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A new Pitzer parameterization for the binary NaOH-H_2O and ternary NaOH-NaCl-H_2O and NaOH-LiOH-H_2O systems up to NaOH solid salt saturation, from 273.15 to 523.15 K and at saturated vapour pressure

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Abstract.

This paper presents a new set of Pitzer specific interaction parameters for the binary NaOH-H_2O system for concentrations up to more than 30 mol·kgw^{-1} and temperatures ranging from 273.15 K to 523.15 K. Assuming that the electrolyte is only partially dissociated, the model requires the adjustment of *i)* the three classical binary interaction parameters $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ}, *ii)* the equilibrium constant of formation of the aqueous complex $NaOH^0$(aq), and *iii)* one binary ($\lambda_{NaOH/NaOH}$) and one ternary ($\zeta_{NaOH/Na+/OH-}$) interaction parameters. This approach, which provides much better results than the approach of fully dissociated electrolyte, was chosen to extend the description of the system to high temperatures and high concentrations. The temperature functions of the solubility products of anhydrous NaOH(cr) and five hydrated salts, NaOH.$n$$H_2O$(cr) (where n = 1, 2, 3.11, 3.5, 4α), were determined. In order to evaluate the quality of the new set of parameters, several tests were run on various properties using various literature data. These include the boiling point elevation in the NaOH-H_2O system and the phase diagrams of the two ternary systems NaOH-NaCl-H_2O and NaOH-LiOH-H_2O. Interaction parameters for the two related binary systems NaCl-H_2O and LiOH-H_2O were taken from previous studies. To ensure consistency, four new mixing parameters were revised ($\zeta_{Na+/Cl-/NaOH}$ and $\Psi_{Cl-/OH-/Na+}$ for the ternary system NaOH-NaCl-H_2O and $\lambda_{Li+/NaOH}$ and $\Psi_{OH-/Na+/Li+}$ for the ternary system NaOH-LiOH-H_2O). Consistent with Pitzer's equations, our new set of parameters can be used to satisfactorily describe the quaternary Na^+-Li^+-Cl^--OH^--H_2O system to very high concentrations and temperatures.

Keywords: sodium hydroxide, Pitzer model, high salinities, thermodynamic excess properties

1. Introduction

Understanding the physico-chemical behaviour of natural and synthetic saline aqueous systems is very important for environmental and industrial purposes. Various models have been developed to describe such systems [1–5]. Pitzer [6] developed one of the most promising and frequently used models. Indeed, researchers have shown that it can represent the physico-chemical solution properties of very low to very high salinities [7] in complex systems [8], and at high temperatures [7], and it has been applied to many different chemical systems ([9], and references therein). The semi-empirical Pitzer approach considers specific interactions between dissolved species and uses interaction parameters, thermodynamic constants for aqueous complexation reactions, and mineral (respectively gas) solubility products for dissolution/precipitation (respectively dissolution/degassing) reactions. All of these parameters are included in thermodynamic databases that can be used by geochemical codes. However, extending these databases to include new species might be problematic in terms of numerical stability and/or model consistency, especially when the previously tabulated parameters are limited by their salinity range of validity. Fundamental systems should therefore be reviewed and updated to extend their thermodynamic characterisation to very high salinities and high temperatures.

Here, we consider the $NaOH$-H_2O binary system because of the very high solubility of NaOH salts [10]. This electrolyte has been widely studied both in the binary system $NaOH$-H_2O and in mixtures. Pitzer and Mayorga [11] worked on this binary system up to 6 $mol \cdot kgw^{-1}$ at 298.15 K. Harvie *et al.* [8] predicted solid-liquid equilibria in the **Na**-K-Mg-Ca-H-Cl-SO_4-**OH**-HCO_3-CO_3-CO_2-H_2O systems at 298.15 K up to 6 $mol \cdot kgw^{-1}$. Pabalan and Pitzer [12] predicted solid-liquid equilibria in the **Na**-K-Mg-Cl-SO_4-**OH**-H_2O at high temperature. Pabalan and Pitzer [13] provided parameters for the binary system $NaOH$-H_2O between

