Effect of Lithium and Sodium Sulfates on the Crystallization of Boric Acid from Aqueous Solutions: Kinetic and Thermodynamic Effects

by

Wilson Alavia Medina

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Director of thesis: Dr. Teófilo A. Graber

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Abstract

This research is intended to determine the effect of Lithium and Sodium Sulfates on the crystallization of boric acid from aqueous solutions from the kinetic and thermodynamic approaches.

The interest of this study is that during the production of boric acid from brines in Northern Chile, after the fractional crystallization process for reducing impurities such as Na\(^+\), K\(^+\), Li\(^+\) and SO\(_4\)^{2-}, the slurry obtained (once it is added to the final brine of this process sulfuric acid at room temperature to crystallize boric acid) when its solution is saturated in sodium sulfate tends to flocculate; therefore, the boric acid concentrate contaminates with this salt and other impurities. In addition, the solubility of the boric acid in the brine could be affected in presence of this salt and potassium sulfate at the working temperatures; consequently affecting the crystallization yield. Also in this stage the crystals of boric acid could be contaminated with traces of Li\(_2\)SO\(_4\)-H\(_2\)O due to an abrupt decreasing of solubility of lithium sulfate by the effect of the common anion (SO\(_4\)^{2-}) which is a precipitating agent. These effects reduce the yield of the obtaining process of boric acid.

Regarding the thermodynamic approach the solubility, density, viscosity and refractive index of the systems: H\(_3\)BO\(_3\)+Na\(_2\)SO\(_4\)+H\(_2\)O and H\(_3\)BO\(_3\)+Li\(_2\)SO\(_4\)+H\(_2\)O for a wider range of concentrations and temperatures, from (293.15 to 313.15) K, and from (0 to 3.3242) mol·kg\(^{-1}\) H\(_2\)O which were respectively measured.

The experimental data were correlated by empirical equations, obtaining a good enough fit to be useful for evaluating the physical properties of aqueous solutions saturated in boric acid, in the range studied of concentrations of these salts and temperatures. The solubility was represented using the Pitzer model.
The results showed that solubility was described satisfactorily using an equation based on Pitzer model to obtain a good enough fit to be useful for evaluating the solubility of boric acid in sodium sulfate, potassium sulfate and lithium sulfate aqueous solutions, in the range studied of concentrations and temperatures. The model parameters are valid to maximum concentration of the salts, 3.3149 mol·kg$^{-1}$ for Li$_2$SO$_4$, 3.380 mol·kg$^{-1}$ for Na$_2$SO$_4$, and 1.245 mol·kg$^{-1}$ for K$_2$SO$_4$ from 293.15 K to 313.15 K.

For the Kinetic approach a methodology was implemented to obtain single crystals of boric acid, the suitable growth face and direction, using a growth cell, and an Atomic Force Microscope (AFM) in situ apparatus to be able to perform continuous crystallization and determine the growth mechanisms and rate of boric acid from aqueous solutions in absence and presence of Na$_2$SO$_4$ and Li$_2$SO$_4$. The solutions used were saturated solutions of boric acid at 25 °C with 0, 5, and 16 % mass for Na$_2$SO$_4$ and 1, 5 and 9 % mass for Li$_2$SO$_4$.

Test batch crystallization by cooling, using a cubic profile, aqueous solutions of boric acid in presence and absence of salts were performed in a RC1 calorimetric reactor. The studied levels of concentrations were from (0, 5, 10, 15, 20, 23 and 30) % mass and (5, 10, 15, 20 and 23) % mass in presence of sodium sulfate and lithium sulfate respectively. In order to determine the effect of Na$_2$SO$_4$ and Li$_2$SO$_4$ in the crystal size, distribution and shape of boric acid were used the FBRM® G400 and PVM® V819 probes.

It was found that the best method to grow single crystals of boric acid suitable for crystal growth studies was the evaporation at low evaporation rate and the suitable growth face the (001) and the direction growth the [1 0 0].

The presence of lithium and sodium sulfates during the crystallization of boric acid from aqueous solutions affect the solubility, crystal growth mechanism and rate, crystal size distribution (CSD) and shape of the boric acid obtained.
Lithium sulfate reduces the solubility therefore increases the supersaturation of boric acid (thermodynamic effect). It promotes nucleation and reduces the growth rate. The solubility drops for the Li\(^+\) behavior as structure maker of water in presence of sulfate ion and the growth rate is decreased by the adsorption of the salt on the actives sites of growth of the boric acid crystal (kinetic effect).

Sodium sulfate increases the solubility therefore reduces the supersaturation of boric acid (thermodynamic effect). It lessens the growth rate. The solubility rises for the Na\(^+\) behavior as structure breaker of water in presence of sulfate ion and the growth rate is decreased by the adsorption of the salt on the actives sites of growth of the boric acid crystal (kinetic effect).

Both salts affect the growth rate but do not affect the growth mechanism (spiral growth). At salt concentration of 10 % the growth rate is the 30 % and 40 % of the growth in absence of the salts \(G_o\), for lithium and sodium sulfate respectively. At 15 % the growth is reduced to 10 % and 30 % of \(G_o\). In absence of agglomeration the growth would reach a minimum, 0.1, at salt concentration of 20 % for both salts, thus a maximum coverage of all active sites on the boric acid surface of 90 %, but in the batch reactor the stirring causes desorption of the salt molecules from the active sites; therefore, growth is expected to be higher during the process. However the results indicate a slightly greater effect of the Li\(^+\) than Na\(^+\) on the reduction of the growth rate of boric acid.

As results in presence of Li\(_2\)SO\(_4\) fines production is increased and the powder, granular, mean size are decreased. Also agglomeration is promoted and the yield reduced. The yield decreases as salt concentration grows. At salt concentration of 5 % of the production is 61% of the production in absence of the salt. Lithium sulfate does not affect the crystal shape due to the fact that Li\(^+\) ion is adsorbed in all the faces equally.
In presence of Na$_2$SO$_4$ fines production is increased and the powder, granular, mean size are decreased. Also agglomeration is promoted and the yield reduced. The yield decreases as salt concentration grows. At salt concentration of 5 % the production are the 50 % of the production in absence of the salt. Also sodium sulfate modifies the shape of boric acid from prismatic to prismatic planar. It can be attributed to the preferentially face adsorption of Na$^+$ ion on the faces(110), (100), (010) and (010).

The effect of Lithium sulfate is greater than the corresponding to sodium sulfate on the growth rate, fines, powder and granular production, the mean size, the yield and the shape of boric acid crystals.

For both salt the thermodynamic effect is greater than the kinetic effect (adsorption of impurities weak to moderate) consequently is enough to wash the crystals with boric acid saturated solution to purify and classify them properly to meet the product specifications.
Dedicatoriy

To God and my family for their love and valuable support during this stage of my life.
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Nomenclature

\(a^a_B\), activity of boric acid in water

\(a_B\), activity coefficient of boric acid in a ternary system

\(A_\phi\), Debye-Hückel constant of the osmotic coefficient.

\(b\), constant, \(1.2 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}\).

\(B\), nucleation rate in nucleus·kg\(^{-1}\)·s\(^{-1}\).

\(B_{ca}\), viral coefficients of second order for the ionic species.

\(B(L)\), birth rate of particles.

\(C_{ca}\), viral coefficients of third order for the ionic species.

\(c\), solute concentration.

\(c^*\), saturation concentration.

\(c^*/Cc\), dimensionless solubility.

\(c_{imp}\), impurity concentration.

\(dL_{\text{mean}}/dt\), variation of the mean size in \(\mu\text{m} \cdot \text{s}^{-1}\).

\(d_m\), molecular diameter in m\(^3\).

\(D_{AB}\), diffusivity of A in B in m\(^2\)·s\(^{-1}\).

\(D(L)\), the death rate of particles.

\(G\), Linear growth rate in m·s\(^{-1}\).

\(k\), constant for the adsorption of solute.

\(k_b\), Boltzmann constant, \(1.381 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}\).

\(k_d\), diffusive coefficient.

\(k_i\), constant for the adsorption of impurity.

\(k_v\), volumetric shape factor.

\(K_{PS}\), solubility product.

\(L\), characteristic dimension of the crystal in m.
$L_{\text{mean}}$, mean size in μm.

$m$, salt molality, mol·kg$^{-1}$H$_2$O.

$m_1$, lithium sulfate molality, mol Li$_2$SO$_4$·kg$^{-1}$H$_2$O.

$m_2$, sodium sulfate molality, mol Na$_2$SO$_4$·kg$^{-1}$H$_2$O.

$m_3$, potassium sulfate molality, mol K$_2$SO$_4$·kg$^{-1}$H$_2$O.

$m_a$, anion species molality, mol·kg$^{-1}$H$_2$O.

$m_B^0$, boric acid solubility in water, mol·kg$^{-1}$H$_2$O.

$m_B$, boric acid solubility in salt aqueous solution, mol·kg$^{-1}$H$_2$O.

$m_c$, cation species molality, mol·kg$^{-1}$H$_2$O.

$m_s$, solvent mass in kg.

$m_n$, neutral species molality, mol·kg$^{-1}$H$_2$O.

$n$, population density in nucleus·kg$^{-1}$·m$^{-1}$.

$n_{\text{ad}}$, number of sites occupied by impurities.

$n_{\text{max}}$, number of sites available for adsorption.

$n_D$, refractive index.

$N$, number of particles.

$N_A$, Avogadro number, 6.022×10$^{23}$ mol$^{-1}$.

$I$, ionic strength, mol·kg$^{-1}$H$_2$O.

$R$, universal gases constant, 83.144 cm$^3$·bar·mol$^{-1}$K$^{-1}$.

$R^2$, coefficient of multiple determination.

$S$, supersaturation.

$t$, time in s.

$t_o$, initial time in s.

$t_f$, final time in s.

$T$, the absolute temperature, K.

$T_o$, initial temperature in °C.
$T_f$, final temperature in °C.

$V$, system volume in m$^3$.

$V_m$, molar volume in kmol/m$^3$.

$x$, mole fraction.

$x_B$, solubility of boric acid in mole fraction.

$x_1$, mole fraction of lithium sulfate.

$x_2$, mole fraction of sodium sulfate.

$x_o$, distance between dislocations in m.

$z_a$, relative charge of the anion.

$z_c$, relative charge of the cation.

**Greek letters**

$\alpha$, efficiency factor

$\alpha_1$, parameters for 1:2 electrolytes, 1.4 kg$^{1/2}$·mol$^{1/2}$.

$\alpha_2$, parameters for 1:2 electrolytes, 12 kg$^{1/2}$·mol$^{-1/2}$.

$\alpha$, efficiency factor

$\beta^{(0)}$, $\beta^{(1)}$ and $\beta^{(2)}$ adjusting parameters.

$\gamma_B^0$, activity coefficient of boric acid in water

$\gamma_B$, activity coefficient of boric acid in a ternary system

$\gamma$, edge work.

$\gamma_{CL}$.

$\epsilon$, water dielectric constant.

$\eta$, dynamic viscosity in mPa·s.

$\theta$, the surface coverage.

$\theta_o$, overall surface coverage.
$\theta$, the coverage of active sites by an impurity.

$\kappa$, electrical conductivity in mS·cm$^{-1}$.

$\lambda_{nn}$, virial coefficients of second order for the neutral species.

$\lambda_{nc}, \lambda_{na}, \mu_{nn}, \mu_{na}$ and $\xi_{nca}$, mixing parameters coming from ionic and neutral interactions.

$\lambda_{Bc}, \lambda_{Ba}, \zeta_{B-a-c}$ are fitting parameters related to the interactions between the boric acid and cation c and anion a, and cation and anion respectively.

$\mu_0, \mu_1, \mu_2$ and $\mu_3$ are the zero, first, second and third moment of the crystal size distribution. $\mu_{nnn}$, virial coefficients of third order for the neutral species.

$\mu^S$, chemical potential of boric acid in solid (S).

$\mu^L$, chemical potential of boric acid in liquid (L).

$\nu_c$, cation coefficient.

$\nu_a$, anion coefficient.

$\rho$, density in kg·m$^{-3}$.

$\rho_c$ is the crystal density in kg·m$^{-3}$.

$\sigma$, Relative supersaturation

$\sigma (x_o)$, the dependent supersaturation on dislocations.

**Abbreviations**

AFM, Atomic force microscope.

BCF, Burton, Cabrera and Frank.

CAM, Competitive adsorption model.

CLD, Chord length distribution.

CSD, Crystal size distribution.

FBRM, Focused beam reflectance measurement.

MAD, Median average deviation.

MZW, Metastable zone width.

PVM, Particle vision and measurement.

SD, Standard error of the estimate.

SPM, Scanning probe microscope.
Chapter I

Introduction
1.1 Background

Crystallization is a separation and purification process used for the production of different materials, from the basic chemical compounds to the special ones (Kellogg and Leeman 2012, Baker, Gulati et al. 2015, Delmar, Bolla et al. 2015, Moreno and Mendoza 2015) and drugs (Morissette, Almarsson et al. 2004, El-Zhry El-Yafi and El-Zein 2015, Veesler and Puel 2015).

Although, industrial crystallization has been used for centuries, unfortunately many problems remain without solution. The purity and morphology of the crystals can determine the product properties (Demopoulos 2009, Navarro, Wu et al. 2009). These parameters could affect the quality of the final product, its dissolution rate in solvents, the transport properties of the suspension in the crystallizer result in drawbacks in the downstream processes such as filtration, settling and drying. The characteristics of the product can be specified based on individual parameters for the crystal, e.g. shape, size and purity, however in the production process the crystals do not have the same shape and size; therefore, the quality of the product is determined by the crystal size distribution, CSD (Schorsch, Ochsenbein et al. 2014, Ghadipasha, Tronci et al. 2015, Hertrampf, Müller et al. 2015, Holaň, Ridvan et al. 2015).

A compound, different than the crystallization one is considered as an impurity; consequently, the solvent used for growing and any other compound added to the medium or present is an impurity. Different names such as additives, aggregates and inhibitor are used in the literature for these types of compounds. Independently of its concentration a chemical intentionally added is called additive. The aggregate concept refers to an impurity added in great amount relatively (to weight percent). An impurity can inhibit or promote the crystal growth processes (Meenan, Anderson et al. 2002). The one which inhibits the growth is called inhibitor and the one which promotes the growth is called promoter (Al-Jibbouri 2002).
To design and optimize properly a crystallization process is necessary to known the kinetic of crystallization (nucleation and growth) (Demopoulos 2009). The nucleation rate is that the speed at tiny nucleus crystals enter to the crystal population and the growth rate is that the crystal presents increases in their size (ter Horst, Schmidt et al. 2015).

The crystal growth takes place in a solution when it is supersaturated. This solution is in this state when the number of growth units present, is greater than the ones present at the equilibrium state at a determined pressure and temperature (solubility). The growth units can be atoms, molecules, ions, complexes, monomers and polymers. When these units are in excess, they make groups forming nucleus if the critical number of units is reached. This number is determined by the minimum energy of the system. The growth units diffuses from the solution of the nucleus surface and adsorb and migrate over it until a suitable place for incorporating is found; this site is called active site, which makes the crystal grows. The slowest step of this process is the controlling step (Vekilov and Chernov 2003, Nielsen, De Yoreo et al. 2013, Vekilov 2015).

**Figure 1.** Illustration of the Atomic Process taking place during the growth of a crystal face. Modified from De Yoreo y Vekilov (De Yoreo and Vekilov 2003).
The crystal surface is formed of terraces and steps. The edges of the steps are formed of growth units. When the links between the edges are broken because of thermal effects or interaction with the medium growth, dislocations are formed. They can be positive, negative and neutral, and the difference between the negative and positive sites determines the surface charge.

To keep the system neutrality, the co-ions, migrate to the surface, forming a fixed layer, known as Stern layer. These ions attract co-ions which disorder the solvent structure, forming a diffuse layer. Both layers compose the double layer. This layer determines the solid–liquid system properties such as: Solubility, energy and interfacial tension (Sahin and Bulutcu 2003, Vekilov 2015). In addition, it sets the diffusion rate of units from and to the surface which determines the step advance on the surface that fixes the growth rate (Vekilov 2015).

The formation of the double layer is a complex process which depends on the interactions between the species present in the solution, the adsorbed species on the surface and the ionic surface groups, as well as the pH, temperature and the stirring rate (Sahin and Bulutcu 2003).

The presence of impurities in the solution modifies the solvent structure, and depending on the affinity of them for the solvent, it makes more or less structure. These impurities interact with the solute, changing its affinity for the solvent molecules and forming complex molecules. The solute, the formed complexes and the impurities compete for the kinks, changing the potential and charge of the surface due to the fact they modified the number of positive, negative and neutral sites on the crystal faces, inhering or promoting the growth rate. The proportion of these sites on the crystal surface determines its stability, as much neutral sites exist on the surface as more stable it is (Yang, Qian et al. 2014, Borsos and Nagy 2015), (Pritula and Sangwal 2015).

**Figure 1.2** Description of the Solid-Liquid interface (Double Layer). Reproduced from Al-Jibbouri (Al-Jibbouri 2002).

Currently it is necessary further research to quantify the impurity effects in the potential surface, charge, and interfacial energy, the dynamic of formation of the double layer, the solvent structure, and the mechanisms involved in the modification of the kinks and edges and their prediction from variables measurable process in the industry. This research is required to be able to obtain phenomenological models to predict the crystal shape, crystal size and shape distribution for modelling, simulation and optimization of crystallization processes.
1.1.1 Kinetic Effect (Crystal side)

The experimental data reported in literature about the effect of impurities deal with different topics such as the habit and morphology modification, growth rate (Markande, Nezzal et al. 2012, Zhang, Jia et al. 2013), advancing speed of crystalline layers, presence of dead zones at low impurities concentration, nucleation and precipitation kinetics (Matsui, Sazaki et al. 2006, Markande, Nezzal et al. 2012) and the chemical composition of the species of impurities.

Many models that describe the impurity effects on the crystal growth processes are based on the concept of adsorption of impurities species (ions, atoms or molecules) on the kinks, steps and terraces over the growth surface (Cabrera and Vermilyea 1958, Févotte and Févotte 2010, Borsos and Nagy 2015).

Cabrera and Vermilyea (Cabrera and Vermilyea 1958) considered theoretically the adsorption of impurity molecules on the terrace surface during the displacement of the edges on the surface. Bliznakov (Bliznakov 1954) presented the reduction model of the number of growth sites on the surface and reported experimental results of soluble compounds in water, that supported it. Sears (Sears 1958) and Dunning and Albon (Dunning 1958) proposed the impurity adsorption model on the edges of the face and they probed its validity over the dependence of the displacement rate of the growth layer with the impurity concentration.

Davey (Davey 1976) and Davey and Mullin (Davey and Mullin 1974, Davey and Mullin 1974), studied the displacement rate of the layers as function of the concentration of impurities and verified the adsorption of kinetic models with experimental data.
Kubota and Mullin (Kubota and Mullin 1995) proposed a new kinetic model for the growth in presence of impurities. The model describes the adsorption of impurities through the steps and define the efficiency factor, $\alpha$ for the impurity adsorption. In this model the factor, $\alpha$, takes values between zero and infinite unlike the factor in the Bliznakov model where $\alpha=1$ therefore, as evidence for different crystals, their model, describes better the kinetic data when the growth units are adsorbed on the active sites in the steps. They used adsorption isotherms of Langmuir related to the fractional coverage, $\theta$, of a two-dimensional surface for impure molecules with the impure concentration in the solution, $c_{imp}$, and a constant adsorption, $K$, defined as the coverage of a one-dimensional step. The authors did not justify the relation of the lineal coverage with the Langmuir isotherm.

Martins et al. (Martins, Rocha et al. 2006) proposed that the impurities and the solute compete for the growth sites on the surface. This competence was described using an extended Langmuir isotherm that depends on the solute and impure concentration, and has two constants $K$ and $K_i$. These constants are used to represent the total surface coverage.

**Figure 1.3** Impurity effect on the growth rate at different values of the efficiency factor $\alpha$. Reproduced from Al-Jibbouri (Al-Jibbouri 2002).
Martins et al. (Martins, Rocha et al. 2006) defined a new effective factor $\beta$. It depends on the specific properties of the impurity and indicates the affinity of the impurities adsorbed on the surface for the active sites. According to the effect of the impurity on the growth rate they were classified as: Actives ($\beta>1$) and slightly actives ($\beta<1$). In addition, they found that the active impurities decreases the growth rate although they are barely adsorbed, e.g. The Tailor made additives.

### 1.1.2 Thermodynamic Effects (Solution side)

The solubility data, available for many multicomponent systems, are barely and sometimes are not reliable therefore they have a limited use for most of the engineering purposes. For that work the complete phase diagram is necessary. This diagram is not obtained in a short time, for this reason many thermodynamic models have been proposed to predict the salt solubility and other compounds in brines.

Some of the most successful models are based on the Pitzer equation to describe the thermodynamic properties of aqueous electrolytes for a broad ionic strength range (Pitzer 1973, Pitzer 1986). It is possible to work at high temperatures with the Pitzer model when empirical functions are added. These functions can be obtained from binary and ternary systems hence the solubility for electrolyte and non-electrolyte solutions can be calculated, based on thermodynamic considerations.

The solubility of species in solution can be modified due to the presence of other species as well as impurities. These species can change the water structure and the hydration characteristics of the present ions; therefore, the physical properties of the saturated solution such as density and metastable zone and not only nucleation, growth and dissolution rate (Kowacz and Putnis 2008, Ruiz-Agudo, Putnis et al. 2009, Ruiz-Agudo, Putnis et al. 2015).
The effect of impurities on the water structure and the solute hydration, and its consequences to the growth and dissolution of crystals was studied by Kowacz and Putnis (Kowacz and Putnis 2008). They measured the advancement rate of steps in situ by atomic force microscopy (AFM) in an supersaturation range from 0.0005 M to 1 M for BaSO\textsubscript{4} in KCl, NaCl, LiCl, CaCl, NaF and NaNO\textsubscript{3} solutions.

The results showed that the dependence of the growth and dissolution of BaSO\textsubscript{4} with impurities could be explained considering the specific effects of the salts on the dynamic of the solvent structure and the hydration of the growth units. They found that hydration of ions in electrolyte solution (\(\Delta E_{i-salt}\)) is determined by the solvent molecules dynamic in the solution (\(E_{0-salt}\)) and for the activation energy for the solvent exhaust from the solvation layer of the ion (\(E_{i-salt}\)). This increases following the order LiCl<NaCl<KCl and NaF<NaCl. \(E_{i-salt}\) is related to the capacity of the ions to be together or separated in the solution and decreases inversely to the salt solubility in the solution in the order CsCl>NaNO\textsubscript{3}>LiCl>NaCl>KCl>NaF.

In regards to the growth Kowacz and Putnis (Kowacz and Putnis 2008, Ruiz-Agudo, Putnis et al. 2015) found that if controlling mechanism is the integration of growth units in the dislocations, then the cations, dehydration rate affects substantially the growth. The dislocation spread is conducted by electrostatic and interrupted by the energy barrier for water molecules removing from the growth units layer and the water bound to the surface. The growth rate resulted to be more dependent on the dynamic water when the growth is controlled through diffusion due to the fact that ions diffusion depends on the solvent exchange frequency. In addition, they found that the similar morphological change, caused by salt addition or temperature implies that morphology can have characteristics of the solvent dynamic structure and the solute hydration in the solution.
1.1.3 Kinetic and Thermodynamic studies

The impurities affect simultaneously the solution and the crystal surface for this reason some studies have been performed so far.

Enqvist et al. (Enqvist, Partanen et al. 2003) studied the influence of organic impurities at high concentrations on the growth rate of KH$_2$PO$_4$ (KDP) from aqueous solutions. The impurities used were urea, 1-propanol and ethanol. In the study, the growth rate in the growth direction [001] for the face (101) of a mono-crystal of KDP was measured using a cell growth placed under an optic microscope coupled to a digital camera. For representing the driving force based on the activity of KDP, they modelled the coefficient activity of KDP using the Pitzer equation and used the mass transfer coefficient, $k_d$, for the binary system KDP-H$_2$O to calculate the growth rate controlled by diffusion for the ternary systems for determining the controlling step. For the system in absence of impurities the controlling step was the surface integration, described by Burton-Cabrera and Frank, BCF equation. This model is specific for growth controlling by the mechanism of surface diffusion. For low growth rates the controlling steps were the integration and diffusion simultaneously. It was described by the two-step model. The experimental and modelling results showed that ethanol and propanol decrease the solubility and the growth rate. They are adsorbed preferentially on the crystal surface occupying the actives sites and inhibiting the growth. This fact can be attributed to their polar behavior.

Jiang et al. (Jiang, Pan et al. 2008) found that the impurities, depending on their nature, affect the crystallization process in different ways. In situ atomic force microscopic studies showed that during the crystallization of calcium sulfate dehydrates in presence of borax, this impurity promotes the secondary nucleation to increase the density steps on the growing faces of the crystal, and reduce the spread rate of the steps by adsorption simultaneously. The double effect of borax is regulated by its concentration. This behavior was described by an equation based on the Birth and Spread model (B+S). This model describes properly the microscopic and macroscopic growth rates.
In addition Jiang et al. found that the nucleation rate is inversely proportional to the interfacial energy, \( \gamma \). They remark the importance of the interfacial properties, specifically the interfacial energy to obtain the full view of the impurity effects on the growth mechanisms.

1.1.4 The crystal size distribution (CSD) and the effect of additives

The quality of the product obtained by crystallization is described by the purity and the crystal size distribution (CSD) (Abbas and Romagnoli 2007). This last parameter is controlled by changing the process conditions, such as supersaturation by cooling profile and / or the adding of additives (Hash and Okorafor 2008). This allows the CSD meet the product quality (Abbas and Romagnoli 2007, Borsos and Nagy 2015). For proper design of crystallization processes and implementation of control strategies, it is needed mathematical models describing the evolution of the CSD, depending on operating conditions of the process (the solution composition, a method of supersaturation, crystallization time, initial seeding) (Sarkar, Rohani et al. 2006, Abbas and Romagnoli 2007, Ward and Yu 2008, Févotte and Févotte 2010, Borsos and Nagy 2015).

To model the evolution of CSD, population balance equation (Sarkar, Rohani et al. 2006, Abbas and Romagnoli 2007, Ouiazzane, Messnaoui et al. 2008, Zhang, Liu et al. 2015) are applied together with mass and energy balances. These equations have symbolic solution only in simple cases (considering only crystal growth), in other cases is needed the application of numerical methods (Qamar and Warnecke 2008). The complexity of the system depends on the kinetic phenomena considered (nucleation, growth, breakup, agglomeration) and fluid dynamics, and determines the numerical method used to solve the mathematical model. The main resolution methods are the method of moments (Falola, Borissova et al. 2013), method of characteristics (Févotte and Févotte 2010), finite volume methods and high scheme (Qamar, Elsner et al. 2006, Sarkar, Rohani et al. 2006, Ouiazzane, Messnaoui et al. 2008, Qamar, Warnecke et al. 2009, Borsos and Nagy 2015).
1.2 Boric Acid

Boric acid is a boron compound interesting for academy and industry due to its applications in agriculture, as fertilizer, as a neutron absorber to control the speed of nuclear fission (He, Su et al. 2014), and as a chemical manufacture to obtain borax and boron compounds (Wang and Zeng 2014).

Boric acid is presented in two specifications: Granular and Powder. Their chemical analysis and granulometry, they are shown below in Table 1.1 and Table 1.2.

<table>
<thead>
<tr>
<th>Component</th>
<th>Unit</th>
<th>Typical Value Normal Sulfate</th>
<th>Typical Value Low Sulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₂O₃</td>
<td>%</td>
<td>56.5</td>
<td>56.5</td>
</tr>
<tr>
<td>SO₄</td>
<td>Ppm</td>
<td>250</td>
<td>105</td>
</tr>
<tr>
<td>Fe</td>
<td>Ppm</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Cl</td>
<td>Ppm</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Water Insoluble</td>
<td>Ppm</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Purity</td>
<td>%</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>


The main sources of boric acid production are seawater and natural brines from evaporate basins, known as salt lakes and whose genesis is associated with intense volcanic activity occurred in the past in these regions; the Searles Lake in California (USA) and the boron province of South America that comprises the Atacama Salt lake in northern Chile, the Uyuni Salt Lake in south western Bolivia and the Dead Man Salt Lake in northwest Argentina, which are the main evaporate resources in the world (Chong 2000).
### Table 1.2 Dry Sieve Analysis for Boric Acid

<table>
<thead>
<tr>
<th>Size in μm</th>
<th>US Mesh</th>
<th>Typical Value Granular (%)</th>
<th>Typical Value Powder (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(+)1000</td>
<td>+18</td>
<td>2.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(+)841</td>
<td>+20</td>
<td>5.5</td>
<td>-</td>
</tr>
<tr>
<td>(+)420</td>
<td>+40</td>
<td>14.0</td>
<td>-</td>
</tr>
<tr>
<td>(+)149</td>
<td>+100</td>
<td>65.0</td>
<td>-</td>
</tr>
<tr>
<td>(-)125</td>
<td>-120</td>
<td>-</td>
<td>75.0</td>
</tr>
<tr>
<td>(+)74</td>
<td>+200</td>
<td>10.0</td>
<td>-</td>
</tr>
<tr>
<td>(-)63</td>
<td>-230</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td>(+)44</td>
<td>+325</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>(-)0.044</td>
<td>-325</td>
<td>0.5</td>
<td>-</td>
</tr>
</tbody>
</table>


In northern Chile the production of boric acid from brines is the most economical method, due to the low cost implied to concentrate it; by solar evaporation. However, the species present in the aqueous systems formed a complex equilibrium then, to control the process and get crystals of high purity is essential to understand the solid-liquid involved equilibrium. This salt water system could be represented as: 

\[
\text{Li}^+\text{-Na}^+\text{-K}^+\text{-Ca}^{2+}\text{-Mg}^{2+}\text{-H}^+\text{-Cl}^-\text{-SO}_4^{2-}\text{-B}_4\text{O}_7^{2-}\text{-OH}^-\text{-HCO}_3^-\text{-CO}_3^-\text{-H}_2\text{O})
\]

(Thompson 1974).

The brines used are high sulfate solutions. In this system the main species present are \(\text{B}^{3+}, \text{Na}^+, \text{K}^+, \text{Li}^+, \text{Mg}^{2+}, \text{Cl}^-\) and \(\text{SO}_4^{2-}\). They formed binary, ternary, quaternary and more multicomponent systems. Considering that during the process the pH of the solution is about 3, to have boron as boric acid, the main system is: 

\[
\text{Li}^+\text{-Na}^+\text{-K}^+\text{-Mg}^{2+}\text{-H}^+\text{-Cl}^-\text{-SO}_4^{2-}\text{-H}_3\text{BO}_3\text{-CO}_3\text{-H}_2\text{O})
\]
A fractional crystallization process for removing impurities such as Na\(^+\), K\(^+\), Li\(^+\) and SO\(_4^{2-}\) is necessary. To the final brine of this process is added sulfuric acid at room temperature to crystallize boric acid. The slurry obtained when its solution is saturated in sodium sulfate tends to flocculate therefore the boric acid concentrate contaminates with this salt and other impurities (Wilson 1975). In addition, the solubility of the boric acid in the brine could be affected in presence of this salt and potassium sulfate at working temperatures therefore affecting the crystallization yield. Also in this stage the crystals of boric acid could be contaminated with traces of Li\(_2\)SO\(_4\)·H\(_2\)O (Pavlovic-Zuvic, Parada-Frederick et al. 1983) due to an abrupt decreasing of solubility of lithium sulfate by the effect of the common anion (SO\(_4^{2-}\)) which is a precipitating agent. These effects reduce the yield of the obtaining process of boric acid.

The optimization of industrial processes by fractional crystallization and / or solvent crystallization requires a large number of mineral solubility and transport properties data in pure water and aqueous electrolyte solutions. In this context, the thermodynamic model and empirical correlations play an important role in the prediction and correlation of these data in ranges of industrial operating conditions (Digiacomo, Brandani et al. 1992).

Also to identify the variables and their behavior that determine the mean crystal size and crystal size distribution is relevant, to avoid problems with downstream purification process and meet the product specifications (see Table 1.2). This can be afforded knowing the kinetic of crystallization of the boric acid from aqueous solutions. This implies to determine the variables, experimental methods to measure, and models to describe the growth mechanism, growth rate and nucleation.
1.3 Boric Acid behavior in water and salt aqueous solution, equilibrium and transport properties and thermodynamic modelling.

The acid–base equilibrium present in the boron solutions does not behave as a weak acid unlike forming polyborates (Peiming Wang 2013) which are associated strongly and difficult to quantify due to the fact of boron can coordinate to three or four oxygen atoms (Galleguillos, Molina et al. 2006). Raposo et al. (Raposo, Zuloa et al. 2003) to estimate the effect of ionic medium in the solution equilibrium, determined that boric acid is dissociated in $\text{H}_2\text{BO}_3^-$ which interacts with the ion presents in the medium (Peiming Wang 2013, Ge, Fang et al. 2014). Tosell (Tosell 2005) to calculate dissociation constants by the ab initio method, found the formation of $\text{B(OH)}_4^-$ instead of $\text{H}_2\text{BO}_3^-$, by the reaction of $\text{B(OH)}_3$ and water, being present a complex intermediate $\text{B(OH)}_3…\text{H}_2\text{O}$ during the dissociation of this acid in water. The presence of these species was verified experimentally by NMR shifts.

Perelygin and Chistyakov (Perelygin and Chityakov 2006) performed the speciation of boric acid solutions for the complete pH range. For a total concentration of 0.1 M, determined that for pH less than 7, $\text{H}_3\text{BO}_3$ is the prevalent specie, at pH 8, the predominant species are $\text{H}_2\text{BO}_3$, $\text{H}_2\text{BO}_3^-$ and $\text{B(OH)}_4^-$, at pH between 10 and 12, $\text{B(OH)}_4^-$, $\text{H}_2\text{BO}_3^-$ and at pH greater than 12, $\text{BO}_3^{3-}$ and HBO$_2^{3-}$.

The solubility, vapor pressure and density for boric acid solutions have been reported in literature (Kolthoff 1926, Linke and Seidell 1958, Brandani, Del Re et al. 1988, Digiacomo, Brandani et al. 1992, Digiacomo, Brandani et al. 1993, Chanson and Millero 2006, Galleguillos, Molina et al. 2006, Wang, Kosinski Jerzy et al. 2013) in absence and presence of impurities. Brandani et al. (Brandani, Del Re et al. 1988) measured vapor pressure for boric acid solutions at a temperature range from 40 °C to 100 °C and together with solubility data from literature, they represented the information by a an equation based on the Wilson model. For this purpose boric acid was considered as a neutral molecule and non-dissociated.
Experimental data of solubility of H$_3$BO$_3$ in water and in aqueous solutions of NaCl, KCl, LiCl, RbCl, CsCl, BaCl$_2$, MgCl$_2$, MgCl$_2$, K$_2$SO$_4$, Na$_2$SO$_4$ at various temperatures and salt concentration were reported in the literature (Digiaco, Brandani et al. 1992) (Linke and Seidell 1958, Digiaco, Brandani et al. 1993, Chanson and Millero 2006).

In presence of sodium and potassium sulfate in aqueous solutions, the solubility of boric acid was reported by Di Giaco et al. (Digiaco, Brandani et al. 1992). They studied a large concentration range from (0 to 3.739) mol·kg$^{-1}$ H$_2$O for Na$_2$SO$_4$ and from (0 to 1.084) mol·kg$^{-1}$H$_2$O for K$_2$SO$_4$, at temperatures from 303 K to 373 K. They find that the solubility of boric acid increases in presence of both salts but the effect of K$_2$SO$_4$ is greater than Na$_2$SO$_4$. To represent the solubility they adjusted the activity coefficient considering the boric acid as non-dissociated; therefore, they combined the Wilson equation for short range interactions and the Debye-Huckel and Born equations for long range interactions due to the presence of ions. The resulting model has binary and ternary parameters, and the melting enthalpy and temperature for boric acid. This equation predicted the solubility with an average deviation less than 1 % but a deviation of 40 % for the activity coefficient.

The solubility in acid chloride aqueous solutions were reported in literature for the salts LiCl, NaCl, KCl, RbCl, and CsCl as a function of the ionic strength at 298.15 K by Chanson and Millero[18]. The solubility of boric acid [B] was determined as a function of ionic strength from (0 to 6) mol·kg$^{-1}$H$_2$O at 25°C. The results were examined using the Pitzer equation (Pitzer 1973, Pitzer 1986). This model has three interaction parameters $\lambda_{Bc}$, $\lambda_{Ba}$, related to the interaction of boric acid with cation c and anion a respectively, and $\zeta_{B-a-c}$ related to the interaction with cation c and anion a. The parameters were obtained using experimental data. To apply the model as a predictive one, Chanson and Millero, designed a methodology to estimate the interaction parameters from systems with common ions. To validate this methodology they predicted the solubility of boric acid (0.866 mol · kg$^{-1}$) in artificial sea water (0.427 mol · kg$^{-1}$ NaCl and 0.055 mol · kg$^{-1}$ MgCl$_2$), being in good agreement with the measured value (0.864 mol·kg$^{-1}$).
As well Chanson and Millero estimated the interactions parameters at 298.15 K for the systems $\text{H}_3\text{BO}_3 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$, $\text{H}_3\text{BO}_3 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$ and $\text{H}_3\text{BO}_3 + \text{Li}_2\text{SO}_4 + \text{H}_2\text{O}$ in average maximum salt concentrations of 2.7 mol·kg$^{-1}$H$_2$O, 2.8 mol·kg$^{-1}$ H$_2$O and 2.8 mol·kg$^{-1}$ H$_2$O respectively.

Therefore is needed to measure the solubility of boric acid in sodium sulfate aqueous solutions for a wider range of concentrations and temperatures, from (293.15 to 313.15)K, and from (0 to 3.3795) mol·kg$^{-1}$ H$_2$O respectively. The results could be represented using an equation based on Pitzer model given by Chanson and Millero (Chanson and Millero 2006). Their parameters estimated and validated estimating the solubility of boric acid in lithium sulfate, sodium sulfate, and potassium sulfate aqueous solutions at different temperatures and salt concentrations.

