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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

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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 Na_2SO_4 concentrations ranging from (0 to 3.3795) mol kg^{-1} H_2O.

The results were represented using an equation based on Pitzer model for the interactions of nonelectrolytes with electrolytes in aqueous solutions, given by Chanson 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 = 0.033 mol kg^{-1} H_2O for $H_3BO_3 + Na_2SO_4 + H_2O$, SD = 0.020 mol kg^{-1} H_2O for $H_3BO_3 + Li_2SO_4 + H_2O$ and SD = 0.030 mol kg^{-1} H_2O for $H_3BO_3 + K_2SO_4 + H_2O$). The model parameters are valid to maximum concentration of the salts, 3.380 mol kg^{-1} for Na_2SO_4, 3.149 mol kg^{-1} for Li_2SO_4 and 1.245 mol kg^{-1} for K_2SO_4 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 $H_3BO_3 + Na_2SO_4 + H_2O$, $H_3BO_3 + Li_2SO_4 + H_2O$ and $H_3BO_3 + K_2SO_4 + H_2O$, it was found that effect of these ions on the decreasing of the solubilty 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 to form 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$^+$–Ca^{2+}–Mg^{2+}–H$^+$–Cl$^-$– SO$_4^{2-}$–B$_4$O$_7^{2-}$–OH$^-$–HCO$_3^-$–CO$_3$–H_2O [4].

The brines used are high sulfate solutions. In this system the main species present are B^{3+}, Na$^+$, K$^+$, Li$^+$, Mg^{2+}, Cl$^-$ and SO$_4^{2-}$ [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$^+$–Mg^{2+}–H$^+$–Cl$^-$–O$_4^{2-}$–H_3BO_3–CO$_3$–H_2O.

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Nomenclature

a^0_B	Activity of boric acid in water
a_B	Activity coefficient of boric acid in a ternary system
A_ϕ	The Debye–Hückel constant of the osmotic coefficient
b	Constant, $1.2 \text{ kg}^{1/2} \text{ mol}^{-1/2}$
B_{ca}	Viral coefficients of second order for the ionic species
C_{ca}	Viral coefficients of third order for the ionic species
I	Ionic strength, $\text{mol kg}^{-1} \text{ H}_2\text{O}$
K_{ps}	Solubility product
m	Salt molality, $\text{mol kg}^{-1} \text{ H}_2\text{O}$
m_a	Anion species molality, $\text{mol kg}^{-1} \text{ H}_2\text{O}$
m^0_B	Boric acid solubility in water, $\text{mol kg}^{-1} \text{ H}_2\text{O}$
m_B	Boric acid solubility in salt aqueous solution, mol kg^{-1} H_2O
m_c	Cation species molality, $\text{mol kg}^{-1} \text{ H}_2\text{O}$
m_n	Neutral species molality, $\text{mol kg}^{-1} \text{ H}_2\text{O}$
MAD	Median average deviation
R	The universal gases constant, $83.144 \text{ cm}^3 \text{ bar mol}^{-1}$ K^{-1}
SD	Standard error of the estimate
T	The absolute temperature, K
z_a	Relative charge of the anion
z_c	Relative charge of the cation

Greek letters

α_1	Parameters for 1:2 electrolytes, $1.4 \text{ kg}^{1/2} \text{ mol}^{-1/2}$
α_2	Parameters for 1:2 electrolytes, $12 \text{ kg}^{1/2} \text{ mol}^{-1/2}$
$\beta^{(0)} \beta^{(1)}$ and $\beta^{(2)}$	Adjusting parameters
λ_{nn}	Viral coefficients of second order for the neutral species
$\lambda_{nc}, \lambda_{na}, \mu_{nnc}, \mu_{nna}$ and ξ_{nca}	Mixing parameters coming from ionic and neutral interactions
$\lambda_{Bc}, \lambda_{Ba}, \zeta_{B-a-c}$	Fitting parameters related to the interactions between the boric acid and cation c and anion a, and cation and anion, respectively
ν_c	Cation coefficient
ν_a	Anion coefficient
μ_{nnn}	Viral coefficients of third order for the neutral species
γ_B^0	Activity coefficient of boric acid in water
γ_B	Activity coefficient of boric acid in a ternary system
μ_B^S	Chemical potential of boric acid in solid (S)
μ_B^L	Chemical potential of boric acid in liquid (L)

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 [6]. 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 therefore affecting the crystallization yield.

Also in this stage the crystals of boric acid could be contaminated with traces of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ [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 equilibria 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_2BO_3^- which interacts with the ion presents in the medium [9,12]. Tosell [13] to calculate dissociation constants by the ab initio method, found the formation of B(OH)_4^- instead of H_2BO_3^-, by the reaction of B(OH)_3 and water, being present an intermediate complex $\text{B(OH)}_3 \ldots \text{H}_2\text{O}$ during the dissociation of this acid in water. The presence of these species was verified experimentally by NMR shifts.

Perelygin and Chistyakov [14] performed the speciation of boric acid solutions for the complete pH range. For a total concentration of 0.1 M, for pH less than 7, H_3BO_3 is the prevalent specie, at pH 8, the predominant species are H_3BO_3, H_2BO_3^- and B(OH)_4^-, at pH between 10 and 12, B(OH)_4^-, H_2BO_3^- and at pH greater than 12, BO_3^{3-} and HBO_3^{2-}.

The solubility, vapor pressure and density for boric acid solutions have been reported in literature [5,8–10,15–19] in absence and presence of impurities. Brandani et al. [15] measured vapor pressure for boric acid solutions at a temperature range from $40\,°\text{C}$ to $100\,°\text{C}$ 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_3BO_3 in water and in aqueous solutions of NaCl, KCl, LiCl, RbCl, CsCl, BaCl_2, MgCl_2, MgCl_2, K_2SO_4, Na_2SO_4 and Li_2SO_4 at various temperatures and salt concentration were reported in the literature [5,8,16–18].

Alavia et al. [5] reported the solubility of H_3BO_3 in aqueous solutions of Li_2SO_4 at 293.15–313.15 K and salt concentrations from (0 to 3.1492) $\text{mol kg}^{-1} \text{ H}_2\text{O}$. 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 3.739) $\text{mol kg}^{-1} \text{ H}_2\text{O}$ for Na_2SO_4 and from (0 to 1.084) $\text{mol kg}^{-1} \text{ H}_2\text{O}$ for K_2SO_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_2SO_4 is greater than Na_2SO_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–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) $\text{mol kg}^{-1} \text{ H}_2\text{O}$ at $25\,°\text{C}$. The results were examined using the Pitzer equation