273.15-623.15 K and up to 10 mol·kgw^{-1} using both osmotic coefficient data and volumetric data such as apparent molar volumes. Simonson *et al.* [14] deduced, from heat capacity and dilution enthalpy measurements in the NaOH-H_2O system, the osmotic coefficient between 273.15 K and 523.15 K and up to 6 mol·kgw^{-1}. They represented these data with Pitzer's model and introduced the interaction parameter $\beta^{(2)}$ in order to improve their fit. Petrenko and Pitzer [15] measured vapor pressure and deduced water activity values. Using a modified version of the original Pitzer model, based on a mole fraction scale instead of a molality scale, they modeled these data between 273.15 and 523.15 K and for molalities ranging from 0 to 249.786 mol·kgw^{-1}. Christov and Møller [16] worked on the H-**Na**-K-**OH**-Cl-HSO_4-SO_4-H_2O system at high temperature (523.15 K). The parameters for the NaOH-H_2O system are valid up to 6 mol·kgw^{-1}. The excess properties of NaOH solutions are described with accuracy up to this concentration limit. In this paper, the authors also underline the non validity of their parameters at higher concentration. However these authors tested with success their parameters to determine the solubility of some hydrated salts up to about 60°C and 50 mol·kgw^{-1}.

The work described here goes further and aims to develop a set of parameters able to represent both the excess properties (e.g. osmotic coefficient, activity coefficient) and the mineral solubility in the NaOH-H_2O binary system to very high salinities, from 273.15 to 523.15 K, using the Pitzer approach. The originality of this study is to propose a model valid up to salt saturation between 273.15 and 523.15 K. Up to our knowledge, no Pitzer model exists on a such system up to so high concentrations (higher than 30 mol·kgw^{-1}). Its compatibility with more complex systems is checked on the LiOH-NaOH-H_2O and NaOH-NaCl-H_2O ternary systems.

2. Theoretical background

Pitzer [6] developed a semi-empirical thermodynamic model to represent the excess properties of electrolyte solutions. He improved on the work of Debye-Hückel [17], whose equation is valid for a low range of molalities, to extend its field of application. Pitzer [6] and Pitzer and Mayorga [11] provided specific interaction parameters (3 for binary systems: $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ}) for 1-1, 2-1, 3-1, 4-1 and 5-1 type electrolytes for maximum molalities of 6 $mol{\cdot}kgw^{-1}$, assuming total dissociation of the electrolytes. Pitzer and Mayorga [18] then showed that an additional parameter ($\beta^{(2)}$) is needed to represent the behaviour of the 2-2 type electrolytes above 0.1 $mol{\cdot}kgw^{-1}$. Pitzer and Kim [19] extended the model to include mixed electrolytes. A few years later, Kim and Frederick [20] provided ion interaction parameters for 304 single salts and for all types of electrolytes. These parameters apply at 298.15 K and generally up to saturation (for instance for NaOH up to 29 $mol{\cdot}kgw^{-1}$). They could give a similar result as the one obtained in case 1 of this study (see below). In order to improve Pitzer's model and its ability to accurately describe experimental data, authors have included virial coefficients of higher orders than C^{Φ} ([21–23]). Ananthaswamy and Atkinson [21] introduced three higher order virial coefficients (D^{Φ}, E^{Φ} and F^{Φ}) to represent the excess properties (osmotic coefficient, apparent molal enthalpy and apparent molal heat capacity) of $CaCl_2$ between 273.15 and 373.15 K up to 9 $mol{\cdot}kgw^{-1}$. Anstiss and Pitzer [22] determined interaction parameters for LiCl up to 20 $mol{\cdot}kgw^{-1}$ by including D^{Φ} and E^{Φ} parameters. Pitzer *et al.* [23] also introduced an ionic strength dependence in the higher order virial coefficients for $CaCl_2$ and $MgCl_2$ systems. But when pushed to more than 27 $mol{\cdot}kgw^{-1}$, these models which rely on the full dissociation hypothesis for the electrolyte, the number of charged species exceeds that of water. The paradoxical situation takes place where charged species are in direct contact with each other but do not form a complex because of the initial hypothesis of full dissociation. Physically, this is hardly justifiable.

Thus, some electrolytes cannot be described if we only consider total dissociation. Indeed, rather than high order virial coefficients, Pitzer and Silvester [24] introduced a neutral species that comes from the partial dissociation of phosphoric acid. Later, several authors successfully introduced the $H_3PO_4^0$(aq) species [25–27] to describe the behaviour of the phosphoric acid system up to 24 mol·kgw^{-1} using either the original Pitzer's model or the modified Pitzer's model [28]. In our model for NaOH-H_2O at high temperature and high salinity, it was necessary to introduce the neutral species $NaOH^0$(aq).

