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Abstract

A data review for vapour liquid equilibrium (VLE) of the boric acid/ water system is conducted from different databases and authors. A void of information for the distribution coefficient for boric acid into the liquid and vapour phases at temperatures below 373.15 K is identified. New experimental data is measured in this work to fill the lack of distribution coefficients values for temperatures below 373.15 K. Values calculated from mathematical correlations for the distribution coefficient are compared with the experimental data. Besides, mixed solvent electrolyte thermodynamic model (MSE) has been computed for VLE equilibrium based on a gamma-phi formulation; thus, it includes a calculation of the speciation equilibrium for boric acid in aqueous solutions. Nevertheless, actual parameters used in MSE model are not adapted to represent the distribution coefficient at temperatures below 500 K. Consistency is evaluated between experimental data and thermodynamic correlations. The correlation presented by Plyasunov (2011) is identified as the correlation that represents the experimental data with less variation among the collected correlations. Finally, a modification in the parameters of volatility for MSE model is proposed to obtain a similar representation of the distribution coefficient than the correlation proposed by Plyasunov (2011).

Keywords : Vapour-liquid equilibrium, Distribution coefficient, Mixed solvent electrolyte model

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1. INTRODUCTION

Vapour liquid equilibria (VLE) of boric acid/water system has been widely studied in different application fields as boron is present in natural water (e.g., seawater and geothermal), and used in many industries (e.g., ceramic, fiberglass, nuclear). For instance, authors like Pouget [1] studied this mixture targeting lithium extraction and purification processes, but also research on geothermal resources has been one of the main interested fields in this VLE and the effect of the temperature [2]. Research concerning the characterization of geothermal sources [3], including additional components different from boric acid, has conducted VLE measures directly over geothermal water for temperatures around 373.15 K. Desalination process also requires the knowledge of the VLE of the boric acid/water system due to the presence of boron in seawater [4], and the legal requirements of boron contents for drinking water production [5].

One of the major challenges for modelling boric acid/water system VLE concerns the boric acid volatility, therefore concentration in the vapour phase ($y_{b.a}$) and the liquid phase ($x_{b.a}$) must be known. Measures of boric acid / water binary systems and vapour/liquid phase composition must still be complemented. This property can be represented as the ratio of the concentration in each phase (eq.1) known as the distribution constant (K_D); this ratio is mainly dependent on the temperature and pressure of the mixture.

$$K_D = \frac{y_{b.a}}{x_{b.a}} \quad (1)$$

As the relative volatility of water and boric acid is the key driving-force in thermal-driven separation technologies, a correct modelling of this property is essential to support the process simulation and design. The calculation of the compositions in liquid and gas phases with respect to thermodynamic conditions is the cornerstone for the study of thermal-driven separation processes such as conventional distillation (temperatures around 370-430 K) [6, 7] or membrane distillations (temperature around 330-370 K) [8], and intervenes also on some applications at high temperature (e.g., nuclear pressurized water reactors).

Considering the various application fields, the VLE of boric acid should be precisely known in a wide temperature range, lying from 330 K up to 645 K depending on the used technology and studied system. However, published data in open literature (see section 2) exhibits two drawbacks: very high discrepancies between experimental values of boric acid volatility between 373 K and 500 K,

and no reported data below 373 K. Consequently, available correlations to predict VLE also show large deviations according to the data on which they are based.

Then, this work aims at presenting new experimental data to fill the void with K_D values at VLE for temperatures below at 375.15 K for the binary system boric acid / water, and identify a thermodynamic correlation able to represent the volatility of boric acid in the whole temperature domain.

2. REVIEW OF EXPERIMENTAL DATA AND MODELS

This section aims at reviewing experimental data reported in scientific literature regarding the vapor-liquid distribution of binary boric acid / water systems, as well as existing correlations to model its dependency with temperature.

2.1. Thermodynamic system

The system H_3BO_3 is an electrolytic system composed for the gas phase of water and boric acid vapour ($H_2O(g)$, $H_3BO_3(g)$), and in the liquid phase of the same species ($H_2O(aq)$, $H_3BO_3(aq)$) in addition to ionic derivatives of boric acid such as borate ions $[B(HO)_4]^-(aq)$. At high concentrations of boric acid, boric acid may crystallize ($H_3BO_3(s)$) or form polyborates ions (e.g., $[B_2(HO)_7]^-(aq)$, $[B_3O_3(HO)_4]^-(aq)$, $[B_4O_5(HO)_4]^-(aq)$, $[B_5O_6(HO)_4]^-(aq)$). This paper focuses on the volatility of boric acid, therefore the emphasis is put on low boric acid concentration where only boric acid and monoborate ion are present in solution.

This phenomenon can be modelled with a gamma-phi formulation according to the eq.(2), therefore, an accurate activity calculation of $H_3BO_3(aq)$ ($\gamma_{b.a}$) and a fugacity coefficient ($\Phi^V_{b.a}$) are important to phase distribution modelling in complex systems [1].

$$y_{b.a}\Phi^V_{b.a}P = x_{b.a}\gamma_{b.a}P_{b.a} \quad (2)$$

Partial pressure of the boric acid is needed to calculate the distribution constant (eq.1) based on the gamma-phi formulation. This value can be obtained from experimental data of temperature and pressure at VLE, and the molar excess Gibbs free energy (g) according to the equation of Gibbs-Duhem (eq.3) [9] and the eq.(4) to calculate the boric acid partial pressure $P_{b.a}$ based on the total pressure of the system (P) and the water activity $x_w\gamma_w$, the fugacity coefficient of the water Φ_w^V and the saturation pressures for the water P_w^{sat} and boric acid $P_{b.a}^{sat}$.

$$g=x_w \ln\gamma_w + x_{b.a} \ln\gamma_{b.a} \tag{3}$$

$$P=\frac{x_w\gamma_w P_w^{sat}}{\Phi_w^V}+\frac{x_w\gamma_{b.a}P_{b.a}^{sat}}{\Phi_{b.a}^V} \tag{4}$$