Density of $\text{H}_3\text{BO}_3$ in water was informed from dilute to saturated solutions at 273.15 K to 373.15 K (Novotny and Sohnel 1988). For the ternary systems $\text{H}_3\text{BO}_3 + \text{KCl} + \text{H}_2\text{O}$ at 293.15 K, 298.15 K and 303.15 K (Galleguillos, Flores et al. 2001), and $\text{H}_3\text{BO}_3 + \text{NaCl} + \text{H}_2\text{O}$, $\text{H}_3\text{BO}_3 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$ and $\text{H}_3\text{BO}_3 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ at 298.15 K, 303.15 K and 308.15 K (Galleguillos, Molina et al. 2006) this property was reported for undersaturated solutions. Also the refractive index for $\text{H}_3\text{BO}_3 + \text{H}_2\text{O}$ and $\text{H}_3\text{BO}_3 + \text{KCl} + \text{H}_2\text{O}$ under-saturated solutions at 293.15, 298.15 and 303.15 K were reported (Galleguillos, Flores et al. 2001).

Density, viscosity, refractive index and electrical conductivity at saturation, in boric acid, have been not reported for the systems $\text{H}_3\text{BO}_3 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ and $\text{H}_3\text{BO}_3 + \text{Li}_2\text{SO}_4 + \text{H}_2\text{O}$ for salt concentrations from (0 to 3.1472) mol·kg$^{-1}$ and temperatures ranging from (293.15 to 313.15).

Therefore is necessary to determine the density, refractive index, viscosity and electrical conductivity for aqueous solutions of sodium sulfate saturated in boric acid. These properties could be described using empirical equations and their behavior discussed by comparison to the properties of the system $\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ (Wolf 1966, Söhnel and Novotný 1985, McCleskey 2011).
1.4 Effect of impurities on the metastable zone width and kinetic of crystallization of H$_3$BO$_3$ from water and salt aqueous solutions

In the literature, it have been reported solubility, metastable zone width and growth rate data for aqueous solutions saturated in boric acid in the presence of sodium sulfate (Taboada and Graber 2007), and sodium chloride (Taboada, Soria et al. 1993). Taboada and Graber (Taboada and Graber 2007) found that growth rate of boric acid is reduced in presence of sodium sulfate.

On the other hand, in a former work (Alavia and Graber 2010) we presented a theoretical explanation of the reduction of the growth rate of boric acid in presence of sodium sulfate. It was found that the presence of this salt, which is an active impurity inhibits the growth rate, because of it promotes the migration and adsorption of sodium and sulfate ions in the active sites on terraces and steps on the surface; reducing the speed of advance of steps. The controlling step of the growth rate is integration by surface diffusion and growth is due to the presence of dislocations in spiral on the crystal surface in absence and presence of sodium sulfate.

For verification of the theoretical explanation found, the crystal growth rate of boric acid must be measured in presence of impurities. Further, the growth mechanism of boric acid in presence of foreign ions and the adsorption isotherms of them on the growth surface of boric acid during the crystal growth should be determined experimentally.

The crystal growth of boric acid has been studied by different methods. Batch (Taboada and Graber 2007), fluidized bed (Sahin 2002) and rotating disc (Sahin and Aslan 2004) techniques have been used to evaluate the growth rate. Those methods are able to evaluate the overall growth rate, but they are not appropriate to determine the mechanisms involved on the growth of specific crystal faces.
The growth rate and mechanisms of growth of specific faces have been studied using a temperature controlled flow cell placed under an optic microscope (Kubota, Otosaka et al. 2000, Enqvist, Partanen et al. 2003, Lovette, Browning et al. 2008, Bianco 2009) but it is limited to image growth processes in situ at the scale equivalent to that of crystal faces (Lovette, Browning et al. 2008).

Since AFM provides the ability to image crystal growth and dissolution processes in situ at micrometer and nanometer-scale resolution (Wu, Wang et al. 2011), it has been used to investigate mechanisms of kink formation (Vekilov 2007), the transition between growth mechanisms and the effects of additives and impurities (Vavouraki, Putnis et al. 2010, Ruiz-Agudo, Putnis et al. 2011, Wu, Wang et al. 2011). Further, it has been applied to study the role of impurities in a surface of modification (Wu, Wang et al. 2011), to distinguish between polymorphs for pharmaceutical compounds (Doherty, Lovette et al. 2008), to study the kinetics of crystallization of amorphous solids by targeting a crystal at the surface (Miyazaki, Aso et al. 2011), to study the crystallization behavior of films at different temperatures (Wu, Liu et al. 2011) and to determine the relative stability of crystal faces (Shindo, Igarashi et al. 2010, Shirota, Niki et al. 2011).

Currently, in crystallization studies, the FBRM (Czapla, Kail et al. 2010) and PVM sensors are applied for determining the evolution of the size distribution of crystals (Barrett and Glennon 2002) and observe the shape of the crystals (Kempkes, Eggers et al. 2008, Acevedo and Nagy 2014, Borsos and Lakatos 2014) respectively, they are widely used (Zhou, Moment et al. 2015). Its usefulness lies in the determination of nucleation, growth rate and determination (Luo, Wu et al. 2013) of agglomeration and glass breaking online (Liu, Wei et al. 2013). This information is useful in the design and optimization of crystallization processes (Zhou, Moment et al. 2015). In literature there have not been reported studies for the systems H₃BO₃+Na₂SO₄+H₂O and H₃BO₃+Li₂SO₄+H₂O.
The studies performed so far, approached the problem either from the kinetics or the thermodynamics however is necessary to assess them from both methods to be able to explain the boric acid crystal growth rate and mechanism from aqueous solutions in presence of impurities experimentally and obtain useful information to optimize the crystallization stage within the industrial processes.

1.5 Objectives

According to what was mentioned above the general objective of this research is to determine the effect of Lithium and Sodium Sulfates on the crystallization of Boric Acid from aqueous solutions from the kinetic and thermodynamic approaches.

The specific objectives are:

• To measure the physical properties of the systems: \( \text{H}_3\text{BO}_3+\text{Li}_2\text{SO}_4+\text{H}_2\text{O} \) and \( \text{H}_3\text{BO}_3+\text{Na}_2\text{SO}_4+\text{H}_2\text{O} \) from 293.15 K to 313.15 K and concentration of the salts from 0 to 3.149 mol·kg\(^{-1}\) for \( \text{Li}_2\text{SO}_4 \) and 3.380 mol·kg\(^{-1}\) for \( \text{Na}_2\text{SO}_4 \).

• To describe the thermodynamic effects of \( \text{Li}_2\text{SO}_4 \) and \( \text{Na}_2\text{SO}_4 \) on the solubility of boric acid in aqueous solutions and their effect on the transport properties studied.

• To implement an experimental apparatus to perform continuous growth crystallization using AFM in situ to determine the growth mechanisms and rate of boric acid from aqueous solutions in absence and presence of \( \text{Li}_2\text{SO}_4 \) and \( \text{Na}_2\text{SO}_4 \) from 293.15K to 313.15 K.

• To determine the effect of \( \text{Li}_2\text{SO}_4 \) and \( \text{Na}_2\text{SO}_4 \) in the crystal size distribution (CSD) and shape of boric acid by batch cooling crystallization using the FBRM® G400 and PVM® V819 probes.
1.6 Scope of the research

The experimental methodology developed in this study: a) Single crystal growth method, b) Determination of the suitable growth face and direction for growth rate and mechanism by AFM, c) Determination of growth rate and mechanism by continuous growth crystallization from aqueous solutions using AFM continuous growth crystallization, d) To determine the effect of the shape of boric acid using the FBRM® G400 and PVM® V819 probes; which could be applied for the study of growth mechanism and rate for other compounds in the presence of impurities and their impact on the distribution of crystal size, shape, and crystallization yield.

1.7 Boundaries of the study

This work focuses only on studying the phenomena related to the kinetics and thermodynamics of crystallization, without considering the suspensions hydrodynamic during the crystal growth process due to its high complexity. Crystallization experiments performed are limited to laboratory scale to meet the conditions of the models. Further studies on the suspension hydrodynamics, is necessary to scale the results and apply them for the design of industrial crystallizers.

For the kinetic approach the main focus is to determine experimentally the growth mechanism of boric acid in presence and absence of impurities and their implications on the CSD and shape, not to develop theoretical models such as the competitive adsorption model (CAM) and population balance equations (PBE) because of they have been broadly studied in literature. However, CAM has been applied to explain the adsorption of impurities and make some comments about the suitability of use the method of moments to calculate the growth and nucleation rates.
1.8 Thesis structure

This thesis is divided in four chapters. In Chapter 1, presents a review of the thermodynamic, kinetic, and thermodynamic and kinetics combined effects of the impurities during the crystallization of inorganic compounds from aqueous solutions. Also, it is reported the thermodynamic and kinetic effects of the impurities during the crystallization of boric acid from aqueous solutions in absence and presence of impurities. The obtaining process for boric acid from brines is described and the problem and objectives of this work is exposed.

In Chapter 2, describes the thermodynamic effects of the impurities, for that purpose are presented the measurements methods and results of the physical properties for the systems \( \text{H}_3\text{BO}_3+\text{Na}_2\text{SO}_4+\text{H}_2\text{O} \) and \( \text{H}_3\text{BO}_3+\text{Li}_2\text{SO}_4+\text{H}_2\text{O} \) from 293.15 K to 313.15 K. These solubility and density are represented by thermodynamic models and the refractive index, viscosity and electrical conductivity are described through empirical correlations.

In Chapter 3, the kinetic effect of the impurities is shown. A methodology is presented and implemented to obtain single crystals of boric acid, in order to determine the suitable growth face and direction using a growth cell, and an AFM in situ apparatus to be able to perform continuous crystallization and determine the growth mechanisms and rate of boric acid from aqueous solutions in absence and presence of \( \text{Na}_2\text{SO}_4 \) and \( \text{Li}_2\text{SO}_4 \) from 293.15K to 313.15 K. Also the effect of \( \text{Na}_2\text{SO}_4 \) and \( \text{Li}_2\text{SO}_4 \) in the crystal size distribution and shape of boric acid were studied by batch cooling crystallization with the FBRM® G400 and PVM® V819 probes.

Finally in chapter 4, the conclusions of this research are presented.
Chapter II

Solid-Liquid Equilibrium and Physical Properties of the systems:

\[ \text{H}_3\text{BO}_3 + \text{Li}_2\text{SO}_4 + \text{H}_2\text{O} \text{ and } \text{H}_3\text{BO}_3 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \]
2.1 Theoretical framework

2.1.1 Solubility

A solution (either gaseous, liquid or solid) is a homogeneous mixture of two or more substances with components called solute and solvent. If small amounts of a solute are added in a vessel containing liquid water (solvent) at a given temperature, initially the solute is dissolved thus forming an unsaturated solution; however, there is a point where water cannot solve as much solute, then a saturated solution is produced, therefore, the concentration of solute in this solution represents the solubility of the solute in water (Lovera 2006).

The solubility of a solid in a liquid depends on temperature. In most cases, it increases proportionally with temperature: although, there are a few exceptions to this rule.

The solubility also depends on the pressure, but its effect is generally imperceptible, pressures up to 2,000 atm and 3,000 atm generally have little or no effect on solubility of inorganic substances. Another factor influencing the solubility is the particle size, a solution can reach more easily saturation equilibrium if the solute particles are very small (Mullin 1972).

Pure solution (solution formed by a solute and a solvent) is only used in analytical laboratories, while the solutions used in crystallization processes at industrial level, are invariably impure (solution formed by a solvent, a main solute and one or more solutes considered as impurities). The presence of impurities in a saturated solution has a significant impact on the solubility characteristics of the main solute.
If on a binary saturated solution, which is made of A (solid solute) and B (a liquid solvent), a certain amount of a third component C (also soluble in B) is added, there are four possibilities (Mullin 1972):

- The system remains in its original state of saturation, although this happens very rarely.
- Component C can chemically react with A to form a complex compound, completely altering the nature of the system.
- The presence of component C causes the supersaturated solution in ratio of component A, which begins to precipitate. This effect is known as salting-out.
- The presence of component C makes the solution turn into unsaturated in relationship to component A. This effect is known as salting-in.

2.1.2Density

The density $\rho$ is a physical property defined as the mass per unit volume of a given substance. Overall, density substances varies when pressure or temperature change. In the case of pure substances such as water, usually with increasing temperature the density decreases, with some exceptions to the rule. Pure water, between 0 °C and 4 °C density increases along with temperature; whereas, from the 4 °C upwards it decreases as the temperature increases.

For simple aqueous solutions there is a different behavior. With increasing temperature, the water molecules begin to move faster, this increase in speed of each molecule creates larger spaces between them, allowing the entry of larger amount of solute in the water structure, hence the solubility increases. Consequently, the mass of the solution increases as the density value. This phenomenon happens in most cases, with some exceptions. In order to explain the change in density multicomponent aqueous solutions, it is necessary to use the concepts of salting-in and salting-out.
2.1.3 Refractive index

The principle of refractometry lies in the change of the propagation speed when the electromagnetic radiation passes through a boundary between two media. According to this principle, the refractive index of $n_D$ is defined as the ratio between the speed of the radiation in vacuum ($c_L = 3 \cdot 10^8$ m/s) and the speed at which $c_b$ through a certain medium of specific features, for a defined light frequency value (Reis, Lampreia et al. 2010).

The measuring principle of the refraction index is based on the change of direction experienced by the beam of light passing from one medium to another, both of different density (Snell Law). This law states that the ratio of the refractive indexes $n_1$ and $n_2$ is proportional to the ratio between the angle of refraction $\theta_2$ and incidence angle $\theta_1$. Snell Law is represented as:

$$\frac{n_1}{n_2} = \frac{\text{sen} \theta_2}{\text{sen} \theta_1}$$  \hspace{1cm} (2.1)

The refractive index has different applications as the qualitative identification of compounds; determining purities of samples and quantitative analysis of solutions.

2.1.4 Viscosity

The dynamic viscosity $\mu$ of a fluid is the property to withstand the speed at which the deformation performs when shear forces act on it. Often the expression $\nu$ kinematic viscosity, which is obtained dividing $\mu$ between fluid density $\rho$ is used.

The temperature influences differently to the viscosity of liquids and gases due to the difference in their molecular structure.
In liquids, if there is low temperature, their molecules are quite close together, with strong cohesive forces between them, resulting in greater resistance to movement. As temperature increases, the cohesive forces between molecules are reduced with a corresponding reduction in the resistance to movement. Because viscosity is an indicator of the resistance to movement, it follows that the viscosity decreases with increasing temperature of a liquid.

In connection to the gas, molecules are sufficiently spaced and intermolecular forces are negligible, in this case for gases resistance to relative movement arises due to exchange of the amount of movement of molecules between adjacent layers. As the molecules are transported from a volumetric region of low speed by the random motion, until they are mixed with molecules of a higher molecular region speed. There is an exchange of momentum that is resistant to relative movement between adjacent layers. Consequently, it is concluded that if the gas temperature is increased randomly, molecular activity increases and as well as its viscosity.

### 2.1.5 Electrical conductivity

Electrical conductivity $\kappa$ is defined as the ability of solutions, for example electrolytes to conduct electrical power. Virtually, pure water does not conduct electricity, however the water with dissolved salt does. Positively charged ions and negatively ones are the leading power, driven amount depends on the number of ions present and its mobility.

In most aqueous solutions, the higher the temperature, the greater the amount of dissolved ions and decrease the viscosity of water, then they will move more quickly, more electric power. This phenomenon occurs to a certain point at which the electrical conductivity starts to decrease, because the solution is so saturated that restricts freedom of movement.
2.2 Solubility, Density, Refractive Index, Viscosity and Electrical Conductivity of Aqueous Solutions of Sodium Sulfate and Lithium Sulfate Saturated in Boric Acid at 293.15, 298.15, 303.15, 308.15 and 313.15 K

The solubility, density, refractive index, viscosity and electrical conductivity for aqueous solutions of Li$_2$SO$_4$ and Na$_2$SO$_4$ saturated in H$_3$BO$_3$, from 0 to 3.380 mol·kg$^{-1}$ for Na$_2$SO$_4$ and 3.1492 mol·kg$^{-1}$ for Li$_2$SO$_4$, over the temperature range from 293.15 K to 313.15 K have been determined. These physical properties were represented by equations as functions of temperature and each salt concentration. This information is useful for evaluating the physical properties of aqueous solutions saturated in H$_3$BO$_3$ in the range of concentrations of Na$_2$SO$_4$ and Li$_2$SO$_4$ and temperatures studied.

2.2.1 Experimental Methodology

Materials

The chemical compounds used and their characteristics are described in Table 2.1.

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Source</th>
<th>Mass Fraction Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boric acid</td>
<td>Merck</td>
<td>0.995</td>
</tr>
<tr>
<td>Lithium sulfate Monohydrated</td>
<td>Merck</td>
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</tr>
<tr>
<td>Sodium sulfate</td>
<td>Sigma-Aldrich</td>
<td>0.995</td>
</tr>
<tr>
<td>(2R, 3R, 4R,5R)-hexan-1,2,3,4,5,6-hexol</td>
<td>Merck</td>
<td>0.995</td>
</tr>
</tbody>
</table>

To remove the humidity of the boric acid and the sodium sulfate, and the water molecule of lithium sulfate monohydrate, boric acid was dried in an oven at 333.15 K and the salts at 393.15 K respectively for 24 h double distilled and deionized water (electrical conductivity of 0.0054 μS·cm$^{-1}$) were used in all procedures.
Apparatus and Procedures

Solution Preparation

Aqueous solutions saturated in boric acid were prepared for every temperature studied, based on the solubility data reported by Linke and Seidell (Linke and Seidell 1958). Boric acid and deionized water were massed and the resulting solution stirred to equilibrium. To prepare the ternary solutions, sodium sulfate or lithium sulfate monohydrate, a saturated solution in boric acid, and an excess of boric acid to ensure saturation in it were massed. An analytical balance with a precision of ± 0.0001g (Denver Instrument Co., model AA-200) was used to mass the reagents.

The solutions prepared were kept under agitation at constant temperature for 96 h (equilibrium time) in a phase equilibrium unit which is composed by a rotatory basket located inside a thermostatically controlled water bath. Ten concentration levels of lithium sulfate and sodium sulfate respectively were studied at temperatures ranging from 293.15 K to 313.15 K. For every concentration, two solutions were prepared to ensure repeatability. To determine the equilibrium time, aqueous solutions of lithium sulfate of 1.7002 mol·kg\(^{-1}\) H\(_2\)O, saturated in boric acid, were prepared and agitated at 303.15 K, using the phase equilibrium unit. Every 24 h a different solution was removed and its density was measured. That procedure was repeated until the density is constant, which indicates the solution has reached the thermodynamic equilibrium. The agitation time needed for the solutions to achieve that state is the equilibrium time.

Physical Properties Measurement

After equilibrium was reached the solutions were left settling for 12 h to improve the solid–liquid separation. For every solution a sample of 7 mL of liquid was removed, using a syringe filter (0.45 μm pore size), and diluted at 250 mL, for its chemical analysis in Na\(^+\) and Li\(^+\) by SM3111B- atomic absorption, 15 SO\(_2^-\) by SM 4500-SO\(_4^2-\)D15 and, H\(_3\)BO\(_3\) by complexation with (2R,3R,4R,5R)-hexan-1,2,3,4,5,6-hexol and titration by NaOH of concentration 0.1004 mol·kg\(^{-1}\) H\(_2\)O.
The composition of the residual wet solid phase was analyzed for Na\(^+\), Li\(^+\), SO\(_4\), and H\(_3\)BO\(_3\) by the methods mentioned above, to settle the solid in equilibrium with the saturated solution. The nature of this solid was determined by XRD when necessary. The reproducibility of the measured data was determined, compared to the H\(_3\)BO\(_3\) solubility data from Linke and Seidell (Linke and Seidell 1958).

To measure the other physical properties of the solutions a proper amount of sample was removed from every solution using a syringe filter (0.45 μm pore size).

Density was measured with a vibrating tube densimeter (Mettler Toledo, model DE50). It has a precision of 0.05 kg·m\(^{-3}\) and reproducibility better than ± 1 kg·m\(^{-3}\). The density was measured in triplicate per sample at each mentioned temperature. The apparatus was calibrated previously, using distilled deionized water as a reference substance, before measuring for every temperature. The densimeter has a temperature control (± 0.1 K). The time needed to reach temperature stability was 600 s. In the measuring cell about 2 mL of solution were introduced; the solution was not allowed to crystallize inside the cell.

Refractive index was measured with a refractometer (Mettler Toledo, model RE40) with a precision and reproducibility of ± 0.0001. These values are measured at the yellow doublet sodium D-line, with \( \lambda = 589 \text{ nm} \). Two drops of the sample were deposited on the prism of the instrument, using an airtight hypodermic syringe. Three measurements were made for each sample. After measurement, the solution was suctioned from the prism by a cleaning syringe; the prism was rinsed with distilled water and dried with tissue paper.
The kinematic viscosity was measured in triplicate for every solution with an automatic laser viscometer system (Schott-Gerate AVS 310). It measures the transit time of a liquid between two points in a capillary with a precision of ± 0.1 s. Two calibrated Micro-Ostwald capillaries with instrument constants, K, 0.01132 mm²·s⁻² and 0.01111 mm²·s⁻², respectively, were used. Their calibration was made using four cannon-certified viscosity standards (N1.0 (b), N2, S3 (a), and N4) to include the whole range of dynamic viscosity measurements. The measurements ranged from 5.2 mPa·s to 0.70 mPa·s at 293.15 K to 313.15 K. To measure the viscosity, 2 mL of solution was poured into the capillary and it was immersed inside a transparent thermostatic bath (Schott-Gerate CT 52) that had a temperature precision of ± 0.05 K. Dynamic viscosity data for every solution was determined using its kinematic viscosity and density measured.

Electrical conductivity was measured in triplicate for every solution using a conductivemeter (Orion, model 19700-27) with a precision < 0.5 % and reproducibility of ± 0.7 %. It was calibrated using a standard KCl solution, fixing a cell constant of 0.604 cm⁻¹. The conductivemeter cell was introduced in the flask containing the solution, and the instrument readings were recorded. After every measurement the flask was rinsed with distilled water and dried with tissue paper. To keep the temperature constant for the measurements, a digital immersion circulator (Thermo Haake, DC3) of 298.15 K to 423.15 K temperature range and a refrigerated water bath vessel (Thermo Haake, V) of 15 L capacity and refrigerant R134A for refrigeration down to 268.15 K were used.

### 2.2.2 Results and discussion

In Table 2.2 and Table 2.3 are presented the solubility $x_B$, density $\rho$, refractive index $n_D$, dynamic viscosity $\eta$, and electrical conductivity $\kappa$ of saturated solutions for $\text{H}_3\text{BO}_3 + \text{Li}_2\text{SO}_4 + \text{H}_2\text{O}$ and $\text{H}_3\text{BO}_3 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ as a function of mole fraction of Li$_2$SO$_4$, $x_1$, and Na$_2$SO$_4$, $x_2$, at temperatures $T$ of (293.15, 298.15, 303.15, 308.15, and 313.15)K.
Table 2.2 Solubility $x_B$, Density $\rho$, Refractive Index $n_D$, Viscosity $\eta$, and Electrical Conductivity $\kappa$ of Aqueous Solutions of Li$_2$SO$_4$ Saturated in H$_3$BO$_3$ $x_B$, for different Na$_2$SO$_4$ mole Fraction, $x_1$, at (293.15, 298.15, 303.15, 308.15 and 313.15) K$^a$

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<th>$\eta$/mPa·s</th>
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|                   |                   |             | \(T = 308.15\)  |      |                 |                 |
| 0.00              | 2.34              | H\(_3\)BO\(_3\) | 1018.8          | 1.3358 | 0.8048          | 0.027           |
| 0.18              | 2.19              | H\(_3\)BO\(_3\) | 1027.0          | 1.3375 | 0.8518          | 1.408           |
| 0.52              | 2.14              | H\(_3\)BO\(_3\) | 1044.4          | 1.3407 | 0.9573          | 3.440           |
| 0.89              | 2.13              | H\(_3\)BO\(_3\) | 1061.2          | 1.3440 | 1.0627          | 5.009           |
| 1.27              | 2.11              | H\(_3\)BO\(_3\) | 1078.4          | 1.3472 | 1.1913          | 6.275           |
| 1.86              | 1.92              | H\(_3\)BO\(_3\) | 1104.4          | 1.3522 | 1.3862          | 7.677           |
| 3.06              | 1.84              | H\(_3\)BO\(_3\) | 1148.7          | 1.3604 | 1.9321          | 9.014           |
| 3.81              | 1.70              | H\(_3\)BO\(_3\) | 1179.2          | 1.3652 | 2.3449          | 9.270           |
| 4.22              | 1.57              | H\(_3\)BO\(_3\) | 1194.5          | 1.3683 | 2.6724          | 9.235           |
| 5.10              | 1.44              | H\(_3\)BO\(_3\)+ Li\(_2\)SO\(_4\) | 1227.0          | 1.373  | 3.6191          | 8.945           |
Table 2.2 Continued

<table>
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<th>x_B · 10^2</th>
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<th>n_D</th>
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*T = 313.15 K

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*aStandard uncertainties u are u(T) = 0.06 K, u(x_B) = 0.0001, u(x_1) = 0.0002, and the combined expanded uncertainties U_c at 0.95 level of confidence and k = 2 are U_c(ρ) = 0.4 kg·m⁻³, U_c(n_D) = 0.0005, U_c(η) = 0.0194 mPa·s and U_c(κ) = 0.303 S·m⁻¹.

The standard uncertainty, u(x_1) is 0.0002 mol fraction and u(x_2), is 0.0003 mol fraction. It was determined following the guidelines for evaluating the uncertainty by NIST (Taylor 2009).

The accuracy of the measured data was determined as compared to the H₃BO₃ solubility data from Seidell and Linke (Linke and Seidell 1958) and its density, estimated using the correlation given by Novotný and Söhnel (Novotny and Sohnel 1988). The reproducibility for solubility is better than 0.0007 mol fraction and for density better than 0.6 kg·m⁻³. It was not possible to determine the accuracy for the other properties because there is no reported data in literature for aqueous solutions saturated in H₃BO₃ and the systems studied. The standard uncertainty for the temperature, u(T), is 0.06 K.
Table 2.3 Solubility $x_B$, Density $\rho$, Refractive Index $n_D$, Viscosity $\eta$, and Electrical Conductivity $\kappa$ of Aqueous Solutions of Na$_2$SO$_4$ Saturated in H$_3$BO$_3$ $x_B$, for different Na$_2$SO$_4$ mole Fraction, $x_2$, at (293.15, 298.15, 303.15, 308.15 and 313.15) K$^a$

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$T = 313.15$ K

$^a$Standard uncertainties $u$ are $u(T) = 0.06$ K, $u(x_B) = 0.0002$, $u(x_2) = 0.0003$, and the combined expanded uncertainties $U_c$ at 0.95 level of reliability and $k = 2$ are $U_c(\rho) = 4.2$ kg·m$^{-3}$, $U_c(n_D) = 0.0005$, $U_c(\eta) = 0.0243$ mPa·s and $U_c(\kappa) = 0.161$ S·m$^{-1}$.

**Solubility**

The data of boric acid determined is reported with repeatability more than 0.0017 and standard uncertainty, $u(x_B) = 0.0001$ mol fraction in presence of Li$_2$SO$_4$ and $u(x_B) = 0.0002$ mol fraction for Na$_2$SO$_4$. By applying the residual wet method (Castellan 1983), it was determined that the solid phase in equilibrium with the saturated solution is H$_3$BO$_3$, but for the last concentration of lithium sulfate and sodium sulfate, at every temperature, the solid phase is H$_3$BO$_3$ + Li$_2$SO$_4$·H$_2$O and H$_3$BO$_3$ + Na$_2$SO$_4$ respectively (eutectic point) as it was confirmed analyzing that points by XRD.
The measured data for the systems were illustrated in Figure 2.1 and Figure 2.2.

Figure 2.1 shows that boric acid solubility decreases with increases of mole fraction of lithium sulfate at constant temperature, due to a salting out effect, given by the structure making characteristic of Li$^+$ ion (Chanson and Millero 2006) and that boric acid solubility increases with mole fraction increases of sodium sulfate at constant temperature (see Figure 2.2), due to a salting in effect, for the structure breaking characteristic of the Na$^+$ ion (Chanson and Millero 2006).

In presence of the salts, the temperature effect was the same as in aqueous solutions of boric acid (Linke and Seidell 1958), increasing solubility with increases of temperature at constant salt concentration. The values of solubility of H$_3$BO$_3$ measured in aqueous solutions of Li$_2$SO$_4$ are smaller than in H$_2$O at the same temperature (Linke and Seidell 1958). The solubility values measured are similar to the ones in LiCl+H$_2$O (Chanson and Millero 2006). In both cases the solubility decreases as salt concentration increases. Mainly it can be assumed as the effect the Li$^+$ ions presence. This behavior, in presence of lithium sulfate, is inverse to that presented in aqueous solutions of NaCl (Digiacomo, Brandani et al. 1993), NaCl+KCl (Digiacomo, Brandani et al. 1993), K$_2$SO$_4$ (Kolthoff 1926, Digiacomo, Brandani et al. 1992), where the solubility of the H$_3$BO$_3$ increases with salt concentration increment.

Solubility increases as sodium sulfate concentration raises as it can be seen in Figure 2.2. This behavior is alike in presence of potassium Chloride (Chanson and Millero 2006), potassium sulfate (Digiacomo, Brandani et al. 1993), and inverse that in presence of lithium sulfate. The behavior of solubility is because of the presence of Na$^+$ ion, which is a structure breaker as K$^+$ ion (Chanson and Millero 2006). The salt effect increases with temperature increments.
Figure 2.1 Solubility, $x_1$, of boric acid as function of lithium sulfate mole fraction, $x_1$: This study (◇, $T = 293.15$ K; □, $T = 298.15$ K, △, $T = 303.15$ K, ○, $T = 308.15$ K, ×, $T = 313.15$ K); −, calculated from equation 2.2.

Figure 2.2 Solubility, $x_1$, of boric acid as function of sodium sulfate mole fraction, $x_2$: This study (◇, $T = 293.15$ K; □, $T = 298.15$ K, △, $T= 303.15$ K, ○, $T =308.15$ K, × , $T = 313.15$ K); −, calculated from equation 2.2.
To describe the experimental data, it was fitted to a curve according to the following equation:

\[
\ln\left(\frac{x_B(x_s, T)}{\text{mole fraction}}\right) = A_0(x_s) + B_0(x_s)\frac{T}{K} \tag{2.2}
\]

with

\[
A_0(x_s) = \sum_{i=0} a_{0i}(x_s/\text{mole fraction})^i \tag{2.3}
\]

\[
B_0(x_s) = \sum_{i=0} b_{0i}(x_s/\text{mole fraction})^i \tag{2.4}
\]

where \(T\) is the absolute temperature, \(i = 0, 1, 2...\) etc., \(s=1\) for \(\text{Li}_2\text{SO}_4\) and \(2\) for \(\text{Na}_2\text{SO}_4\). The nomenclatures for the salts are kept in all the manuscript. The coefficients \(a_{0i}\) and \(b_{0i}\) are constants and were estimated using the least-squares method. Four constants \((a_{00}, a_{01}, a_{02}, \text{ and } b_{00})\) and five constants \((a_{00}, a_{01}, a_{02}, a_{03}, \text{ and } b_{00})\) of the model were necessary to describe the experimental data in presence of lithium and sodium sulfates respectively. The values obtained for the constants are shown in Table 2.4 and Table 2.5. The 99.43 \%, in presence of \(\text{Li}_2\text{SO}_4\), and 99.83 \%, in presence of \(\text{Na}_2\text{SO}_4\), of the variance of the experimental data are explained by the model as was proven by the coefficients of multiple determination \(R^2 = 0.9943\) and \(R^2 = 0.9983\) respectively. The standard error of estimate is given by

\[
SD = \sqrt{\frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{n-p}} \tag{2.5}
\]

where \(y, \hat{y}, n,\) and \(p\) represent the observed value, predicted value, number of data points, and parameters, respectively. The calculated value of is 0.0003 mol fraction and 0.0002 mol fraction of \(\text{H}_3\text{BO}_3\) in presence of lithium sulfate and sodium sulfate respectively. Equation 2.5 is applied to calculate the fit estimating error for the rest of correlations reported in this study.
Density and Refractive index

Density values were measured with a repeatability more than 1.8 kg·m$^{-3}$. Figure 2.3 and Figure 2.4 present the experimental values as function of the lithium sulfate and sodium sulfate concentration for every temperature studied. It can be observed that density depends on the sulfate salt concentration, increasing its value as salt concentration increases. Regarding the temperature effect, density typically decreases with temperature increases for aqueous solutions, but it does not in the presence of lithium sulfate and sodium sulfate. This can be explained due to the fact that the solubility of boric acid increases with temperature at the same concentration of the sulfate salt; thus, increasing the total solid concentration.

The density values measured for the solutions of boric acid in presence of lithium sulfate were compared to the ones for aqueous solutions of this salt, at the same temperatures and concentrations, reported by Carton et al. (Carton, Sobron et al. 1995). It was found that the density measured has the same behavior with respect to the salt concentration and value as density of this salt in water; it is shown in Figure 2.3. This fact can be explained due to the fact that the lithium sulfate decreases the solubility of boric acid, its contribution being small to the density value. The behavior in presence of sodium sulfate is similar to the one described above, when it is compared to aqueous solutions of sodium sulfate.

Refractive index data were obtained having repeatability less than 0.0016. The refractive index depends on salt sulfate concentration, increasing as salt concentration increases, but it does not depend on temperature. This behavior is similar to the one shown by the density and it can be assumed that the total solid concentration increases with temperature.
Because the density and refractive index present similar conducts, they are described by the same relation with sulfate concentration. That function is expressed mathematically by equation 2.6.

\[ Y_j(x_s) = \sum_{i=0} a_{ij}(x_s/\text{mole fraction})^i \]  

(2.6)

where \( Y_j \) represents the density or the refractive index (it means, \( j = 1 \) or \( 2 \), respectively); the \( i \) subscript ranges as before. The coefficients \( a_{ij} \) are parameters of the model. The values of the parameters obtained are given in Table 2.4 and Table 2.5 for lithium sulfate and sodium sulfate respectively.

The density data were represented well by the model verifying that the influence of temperature is negligible as compared to that one of the salt concentration. The estimated error are 3.9 kg·m\(^{-3}\), in presence of Li\(_2\)SO\(_4\) and 3.6 kg·m\(^{-3}\) in presence of Na\(_2\)SO\(_4\). The combined expanded uncertainty, \( U_c \), was determined following the guidelines for evaluating the uncertainty by NIST (Taylor 2009). The value found at 0.95 level of confidence and \( k = 2 \), are \( U_c(\rho) = 0.4 \text{ kg·m}^{-3} \) and \( U_c(\rho) = 4.2 \text{ kg·m}^{-3} \) for Li\(_2\)SO\(_4\) and Na\(_2\)SO\(_4\) respectively. The model describes 99.72 % and 99.84 % of the variability of the experimental data (\( R^2 = 0.9972 \) and \( R^2 = 0.9984 \)) for the system in presence of Li\(_2\)SO\(_4\) and Na\(_2\)SO\(_4\) respectively. The calculated values are illustrated in Figure 2.3 and Figure 2.4.

The refractive index of the ternary solutions were fitted to the empirical model using \( a_{20} \) and \( a_{21} \); and \( a_{20}, a_{21} \) and \( a_{23} \) parameters (\( R^2 = 0.9951 \) and \( R^2 = 0.9868 \)) for the system in presence of Li\(_2\)SO\(_4\) and Na\(_2\)SO\(_4\) respectively. The values of the parameters obtained are given in Table 2.4 and Table 2.5. The calculated values are illustrated in Figure 2.5 and Figure 2.6.
Figure 2.3 Density $\rho$ of aqueous solutions of lithium sulfate saturated in boric acid as a function of lithium sulfate mole fraction, $x_1$: This study ($\bigcirc, T = 298.15$ K, $\Delta, T = 303.15$ K, $\blacklozenge, T = 308.15$ K, $\times, T = 313.15$ K); $-$, calculated from equation 2.6. Reference (Carton, Sobron et al. 1995) ($\bullet, T = 298.15$ K, $\blacktriangle, T = 303.15$ K, $\blacklozenge, T = 308.15$ K, $+$, $T = 313.15$ K).

Figure 2.4 Density $\rho$ of aqueous solutions of sodium sulfate saturated in boric acid as a function of sodium sulfate mole fraction, $x_2$: This study ($\bigcirc, T = 298.15$ K, $\Delta, T = 303.15$ K, $\blacklozenge, T = 308.15$ K, $\times, T = 313.15$ K); $-$, calculated from equation 2.6.
Figure 2.5 Refractive index $n_D$ of aqueous solutions of lithium sulfate saturated in boric acid as a function of lithium sulfate mole fraction, $x_1$: This study (◇, $T = 293.15$ K, □, $T = 298.15$ K, Δ, $T = 303.15$ K, ○, $T = 308.15$ K, ×, $T = 313.15$ K); —, calculated from equation 2.6.

Figure 2.6 Refractive Index $n_D$ of aqueous solutions of sodium sulfate saturated in boric acid as a function of sodium sulfate mole fraction, $x_2$: This study (◇, $T=293.15$ K, □, $T = 298.15$ K, Δ, $T = 303.15$ K, ○, $T=308.15$ K, ×, $T = 313.15$ K); —, calculated from equation 2.6.
Table 2. 4 Coefficients of equations 2.2 to 2.10 for the system H$_3$BO$_3$+Li$_2$SO$_4$+H$_2$O

<table>
<thead>
<tr>
<th>Property</th>
<th>$a_{i0}$</th>
<th>$a_{i1}$</th>
<th>$a_{i2}$</th>
<th>$b_{i0}$</th>
<th>$b_{i1}$</th>
<th>$b_{i2}$</th>
<th>$b_{i3}$</th>
<th>$R^2$</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_B$</td>
<td>-12.218</td>
<td>-4.5364</td>
<td>-80.777</td>
<td>0.027270</td>
<td></td>
<td></td>
<td></td>
<td>0.9943</td>
<td>0.0003</td>
</tr>
<tr>
<td></td>
<td>±0.236</td>
<td>±1.1983</td>
<td>±25.425</td>
<td>±0.000773</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\rho$</td>
<td>1022.0</td>
<td>4115.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.9972</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>±1.7</td>
<td>±63.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n_D$</td>
<td>1.3371</td>
<td>0.75684</td>
<td>-0.023667</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.9951</td>
<td>0.0009</td>
</tr>
<tr>
<td></td>
<td>±0.0004</td>
<td>±0.01534</td>
<td>±0.001169</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\eta$</td>
<td>6.9865</td>
<td>53.564</td>
<td>0.03044</td>
<td>0.088997</td>
<td></td>
<td></td>
<td></td>
<td>0.9974</td>
<td>0.0587</td>
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<tr>
<td></td>
<td>±0.3461</td>
<td>±32.870</td>
<td>±0.012870</td>
<td>±0.00683</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The confidence interval for all the parameters is reported at 0.95 level of confidence.