However, considering the existence of a neutral species in solution is not inconsequential and particular attention must be paid to the meaning of the available experimental data, especially when these have been acquired with isopiestic or electromotive force (e.m.f.) methods. For example, osmotic coefficient data given in the literature (ϕ^{lit}) generally consider full dissociation of the electrolytes. But when using a geochemical calculation code, the osmotic coefficients of a solution (ϕ) and other excess properties (such as mean activity coefficients) are calculated by considering the detailed speciation of the solution. This is the case of PHREEQC v2.18 [29], which is the geochemical calculation code we used in this study. In order to be able to compare the modelled values with literature data, we had to correct the calculated osmotic coefficient by taking the partial dissociation into account. The osmotic coefficient (ϕ) was then calculated using the equation of Clegg and Whitfield [30] who developed the Pitzer's model equations for a system containing an indefinite number of both neutral and ionic solutes (see the Online Resource 1). The correction is as follows:

$$\phi' = \phi \sum_i m_i \Big/ \sum_i \nu_i m_i \qquad (1a)$$

where ν_i is the number of ions formed by the complete dissociation of one molecule of solute and m_i is the molality of solute in mol·kgw^{-1}. In the case of the NaOH-H_2O system:

$$\phi' = \phi\,(m_{Na+} + m_{OH-} + m_{NaOH})/(m_{Na+} + m_{OH-} + 2 * m_{NaOH}) \tag{1b}$$

We can now compare ϕ' with the literature data (ϕ^{lit}). The mean activity coefficient also had to be corrected. Indeed, like the osmotic coefficient, the activity coefficient provided in the literature (γ^{lit}) is based on the total dissociation of the electrolyte. In order to compare literature data and PHREEQC calculations ($\gamma_{\pm}$), we calculated the corrected activity coefficient ($\gamma'_{\pm}$) using the following equation [25]:

$$\ln\gamma'_{\pm} = \left(\frac{m_{Na+}}{m_{Na+} + m_{NaOH}}\right)\ln\gamma_{\pm} \tag{2a}$$

$$\ln\gamma_{\pm} = (\ln\gamma_{Na+} + \ln\gamma_{OH-})/2 \tag{2b}$$

The activity of water does not need to be corrected. It is calculated in coherence with the aqueous speciation using the following equation:

$$\ln a_w = \left(-\phi M_w \sum_i m_i\right)/1000 \tag{3}$$

where $M_w$is the molar mass of water (18.0153 g·mol^{-1}).

3. Model parameterization and results

3.1.Methodology

We used the theories described above to develop a two-step procedure. We first developed the simplest model and then increased its complexity until the model results matched the available experimental data (e.g. for osmotic coefficient or water activity). We started parameter fitting using the fully dissociated approach considering only 3 parameters: $\beta^{(0)}$, $\beta^{(1)}$ (with its associated parameter α_1 equal to 2) and C^{ϕ}. If this model was not able to correctly reproduce the experimental thermodynamic properties, we added another adjustable interaction parameter $\beta^{(2)}$ and its adjusted associated parameter, α_2. In this last case, the parameter α_1 is equal to 1.4 (see the Online Resource 1 which describes the Pitzer equations) [18]. Several authors reported that when they are unable to reproduce excess properties on the concentration and temperature ranges under consideration, they introduce the binary interaction parameter $\beta^{(2)}$ and the associated parameter α_2 rather than considering partial dissociation [9, 14]. The $\beta^{(2)}$ parameter was first introduced by Pitzer and Mayorga [18] to describe the aqueous properties of 2-2 electrolytes. In Pitzer's classic theory, $\alpha_1 = 1.4$ and $\alpha_2 = 12$ [18]. However, to obtain a better fit, Filippov [31] proposed a value of 1 or -1, and Christov [9] considered it to be an adjustable parameter. If these α variations cannot reproduce the experimental results over the entire range of concentrations and temperatures under consideration, the alternative used by Pitzer and Silvester [24] consists in introducing a neutral and/or aqueous complex species together with the associated binary and ternary interaction parameters, and its thermodynamic equilibrium constant (K) of formation. In this case, the $\beta^{(2)}$ and associated α_2 parameters for the charged species are redundant and must be removed from the model.

We coupled an optimization software with PHREEQC v2.18 [29] to estimate the parameters after modifying the temperature dependence of interaction parameters ($\beta^{(0)}$, $\beta^{(1)}$,C^{ϕ}, $\lambda_{NaOH/NaOH}$ and $\zeta_{NaOH/Na+/OH-}$) so that the sets of parameters of both Møller [32] and Christov and Møller [16] could be used without further adjustment :

$$Para(T_k) = a_1 + a_2T_k + a_3T_k^2 + a_4T_k^3 + a_5/T_k + a_6 \ln T_k + a_7/(T_k - 263) + a_8/(680 - T_k) + a_9/(T_k - 227) \quad (4)$$

where T_k is the temperature in Kelvin and a_i are adjustable parameters.