Nevertheless, the low concentration of boric acid in aqueous solutions due to the solubility [10] enables to use Henry's law approach. Thus, Henry constant for boric acid is included into the gamma-phi model (eq.2), then eq.(5) is obtained where Hb.a corresponds to Henry's constant for boric acid in water, Π is the Poynting correction factor [11] and P is the system pressure.

$$y_{b.a}\Phi_{b.a}^V P = x_{b.a}\gamma_{b.a}H_{b.a}\Pi \tag{5}$$

Henry's constant correlations are functions of the temperature and it is intended for low concentration dilutions, thus, the effect of boric acid concentration requires an adapted activity coefficient model to calculate the K_D according to the eq.(6).

$$K_D=\frac{\gamma_{b.a}(x,T,P)*H_{b.a}(T)*\Pi(P,T)}{\Phi_{b.a}^V(T)*P} \tag{6}$$

Moreover, calculation of activity coefficients of H_3BO_3(aq) can be conducted using an electrolytic model to estimate the non-idealities of the system. This

approach take into account the different interactions among the species present in the aqueous solution. Eq.(7) enables the estimation of a total activity coefficient including long-range ($\gamma_{b.a}^{LR}$), medium-range ($\gamma_{b.a}^{MR}$) and short-range ($\gamma_{b.a}^{SR}$) interactions.

According to [12] the short-range interaction contribution to electrolytic systems can be neglected, nevertheless, the interaction molecule-molecule $H_2O(aq)$ - $H_3BO_3(aq)$ is taken into account as a medium-range interaction. Besides, the interaction between ions is also taken into account in the long-range contribution.

$$\gamma_{b.a} = \gamma_{b.a}^{SR} * \gamma_{b.a}^{MR} * \gamma_{b.a}^{LR} \quad (7)$$

Calculation of medium-range ($\gamma_{b.a}^{MR}$) and short-range ($\gamma_{b.a}^{SR}$) interactions depends on the moles number for each specie besides other properties like temperature, ionic force and charge. Likewise, boric acid does not dissociate completely in water, then, the calculation of the activity should include the chemical equilibrium.

Behaviour of boric acid has been studied for different authors to calculate the possible species present in the aqueous solutions [13, 14]. The main equilibrium corresponds to the acid-basic equilibrium of $H_3BO_3(aq)$ with its conjugated base, the borate ion $B(OH)^-_4(aq)$, reporting an acid constant equilibrium of 9.24 (Eq.8) [15, 16].

$$H_3BO_{3(aq)} + 2H_2O \rightleftharpoons B(OH)^-_{4(aq)} + H_3O^+ \quad (8)$$

Moreover, polyborates molecules has been reported by [17, 18, 19], leading to the formation of mainly four polyborate species (Eq.9 - Eq.12)

$$2H_3BO_{3(aq)} + H_2O \rightleftharpoons B_2O(OH)^-_{5(aq)} + H_3O^+ \quad (9)$$

$$3H_3BO_{3(aq)} \rightleftharpoons B_3O_3(OH)^-_{4(aq)} + H_3O^+ + H_2O \quad (10)$$

$$4H_3BO_{3(aq)} \rightleftharpoons B_4O_5(OH)^{-2}_{4(aq)} + 2H_3O^+ + H_2O \quad (11)$$

$$5H_3BO_{3(aq)} \rightleftharpoons B_5O_6(OH)^{-3}_{6(aq)} + 3H_3O^+ \quad (12)$$

However, major species for the diborate and pentaborate (eq.13 and eq.14) are identified in more recent researches [20, 21]

$$2H_3BO_{3(aq)} + OH^- \rightleftharpoons B_2(OH)^-_{7(aq)} \quad (13)$$

$$5H_3BO_{3(aq)} + OH^- \rightleftharpoons B_5O_6(OH)^-_{4(aq)} + 6H_2O \quad (14)$$

Concentration of boric acid in the liquid phase H_3BO_3(aq) is affected by its low solubility in water, thus, solid-liquid equilibrium might be taken into account. [22, 23, 10] have identify three solid phases in equilibrium with the liquid phase, those phases correspond to boric acid H_3BO_3(s) and two monomeric molecules, metaboric acid HBO_2(s) and crystalline oxide B_2O_3(s), then, equilibrium at the liquid phase with neutral species is also included into the reactive system according to the eq.(15) and eq.(16) for the liquid phase [24]. Solubility values for each specie can be calculated with a solubility expression in function of the temperature [25].

$$H_3BO_{3(aq)} \rightleftharpoons HBO_{2(aq)} + H_2O \quad (15)$$

$$H_3BO_{3(aq)} \rightleftharpoons B_2O_{3(aq)} + 3H_2O \quad (16)$$

Equilibrium constant and the effect of the temperature for each one of the equilibriums is detailed in different works e.g [26, 27] for polyborates, [28, 29, 30] for HBO_2(aq) and B_2O_3(aq).

Mixed solvent electrolyte model (MSE) [31] presents a theoretical approach to calculate each interaction of the eq.(7) based on the excess Gibbs energy

calculation. However, this model requires the setting of the binary interaction parameters based in experimental data [32]. In this model, chemical equilibrium for speciation calculation is based on the excess properties and the Helgeson-Kirkham-Flowers equations (HKF) [20]. This model includes the speciation of the pentaborate as the trivalent anion ($[B_5O_6(OH)_6]^{-3}$(aq)) instead of the monovalent anion ($[B_5O_6(OH)_4]^-$ (aq)), besides it does not includes the equilibrium for the specie ($[B_2(OH)_7]^-$(aq)).

For this work, K_D experimental data is presented as the ratio of total Boron concentration for each phase, thus, the different species in the aqueous phase are considered, even though H_3BO_3(aq) is the main specie in the liquid phase at the concentrations and pH conditions of the experimental points.