Table 2. 5 Coefficients of equations 2.2 to 2.10 for the system H$_3$BO$_3$+Na$_2$SO$_4$+H$_2$O

<table>
<thead>
<tr>
<th>Property</th>
<th>$a_{j0}$</th>
<th>$a_{j1}$</th>
<th>$a_{j2}$</th>
<th>$a_{j3}$</th>
<th>$b_{j0}$</th>
<th>$b_{j1}$</th>
<th>$R^2$</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_B$</td>
<td>-11.595</td>
<td>18.5</td>
<td>-312.63</td>
<td>2063.2</td>
<td>0.02519</td>
<td></td>
<td>0.9983</td>
<td>0.0002</td>
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<td></td>
<td>±0.131</td>
<td>±1.3</td>
<td>±59.72</td>
<td>±711.3</td>
<td>±0.00043</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\rho$</td>
<td>1018.8</td>
<td>6608.6</td>
<td>-21522</td>
<td></td>
<td></td>
<td></td>
<td>0.9984</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>±1.9</td>
<td>±208.8</td>
<td>±4082.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n_D$</td>
<td>1.3359</td>
<td>1.16057</td>
<td>-11.192</td>
<td>70.715</td>
<td></td>
<td></td>
<td>0.9986</td>
<td>0.0005</td>
</tr>
<tr>
<td></td>
<td>±0.0003</td>
<td>±0.06270</td>
<td>±3.002</td>
<td>±37.536</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\eta$</td>
<td>6.2175</td>
<td></td>
<td></td>
<td></td>
<td>-0.0208</td>
<td>-0.08760</td>
<td>0.9963</td>
<td>0.0477</td>
</tr>
<tr>
<td></td>
<td>±0.3862</td>
<td></td>
<td></td>
<td></td>
<td>±0.0013</td>
<td>±0.00158</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\kappa$</td>
<td>0.24250</td>
<td>592.21</td>
<td>-11993</td>
<td>81071</td>
<td></td>
<td></td>
<td>0.9958</td>
<td>0.236</td>
</tr>
<tr>
<td></td>
<td>±0.1471</td>
<td>±30.450</td>
<td>±1458.0</td>
<td>±18230</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The confidence interval for all the parameters is reported at 0.95 level of confidence.
**Dynamic Viscosity**

Dynamic viscosity data were measured with a repeatability of 0.0148 mPa·s. It was observed that viscosity increases as salt concentration increases at constant temperature. The viscosity decreases as the temperature value increases, because the solution packing decreases as the temperature rises. Therefore, the following equation was chosen to describe these data:

\[
\ln \frac{\eta(x_s,T)}{\text{mPa} \cdot \text{s}} = A_3(x_s) + B_3(x_s)\frac{T}{K}
\]

with

\[
A_3(x_s) = \sum_{i=0} a_{ij} (x_s/\text{mole fraction})^i
\]

\[
B_3(x_s) = \sum_{i=0} b_{ij} (x_s/\text{mole fraction})^i
\]

A_3 and B_3 represent potential series of x.

The experimental data are represented well by the model, using four parameters of the potential series (\(a_{30}, a_{32}, \text{and } b_{30} \text{ and } b_{31}\)) in presence of Li_2SO_4, with an estimated error of 0.0587 mPa·s, and three parameters (\(a_{30}, b_{30} \text{ and } b_{31}\)) in presence of Na_2SO_4, with an estimated error of 0.0477 mPa·s. The model explains 99.74 % and 99.63 % of the variability of the experimental data (\(R^2= 0.9974 \text{ and } R^2= 0.9963\)) for the systems in presence of Li_2SO_4 and Na_2SO_4 respectively. The values of the parameters obtained are given in Table 2.4 and Table 2.5. The calculated values are illustrated in Figure 2.7 and Figure 2.8.
**Figure 2.7** Viscosity $\eta$ of aqueous solutions of lithium sulfate saturated in boric acid as a function of lithium sulfate mole fraction, $x_1$: This study ($\bigtriangleup$, $T = 298.15$ K, $\bigcirc$, $T = 303.15$ K, $\times$, $T = 308.15$ K, $\times$, $T = 313.15$ K); $-$, calculated from equation 2.7. Reference (Carton, Sobron et al. 1995) ($\blacklozenge$, $T = 298.15$ K, $\blacktriangle$, $T = 303.15$ K, $\bullet$, $T = 308.15$ K, $+$, $T = 313.15$ K).

**Figure 2.8** Viscosity $\eta$ of aqueous solutions of sodium sulfate saturated in boric acid as a function of sodium sulfate mole fraction, $x_2$: This study ($\bigtriangleup$, $T = 298.15$ K, $\bigcirc$, $T = 303.15$ K, $\times$, $T = 308.15$ K, $\times$, $T = 313.15$ K); $-$, calculated from equation 2.7.
For the system $\text{H}_3\text{BO}_3+\text{Li}_2\text{SO}_4+\text{H}_2\text{O}$, the viscosity values measured, were compared to the viscosity of solutions of salt in water, at the same temperatures and concentrations, reported by Carton et al. (Carton, Sobron et al. 1995). It was found that the viscosities measured have the same behavior, in regards to the salt concentration and higher value than viscosities of this salt in water, as can be observed in Figure 2.7. It can be explained by a decrease in the solubility of boric acid by lithium sulfate; the acid contribution to the viscosity value being small.

**Electrical conductivity**

Electrical conductivity data were reported with a repeatability more than 1.01 S·m$^{-1}$. The conductivity depends on salt concentration, conductivity value increases with salt concentration until reaching a maximum level, after which it decreases. The presence of that maximum could be explained by the system reaching the maximum ionic mobility at the salt concentrations shown in Figure 2.9 and Figures 2.10 for $\text{Li}_2\text{SO}_4$ and $\text{Na}_2\text{SO}_4$ respectively. A further increase of concentration results in the reduction of the ionic mobility by complex species formation. Temperature affects the conductivity as well, increasing its value for the promotion of the ionic mobility of $\text{SO}_4^{2-}$, $\text{Li}^+$ and $\text{Na}^+$ ions because of the viscosity decreases. Thus a regression curve for electrical conductivity ($\kappa$) function of mole fraction of the salt ($x$) and temperature ($T$) was chosen. It is expressed by

$$\kappa(x_s, T)/\text{S} \cdot \text{m}^{-1} = A_4(x_s) + B_4(x_s) \frac{1}{T/\text{K}}$$

where $A_4$ and $B_4$ depend on $x_s$ exclusively, and it has the same functional behavior as equations 2.8 and 2.9, respectively. The parameters $a_{40}$, $a_{41}$, $b_{40}$, $b_{41}$, $b_{42}$, and $b_{43}$ were needed to describe the data with the model in presence of $\text{Li}_2\text{SO}_4$, with an estimated error of 0.204 S·m$^{-1}$, and five parameters ($a_{40}$, $a_{41}$, $a_{42}$, and $a_{43}$) in presence of $\text{Na}_2\text{SO}_4$, with an estimated error of 0.236 S·m$^{-1}$. 
The parameter values and the goodness of fit are given in Table 2.4 and Table 2.5. The conductivity data were fitted well ($R^2 = 0.9962$ and $R^2 = 0.9958$) as can be seen in Figure 2.10 and Figure 2.11 for Li$_2$SO$_4$ and Na$_2$SO$_4$ respectively.

**Figure 2.9** Electrical conductivity $\kappa$ of aqueous solutions of lithium sulfate saturated in boric acid as a function of lithium sulfate mole fraction, $x_1$: This study (◦, $T = 293.15$ K, □, $T = 308.15$ K, ×, $T = 313.15$ K); calculated from equation 2.10. Reference (Carton, Sobron et al. 1995)(●, $T = 293.15$ K; ●, $T = 298.15$ K, ▲, $T = 303.15$ K, $T = 308.15$ K, +, $T = 313.15$ K).

**Figure 2.10** Electrical conductivity $\kappa$ of aqueous solutions of sodium sulfate saturated in boric acid as a function of sodium sulfate mole fraction, $x_2$: This study (◦, $T = 293.15$ K, □, $T = 308.15$ K, ×, $T = 313.15$ K); calculated from equation 2.10.
The electrical conductivity in presence of lithium sulfate measured values was compared to the electrical conductivity of solutions of this salt in water at the same temperatures and concentrations reported by Carton et al. (Carton, Sobron et al. 1995).

It was observed that the electrical conductivity measured has the same behavior regarding the salt concentration and smaller value than the conductivity of this salt in water as shown in Figure 2.9. It can be attributed to the weak dissociation of boric acid, its contribution to the electrical conductivity value, being negligible compared to the lithium sulfate one and the fact than ionic mobilities of SO$_4^{2-}$ and Li$^+$ ions are lower than those ones corresponding to an aqueous solution of Li$_2$SO$_4$, because of the higher viscosity of the solutions studied.

In presence of Na$_2$SO$_4$ the solution conductivity does not depend on the temperature as it can be seen in Figure 2.10. The value of conductivity is determined by the salt concentration. The contribution of boric acid is negligible due to the fact it behaves as a non-electrolyte (Digiacomo, Brandani et al. 1992, Chanson and Millero 2006, Galleguillos, Molina et al. 2006). It was found that comparing the conductivity measured to the corresponding to sodium sulfate solution (McCleskey 2011). This is illustrated in Figure 2.14 at 298.15 K. The effect of temperature is negligible. It is attributed to the slightly increase of the conductivity of Na$_2$SO$_4$ in aqueous solutions with temperature raises (McCleskey 2011).

**Effect of the cation on the transport properties**

To analyze the effect of the cation on the properties, the measurements of the systems were compared to the corresponding of the system Na$_2$SO$_4$+H$_2$O (Wolf 1966, Söhnel and Novotný 1985, McCleskey 2011).

In Figure 2.11 and 2.12 are presented the comparison of the density and refractive index for the systems studied with sodium sulfate solutions (Söhnel and Novotný 1985) at 293.15 K. This comparison was made only at one temperature due to the insignificant effect of temperature in both ternary systems.
Figure 2.11. Density $\rho$ of aqueous solutions as a function of salt mole fraction, $x$, at $T=293.15$ K: (○, sodium sulfate solution saturated in boric acid, ●, lithium sulfate solution saturated in boric acid, ◊, sodium sulfate solution, reference (Söhnel and Novotný 1985)).

Figure 2.12. Refractive index $n_D$ of aqueous solutions as a function of salt mole fraction, $x$, at $T=293.15$ K: (○, sodium sulfate solution saturated in boric acid, ●, lithium sulfate solution saturated in boric acid, ◊, sodium sulfate solution, reference (Wolf 1966)).
It was found that the values of both properties in presence of sodium sulfate are greater than in lithium sulfate solutions, this difference can be attributed to the cation behavior, due to Na\(^+\) which is considered as a structure breaker with a higher ionic radii (1.07 Å) than Li\(^+\) (0.79 Å) (Mähler and Persson 2012) therefore it increases the boric acid solubility (see Figure 2.2) and the total mass per volume ratio.

In Figure 2.13 it can be seen that the effect of Li\(^+\) is greater than Na\(^+\) on the viscosity increment. This is explained due to the Li\(^+\) (water structure maker) compresses the volume solution, increasing the cohesion between species in solution. Therefore, the shear stress needed to initiate the movement.

**Figure 2.13** Viscosity $\eta$ of aqueous solutions as a function of salt mole fraction, $x$, at $T=293.15$ K: (○, sodium sulfate solution saturated in boric acid, ●, lithium sulfate solution saturated in boric acid, ◊, sodium sulfate solution, reference(Wolf 1966)).
For the electrical conductivity the Na\textsuperscript{+} has greater effect in the increasing of this property than Li\textsuperscript{+} as shown in Figure 2.14. This is due to the fact that Na\textsuperscript{+} increases the free spaces on the water structure, promoting the sodium ion mobility, unlike lithium ion that is a structure maker (Chanson and Millero 2006).

Figure 2. 14 Electrical Conductivity $\kappa$ of aqueous solutions as a function of salt mole fraction, $x$, at $T=298.15$ K: (○, sodium sulfate solution saturated in boric acid,●, lithium sulfate solution saturated in boric acid, ◊, sodium sulfate solution, reference (McCleskey 2011)).

2.3 Thermodynamic Modeling of the Solubility of the Systems H\textsubscript{3}BO\textsubscript{3}+Li\textsubscript{2}SO\textsubscript{4}+H\textsubscript{2}O and H\textsubscript{3}BO\textsubscript{3}+Na\textsubscript{2}SO\textsubscript{4}+H\textsubscript{2}O at 293.15 K to 313.15 K

To evaluate the impact of these impurities concentration in the crystallization yield and purity of the boric acid from brines, the measured data in the previous section were modeled. The solubility was fit using the Pitzer model.
2.3.1 Methodology

Thermodynamic Background

Pitzer Model

The general equation of the Free Excess Gibbs Energy given by the Pitzer model (Pitzer 1973, Pitzer 1986) could be simplified to represent the ternary system salt + neutral + water, obtaining the expression:

\[
\frac{G^{ex}}{RT} = f(I) + 2m_1m_2 (B_{ca} + m_2 \zeta C_{ca}) + 2m_1m_4 \lambda_{na} + 2m_1m_4 \lambda_{na} + m_4^2 \lambda_{mn} \\
+ m_4^3 \mu_{nan} + 3m_4^2 m_5 \mu_{nnn} + 3m_4^2 m_5 \mu_{nna} + m_4 m_5 \zeta_{nca} \tag{2.11}
\]

where

\[
f(I) = -\frac{4IA_0}{b} \ln(1 + bI^{1/2}) \tag{2.12}
\]

\[
B_{ca} = \beta_{ca}^{(0)} + \beta_{ca}^{(1)} h(x_1) + \beta_{ca}^{(2)} h(x_2) \tag{2.13}
\]

\[
h(x) = \frac{2}{x^2} [1 - (1 + x) \exp(-x)] \tag{2.14}
\]

\[
x_1 = \alpha_1 I^{1/2}, x_2 = \alpha_2 I^{1/2} \tag{2.15}
\]

\[
\zeta_{nca} = 6 \mu_{nca} + 3 \left( \frac{\mu_{nca}}{z_a} \right) + 3 \left( \frac{\mu_{nca}}{z_c} \right) \tag{2.16}
\]

The first term on the right side in equation (2.11) describes the electrostatic contribution of long range given by the modified Debye-Hückel expression (2.12).
In equation 2.11 the other terms represent the viral contributions of short range. The symbol \( R \) is the universal gases constant \( (R = 83.144 \text{ cm}^3\text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \), \( T \) the absolute temperature in K; \( m_c, m_a \) and \( m_n \) represent the cation, anion and neutral species molality respectively; \( z_c \) is the relative charge of the cation, and \( z_a \) corresponds to the anion; \( B_{ca} \) and \( \lambda_{nn} \) are the viral coefficients of second order for the ionic and neutral species respectively; \( C_{ca} \) and \( \mu_{nn} \) are the viral coefficients of third order. The coefficients \( \lambda_{nc}, \lambda_{nna}, \lambda_{nnc}, \mu_{nnc} \) and \( \xi_{nca} \) are mixing parameters coming from ionic and neutral interactions.

In the equation (2.12), \( A_\phi \) is the Debye-Hückel constant of the osmotic coefficient, \( b \) is a constant and has the value of 1.2 kg\(^{1/2} \cdot \text{mol}^{-1/2}\). In all equations the symbol \( I \) represents the ionic strength and is defined as:

\[
I = \frac{1}{2} \sum_{\text{ion}} m_{\text{ion}} z_{\text{ion}}^2 \tag{2.17}
\]

The terms \( \beta^{(0)} \), \( \beta^{(1)} \), \( \beta^{(2)} \) and \( C \) are adjusting parameters and have the typical meaning as in the Pitzer model; \( \alpha_1 = 1.4 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} \) and \( \alpha_2 = 12 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} \) which are parameters for 2:2 electrolytes. For other electrolytes the given values are \( \alpha_1 = 1.4 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} \) and \( \alpha_2 = 12 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} \).

**Solubility**

The solid-liquid equilibrium of aqueous solutions saturated in boric acid with is solid can be represented as:

\[
H_3BO_3(s) = H_3BO_3(aq) \tag{2.18}
\]

where the boric acid is considered in liquid phase as neutral specie. In equilibrium, the chemical potential of boric acid in solid (S) and liquid (L) phases are equal:

\[
\mu_B^S = \mu_B^L \tag{2.19}
\]
Relating equation 2.19 to the activity is obtained:

\[ \ln K_{PS} = \ln a_B^0 \]  
(2.20)

where \( K_{PS} \) is the solubility product and \( a_B^0 \) is the activity of boric acid in water (binary system). The activity of pure boric acid in solid phase is considered as the unity. The \( K_{PS} \) value is the same for salt aqueous solutions saturated in boric acid because of it depends on temperature only, consequently:

\[ \ln K_{PS} = \ln a_B^0 = \ln a_B \]  
(2.21)

and the solid -liquid equilibrium equation is:

\[ \ln \left[ \frac{m_B^0}{m_B} \right] = \ln \left[ \frac{\gamma_B}{\gamma_B^0} \right] \]  
(2.22)

with \( m_B^0, m_B, \gamma_B^0, \gamma_B \) are the boric acid solubility and activity coefficient in water and in a salt aqueous solution, respectively. The activity coefficient is obtained from the partial derivation of the excess Gibbs energy (equation 2.11) respect to boric acid moles at constant temperature.

Combining the activity coefficients for the binary and ternary systems with the solid-liquid equilibrium condition, Chanson and Millero (Chanson and Millero 2006) establish an equation to calculate the boric acid solubility in salt aqueous solutions which is referenced in this work:

\[ \ln \left[ \frac{m_B^0}{m_B} \right] = (2v_c \lambda_{Bc} + 2v_a \lambda_{Ba})m + v_c v_a \zeta_{Ba} m^2 \]  
(2.23)

where \( v_c \) is the cation coefficient and \( v_a \) the anion one, \( \lambda_{Bc}, \lambda_{Ba}, \zeta_{Ba-c} \) are fitting parameters related to the interactions between the boric acid and cation c and anion a, and cation and anion respectively, \( m \) is the salt molality. It must be noted, in equation 2.23, that to calculate the solubility, the \( K_{PS} \) is not necessary due to the fact that this parameter is replaced by the activity equality (equation 2.21).
The equation 2.23 can be expressed as:

\[ \ln[m_b] = a + bm + cm^2 \]  \hspace{1cm} (2.24)

The coefficients \(a\), \(b\) and \(c\) are related to the Pitzer parameters by:

\[ a = \ln[m_b^0] \]  \hspace{1cm} (2.25)

\[ b = -2(\nu_c \lambda_{bc} + 2\nu_a \lambda_{ba}) \]  \hspace{1cm} (2.26)

\[ c = -\nu_c \nu_a \zeta_{Bac} \]  \hspace{1cm} (2.27)

The \(a\) coefficient is estimated from the solubility of boric acid in water by the method of linear regression using experimental data from literature (Linke and Seidell 1958). The parameters, \(b\) and \(c\), are obtained by fitting the solubility of boric acid in the ternary system (in presence of a salt) using the least-squares method, minimizing the objective function:

\[ \sum_{i=1}^{n}(m_{B,exp} - m_{B,cal})^2 \]  \hspace{1cm} (2.28)

The mixing salt parameters (\(\lambda_{Bc}, \lambda_{Ba}, \zeta_{B-a-c}\)) can be calculated following the procedure given by Chanson and Millero (Chanson and Millero 2006). In this case, first the \(b\) parameters for the systems \(H_3BO_3+KCl+H_2O\) (1) and \(H_3BO_3 + K_2SO_4+H_2O\) (2) were estimated and applied them to the equation (2.26) obtaining:

\[ b_1 = -(2\lambda_{BK} + 2\lambda_{BCl}) \]  \hspace{1cm} (2.29)

\[ b_2 = -(2\lambda_{BK} + 2\lambda_{SO4}) \]  \hspace{1cm} (2.30)

In equation (2.29) \(\lambda_{BCl}\) is set to zero and \(\lambda_{BK}\) is obtained. This parameter, \(\lambda_{BK}\), is replaced in equation (2.30) and \(\lambda_{BSO4}\) obtained. The \(\lambda_{Na}\) or \(\lambda_{Li}\) are calculated replacing the \(\lambda_{BSO4}\) already obtained, in equation 2.26, using the respective \(b\) value for each system. The coefficient \(\zeta_{B-a-c}\) is estimated from equation (2.27) using the \(c\) estimated for the studied systems.
2.3.2 Results and Discussion

The solubility of boric acid in water measured and the reported by Linke (Linke and Seidell 1958) where used to obtain the $a$ parameter from equation 2.25. This parameter depends on temperature like the solubility. This parameter was expressed using a function of temperature according to the work of Chanson and Millero (Chanson and Millero 2006):

$$a = a_0 + a_1 T$$

(2.31)

where $a_0$ and $a_1$ are fitting parameters and $T$ is the absolute temperature. The coefficients $b$ and $c$ of equation 2.24 where fitted to the solubility of boric acid in the systems $\text{H}_3\text{BO}_3+\text{Na}_2\text{SO}_4+\text{H}_2\text{O}$, measured in this work, $\text{H}_3\text{BO}_3+\text{Li}_2\text{SO}_4+\text{H}_2\text{O}$, $\text{H}_3\text{BO}_3+\text{K}_2\text{SO}_4+\text{H}_2\text{O}$ at 298.15, 308.15 K (Linke and Seidell 1958), 305.15 K and 312.15 K (Digiacomo, Brandani et al. 1992), and $\text{H}_3\text{BO}_3+\text{KCl}+\text{H}_2\text{O}$ at 298.15 K, 308.15 K (Linke and Seidell 1958), 298.15 K (Chanson and Millero 2006), and at 303 K and 313 K (Linke and Seidell 1958). It was found that these coefficients are independent of temperature. The optimal values of the coefficients estimated ($a_0$, $a_1$, $b$, and $c$) are presented in Table 2.6.

### Table 2.6 Parameters and standard deviation of equation 2.24 for modeling boric acid solubility in salt aqueous solutions from 293.15 K to 313.15 K

<table>
<thead>
<tr>
<th>Salt</th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$b$</th>
<th>$c$</th>
<th>$R^2$</th>
<th>$SD$</th>
<th>$m_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$SO$_4$</td>
<td>-8.5077</td>
<td>0.0283</td>
<td>-0.0457</td>
<td>-0.0275</td>
<td>0.9916</td>
<td>0.02</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>$\pm0.4996$</td>
<td>$\pm0.0016$</td>
<td>$\pm0.0145$</td>
<td>$\pm0.0062$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>-8.5077</td>
<td>0.0283</td>
<td>0.2980</td>
<td>-0.0478</td>
<td>0.9947</td>
<td>0.03</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>$\pm0.4996$</td>
<td>$\pm0.0016$</td>
<td>$\pm0.0134$</td>
<td>$\pm0.0050$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>-8.5077</td>
<td>0.0283</td>
<td>0.5546</td>
<td>-0.1388</td>
<td>0.9928</td>
<td>0.03</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>$\pm0.4996$</td>
<td>$\pm0.0016$</td>
<td>$\pm0.0442$</td>
<td>$\pm0.0395$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>-8.5077</td>
<td>0.0283</td>
<td>0.0470</td>
<td>0.0042</td>
<td>0.9772</td>
<td>0.06</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>$\pm0.4996$</td>
<td>$\pm0.0016$</td>
<td>$\pm0.0198$</td>
<td>$\pm0.0039$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$The confidence intervals for all the parameters are reported at 0.95 level of reliability.
In Figures 2.15 to 2.17 the experimental and estimated solubility are compared to verify the goodness of the fitting for the systems Li$_2$SO$_4$ + H$_3$BO$_3$ + H$_2$O, Na$_2$SO$_4$ + H$_3$BO$_3$ + H$_2$O and K$_2$SO$_4$ + H$_3$BO$_3$ + H$_2$O. The estimations of the solubility of boric acid in the systems at 300.65 K, 305.65 K and 310.65 K are also presented, in these figures, to demonstrate the suitability of the model to calculate the solubility at different temperatures.

In Figure 2.16 it can be observed that adding lithium sulfate, the solubility of boric acid decreases. It could be attributed to the competence of ions and boric acid for water molecules, therefore a salting out effect is produced. The magnitude of this effect depends on the sign and value of the $c$ coefficient of equation 2.24, and is proportional to the square of the salt molality $m_1$. The $c$ value is shown in Table 2.7.

**Figure 2.15** Solubility of boric acid $m_B$ as a function of lithium sulfate molality $m_2$:

This study (◇, $T = 293.15$ K; □, $T = 298.15$ K, △, $T = 303.15$ K, ○, $T = 308.15$ K, ●, $T = 313.15$ K); ---, $T=300.65$ K, --, $T=305.65$ K, ···, $T=310.65$ K ,—, $T=293.15K$, 298.15 K, 303.15 K, 308.15 K, 313.15 K calculated from equation 2.24.
Figure 2.16 Solubility of boric acid $m_B$ as a function of sodium sulfate molality $m_2$: This study (◇, $T = 293.15$ K; □, $T = 298.15$ K, Δ, $T = 303.15$ K, ◦, $T = 308.15$ K, ●, $T = 313.15$ K); ---, $T=300.65$ K, ---, $T=305.65$ K, ⋆, $T=310.65$ K, —, $T=293.15$ K, 298.15 K, 303.15 K, 308.15 K, 313.15 K calculated from equation 2.2.4.

The Figure 2.16 shows that the solubility of boric acid increases for the whole range of sodium sulfate, $m_2$, solutions studied (0 to 3.4) mol/kg$^{-1}$ at (293.15 to 313.15) K. It is due to the interactions between acid and water molecules are promoted, being the salting in effect the main one. This fact is supported by the great positive value of the coefficient $b$ shown in Table 2.6.

Figure 2.17 Solubility of boric acid $m_B$ as a function of potassium sulfate molality $m_3$: This study (□, $T = 298.15$ K, Δ, $T = 305.15$ K, ●, $T = 313.15$ K); ---, $T=300.65$ K, ---, $T=308.15$ K, ⋆, $T=310.65$ K , —, $T=293.15$ K, 298.15 K, 303.15 K, 308.15 K, 313.15 K calculated from equation 2.24.
In presence of potassium sulfate ($m_3$), the solubility of boric acid increases as shown in Figure 2.17. It is the same behavior as in presence of sodium sulfate (see Figure 2.12). It can be explained by a salting in effect, produced by the presence of the K$^+$ ion. The extent of this effect depends on the sign and value of the $b$ coefficient of equation 2.24. The $b$ value is shown in Table 2.6.

It was found that the values of the $b$ and $c$ coefficients do not depend on concentration neither temperature at the concentration nor temperature ranges studied, but the $a$ parameter is temperature dependent. That is why parallel curves are obtained to represent the salting in and salting out effects at different temperatures.

<table>
<thead>
<tr>
<th>Salt</th>
<th>$\lambda_{BC}$</th>
<th>$\lambda_{Ba}$</th>
<th>$\zeta_{B,a-c}$</th>
<th>$m_{max}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$SO$_4$</td>
<td>0.127</td>
<td>-0.230</td>
<td>0.014</td>
<td>5.2</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>0.087$^b$</td>
<td>-0.205$^c$</td>
<td>-0.055$^c$</td>
<td>2.8</td>
<td>(Chanson and Millero 2006)</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>0.041</td>
<td>-0.230</td>
<td>0.024</td>
<td>3.4</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>0.028$a$</td>
<td>-0.205$^c$</td>
<td>-0.065$^d$</td>
<td>2.7</td>
<td>(Chanson and Millero 2006)</td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>-0.024</td>
<td>-0.230</td>
<td>0.069</td>
<td>1.2</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>-0.026$^f$</td>
<td>-0.205$^c$</td>
<td>-0.043$^g$</td>
<td>2.8</td>
<td>(Chanson and Millero 2006)</td>
</tr>
</tbody>
</table>

$^a$ It was estimated using the average $b=0.4065$ ($a=-0.4065$) from the system H$_3$BO$_3$+LiCl+H$_2$O at 298.15 K and $m_{max}=5.2$, $\lambda_{BC}=0$.

$^b$ It was estimated using the average $b=-0.0545$ ($a=0.0545$) from the system H$_3$BO$_3$+NaCl+H$_2$O at 29815 K and $m_{max}=4.8$, $\lambda_{BC}=0$.

$^c$ It was estimated using the average $b=-0.1725$ ($a=0.1725$) from the systems H$_3$BO$_3$+Na$_2$SO$_4$+H$_2$O and H$_3$BO$_3$+K$_2$SO$_4$+H$_2$O at 298.15 K. and $m_{max}=0.5$, $\lambda_{BC}=0$.

$^d$ It was estimated using the average $b=-0.01725$ ($a=0.1725$) from the systems H$_3$BO$_3$+Na$_2$SO$_4$+H$_2$O and H$_3$BO$_3$+K$_2$SO$_4$+H$_2$O at 298.15 K. and $m_{max}=0.5$, $\lambda_{BC}=0$.

$^e$ It was estimated using the average $\zeta_{B,SO_4,Li}=2\zeta_{B,Cl,Li}+\zeta_{B,SO_4,Na}^a2\zeta_{B,Cl,Na}$. $\zeta_{B,Cl,Li}$ = -0.004, $\zeta_{B,SO_4,Na}=-0.065$ and $\zeta_{B,Cl,Na}=0.008$.

$^f$ It was estimated using the average $c=0.065$ ($b=-0.065$) from the system H$_3$BO$_3$+Na$_2$SO$_4$ at 298.15 K. and $m_{max}=0.5$

$^g$ It was estimated using the average $c=0.0505$ ($a=-0.0505$) from the system H$_3$BO$_3$+KCl+H$_2$O at 298.15 K. and $m_{max}=3.978$, $\lambda_{BC}=0$.

$^h$ It was estimated using the average $c=0.043$ ($b=-0.043$) from the system H$_3$BO$_3$+K$_2$SO$_4$ at 298.15 K. and $m_{max}=0.5$.
The mixing salt parameters were calculated following the procedure described in the solubility section (equations 2.26 to 2.29). The values of the coefficient $b$ for the systems used are given in Table 2.6. The determined parameters and their average maximum salt concentration of validity are presented in Table 2.7.

The parameters obtained were compared to the reported by Chanson and Millero (Chanson and Millero 2006). They estimated the interaction parameters shown in Table 2.7 using fitting parameter $a$ and $b$ which are equivalent to the $-b$ and $-c$ coefficients of this study respectively. The detailed procedure of estimation for each interaction parameter and their equivalents $b$ and $c$ are described below. The original parameters from (Chanson and Millero 2006) are given in brackets.

It was found that the value of the parameter $\lambda_{BSO4}$ estimated in this study is similar to the literature value as exposed in Table 2.7. Chanson and Millero used the systems $H_3BO_3+Na_2SO_4+H_2O$ and $H_3BO_3+K_2SO_4+H_2O$ at 298.15 K and $m_{max}=0.5$, with an average $b= -0.1725$ ($a=0.1725$) to calculate the interaction parameters. In this study the systems employed were $H_3BO_3+KCl+H_2O$, $H_3BO_3+K_2SO_4+H_2O$ from 293.15 K to 313.15 K and $m_{max}=3.5$.

The parameter $\lambda_{BLi}$ is 1.5 times higher than the one reported by Chanson and Millero. In this case the references system used was $H_3BO_3+Li_2SO_4+H_2O$ and the $\lambda_{BSO4}$ previously estimated, unlike the literature parameter that was estimated from the system $H_3BO_3+LiCl+H_2O$ at 29815 K and $m_{max}=5.2$, making the $\lambda_{BCl}=0$, and using an average $b= 0.4065$ ($a=-0.4065$).

The parameter $\lambda_{BNa}$ is 1.5 times greater than the literature value. This variance is mainly caused by the reference systems used. In this study, the parameter was obtained from the $b$ corresponding to the system $H_3BO_3+Na_2SO_4+H_2O$ and the $\lambda_{BSO4}$ previously estimated, but in literature the parameter was estimated from the system $H_3BO_3+NaCl+H_2O$ at 298.15 K and $m_{max}=4.8$, making the $\lambda_{BCl}=0$, and using an average $b= -0.0545$ ($a=0.0545$).
The parameter $\lambda_{BK}$ is similar to the one reported in literature. This is due to the reference system used was the same, $H_3BO_3+KCl+H_2O$, making $\lambda_{BCl}=0$ and it is in the range of concentration studied, $m_{max}=3.978$.

The parameter $\zeta_{B-SO4-Li}$ has opposite sign and it is 0.6 times smaller than the one reported by Chanson an Millero (Chanson and Millero 2006). This coefficient was calculated from equation 2.27, the c value used is shown in Table 2.7, for the system $H_3BO_3+Na_2SO_4+H_2O$. Chanson and Millero assessed this value using an additive rule. It was estimated adding the parameter $\zeta_{B-Cl-Li}=-0.008$, $\zeta_{B-SO4-Na}=-0.065$ and $\zeta_{B-Cl-Na}=-0.004$ for the systems $H_3BO_3+LiCl+H_2O$, $H_3BO_3+Na_2SO_4+H_2O$ and $H_3BO_3+NaCl+H_2O$ respectively at 298.15 K. The equation used was: $\zeta_{B-SO4-Li}=2\zeta_{B-Cl-Li}+\zeta_{B-SO4-Na}-2\zeta_{B-Cl-Na}$. This parameter is valid until 2.8 mol·Kg$^{-1}$.

The parameter $\zeta_{B-SO4-Na}$ has opposite sign and it is 2.7 times smaller than the one reported by Chanson and Millero. This value was obtained directly from equation 2.27, using the c value given in Table 2.7 for the system $H_3BO_3+Na_2SO_4+H_2O$. The value estimated by Chanson and Millero, was obtained following the same procedure. They used the average $c=0.065$ ($b=-0.065$) for the system $H_3BO_3+Na_2SO_4$ at 298.15 K. and $m_{max}=0.5$. It was observed that its $\zeta_{B-SO4-Na}$ does not reproduce the c value from where it was calculated. To verify if it was a tipping mistake, this parameter was re-estimated from their reference data (Digiacomo, Brandani et al. 1993), the c value obtained was 0.130.

The parameter $\zeta_{B-SO4-K}$ has opposite sign and it is 3.9 times greater than the reported by Chanson an Millero (Chanson and Millero 2006). This value was obtained directly from equation 2.26, using the c value given in Table 2.7 for the system $H_3BO_3+K_2SO_4+H_2O$. Chanson and Millero, obtained this parameter using the average $c=0.043$ ($b=-0.043$) for the system $H_3BO_3+K_2SO_4$ at 298.15 K. and $m_{max}=0.5$. As in the case of $\zeta_{B-SO4-Na}$, it was found that $\zeta_{B-SO4-K}$ does not reproduce the c value from where it was calculated. To verify it the c value was re-estimated from their reference data (Linke and Seidell 1958), the value estimated is 0.139.
The comparison of the fitting of the solubility of boric acid in lithium, sodium and potassium sulfates, by the model proposed in this work, are shown in Figures 2.18 to 2.21. The results showed that the proposed model represents the experimental data very well, but the one proposed by Chanson and Millero (Chanson and Millero 2006) does not.

**Figure 2.18** Solubility of boric acid $m_B$ as a function of lithium sulfate molality $m_1$ at 298.15 K (○, experimental, --, calculated from equation 2.24,···, calculated from equation 2.23 using the mixing parameters from (Chanson and Millero 2006) given in Table 2.7).

For the system $\text{H}_3\text{BO}_3+\text{Li}_2\text{SO}_4+\text{H}_2\text{O}$ the results showed fit well with the data by the model used in this study, but the Chanson model, using the mixing parameters estimated from systems with common ion, fits the data until concentration of 0.301 molkg$^{-1}$ as shown in Figures 2.18.

For the system $\text{H}_3\text{BO}_3+\text{Na}_2\text{SO}_4+\text{H}_2\text{O}$ the results showed that the proposed model represents the experimental data very well, but the one, proposed by Chanson and calculated using the mixing parameters estimated from systems with common ion, fits the data until concentration of 0.563 molkg$^{-1}$ as shown in Figures 2.19.
Figure 2.19 Solubility of boric acid $m_B$ as a function of sodium sulfate molality $m_2$ at 298.15 K (○, experimental, —, calculated from equation. 2.24, ⋯, calculated from equation. 2.23 using the mixing parameters from (Chanson and Millero 2006) given in Table 2.7).

Figure 2.20 Solubility of boric acid $m_B$ as a function of potassium sulfate molality $m_3$ at 298.15 K (○, experimental, —, calculated from equation 2.24, ⋯, calculated from equation 2.23 using the mixing parameters from (Chanson and Millero 2006) given in Table 2.7).
Figure 2.21 Solubility of boric acid \( m_B \) as a function of potassium sulfate molality \( m_3 \) at 298.15 K (○, experimental, –, calculated from equation 2.24, ..., calculated from equation 2.23 using the mixing parameters from (Chanson and Millero 2006) given in Table 2.7).

In the case of the system \( \text{H}_3\text{BO}_3 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O} \) the results showed that both models, this study and the Chanson and Millero represented well the experimental data at 298.15 K as can be seen in Figure 2.20.

For the system \( \text{H}_3\text{BO}_3 + \text{Li}_2\text{SO}_4 + \text{H}_2\text{O} \) and \( \text{H}_3\text{BO}_3 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \) the behavior of the model is similar to the presented in Figures 2.18 and 2.19 at the other temperatures studied, but for the system \( \text{H}_3\text{BO}_3 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O} \) deviation from the experimental data are presented at higher temperatures for the Chanson model as shown in Figure 2.21 due to their parameters are only valid at 298.15 K.