The equilibrium constants of the reactions are also dependant on temperature according to the following equation:

$$\mathrm{Log}_{10} K = A_1 + A_2T_k + A_3/T_k + A_4 \log_{10} T_k + A_5/T_k^2 \quad (5)$$

3.2. Application to the binary NaOH-H_2O system

3.2.1. Data selection

The data used for the parameterization of the NaOH-H_2O system are osmotic coefficients and water activity measurements issued from literature (Fig. 1 and Table 1). Osmotic coefficient data for NaOH solutions at 298.15 K are taken from Hamer and Wu [33] for molalities ranging from 0.001 to 29 mol·kgw^{-1}. These authors compiled isopiestic data from Robinson and Stokes [34], and vapour pressure data from Kangro and Groeneveld [35]. Simonson *et al.* [14] also provided osmotic coefficients for NaOH molalities ranging from 0.01 to 6 mol·kgw^{-1} and temperatures from 273.15 to 523.15 K, calculated using Pitzer interaction parameters optimized from heat capacity and heat of dilution measurements. Water activity data are taken from Petrenko and Pitzer [15] for molalities ranging from 0.28 to 249.786 mol·kgw^{-1} between

273.15 and 523.15 K. Petrenko and Pitzer [15] computed water activity data from measured vapour pressures [35–38].

Holmes and Mesmer [39] also gave osmotic coefficient data for sodium hydroxide systems up to 7 mol·kgw^{-1} at three temperatures (383.25, 413.12 and 443.09 K). These authors measured osmotic coefficients directly using the isopiestic method, with NaCl as the reference electrolyte. Because of the limited range of concentrations (up to 7 mol.kgw^{-1}) of this latter set of experimental data, we decided not to use it. Indeed, in the optimization process, we worked temperature by temperature. Consequently, if we had optimized parameters on these data at one temperature, the resulting interaction parameters would have been valid up to 7 mol.kgw^{-1} only. Therefore, this set of parameters would have not been coherent with the sets of parameters determined for other temperatures. The activity coefficient data are not used for the optimisation. But the values obtained with our model are compared with values provided by literature [14, 15, 33, 34, 39].

Solubility data for NaOH.nH_2O minerals were from Pickering [10], who identified anhydrous NaOH(cr) and eight hydrates of sodium hydroxide (1-2-3.11-3.5-4α-4β-5-7). For temperatures above 273.15 K only anhydrous NaOH(cr) and five hydrates can exist (1-2-3.11-3.5-4α. Pickering's [10] measurements were verified by Cohen-Adad *et al.* [40]. Experimental invariant points are reported in Table 2 for comparison. The principal difference is for NaOH:3.5 H_2O + NaOH:H_2O. These data from Pickering [10] and Cohen-Adad *et al.* [40] are compared with those compiled by Zdanovskii [41] and Linke [42] for ternary systems. The sets of data are coherent. For anhydrous NaOH(cr) we used those provided by Cohen-Adad *et al.* [40], Linke [42] and Zdanovskii [41].

3.2.2. Model parameterization

Our objective was to determine the excess properties of NaOH solutions up to 523.15 K and from pure water to saturation with respect to the most soluble phase of $NaOH.nH_2O$ hydrate minerals. In a first step, we began with the simplest model at 298.15 K only, simply considering the three interaction parameters $\beta^{(0)}_{Na+/OH-}$, $\beta^{(1)}_{Na+/OH-}$ (α_1=2) and $C^{\phi}_{Na+/OH-}$ (Case 1). In this first case, the calculated standard deviation, σ (calculated on 76 measured data from [14], [15], [33]-Table 1), on the osmotic coefficient is 0.0808. This model did not correctly represent osmotic coefficient data throughout the entire domain of molalities at 298.15 K. The adjustable interaction parameter $\beta^{(2)}_{Na+/OH-}$ was therefore added with α_1=1.4 and α_2=12 (Case 2, σ=0.0805). As described in the methodology part the α_2 value was also tentatively optimized whereas α_1 is kept equal to 1.4. The best fit is obtained with α_2=0.695 (Case 3, σ=0.0285). Finally, we removed the $\beta^{(2)}$ term and we included the neutral species $NaOH^0$(aq) in the speciation calculation (Case 4, σ=0.00354). The equilibrium constant (K_{NaOH}) and two additional ternary ($\zeta_{Na+/OH-/NaOH}$) and binary ($\lambda_{NaOH/NaOH}$) interaction parameters were added to $\beta^{(0)}_{Na+/OH-}$, $\beta^{(1)}_{Na+/OH-}$ (α_1=2) and $C^{\phi}_{Na+/OH-}$. Several other studies [43–50] consider the neutral species $NaOH^0$(aq). In particular, Sharma and Kashyap [50] have experimentally identified this ion pair in concentrated aqueous solutions of sodium hydroxide, using a Raman spectrometer. The lowest standard deviation is obtained for Case 4 when the partial dissociation of NaOH is considered. Moreover, at 298.15 K, this approach also enables us to accurately represent the mean activity coefficient of 52 data points ([33]-Table 3).