2.2. Experimental data for the boric acid VLE distribution constant

An extensive review is conducted to gather information from different authors. Thermodynamic databases e.g, NIST, DECHEMA, KDB and MULTEQ were consulted for VLE data of the binary system water/boric acid. Compiled data from thermodynamic databases such as NIST and DECHEMA does not provide information for phases compositions and only report measurements of pressure for given temperature and total boric acid concentrations in water (no measurements of boric acid concentrations in resulting liquid and vapour phases). Therefore, the review was completed by a dedicated literature review, searching for K_D distribution constants, obtained from measurements of the boric acid concentration in both liquid and vapour phases.

Another reference point is provided by the code MULTEQ from the Electrical Power Research Institute (EPRI). This value is obtained as a result of the theoretical calculation of the equilibrium based on the Gibbs energy [33] calculated with enthalpy and entropy data reported in CODATA [34] and NIST-JANAF Thermochemical Tables [35] for H_3BO_3 in the liquid and vapour phase at a temperature of 298.15 K. However, it is not taken as an experimental value for this work.

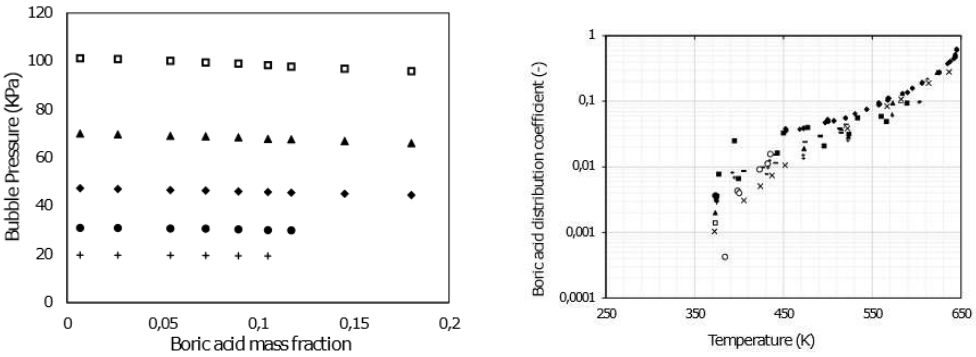
Table 1 presents a summary of the range and points collected for the boric acid volatility expressed as bubble point pressure and K_D for the boric acid / water system. Published data are collected from different sources, conditions and methods.

Table 1: Summary of published data for bubble point and distribution constant of boric acid/water systems

Temperature (K)	Concentration range ($mg_{H_3BO_3}/kg$)	Experimental points	Measured system	Reference
Bubble point measurements				
373.4 – 374.8	24700 - 164165	8	H_3BO_3/Water	[36]
313.2 – 373.2	6823 - 171353	47	H_3BO_3/Water	[37]
373.2	29987 - 198281	6	H_3BO_3/Water	[38]
373.4 - 376.2	30640 - 266900	12	H_3BO_3/Water	[39]
452.1 - 481.5	909 - 1667	8	H_3BO_3/Water	[40]
K_D distribution constant				
372.1 – 363.6	197 - 21526	10	H_3BO_3/Water	[41]
452.7 – 644.5	1100 - 7000	50	H_3BO_3/Water	[42]
384.1 – 434.8	15 - 28	6	Geothermal water	[43]
373.6 – 375.4	68013 - 259686	10	H_3BO_3/Water	[44]
398.3 – 531.2	16 - 38	23	Geothermal water	[45]
377.1 – 589.1	4922 – 74399	14	H_3BO_3/Water	[46]
377.3	Not reported	1	H_3BO_3/Water	[47]
373.1 - 623.1	61830	5	H_3BO_3/Water	[48]
373.1	16000 - 245000	29	H_3BO_3/Water	[49]
394.6 - 603.8	500 - 4900	11	H_3BO_3/Water	[50]

Appendix 2 presents a compilation of the data retrieved from these publications.

The compilation of data is presented in the Appendix, see Tables 9 and 10.



□ : 373.15 K ; ▲363.15 K ; □ 353.15 K ; 343.15 K ; + 333.15 K ;□ [46]; □: [42]; ●: [47]; ○ [43] ;× : [51]; - : [45]; ▲ [48]; □: [49]; +:[50]

Figure 1: Experimental points reported in literature for binary boric acid / water system: bubble pressure (left) at different temperatures and K_D vapour-liquid boric acid distribution coefficient repported by different authors (right).

For all temperatures from 333.15 K to 373.15 K, it appears that the bubble pressure is little sensitive to the boric acid concentration (see Figure 1, left). The bubble pressure remains very close to the vapour pressure of pure water, due to the low relative volatility of boric acid compared to water. Information on the acid boric concentration in both phases are then required to assess such low-volatility system, as pictured on Figure 1, right.

2.3. Models for the boric acid VLE distribution constant

Various correlations (Table 2) are proposed to calculate the K_D at different temperatures. Glover [45] presents in his work two correlations in function of the temperature, these are obtained from parametric regression over experimental

data (eq.17 and eq.19). Then, Glover presents another correlation based on the ratio of the steam and water density (Eq.20), nevertheless, all of them are limited at 373.15 K. Other authors like Plyasunov [52] propose an expression resulting from fitting an expression based on a correlation's modification for the expansion of the Helmholtz energy of the boric acid / water system, this expression includes a proposed value for the Krichevskii parameter A_{Kr} (eq. 21).