The reason why the model given by Chanson and Millero (Chanson and Millero 2006) does not describe properly the solubility of boric acid in the system studied, is the difference of the values of \( \zeta_{B,a,c} \) as can be seen in Table 2.7. For all the systems studied, this parameter is negative, 2.7 and 3.9 times greater than the values found for \( \text{H}_3\text{BO}_3 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \) and \( \text{H}_3\text{BO}_3 + \text{Li}_2\text{SO}_4 + \text{H}_2\text{O} \) and 0.6 times smaller for \( \text{H}_3\text{BO}_3 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O} \); although, the concentration range is slightly smaller than the corresponding to the systems, 3.4 mol\cdot kg\(^{-1}\). This difference can be attributed to the estimation of the \( b \) coefficient (\( c \) in the reference (Chanson and Millero 2006)) mainly, restricted only to temperature of 298.15 K.
To show the effect of different cations with common anion in the solubility of boric acid, in Figure 2.22 the solubility of boric acid in lithium sulfate, sodium sulfate and potassium sulfate at 313.15 K is presented. They were estimated using equation 2.24. The behavior of solubility at the other temperatures is similar.

Figure 2.22 Solubility of boric acid $m_B$ as a function of salt sulfate molality $m$ at 313.15 K (--, Li$_2$SO$_4$, - - , Na$_2$SO$_4$, ---, K$_2$SO$_4$) calculated from equation 2.24.

The Figure 2.22 shows that the presence of different cations with common anion affects in a different way to the solubility of boric acid. The effect follows this order, determined according to the decrease of boric acid solubility or by the value of the $b$ parameter (salting coefficient) at 313.15 K: Li$^+$ $>$ Na$^+$ $>$ K$^+$, which can be attributed to the increase of their ionic radii coordinated with 6 water molecules (Li$^+$=0.79 Å, Na$^+$=1.07 Å and K$^+$=1.38 Å) (Mähler and Persson 2012); therefore, the capacity to form hydration shells. This classification is only valid in aqueous sulfate solutions due to the effect of the structure makers (Li$^+$) or structure breakers (Na$^+$ and K$^+$) is also related to the salting coefficient which is a function of the cation – boric acid interaction, $\lambda_{Bc}$, and the anion (common ion) – boric acid interaction, $\lambda_{Ba}$. That is, boric acid is more soluble in sulfate salt solutions than in chloride solutions. (Chanson and Millero 2006)
It can be inferred from these results that lithium sulfate is a precipitant agent for boric acid and that its behavior is attributed to the salting out effect of Li$^+$ ion, sodium sulfate and potassium sulfates increase the boric acid solubility, this salting in effect is due to the presence of Na$^+$ and K$^+$ ions. The presence of these salts can be unfavorable for the crystallization of boric acid, due to decreases the supersaturation therefore the yield of the process.

2.3 Effect of sulfate ion

The SO$_4^{2-}$ ion modifies the water structure. It attracts negatively charged water molecules from the solution, which focused on the positive side of the dipole form layers of hydration around that ion (Al-Jibbouri, 2002; Kowacz and Putnis, 2008), whose process is favorable because of high sulfate hydration enthalpy (-1145 kJ / mol), the result making more structured the solution; but the final effect of the sulfate salt on the solubility and the transport properties is determined by the cation.

Experimental data show that density, refractive index and viscosity increase with increasing salt sulfates concentration in presence of lithium, sodium and potassium ions. This is explained by the interactions of Li$^+$, Na$^+$, K$^+$ and SO$_4^{2-}$ ions with boric acid, as suggested the parameters associated with the concentration of salt sulfates in correlations of viscosity, refractive index and electrical conductivity.

In the case of solubility the final result (increase or decrease) depends on the cation as discussed above. In presence of Li$^+$ the solubility decreases (water structure is increased) but in company to Na$^+$ and K$^+$ the solubility decreases (water structure is decreased).
2.4 Conclusions

This work provides reliable data of solubility of boric acid, density, refractive index, dynamic viscosity, and electrical conductivity data of aqueous solutions of lithium and sodium sulfates saturated in boric acid at temperature ranges from (293.15 to 313.15)K. The experimental data were correlated by empirical equations, obtaining a good enough fit to be useful for evaluating the physical properties of aqueous solutions saturated in boric acid, in the range studied of concentrations of lithium sulfate and temperatures.

The solubility was described satisfactorily using an equation based on Pitzer model to obtain a good enough fit to be useful for evaluating the solubility of boric acid in sodium sulfate, potassium sulfate and lithium sulfate aqueous solutions, in the range studied of concentrations and temperatures. The model parameters are valid to maximum concentration of the salts, 3.3149 mol·kg\(^{-1}\) for \(\text{Li}_2\text{SO}_4\), 3.380 mol·kg\(^{-1}\) for \(\text{Na}_2\text{SO}_4\), and 1.245 mol·kg\(^{-1}\) for \(\text{K}_2\text{SO}_4\) from 293.15 K to 313.15 K.

The effect of the ions on the solubility of boric acid, in aqueous sulfate solutions, follows this order: \(\text{Li}^+ > \text{Na}^+ > \text{K}^+\), which can be attributed to the increase of their ionic radii, coordinated with 6 water molecules therefore the capacity to form hydration shells. It was determined that the lithium sulfate is a precipitant agent for boric acid and its behavior is attributed to the salting out effect of \(\text{Li}^+\) ion therefore its presence is favorable for the crystallization of boric acid, due to it the supersaturation increases; consequently, the yield of the process. Sodium sulfate and potassium sulfates increase the boric acid solubility; this salting in effect is due to the presence of \(\text{Na}^+\) and \(\text{K}^+\) ions. The presence of these salts can be unfavorable for the crystallization of boric acid, due to the decreasing of the supersaturation hence the yield.

It was found that the values of density and refractive index in presence of sodium sulfate are greater than in lithium sulfate solutions, this difference can be attributed to the cation behavior, due to \(\text{Na}^+\) is considered as a breaker structure with a higher ionic radii (1.07 Å) than \(\text{Li}^+\) (0.79 Å); therefore, it increases the boric acid solubility and the total mass per volume ratio.
The effect of Li\(^+\) is greater than Na\(^+\) on the viscosity increasing. This is explained due to the Li\(^+\) (water structure maker) compresses the volume solution, increasing the cohesion between species in solution, thus the shear stress needed to initiate the movement. For the electrical conductivity the Na\(^+\) has greater effect in the increasing of this property than Li\(^+\). This is due to the fact that Na\(^+\) increases the free spaces on the water structure, promoting the sodium ion mobility, unlike lithium ion that is a structure maker.
Chapter III

Effect of impurities on the crystallization of H$_3$BO$_3$ from the systems:

H$_3$BO$_3$+Na$_2$SO$_4$+H$_2$O and H$_3$BO$_3$+ H$_2$O+ Li$_2$SO$_4$: Growth rate and mechanism by atomic force microscopy, AFM and crystal size by batch crystallization and the FBRM and PVM probes
3.1 Theoretical framework

Crystallization can be defined as a phase change of the crystalline product which is obtained from a solution. A solution is a mixture of two or more species that form a single homogeneous phase. Typically a solution is formed by a solvent liquid and a solid solute at constant temperature $T$ and pressure $P$. The solution to be crystallized should be supersaturated. A solution is called supersaturated when the solute concentration exceeds the concentration of solute in the steady state (saturated) at a given temperature. The main methods to generate supersaturation are: Temperature change (mainly cooling), solvent evaporation, chemical reaction and changing the composition of the solvent (salting out) (Mersmann 2001).

The Ostwald-Myers diagram (Mersmann 2001), shown in Figure 3.1, illustrates the basis of all growth methods from solutions. The solid line represents a section of the curve for the solute / solvent system. The upper dotted line refers to the saturation line, which denotes the concentration and temperature where spontaneous nucleation occurs. The diagram can be evaluated based on three areas: a) The stable area (undersaturated), where crystallization is impossible b) The metastable zone (supersaturated), where the spontaneous nucleation is unlikely, but a crystal located in this area will grow and c) Unstable or labile zone where spontaneous nucleation and growth are likely.

![Ostwald-Miers diagram](image)

**Figure 3.1** Ostwald-Miers diagram for a solute / solvent system. Reproduced from (Mersmann 2001).
The crystallization of solutions is a 2 step process; the first step is the separation of the phase by the birth of crystals. The birth of crystals, is called nucleation, in which, solute molecules have formed the smallest possible size particles under the conditions present in the solution. The next step of the crystallization process is further growth of the nuclei, by addition of solute molecules from the supersaturated solution; this part of the crystallization process is known as crystal growth. The study of the kinetics of these processes is important because they together, with the residence time, determine the characteristics of the particulate product obtained in crystallizers (Mersmann 2001, Demopoulos 2009). The nucleation defines the initial shape and the crystals growth and size.

### 3.1.1 Nucleation

Depending on the mechanisms involved, nucleation is divided into: Primary nucleation (homogeneous and heterogeneous) and secondary nucleation (Demopoulos 2009).

The nucleation rate is defined as the rate at which nuclei formed (nuclei which have reached the critical size) enter the solution. This can be expressed as:

\[
B = \frac{1}{m} \frac{dN}{dt}
\]  

(3.1)

where \(N\) is the number of particles, \(t\) time, \(m\) solvent mass and \(B\) nucleation rate. Factors affecting the rate of nucleation are: supersaturation, presence of impurities, temperature, and agitation, among others (Mersmann 2001).

### 3.1.2 Growth

Crystals grows due to various mechanisms, which can be discussed under the following general approaches (Mersmann 2001): a) Theories of surface energy b) Theories of adsorption layer c) Kinematic theories c) Theories of reaction-diffusion and d) Birth and dispersion models.
The representation of a crystal growth from solution is often made by the two step model, which is based on kinematic theories. This model describes the growth of crystals as a superposition of two resistors: The diffusion through the boundary layer mass transfer, for example diffusion step, and incorporation of growth units in the crystal lattice, for example integration step. The slower step of the above is the controlling. Depending on the system, hydrodynamic, saturation, the first or second step can determine the whole process, or both steps can control the growth at different levels.

The complete concentration gradient, is divided into two parts, the first part c-c* within a diffusive-convective layer that causes transport diffusive-convective, while the second, cI-c* (I is the interface), it is decisive for the reaction of integration in the reaction layer. Growth is completely determined by diffusion and convection if: 
\[ c_I - c^* \ll c - c_I \], otherwise, it is controlled by the reaction of integration.

When the diffusive-convective transport takes place rapidly, the diffusive coefficient \( k_d \to \infty \), or reaction of integration takes place very slowly, the crystal growth is controlled by the reaction of integration that occurs in the crystal surface. The individual processes involved can be diverse and complex, so difficult to understand (Mersmann 2001).

A possible inhibition of integration may be, for example adsorption of impurities or foreign particles in the crystal surface (Demopoulos 2009). Then the particles should be desorbed or overgrown, which are processes that sometimes occur only at high supersaturation of the crystallizing substance. Large integration units, for example, organic substances are transported slowly by surface diffusion to the crystal surface, and must rotate about integration sites, until they are in a position to be integrated.
Surface structure and growth mechanism

During crystal growth, units collide with the crystal and are adsorbed on the surface due to the fact that the chemical bonds between the unit and the plane of the crystal face are strong enough for adsorption, but not to be adsorbed at a single site of the structure, the adsorbed units must move to find a place energetically favorable to integrate permanently; otherwise, the unit will return to the solution after a certain diffusion distance. This favorable integration sites come from the topology of the crystal surface, in other words, from the molecular structure of the crystal surface, and can be classified into terraces, steps and dislocations.

If in molecular terms, the surface is rough and has many dislocations, continued growth will occur, because the thermodynamic barriers are overcome. After a short distance of surface diffusion, each unit of growth that reaches the surface in a supersaturated solution is integrated in the crystal structure. If the crystal structure on the molecular scale is softer, growth is more difficult due to limited integration favorable sites. Different sources for sites of dislocations and steps, such as surface nucleation and screw dislocations, must be taken into account to describe quantitatively the growth rates in this case (See Figure 3.2).

Figure 3.2 Growth mechanisms. Reproduced from (Doherty, Lovette et al. 2008)
The crystal surface for high surface energies is soft. Therefore, it does not provide growth sites for growth units arriving. In practice, this is idealism is not met due to imperfections in the crystal lattices. Frank (1949) according to Mersmann (Mersmann 2001) assumes that the presence of dislocations in a spiral ending anywhere on the crystal surface are sources of favorable integration sites. Burton, Cabrera and Frank (Burton, Cabrera et al. 1951) developed a model (BCF) for growing crystals in which the surface of the crystal grows by the addition of growth units in dislocation sites, in an endless series of equidistant steps.

**Surface diffusion**

The BCF model describes the flow to dislocations for crystal growth from solutions when the diffusion of solute molecules either through the solution on the surface or edge of the steps is much slower than in the free crystal surface. For low supersaturation growth rate, $v_{BCF}$, is parabolic and is described by:

$$v_{BCF} = \frac{c^* N_A V_m D_{AB} k_b T}{2x_0 \gamma} \left[ \sigma(x_0) \right]^2$$

where $\gamma$ is the edge work, $N_A$ Avogadro number, $V_m$ molar volume in kmol/m$^3$, $k_b$ Boltzmann constant, $1.381 \times 10^{-23}$ J-K$^{-1}$, $D_{AB}$ diffusivity of A in B, m$^2$-s$^{-1}$, $T$ temperature in K, $c^*$ saturation concentration, $x_0$ distance between dislocations in m. and $\sigma(x_0)$ the dependent supersaturation on dislocations. Replacing the equivalence of $\gamma$ in equation 3.2 is obtained:

$$v_{BCF} = \frac{D_{AB} \left( \frac{c^*}{C_c} \right)^{4/3} \sqrt{S}}{0.828 d_m \ln \left( \frac{c^*}{C_c} \right)} \left[ \sigma(x_0) \right]^2$$

$d_m$ is the molecular diameter in m$^3$, $S$ the supersaturation and $c^*/C_c$ the dimensionless solubility.
The dependent supersaturation on dislocations, \( \sigma(x_0) \) is a function of the distances \( x_0 \) and \( y_0 \) which are dependent on supersaturation, \( \sigma \), the supersaturation ratio under these BCF model is represented by the equation:

\[
\frac{\sigma(x_0)}{\sigma} = \left[ 1 + \frac{2\pi a (\delta - y_0)}{x_0 y_0} + \frac{2a}{x_0} \ln \left( \frac{y_0}{x_0} \right) \right]^{-1}
\]

(3.4)

where \( a \) is the distance between steps and dislocations.

For low supersaturations, \( \sigma(x_0)/\sigma \) it is reduced to:

\[
\frac{\sigma(x_0)}{\sigma} = \left[ 1 + \frac{2a}{x_0} \ln \left( \frac{y_0}{x_0} \right) \right]^{-1}
\]

(3.5)

For high suspensions densities and crystal sizes larger than 100 μm, the surfaces do not present ideal spirals due to the fact they are deformed by collisions between the crystals and the impeller. The resultant surfaces have also fractures (sources of new dislocations, steps and macrosteps). Therefore the equation 3.4 should be modified according to experimental results. Replacing \( \sigma(x_0) \) by \( \sigma \) and adding a correction parameter \( A \), which may depend on the distances \( x_0 \) and \( y_0 \) which are functions of the \( \sigma \) and solubility \( c^*/C_c \), obtaining:

\[
\nu_{\text{BCF}} = A \frac{D_{AB}(c^*/C_c)^{4/3} \sqrt{S}}{d_m \ln (C_c / c^*)} \sigma^2
\]

(3.6)

For systems highly soluble \( 0.1 < c^*/C_c < 1 \), which are usually crystallized at low supersaturation, \( \sigma < 0.1 \), the ratio \( \sigma(x)/\sigma \) is about 0.1 as shown in Figure 3.3.
The linear growth rate, $G$, is the double of the $v_{BCF}$. Also the linear growth rate can be expressed as:

$$G = \frac{dL}{dt}$$  \hspace{1cm} (3.7)

where $L$ is the characteristic dimension of the crystal. The growth rate is affected by the supersaturation, presence of impurities, temperature, and agitation (Demopoulos 2009).

**Figure 3.3** Ratio $\sigma (x) / \sigma$ as a function of relative supersaturation, $\sigma$, for different dimensionless solubilities, $c^*/C_c$. Reproduced from (Mersmann 2001).

**Effect of impurities on the crystal growth**

In the crystal growth from solutions containing impurities, dislocations sites in the crystal surface are preferred for capturing impurities found in motion on the surface. Consequently, the kinetic effect of an impurity on the speed step advance and the growth rate can be considered to involve three steps: 1) Adsorption of impurities on the surface of diffusing impurities from the solution. 2) Migration of impurities adsorbed on the terraces of the surface 3) Adsorption of impurities migrating over the surface in areas free of steps and dislocations steps (kinks).
In the analysis of the kinetics of crystal growth from solutions containing impurities it is believed that the surface diffusion is important. Consequently, the direct integration of impurities at dislocations (kinks) is not significant (Sangwal 2007).

Kubota-Mullin model (Kubota and Mullin, 1995) essentially describes the steps 2 and 3. This assumes that impurities are adsorbed strongly along steps and act as barriers to their movement, being physically possible.

### 3.1.3 Surface coverage

During growth for established conditions, the crystal surface has a fixed number of sites available for adsorption, \( n_{\text{max}} \), a fraction of which is occupied if impurities are present. The amount of adsorption sites per occupied unit area on the surface, at a given temperature and impurity concentration, \( c_{\text{imp}} \), can be expressed by:

\[
\theta = \frac{n_{\text{ad}}}{n_{\text{max}}}
\]

where \( \theta \) is the surface coverage and \( n_{\text{ad}} \) is the number of sites occupied by impurities. In the absence of impurities \( n_{\text{ad}} = 0 \) because of adsorption sites are empty. Adsorption sites are fully occupied, when an increase of the impurity concentration increases the value of \( \theta \) to 1.

The surface coverage is approximated frequently by adsorption isotherms, being Langmuir isotherm the most used. This is used to describe highly localized chemical adsorption and restricted to the monomolecular layer but also it is suitable to represent physical adsorption processes.

Sangwal (Sangwal 2007) mentions that to have simple mathematical expressions of adsorption isotherms, it is assumed that impurities occupy adsorption sites only, but in reality the crystal growth in impure solutions comprising a multicomponent sorption phenomenon where sites adsorption are disputed by impurities and solute (Martins, Rocha et al. 2006).
3.1.4 Competitive Adsorption model

To explain the effect of impurities on the crystal growth rate Martins et al. (Martins, Rocha et al. 2006) have proposed the Competitive Adsorption Model (CAM) that describes crystal growth in the presence of impurities as a competition between solute crystallizing units and impurities because adsorption on the actives sites over the crystal surface. The determinant factors of success of each type of species are related to its concentration, mobility and physicochemical affinity to the crystal surface. Also in this model it is assumed that solution properties are not changed by impurities and the system is in steady state. In the CAM to represent the competition between solute molecules and impurities, the overall surface coverage, $\theta_s$, is given by an extended Langmuir isotherm, obtaining:

$$\theta_s = \frac{K_i c_{imp}}{K_i c_{imp} + K\sigma + 1}$$  \hspace{1cm} (3.8)

where $c$ and $c_{imp}$ are the solute and impurity concentrations in the solution. Representing this equation as a function of supersaturation, $\sigma$, is obtained:

$$\theta_s = \frac{k_i c_{imp}}{k_i c_{imp} + k\sigma + 1}$$  \hspace{1cm} (3.9)

where $c^*$, is the solute solubility, $k_i=K_i/(1+Kc^*)$ and $k=Kc^*/(1+Kc^*)$ are constant for the adsorption of solute and impurity respectively.

In the case of crystal growth from impure solutions the following steps are considered:
1) Surface adsorption of the impurity molecules diffusing it from the solution. 2) Migration of impurities ad molecules across the surface. 3) Step/kink adsorption of impurity molecules migrating on the surface.

These processes are associated with changes of thermodynamic energy, whose relative values determine if and how adsorption occurs.
The coverage of active sites by an impurity, $\theta_i$, will be proportional to overall surface coverage, $\theta_s$. It is represented by:

$$\theta_i = \beta_i \theta_s$$  \hspace{1cm} (3.10)

The parameter $\beta_i$ can take high values when the second and third steps are thermodynamically favorable. For very mobile impurities $\beta_i$ it is greater than one, indicating that the impurities concentrate on the active sites (kinks). For favorable adsorption on the surface, $\beta$ takes small positive values ($0<\beta_i<<1$) (Martins, Rocha et al. 2006).

Assuming that Burton Cabrera and Frank diffusion mechanism (Burton, Cabrera et al. 1951) describes crystal growth, the ratio between linear growth rate in impure, $G$, and pure, $G_o$, solutions is given by (Martins, Rocha et al. 2006):

$$\frac{G}{G_o} = 1 - \theta_i$$  \hspace{1cm} (3.11)

Replacing the equations 3.9 and 3.10 at 3.11 is obtained:

$$\frac{G}{G_o} = 1 - \beta_i \frac{k_c \text{imp}}{k_i c_{\text{imp}} + k \sigma + 1}$$  \hspace{1cm} (3.12)

In the case of low affinity of impurities, $k_i$ is low, the solute solubility, $c^*$, is high (high $k$ and low $k_i$) and the impurity concentrations and the surface coverage are low.

### 3.1.5 Crystal size distribution (CSD)

The particle size distribution is characterized by the population density $n$, which is defined as:

$$n = \frac{1}{m} \frac{dN}{dL}$$  \hspace{1cm} (3.13)

where $N$ is the number of crystals and $m$ the volume or mass suspension.
The CSD is dynamic; therefore, it is necessary to know how $n$ changes with time and due to kinetic effects described above. The evolution of the CSD can be evaluated coupling the mass, energy and population balances for the crystallization process. The balance mass is given by:

$$\frac{dc}{dt} = -3 \cdot \rho_c \cdot k_v \cdot \int_0^\infty G(\Delta C, L, t) \cdot n(L, t) \cdot L^2 dL$$  \hspace{1cm} (3.14)

$$c(0) = c_0$$  \hspace{1cm} (3.15)

$\rho_c$ is the crystal density and $k_v$ is the volumetric shape factor.

For batch cooling crystallization using the cubic profile, the energy balance is simplified to:

$$T = T_0 - (T_0 - T_f) \cdot \left(\frac{t}{t_f}\right)^3$$  \hspace{1cm} (3.16)

where $T_0$ and $T_f$ are the initial and final temperature, and $t_f$ is the final time. This profile is used to crystallize within the metastable zone thus the primary nucleation is minimized and the growth is promoted.

The population balance equation (PBE) for a batch system is given by:

$$\frac{\partial n}{\partial t} + \frac{\partial (\bar{\rho}n)}{\partial L} + n \frac{\partial V}{\partial t} + D(L) - B(L) = 0$$  \hspace{1cm} (3.17)

where $V$ is the system volume, $B(L)$ is the birth rate and $D(L)$ the death rate taking into account the agglomeration, attrition, breakage and nucleation which depend on the fluid dynamics and/or crystallization kinetics (Mersmann, Braun et al. 2002).
Assuming that agglomeration, attrition and breakage are negligible equation 3.17 is reduced to:

\[
\frac{\partial n}{\partial t} + G \frac{\partial n}{\partial L} = 0
\]  
(3.18)

\[
n(0,t) = \frac{B}{c}
\]  
(3.19)

\[
n(L,0) = n_0
\]  
(3.20)

The eq. 3.18 can be solved by using the method of moments. The \(\mu_j\)th moment of the PBE is defined as:

\[
\mu_j = \int_0^\infty L^j n(L,t) dL
\]  
(3.21)

Applying eq. 3.21 to 3.18 the moments are:

\[
\frac{du_0}{dt} = B
\]  
(3.22)

\[
\frac{du_j}{dt} = jG u_{j-1} + BL_0^j \quad j=1,2,\ldots N
\]  
(3.23)

\(L_0\) is the seed size. The \(\mu_0, \mu_1, \mu_2\) and \(\mu_3\) are related to total numbers, length, area and volume of the crystals.

In absence of seed the boundary condition (equation 3.20) is equal to zero and equation 3.23 is:

\[
\frac{du_j}{dt} = jG u_{j-1} \quad j=1,2,\ldots N
\]  
(3.24)
3.2 Experimental procedure

3.2.1 Preparation of single crystals of H$_3$BO$_3$ for crystal growth cell and AFM growth experiments

There are many methods to growth single crystal (Shead 1967, Oaki and Imai 2003), but the Vapor diffusion and liquid-liquid diffusion methods were reported to be the most suitable (Müller). Therefore, those were tested using acetone as the precipitant, and water as the solvent. In addition, the classical methods of slow cooling (for pure boric acid solutions in presence and absence of hydrochloric acid) and evaporation were performed. For the single crystal experiments, water was the best solvent and the precipitant acetone.

In the Vapor diffusion method, the effect of the ratio solvent/precipitant was studied. A solution saturated in boric acid at 10°C was prepared by dissolving 0.7562 g of boric acid (99.99%, Acros) in 20.0001 g of ultrapure water produced with a Milli-Q plus apparatus (Millipore Bedford, MA, USA). 1.03 ml of solution was pour into vials. Each vial was introduced in a flask with lid. They were left at room temperature for three days.

3.2.2 Crystal growth cell measurements

Single crystal growth of boric acid was studied in a crystal growth cell using a single crystal of approximately 2 mm of size. The crystal was glued on the sample holder of the cell. Supersaturated solution was pumped through the cell at 4.7 ml/min using a peristaltic pump. The experimental set up is shown in Figure 3.4. The supersaturated solution was obtained using two vessels ($V_1$) and ($V_2$). In $V_2$ a saturated solution was stored at 20 ºC. It was pumped to another reservoir at 19 ºC ($V_1$) to get a relative supersaturation, $\sigma$, of 0.02, before going to the cell. This undercooling is enough to promote growth and minimize nucleation ($\Delta T_{\text{max}} = 1.7$ ºC).
Pictures were taken every 20 min for 8 h by a camera mounted on the top of an optical microscope. The solutions saturated in boric acid at 20 °C were prepared using the composition described in Table 2.2 and the procedure described in section 2.2.1.

![Experimental apparatus diagram](image)

**Figure 3.4** A Schematic diagram of the experimental apparatus for single crystal growth of boric acid. Modified from (Bianco 2009).

### 3.2.3 AFM crystal growth measurements

An Agilent 5500 AFM/SPM microscope with an open flow through cell of 0.5 cm³, held at 23 °C by a temperature controller, was used to follow the surface changes of a single crystal of boric acid during growth. The scans were taken in contact mode. An uncoated silicon cantilever with a force constant of 0.2 N/m has been used at this stage. The experimental set up is shown below in Figure 3.5.
For each experiment, one single crystal of boric acid was glued on a glass slide, using two parts of glue to expose the (001) face, and put it inside the flow cell. Growth solutions were pumped through the cell using a peristaltic pump at 0.85 ml/min, to fill and change the solution in the cell, and 0.07 ml/min to shift fresh solution and assure that growth is controlled by integration step. The solution were not recirculated to avoid that the salt concentration increases. Images were taken every 64 s and the scanned area was 20x20 µm². The bulk supersaturation (σ =0.05) was generated cooling down 2 °C a saturated solution of boric acid at 25 °C in a thermostatic vessel. This sub cooling is enough to encourage growth and minimize nucleation (ΔT_max= 2.8 °C).

**Figure 3.** Set up of the AFM open flow through cell for single crystal growth measurement. Details are described on the text.

The solutions were prepared by dissolving the suitable amount of H₃BO₃ (Acros organics, 99.99 %), Na₂SO₄ (Sigma-Aldrich, ≥99.0 %) or Li₂SO₄·H₂O (Sigma-Aldrich, 99.0% dry basis) in ultrapure water produced with a Milli-Q Plus apparatus (Millipore Bedford, MA, USA). The solutions used were saturated solutions of boric acid at 25 °C with 0, 1, 5, and 16 % mass for Na₂SO₄ and 1, 5 and 8 % mass for Li₂SO₄.

To choose the surface of study, a crystal surface of 90 x 90 µm² area was scanned in air. A 20x20 µm² area of the chosen surface was scanned to verify the presence of characteristic points (steps, edges and dislocations) and that the highest point is less than 4 µm (height limit of the scanner).
3.2.4 Batch cooling crystallization

Batch cooling crystallization of boric acid in absence and presence of sodium and lithium sulfates were done, using a cooling cubic profile, in a RC1 calorimetric reactor (Mettler Toledo). The evolution of the crystal size distribution and crystal habit was determined in line with the FBRM G400 ® and PVM ® V819 probes (Mettler Toledo) respectively. The experimental conditions are given in the Table 3.1 and the setup is shown in Figure 3.6.

The FBRM G400 ® is a probe that tracks changes to particle size distribution and count in real time. The probe is immersed into the crystallizer, and by means of a focused laser which scans the surface of the probe window to track individual chord lengths - measurements of particle size, shape and count. The results are presented as a chord length distribution (CLD) which is proportional to the CSD (MettlerToledo). PVM ® V819 is a probe-based real time microscope for crystal, particles and droplets (MettlerToledo 2007).

First solutions saturated in boric acid at different concentrations of lithium and sodium sulfates were prepared. Every solution was left in the saturation vessel for 12 h which is the equilibrium time using a paddle stirrer. The solutions were prepared by dissolving the suitable amount of \( \text{H}_3\text{BO}_3 \) (Merck, 99.99 %), \( \text{Na}_2\text{SO}_4 \) (Merck, ≥99.0 %) or \( \text{Li}_2\text{SO}_4 \cdot\text{H}_2\text{O} \) (Merck, 99.0% dry basis) in ultrapure water (\( \mu= 0.0054 \text{ mΩ/cm} \)). To remove the humidity of the boric acid, the sodium sulfate, and the water molecule of lithium sulfate monohydrate, the boric acid was dried in an oven at 333.15 K and the salts at 393.15 K respectively for 24 h.

The levels of concentrations studied were from (0, 5, 10, 15, 20, 23 and 30) % mass and (5, 10, 15, 20 and 23) % mass in presence of sodium sulfate and lithium sulfate respectively. Every experiment was made twice to assure repeatability. After that the solution was transferred to the vessel (crystallizer) of the RC1. The pH, FBRM, PVM probes and seed were introduced to the vessel. After that the cooling was started.
To verify the supersaturation of the solution, samples were taken at the beginning, during and the final stage of the experiment. After the test, the suspension crystallized (residual liquid and crystals), were deposited in a 1000 ml beaker. The crystals remaining in the crystallizer walls were removed with water using a squeeze bottle.

**Figure 3.6** Experimental setup for batch crystallization by cooling using RC1 calorimetric reactor with FBRM G400 ® and PVM ® V819 probes.

**Table 3.1** Experimental conditions for batch cooling crystallization tests

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Mass seed (g)</td>
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</tr>
<tr>
<td>Tyler Mesh:</td>
<td>-100+120</td>
</tr>
<tr>
<td>Initial Temperature (°C)</td>
<td>50</td>
</tr>
<tr>
<td>Final temperature (°C)</td>
<td>25</td>
</tr>
<tr>
<td>Cooling profile</td>
<td>Cubic</td>
</tr>
<tr>
<td>Experiment time (min)</td>
<td>120</td>
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<tr>
<td>Stirring rate (rpm)</td>
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</tr>
<tr>
<td>Solution Volume (ml)</td>
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</tr>
</tbody>
</table>
3.3 Results and discussion

3.3.1 Preparation of single crystals of H$_3$BO$_3$ for crystal growth cell and AFM growth experiments

Vapor diffusion

After 3 days the experiment started any crystal was observed inside the flasks with solution. It could be that acetone amount diffused was not enough to supersaturate the solution. Therefore, different ratios water/solution was studied to supersaturate the solution as shown in Table 3.2. It was found that the ratio water / acetone are not important for improving supersaturation and any crystal was observed.

Liquid-liquid diffusion

Firstly, the effect of the position of the solution and precipitant was studied. 0.1 ml of solution and 0.5ml of precipitant were put in vials in two different positions; first solution was on the top and precipitant on the bottom and vice versa. It was found that crystallization is independent of solution and precipitant position, and they do not improve the mixing and supersaturation. In any of the samples, crystal formation was observed. It may be that supersaturation was not enough.

Slow cooling

Boric acid solutions saturated at 25 °C were prepared by dissolving 0.27 g of boric acid (99.99%, Acros) in ultrapure water produced with a Milli-Q Plus apparatus (Millipore Bedford, MA, USA). They were heated up to 30 °C to dissolve solid boric acid by a thermostatic bath. After they were cooled down at room temperature for 1.25 hours. The nucleuses formed were separated and the clear solution was left to cool down at room temperature for 6 days. The solutions were prepared with an error less than 0.33 %. Only in the samples after 6 day time, big crystals were observed; although, they were agglomerated.
On other hand, test at a greater cooling rate with and without seed were made. Growth solutions were prepared by dissolving 0.1889 g of boric acid in 5.009 g of ultrapure water. Seed of size 150 µm were introduced in the samples and left inside a refrigerator at 4 °C for 6 days. In addition, 3.2716 g of solution (without seed) were put store in a refrigerator at 4 °C. In the samples with and without seed were formed dendritic crystals. It could be due to the fact that supersaturation was high; consequently, primary nucleation occurred.

Table 3.2 Ratio water / acetone and volume of solution and precipitant studied in the Vapor diffusion method.

<table>
<thead>
<tr>
<th>No</th>
<th>ratio water/acetone</th>
<th>Volume solution (ml)</th>
<th>Volume precipitant (ml)</th>
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</thead>
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<tr>
<td>1</td>
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<td>1.0</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1.0</td>
<td>0.5</td>
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<tr>
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<tr>
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<td>1.0</td>
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<tr>
<td>10</td>
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<td>1.0</td>
<td>15.0</td>
</tr>
</tbody>
</table>

Evaporation

Solutions of boric acid saturated at 20 ºC were prepared. They were evaporated at room temperature at constant evaporation rate by a fume cupboard and variable evaporation rate.
The samples evaporated at constant evaporation rate presented flat hexagonal crystals without internal fractures as shown in Figure 3.7. The samples evaporated at variable rate presented flat hexagonal crystals too, but agglomerated.

Consequently the best method to grow single crystals suitable for crystal growth studies is the evaporation at constant evaporation rate.

Figure 3.7 Single crystal of boric acid grown by evaporation from boric acid solutions saturated at 20°C.

Therefore, to obtain the single crystal for the growth cell and AFM studies, single crystal was obtained by this method. Solutions of boric acid saturated at 20 °C were prepared. They were evaporated at room temperature inside a desiccator for 20 days. The crystals obtained were flat hexagonal without internal fractures and about 2 mm of size. Their crystalline structure was verified by XRD.
3.3.2 Crystal growth measurements in the crystal growth cell

Boric acid is a layered material parallel to the basal plane of a triclinic crystal structure. The triclinic unit cell, containing four molecules of B(OH)$_3$, has the dimensions $a=0.7039$ nm, $b=0.7053$ nm, $c=0.6578$ nm, $\alpha=92.58^\circ$, $\beta=101.17^\circ$ and $\gamma=119.83^\circ$ (Erdemir 1991). In each layer, one boron atom is surrounded by three oxygen atoms to form a triangular BO$_3$ group. Hydrogen bonds link the BO$_3$ planar groups together to form endless layers of nearly hexagonal symmetry (Erdemir 1991). The electronegativity of boron is 2 and 3.5 for oxygen, being the bonding between them described as mostly covalent with some ionic character (Cooper, Larsen et al. 1973). The bond distances within a B(OH)$_3$ molecule are B-O= 0.136 nm, O-H= 0.088 nm, with a value of 114° for the oxygen bond angle. The O-H $\cdots$ O distance between molecules is 0.270 nm. The layers are 0.318 nm apart and are held together by weak van- der- Waals forces (Zachariasen 1954). The volume of the unit cell is 0.263 nm$^3$, which contains four boric acid molecules (Erdemir 1991). The faces of the boric acid crystal are shown in Figure 3.8.

![Figure 3.8](image_url)
For the single crystal of boric acid the (001) face was studied because of it is the cleavage plane. It was observed that boric acid grows layer by layer; it could be seen in Figure 3.9. The biggest face, (001), grew more favorable in directions [100] and [110] than the other growth directions to complete the growth of each layer. The growth in the direction [100] is the fastest. In addition, it was observed a perpendicular growth, that is greater than tangential growth for the (001) face and the formation of the (011) face. It could be explained for the growth of the layers by spiral growth as shown in Figure 3.11.

Figure 3.9 Single crystal growth of boric acid from a supersaturated solution at $\sigma=0.02$ and 19 °C.

Also the growth directions [010], [010], [110] and [100] are the slowest; therefore, it can be better determined. For that reason, the slowest growth direction, [110] was chosen for the study.
3.3.3 Crystal growth measurements studied by AFM

Atomic surface structure

AFM scans of boric acid taken in air shown that the surface is composed by dislocations, edges, steps and macrosteps. The angle measured on the edges of the face exposed is 121.3° which agrees with the $\gamma = 119.83^\circ$ of the unit cell verifying that (001) face is exposed. That is shown in Figure 3.10.

![Image showing dislocation, edges, steps, and macrosteps with angles and scale](image)

**Figure 3.10** Topography of the (001) face of a single crystal of boric acid taken by AFM in air at room temperature.

Crystal growth of boric acid

After 8.01 min. since the crystal growth started, it was observed that the surface grew by multilayer growth, following the trend of a spiral in counterclockwise direction, as shown in Figure 3.11. The sources of steps for growing were dislocations on the surface. Consequently, the mechanisms of growth and dissolution of boric acid at $\sigma = 0.05$, corresponding to an undercooling of 2 °C, at 23 °C is derived to be spiral growth. The molecules of boric acid diffuse from solution to the active sites at the steps present in dislocations, where they integrate making the step advance to complete a crystal face and make the crystal growth. That fact verified the spiral growth determined by the studies in the growth cell.
During the growth of the surface, the direction of advance of the followed steps was \([\bar{1}10]\). The velocity of the steps’ advance was calculated measuring the change of length of the selected steps (e.g. step 1 and step 2 in Figure 3.11) in counterclockwise direction. The average value obtained was \(66 \pm 9 \text{ nm/s}^{\text{1}}\).

**Figure 3.11** Evolution of steps advance on the (001) face of boric acid during grown in its aqueous solutions at 23 °C and at \(\sigma = 0.05\) a) at 8.01 min. b) at 9.05 min. c) at 12.17 min. d) at 13.21 min. On the scans, the steps’ advance following a spiral trend in counterclockwise direction can be observed.
Measuring the change in height of the total surface in time, it was possible to calculate the perpendicular growth rate. The value found is 2 nm·s\(^{-1}\) or 2·10\(^{-9}\) m·s\(^{-1}\). To verify if that value is representative for the whole crystal, it was compared with an overall growth rate extrapolated from growth rate obtained in a fluidized bed (Sahin 2002), that value is 3.7·10\(^{-8}\) m·s\(^{-1}\). It shows that growth rate of boric acid is not quantified only for the perpendicular growth of the (001) face. Therefore, it is necessary to take into account the growth in directions perpendicular and tangential, and the other faces to quantify the overall growth rate from faces growth measurements by AFM. It is also necessary to make later statistical studies to get representative values for the whole crystal (Piskunova and Rakin 2005).