In the following step, we therefore used the same optimization approach at temperatures other than 298.15 K. The interaction parameters were adjusted using both the osmotic coefficients given by Simonson *et al.* [14] up to 6 $mol\cdot kgw^{-1}$ and the water activity data given by Petrenko and Pitzer [15] up to saturation with respect to hydrated minerals. The results cover a wide range of temperatures, from 273.15 to 523.15 K.

The osmotic coefficient and water activity can be represented up to x_2=0.82 (≈ 250 mol·kgw^{-1}) (Fig. 2), where x_2 is the molar fraction of total of Na in the aqueous solution, defined by:

$$x_2 = n_{tot\ Na}/(n_{tot\ Na} + n_w) \tag{6}$$

where n_w is the number of moles of water.

The osmotic coefficients from Petrenko and Pitzer [15] were calculated from water activity data using a rearrangement of Eq. 3. Here, the osmotic coefficient is calculated assuming total dissociation and we could compare these values with model results. They are consistent with Simonson *et al.*'s data [14].

The standard deviation (σ) obtained with our model for each experimental data set of osmotic coefficients is given in Table 1. Values of σ illustrate the good match both for the data used for the parameterization and for the data used from Holmes and Mesmer [39]. The regression coefficients of Eq. 4 are given in Table 4.

The mean activity coefficient of NaOH was also calculated according to temperature. The speciation of the aqueous solution and the partial dissociation were taken into account according to Eq. 2. The mean activity coefficients calculated with this equation are given in Table 3 together with literature values given for comparison. Although the values are extremely variable (γ=42.8 at 22 mol·kgw^{-1} and 273.15 K and γ<1 at 523.15 K for the same molality), our values are similar to those recommended by several authors [14, 15, 33, 34, 39]. For instance, the comparison with the experimental values compiled by Hamer and Wu [33] at 298.15 K, shows that our model better represents the data than the other models up to 22 mol.kgw^{-1}.

The speciation of dissolved NaOH is plotted on Fig. 3 in terms of molar percentage of NaOH^0(aq) as a function of the total NaOH molality at various temperatures. Up to 423.15 K, the species $NaOH^0(aq)$ appears when the total NaOH molality is around 10 mol·kgw^{-1}. It becomes increasingly predominant when the concentration of total NaOH increases. For instance, at 30 mol·kgw^{-1}, the proportion of $NaOH^0(aq)$ ion pair reaches 35 %, except at 273.15 and 298.15 where 50 % only of the total dissolved NaOH is dissociated. This suggests that at high temperature (>423.15 K) or at high molality (>10 mol·kgw^{-1}), the species $NaOH^0(aq)$ should not be disregarded. A more complete discussion about Fig. 3 is provided in Discussion paragraph.

Once the aqueous properties of the $NaOH\text{-}H_2O$ system had been properly described, salt solubility could be studied and we estimated the temperature functions of equilibrium constants for the dissolution reaction of anhydrous NaOH(cr) and hydrated $NaOH.nH_2O(cr)$ salts [n=1, 2, 3.11, 3.5 or 4α]. The irreversible general dissolution reaction is:

$$NaOH.nH_2O(cr) \rightarrow Na^+ + OH^- + nH_2O$$

The temperature functions of the equilibrium constants are plotted in Fig. 4 and the corresponding coefficients (see Eq. 5) are given in Table 5. On Fig. 4, the lines are the values determined in this study. The white symbols are the values determined by Christov and Møller [16] and the grey symbols were calculated using the standard thermodynamic properties of formation ($\Delta H°_f$, S° and C_p) of $NaOH.H_2O$ provided by Wagman *et al.* [51]. The solubility of the different hydrated NaOH salts in water is plotted against temperature on Fig. 5. Model calculations (lines) are consistent with experimental data (symbols) from Pickering [10] and the invariant points (black symbols) are well reproduced by calculations (see also Table 1). Although $NaOH.nH_2O$ [with n=2, 3.5 or 4] are not stable at 298.15 K, the log K of those three salts can be calculated which gives 3.95, 2.5 and 2.11, respectively. These values are close to the values proposed by Christov and Moller [16] who found 3.56, 2.23 and 1.93 for $NaOH.2H_2O$, $NaOH.3.5H_2O$ and $NaOH.4H_2O$, respectively.