Table 2: Empirical correlations for K_D calculation for different temperatures found in the literature for boric acid/water system

Author of the corr.	Correlation	Ref
Tonami (1970)	$\log(K_D) = 7.751 - \frac{3788}{T}$ (17) for 373.15 K < T < 414.15 K $\log(K_D) = 0.1899 - \frac{657}{T}$ (18) for 414.15 K < T	[45]
Tonami average	$\log(K_D) = 2.81 - \frac{2088}{T}$ (19) for 373.15 K < T	[45]
Glover	$1/(K_D) = 10^{(3.0506 - 0.0069*(T-273,15))}$ (20) For 423.15 K < T < 593.15 K	[45]
Plyasunov	$RT*\ln(K_D) = A_{Kr}\frac{2*(\delta_1(L)-\delta_c)}{\delta_c^2} * \left(1 + C_1\left(1-\frac{T}{T_C}\right)^3 + C_2\left(1-\frac{T}{T_C}\right)^4 + C_3\left(1-\frac{T}{T_C}\right)^5\right)$ (21) for 273.15 K < T <T_c with T_c: Critical temperature; $\delta_1(L)$:Liquid solvent (water) density at T [mol/cm^3]; δ_c: Critical solvent (water) density; A_{Kr}:-75 MPa C_1: 6.174; C_2:-1.553; C_3: 20.380	[52]

Moreover, K_D values in function of the temperature can be obtained from the code MULTEQ by the Electrical Power Research Institute (EPRI). This correlation is based in the data published in Weres [53] and CODATA.

Another approach corresponds to a parametrisation of the MSE model for the system boric acid/ water proposed by Wang et al. [18]. In this work, binary interaction parameters for each specie are published. Likewise, the chemical equilibrium parameters based on HKF equations is presented. This approach enables to take into account the different species present in the liquid phase e.g polyborates.

MSE model is available in the thermodynamic Library of the commercial software Simulis® Thermodynamics from PROSIM®, K_D calculation is based on Henry's law (Eq.6). Henry's constant values are obtained from an empirical correlation (Eq 22) obtained from a parametric fitting in function of the temperature. The proposed parameters values are A = -49.92, B = 8759.16, C= 5.85, D= 1.29e-25 E=9 [1] where Henry's constant is obtained in mol ⋅ l^{-1} ⋅ atm^{-1}.

$$\ln(H_{b.a}) = A + \frac{B}{T} + C\ln T + DT^{E} \qquad (22)$$

Even when there are different correlations to calculate K_D at VLE for water / Boric acid published in the literature, these are limited by the authors for temperatures below 373.15 K. Only the parameterization for Wang et al. [18] model (MSE), MULTEQ-EPRI correlation and the correlation from Plyasunov [52] (eq.21) are proposed for systems at a temperature below 373.15 K, besides experimental validation is not presented for temperatures between 273.15 K and 373.15 K. Moreover, K_D experimental data published by some authors e.g Plyasunov [52], Glover [45] report deviations depending on the source of information for temperatures between 373 K and 500 K. Generally speaking, just K_D experimental data for temperatures over 500 K present a consensus for models validation.

K_D not only depends on the temperature, it also depends on the concentration as seen in the eq.(6). However, thermodynamic correlations are expressed as a function of temperature, only MSE model enables incorporate the concentration in the calculation. Figure 2 summarizes the different correlations for K_D and their temperature ranges.

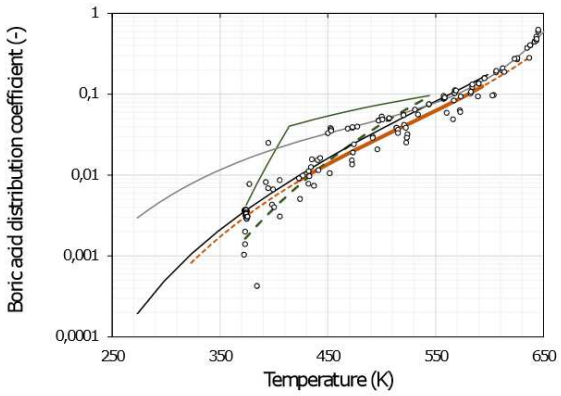


Figure 2: Published correlations for boric acid distribution coefficient and comparison with experimental data. Gray line: MSE model; green line: eq.(17) and eq.(18); dotted green line eq.(19); Orange line: eq.(20); dotted orange line: MULTEQ-EPRI VLE simulation; black line eq.(21); ○ Experimental data.

2.4. Exhibiting the need for new experimental data

The literature review exhibits that there is a lack of experimental values for K_D at temperatures below 373.15 K. Therefore, models based on the various sources will be inconsistent in this interval of temperature. Furthermore, existing experimental measures above 373.15 K require a data reconciliation. In general, K_D experimental data is not thermodynamically consistent with Henry's law parameterization for Wang et al. [18] (MSE) model neither with the other correlations. Experimental K_D values for VLE at temperature below 373.15 K are obtained in this work, then, data is compared to the thermodynamic models and correlations to choose the most appropriate representation of boric acid volatility.

3. EXPERIMENTAL METHODOLOGY

This section aims to present the experimental protocol to calculate K_D values in a range of temperature between 333.15 k and 373.15 K, besides, the uncertainty calculation and the consistency evaluation method are also presented.

3.1. Experimental apparatus

The experimental apparatus deployed in this work is an ebulliometer (PIGNAT model EEA 3000). This apparatus assures the dynamic equilibrium of the liquid and vapour phases inside an adiabatic equilibrium chamber. In addition, the equilibrium chamber is equipped with a platinum resistance thermometer (Hart Scientific 5615) to measure the chamber temperature and a pressure measure devise (MKS type 250 E). In order to get samples of VLE at temperature close to 373 K, vacuum is not used, otherwise, for VLE at temperatures lower than 373 K different values of vacuum are applied. Figure 3 presents a schema of the ebulliometer.