**Growth of boric acid in presence of impurities**

In order to study the effect of impurities, the measurement of the steps’ advance was taken into account. The advance of steps in presence of 1 % mass of Na\(_2\)SO\(_4\) was inhibited due to this salt adsorbed on the steps (step pinning); in addition, it was observed that the upper steps advance is faster than the undersides steps.

In presence of 5 % mass of Na\(_2\)SO\(_4\) the dislocations on the face are the main sources of active sites. At 5 % mass of sodium sulfate the advance of the steps was negligible, there was no nucleus and the surface became soft so there were no more dislocations for growing. In presence of 1 % mass of Li\(_2\)SO\(_4\) formation of new steps was already stopped. At higher concentrations of that salt the surface became soft and the advance of the steps was negligible. The effect of those impurities is shown in Figure 3.12.

The advance of steps in presence of impurities calculated was used to evaluate the relative advance of steps, \(v/v_o\), where \(v_o\), is the velocity of advance of steps without impurities. They were used to estimate the relative growth rate, \(G/G_o\), due to they are proportional (Tang, Jiang et al. 2007). The results are shown in Figure 3.13.
It was found that both impurities inhibit the growth rate, but lithium sulfate has greater effect than sodium sulfate at lower concentrations. The topography of the surface in presence of these impurities suggests that the inhibition of the growth rate is due to their adsorption on the active sites of the crystal surface of boric acid.

![Image of crystal surface with impurities](image.png)

**Figure 3.** Advance of steps on the (001) face of boric acid in presence of Na$_2$SO$_4$ or Li$_2$SO$_4$ at 23 °C at $\sigma=0.05$.

To support the interpretation of effect of those salts, the adsorption isotherms of Na$_2$SO$_4$ and Li$_2$SO$_4$ onto boric acid are needed. Considering that mutual effect of change of the solubility exits, between sodium sulfate and boric acid (Digiacomo, Brandani et al. 1992), and boric acid crystal habit is composed of different crystallographic faces; adsorptions’ measurements could not be made for the specific faces’ growth rate measured by classic methods. The alternative tool verify the adsorption of the impurities on the active sites is to use Molecular Modeling simulations (Jiang, Pan et al. 2008) or applied a theoretical model, hence the CAM model was applied in this study.
It was determined that, the adsorption of sodium sulfate and lithium sulfate on the surface was independent of the supersaturation \((k=0)\), they were adsorbed preferentially on the adsorption sites on the crystal surface \((k_i \gg k \text{ and } \beta_i \approx 1)\). The affinity for active sites of \(\text{Li}_2\text{SO}_4\) is greater than \(\text{Na}_2\text{SO}_4\) \((\beta_{\text{Li}_2\text{SO}_4} > \beta_{\text{Na}_2\text{SO}_4})\), that fact explains the greater effect of \(\text{Li}_2\text{SO}_4\) compared to \(\text{Na}_2\text{SO}_4\) on the growth rate of boric acid. The parameters of the model are shown in Table 3.3.

As shown in Figure 3.14, the adsorption of lithium sulfate was higher than sodium sulfate at lower concentrations, that fact explained the greater inhibition of the advance of steps in presence of lithium sulfate.

![Figure 3.13](image)

**Figure 3.13** Relative growth rate \(G/G_0\) of boric acid in presence, \(c_{\text{imp}}\), in % mass of \(\text{Li}_2\text{SO}_4\), ■, and \(\text{Na}_2\text{SO}_4\), ▲, at 23 °C and \(\sigma = 0.05\).—, calculated from equation 3.12.

Also it was found that a thermodynamic effect is involved in the inhibition of the growth rate of boric acid in presence of lithium sulfate. This is related to the increasing of the supersaturation by the reduction of the solubility, as shown in Figure 2.1. Therefore, promoting the nucleation (fines productions) and reducing the crystal growth as shown in Figure 3.13. This fact implies that the crystal shape of equilibrium (hexagonal) is no affected by the presence of lithium sulfate. Due to nucleation rate is faster than the growth rate, the thermodynamic effect is the greatest.
The coverage of active sites by an impurity, $\theta_i$, for the boric acid crystal surface in presence of, $c_{imp}$, Li$_2$SO$_4$, ■, and Na$_2$SO$_4$, ▲, —, calculated from equation 3.10 at 23 °C and $\sigma$ =0.05.

![Graph showing the coverage of active sites by impurities](image)

**Figure 3. 14** The coverage of active sites by an impurity, $\theta_i$, for the boric acid crystal surface in presence of impurities, Li$_2$SO$_4$, ■, and Na$_2$SO$_4$, ▲, calculated from equation 3.10 at 23 °C and $\sigma$ =0.05.

**Table 3. 3** Parameters of CAM obtained for the growth of H$_3$BO$_3$ from aqueous solutions of Na$_2$SO$_4$ or Li$_2$SO$_4$ at 23°C and $\sigma$=0.05

<table>
<thead>
<tr>
<th>$k_i$ (100 g solution/g solute)</th>
<th>$k$</th>
<th>$\beta_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.04</td>
<td>0</td>
<td>0.87</td>
</tr>
<tr>
<td>6.50</td>
<td>0</td>
<td>0.95</td>
</tr>
</tbody>
</table>

In presence of sodium sulfate, the growth rate is reduced by the decreasing supersaturation. This is because of the inverse behavior of boric acid in presence of Na$^+$ ion (See Figure 2.2 and Figure 2.22). Further PVM studies are needed to determine the controlling effect, the shape, controlling effect (thermodynamic or kinetic).

At concentration greater than 5 % mass for both impurities some nucleus were formed inside the fluid cell. It could be for contact with the cantilever, vibration of the fluid by the peristaltic pump or evaporation of the solution inside the cell by the AFM laser.
3.3.4 Effect of the salt concentration on the particle size distribution of boric acid

To analyze the effect of the sulfate salt concentration on the particle size of boric acid (the pH was about 3 for all the tests assuring the production of $\text{H}_3\text{BO}_3$ only and an average supersaturation in absence of impurities $\sigma = 0.01$), it is necessary to specify the interesting size ranges. The ranges chosen were:

- (10-60) $\mu$m. This range reflects the nucleation and breaking processes.
- (60-125) $\mu$m. This is the main range for the powder boric acid (See Table 1.2).
- (148-1000) $\mu$m. This is the main range for the granular boric acid (See Table 1.2).
- (1000-2000) $\mu$m. The crystals that are in this range are out of the specifications.

The FBRM probe provides a signal (count/s) and the Chord Length Distribution (CLD) that are proportional to the number of particles and the CSD in the system. As the counts for the studied size ranges are shown in Figure 3.15.

It can be seen in Figure 3.15 the predominance of fines and granular particles, a lower amount of powder and few coarse crystals.

The presence of the fines explain the decreasing of the crystals mean size from 179 $\mu$m at the beginning of the process to 148 $\mu$m for the final CSD, as shown in Figure 3.16. The production of the small crystals can be explained by secondary surface nucleation due to the presence of the seeds and the collisions of the solute molecules with the stirrer and the walls of the crystallizer. Also, the reduction of the mean size could be explained by attrition (breaking of crystals) caused by their needle shape.

From the CLD measurements we can calculate the percentage of fines, powder and granular crystal produced in crystallization conditions given in Table 3.1 and in absence of impurities. To estimate it, the count for each size is divided by the total number of counts and multiplied by 100. The values are presented in Figure 3.17.
In Figure 3.17, it can be observed that a maximum granular (36.84 %) and minimum fines production (29.64 %) is present at 47 min (red dotted line). The mean size, working temperature and the third moment of the CLD, $\mu_3$ (Total Volume of Crystals) were plotted in the same figure. The resulting figure could be thought that the optimal work temperature is 38.8 °C (to increase the production of powder and granular, mean size (159 µm), mass ($\mu_3=1.3\cdot 10^{10}$) and decrease the fines particles) but observing the variation of the total number of counts, it could be realized that for each maximum size a minimum number of counts is also presented as shown in Figure 3.18. This behavior indicates the formation of agglomerated particles. These groups formed and destroyed continuously during the crystallization; this can be observed graphically as hills in the mean size and valleys for the total number of counts.

It must be mentioned that although the third moment does not give the mass of crystals achieved. It is proportional, thus valid as an indicator of the mass obtained.

If there was no agglomeration, the clearly optimal point would be at 47 min, and the other suboptimal points at 1 h and 3 min and 1 h and 17 min. Consequently, it could be defined an optimal region to work between 47 min and 1 h and 17 min (38.8 °C and 34.9 °C) to obtain powder (from 18.80 to 19.21) %, granular (from 34.69 and 36.86) %, fines (from 29.79 to 32.72)% , mean size (from 152.70 to 159.73) µm and $\mu_3$ (from 1.2· $10^{10}$ to 1.3· $10^{10}$) µm$^3$.

At the moment to choose the optimal conditions, the main target must be taken into account. In other words, whether the yield, or the quality of the process is more important. A middle point provides a good quality and yield but not the optimal ones. In this case, there are many points until 39 min (39.4 °C). After that time agglomeration is spent. This zone lasts until the end of the process. Another interesting point is present at 1 h and 23 min, where the production of fines is greater than granular and powder. One should work before this point to avoid further separation problems ($\sigma =0.04$).
The agglomeration phenomena are attributed to the hydrogen bonds formation, between the three molecules of boric acid-water-boric acid for their polar behavior (Sahin and Bulutcu 2003). As a consequence to the required CSD, further separation and screening process are needed.

The agglomeration problem could be addressed using additives. (Puri, Fairchild et al. 1986, Gao, Rafaniello et al. 2015)

During the crystallization of boric acid not only growth and nucleation take place, but also agglomeration and attrition; therefore, it is not appropriate to use the method of moments presented in equation 3.22 and equation 3.23 to estimate the crystal growth and nucleation rates.

The variation of the mean length with time could be used as indicator of the growth rate. It is shown in Figure 3.19. Due to a value to contrast the effect of impurities on the growth rate is needed; an average value of the \( \frac{dL_{\text{mean}}}{dt} \) before agglomerations appears could be taken (until 39 min). The value is \( 3.0 \cdot 10^{-8} \text{ m \cdot s}^{-1} \). It is close to the value reported in literature (Sahin 2002), \( 3.7 \times 10^{-8} \text{ m \cdot s}^{-1} \). The difference is explained for the different hydrodynamic conditions due to it was obtained in a fluidized bed.

The nucleation rate from the variation of the total number of counts was tried to be estimated with time and the zero moment. It was found that \( \mu_0 \) is equal to total number of counts. Also, the variation of it is alternative negative and positive. The negative values indicate disappearance of particles which is given by agglomeration; therefore, it is not possible to calculate the nucleation rate.
Figure 3.15 Number of chord lengths counted per second between: —, 10-60 µm (Fines), —, 60-125 µm (Powder), —, 149-1000 µm (Granular), —, 1000-2000 µm (Coarse), for the batch cooling crystallization of boric acid from aqueous solutions. Relative time is given in h and minutes.
Figure 3.16  Boric acid crystals mean size in μm, number of chord lengths counted per second between: , 10-60 μm (Fines), , 60-125 μm (Powder), , 149-1000 μm (Granular), , 1000-2000 μm (Coarse), for the batch cooling crystallization of boric acid from aqueous solutions. Relative time is given in h and minutes.
Figure 3.17  Boric acid crystals mean size in μm, −, working temperature T in °C, −, Third moment of the CLD μ₃ in μm³, −, and % crystals: —, 10-60 μm (Fines), —, 60-125 μm (Powder), —, 149-1000 μm (Granular) for the batch cooling crystallization of boric acid from aqueous solutions. Relative time is given in h and minutes. The red dot lines, —, indicate the false optimal working region.
Figure 3. 18  Boric acid crystals mean size in μm, —, number of chord lengths counted per second: total, —, and between: —, 10-60 μm (Fines), —, 60-125 μm (Powder), —, 149-1000 μm (Granular), —, 1000-2000 μm (Coarse), for the batch cooling crystallization of boric acid from aqueous solutions. Relative time is given in h and min.
Figure 3. 19  Boric acid crystals mean size in μm, —, working temperature T in ºC, —, variation of the mean size with time $dL_{\text{mean}}/dt$ in μm·s$^{-1}$, ⋯, and total number of counts, —. Relative time is given in h and minutes.
**Sodium sulfate effect**

The effect of the presence of sodium sulfate on the production of fines, powder, granular and coarse particles was studied, as well as the effect on the mean size and the total number of counts. To explain the found behaviors the derivate quantities (variation of the mean size and the third moment of CLD) were used.

The production of fines increases with salt concentration, rising as shown in Figure 3.23. It is greater than in absence of sodium sulfate, but about 40 min it decreases and at 53 min and 5% mas it becomes smaller than the system in absence of this salt. This reduction can be explained by agglomeration. It is supported by the decreasing of the total number of accounts (see Figure 3.27) and the images taken by PVM (see Figure 3.20).

In Figure 3.20 it can be observed that fines stick on bigger particles therefore reducing their number. After that zone, the fines increase due to the supersaturation ($\sigma = 0.05$) growths for faster cooling (characteristic of the cubic profile) promoting nucleation (thermodynamic effect) as show in Figure 3.21.

In presence of sodium sulfate, powder and granular particles decrease. This reduction is promoted with salt concentration elevations, as shown in Figures 3.23 and 3.24 respectively. This behavior can be explained by the reduction of the growth rate of boric acid by the adsorption of salt on the active sites as sodium sulfate concentration rises (See figures 3.13 and 3.14).

The increasing of powder at the end of the process can be attributed to two effects: The growth rate rises by faster cooling (bigger supersaturation) and the agglomeration of fines as shown in Figure 3.20.
Figure 3.20 Crystal agglomeration during crystallization of boric acid from sodium sulfate aqueous solutions at salt concentrations in % mass: a) 5 b) 10 c) 20 and d) 30.

Coarse particles do not present a clear tendency with the variation of salt concentration as can be observed in Figure 3.25. The fact, that could be highlighted, is that this range reflects the agglomeration when it takes place in granular particles. The agglomeration increases with salt concentration rises as shown in Figure 3.36 (coarse particle increasing). This effect could be attributed to the sodium ion which is adsorbed on the active sites of boric acid surface (see Figure 3.14) forming more hydration shells (Mähler and Persson 2012) and promoting the formation of hydrogen bonds between boric acid molecules.
When agglomeration happens in fines and powder particles the result is the proliferation of counts of powder and granular ones. This fact can indicate falsely the increase of production of both sizes and the mean size as shown as hills in the trends in Figures 3.23, 3.24 and 3.26 respectively. However, the mean size is clearly reduced by the salt as illustrated in Figure 3.26. Due to agglomeration increases as salt concentration rises as shown in Figure 3.20 and the valleys and hills for total number of count and the mean size at the same period of time, it is not advisable to estimate the percentage of crystal of fines, powder and granular from the CLD.

**Figure 3.21** Crystal agglomeration at the end of the crystallization of boric acid from sodium sulfate aqueous solutions at salt concentrations in % mass: a) 5 b) 10 c) 20 and d) 30.

Also it is not advisable to estimate the kinetic of crystallization using equations 3.22 and 3.23. Therefore for comparison purposes, the variation of the mean size with time is calculated (see figure 3.28) and focus on the region present before agglomeration (at the begging) to determine the effect of sodium sulfate on the growth rate.
**Figure 3.22** Number of chord lengths counted per second between 10-60 μm (Fines) for the batch cooling crystallization of boric acid from sodium sulfate aqueous solutions at salt concentrations in % mas: –, 0, ■, 5, ◆, 10, ×, 20. Relative time is given in h and minutes.
Figure 3. 23 Number of chord lengths counted per second between 60-125 μm (Powder) for the batch cooling crystallization of boric acid from sodium sulfate aqueous solutions at salt concentrations in % mas: —, 0, ■, 5, ▲, 15, +, 30. Relative time is given in h and minutes.
**Figure 3. 24** Number of chord lengths counted per second between 148-1000 µm (Granular) for the batch cooling crystallization of boric acid from sodium sulfate aqueous solutions at salt concentrations in % mas: –, 0, ■, 5, ▲, 15, ×, 20, ●, 23. Relative time is given in h and minutes.
Figure 3. 25 Number of chord lengths counted per second between 1000-2000 μm (Granular) for the batch cooling crystallization of boric acid from sodium sulfate aqueous solutions at salt concentrations in % mas: – , 0, ◆, 10, ▲, 15, ×, 20, ●, .23. Relative time is given in h and minutes.
Figure 3. 26  Boric acid crystals mean size in μm for the batch cooling crystallization of boric acid from sodium sulfate aqueous solutions at salt concentrations in % mas: —, 0, ■, 5, ▲, 15, ×, 20. Relative time is given in h and minutes.
Figure 3.27 Total number of chord lengths counted per second of boric acid crystals for the batch cooling crystallization of boric acid from sodium sulfate aqueous solutions at salt concentrations in % mas: –, 0, ■, 5, ▲, 15, +, 30. Relative time is given in h and minutes.
**Figure 3.** Variation of the boric acid crystals mean size, $dL_{\text{mean}}/dt$, in $\mu\text{m} \cdot \text{s}^{-1}$ for the batch cooling crystallization of boric acid from sodium sulfate aqueous solutions at salt concentrations in % mas: –, 0, ■, ▲, ×, 15, ×, 20. Relative time is given in h and minutes.
Figure 3. 29 Boric acid crystals mean size, –, working temperature T in °C, –, and Third moment of the CLD $\mu_3$ in $\mu m^3$ for the batch cooling crystallization of boric acid from sodium sulfate aqueous solutions at salt concentrations in % mas: –, 0, ■, 5, ◆, 10, ▲, 15, △, 20. Relative time is given in h and minutes.
As expected, the growth rate of boric acid decreases with sodium sulfate rises, supporting the finding by AFM experiments. For example, at 12 min the rate is: 0.030 μm·s⁻¹ (3.0·10⁻⁸ m·s⁻¹) at 0 %, 0.030 μm·s⁻¹ (3.0·10⁻⁸ m·s⁻¹) at 5 %, 0.016 μm·s⁻¹ (1.6·10⁻⁸ m·s⁻¹) at 15 % and 0.008 μm·s⁻¹ (0.8·10⁻⁸ m·s⁻¹) at 20 %. In Figure 3.30 a comparison of the relative growth rate from both methods is shown.

![Figure 3.30](image-url)

**Figure 3.30** Comparison of the relative growth rate $G/G_0$ of boric acid in presence of Na₂SO₄, % mass, estimated from AFM in situ crystal growth, ■, and batch cooling crystallization using FBRM probe, ♦. — is the trend line.

At salt concentrations greater than 15 % the growth should be stopped completely (see Figure 3.14 and 3.30) for the coverage of all active sites by the salt. This fact does not happen due to the different hydrodynamic conditions for both experiments. In the AFM the flow is slow but in the batch reactor the stirring causes desorption of the salt molecules from the active sites; therefore, growth takes place but slower than in absence of the salt. However, the result of the AFM indicates the global effect of the impurity in the growth rate (reduction).
Also, the reduction of the adsorption strength suggests that it is enough to wash the crystals with saturated solution, vigorously stirred to remove the sodium sulfate impurity from the crystal surface.

The trend of the yield of the process could be explained by a third moment as shown in Figure 3.29. It is observed that the yield decreases as salt concentration grows. This fact is explained by the reduction of the average superstation with salt concentration raises (thermodynamic effect $\sigma < 0.01$). At 5 % mass the production is the half of the production in absence of the salt.

**Lithium sulfate effect**

It was not only studied the effect of the presence of lithium sulfate on the production of fines, powder, granular and coarse particles; but also the effect on the mean size and the total number of counts. To explain the behaviors found the derivate quantities (variation of the mean size and the third moment of CLD) were used.

Fines are produced for secondary surface nucleation on the seeds, the crystallization vessel, the stirrer and the probes surface (see Figure 3.31). Their number increases with salt concentration raises, as shown in Figure 3.33. This is attributed to the reduction of the metastable zone width and increasing of the average supersaturation ($\sigma =0.01$, $\sigma =0.08$, $\sigma =0.13$, $\sigma =0.18$, $\sigma =0.27$ and $\sigma =0.35$ at 0 %, 5 %, 10 %, 15 %, 20 % and 23 % respectively).

At the beginning, the number of fines is greater than in absence of lithium salt. After that the number decreases because they agglomerate with the seeds, as shown in Figure 3.31 and Figure 3.38 (reduction of the total number of counts).

The agglomeration increases with salt concentration rises, as shown in Figure 3.36 (coarse particle increasing). This effect could be attributed to the lithium ion which is adsorbed on the active sites of boric acid surface (see Figure 3.14) forming more hydration shells (Mähler and Persson 2012) and promoting the formation of hydrogen bonds between boric acid molecules.
After 1 h to end the fines increase (see figure 3.33) due to the supersaturation ($\sigma > 0.01$, $\sigma > 0.06$, $\sigma > 0.13$, $\sigma > 0.17$, $\sigma > 0.27$ and $\sigma > 0.35$ at 0 %, 5 %, 10 %, 15 %, 20 % and 23 % respectively) growths for faster cooling (characteristic of the cubic profile) promoting nucleation (thermodynamic effect) as exposed in Figure 3.32.

The amount of powder and granular boric acid are also affected by agglomeration as revealed in Figure 3.34 and 3.35. In fact the agglomeration of fines increase the corresponding to powder, and the agglomeration of powder has the same result for granular. This fact can indicate falsely the increase of production of both sizes and the mean size. This appears in the trends as hills in Figures 3.34, 3.35 and 3.37 respectively. However the mean size is clearly reduced by the salt as illustrated in Figure 3.37.

**Figure 3.31** Crystal agglomeration during crystallization of boric acid from lithium sulfate aqueous solutions at salt concentrations in % mass: a) 5 b) 10 c) 15 and d) 20.
It was also found that comparing Figures 3.35 and 3.37 that granular counts determine the mean size.

In this case is not advisable to estimate the % crystal of fines, powder and granular from the CLD because of agglomeration.

The effect of the salt on the growth rate is implied for powder and granular particles decrease. This is reduced by the adsorption of the salt on the active sites as lithium sulfate concentration rises (See figures 3.13 and 3.14).

![Image](image_url)

**Figure 3.32** Crystal agglomeration at the end of the crystallization of boric acid from lithium sulfate aqueous solutions at salt concentrations in % mass: a) 5 b) 10 c) 15 and d) 20.

Also it is not advisable to estimate the kinetic of crystallization using equations 3.22 and 3.23, but for comparison purposes, the variation of the mean size with time is calculated (see Figure 3.39) and at the begging to determine the effect of lithium sulfate on the growth rate.
Figure 3. Number of chord lengths counted per second between 10-60 μm (Fines) for the batch cooling crystallization of boric acid from lithium sulfate aqueous solutions at salt concentrations in % mas: —, 0, ■, 5, ◆, 10, ✗, 20. Relative time is given in h and minutes.
Figure 3. 34 Number of chord lengths counted per second between 60-125 µm (Powder) for the batch cooling crystallization of boric acid from lithium sulfate aqueous solutions at salt concentrations in % mas: - , 0, ■, 5, •, 10, ×, 20. Relative time is given in h and minutes.
Figure 3.35 Number of chord lengths counted per second between 148-1000 µm (Granular) for the batch cooling crystallization of boric acid from lithium sulfate aqueous solutions at salt concentrations in % mas: — 0, ■ 5, ▲ 15, × 20. Relative time is given in h and minutes.
Figure 3.36 Number of chord lengths counted per second between 1000-2000 μm (coarse) for the batch cooling crystallization of boric acid from lithium sulfate aqueous solutions at salt concentrations in % mas: ─, 0, ■, ♦, 10, ▲, 15, ×, 20, ●, 23. Relative time is given in h and minutes.
Figure 3. 37 Boric acid crystals mean size in μm for the batch cooling crystallization of boric acid from lithium sulfate aqueous solutions at salt concentrations in % mas: —, 0, ■, 5, ▲, 15, ×, 20. Relative time is given in h and minutes.
Figure 3. 38 Total number of chord lengths counted per second of boric acid crystals for the batch cooling crystallization of boric acid from lithium sulfate aqueous solutions at salt concentrations in % mas: —, 0, ◆, 10, ▲, 15, ●, 23. Relative time is given in h and minutes.
Figure 3.9 Variation of the boric acid crystals mean size, $\frac{\text{d}L_{\text{mean}}}{\text{d}t}$, in $\mu\text{m} \cdot \text{s}^{-1}$ for the batch cooling crystallization of boric acid from lithium sulfate aqueous solutions at salt concentrations in % mas: $-\text{, 0, 5, 10}$. Relative time is given in h and minutes.
Figure 3. 40 Boric acid crystals mean size, —, working temperature $T$ in °C, —, and Third moment of the CLD $\mu_3$ in $\mu$m$^3$ for the batch cooling crystallization of boric acid from sodium sulfate aqueous solutions at salt concentrations in % mas: —, 0, ■, 5, ▲, 15, ●, 23. Relative time is given in h and minutes.
As expected, the growth rate of boric acid decreases, with lithium sulfate rises, supporting the finding by AFM experiments. For example at 12 min the rate is: 0.030 μm·s⁻¹ (3.0·10⁻⁸ m·s⁻¹) at 0 %, 0.027 μm·s⁻¹ (2.7·10⁻⁸ m·s⁻¹) at 5 % and 0.008 μm·s⁻¹ (0.8·10⁻⁸ m·s⁻¹) at 10 %. In Figure 3.41 a comparison of the relative growth rate is shown from both methods.

![Figure 3.41](image)

**Figure 3.41** Comparison of the relative growth rate $G/G_0$ of boric acid in presence of Li$_2$SO$_4$, % mass, estimated from AFM in situ crystal growth, ■, and batch cooling crystallization using FBRM probe, ◆, is the trend line.

As can be seen in Figure 3.41 there are differences in the values of growth rate, especially at 5 %. This fact reveals that the growth rate calculated using FBRM is also counting the agglomeration. This effect is neither possible to separate nor avoid, because it takes place during the whole crystallization. Whereas using the AFM in situ, it is possible to control better the experiment to avoid agglomeration, minimize nucleation and obtain more representative growth rate values.

As in presence of Na$_2$SO$_4$ for Li$_2$SO$_4$ adsorption strength is also reduced suggesting that is enough washing the crystals with saturated solution vigorously stirred to remove this impurity from the crystal surface.

In Figure 3.40 the reduction of the third moment indicates the effect of lithium sulfate. It reduces the yield for the thermodynamic effect mainly. At 5 % the production is the 61 % of the production in absence of Li$_2$SO$_4$. 


Comparison of the effect of sodium sulfate and lithium sulfate

The production of fines, powder and granular particles, the mean size, the total number of counts, the variation of the mean size and the third moment of CLD were compared in presence of sodium and lithium sulfates. This comparison is useful to understand the effect of the cation (common anion).

The production of fines in presence of Li$_2$SO$_4$ is greater than for Na$_2$SO$_4$ as shown in Figure 3.42. It is attributed to a bigger effect of Li$^+$ (structure maker) than Na$^+$ ion (structure breaker) on the solubility of boric acid in water (see chapter 2) and the metastable zone width (MZW). Li$^+$ reduces the solubility and the MZW and increases the average supersaturation, therefore promotes nucleation (fines) but Na$^+$ increases the solubility and the MZW but it reduces the average supersaturation.

Agglomeration in presence of Li$^+$ is bigger than Na$^+$ this is also related to more preferential adsorption of Li$^+$ than Na$^+$ ions on the actives sites of boric acid surface. In the case of powder particles the effect of lithium sulfate is more complex than sodium sulfate as shown in Figure 3.43 because of the strong impact of agglomeration. It falsely indicates a higher amount of powder than in absence of boric acid and sodium sulfate; although, these have greater growth rate as exposed in Figure 3.47. The increasing of powder at the end of the process can be attributed to two effects: The growth rate rises by faster cooling (bigger supersaturation) and the agglomeration of fines.

In Figure 3.44, it can be seen that granular counts in presence of sodium sulfate are bigger than in lithium sulfate. It is the result of a greater growth rate with Na$_2$SO$_4$ and higher production of fines with Li$_2$SO$_4$ (it reduces the mean size). Therefore, the mean size is larger with sodium sulfate than lithium sulfate (see figure 3.45). The deviation, at the end, is the result of higher agglomeration for Li$_2$SO$_4$. However, in presence of both impurities the mean size is smaller than in absence of them, caused mainly by the reduction of the growth rate (see Figure 3.13 and 3.47) and increasing of fines production.
Figure 3. 42 Comparison of the number of counts per second of fine crystals for the batch cooling crystallization of boric acid from aqueous solutions in absence, —, and presence of 10 % mass of lithium sulfate, ◆, and sodium sulfate, ◆. Relative time is given in h and minutes.
Figure 3. Comparison of the number of counts per second of powder crystals for the batch cooling crystallization of boric acid from aqueous solutions in absence, —, and presence of 10 % mass of lithium sulfate, ♦, and sodium sulfate, ◆. Relative time is given in h and minutes.
Figure 3. 44 Comparison of the number of counts per second of granular crystals for the batch cooling crystallization of boric acid from aqueous solutions in absence, —, and presence of 10% mass of lithium sulfate, ◊, and sodium sulfate, ♦. Relative time is given in h and minutes.
Figure 3.45 Comparison of the mean size of crystals in μm for the batch cooling crystallization of boric acid from aqueous solutions in absence, —, and presence of 10 % mass of lithium sulfate, ♦, and sodium sulfate, ♣. Relative time is given in h and minutes.
Figure 3. 46 Comparison of total number of counts in counts /s for the batch cooling crystallization of boric acid from aqueous solutions in absence, —, and presence of 10 % mass of lithium sulfate, ◆, and sodium sulfate, ◆. Relative time is given in h and minutes.
Figure 3. 47 Comparison of the variation of the mean size, $dL_{\text{mean}}/dt$, in μm·s$^{-1}$ for the batch cooling crystallization of boric acid from aqueous solutions in absence, —, and presence of 10 % mass of lithium sulfate, ♦, and sodium sulfate, ◦. Relative time is given in h and minutes.
Figure 3. Comparison of the third moment of CLD $\mu_3$ in $\mu m^3$ for the batch cooling crystallization of boric acid from aqueous solutions in absence, —, and presence of 5% mass of lithium sulfate, ■, and sodium sulfate, ■. Relative time is given in h and minutes. $T$ is the working temperature, —, in °C.
To discuss the effect of the salts on the growth rate, the estimated value from the CLD is used so as to have the same conditions for comparison, at 12 min. As shown in Figure 3.49.

![Figure 3.49](image)

**Figure 3.49** Comparison of the relative growth rate $G/G_0$ of boric acid in presence of sodium sulfate, ▲, and lithium sulfate, ●, estimated from batch cooling crystallization using FBRM probe. —, is the trend line.

The growth rate of boric acid is more reduced by lithium sulfate than sodium sulfate rises, supporting the finding by AFM experiments. At salt concentration of 10 % the growth rate is the 30 % and 40 % of the growth in absence of the salts $G_0$, for lithium and sodium sulfate respectively. At 15 % the growth is reduced to 10 % and 30 % of $G_0$.

Also from the Figure 3.47 it is deduced than in absence of agglomeration growth would reach a minimum, 0.1, at salt concentration of 20 % for both salts; consequently, a maximum coverage of all active sites on the boric acid surface of 90 % (calculated from equation 3.11), but in the batch reactor the stirring causes desorption of the salt molecules from the active sites; therefore, growth is expected to be higher for the during process. However, the results indicate a slightly greater effect off the Li$^+$ than Na$^+$ on the reduction of the growth rate of boric acid, as shown in Figures 3.47 and 3.49.
The third moment (yield) is bigger in presence of Na₂SO₄ than Li₂SO₄ as shown in Figure 3.48. This is due to the fact that mean size is bigger. Although Li₂SO₄ decreases the solubility, thus, increases the supersaturation. It produces fines which do not contribute to the yield.

The yield decreases as salt concentration grows. At salt concentration of 5% the production are the 50% and 61% of the production in absence of the salt, for Na₂SO₄ and Li₂SO₄ respectively.

### 3.3.5 Effect of salt on the shape of boric acid crystal

To determine the effect of the salts on the shape of the boric acid crystal the pictures taken with the PVM were contrasted to the topography obtained by AFM in situ. It was found that the shape described on the face (001), highlighted by a red line in Figure 3.50, and is similar to the obtained one by batch crystallization.

**Figure 3.50** Comparison of the shape of boric acid obtained from a) AFM in situ b) PVM during batch crystallization of boric acid from aqueous solutions.
Due to the growth mechanism, it is spiral growth in perpendicular direction to the face (001). The crystal grows in direction [001] forming also the (011) face, thus a prismatic shaped. Through computer simulations, it was determined that at higher supersaturations the (001) face growth increases disappearing and reducing the crystal volume (forming fine particles). In the case of the (001̅) face the growth is promoting, resulting needle shaped crystals. Both type of shapes (fines and needles) mean technical problems for the further downstream separation and transport process.

In presence of sodium sulfate the crystal shape is modified as can be seen in Figure 3.51. The boric acid crystals obtained were prismatic plane shaped at salt concentration of 5%. This shape does not change with salt concentration raises. This fact reveals that sodium sulfate adsorbs preferentially on the faces (110), (100), (010) and (010̅) therefore, it reduces the advance step in the growth directions [110], [100], [010] and [010̅] but does not affect the growth in [110̅] and [001]. This fact was supported by computer simulations of the growth faces (Kaminsky 2007) based on the crystal structure reported by Zachariasen (Zachariasen 1954).

**Figure 3.51** Comparison of the shape of boric acid obtained from a) AFM in situ b) PVM during batch crystallization of boric acid from sodium sulfate aqueous solutions at concentration of 5% mass.
In the case of lithium sulfate, the crystal shape is not modified as shown in Figure 3.52. This shows that lithium sulfate is adsorbed equally in all the faces of the steps thus it reduces their advance in the corresponding growth directions.

**Figure 3.52** Comparison of the shape of boric acid obtained from a) AFM in situ b) PVM during batch crystallization of boric acid from lithium sulfate aqueous solutions at concentration of 20% mass.

The greater effect of sodium sulfate than lithium sulfate on the shape of boric acid can be attributed to the preferentially face adsorption. Na⁺ ion is preferentially adsorbed on the faces (110), (100), (010) and (001) but Li⁺ ion is not. It is adsorbed in all the faces equally.

### 3.4 Summary and conclusions

A methodology was implemented to obtain single crystals of boric acid, to determine the suitable growth face and direction using a growth cell, and an AFM in situ apparatus to be able to perform continuous crystallization and determine the growth mechanisms and rate of boric acid from aqueous solutions in absence and presence of Na₂SO₄ and Li₂SO₄ from 293.15K to 313.15 K.
Also the effect of Na$_2$SO$_4$ and Li$_2$SO$_4$ in the crystal size distribution and shape of boric acid were studied by batch cooling crystallization with the FBRM® G400 and PVM® V819 probes. The levels of concentrations studied were from (0, 5, 10, 15, 20, 23 and 30) % mass and (5, 10, 15, 20 and 23) % mass in presence of sodium sulfate and lithium sulfate respectively.

The best method to grow suitable single crystals for crystal growth studies was the evaporation at low evaporation rate, obtaining pseudo suitable hexagonal crystals to perform measurements in the growth cell and the AFM in situ.

In the growth cell was observed that boric acid grows layer by layer. The studied face is the (001). It grows more favorable in directions [100] and [110] to complete the growth of each layer. The growth direction [100] is the fastest. The slowest directions [010], [010] and [110] can be better determined. For that reason, the slowest growth direction,[110], was chosen for the study. In addition it was observed a perpendicular growth, that is greater than tangential growth for the (001) face. It could be explained by the growth of the layers, by spiral growth.

In the AFM in situ, it was determined that growth mechanism of the (001) face of boric acid crystal from aqueous solutions is governed by spiral growth in absence and presence of sodium and lithium sulfate. It shows that growth rate of boric acid is not quantified only for the perpendicular growth of the (001) face. Therefore, it is necessary to take into account both growths, perpendicular and tangential, and other faces, to quantify the overall growth rate. As well, it is necessary to make later statistical studies to get representative values of the whole crystal. However, the relative growth rates obtained from the advance of steps in direction [110] are enough for the comparison of the effect of the sulfate salts studied on the growth of boric acid.
In presence of sodium and lithium sulfate the relative growth rate of boric acid is reduced. It could be explained for the inhibition of the advance of the steps, of the (001) face in the direction growth[110], by the adsorption of those salts on the actives sites, and the inhibition of the formation of sources of steps such as dislocations.

It was found that a thermodynamic effect is involved in the inhibition of the growth rate of boric acid in presence of both salts. For the first salt this effect is greater than kinetic. It is related to the increasing of the supersaturation by the reduction of the solubility; therefore, promoting the nucleation (fines productions) and reducing the crystal growth. For the sodium salt the growth rate is reduced by the supersaturation decreasing. This is because of the inverse behavior of boric acid in presence of Na⁺ ion.

In the batch cooling crystallization with PVM, FBRM and pH probes were found that during the crystallization of boric acid in absence and presence of sodium sulfate and lithium sulfate (the pH was about 3 for all the tests assuring the production of H₃BO₃ only and an average supersaturation in absence of impurities σ = 0.01) not only growth and nucleation take place but also agglomeration and attrition. Therefore, it is not appropriate to use the method of moments presented in equations 3.22 and 3.23 to estimate the crystal growth and nucleation rates.

The variation of the mean size with time (before agglomeration at 12 min) was used as indicator of the growth rate to contrast the effect of impurities on the growth rate. The value found in absence of impurities is 3.0·10⁻⁸ m·s⁻¹. It is close to the value reported in literature (Sahin 2002), 3.7·10⁻⁸ m·s⁻¹. The difference is explained for the different hydrodynamic conditions due to it, it was obtained in a fluidized bed.

It was tried to estimate the nucleation rate from the variation of the total number of counts with time and the zero moment. It was found that μ₀ is equal to total number of counts. Also the variation of it, it is alternative, negative and positive. The negative values indicate disappearing of particles which is given by agglomeration. Consequently, it is not possible to calculate the nucleation rate.
The agglomeration is attributed to the hydrogen bonds formation between boric acid-water-boric acid for their polar behavior. As a consequence to the CSD requirement, further separation and screening process are needed. The agglomeration problem could be addressed using additives.