4. Testing against boiling point, ternary systems and discussion

4.1.Boiling point elevation

The parameterization of the NaOH-H_2O binary system was tested by calculating an independent property that is the boiling point elevation of this system depending on the NaOH concentration. The boiling point elevation,Θ_B, is equal to the difference between the boiling temperature (T_B) of a given solution and that of the pure solvent at the same pressure. Ge and Wang [52] proposed an equation in coherence with the Pitzer theory. They demonstrated that the boiling point elevation can be calculated with the following equation:

$$\Theta_B = \frac{-\Delta H_{0,T_B}^{vap} - 2RT_B \ln a_{liq} + \sqrt{\left(\Delta H_{0,T_B}^{vap}\right)^2 - 2\Delta C_p^{vap} T_B^2 R \ln a_{liq}}}{2\left(\frac{\Delta H_{0,T_B}^{vap}}{T_B} + 0.5\Delta C_p^{vap} + R \ln a_{liq}\right)} \qquad (7)$$

where $\Delta H_{0,T_B}^{vap}$ is the enthalpy of vaporization of a pure solvent at its normal boiling point T_B and ΔC_p^{vap} is the difference in heat capacity between the vapor (C_p^V) and liquid (C_p^L) phases at the normal boiling point of the pure solvent. The values of these parameters are given in Online Resource 2 and are provide by Lide [53]. a_{liq} is the water activity in the aqueous solution at $T_B + \Theta_B$.

The boiling point elevation was determined by iteration. We set an arbitrary initial value for Θ_B and the corresponding water activity was calculated with PHREEQC. By applying Eq. 8, we obtained a new value for Θ_B. If this value was different from the previous one, it was used to recalculate the water activity. This iterative procedure was continued as long as the boiling point rise obtained at two successive steps were different.

The results of these calculations are given in Fig. 6 and compared with the experimental data. Kirschstein [54] provided boiling point values for molalities ranging from 1.31 to 141.7 mol·kgw^{-1}. The range of molalities studied by Bialik *et al.* [55] is from 0.9876 to 9.77 mol·kgw^{-1}. We also plotted the values predicted with the Dühring equation [56]. This empirical law assumes that the boiling point of a given solution is a linear function of the boiling point of pure water at the same pressure. We then calculated the boiling point elevation with the interaction parameters of Christov and Møller [16]. The various boiling point elevation values are given in Online Resource 2. The interaction parameters defined in this study can accurately predict the boiling point elevation up to 75 mol·kgw^{-1} without any further optimization.

4.2.Ternary system NaOH-NaCl-H_2O

To check the validity of our interaction parameters for the NaOH binary system (Table 4), we studied the ternary system NaOH-NaCl-H_2O and the solubility of halite in NaOH solutions as a function of temperature. The interaction parameters of the binary system NaCl-H_2O are provided by Møller [32] who considers NaCl to be completely dissociated (Table 6). The binary parameter interaction $\theta_{OH-/Cl-}$ is given by Christov and Møller [16]. The equilibrium constant of halite is provided by Chase [57], consistent with the Thermoddem database [58]. Only two additional interaction parameters ($\psi_{Na+/Cl-/OH-}$ and $\zeta_{Na+/Cl-/NaOH}$) were optimized. The results are shown in Fig. 7. Experimental solubility data come from several authors and were compiled by Linke [42] and Zdanovskii *et al.* [41]. By optimizing the ternary parameters $\psi_{Na+/Cl-/OH-}$ and $\zeta_{Na+/Cl-/NaOH}$, the halite solubility can be satisfactorily reproduced up to 423.15 K and up to saturation of NaOH. Except at 423.15 K, where we represented solubility up to 55 mol·kgw^{-1}. The regression coefficients of Eq. 4 are given in Table 7 for the interaction parameters ($\psi_{Na+/Cl-/OH-}$ and $\zeta_{Na+/Cl-/NaOH}$).