As an operation protocol, a solution of water/ boric acid is loaded into the homogenization chamber (1); vacuum is applied to the system (using the vacuum pump) for experiments at reduced pressure set between 20 kPa and 90 kPa, therefore, a VLE temperature between 323.15 K and 373.15 K is obtained, then the solution is heated in the boiling chamber (2) (using an electrical resistance) until the ebullition and vapour is driven to the VLE chamber (3). Temperature and pressure of the chamber are measured constantly until the values are constant for 30 minutes when VLE is assumed and sampling is conducted.

Once the vapour phase is produced at the VLE in the equilibrium chamber (3), it goes through a total condensation using a heat exchanger operated with a cooling fluid at 273.15 K of inlet temperature (controlled with a chiller), likewise, the vacuum line is connected to a cryogenic cold trap, thus, total condensation is ensured. Both liquid and vapour phases are recirculated into the homogenization chamber equipped with magnetic agitation (1) until VLE is achieved. Then, this apparatus allows sampling of the liquid phase at sampling outlet (5), and the sample corresponding to the vapour phase is collected as liquid after condensation at sampling outlet (6).

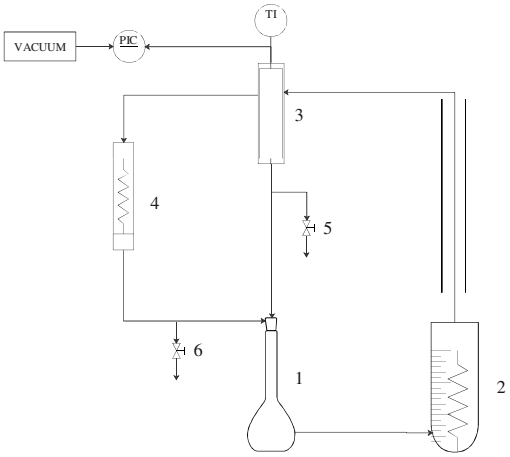


Figure 3: Schema of experimental apparatus for VLE measures. (1) Homogenization chamber. (2) Boiling chamber. (3) Adiabatic equilibrium chamber. (4) Vapour condenser. (5) Liquid phase sampling valve. (6) Vapour condensed sampling valve. (PIC) Equilibrium chamber pressure controller and indicator. (TI) Equilibrium chamber temperature indicator.

3.2. Sample preparation and analysis

Samples are prepared in a range of concentration between 500 and 3500 mg of total boron per liter of solution assuring being below the solubility limits for the boric acid in water Wang et al. [54]. The concentration of each sample is analysed and reported in the results.

Samples were prepared in the laboratory using solid boric acid reagent at a ≥ 99.5 w% purity obtained from Sigma Aldrich.

Samples dilution for composition analysis was carried out with a nitric acid solution at 2.0 vol% prepared in the laboratory using analytical degree reagent (70 vol%) obtained from Fisher. Table 3 contains a summary of the reagents. Volumetric material used for dilutions and samples preparations are reported in the table 4.

Table 3: List of reagents

Name	Purity	Cast number	Supplier
Boric acid	≥ 99.5 w%	10043-35-3	Sigma Aldrich
Nitric acid	70 vol%	7697-37-2	Fisher Sci

Table 4: List of volumetric material and manufacturer's specification

Type	Volume	Reported error
Pipette	0.5 ml	+/- 0.005 ml
Pipette	1.0 ml	+/- 0.01 ml
Pipette	2.0 ml	+/- 0.05 ml
Pipette	5.0 ml	+/- 0.05 ml
graduated flask	50.0 ml	+/- 0.06 ml

3.3. Analytical method

Composition analysis is carried out after collecting samples. Inductively coupled plasma optical emission spectrometer technique (ThermoScientific ICP-OES ICAP 6300) is the analytical method chosen for the quantification of elementary boron in the liquid and the condensed vapour phase. Analytical method is calibrated with six standardized solutions covering a range of concentration between 1 and 50 ppm of elementary boron concentration [55].
Samples are diluted with distillate water acidified with nitric acid at 2.0 vol% to obtain a final concentration between 1 and 50 ppm of elementary boron. For the liquid phase, dilution ratio is calculated following the eq.(23) where V_1 is the volume of the pipette to measure the sample and (V_2) is the volume of the graduated flask.
Instead, the dilution of condensate vapour phase was conducted on the way to obtain the lowest possible dilution ratio. Samples were measured with pipettes of different volumes (V_{pi}), then water was added with another pipette until a final volume between 4.0 ml and 5.0 ml. For example, for a 2.5 ml sample (V_1) is resultant from a first measure with a 2.0 ml pipette followed by a measure with a 0.5 ml pipette, thus (V_2) correspond to 4.5 after adding 2.0 ml of water.

$$DR = \frac{\sum V_1}{V_2} = \frac{\sum V_{Pi}}{V_2} \quad (23)$$

The samples are analysed three times using a quartz torch in three different wavelengths corresponding to 182.641 mm, 208.959 mm measured in axial mode and 249.773 mm measured in radial mode. Thus, the average value of all the measures is taken as boron concentration $C_{B,ICP}$, then, the reported boron concentration of the sample is calculated using the eq.(24). Finally, density of the solution at 293.15 K is used to calculate and report the concentration in mass fraction.

$$C_{B,sample}(mg/L) = \frac{\sum V_{Pi}}{V_2 * C_{B,ICP}} \quad (24)$$

3.4. Experimental uncertainties analysis

Uncertainties for the reported pressure and temperature correspond to the error reported by the equipment manufacturer. In the case of K_D values, different sources of uncertainties were identified and considered for the final value. Moreover, an analysis of uncertainties is conducted to calculate a global uncertainty S_{global} for each value.

3.4.1. Sources of uncertainties and type

Uncertainties are classed depending on the source; those uncertainties associated with the composition measure and those associated with the dilution of samples for ICP analysis are taken into account for all reported values. In addition, an uncertainty due to the reproducibility of the points, where pressure was not modified, is calculated.