In absence of impurities the crystals mean decreases size from 179 µm at the beginning of the process to 148 µm for the final CSD. This is explained by the presence of the fines. They are produced by secondary surface nucleation due to the presence of the seeds and the collisions of the solute molecules with the stirrer and the walls of the crystallizer. Also the reduction of the mean size could be explained by attrition caused by their needle shape.

It was determined that working temperatures until at 39.4 °C assure a good yield and quality. After that point, agglomeration takes place. Another interesting point to obtain greater production of powder than fines is at 37.5 °C. It should be worked before this point to avoid further separation problems.

To determine the effect of lithium and sodium sulfates on the CSD of boric acid, they were compared (in absence and presence of the salts) the production of fines, powder and granular particles, the mean size, the total number of counts, the variation of the mean size and the third moment of CLD. This comparison is useful to understand the effect of the cation (common anion).

Lithium sulfate increasing concentration reduces the growth rate of boric acid more than sodium sulfate rises, supporting the finding by AFM experiments. At salt concentration of 10 % the growth rate is the 30 % and 40 % of the growth in absence of the salts $G_o$, for lithium and sodium sulfate respectively. At 15 % the growth is reduced to 10 % and 30 % of $G_o$. In absence of agglomeration, the growth would reach a minimum, 0.1, at salt concentration of 20 % for both salts; therefore, a maximum coverage of all actives sites on the boric acid surface of 90 %, but in the batch reactor the stirring causes desorption of the salt molecules from the active sites; therefore, growth is expected to be higher during the process. However the results indicate a slightly greater effect off the Li$^+$ than Na$^+$ on the reduction of the growth rate of boric acid.
The production of fines in presence of Li$_2$SO$_4$ is greater than for Na$_2$SO$_4$. It is attributed to the bigger effect of Li$^+$ (structure maker) than Na$^+$ ion (structure breaker) on the solubility of boric acid in water (see chapter 2) and the metastable zone width (MZW), and the supersaturation. Li$^+$ reduces the solubility and the MZW, and increases the supersaturation consequently, promotes nucleation (fines) but Na$^+$ increases the solubility and the MZW, and reduces the supersaturation.

Agglomeration in presence of Li$^+$ is bigger than for Na$^+$ this is also related to more adsorption of Li$^+$ than Na$^+$ ions on the actives sites of boric acid surface.

In the case of powder particles the effect of lithium sulfate is more complex than sodium sulfate due to the strong impact of agglomeration. It falsely indicates a higher amount of powder than in absence of boric acid and sodium sulfate; although, these have greater growth rate. The increasing of powder at the end of the process can be attributed to two effects: The growth rate rises by faster cooling (bigger supersaturation) and the agglomeration of fines.

The granular counts in presence of sodium sulfate are bigger than for lithium sulfate. It is the result of a greater growth rate with Na$_2$SO$_4$ and higher production of fines with Li$_2$SO$_4$ (it reduces the mean size). Therefore, the mean size is larger with sodium sulfate than lithium sulfate. The deviation at the end is the result of higher agglomeration for Li$_2$SO$_4$. However, in presence of both impurities the mean size is smaller than in absence of them caused mainly by the reduction of the growth rate and increasing of fines production.

The yield (third moment) is bigger in presence of Na$_2$SO$_4$ than Li$_2$SO$_4$. This is due to the fact that mean size is bigger. Although, Li$_2$SO$_4$ decreases the solubility thus increases the supersaturation, it produces fines which do not contribute to the yield. The yield decreases as salt concentration grows. At salt concentration of 5 % the production are the 50 % and 61 % of the production in absence of the salt, for Na$_2$SO$_4$ and Li$_2$SO$_4$ respectively.
The boric acid crystal shape was prismatic as already found by AFM in situ and growth cell methods. This shape is the result of the growth mechanism (spiral growth) in the direction [001] which is perpendicular to the face (001). At higher supersaturations the (001) face growth increases disappearing and reducing the crystal volume (forming fine particles). In the case of the (00$\bar{1}$) face the growth is promoting, resulting needle shaped crystals. Both type of shapes (fines and needles) mean technical problems for the further downstream separation and transport process.

In the case of lithium sulfate the crystal shape is prismatic. This fact indicates that lithium sulfate is adsorbed equally in all the faces of the steps thus it reduces their advance in the corresponding growth directions.

In presence of sodium sulfate, boric acid, prismatic plane shaped crystals were obtained. This shape does not change with salt concentration raises. This fact reveals that sodium sulfate adsorbs preferentially on the faces($\bar{1}10$), ($\bar{1}00$), (010) and (0$\bar{1}$0) therefore, it reduces the advance step in the growth directions[$\bar{1}10$], [$\bar{1}00$], [010] and [0$\bar{1}$0] but does not affect the growth in [110] and [100].

The greater effect of sodium sulfate than lithium sulfate on the shape of boric acid can be attributed to the preferentially face adsorption. Na$^+$ ion is preferentially adsorbed on the faces($\bar{1}10$), ($\bar{1}00$), (010) and (0$\bar{1}$0) but Li$^+$ ion is not. It is adsorbed in all the faces equally.
Chapter IV

Conclusions and Outlook
4.1 Conclusions

4.1.1 Specific objective 1: To measure the physical properties of the systems: H$_3$BO$_3$+Na$_2$SO$_4$+H$_2$O and H$_3$BO$_3$+Li$_2$SO$_4$+H$_2$O from 293.15 K to 313.15 K and concentration of the salts from 0 to 3.149 mol·kg$^{-1}$ for Li$_2$SO$_4$ and 3.380 mol·kg$^{-1}$ for Na$_2$SO$_4$.

This research provides reliable data of solubility of boric acid, density, refractive index, dynamic viscosity, and electrical conductivity data of aqueous solutions of lithium and sodium sulfates saturated in boric acid at temperature ranges from (293.15 to 313.15)K. The experimental data were correlated by empirical equations, obtaining a good enough fit to be useful for evaluating the physical properties of aqueous solutions saturated in boric acid, in the range studied of concentrations of lithium sulfate and temperatures.

4.1.2 Specific objective 2: To describe the thermodynamic effects of Li$_2$SO$_4$ and Na$_2$SO$_4$ on the solubility of boric acid in aqueous solutions and their effect on the transport properties studied.

The solubility was described satisfactorily using an equation based on Pitzer model to obtain a good enough fit to be useful for evaluating the solubility of boric acid in sodium sulfate, potassium sulfate and lithium sulfate aqueous solutions, in the range studied of concentrations and temperatures. The model parameters are valid to maximum concentration of the salts, 3.3149 mol·kg$^{-1}$ for Li$_2$SO$_4$, 3.380 mol·kg$^{-1}$ for Na$_2$SO$_4$, and 1.245 mol·kg$^{-1}$ for K$_2$SO$_4$ from 293.15 K to 313.15 K.

It was determined that the lithium sulfate is a precipitant agent for boric acid and its behavior is attributed to the salting out effect of Li$^+$ ion; therefore, its presence is favorable for the crystallization of boric acid, for which the supersaturation increases therefore the yield of the process. Sodium sulfate and potassium sulfates increase the boric acid solubility; this salting in effect is due to the presence of Na$^+$ and K$^+$ ions. The presence of these salts can be unfavorable for the crystallization of boric acid, due to the decreasing of the supersaturation; therefore, the yield.
The effect of the ions on the solubility of boric acid, in aqueous sulfate solutions, follows the following order: \( \text{Li}^+ > \text{Na}^+ > \text{K}^+ \), which can be attributed to the increase of their ionic radii, coordinated with 6 water molecules therefore the capacity to form hydration shells.

It was found that the values of density and refractive index in presence of sodium sulfate are greater than in lithium sulfate solutions, this difference can be attributed to the cation behavior, due to \( \text{Na}^+ \) is considered as a structure breaker with a higher ionic radii (1.07 Å) than \( \text{Li}^+ \) (0.79 Å); consequently, it increases the boric acid solubility and the total mass per volume ratio.

The effect of \( \text{Li}^+ \) is greater than \( \text{Na}^+ \) on the viscosity increasing. This is explained due to the \( \text{Li}^+ \) (water structure maker) compresses the volume solution, increasing the cohesion between species in solution, thus the shear stress needed to initiate the movement. For the electrical conductivity, the \( \text{Na}^+ \) has greater effect in the increasing of this property than \( \text{Li}^+ \). This is due to the fact that \( \text{Na}^+ \) increases the free spaces on the water structure, promoting the sodium ion mobility, unlike lithium ion that is a structure maker.

4.1.3 Specific objective 3: To implement an experimental apparatus to perform continuous growth crystallization using AFM in situ to determine the growth mechanisms and rate of boric acid from aqueous solutions in absence and presence of \( \text{Li}_2\text{SO}_4 \) and \( \text{Na}_2\text{SO}_4 \) from 293.15K to 313.15 K.

An experimental apparatus was implemented to perform continuous growth crystallization using AFM in situ to determine the growth mechanisms and rate of boric acid from aqueous solutions in absence and presence of \( \text{Li}_2\text{SO}_4 \) and \( \text{Na}_2\text{SO}_4 \) from 293.15K to 313.15 K. This apparatus proved to be useful for determining the growth mechanism and relative rate of boric acid; also, to study the growth of specific faces and their directions. This information together with growth cell results is useful to determine the final shape of the crystal in absence and presence of impurities.
To obtain suitable crystals for the measurements, the best method found was the evaporation at low evaporation rate, obtaining pseudo hexagonal crystals.

In the growth cell, it was observed that boric acid grows layer by layer. The studied face is the (001). It grows more favorable in directions [100] and [110] to complete the growth of each layer. The growth direction [100] is the fastest. The slowest directions [010], [01̅0] and [110] can be better determined. For that reason, the slowest growth direction, [110], was chosen for the study. In addition it was observed a perpendicular growth, that is greater than tangential growth for the (001) face. It could be explained by the growth of the layers, by spiral growth.

In the AFM in situ, it was determined that growth mechanism of the (001) face of boric acid crystal from aqueous solutions is governed by spiral growth in absence and presence of sodium and lithium sulfate. It shows that growth rate of boric acid is not quantified only for the perpendicular growth of the (001) face. Therefore, it is necessary to take into account both growths, perpendicular and tangential, and other faces, to quantify the overall growth rate. As well, it is necessary to make later statistical studies to get representative values of the whole crystal. However, the relative growth rates obtained from the advance of steps in direction [110] are enough for the comparison of the effect of the sulfate salts studied on the growth of boric acid.

In presence of sodium and lithium sulfate, the relative growth rate of boric acid is reduced. It could be explained that for the inhibition of the advance of the steps, of the (001) face in the direction growth[110], by the adsorption of those salts on the active sites, and the inhibition of the formation of sources of steps such as dislocations.

It was found that a thermodynamic effect is involved in the inhibition of the growth rate of boric acid in presence of both salts. For the lithium sulfate, this effect is greater than kinetic. It is related to the increasing of the supersaturation by the reduction of the solubility; consequently, promoting the nucleation (fines productions) and reducing the crystal growth. For the sodium salt the growth rate is reduced by the supersaturation decreasing. This is because of the inverse behavior of boric acid in presence of Na⁺ ion.
4.1.4 **Specific objective 4:** To determine the effect of Li$_2$SO$_4$ and Na$_2$SO$_4$ in the crystal size distribution (CSD) and shape of boric acid by batch cooling crystallization using the FBRM® G400 and PVM® V819 sensors.

In the batch cooling crystallization with PVM, FBRM and pH, probes were found that during the crystallization of boric acid in absence and presence of sodium sulfate and lithium sulfate not only growth and nucleation take place, but also agglomeration and attrition. Therefore, it is not appropriate to use the method of moments presented in equations 3.22 and equations 3.23 to estimate the crystal growth and nucleation rates.

The variation of the mean size with time (before agglomeration at 12 min) was used as indicator of the growth rate to contrast the effect of impurities on the growth rate. The value found in absence of impurities is $3.0 \times 10^{-8} \text{ m} \cdot \text{s}^{-1}$. It is close to the value reported in literature (Sahin 2002), $3.7 \times 10^{-8} \text{ m} \cdot \text{s}^{-1}$. The difference is explained for the different hydrodynamic conditions due to it was obtained in a fluidized bed.

The nucleation rate from the variation of the total number of counts with time and the zero moment was tried to be estimated. It was found that $\mu_0$ is equal to the total number of counts whose variation is alternatively negative and positive. The negative values indicate disappearance of particles which is given by agglomeration; consequently, it is not possible to calculate the nucleation rate.

The pH was about 3 for all the tests assuring the production of H$_3$BO$_3$ only.

The agglomeration is attributed to the hydrogen bonds formation between boric acid-water-boric acid for their polar behavior. As a consequence to the required CSD further separation and screening process are needed. The agglomeration problem could be addressed using additives.
In absence of impurities, the crystals mean decreases size from 179 µm at the beginning of the process to 148 µm for the final CSD. This is explained for the presence of the fines. They are produced by secondary surface nucleation due to the presence of the seeds and the collisions of the solute molecules with the stirrer and the walls of the crystallizer. Also, the reduction of the mean size could be explained by attrition caused by their needle shape.

It was determined that working temperatures until 39.4 °C assure a good yield and quality. After that point, agglomeration takes place. Another interesting point to obtain greater production of powder than fines is at 37.5 °C. It should be worked before this point to avoid further separation problems.

To determine the effect of lithium and sodium sulfates on the CSD of boric acid (in absence and presence of the salts) the production of fines, powder and granular particles, the mean size, the total number of counts, the variation of the mean size and the third moment of CLD were compared. This comparison is useful to understand the effect of the cation (common anion).

Lithium sulfate concentration increasing reduces the growth rate of boric acid more than sodium sulfate rises, supporting the finding by AFM experiments. At salt concentration of 10 % the growth rate is the 30 % and 40 % of the growth in absence of the salts G₀, for lithium and sodium sulfate respectively. At 15 % the growth is reduced to 10 % and 30 % of G₀. In absence of agglomeration, the growth would reach a minimum, 0.1, at salt concentration of 20 % for both salts therefore a maximum coverage of all active sites on the boric acid surface of 90 %, but in the batch reactor the stirring causes desorption of the salt molecules from the active sites; therefore, growth is expected to be higher during the process. However the results indicate a slightly greater effect off the Li⁺ than Na⁺ on the reduction of the growth rate of boric acid.
The production of fines in presence of Li$_2$SO$_4$ is greater than for Na$_2$SO$_4$. It is attributed to the bigger effect of Li$^+$ (structure maker) than Na$^+$ ion (structure breaker) on the solubility of boric acid in water (see chapter 2) and the metastable zone width (MZW), and the supersaturation. Li$^+$ reduces the solubility and the MZW, and increases the supersaturation consequently, promotes nucleation (fines) but Na$^+$ increases the solubility and the MZW, and reduces the supersaturation.

Agglomeration in presence of Li$^+$ is bigger than for Na$^+$ this is also related to more adsorption of Li$^+$ than Na$^+$ ions on the active sites of boric acid surface.

In the case of powder particles, the effect of lithium sulfate is more complex than sodium sulfate due to the strong impact of agglomeration. It falsely indicates a higher amount of powder than in absence of boric acid and sodium sulfate; although, these have greater growth rate. The increasing of powder at the end of the process can be attributed to two effects: The growth rate rises by faster cooling (bigger supersaturation) and the agglomeration of fines.

The granular counts in presence of sodium sulfate are bigger than for lithium sulfate. It is the result of a greater growth rate with Na$_2$SO$_4$ and higher production of fines with Li$_2$SO$_4$ (the mean size is reduced). Therefore the mean size is larger with sodium sulfate than lithium sulfate. The deviation at the end is the result of higher agglomeration for Li$_2$SO$_4$. Nevertheless, in presence of both impurities the mean size is smaller than in absence of them caused mainly by the reduction of the growth rate and increasing of fines production.

The yield (third moment) is bigger in presence of Na$_2$SO$_4$ than Li$_2$SO$_4$. This is due to the fact that mean size is bigger. Although, Li$_2$SO$_4$ decreases the solubility thus increases the supersaturation, it produces fines which do not contribute to the yield. The yield decreases as salt concentration grows. At salt concentration of 5 % the production is 50 % and 61 % of it in absence of the salt, for Na$_2$SO$_4$ and Li$_2$SO$_4$ respectively.
The boric acid crystal shape was prismatic as already found by AFM in situ and growth cell methods. This shape is the result of the growth mechanism (spiral growth) in the direction [001] which is perpendicular to the face (001). At higher supersaturations the (001) face growth increases disappearing and reducing the crystal volume (forming fine particles). In the case of the (001̅) face the growth is promoting, resulting needle shaped crystals. Both type of shapes (fines and needles) mean technical problems for the further downstream separation and transport process.

In the case of lithium sulfate the crystal shape is prismatic. This fact indicates that lithium sulfate is adsorbed equally in all the faces of the steps thus it reduces their advance in the corresponding growth directions.

In presence of sodium sulfate, boric acid, prismatic plane shaped crystals were obtained. This shape does not change with salt concentration raises. This fact reveals that sodium sulfate adsorbs preferentially on the faces(110), (100), (010) and (010̅) therefore, it reduces the advance step in the growth directions[110], [100], [010] and [010̅] but does not affect the growth in [110] and [100].

The greater effect of sodium sulfate than lithium sulfate on the shape of boric acid, it can be attributed to the preferentially face adsorption. Na⁺ ion is preferentially adsorbed on the faces(110), (100), (010) and (010̅) but Li⁺ ion is not. It is adsorbed in all the faces equally.

4.1.5 General objective: To determine the effect of Lithium and Sodium Sulfates on the crystallization of Boric Acid from aqueous solutions from the kinetic and thermodynamic approaches.

The presence of lithium and sodium sulfates during the crystallization of boric acid from aqueous solutions affect the solubility, crystal growth mechanism and rate, CSD and shape of the boric acid obtained.
Lithium sulfate reduces the solubility thus it increases the supersaturation of boric acid (thermodynamic effect). It promotes nucleation and reduces the growth rate. The solubility drops for the Li\(^+\) behavior as structure maker of water in presence of sulfate ion, and the growth rate is decreased by the adsorption of the salt on the active sites of growth of the boric acid crystal (kinetic effect).

Sodium sulfate increases the solubility; therefore, it reduces the supersaturation of boric acid (thermodynamic effect). It lessens the growth rate. The solubility rises for the Na\(^+\) behavior as structure breaker of water in presence of sulfate ion, and the growth rate is decreased by the adsorption of the salt on the active sites of growth of the boric acid crystal (kinetic effect).

Both salts affect the growth rate but do not the growth mechanism (spiral growth). At salt concentration of 10 % the growth rate is the 30 % and 40 % of the growth in absence of the salts \(G_0\), for lithium and sodium sulfate respectively. At 15 % the growth is reduced to 10 % and 30 % of \(G_0\). In absence of agglomeration, the growth would reach a minimum, 0.1, at salt concentration of 20 % for both salts; consequently, a maximum coverage of all active sites on the boric acid surface of 90 %, but in the batch reactor the stirring causes desorption of the salt molecules from the active sites, thus growth is expected to be higher during the process. However, the results indicate a slightly greater effect off the Li\(^+\) than Na\(^+\) on the reduction of the growth rate of boric acid.

As results in presence of Li\(_2\)SO\(_4\) fines production is increased and the powder, granular, mean size are decreased. Also, agglomeration is promoted and the yield reduced. The yield decreases as salt concentration grows. At salt concentration of 5 % the production is 61 % of it in absence of the salt. Lithium sulfate does not affect the crystal shape due to the fact that Li\(^+\) ion is adsorbed in all the faces equally.
In presence of Na$_2$SO$_4$ fines production is increased and the powder, granular, mean size are decreased. Also, agglomeration is promoted and the yield reduced. The yield decreases as salt concentration grows. At salt concentration of 5 % the production is 50 % of the it in absence of the salt. Also, sodium sulfate modifies the shape of boric acid from prismatic to prismatic planar. It can be attributed to the preferentially face adsorption. Na$^+$ ion is preferentially adsorbed on the faces (110), (100), (010) and (010).

The effect of Lithium sulfate is greater than the corresponding to sodium sulfate on the growth rate, fines, powder and granular production, the mean size, the yield and the shape of boric acid crystals.

For both salts the thermodynamic effect is greater than the kinetic effect; consequently, it is enough to wash the crystals with boric acid saturated solution to purify and classify them properly to meet the product specifications.

4.2 Outlook

The experimental methodology developed in this study could be applied for the study of growth mechanism and rate for other compounds in the presence of impurities and their impact on the distribution of crystal size, shape, and crystallization yield. It has the following components:

1) Thermodynamic: Equilibrium and transport properties

2) Kinetic: a) Single crystal growth method b) Determination of the suitable growth face and direction for growth rate and mechanism by AFM c) Determination of growth rate and mechanism by continuous growth crystallization from aqueous solutions using AFM continuous growth crystallization d) To determine the effect of the shape of boric acid using the FBRM® G400 and PVM® V819 probes.
References


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Annex

Journal Publications and Conference Procedures
Journal Publications

- Alavia, W.; Lovera, J. A.; Cortez, B. A.; Graber, T. A., Solubility, Density, Refractive Index, Viscosity, and Electrical Conductivity of Boric Acid + Lithium Sulfate + Water System at (293.15, 298.15, 303.15, 308.15 and 313.15) K. *Journal of Chemical & Engineering Data* 2013, 58, (6), 1668-1674.

- Alavia, W.; Lovera, J.; Graber, T. A., Thermodynamic modeling of the solubility of boric acid in the systems boric acid + lithium sulfate + water, boric acid + sodium sulfate + water and boric acid + potassium sulfate + water at 293.15–313.15 K. *Fluid Phase Equilibria* 2015, 398, (0), 63-71.

- Alavia, W.; Graber, T. A., Density, Refractive Index, Viscosity, and Electrical Conductivity of Aqueous Solutions of Sodium Sulfate Saturated in Boric Acid at (293.15, 298.15, 303.15, 308.15 and 313.15) K (In preparation).
Solubility, Density, Refractive Index, Viscosity, and Electrical Conductivity of Boric Acid + Lithium Sulfate + Water System at (293.15, 298.15, 303.15, 308.15 and 313.15) K

Wilson Alavia, Jorge A. Lovera, Brenda A. Cortez, and Teofilo A. Gruber*
CITETM, Departamento de Ingeniería Química, Universidad de Antofagasta, Av. Universidad de Antofagasta 02800, Antofagasta, Chile

ABSTRACT: The solubility, density, refractive index, viscosity, and electrical conductivity for aqueous solutions of Li₂SO₄ from (0 to 3.1472) mol·kg⁻¹ H₂O, saturated in H₃BO₃, over the temperature range from (293.15 to 313.15) K have been determined. These physical properties were represented by equations as functions of temperature and Li₂SO₄ concentration. This information is useful for evaluating the physical properties of aqueous solutions saturated in H₃BO₃ in the range of concentrations of Li₂SO₄ and temperatures studied.

INTRODUCTION
Boric acid is a weak inorganic acid that has many applications, such as, antiseptic agent, flame retardant, and food preservative. It is useful in preparing synthetic organic borate salts and other boron compounds. As well, it is used as a chemical slime in pressurized water reactors in nuclear power plants. This acid is produced industrially by crystallization from brines or boron (3+) minerals. Brines are aqueous solutions from salt lakes that contain Ba²⁺, Na⁺, K⁺, Li⁺, Mg²⁺, Cl⁻, and SO₄²⁻ species. The main boron (3+) minerals are boronatrolite, sodium tetraborate dehydrate, and hydrated calcium borate. The brines and boron (3+) mineral deposits in Chile are located in the northern region with the Salar de Atacama being the main source for boric acid production due to the high content of boron (3+) species in its brines.

The boric acid production from brines starts with concentrating the brine by solar evaporation in ponds. In the first one NaCl is crystallized. The residual brine saturated in K⁺ and SO₄²⁻ ions is sent to a second group of evaporation ponds, where NaCl, KCl, and some K₂SO₄·MgSO₄·6H₂O is crystallized. In the third group of ponds MgSO₄·KCl·3H₂O, K₂SO₄·MgSO₄·6H₂O, LiKSO₄·KCl, and KMgCl·4H₂O crystallize. These salts are harvested from the ponds to be further processed. The final brine is used to produce boric acid by adding sulfuric acid. During this step, Li₂SO₄ could crystallize as Li₂SO₄·H₂O due to a salting out effect. Thus it is necessary to leach the crystals obtained before sending them to the drying stage. The impact of this impurity concentration in the crystallization yield and purity of the boric acid is evaluated, if its solubility in aqueous solution of lithium sulfate and the physical properties of its saturated solutions are known. As well that information is useful for the design and optimization of boric acid crystallization from brines.

Because the effect of the physical properties of lithium sulfate in the boric acid production is important, we report in this contribution the solubility, density, refractive index, viscosity, and electrical conductivity for aqueous solutions of lithium sulfate saturated in boric acid at temperatures from (293.15 to 313.15) K and Li₂SO₄ concentrations ranging from (0 to 3.1472) mol·kg⁻¹ H₂O.

In the literature physical properties data of aqueous solutions of sulfate salts that contain boron (3+) compounds are scarce. Linke and Seidell[8] reported the solubility of H₃BO₃ in water at the temperature range from (273.15 to 454.15) K. As well they collected the solubility of H₃BO₃ in aqueous solutions of NaCl, KCl, LiCl at (283.15, 289.00, and 297.00) K, RbCl and CsCl at 291.15 K, BaCl₂, MgCl₂, and MgCl₂ at 291.00 K, and Na₂SO₄ at (293.45, 298.65, 298.15, 301.65, 308.15, and 348.15) K. Koltunoff[9] presented solubility of H₃BO₃ in aqueous solutions of NaCl, KCl, LiCl, K₂SO₄ at 293.15 K and Na₂SO₄ at 291.15 K. Chanson and Müller[10] determined the solubility of H₃BO₃ in electrolyte solutions (LiCl, NaCl, KCl, RbCl, and CsCl) as a function of the ionic strength at 298.15 K. Di Giacomo et al.[11] measured the solubility of H₃BO₃ in aqueous solutions of NaCl, KCl, NaCl-KCl, K₂SO₄, Li₂SO₄, and K₂SO₄-Na₂SO₄ at a large range of concentrations at temperatures from (303.21 to 373.15) K. Nowotny and Sühnel[15] developed a correlation to estimate the densities of aqueous solutions of several inorganic substances including H₃BO₃ as a function of concentration and temperature. Galleguillos et al.[16] measured experimental data of density and refractive index of aqueous solutions of H₃BO₃ and KCl at (293, 298, 303, and 308.15) K. In a later work Galleguillos et al.[17] reported the density of ternary aqueous

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systems that contain H$_2$BO$_3$ with different electrolytes (NaCl, K$_2$SO$_4$, and Na$_2$SO$_4$) at (298.15, 303.15 and 308.15) K.

**EXPERIMENTAL SECTION**

**Materials.** The chemical compounds used and their characteristics are described in Table I. To remove the humidity of the boric acid and the water molecule of lithium sulfate monohydrate, the compounds were dried in an oven at (333.15 and 393.15) K respectively for 24 h. Double distilled and deionized water (electrical conductivity of 0.0005 μS cm$^{-1}$) were used in all procedures.

**Apparatus and Procedures.** Solution Preparation. Aqueous solutions saturated in boric acid were prepared for every temperature studied, based on the solubility data reported by Linke and Siddell. Boric acid and deionized water were mixed and the resulting solution stirred to equilibrium. To prepare the ternary solutions, lithium sulfate monohydrate, a saturated solution in boric acid, and an excess of boric acid to ensure saturation in it were mixed. An analytical balance with a precision of ±0.0001 g (Denver Instrument Co., model AA-200) was used to mass the reagents. The solutions prepared were kept under agitation at constant temperature for 96 h (equilibrium time) in a phase equilibrium unit which is composed by a rotating basket located inside a thermostatically controlled water bath. Ten concentration levels of lithium sulfate were studied at temperatures ranging from (298.15 to 313.15) K. For every concentration, two solutions were prepared to ensure repeatability. The lithium sulfate concentrations prepared ranged from (0 to 3.1472) mol kg$^{-1}$ H$_2$O.

To determine the equilibrium time, aqueous solutions of lithium sulfate of 1.702 mol kg$^{-1}$ H$_2$O saturated in boric acid, were prepared and agitated at 303.15 K, using the phase equilibrium unit. Every 24 h a different solution was removed and its density was measured. That procedure was repeated until the density is constant, which indicates the solution has reached the thermodynamic equilibrium. The agitation time needed for the solutions to achieve that state is the equilibrium time.

**Physical Property Measurements.** After equilibrium was reached the solutions were left settling for 12 h to improve the solid–liquid separation. For every solution a sample of 7 mL of liquid was removed, using a syringe filter (0.45 μm pore size), and diluted to 250 mL, for its chemical analysis in Li$^+$ by SM311B-atomic absorption,$^{11}$ SO$_4^{2-}$ by SM 4560-S04-D$^{15}$ and, H$_2$BO$_3$ by complexation with (2R,3R,5AR)-hexanol-1,2,3,4,5-hexanol and titration by NaOH of concentration 0.1004 mol kg$^{-1}$ H$_2$O. The composition of the residual wet solid phase was analyzed for Li$^+$, SO$_4^{2-}$, and H$_2$BO$_3$ by the methods mentioned above, to settle the solid in equilibrium with the saturated solution. The nature of this solid was determined by XRD when necessary. The accuracy and reproducibility of solution chemical composition measurements were better than (0.0004 and 0.00074) mole fraction, respectively. The reproducibility of the measured data was determined compared to the H$_2$BO$_3$ solubility data from Linke and Siddell.

To measure the other physical properties of the solutions a proper amount of sample was removed from every solution using a syringe filter (0.45 μm pore size).

Density was measured with a vibrating tube densimeter (Mettler Toledo, model DE30). It has a precision of 0.05 kg m$^{-3}$ and reproducibility better than ± 1 kg m$^{-3}$. The density was measured in triplicate per sample at each mentioned temperature. The apparatus was calibrated previously, using distilled deionized water as a reference substance, before measuring for every temperature. The densimeter has a temperature control (± 0.1 K). The time needed to reach temperature stability was 600 s. In the measuring cell about 2 mL of solution was introduced; the solution was not allowed to crystallize inside the cell.

Refractive index was measured with a refractometer (Mettler Toledo, model RE-60) with a precision and reproducibility of ± 0.0001. These values are measured at the yellow doublet sodium D-line, with n = 589 nm. Two drops of the sample were deposited on the prism of the instrument, using an airtight hypodermic syringe. These measurements were made for each sample. After measurement, the sample was suctioned from the prism by a cleaning syringe; the prism was rinsed with distilled water and dried with tissue paper.

The kinematic viscosity was measured in triplicate for every solution using an automatic laser viscometer system (Schott-Gerate AVS 310). It measures the transit time of a liquid between two points in a capillary with a precision of ± 0.1 s. Two calibrated Micro-Ostwald capillaries with instrument constants, K, (0.01312 and 0.01111) mm$^2$s$^{-1}$, respectively, were used. Their calibration was made using four certified viscosity standards (N1.0 (b), N2, N3 (a), and N4) to include the whole range of dynamic viscosity measurements. The measurements ranged from 5.2 mPa·s to 0.70 mPa·s at (298.15 to 313.15) K. To measure the viscosity, 2 mL of solution was poured into the capillary and it was immersed inside a transparent thermostatic bath (Schott-Gerate CT 52) that had a temperature precision of ± 0.05 K. Dynamic viscosity data for every solution was determined using its kinematic viscosity and density measured.

Electrical conductivity was measured in triplicate for every solution using a conductimeter (Orion, model 19700-27) with a precision of ± 0.5 % and reproducibility of ± 0.7 %. It was calibrated using a standard KCl solution, fixing a cell constant of 0.664 cm$^{-1}$. The conductimeter cell was introduced in the flask containing the solution, and the instrument readings were recorded. After every measurement the flask was rinsed with distilled water and dried with tissue paper. To keep the temperature constant for the measurements, a digital immersion circulator (Thermo Haake, DC3) of (298.15 to 423.15) K temperature range and a refrigerated water bath vessel (Thermo Haake, V1) of 15 L capacity and refrigerant R134A for refrigeration down to 288.15 K were used.

**RESULTS AND DISCUSSION**

Table 2 is presents the solubility $x_0$, density $\rho$, refractive index $n$, dynamic viscosity $\eta$, and electrical conductivity $\sigma$ of saturated solutions for H$_2$BO$_3$ + Li$_2$SO$_4$ + H$_2$O as a function of mole fraction of Li$_2$SO$_4$, $x_0$, at temperatures T of (293.15, 298.15, 303.15, 308.15, and 313.15) K. The standard uncertainty, $u(x_0)$, is 0.0002 mol fraction. It was determined using the best fit method.
Table 2. Solubility $x$, Density $\rho_c$, Refractive Index $n_c$, Viscosity $\eta_c$, and Electrical Conductivity $\kappa_c$ of Aqueous Solutions of Li$_2$SO$_4$ Saturated in H$_2$BO$_3$ for different Li$_2$SO$_4$ Mole Fraction, $x$, at (293.15, 298.15, 303.15, 308.15, and 313.15) K

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<th>$x_c$, $\text{mol} %$</th>
<th>$\rho_c$, $\text{kg/m}^3$</th>
<th>$n_c$</th>
<th>$\eta_c$, $\text{mPa.s}$</th>
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*Standard uncertainties are $\sigma(T) = 0.08 \text{K}, \sigma(x_c) = 0.0001$, $\sigma(n_c) = 0.0002$, and the combined expanded uncertainties $U$ at 0.99 level of confidence and $k = 2$ are $U(\rho_c) = 0.04 \text{ kg/m}^3$, $U(n_c) = 0.0005$, $U(\eta_c) = 0.0014 \text{ mPa.s}$ and $U(\kappa_c) = 0.033 \text{ S/m}$.

Cite: doi.org/10.1021/jacs.0e01586a. J. Chem. Eng. Data XXXX, XXX, XXX-XXX
following the guidelines for evaluating the uncertainty by NIST.16 The accuracy of the measured data was determined as compared to the \( H_2BO_3 \) solubility data from Seidell and Link8 and its density, estimated using the correlation given by Novotný and Sühlner.13 The reproducibility for solubility is better than 0.0007 mol fraction and for density better than 0.6 kg m\(^{-3}\). It was not possible to determine the accuracy for the other properties because there is no reported data in literature for aqueous solutions saturated in \( H_2BO_3 \) and the system studied. The standard uncertainty for the temperature, \( u(T) \), is 0.08 K.

The data of boric acid determined is reported with repeatability better than 0.0017 and standard uncertainty, \( u(x) \), of 0.0061 mol fraction. By applying the residual test method,1 it was determined that the solid phase in equilibrium with the saturated solution is \( H_2BO_3 \) but for the last concentration of lithium sulfate, at every temperature, the solid phase is \( H_2BO_3 \) + Li\(_2\)SO\(_4\)·H\(_2\)O (eutectic point) as it was confirmed analyzing that point by XRD.

The measured data were illustrated in Figure 1. It shows that boric acid solubility decreases with increases of mole fraction of lithium sulfate at constant temperature, due to a salting out effect, given by the structure making characteristics of Li\(^+\) ions.11 The temperature effect was the same as the effect in aqueous solutions of boric acid, increasing solubility with increases of temperature.

The values of solubility of \( H_2BO_3 \) measured in aqueous solutions of Li\(_2\)SO\(_4\) are smaller than in H\(_2\)O at the same temperature.1 The solubility values measured are similar to the ones in LiCl + H\(_2\)O.15 In both cases the solubility decreases as salt concentration increases. Mainly it can be assumed as the effect of the presence of Li\(^+\) ions. This behavior is inverse to that presented in aqueous solutions of NaCl,8 KCl,9 Na\(_2\)SO\(_4\)·10\(_2\), and Na\(_2\)SO\(_4\)·12\(_2\), where the solubility of the \( H_2BO_3 \) increases with salt concentration increasing.16,11,12

To describe the experimental data, it was fitted to a curve according to the following equation:

\[
\ln(x_2/x_1, T)/\text{mole fraction} = A_0(x_2) + B_0(x_2)T/K
\]

with

\[
A_0(x_2) = \sum_{i=0}^{n} a_{0i}(x_2/\text{mole fraction})^i
\]

\[
B_0(x_2) = \sum_{i=0}^{n} b_{0i}(x_2/\text{mole fraction})^i
\]

where \( T \) is the absolute temperature, \( i = 0, 1, 2, \ldots \) etc. The coefficients \( a_{0i} \) and \( b_{0i} \) are constants and were estimated using the least-squares method.

Four constants \( (a_{00}, a_{01}, a_{02}, \text{and } b_{00}) \) of the model were necessary to describe the experimental data. The values obtained for the constants are in Table 3. The curve families of tendency of the logarithm of the solubility are parabolas. The 99.43 % of the variance of the experimental data are explained by the model as was proven by the coefficient of multiple determination \( R^2 = 0.9943 \). The standard error of estimate is given by

\[
SD = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - p}}
\]

where \( y_i \), \( \bar{y} \), \( n \), and \( p \) represent the observed value, predicted value, number of data points, and parameters respectively. The calculated value is 0.0003 mol fraction of Li\(_2\)SO\(_4\) and the maximum residual between experimental and predicted values is 0.0014 mol fraction. Equation 4 is applied to calculate the fit estimating error for the rest of correlations reported in this study.

Density values were measured with a repeatability better than 1.8 kg m\(^{-3}\). Figure 2 presents the experimental values as function of the lithium sulfate concentration for every temperature studied. It can be observed that density depends on the sulfate salt concentration, increasing its value as salt concentration increases. With respect to the temperature effect, density typically decreases with temperature increases for aqueous solutions, but it does not in the presence of lithium sulfate. This can be explained due to the fact that the solubility of boric acid increases with temperature at the same concentration of lithium sulfate, thus increasing the total solid concentration.

The density values measured were compared to the ones for aqueous solutions of this salt, at the same temperatures and concentrations, reported by Carton et al.18 It was found that the density measured has the same behavior with respect to the salt concentration and value as density of this salt in water: it is shown in Figure 2. This fact can be explained due to the fact that the lithium sulfate decreases the solubility of boric acid, its contribution being small to the density value.

Refractive index data were obtained having a repeatability less than 0.0004. The refractive index depends on lithium sulfate concentration, increasing as salt concentration increases, but it does not depend on temperature. This behavior is similar to that shown by the density and it can be assumed that the total solid concentration increases with temperature.