With this full parameterization, we calculated osmotic coefficients for the ternary system NaCl-NaOH-H_2O at three temperatures (298.15, 323.15 and 373.15 K) (Fig. 8). They are similar to the isopiestic measurements of Königsberger *et al.* [59]. The standard deviations are 0.0113, 0.0069 and 0.0202 for 298.15, 323.15 and 373.15 K, respectively. Harned and Harris [60] and Harned and Cook [61] recommended activity coefficient values in ternary solutions and for four total constant molalities ($m_{\mathrm{NaOH}} + m_{\mathrm{NaCl}}$) (Fig. 9). Our calculations give standard deviations for the mean activity coefficients of NaOH of 0.00489, 0.00544, 0.0112 and 0.0429 for the total molalities of 0.5, 1, 3 and 5 $\mathrm{mol \cdot kgw^{-1}}$, respectively. For the mean activity coefficients of NaCl, we obtained standard deviations of 0.008 and 0.00609 at total molalities of 0.5 and 1 $\mathrm{mol \cdot kgw^{-1}}$, respectively.

4.3.Ternary system NaOH-LiOH-H_2O

We also studied the ternary system NaOH-LiOH-H_2O. This system was studied by Lassin *et al.* [28] using the interaction parameters provided by Christov and Møller [16] for the NaOH-H_2O system. Because of the concentration limits of this set of parameters, we reconsidered the system and used the NaOH parameterisation determined in this study. The interaction parameters of the binary system LiOH-H_2O come from Lassin *et al.* [28] who consider dissolved LiOH to be completely dissociated (additional data are given in Online Resource 2).

Few experimental data exist on this system [41, 62] and these authors publish inconsistent values. Some of these authors gave solubility data for the NaOH-H_2O system also. This enabled us to compare their values with the data from Pickering [10] and to choose the set of data which seems to be the most coherent namely Evteeva (1965) and Itkina *et al.* (1963, 1966, 1968) compiled by Zdanovskii *et al.* [41].

Two mixing parameters ($\psi_{\mathrm{Li+/Na+/OH-}}$ and $\lambda_{\mathrm{Li+/NaOH}}$) were added to the model and were optimised on solubility data of LiOH in NaOH solutions as a function of temperature (303.15, 323.15, 373.15 and 423.15 K) (Table 8). At moderately high molalities (around NaOH = 10-15 mol·kgw^{-1}), only the ternary interaction parameter $\psi_{Li+/Na+/OH-}$ has an influence on the calculated results since the concentration of the NaOH^0(aq) ion pair is small (see previous sections). We therefore first optimised this parameter before adjusting $\lambda_{Li+/NaOH}$ to tentatively extend the representation of the solubility of LiOH in NaOH solutions to the entire molality range (Fig. 10). Calculation results are consistent with experimental data except at 373.15 K where the predicted LiOH solubility is lower than measured data. However, there is too little experimental data to draw meaningful conclusions.

This new parameterization greatly improves the thermodynamic description of the LiOH-NaOH-H_2O system by Lassin *et al.* [28]. However, due to the scarcity of measured data, we are unable to further improve the model developed in this study. Additional experimental data are needed.

4.4.Discussion

The results obtained on the NaOH-H_2O system show that the proposed set of parameters is able to represent most of the excess properties up to saturation between 273.15 and 523.15 K. Using the classical Pitzer equations, a good match between numerical results and measurements cannot be achieved without the use of the neutral ion pair NaOH^0(aq) in the speciation calculations. Pokrovskii and Helgeson [63] determined log K values between 273.15 and 623.15 K with data up to 6 mol·kgw^{-1}. They found -0.75, -0.66 and -0.21 at 298.15, 373.15 and 473.15 K, respectively, for the reaction $Na^+ + OH^- = NaOH^0(aq)$. We estimated Pitzer interaction parameters by first using the log K values proposed by Pokrovskii and Helgeson [63]. The resulting set of parameters was not able to reproduce excess properties over the entire range of concentrations. It could represent the data only up to 14 mol·kgw^{-1}. We therefore had to propose new values for the formation constant of the

$NaOH^0$(aq) species to represent the excess properties over the entire range of concentrations, without losing accuracy at low molalities. At 298.15 K, 373.15 K and 473.15 K, we found -3.5, -3.16 and -1.35, respectively, which is consistent with the calorimetric data of Chen *et al.* [44] for temperatures above 523.15 K. New experimental data concerning speciation is needed to enable us to reduce this uncertainty.