While reporting a concentration of total boron in each sample, this value required an estimated error; this is calculated from a combination of different uncertainties. One source of error is due to the laboratory manipulations of the samples e.g dilutions for analysis conditioning. Likewise, errors are calculated as type B (classification NIST) [56], thus, values for each reported uncertainty depend on each pipette and graduated flask used in the dilution process; it corresponds to the manufacturer's specifications.

For the ICP analysis, there is set an equation to correlate the measured intensities and the boron concentration. This equation is parameterized using

standard solutions of known concentration (prepared in the laboratory). Then, all the standard solutions are analysed and results allow setting the calibration curve. Standard deviations between the set value and the calibration curve is calculated and taken as the value of the uncertainty (S_{itp}).

Likewise, 9 measures to each sample are taken as described in the analytical method, then, reported concentration is the average value (X_{avg}). The ICP uncertainty (S_{icp}) corresponds to the combination of the standard deviation due to the reliability (S_{ms}) and the deviation from the calibration curve (eq.25). For each experience, the value of the relative standard deviation is reported (RSD_{icp}).

Table 5: Source and probabilistic distribution for each type of uncertainty

Uncertainty source	Distribution	Parameters
Volumetric material	Uniform distribution	Manufacturer's specification
ICP analyse	Normal distribution	Standard deviation from calibration curve and reliability
Repeatability of the measurements	Confidence interval	Standard deviation and mean from independent observations

$$S_{icp}=\sqrt{S_{itp}^2+S_{ms}^2} \tag{25}$$

A probabilistic distribution for each type of uncertainty is identified. Table 5 present the type of uncertainty taken into account for this work.

Uncertainties are combined according to the corresponding probabilistic distribution set for each type of error. The propagation is conducted under the Monte Carlo method [57] for K_D calculation. As a result, it is obtained an average value K_D^{MC} for each experimental measure and an associated standard deviation depending on all the probabilistic distributions S_{global}.

Moreover, for the points close to 373.15 K where pressure was not modified. A single value is calculated for an average temperature (AVGMC), and uncertainty corresponds to the standard deviation of K_D^{MC} of each experiment (reproducibility error).

4. MODELLING METHODOLOGY

4.1. Thermodynamic modelling

In this work, the MSE model is used as basis for the thermodynamic modelling as it allows the calculation of the chemical and physical properties of each phase. Likewise, it enables the computation of more complex systems, while studying multi-component systems with several other ions beyond binary systems, crystallization of boric acid and precipitations of borate salts.

MSE model is consistent with the bubble point (T,P) experimental data according to Wang et al. [18] and validated with the experimental data for bubble point of the section in the 2.2 according to the method described in Valderrama and Alvarez [58] since there is no deviation greater than 10 %. Then, experimental points obtained in this work were sorted according to a thermodynamic consistency test (TCT) for T,P at VLE using the eq.(26). Therefore, VLE is assumed achieved if each experimental pressure has less than 10 percent of deviation with the pressure calculated by MSE for the conditions of temperature and composition of the experiments.

$$\Delta P(\%) = 100 * \frac{|P^{cal} - P^{exp}|}{P^{exp}} \quad (26)$$

4.2. VLE validation

Deviation of boric acid concentration in the gas phase $y_{b.a}$ was calculated as suggested by Trejos et al. [59] for data consistency between experimental values and thermodynamic correlations. Deviation between K_D values from models and experimental data set were calculated by eq.(27). For this analysis, all the correlations are tested even when data is out of the range of temperature recommended for the author. This evaluation is conducted over three different cases: 1. Experimental data obtained in this work 2. Experimental data published previously 3. Data from this work + experimental data published previously.

$$\Delta y_{b.a}(\%) = \frac{100}{N} * \sum \frac{|y_{b.a}^{cal} - y_{b.a}^{exp}|}{y_{b.a}^{exp}} \quad (27)$$

Since the MSE model calculates the pressure and temperatures at the VLE based on the activity coefficient and the non-idealities in the liquid phase, thus, the formulation of MSE model allows further calculations e.g. the effect of other components over the VLE and the effect of concentration in the K_D, the identification of a well-adapted correlation lead to a new parameterization of Henry's law correlation to use Wang et al. [18] (MSE) model.

Deviation is calculated for each data set and each one of the thermodynamic correlation. Then, the equation having the minimum deviation

with the data set is taken as a correlation of reference. Moreover, the eq.(22) is adapted to model the chosen correlation by minimizing the error. Fitting parameters is conducted according to the eq.(28) where $K_{D,T}^{MSE.Mod}$ stand for the K_D obtained from new parameterization of Wang et al. [18] (MSE) model for a temperature (T), $K_{D,T}^{corr}$ is the value obtained from the correlation chosen as reference and N correspond to the number of evaluations in a range of temperature from 273.15 K to 603.15 K with a ΔT = 5.

$$\min.Std.Error(\%) = \frac{100}{N} * \sum \frac{|K_{D,T}^{MSE.Mod} - K_D^{corr}|}{K_{D,T}^{corr}} \quad (28)$$

Finally, this modification of MSE model should better reproduce the experimental data set for temperatures below 373.15 K than the MSE model with the initial parameters of Wang et al. [18].

5. RESULTS

As a result, 17 experimental points were obtained, then the composition of the initial sample (Z), liquid phase (X) and vapour phase after total condensation (Y) in phase equilibrium were analysed at a set pressure and corresponding temperature for the VLE. Results of boron concentration in each phase expressed as mg of boron per litre of solution in liquid phase, VLE pressure and temperature and calculated K_D for each experience are presented in the table 6.

In addition, points taken with no modified pressure are post-treated to present an average value (AvgMC). As a general result, K_D at atmospheric pressure present the highest standard deviation due to the reproducibility uncertainty.