Because the density and refractive index present similar conducts, they are described by the same relation with sulfate concentration. That function is expressed mathematically by

\[
Y_i (x_2) = \sum_{j=0}^{n_{j}} a_{ij}(x_2/\text{mole fraction})^j
\]

where \( Y_i \) represents the density or the refractive index (it means, \( j = 1 \) or \( 2 \), respectively): the \( i \) subscript changes as before. The coefficients \( a_{ij} \) are parameters of the model.

The density data were represented well by the model using two parameters \( (a_{00} \text{ and } a_{10}) \), verifying that the influence of temperature is negligible as compared to that of the salt concentration. The estimated error is 3.9 kg m\(^{-3}\), and the maximum residual is 7.7 kg m\(^{-3}\). The combined expanded uncertainty, \( U_{cp} \), was determined following the guidelines for evaluating the uncertainty by NIST.16 The value found, at 6.95
Figure 2. Density $\rho$ of aqueous solutions of lithium sulfate saturated in boric acid as a function of lithium sulfate mole fraction, $x_2$; this study ($\bigcirc$, $T = 293.15$ K; $\square$, $T = 298.15$ K; $\Delta$, $T = 303.15$ K; $\bigcirc$, $T = 308.15$ K; $\nabla$, $T = 313.15$ K, $\bigtriangledown$, $T = 318.15$ K, $\bigcdot$, $T = 323.15$ K). The level of confidence and $k = 2$, is $U_r(\rho_0) = 0.4$ kg m$^{-3}$. The model describes $99.72\%$ of the variability of the experimental data ($R^2 = 0.9972$). The values of the parameters obtained are given in Table 3 and the calculated values are illustrated in Figure 3.

The refractive index of the ternary solution was fitted to the empirical model using $a_{20}$ and $a_{41}$ parameters, $99.51\%$ being the variability of the refractive index data described by the model ($R^2 = 0.9951$), with an estimated error of 0.0009 and maximum residual of 0.0016. The combined expanded uncertainty, at the 0.95 level of confidence and $k = 2$, is $U_r(n_0) = 0.0005$. The corresponding values to the model are shown in Table 3 and the calculated values are illustrated in Figure 3.

Figure 3. Refractive Index $n_0$ of aqueous solutions of lithium sulfate saturated in boric acid as a function of lithium sulfate mole fraction, $x_2$; this study ($\bigcirc$, $T = 293.15$ K; $\square$, $T = 298.15$ K; $\Delta$, $T = 303.15$ K; $\bigcirc$, $T = 308.15$ K; $\nabla$, $T = 313.15$ K, $\bigtriangledown$, $T = 318.15$ K, $\bigcdot$, $T = 323.15$ K). The coefficients are reported at 0.95 level of confidence.

Dynamic viscosity data were measured with a repeatability of 0.0148 mPa·s. It was observed that viscosity increases as salt concentration increases at constant temperature, for the structure maker effect of Li$^+$ ion which leads to greater packing of the solution. The viscosity decreases as the temperature value increases, because the solution packing decreases as the temperature rises. Therefore the following equation was chosen to describe these data:

$$\ln \eta(x_1, T)/mPa \cdot s = A_0 (x_1) + B_1 (x_1) T/K$$

$$A_0 (x_2) = \sum_{i=0}^{n} a_i (x_2/\text{mole fraction})^i$$

where $\eta$ is the viscosity, $x_1$ and $x_2$ are the mole fractions of lithium sulfate and boric acid, respectively, $T$ is the temperature, and $A_0(x_1), B_1(x_1)$, and $a_i$ are empirical coefficients.
\[ B_i(x_2) = \sum_{i=0}^{n} b_i(x_2 \text{ mole fraction})^i \]

Equation (8)

\(A_i\) and \(B_i\) represent potential series of \(x_2\).

The experimental data are represented well by the model, using four parameters of the potential series \((a_0, a_1, b_0, b_1)\) and \((b_2, b_3)\), with an estimated error of 0.0587 mPa·s and maximum residual of 0.1091 mPa·s. The combined expanded uncertainty, at 0.95 level of confidence and \(k = 2\), is \(U_e = 0.0194\) mPa·s.

The viscosity values were measured compared to the viscosity of solutions of this salt in water, at the same temperatures and concentrations, reported by Carton et al.\textsuperscript{16} It was found that the viscosities measured have the same behavior with respect to the salt concentration and higher value than viscosities of this salt in water, as can be observed in Figure 4. It can be explained for a decrease in the solubility of boric acid by lithium sulfate; the acid contribution to the viscosity value being small.

Electrical conductivity data were reported with a repeatability better than 1.01 S·m\(^{-1}\). The conductivity depends on lithium sulfate concentration, increasing with salt concentration increases until reaching a maximum value, after which it decreases. The presence of that maximum may be explained by the system reaching the maximum ionic mobility at the salt concentrations shown in Figure 5, a further increase of concentration results in the reduction of the ionic mobility by complex species formation. Temperature affects the conductivity as well, increasing its value for the promotion of the ionic mobility of \(SO_4^{2-}\) and \(Li^+\) ions because of the viscosity decreases.

The viscosity values are given in Table 3. The conductivity data were fitted well (\(R^2 = 0.9966\)) as can be seen in Figure 5. The estimating error of ionic conductivity calculated is 0.204 S·m\(^{-1}\) and the maximum residual is 0.275 S·m\(^{-1}\). The combined expanded uncertainty, at 0.95 level of confidence and \(k = 2\), is \(U_e = 0.303\) S·m\(^{-1}\).

The electrical conductivity measured values were compared to the electrical conductivity of solutions of this salt at water at the same temperatures and concentrations reported by Carton et al.\textsuperscript{13} It was observed that viscosities measured have the same behavior with respect to the salt concentration and smaller values than viscosities ionic mobility of \(SO_4^{2-}\) and \(Li^+\) ions are lower than that corresponding to an aqueous solution of LiSO\(_4\) because of the higher viscosity of the solutions studied.

**CONCLUSIONS**

This work provides reliable data of solubility of boric acid, density, refractive index, dynamic viscosity, and electrical conductivity data of aqueous solutions of lithium sulfate saturated in boric acid at temperature ranges from 293.15 to 313.15 K. The experimental data were correlated by empirical equations, obtaining a good enough fit to be useful for evaluating the physical properties of aqueous solutions saturated in boric acid, in the range studied of concentrations of lithium sulfate and temperatures.

**AUTHOR INFORMATION**

*E-mail: tgraben@uantof.cl. Tel.: 56 55 637313. Address: Av. Angamos 601. Antofagasta, Chile.

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**Notes**

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Thermodynamic modeling of the solubility of boric acid in the systems boric acid + lithium sulfate + water, boric acid + sodium sulfate + water and boric acid + potassium sulfate + water at 293.15–313.15 K

Wilson Alavia, Jorge Lovera, Teófilo A. Graber*
Departamento de Ingeniería Química, Universidad de Antofagasta, Av. Universidad de Antofagasta 02800, 127000 Antofagasta, Chile

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Abstract
In this contribution the experimental solubility of boric acid in sodium sulfate aqueous solution was measured at different temperatures from 293.15 to 313.15 K, and Na2SO4 concentrations ranging from 0 to 3.3795 mol kg−1 H2O.

The results were represented using an equation based on Pitzer model for the interactions of nonelectrolytes with electrolytes in aqueous solutions, given by Clasen and Millero (2006) [18]. The model parameter was estimated and validated estimating the solubility of boric acid in lithium sulfate, sodium sulfate and potassium sulfate aqueous solutions at different temperatures and salt concentrations. The model represented satisfactorily the data for the systems (SD = 0.013 mol kg−1 H2O for H3BO3 + Na2SO4 + H2O; SD = 0.023 mol kg−1 H2O for H3BO3 + Li2SO4 + H2O and SD = 0.010 mol kg−1 H2O for H3BO3 + K2SO4 + H2O). The model parameters are valid to maximum concentration of the salts, 3.3800 mol kg−1 for Na2SO4, 3.489 mol kg−1 for Li2SO4 and 2.435 mol kg−1 for K2SO4 from 293.15 K to 313.15 K.

Based on the results it was determined that lithium sulfate is a precipitant agent for boric acid and its behavior is attributed to the salting out effect of Li+ ion; sodium and potassium sulfates increase the boric acid solubility; this salting in effect is due to the presence of Na+ and K+ ions. The presence of these salts can be unfavorable for the crystallization of boric acid due to the increase of solubility which decreases the supersaturation, therefore the yield of the process.

Comparing the parameters for the system H3BO3 + Na2SO4 + H2O, H3BO3 + Li2SO4 + H2O and H3BO3 + K2SO4 + H2O, it was found that effect of these ions on the decreasing of the solubility of boric acid in aqueous sulfate solutions follows the order: Li+ > Na+ > K+ which can be attributed to the increase of their ionic radii, coordinated with 6 water molecules therefore the capacity for formation hydration shells.

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1. Introduction
Boric acid is a boron compound interesting for academy and industry due to its applications in agriculture, as fertilizer, as a neutron absorber to control the speed of nuclear fission [1], and in chemical manufacture to obtain borax and boron compounds [2]. The main sources of production of boric acid are seawater and natural brines from evaporite basins, known as salt lakes and whose genesis is associated with intense volcanic activity occurred in the past in these regions. The Searles Lake in California (USA) and the Boron province of South America that comprise the Salar de Atacama in northern Chile, the Salar de Uyuni in southwestern Bolivia and the Dead Man Salar in northwest Argentina, are the main evaporite resources in the world [3].

In northern Chile the production of boric acid from brines is the most economically method, due to the low cost implied to concentrate it, by solar evaporation. This is attributed to the high evaporation rates by the high radiation and low rainfall levels in this region. Although this is a competitive advantage, the species present in the aqueous systems form complexes equilibria then to control the process and get crystals of high purity is imprescindible to understand the solid-liquid equilibria involved. This salt water system could be represented as: Li+–Na+–K+–Ca2+–Mg2+–H+–Cl––SO42−–B2O3−–OH−–HCO3−–CO32−–H2O.

The brines used are high sulfate solutions. In this system the main species present are B3+, Na+, K+, Li+, Mg2+–Cl− and SO42− [5]. They formed binary, ternary, quaternary and more multicomponent systems. Considering that during the process the pH of the solution is about 3, to have boron as boric acid, the main system is: Li+–Na+–K+–Mg2+–H+–Cl––SO42−–H2BO3–CO32−–H2O.

* Corresponding author. Tel.: +56 55 2017313.
E-mail address: teophilograber@uantof.cl (T.A. Graber).
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Nomenclature

\( a^b \) Activity of boric acid in water
\( \alpha_a \) Activity coefficient of boric acid in a ternary system
\( A_0 \) The Debye–Hückel constant of the osmotic coefficient
\( b \) Constant, 1.2 kg mol\(^{-1/2}\) mol\(^{-1/2}\)
\( B_{io} \) Viral coefficients of second order for the ionic species
\( C_{io} \) Viral coefficients of third order for the ionic species
\( I \) Ionic strength, mol kg\(^{-1}\) H\(_2\)O
\( K_{sp} \) Solubility product
\( m \) Salt molarity, mol kg\(^{-1}\) H\(_2\)O
\( m_a \) Anion species molarity, mol kg\(^{-1}\) H\(_2\)O
\( m_b \) Boric acid solubility in water, mol kg\(^{-1}\) H\(_2\)O
\( m_n \) Boric acid solubility in salt aqueous solution, mol kg\(^{-1}\) H\(_2\)O
\( m_c \) Cation species molarity, mol kg\(^{-1}\) H\(_2\)O
\( m_a \) Neutral species molarity, mol kg\(^{-1}\) H\(_2\)O
\( \text{MAD} \) Median average deviation
\( R \) The universal gases constant, 8.3144 cm\(^2\) bar mol\(^{-1}\) K\(^{-1}\)
\( \text{SD} \) Standard deviation of the estimate
\( T \) The absolute temperature, K
\( z_a \) Relative charge of the anion
\( z_c \) Relative charge of the cation

Greek letters

\( \alpha_1 \) Parameters for 1:2 electrolytes, 1.4 kg\(^{1/2}\) mol\(^{-1/2}\)
\( \alpha_2 \) Parameters for 1:2 electrolytes, 12 kg\(^{1/2}\) mol\(^{-1/2}\)
\( \beta^{(1)} \) and \( \beta^{(3)} \) Adjusting parameters
\( \lambda_{io} \) Viral coefficients of second order for the neutral species
\( \lambda_{io} \) Mixing parameters coming from ionic and neutral interactions
\( \lambda_{io} \) Fitting parameters related to the interactions between the boric acid and cation c and anion a, and cation and anion, respectively
\( \nu_a \) Cation coefficient
\( \nu_a \) Anion coefficient
\( \mu_{io} \) Viral coefficients of third order for the neutral species
\( \gamma_a \) Activity coefficient of boric acid in water
\( \gamma_a \) Activity coefficient of boric acid in a ternary system
\( \mu_a \) Chemical potential of boric acid in solid (S)
\( \mu_a \) Chemical potential of boric acid in liquid (L)

Also in this stage the crystals of boric acid could be contaminated with traces of Li\(_2\)SO\(_4\)·H\(_2\)O [7] due to an abrupt decreasing of solubility of lithium sulfate by the effect of the common anion (SO\(_4^{2-}\)) which is a precipitating agent. These effects reduce the yield of the obtaining process of boric acid.

The optimization of industrial processes by fractional crystallization and/or solvent crystallization requires a large number of mineral solubility data in pure water and aqueous electrolyte solutions. In this context, the thermodynamic model plays an important role in the prediction and correlation of solubility data in ranges of industrial operating conditions [8].

The acid-base equilibrium present in the boron solutions does not behave as a weak acid unlike forming polyborates [9] associated strongly, difficult to quantify due to the fact that boron can coordinate to three or four oxygen atoms [10]. Raposo et al. [11] to estimate the effect of ionic medium in the solution equilibria, determined that boric acid is dissociated in H\(_3\)BO\(_3\) which interacts with the ion present in the medium [0,12]. Tolstoi [13] to calculate dissociation constants by the ab initio method, found the formation of B(OH)\(_4\) instead of H\(_3\)BO\(_3\), by the reaction of B(OH)\(_4\) and water, being present an intermediate complex B(OH)\(_3\)·H\(_2\)O during the dissociation of this acid in water. The presence of these species was verified experimentally by NMR shifts.

Pereygin and Chistyakov [14] performed the speciation of boric acid solutions for the complete pH range. For a total concentration of 0.1 M, for pH lower than 7, H\(_3\)BO\(_3\) is the prevalent specie, at pH 8, the predominant species are H\(_4\)BO\(_3\), H\(_5\)BO\(_3\), and B(OH)\(_4\), at pH between 10 and 12, B(OH)\(_3\)·H\(_2\)O, and at pH greater than 12, B\(_4\)O\(_5\)\(^{3-}\) and HBO\(_2\)\(^{2-}\).

The solubility, vapor pressure and density for boric acid solutions have been reported in literature [3,8,10,15-19] in absence and presence of impurities. Brandani et al. [15] measured vapor pressure for boric acid solutions at a temperature range from 40 °C to 100 °C and together with solubility data from literature, they represented the information by an equation based on the Wilson model. For this purpose boric acid was considered as a neutral molecule and non-dissociated.

Experimental data of solubility of H\(_3\)BO\(_3\) in water and in aqueous solutions of NaCl, KCl, LiCl, RbCl, CsCl, BaCl\(_2\), MgCl\(_2\), Mg\(_2\)(CO\(_3\))\(_2\), Na\(_2\)SO\(_4\), Na\(_2\)SO\(_3\), and Li\(_2\)SO\(_4\) at various temperatures and salt concentration were reported in the literature [3,8,16-18].

Alavia et al. [5] reported the solubility of H\(_2\)BO\(_3\) in aqueous solutions of Li\(_2\)SO\(_4\) at 293.15–313.15 K and salt concentrations from (0 to 3.1492) mol kg\(^{-1}\) H\(_2\)O. In presence of sodium and potassium sulfate in aqueous solutions, the solubility of boric acid was reported by Di Giacomo et al. [8]. They studied a large concentration range from (0 to 3.75) mol kg\(^{-1}\) H\(_2\)O for Na\(_2\)SO\(_4\), and from (0 to 1.084) mol kg\(^{-1}\) H\(_2\)O for K\(_2\)SO\(_4\), at temperatures from 303 K to 373 K. They found that the solubility of boric acid increases in presence of both salts but the effect of K\(_2\)SO\(_4\) is greater than Na\(_2\)SO\(_4\). To represent the solubility they adjusted the activity coefficient considering the boric acid as non-dissociated therefore combining the Wilson equation for short range interactions and the Debye–Hückel and Born equations for long range interactions due to the presence of ions. The resulting model has binary and ternary parameters, and the melting enthalpy and temperature for boric acid. This equation predicted the solubility with an average deviation less than 1% but a deviation of 40% for the activity coefficient.

The solubility in acid chloride aqueous solutions were reported in literature for the salts Li\(_2\)Cl, Na\(_2\)Cl, KCl, RbCl, and CsCl as a function of the ionic strength at 298 K by Ghosh and Miller [18]. The solubility of boric acid [18] was determined as a function of ionic strength from (0 to 6) mol kg\(^{-1}\) H\(_2\)O at 25 °C. The results were examined using the Pitzer equation.
This model has three interaction parameters \( \lambda_a, \lambda_{ax}, \lambda_{ax} \), related to the interaction of boric acid with cations \( a \) and anions \( c \), and \( \Delta_{ac} \), related to the interaction of cation \( c \) and anion \( a \). The parameters were obtained using experimental data. To apply the model as a predictive one, Thamson and Milero designed a methodology to estimate the interaction parameters for systems with common ions. To validate this methodology they predicted the solubility of boric acid (0.866 mol kg\(^{-1}\)) in artificial sea water (0.427 mol kg\(^{-1}\) NaCl and 0.953 mol kg\(^{-1}\) MgCl\(_2\)) in good agreement with the measured value (0.864 mol kg\(^{-1}\)). As well they estimated the interactions parameters at 298.15 K for the systems H\(_3\)BO\(_3\) + Na\(_2\)SO\(_4\)+H\(_2\)O, H\(_3\)BO\(_3\)+Li\(_2\)SO\(_4\)+H\(_2\)O, and H\(_3\)BO\(_3\)+Mg\(_2\)SO\(_4\)+H\(_2\)O for average maximum salt concentrations of 2.7 mol kg\(^{-1}\) H\(_2\)O and 2.8 mol kg\(^{-1}\) H\(_2\)O, respectively.

Therefore, in this work is informed the measured solubility of boric acid in sodium sulfate aqueous solutions for a wider range of concentrations and temperatures, from (293.15 to 313.15) K, and from (0 to 3.7375) mol kg\(^{-1}\) H\(_2\)O, respectively.

The results were represented using an equation based on the Djerassi model modified for boric acid.

The parameters were estimated and validated estimating the solubility of boric acid in lithium sulfate, sodium sulfate, and potassium sulfate aqueous solutions at different temperatures and salt concentrations.

2. Materials and method

The materials and methods used to measure the solubility of boric acid in aqueous solutions of sodium sulfate are presented below.

2.1. Materials

Boric acid (Merk, 0.995 mass fraction purity), sodium sulfate (Sigma-Aldrich, 0.995 mass fraction purity), and deionized water with low electrical conductivity, 0.0054 ps cm\(^{-1}\), were used to prepare the solutions. The acid and the salt were dried in an oven, at 31315 K and 303.15 K correspondingly for 24 h, to be able to mass them properly.

2.2. Apparatus and procedures

The solubility of boric acid in aqueous solutions of sodium sulfate at (293.15, 298.15, 303.15, 308.15 and 313.15) K was measured by the dissolution isothermal method described by Alavia et al. [5].

First, based on the data of solubility of boric acid in water [Linke and Sedell (17)], aqueous solutions saturated in boric acid were prepared in 20 cm\(^3\) Pyrex bottles at a given temperature. Second, to each prepared solution, sodium sulfate salt was added in different amounts (in the range from 0 mol kg\(^{-1}\) to 3.7375 mol kg\(^{-1}\) and finally boronic acid was added in excess to assure the saturation of the solutions, each sample has a replica. The mass of each reagent was recorded from an analytical balance with an accuracy of 0.0001 g (Denver Instrument Co., model AA-201). Third, the solutions prepared were capped tightly and were immersed in a thermostatic water bath with temperature control \( \pm \)0.01 K (Thermo Haake DC3), the jars were fixed on a rotating basket. The bath water was stirred to accelerate obtaining thermal equilibrium. The advance of the state of equilibrium of the mixtures was followed by measuring the density with an accuracy \( \pm \)0.0001 g cm\(^{-3}\) (Mettler Toledo densimeter model EDS50) for an aqueous solution of sodium sulfate of 0.0734 mol kg\(^{-1}\) H\(_2\)O, saturated in boric acid at 293.15 ± 0.01 K. The rotation system was immediately stopped after 96 h (equilibrium time) and for better separation of the solid–liquid phase mixtures, the samples were allowed to stand for 12 h at constant temperature. The solid and liquid phases are separated from each bottle using a syringe with a membrane microfilter, 0.45 \( \mu \)m, and for each sample 7 ml of solution was extracted to analyze its composition. Each solid phase was divided into two parts: one part was dissolved in distilled water for analysis by chemical methods and the other part was dried and analyzed by a diffracon X-ray. Liquid samples were analyzed for sodium and sulfate for absorption atomic [22] and boric acid by complexation with (2R,3R,4R,5S)-hexan-1,2,3,4,5,6-hexol and titration by NaOH concentration of 0.004 mol kg\(^{-1}\) H\(_2\)O. All methods were standard.

1. Thermodynamic background

3.1. Djerassi model

The general equation of the free excess Gibbs energy given by the Djerassi model [20,21] could be simplified to represent the ternary system salt + neutral + water obtaining the expression:

\[
\Delta G^\text{ex} = f(l) + 2m_m \mu_a + m_c \mu_c \text{Ca} + 2m_m \mu_m \lambda_a + 2m_m \mu_m \lambda_m + m_m \mu_m \lambda_m \text{Ca} + 2m_m \mu_m \lambda_m \text{Ca} + m_m m_c \mu_m \text{Ca} + m_m m_c \mu_m \text{Ca} + \beta_{\text{Ca}} \mu_m \text{Ca}
\]

where

\[
f(l) = -\frac{4A_{\text{H}}}{b} \ln(1 + b/l^2)
\]

\[
\beta_a = \beta_a^0 + \beta_a^1 \ln(x_a) + \beta_a^2 \ln(x_a)
\]

\[
k(x) = \frac{2}{x^2}[1 - (1 + x) \exp(-x)]
\]

\[
x_a = \alpha_1 l^{1/2}, x_c = \alpha_2 l^{1/2}
\]

\[
\beta_{\text{Ca}} = 6 \mu_m + 3 \beta_{\text{Ca}} \mu_m + 3 \beta_{\text{Ca}} \mu_m
\]

The first term on the right side in Eq. (1) describes the electrostatic contribution of long range given by the modified Debye–Hückel expression (Eq. (2)). The other terms represent the virial contributions of short range. The symbol \( R \) is the universal gas constant (8.3144 cm\(^3\) bar mol\(^{-1}\) K\(^{-1}\)); \( T \) the absolute temperature; \( m_m \) and \( m_c \) represent the cation, anion and neutral species molality, respectively; \( z_a \) is the relative charge of the cation and \( z_c \) corresponds to the anion; \( \beta_a \) and \( \lambda_a \) are the virial coefficients of second order for the ionic and neutral species, respectively; \( \beta_{\text{Ca}} \) and \( \lambda_{\text{Ca}} \) are the virial coefficients of third order.

The coefficients \( \lambda_a, \lambda_m, \mu_m, \mu_m \text{Ca} \), and \( \beta_{\text{Ca}} \) are mixing parameters coming from ionic and neutral interactions. In Eq. (2), \( \alpha_a \) is the Debye–Hückel constant of the osmotic coefficient, \( b \) is a constant and has the value of 1.2 kg\(^{-1}\) mol\(^{-1}\) \( \cdot \) L\(^{3}\). In all equations the symbol \( l \) represents the ionic strength and is defined as:

\[
l = \frac{1}{2} \sum_{a \neq a} n_m c_{m_a}
\]

The terms \( \beta(1), \beta(2), \beta(3) \) and \( \lambda \) are adjusting parameters and has the typical meanings in the Djerassi model: \( \alpha \approx 14 \text{ kg}^{-1} \text{ mol}^{-1} \cdot \text{L}^{-1} \) and \( \alpha_c \approx 12 \text{ kg}^{-1} \text{ mol}^{-1} \cdot \text{L}^{-1} \) are parameters for 2:2 electrolytes. For other electrolytes the given values are \( \alpha \approx 1.4 \text{ kg}^{-1} \text{ mol}^{-1} \cdot \text{L}^{-1} \) and \( \alpha_c \approx 12 \text{ kg}^{-1} \text{ mol}^{-1} \cdot \text{L}^{-1} \).
3.2. Solubility

The solid-liquid equilibrium of aqueous solutions saturated in boric acid with solid can be represented as:

\[ \text{H}_3\text{BO}_3(s) = \text{H}_3\text{BO}_3(aq) \]  

where the boric acid is considered in liquid phase as neutral specie. In equilibrium, the chemical potential of boric acid in solid (S) and liquid (L) phases are equal:

\[ \mu_S = \mu_L \]  

Relating this equality to the activity is obtained:

\[ \ln K_{ps} = \ln \frac{a_S}{a_L} \]  

where \( K_{ps} \) is the solubility product and \( a_S \) is the activity of boric acid in water (binary system). The activity of pure boric acid in solid phase is considered as the unity. The \( K_{ps} \) value is the same for salt aqueous solutions saturated in boric acid because it depends on temperature only, consequently:

\[ \ln K_{ps} = \ln \frac{a_L}{a_S} \]  

and the solid-liquid equilibrium equation is:

\[ \ln \left( \frac{m_S}{m_L} \right) = \ln \left[ \frac{\gamma_S a_S^{m_S}}{\gamma_L a_L^{m_L}} \right] \]  

with \( m_S \), \( m_L \), \( \gamma_S \) and \( \gamma_L \) are the boric acid solubility and activity coefficient in water and in a salt aqueous solution, respectively. The activity coefficient is obtained from the partial derivative of the excess Gibbs energy (Eq. (1)) with respect to boric acid mole at constant temperature.

Combining the activity coefficients for the binary and ternary systems with the solid-liquid equilibrium condition, Chanson and Millero [18] established an equation to calculate the boric acid solubility in salt aqueous solutions which is referenced in this work:

\[ \ln \frac{m_S}{m_L} = \left[ 2 \gamma_S \lambda_{\text{Be}} + \gamma_L \lambda_{\text{Na}} \right] m + \gamma_L \lambda_{\text{Na}} \]  

where \( \gamma_S \) is the cation coefficient and \( \gamma_L \) the anion coefficient, \( \lambda_{\text{Be}} \) and \( \lambda_{\text{Na}} \) are fitting parameters related to the interactions between the boric acid and cation \( c \) and anion \( a \), and cation and anion, respectively, \( m \) is the salt molarity. It must be noted, in Eq. (13), that to calculate the solubility, the \( K_{ps} \) is not necessary due to the fact that this parameter is replaced by the activity equality (Eq. (11)).

Eq. (13) can be expressed as:

\[ \ln \frac{m_S}{m_L} = \frac{a + bm + cm^2}{m_L} \]  

The coefficients \( a, b \) and \( c \) are related to the Fixzer parameters by:

\[ a = \ln \gamma_S \]  

\[ b = -2 \gamma_S \lambda_{\text{Be}} + 2 \gamma_L \lambda_{\text{Na}} \]  

\[ c = -\gamma_L \lambda_{\text{Na}} \]  

The \( a \) coefficient is estimated from the solubility of boric acid in water by the method of linear regression using experimental data from literature [17]. The parameters, \( a, b \) and \( c \), are obtained by fitting the solubility of boric acid in the ternary system (in presence of a salt) using the least-squares method, minimizing the objective function:

\[ \sum_{i=1}^{n} \left( m_{\text{exp}} - m_{\text{cal}} \right)^2 \]

The mixing salt parameters (\( \lambda_{\text{Be}}, \lambda_{\text{Na}}, \gamma_{c-a} \)) can be calculated following the procedure given by Chanson and Millero [18]. In our case first the \( b \) parameters for the systems \( \text{H}_3\text{BO}_3 + \text{KCl} + \text{H}_2\text{O} \) (1) and \( \text{H}_3\text{BO}_3 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O} \) (2) were estimated and applied them to Eq (16) obtaining:

\[ b_1 = -(2 \lambda_{\text{Be}} + 2 \lambda_{\text{Na}}) \]  

\[ b_2 = -(2 \lambda_{\text{Be}} + 2 \lambda_{\text{Na}}) \]  

In Eq. (18), \( \lambda_{\text{Na}} \) is set to zero and \( \lambda_{\text{Be}} \) is obtained. This parameter, \( \lambda_{\text{Be}} \), is replaced in Eq. (19) and \( \lambda_{\text{Na}} \) obtained. The \( \lambda_{\text{Be}}, \gamma_{c-a} \) are estimated from Eq. (17) using the \( c \) estimated for the studied systems.

| Table 1 | Solubility \( m_p \) of boric acid in aqueous solutions of \( \text{Na}_2\text{SO}_4 \) saturated in \( \text{H}_3\text{BO}_3 \) for different \( \text{Na}_2\text{SO}_4 \) molarities, \( m \), at 293.15, 298.15, 303.15, 308.15 and 313.15 K |
|---------|-----------------|-----------------|-----------------|-----------------|
| TK      | \( m_p \) (mol) | \( m_{\text{Na}_2\text{SO}_4} \) | \( m_{\text{H}_3\text{BO}_3} \) | \( m_{\text{H}_2\text{O}} \) |
| 293.15  | 0.0000          | 1.1810          | 1.0000          | 1.0000          |
| 293.15  | 0.0034          | 1.2352          | 1.0034          | 1.0034          |
| 293.15  | 0.0064          | 1.2777          | 1.0064          | 1.0064          |
| 293.15  | 0.0095          | 1.3195          | 1.0095          | 1.0095          |
| 293.15  | 0.0126          | 1.3613          | 1.0126          | 1.0126          |
| 293.15  | 0.0157          | 1.4031          | 1.0157          | 1.0157          |
| 293.15  | 0.0189          | 1.4449          | 1.0189          | 1.0189          |
| 293.15  | 0.0221          | 1.4867          | 1.0221          | 1.0221          |
| 293.15  | 0.0253          | 1.5285          | 1.0253          | 1.0253          |
| 293.15  | 0.0285          | 1.5703          | 1.0285          | 1.0285          |
| 293.15  | 0.0317          | 1.6121          | 1.0317          | 1.0317          |
| 293.15  | 0.0349          | 1.6539          | 1.0349          | 1.0349          |
| 293.15  | 0.0381          | 1.6957          | 1.0381          | 1.0381          |
| 293.15  | 0.0413          | 1.7375          | 1.0413          | 1.0413          |
| 293.15  | 0.0445          | 1.7793          | 1.0445          | 1.0445          |
| 293.15  | 0.0477          | 1.8211          | 1.0477          | 1.0477          |
| 293.15  | 0.0509          | 1.8629          | 1.0509          | 1.0509          |
| 293.15  | 0.0541          | 1.9047          | 1.0541          | 1.0541          |
| 293.15  | 0.0573          | 1.9465          | 1.0573          | 1.0573          |
| 293.15  | 0.0605          | 1.9883          | 1.0605          | 1.0605          |

* Standard uncertainties \( u \) are \( u(\text{m}) = 0.0009 \text{ mol kg}^{-1} \), and the combined expanded uncertainties \( U \), at 0.95 level of confidence and \( k=2 \), are \( u(m_p) = 0.0159 \text{ mol kg}^{-1} \).
4. Results and discussion

The solubility measurements for boric acid in aqueous solutions of sodium sulfate are presented in Table 1 at temperatures from (293.15 to 303.15) K for different sodium sulfate concentrations, m. Based on the guidelines given by NIST [23] the standard uncertainties were estimated for the temperature, \( T \), and salt concentration \( m \). In the case of solubility the combined, \( u \), and expanded, \( U \), at 0.95 level of confidence and \( k = 2 \), where the most appropriate to describe its accuracy. The values found are: \( u(T) = 0.066 \), \( u(m) = 0.0597 \), and \( U(m) = 0.0113 \) mol kg\(^{-1}\).

The solubility of boric acid in water measured was compared to the data presented by Blasdale and Slansky [24] due to this is the primary reference for the most cited values in literature which are reported by Linke [17], Perry [25], and Langer [26]. This comparison is shown in Fig. 1. Although the equilibrium time is different, 96 h in this work and 24 h in the study from Blasdale and Slansky, the deviation between them, calculated using the mean average deviation given by Eq. (20), is 0.0294 mol kg\(^{-1}\) H\(_2\)O.

\[
\text{MAD} = \frac{1}{N} \sum_{i=1}^{N} |x_{\text{lit}} - x_{\text{exp}}|
\]

The measured data for the solubility of boric acid in sodium sulfate aqueous solutions were compared to the data presented by Di Giacomo et al. [8] at 303.15K and 313.15K, due to the fact that they do not report the solubility for the other temperatures of this study. To be able to compare the data for the same sodium sulfate concentrations their data were adjusted to an empirical equation [6] for each temperature. The equation used is shown below and their corresponding parameters, coefficient of multiple determination, \( R^2 \), and the standard error of the estimate, SD [6], for every temperature are presented in Table 2.

\[
\ln m_b = s_0 + s_1 m + s_2 m^2 + s_3 m^3
\]

The experimental solubility follows the same trend as the values reported by Di Giacomo et al. [8] as can be seen in Fig. 2. The values at 303.15 K present a small mean average deviation, 0.0284 mol kg\(^{-1}\) H\(_2\)O, but at 303.15 K the deviation is considerable, 0.1117 mol kg\(^{-1}\) H\(_2\)O at 313.15K; this variance can be attributed to the different mixing method they used to reach the equilibrium which could promote the evaporation of the solution at high temperatures resulting in greater values of solubility.

Di Giacomo et al. [8] used a jacketed glass cell as equilibrium cell. The solution temperature was kept constant by fluid circulation through the jacket from a thermostatically controlled water bath which is suitable to obtain a good mixing and avoid evaporation from the close bottle thus obtaining more representative solubility.

The repeatability of the solubility measured was calculated from the repeated samples. It is smaller than 0.0994 mol kg\(^{-1}\) H\(_2\)O. The value of the relative standard deviation is 1.7 times greater than the \( u_b(m_b) \), but it is 0.8 times smaller than the expanded uncertainty \( U_b(m_b) \). This fact supports the validity of the measurements presented in this work.

The remaining solid phase after the solutions reached the equilibrium, was identified using the residual wet method [27] and verified by XRD. The solid is boric acid, except for the last concentration of sodium sulfate, where the solid presents a mix of boric acid and sodium sulfate. This behavior is the same for all the temperatures studied.

The measured data shows that boric acid solubility increases with rises of molality of sodium sulfate at constant temperature, due to a salting in effect, given by the structure breaking characteristic of Na\(^+\) ion [18].

The solubility of boric acid in water measured and the reported by Linke [17] were used to obtain the \( a \) parameter from Eq. (15). This parameter depends on temperature like the solubility. This parameter was expressed using a function of temperature according to the work of Chanson and Millemo [18]:

\[
\ell = a_0 + a_1 T
\]

where \( a_0 \) and \( a_1 \) are fitting parameters and \( T \) is the absolute temperature. The coefficients \( b \) and \( c \) of Eq. (14) were fitted to the solubility of boric acid in the systems H\(_3\)BO\(_3\)+Na\(_2\)SO\(_4\)+H\(_2\)O, measured in this work, H\(_3\)BO\(_3\)+Li\(_2\)SO\(_4\)+H\(_2\)O [5], H\(_3\)BO\(_3\)+

<table>
<thead>
<tr>
<th>T/K</th>
<th>( x_0 )</th>
<th>( x_1 )</th>
<th>( x_2 )</th>
<th>( x_3 )</th>
<th>SD</th>
<th>( R^2 )</th>
<th>mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>303.15</td>
<td>0.015 ± 0.0049</td>
<td>0.3299 ± 0.0479</td>
<td>-0.0888 ± 0.0244</td>
<td>0.0096 ± 0.0039</td>
<td>0.0044</td>
<td>0.9997</td>
<td>3.003</td>
</tr>
<tr>
<td>313.15</td>
<td>0.0743 ± 0.0077</td>
<td>0.2860 ± 0.0227</td>
<td>-0.0733 ± 0.0070</td>
<td>0.0081 ± 0.0028</td>
<td>0.0046</td>
<td>0.9708</td>
<td>3.250</td>
</tr>
</tbody>
</table>

* The confidence intervals for all the parameters are reported at 0.95 level of confidence.
K$_2$SO$_4$ + H$_2$O at 298.15, 308.15 K [17], 305.15 K and 312.15 K [8], and H$_2$BO$_3$ + KCl + H$_2$O at 298.15K, 308.15 K [17], 298.15 K [18], and at 303 K and 313 K [7].

It was found that these coefficients are independent of temperature. The optimal values of the coefficients estimated ($a_0$, $a_1$, $b$, and $c$) are presented in Table 3.

In Figs. 3–5 the experimental and estimated solubility are compared to verify the goodness of the fitting for the systems Na$_2$SO$_4$ + H$_2$BO$_3$ + H$_2$O, Li$_2$SO$_4$ + H$_2$BO$_3$ + H$_2$O and K$_2$SO$_4$ + H$_2$BO$_3$ + H$_2$O. The estimations of the solubility of boric acid in the systems at 300.65K, 305.65 K or 308.15 K and 310.65 K are also presented, in these figures, to demonstrate the suitability of the model to calculate the solubility at different temperatures.

Fig. 3 shows that the solubility of boric acid increases for the whole range of sodium sulfate solutions studied (0–3.795) mol kg$^{-1}$ at (293.15–313.15)K. It is due to the interactions between acid and water molecules are promoted, being the salting out effect the principal one. This fact is supported by the great positive value of the coefficient b shown in Table 3.

It can be observed in Fig. 4 that adding lithium sulfate the solubility of boric acid decreases. It could be attributed to the competence of ions and boric acid for water molecules, therefore a salting out effect is produced. The magnitude of this effect depends on the sign and value of the $c$ coefficient of Eq. (13), and is proportional to the square of the salt molality $m$. The value is shown in Table 3.

In presence of potassium sulfate the solubility of boric acid increases as shown in Fig. 5. It is the same behavior as in presence of sodium sulfate (see Fig. 3). It can be explained by a salting in effect, produced by the presence of the K$^+$ ion. The extent of this effect depends on the sign and value of the $b$ coefficient of Eq. (13). The $b$ value is shown in Table 3.

It was found that the values of the $b$ and $c$ coefficients do not depend on concentration neither temperature at the concentration and temperature ranges studied, but the $a$ parameter is temperature dependent. That is the reason parallel curves are obtained to represent the salting in and salting out effects at different temperatures.

The mixing salt parameters were calculated following the procedure described in the solubility section (Eqs. (16)–(19)). The values of the coefficient $b$ for the systems used are given in Table 3. The determined parameters and their average maximum salt concentration of validity are presented in Table 4.

The parameters obtained were compared to the reported by Chanson and Millero [18]. They estimated the interaction parameters shown in Table 4 using fitting parameter $a$ and $b$ which are equivalent to the $-b$ and $-c$ coefficients of this study, respectively. The detailed procedure of estimation for each interaction parameter and their equivalents $b$ and $c$ are described below. The original parameters from [8] are given in brackets. It was found that the value of the parameter $A_{diss}$ estimated in this study is similar to the literature value as exposed in Table 4. Chanson and Millero used the systems H$_2$BO$_3$ + Na$_2$SO$_4$ + H$_2$O and H$_2$BO$_3$ + K$_2$SO$_4$ + H$_2$O at 298.15 K and $m_{max} = 0.511$ with an average...
Table 4
Mixing parameters for the Pitzer model, Eq. (8), for modeling basic acid solubility in salt aqueous solutions from 293.15K to 313.15K

<table>
<thead>
<tr>
<th>Salt</th>
<th>( \lambda_{\text{Na}^+} )</th>
<th>( \lambda_{\text{H}^+} )</th>
<th>( c_{\text{Na}^+} )</th>
<th>( m_{\text{Na}^+} )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(_2)SO(_4)</td>
<td>0.041</td>
<td>0.230</td>
<td>0.024</td>
<td>3.380</td>
<td>This study</td>
</tr>
<tr>
<td>Li(_2)SO(_4)</td>
<td>0.028</td>
<td>0.205</td>
<td>0.035</td>
<td>1.956</td>
<td>This study</td>
</tr>
<tr>
<td>K(_2)SO(_4)</td>
<td>0.017</td>
<td>0.181</td>
<td>0.046</td>
<td>2.014</td>
<td>This study</td>
</tr>
</tbody>
</table>

* It was estimated using the average \( b = 0.0545 \) (\( a = 0.0545 \)) from the system H\(_3\)BO\(_3\) + Na\(_2\)SO\(_4\) + H\(_2\)O at 298.15K and \( m_{\text{Na}^+} = 4.793 \), \( \lambda_{\text{Na}^+} = 0 \).
* It was estimated using the average \( b = 0.0405 \) (\( a = 0.0405 \)) from the system H\(_3\)BO\(_3\) + Li\(_2\)SO\(_4\) + H\(_2\)O at 298.15K and \( m_{\text{Li}^+} = 5.172 \), \( \lambda_{\text{Li}^+} = 0 \).
* It was estimated using the average \( b = 0.057 \) (\( a = 0.057 \)) from the systems H\(_3\)BO\(_3\) + Na\(_2\)SO\(_4\) + H\(_2\)O and H\(_3\)BO\(_3\) + K\(_2\)SO\(_4\) + H\(_2\)O at 298.15K and \( m_{\text{Na}^+} = 0.511 \lambda_{\text{Na}^+} = 0 \).
* It was estimated using the average \( b = 0.005 \) (\( a = 0.005 \)) from the system H\(_3\)BO\(_3\) + Na\(_2\)SO\(_4\) at 298.15K and \( m_{\text{Na}^+} = 0.561 \).
* It was estimated by \( c_{\text{Na}^+} \times 2 = c_{\text{Li}^+} \times 2 = c_{\text{K}^+} \times 2 = 0.004 \) (\( a = 0.004 \)) and \( c_{\text{Na}^+} = 0 \) and \( c_{\text{Li}^+} = 0 \) and \( c_{\text{K}^+} = 0 \).
* It was estimated using the average \( b = 0.005 \) (\( a = 0.005 \)) from the system H\(_3\)BO\(_3\) + K\(_2\)SO\(_4\) at 298.15K and \( m_{\text{K}^+} = 0.459 \).

The parameter \( \lambda_{\text{Na}^+} \) is 1.5 times greater than the literature value. This variance is mainly caused by the reference systems used. In this study the parameter was obtained from the \( b \) corresponding to the system H\(_3\)BO\(_3\) + Na\(_2\)SO\(_4\) + H\(_2\)O and the \( \lambda_{\text{Na}^+} \) previously estimated, but in literature the parameter was estimated from the system H\(_3\)BO\(_3\) + Na\(_2\)SO\(_4\) + H\(_2\)O at 298.15K and \( m_{\text{Na}^+} = 4.793 \), making \( \lambda_{\text{Na}^+} = 0 \), and using an average \( b = 0.0545 \) (\( a = 0.0545 \)).

The parameter \( \lambda_{\text{K}^+} \) is 2.7 times greater than the one reported by Chanson and Miliero. In this case the references system used was H\(_3\)BO\(_3\) + Li\(_2\)SO\(_4\) + H\(_2\)O and the \( \lambda_{\text{Li}^+} \) previously estimated, unlike the literature parameter that was estimated from the system H\(_3\)BO\(_3\) + Li\(_2\)SO\(_4\) + H\(_2\)O at 298.15K and \( m_{\text{Li}^+} = 5.172 \), making \( \lambda_{\text{Li}^+} = 0 \), and using an average \( b = 0.0405 \) (\( a = 0.0405 \)).

The parameter \( \lambda_{\text{Li}^+} \) is similar to the one reported in literature. This is due to the reference system used was the same, H\(_3\)BO\(_3\) + K\(_2\)SO\(_4\) + H\(_2\)O in the range of concentration studied, \( m_{\text{K}^+} = 3.978 \).

The parameter \( c_{\text{Na}^+\text{+K}^+} \) has opposite sign and is 2.7 times greater than the one reported by Chanson and Miliero. This value was obtained directly from Eq. (16), using the \( c \) value given in Table 4 for the system H\(_3\)BO\(_3\) + Na\(_2\)SO\(_4\) + H\(_2\)O. The value estimated by Chanson and Miliero was obtained following the same procedure. They used the average \( c = 0.065 \) (\( b = 0.057 \)) for the system H\(_3\)BO\(_3\) + Na\(_2\)SO\(_4\) at 298.15K and \( m_{\text{Na}^+} = 0.563 \). It was observed that its \( c_{\text{Na}^+\text{+K}^+} \) does not reproduce the \( c \) value from where it was calculated. To verify if it was a tipping mistake, this parameter was re-estimated from their reference data [16], the \( c \) value obtained was 0.013.

The parameter \( c_{\text{Na}^+\text{+Li}^+} \) has opposite sign and is 0.3 times smaller than the one reported by Chanson and Miliero [18]. This coefficient was calculated from equation 16, the \( c \) value used is shown in Table 4, for the system H\(_3\)BO\(_3\) + Na\(_2\)SO\(_4\) + H\(_2\)O. Chanson and Miliero assessed this value using an additive rule. It was estimated adding the parameter \( c_{\text{Na}^+\text{+Li}^+} = 0.004 \) (\( a = 0.004 \)) and \( c_{\text{Na}^+\text{+K}^+} = 0.008 \) for the systems H\(_3\)BO\(_3\) + Li\(_2\)SO\(_4\) + H\(_2\)O and H\(_3\)BO\(_3\) + Na\(_2\)SO\(_4\) + H\(_2\)O, respectively at 298.15K and \( m_{\text{Na}^+} = 3.509 \). The equation used was:

\[
c_{\text{Na}^+\text{+Li}^+} = 2c_{\text{Na}^+\text{+K}^+} - c_{\text{Na}^+\text{+Li}^+} \]

This parameter is valid until 2.800 mol kg\(^{-1}\).

The parameter \( c_{\text{Na}^+\text{+K}^+} \) has opposite sign and is 1.6 times greater than the reported by Chanson and Miliero [18], this value was obtained directly from Eq. (16), using the \( c \) value given in Table 4 for the system H\(_3\)BO\(_3\) + K\(_2\)SO\(_4\) + H\(_2\)O. Chanson and Miliero, obtained this parameter using the average \( c = 0.043 \) (\( b = 0.043 \)) for the systems H\(_3\)BO\(_3\) + K\(_2\)SO\(_4\) + H\(_2\)O at 298.15K and \( m_{\text{K}^+} = 0.456 \). As in the case of \( c_{\text{Na}^+\text{+K}^+} \), it was found that \( c_{\text{Na}^+\text{+K}^+} \) does not reproduce the \( c \) value from where it was calculated, to verify if the \( c \) value was re-estimated from their reference data [17], the value estimated is 0.139.

The comparison is shown in Figs. 5–9. The results showed that the proposed model represents the experimental data very well, but the one proposed by Chanson and Miliero [18] does not.

For the system H\(_3\)BO\(_3\) + Na\(_2\)SO\(_4\) + H\(_2\)O the results showed that the proposed model represents the experimental data very well, but the one, proposed by Chanson and calculated using the mixing parameters estimated from systems with common ion, fits the data until concentration of 0.561mol kg\(^{-1}\) as shown in Fig. 5.

![Graph 1](image1.png)

![Graph 2](image2.png)
Fig. 8. Solubility of boric acid $m_m$ as a function of potassium sulfate molality $m$ at 298.15 K [1]. Experimental, –, calculated from Eq. [14], ..., calculated from Eq. [15] using the mixing parameters from [16] given in Table 4.

Fig. 9. Solubility of boric acid $m_m$ as a function of potassium sulfate molality $m$ at 313.15 K [1]. Experimental, –, calculated from Eq. [14], ..., calculated from Eq. [15] using the mixing parameters from [16] given in Table 4.

For the system $\text{H}_2\text{BO}_3 + \text{Li}_2\text{SO}_4 + \text{H}_2\text{O}$ the results showed that the proposed model represents the experimental data very well, but the one proposed by Chanson and calculated using the mixing parameters estimated from systems with common ion, its the data until concentration of 0.30 mol kg$^{-1}$ as shown in Fig. 7.

In the case of the system $\text{H}_2\text{BO}_3 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$ the results showed that both models, this study and the Chanson and Millero represented well the experimental data at 298.15 K as can be seen in Fig. 8. Deviation from the experimental data are presented at higher temperatures for the Chanson model as shown in Fig. 9 due to their parameters are only valid at 298.15 K.

For the systems $\text{H}_2\text{BO}_3 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ and $\text{H}_2\text{BO}_3 + \text{Li}_2\text{SO}_4 + \text{H}_2\text{O}$ the behavior of the model is similar to that presented in Figs 6 and 7 at the other temperatures studied.

The reason why the model given by Chanson and Millero [18] does not describe properly the solubility of boric acid in the systems studied, is the difference of the values of $c_{\text{ex}}$ as can be seen in Table 4. For all the systems studied, its parameter is negative, 2.7 and 3.9 times greater than the values estimated in this study for $\text{H}_2\text{BO}_3 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ and $\text{H}_2\text{BO}_3 + \text{Li}_2\text{SO}_4 + \text{H}_2\text{O}$ and 0.6 times smaller for $\text{H}_2\text{BO}_3 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$. This fact can be attributed to the maximum salt concentrations they used (0.563 mol $\text{Na}_2\text{SO}_4$ kg$^{-1}$ H$_2$O and 0.450 mol $\text{K}_2\text{SO}_4$ kg$^{-1}$ H$_2$O) are smaller than this study (3.380 mol $\text{Na}_2\text{SO}_4$ kg$^{-1}$ H$_2$O and 1.245 mol $\text{Li}_2\text{SO}_4$ kg$^{-1}$ H$_2$O) except for the system $\text{H}_2\text{BO}_3 + \text{Li}_2\text{SO}_4 + \text{H}_2\text{O}$ where the salt concentration (3.301 mol $\text{Li}_2\text{SO}_4$ kg$^{-1}$ H$_2$O) is slightly greater than this study (3.149 mol $\text{Li}_2\text{SO}_4$ kg$^{-1}$ H$_2$O). This difference can be attributed to the estimation of the $b$ coefficient in the reference [18], restricted only to 298.15 K.

To show the effect of different cations with common anion in the solubility of boric acid in the Fig. 10 is presented the solubility of boric acid in lithium sulfate, sodium sulfate and potassium sulfate at 313.15 K. They were estimated using Eq. [14]. The behavior of solubility at the other temperatures is similar.

The Fig. 10 shows that the presence of different cations with common anion affects in a different way to the solubility of boric acid. The effect follows this order, determined according to the decrease of boric acid solubility or by the value of the $b$ parameter (salting coefficient) at 313.15 K: $\text{Li}^+ > \text{Na}^+ > \text{K}^+$, which can be attributed to the increase of their ionic radii coordinate with 6 water molecules ($\text{Li}^+ = 0.79 \AA$, $\text{Na}^+ = 1.07 \AA$ and $\text{K}^+ = 1.38 \AA$) [28] therefore the capacity to form hydration shells. This classification is only valid in aqueous solution due to the effect of the structure makers ($\text{Li}^+$) or structure breakers ($\text{Na}^+$ and $\text{K}^+$) also related to the salting coefficient, is a function of the cation – boric acid interaction, $\lambda_{\text{cc}}$, and the anion (common ion) – boric acid interaction, $\lambda_{\text{an}}$. That is, boric acid is more soluble in salt solutions than in chloride solutions [18].

It can be inferred from this results that lithium sulfate is a precipitant agent for boric acid and that its behavior is attributed to the salting out effect of $\text{Li}^+$ ion, sodium sulfate and potassium sulfates increase the boric acid solubility; this salting in effect is due to the presence of $\text{Na}^+$ and $\text{K}^+$ ions. The presence of these salts can be unfavorable for the crystallization of boric acid, due to decreases the supersaturation therefore the yield of the process.

5. Conclusions

This work provides reliable data of solubility of boric acid in sodium sulfate aqueous solutions and an equation based on the Pitzer model to obtain a good enough fit to be useful for evaluating the solubility of boric acid in sodium sulfate, potassium sulfate and lithium sulfate aqueous solutions, in the range studied of concentrations and temperatures. The model parameters are valid to maximum concentration of the salts, 3.380 mol kg$^{-1}$ for $\text{Na}_2\text{SO}_4$, 3.149 mol kg$^{-1}$ for $\text{Li}_2\text{SO}_4$ and 1.245 mol kg$^{-1}$ for $\text{K}_2\text{SO}_4$ from 281.15 K to 313.15 K.

It was determined that the lithium sulfate is a precipitant agent for boric acid and that its behavior is attributed to the salting out effect of $\text{Li}^+$ ion, sodium sulfate and potassium sulfates increase the boric acid solubility, this salting in effect is due to the presence of $\text{Na}^+$ and $\text{K}^+$ ions. The presence of these salts can be unfavorable for the crystallization of boric acid, due to decreases the supersaturation therefore the yield of the process.
The effect of the ions on the decreasing of the solubility of boric acid in aqueous sulfate solutions, follows this order: Li⁺ > Na⁺ > K⁺, which can be attributed to the increase of their ionic radii, coordinated with 6 water molecules therefore the capacity to form hydration shells.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fluid.2015.04.012.

References

Density, Refractive Index, Viscosity, and Electrical Conductivity of Aqueous Solutions of Sodium Sulfate Saturated in Boric Acid at (293.15, 298.15, 303.15, 308.15 and 313.15) K.

Wilson Alavia, and Teofilo A. Graber*

Departamento de Ingeniería Química, Universidad de Antofagasta, Avenue Universidad de Antofagasta 02800, Antofagasta, Chile.

**ABSTRACT:** Density, refractive index, viscosity and electrical conductivity for aqueous solutions of sodium sulfate saturated in boric acid have been determined. The salt concentration and temperatures ranges studied were from (0 to 0.0559) molar fraction and from (293.15 to 313.15) K respectively. The properties were represented using equations which are functions of temperature and salt concentration.

The properties depend on the salt concentration, increasing as salt amount rises but the temperature effect is negligible except for viscosity. It decreases with temperature increments. The behavior of the properties is attributed to the sodium ion, which is a structure breaker. When the salt concentration rises it compresses the volume of the solution and with sulfate ion change the electromagnetic field. Also the electrical conductivity is function of the ionic mobilities of sodium and sulfate ions.

**KEYWORDS.** Boric Acid, Sodium Sulfate, Density, Viscosity, Electrical Conductivity, Refractive Index.

* To whom correspondence should be addressed. Tel.: 56 55 2 637313. Avenue Universidad de Antofagasta 02800, Antofagasta, Chile. Email: teofilo.graber@uantof.cl.
Introduction

Boric acid produced from high sulfate brines that contain Na+, K+, Li+ and Mg2+ ions could be contaminated with sodium sulfate by impregnation and lithium sulfate monohydrate by coprecipitation at room temperature. Also the crystallization yield is affected by increase of the solubility in sodium sulfate and potassium sulfate aqueous solutions. The problem mentioned could happen to produce boric acid from the Atacama Salt Lake in Chile mainly during spring and winter. In these seasons the sulfate salts concentrations reach higher levels because of the increase of solar evaporation of water from the brines, affecting the overall efficiency. The ions effect over the production could be evaluated using the physical properties of the solutions saturated in boric acid involved and further modeling and optimization is also possible. The interest properties are the solubility, density, viscosity, refractive index and electrical conductivity at saturation.

Boric acid solubility have been reported in solutions of H$_3$BO$_3$+H$_2$O, H$_3$BO$_3$+Na$_2$SO$_4$+H$_2$O, H$_3$BO$_3$+K$_2$SO$_4$+H$_2$O, H$_3$BO$_3$+Na$_2$SO$_4$+H$_2$O from 303.00 K to 373.00 K, H$_3$BO$_3$+Li$_2$SO$_4$+H$_2$O from (0 to 3.1472) mol·kg$^{-1}$H$_2$O at temperatures ranging from 293.15 K to 313.15 K and H$_3$BO$_3$+Na$_2$SO$_4$+H$_2$O from (0 to 3.3795) mol·kg$^{-1}$H$_2$O and temperature ranging from 293.15 K to 313.15 K.

Density of H$_3$BO$_3$+H$_2$O was informed from dilute to saturated solutions at 273.15 K to 373.15 K. For the ternary systems H$_3$BO$_3$+KCl+H$_2$O at 293.15 K, 298.15 K and 303.15 K, and H$_3$BO$_3$+NaCl+H$_2$O, H$_3$BO$_3$+K$_2$SO$_4$+H$_2$O and H$_3$BO$_3$+Na$_2$SO$_4$+H$_2$O at 298.15 K, 303.15 K and 308.15 K this property was reported for undersaturated solutions. Also the refractive index for H$_3$BO$_3$+H$_2$O and H$_3$BO$_3$+KCl+H$_2$O undersaturated solutions at 293.15, 298.15 and 303.15 K were reported.

Density, viscosity, refractive index and electrical conductivity at saturation, in boric acid, have been reported only for the system H$_3$BO$_3$+Li$_2$SO$_4$+H$_2$O for salt concentrations from (0 to 3.1472) mol·kg$^{-1}$ and temperatures ranging from (293.15 to 313.15). Therefore we report in this contribution the density, refractive index, viscosity and electrical conductivity for aqueous solutions of sodium sulfate saturated in boric acid. The salt concentrations and temperatures studied are from (0 to 0.0559) molar fraction and temperatures from (293.15 to 313.15) K respectively. These properties are described using
empirical equations and their behavior is discussed by comparison to the properties of the system Na₂SO₄+H₂O¹⁴,¹⁶ and H₃BO₃+Li₂SO₄+H₂O¹⁰.

**Experimental section**

**Materials**

The characteristics of the reagents used are presented in Table 1.

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Source</th>
<th>Purity (Mass fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boric Acid</td>
<td>Merck</td>
<td>0.995</td>
</tr>
<tr>
<td>Sodium Sulfate</td>
<td>Sigma-Aldrich</td>
<td>0.995</td>
</tr>
<tr>
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<td>Merck</td>
<td>0.990</td>
</tr>
</tbody>
</table>

The boric acid and sodium sulfate were dried before using at 333.15 K and 393.15 K respectively for 24 h.³ For all the procedures deionized and distilled water were employed.

**Apparatus and Procedures**

The samples were prepared twice, to control repetability, mixing a boric acid saturated solution, sodium sulfate and an excess of boric acid to ensure saturation. The compositions were determined in a previous work.³ Reagents were massed with an analytical balance (Denver Instrument Co., model AA-200), with a precision of ± 0.0001g. To assure saturation the samples were stirred for 96 hours at constant temperature in a phase equilibrium unit. Afterwards the solid and liquid phases were separated by settling the suspensions for 12 h.³ The solutions compositions were verified following the procedure given in literature.³,¹⁰

**Physical Properties Measurement**

To measure a sample proper volume to measure in triplicate every property was taken from every solution with a syringe filter (0.45 μm pore size).

A vibrating tube densimeter, Mettler Toledo model DE50, with a precision of 0.05 kg m⁻³ and reproducibility better than ± 1 kg m⁻³ was used to measure the density. The apparatus
was adjusted before measuring with distilled deionized water as reference substance for every temperature. The densimeter has a temperature control of ± 0.1 K and the temperature stability time was 600 s. About 2mL of solution were injected in the measuring cell, avoiding the solution to crystallize within the cell.

A refractometer (Mettler Toledo, model RE40) with a precision and reproducibility of ± 0.0001. Two sample drops were placed on the prism of the instrument using a syringe. After measuring the solution was removed with a cleaning syringe. The prism was rinsed with distilled water and dried with tissue paper. The measurement were made at the yellow doublet sodium D-line, with λ = 589 nm. An automatic laser viscosimeter, Schott-Gerate AVS 310, was used to measure the kinematic viscosity of the solutions with a precision of ± 0.1 s. The equipment was calibrated following the procedure described in a former work. The temperature was kept constant using a thermostatic bath (Schott-Gerate CT 52) with a temperature precision of ± 0.05 K. To measure the property 2 mL of solution was transferred to the capillary which was inside the bath. The dynamic viscosity was obtained multiplying the kinematic viscosity by its corresponding density.

A conductivimeter, Orion, model 19700-27, with a precision < 0.5% and reproducibility of ± 0.7%. The equipment was calibrated with a standard KCl solution, fixing a cell constant of 0.604 cm⁻¹. To measure the conductivity of the solutions, the measuring cell of the equipment was submerged on every container flasks, and the instrument readings registered. Subsequently the cell was cleaned with distilled water and dried with soft paper. The temperature of the sample was maintained constant using a thermostatic bath.

**Results and discussion**

In Table 3 is presented the solubility \( x_1 \), density \( \rho \), refractive index \( n_{20} \), dynamic viscosity \( \eta \), and electrical conductivity \( \kappa \) for solutions of sodium sulfate saturated in boric acid at different mole fractions of \( \text{Na}_2\text{SO}_4 \) \( x_2 \) and temperatures \( T \) (293.15, 298.15, 303.15, 308.15, and 313.15) K.

The standard uncertainty \( \mu \) for \( x_1 \), \( x_2 \) and the combined uncertainties \( \sigma \) for the other properties were determined following the guidelines given by NIST.
<table>
<thead>
<tr>
<th>$x_2 \cdot 10^2$</th>
<th>$x_1 \cdot 10^2$</th>
<th>$\rho / \text{kg m}^{-3}$</th>
<th>$n_D$</th>
<th>$\kappa / \text{S m}^{-1}$</th>
<th>$\eta / \text{mPa s}$</th>
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$T = 293.15 \text{ K}$

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<th>$n_D$</th>
<th>$\kappa/ \text{S} \cdot \text{m}^{-1}$</th>
<th>$\eta/ \text{mPa} \cdot \text{s}$</th>
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$T = 303.15 \text{ K}$

| 0.00              | 2.15              | 1018.8          | 1.3358 | 0.027        | 0.8048        |
| 0.13              | 2.23              | 1028.2          | 1.3372 | 1.013        | 0.8607        |
| 0.41              | 2.33              | 1046.6          | 1.3400 | 2.535        | 0.9306        |
| 0.70              | 2.44              | 1064.7          | 1.3429 | 3.813        | 1.0110        |
| 0.96              | 2.54              | 1084.1          | 1.3458 | 4.935        | 1.0942        |
| 1.31              | 2.61              | 1111.5          | 1.3500 | 6.345        | 1.2267        |
| 2.08              | 2.82              | 1158.0          | 1.3569 | 8.155        | 1.5140        |
| 3.23              | 3.02              | 1211.7          | 1.3639 | 9.345        | 1.9894        |
| 4.33              | 3.16              | 1262.2          | 1.3707 | 9.885        | 2.6353        |
| 5.59              | 3.29              | 1318.6          | 1.3776 | 9.865        | 3.5516        |
Table 2. Continued

<table>
<thead>
<tr>
<th>$x_2 \cdot 10^{-2}$</th>
<th>$x_1 \cdot 10^{-2}$</th>
<th>$\rho / \text{kg} \cdot \text{m}^{-3}$</th>
<th>$\eta_{\text{D}}$</th>
<th>$\kappa / \text{S} \cdot \text{m}^{-1}$</th>
<th>$\eta / \text{mPa} \cdot \text{s}$</th>
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</table>

$^a$Standard uncertainties are $u(T) = 0.06$ K, $u(x_1) = 0.0002$, $u(x_2) = 0.0003$, and the combined expanded uncertainties $U_c$ at 0.95 level of confidence and $k = 2$ are $U_c(\rho) = 4.2$ kg·m$^{-3}$, $U_c(\eta_{\text{D}}) = 0.0005$, $U_c(\kappa) = 0.0243$ mPa·s and $U_c(\eta) = 0.161$ S·m$^{-1}$.

Solubility increases as sodium sulfate concentration raises as can be seen in Figure 1. This behavior is alike in presence of potassium Chloride$^{19}$, potassium sulfate$^{20}$, and inverse that in presence of lithium sulfate$^3$. The behavior of solubility is because of the presence of Na$^+$ ion, which is a structure breaker as K$^+$ ion.$^{3, 19}$ The salt effect increases with temperature increments.

Due to solubility is function of temperature and salt concentration, it was represented by the following equation$^{10}$:

$$\ln x_1(x_2, T)/\text{mole fraction} = A_0(x_2) + B_1(x_2)T/K \quad (1)$$

with

$$A_0(x_2) = \sum_{i=0}^{N} a_i(x_2/\text{mole fraction})^i \quad (2)$$
\[
B_0(x_2) = \sum_{i=0}^{n} b_{i0}(x_2/mole\ fraction)^i
\]

where \( T \) is the absolute temperature, \( i = 0, 1, 2 \ldots n \). The coefficients \( a_{0i} \) and \( b_{0i} \) are constants and were calculated applying the least-squares method. The solubility was described using \( a_{00}, a_{01}, a_{02}, a_{03} \) and \( b_{00} \). Their values are shown in Table 3. The standard error of estimate is given by:

\[
SD = \sqrt{\frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{n-p}}
\]

where \( y_i, \hat{y}_i, n, \) and \( p \) represent the observed value, predicted value, number of data points, and parameters respectively. \( SD = 0.0002 \) mol fraction is equal to the standard uncertainty (0.0002 mol fraction). The \( R^2 = 0.9983 \) Therefore the model represent properly the experimental solubility as exposed in Figure 1.

![Figure 1. Solubility, \( x_1 \), of boric acid as function of sodium sulfate mole fraction, \( x_2 \): (○, \( T = 293.15 \) K; □, \( T = 298.15 \) K; △, \( T = 303.15 \) K; ◆, \( T = 308.15 \) K; ●, \( T = 313.15 \) K); –, calculated from Eq. 1.](image)

Eq. 4 is employed to calculate the adjustment error for all the models in this study.

Density is informed with reproducibility better than 0.6 kg m\(^{-3}\). It was determined comparing to the calculated values from Novotný and Söhnel.\(^1\) Repeatability is better than 5.0 kg m\(^{-3}\).

Refractive index has repeatability less than 0.0016.
Density and refractive index present the same behavior with salt concentration and temperature as can be seen in Figures 2 and 3. The values increase as salt concentration rises, but they are independent of temperature. This untypical behavior with temperature could be explained by the increase of the total mass because of solubility of boric acid grows as temperature rises as shown in Figure 1. This fact compensates the decrease of density with temperature raises and keeps almost constant its value. The effect of salt concentration is attributed to the Na$^+$ ion. This cation compresses the volume of the solution caused by decreasing the excess volume.\textsuperscript{15}

Therefore to represent both properties the following equation\textsuperscript{10} is used:

$$Y_j(x_2) = \Sigma_{i=0} a_{ji}(x_2/molefraction)^i$$

(5)

where $Y_j$ represents the density or the refractive index (it means, $j = 1$ or 2, respectively). The i subscript ranges as before. The coefficients $a_{ji}$ are parameters of the model.

The density and refractive index were described using the parameters $a_{10}, a_{11}, a_{12}$ and $a_{20}, a_{21}, a_{22}, a_{23}$ respectively. Their values are given in Table 3.

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<thead>
<tr>
<th>Property</th>
<th>$a_{0}$</th>
<th>$a_{1}$</th>
<th>$a_{2}$</th>
<th>$a_{3}$</th>
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<th>SD</th>
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<td>±0.1471</td>
<td>±30.450</td>
<td>±1458.0</td>
<td>±18230</td>
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\textsuperscript{1}The confidence interval for all the parameters is reported at 0.95 level of confidence.
Figure 2. Density $\rho$ of aqueous solutions of sodium sulfate saturated in boric acid as a function of sodium sulfate mole fraction, $x_2$: (○, $T = 298.15$ K; ○, $T = 298.15$ K; ○, $T = 303.15$ K; ○, $T = 308.15$ K; •, $T = 313.15$ K); ---, calculated from Eq. 5.
Figure 3. Refractive Index $n_D$ of aqueous solutions of sodium sulfate saturated in boric acid as a function of sodium sulfate mole fraction, $x_2$ (○, $T = 293.15$ K; □, $T = 298.15$ K; △, $T = 303.15$ K; ◯, $T = 308.15$ K; ●, $T = 313.15$ K); --, calculated from Eq. 5.
For density $\rho = 3.6 \text{ kg m}^{-3}$, which is slightly larger than the combined uncertainty, 4.2 $\text{kg m}^{-3}$. The $R^2 = 0.9984$. In the case of refractive index the estimated error is 0.0005, which is similar to the combined uncertainty and $R^2 = 0.9986$. Consequently the model represents properly both properties as shown in Figure 2 and 3.

Dynamic viscosity has repeatability of 0.1847 mPa·s. This property raises with salt concentration increments at constant temperature and decreases with temperature rises at constant concentration as shown in Figure 4. This diminution can be explicated by the promotion of solution compression by sulfate and sodium ions with temperature elevations.\(^{13}\) Thus to fit the measured data a temperature and sodium sulfate dependent equation\(^ {10}\) was applied:

$$\ln \eta_s(x_2, T)/\text{mPa} \cdot \text{s} = A_3(x_2) + B_3(x_2)T/K$$  \hspace{0.5cm} (6)

with

$$A_3(x_2) = \sum_{i=0}^{n} a_i(x_2/\text{mole fraction})^i$$  \hspace{0.5cm} (7)

$$B_3(x_2) = \sum_{i=0}^{n} b_i(x_2/\text{mole fraction})^i$$  \hspace{0.5cm} (8)

$A_3$ and $B_3$ represent potential series of $x_2$.

The viscosity was adjusted using three parameters ($a_3$, $b_3$ and $b_3$) with an estimated error of 0.0477 mPa·s, smaller than its combined uncertainty (0.0243 mPa·s). The model explains 99.63 % of the variability of the experimental data ($R^2 = 0.9963$) as shown in Figure 4. The values of the parameters obtained are given in Table 3.

![Graph](image)

Figure 4. Viscosity $\eta$ of aqueous solutions of sodium sulfate saturated in boric acid as a function of sodium sulfate mole fraction, $x_2$: ($\circ$, $T = 293.15$ K; $\square$, $T = 298.15$ K, $\triangle$, $T = 303.15$ K, $\Diamond$, $T = 308.15$ K, $*$, $T = 313.15$ K); --, calculated from Eq. 6.
The value of conductivity is determined by the salt concentration, the contribution of boric acid is negligible, due to it behaves as a non-electrolyte. It was found comparing the conductivity measured with the corresponding to sodium sulfate solution. This is illustrated in Figure 9 at 298.15 K.

The effect of temperature is negligible it is attributed to the slightly increase of the conductivity for Na$_2$SO$_4$·H$_2$O solutions with temperature raises. The conductivity repeatability is better than 0.0630 S·m$^{-1}$.

![Figure 5. Electrical Conductivity $\kappa$ of aqueous solutions of sodium sulfate saturated in boric acid as a function of sodium sulfate mole fraction, $x_2$: (o, $T$= 293.15 K; □, $T$= 298.15 K, λ, $T$= 303.15 K, ▲, $T$= 308.15 K, ●, $T$= 313.15 K); --, calculated from Eq. 5 at 308.15 K.](image)

Analyzing the Figure 5. it was found a maximum for salt concentrations higher than 0.0411 molar fraction at temperatures from 303.15 K to 313.15 K. At 303.15 K, 308.15 K and 313.15 K the maximum is present at (0.0417, 0.0433 and 0.0439) molar fraction respectively. A further concentration increment decreases the conductivity due to the reduction of ionic mobility by complex species formation and rise of viscosity.

Based on those observations Eq. 5 was chosen to describe the electrical conductivity. In this case the subscript $j$ is equal to 3. The parameters used and their values are presented in Table 3. The model explain well the data ($R^2 = 0.9958$) as can be seen in Figure 5. The estimated error is 0.236 S·m$^{-1}$, 1.5 times greater than its combined uncertainty (0.161 S·m$^{-1}$).
To analyze the effect of the cation on the properties, the measurements were compared to the corresponding to the systems \( H_3BO_3 + Li_2SO_4 + H_2O \) and \( Na_2SO_4 + H_2O \).

In Figure 6 and 7 are presented the comparison of the density and refractive index for the system studied with lithium sulfate solutions saturated in boric acid and sodium sulfate solutions at 293.15 K. This comparison was made only at one temperature due to the insignificant effect of temperature in both ternary systems.

**Figure 6.** Density \( \rho \) of aqueous solutions as a function of salt mole fraction, \( x_2 \), at \( T=293.15 \) K: (\( \cdot \), sodium sulfate solution saturated in boric acid, (\( \cdot \), lithium sulfate solution saturated in boric acid, reference\(^{10,15}\), sodium sulfate solution, reference\(^{14}\)).

**Figure 7.** Refractive index \( n_D \) of aqueous solutions as a function of salt mole fraction, \( x_2 \), at \( T=293.15 \) K: (\( \cdot \), sodium sulfate solution saturated in boric acid, (\( \cdot \), lithium sulfate solution saturated in boric acid, reference\(^{10,15}\), sodium sulfate solution, reference\(^{15}\)).
It was found that the values of both properties in presence of sodium sulfate are greater than in lithium sulfate solutions, this difference can be attributed to the cation behavior, due to Na\(^+\) is considered as a structure breaker. The boric acid contribution to the properties is appreciable for the system studied unlike the reported in presence of lithium sulfate, therefore the density is mainly function of the total mass concentration.

Figure 8. Viscosity $\eta$ of aqueous solutions as a function of salt mole fraction, $x_2$, at $T=293.15$ K: (•, sodium sulfate solution saturated in boric acid, ●, lithium sulfate solution saturated in boric acid, reference$^{10,15}$, sodium sulfate solution, reference$^{15}$).

Figure 9. Electrical Conductivity $\kappa$ of aqueous solutions as a function of salt mole fraction, $x_2$, at $T=298.15$ K: (•, sodium sulfate solution saturated in boric acid, ●, lithium sulfate solution saturated in boric acid, reference$^{10,16}$, sodium sulfate solution, reference$^{16}$).
In Figure 8 and 9 can be seen that the effect of Na$^+$ is greater than Li$^+$ on the viscosity and electrical conductivity. This is explained by the structure breaker characteristic of sodium ion, unlike lithium ion that is a structure maker.\(^1\)

**Conclusions**

Values and equations reliable for the density, refractive index, viscosity and electrical conductivity for aqueous solutions of sodium sulfate saturated in boric acid are provided. They are valid for the complete ranges of concentration and temperatures studied. The effect of the salt on the density, refractive index and viscosity can be explained by the presence of the sodium ion, which is a structure breaker. It compresses the volume of the solution and together with sulfate ions modified the electromagnetic field. The electrical conductivity is a function of the ionic mobilities of sodium and sulfate ions and the temperature effect is negligible.

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Recognitions

1) “To apply Atomic Force Microscopy (AFM) to study the crystal growth of boric acid from aqueous solution in presence and absence of impurities” from the Head of the Crystallization Group, Max Planck Institute for Dynamics of Complex Technical Systems Physical and Chemical Foundations of Process Engineering, Magdeburg, Germany.
To whom it may concern:

Reference letter for Mr. Wilson Alavia Medina

Mr. Wilson Alavia Medina has been for a research stay at Max Planck Institute for Dynamics of Complex Technical Systems between September 2010 and March 2012. During this period I had the pleasure to accompany his work, which is part of his doctoral thesis.

Besides using a single crystal growth cell, he started to apply Atomic Force Microscopy (AFM) to study the crystal growth of boric acid from aqueous solution in presence and absence of impurities. The latter method was applied first time for evaluating faces growth rates in solution in our group and provided promising results. At the moment he is investigating the transferability of the obtained results to real batch cooling crystallization processes.

During his stay, Mr. Wilson Alavia Medina proved to be a very active, committed and thoroughly working person, encouraging own research ideas. Also he quickly and well integrated himself in our research group.

Magdeburg, April 23rd, 2012

apl. Prof. H. Lorenz
Head of the crystallization research group
Awards, Grants and Scholarships

1) Scholarship: Scholarship of the Ministerio de educación de Chile, through program MECE2, Educación superior (2) for doctoral studies in a national program.

2) Grant for participation in Events and short courses for PhD students, CONYCIT, Chile.

3) Accommodation grant for participation in the International School of Crystallization 2012 (ISC2012), Granada, Spain, by The International School of Crystallization-Granada, Spain.

4) Scholarship for a Research Stay at Max Planck Institute for Dynamics of Technical Complex Systems, Germany.