Table 6: Experimental results of initial sample (Z), liquid phase (X) and condensed vapour phase (Y) in mg of boron per litre of solution. **Composition analysis is conducted after total condensation of the vapour phase (Y); boron analysis is conducted for X, Y, Z in liquefied state at 293.15 K and 1 atm.** Calculated equivalent mass boron fraction for initial sample (Z_B), Liquid phase (Y_B) and condensed vapour phase (X_B). Uncertainties as standard deviation due to the analytical method RSD_{icp} for liquid and condensed vapour phase. Calculated distribution coefficient K_D of H_3BO_3/Water system expressed in equivalent boron using Eq. (1), average value of distribution coefficient K_D^{MC} after uncertainty propagation with Monte-Carlo method and uncertainty expressed as standard deviation S_{global} for each experiment.

ID	Total pressure (Pa)			T(K)		Z (mg Boron/l)	Z_B	Y (mg Boron/l)	Y_B	RSD_{icp} for Y [%]	X (mg Boron/l)	X_B	RSDicp for X [%]	K	K_D^{MC}	S_{global}
1	23464	+/-	1%	335.15	+/-0.05	1697	1.70x10−3	3.49	3.50x10−6	9.2	1553	1.55x10−3	8.6	0.00225	0.00229	0.00029
2	29797	+/-	1%	342.13	+/-0.05	1123	1.12x10−3	3.09	3.10x10−6	10.0	1345	1.35x10−3	5.0	0.00230	0.00226	0.00026
3	35330	+/-	1%	346.10	+/-0.05	3227	3.22x10−3	5.83	5.85x10−6	8.9	3261	3.26x10−3	5.1	0.00179	0.00178	0.00018
4	42103	+/-	1%	350.32	+/-0.05	2006	2.01x10−3	5.55	5.57x10−6	7.6	2264	2.26x10−3	4.9	0.00245	0.00241	0.00022
5	51396	+/-	1%	355.32	+/-0.05	2006	2.01x10−3	6.75	6.77x10−6	7.7	2327	2.33x10−3	4.6	0.00290	0.00285	0.00026
6	82126	+/-	1%	367.42	+/-0.05	2006	2.01x10−3	11.31	1.14x10−5	9.0	2219	2.22x10−3	4.6	0.00510	0.00503	0.00051
7	97938	+/-	1%	372.17	+/-0.05	542	5.43x10−4	2.51	2.52x10−6	4.5	683	6.84x10−4	6.1	0.00367	0.00374	0.00029
8	97925	+/-	1%	372.19	+/-0.05	560	5.62x10−4	3.41	3.42x10−6	5.3	651	6.52x10−4	6.0	0.00524	0.00515	0.00042
9	99592	+/-	1%	372.65	+/-0.05	548	5.49x10−4	1.82	1.82x10−6	7.1	545	5.47x10−4	6.5	0.00334	0.00322	0.00032
10	99592	+/-	1%	372.65	+/-0.05	1741	1.74x10−3	6.66	6.68x10−6	6.3	1860	1.86x10−3	6.4	0.00358	0.00353	0.00032
11	99592	+/-	1%	372.65	+/-0.05	1559	1.56x10−3	8.42	8.44x10−6	6.1	1890	1.89x10−3	6.4	0.00446	0.00439	0.00040
12	99592	+/-	1%	372.67	+/-0.05	554	5.56x10−4	3.72	3.73x10−6	6.4	747	7.49x10−4	6.9	0.00498	0.00491	0.00047
13	99805	+/-	1%	372.86	+/-0.05	3279	3.28x10−3	15.47	1.55x10−5	8.4	3620	3.61x10−3	5.9	0.00427	0.00330	0.00033
14	100418	+/-	1%	372.90	+/-0.05	2126	2.13x10−3	11.95	1.20x10−5	8.7	2226	2.23x10−3	5.1	0.00537	0.00527	0.00054
15	100191	+/-	1%	372.93	+/-0.05	3229	3.23x10−3	11.07	1.11x10−5	5.7	2875	2.87x10−3	6.0	0.00385	0.00383	0.00032
16	100071	+/-	1%	372.95	+/-0.05	3378	3.37x10−3	11.76	1.18x10−5	5.8	3543	3.54x10−3	5.5	0.00332	0.00329	0.00026
17	100658	+/-	1%	372.99	+/-0.05	1066	1.07x10−3	6.17	6.19x10−6	7.5	1425	1.43x10−3	5.9	0.00433	0.00435	0.00042
AvgMC	99592	+/-	1%	372,69	+/-0,05										0,00471	

From uncertainties results, there is important to highlight that the main source of error comes from the ICP measure (calibration curve and reliability error combined). As seen, for all the values of RSD in both phases, error is not lower than 4.5%. Consequently, the calculated value for K_D is reported with a high standard deviation of 10% average while combining all the uncertainties using Monte Carlo.

Then, experimental data for VLE is validated in terms of pressure and temperature. VLE pressure was obtained from MSE model, and after, deviation was calculated according to eq.(26). Table 7 presents those results; experiments present consistency in terms of pressure and temperature at VLE due to the low deviation (less than 10 %) while comparing the experimental pressure (P^{exp}) and the pressure calculated with MSE model (P^{cal} MSE). The experiment conducted at 335.15 K presents 7.08% pressure deviation; P^{exp} for this temperature is higher than the calculated pressure (P^{cal} MSE).

Table 7: Pressure deviation calculation between MSE model and experimental data for boric acid / water VLE

Id sample	Z [mg Boron/l]	Temperature [K]	P_{exp} [Pa]	P^{cal} MSE [Pa] - initial parameters [18]	ΔP(%)	Reduced pressure
1	1697	335.20 +/-0.05	23464 +/- 1%	21803	7.08	Yes
2	1123	342.13 +/-0.05	29797 +/- 1%	29762	0.12	Yes
3	3227	346.10 +/-0.05	35330 +/- 1%	35187	0.41	Yes
4	2006	350.32 +/-0.05	42103 +/- 1%	42033	0.17	Yes
5	2006	355.32 +/-0.05	51396 +/- 1%	51486	0.18	Yes
6	2006	367.42 +/-0.05	82126 +/- 1%	81936	0.23	Yes
7	542	372.17 +/-0.05	97938 +/- 1%	97670	0.27	No
8	560	372.19 +/-0.05	97925 +/- 1%	97738	0.19	No
9	948	372.65 +/-0.05	99592 +/- 1%	99379	0.21	No
10	1741	372.65 +/-0.05	99592 +/- 1%	99166	0.043	No
11	1559	372.65 +/-0.05	99592 +/- 1%	99160	0.43	No
12	554	372.67 +/-0.05	99592 +/- 1%	99414	0.18	No
13	3279	372.86 +/-0.05	99805 +/- 1%	99623	0.18	No
14	2126	372.90 +/-0.05	100418 +/- 1%	99995	0.42	No
15	3229	372.93 +/-0.05	100191 +/- 1%	99995	0.20	No
16	3378	372.95 +/-0.05	100071 +/- 1%	99960	0.11	No
17	1066	372.99 +/-0.05	100658 +/- 1%	100431	0.23	No

5.1. Models evaluation

Once experimental data set are complemented with K_D values at temperatures below 375.15 K obtained in this work, the deviation analysis of the correlations is conducted.

Table 8 presents the comparison between experimental data and K_D correlations using the eq.(27). Eq.(21) is identified as the most adapted correlation to calculate the concentration of boric acid in the gas phase while comparing with the experimental data of this work. Thus, this correlation is taken as a reference to do the parametric fitting of the eq.(22).

The resultant values for eq.(22) after parametric fitting are: A = -38.4766 , B = 9479,17, C = 3,82149, D= -1.04939E-25, E=9 . Table 8 present a comparison of K_D deviation from experimental data using Wang et al. [18] (MSE) model using the initial parameters for Henry's law expression and Wang et al. [18] (MSE) model with the new parameters obtained in this work. These new parameters reduced the deviation at a similar level compared to the correlation (Eq.21). Figure 4 presents the total experimental points, the (MSE) model using the initial parameters and correlation eq.(21).

Experimental data obtained in this work is consistent with the Plyasunov [52] correlation (considering the experimental uncertainties). However, the experimental point measured at 335.2 K present a deviation, and correspond to the inferior limit of the existent experimental data. Then, further works might

be conducted to extend and complete the evaluation at lower temperatures. Wang et al. [18] (MSE) model with the new parameters obtained in this work is intended to process simulation applications. Extrapolation for the near-critical region or temperatures below 335.2 K of this correlation is not reliable. The asymptotic behaviour of Henry's constant while approaching the water critical temperature requires a consistency validation.

Table 8: deviation calculation between experimental data set and each thermodynamic correlation for the boric acid / water system.

Dataset	Temperature range	Deviation with Eq.(17) and Eq.(18)	Deviation with Eq.(19)	Deviation with Eq.(20)	Deviation with Eq.(21)	Deviation with MULTEQ	Deviation with MSE model - initial parameters [18]	Deviation with MSE model - new parameters
This work	(335 K - 373 K)	33.6 %	66.1 %	19.5%	19.1%	31.3%	289.0 %	18.0%
Previously published data	(372 K - 645 K)	114.8 %	45.5 %	42.8%	39.0%	35.5%	145.0 %	38.1%
This work + previously published data	(335 K - 645 K)	126.9 %	48.2 %	39.8%	36.4 %	35.0 %	182.7 %	35.4 %

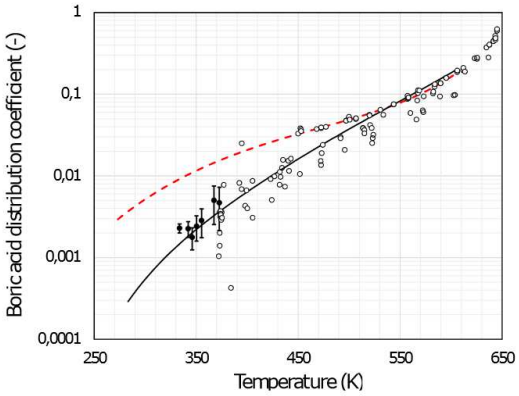


Figure 4: Summary of K_D values for the boric acid / water system. New points (•) from this work with their standard deviation compared to previous published data (○). And simulations using the MSE model with initial parameters [18] (---), as well as correlation Eq.(21) and reparametrization of MSE model in this work (—)

6 CONCLUSION

Plyasunov [52] correlation is identified as the most adapted mathematical equation to model K_D of the boric acid / water system. In addition, the experimental data obtained on this work complement the validation of this theoretical approach. Nevertheless, this correlation is not available on commercial process simulation software like ProSimPlus® or Aspen® and it requires further modifications in the case of complex mixtures e.g. seawater or geothermal water.

By contrast, Wang et al. [18] model is already implemented in commercial simulators as MSE model. Thus, as a main result of this work, new setting of parameters for Henry's law constant is obtained for boric acid while using MSE model to simulate thermal driven technologies containing the boric acid / water system. A modification of the polyborates speciation is required for the case of mixtures at modified pH.

6. CONCLUSION

New experimental data of the boric acid distribution for the VLE is added to the literature for temperatures below 373.15 K. These experimental values are thermodynamically consistent with the K_D correlation proposed by Plyasunov [52]. Thus, for cases where concentrations are not close to the solubility limits, this correlation can be deployed to estimate the total boron concentration of the liquid and vapour phase at the equilibrium.
Instead, MSE model allows to compute a more detailed calculation for complex systems like multi-component systems, while using the modified parametric setting for Henry's law using Wang et al. [18] (MSE) model at temperatures between 346 K to 450 K compared to the original parameters. However, further experimental points should be obtained to complement the state-of-art of the boric acid / water system to improve and reduce the uncertainties.

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