It is questionable whether or not such complex species ($NaOH^0$(aq)) can be used in the Pitzer theory since Pitzer [6] originally developed his model considering the electrolyte to be fully dissociated. This is valid for many salts and strong acids and bases. However, a few years later Pitzer, extended his model [24] to solutions using a dissociation equilibrium. In some cases, Pitzer and Silvester [24] showed that the partial dissociation of the electrolyte needed to be taken into account and that neutral species (and ionic aqueous complexes) could be added to the speciation calculations. To do this, they took the example of phosphoric acid, which they considered to be partially dissociated. The neutral aqueous species $H_3PO_4^0$(aq) was added to the model together with the equilibrium constant of the corresponding dissociation reaction, and parameters for the interaction between $H_3PO_4^0$(aq) and the other species in solution. The equations are similar to the original model. They simply include a correction of the osmotic coefficient to integrate the partial dissociation. This model was improved by Cherif *et al.* [27], who introduced additional complex ions based on Raman spectroscopy measurements [64].

Pitzer *et al.* [65] also used sulphuric acid as another example of the integration of ionic association. They assumed that the second dissociation was partial and they added the aqueous complex HSO_4^-(aq). This approach was used later by Christov and Møller [16]. Felmy *et al.* [66] successfully developed a model for polymerized silica species at high ionic strength based on the classical Pitzer equations. Møller *et al.* [67] added the neutral aqueous species $Al(OH)_3^0$(aq) to describe the solubility of gibbsite and boehmite over a wide pH range.

On the other hand, Møller [32] studied the Na-Ca-Cl-SO_4-H_2O system between 298.15 and 523.15 K and up to 8 mol·kgw^{-1}. She introduced the species $CaSO_4^0$(aq) to reproduce the solubility data. She determined the dissociation constant but fixed the interaction parameter with this neutral species equal to zero. When Greenberg and Møller [7] extended the model of Møller [32], they retained the species $CaSO_4^0$(aq). With such an approach, the extension of the chemical system to other elements became very difficult. This led Christov [68] to propose a new parameterization without $CaSO_4^0$(aq). Harvie *et al.* [8] studied the solubility of the Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system and introduced several complex ions ($MgOH^+$, HCO_3^-, HSO_4^-, $CaCO_3^0$(aq), $MgCO_3^0$(aq)). But it is questionable whether these aqueous complexes will enable the extension to larger chemical systems since parameters should, theoretically, be estimated for specific interactions between parameters and for every new species added to the chemical system. Moreover, the compatibility of parameter sets based on ion association and parameter sets based on 4-parameter descriptions is an open debate.

Finally, the Pitzer model can combine an association equilibrium with solute interactions treated by using virial coefficients [24]. When the classical approach fails at high molality assuming full dissociation, introducing the ion association can significantly improve the results. Nevertheless, for the sake of physical significance, the species added to the model should be compatible with the actual composition of the aqueous solution and should therefore rely on its characterization. Experience suggests that, for a given element, the aqueous complexes introduced in the model should be, at least, present in significant amounts if not predominant, in the solution.

Concerning the fraction of $NaOH^0(aq)$ present in solution, at total NaOH concentrations above about 10 mol·kgw^{-1}, the concentration of $NaOH^0(aq)$ is higher at low temperatures (273.15 and 298.15 K) (Fig. 4). This is surprising since the ionic association should be stronger at high temperatures because of the decrease in the dielectric constant of water. A possible explanation might be a competitive influence of both the dielectric constant and the equilibrium constant of the reaction of formation of the aqueous complex $NaOH^0(aq)$. Indeed, in the model presented here, these equilibrium constant increases at low temperature, and therefore stabilizes the aqueous complex, with a minimum at 298.15 K. The real weight of physical and thermodynamic contributions is hard to evaluate, mainly because there are few available data on aqueous speciation. New data are needed to clarify this point. Currently, the parameters retained in this study provide the best fit with the available excess properties (osmotic coefficient, activity of water).

We have seen that we can represent thermodynamic excess properties up to saturation. At 523.15 K, for instance, we can represent the excess properties up to 250 mol·kgw^{-1}, at which point the water activity is very low (0.012356). We are aware that an “aqueous solution” with such a low water activity is very unusual, but the aim of our study was not to provide new information concerning the structure and behavior of water under such extreme conditions. We show here, for the first time to our best knowledge, the robustness of the Pitzer’s approach and the ability of the model to represent these aqueous properties at very high molality and we provide a comprehensive set of parameters that can be used with confidence and be extended to others chemical systems. This is illustrated by the extension of the binary NaOH-H_2O system to two ternary systems and the calculation of independent data such as the boiling point rise. At this stage, we consider that the proposed set of parameters constitutes a sound basis for describing the quaternary system NaOH-LiOH-NaCl-LiCl-H_2O up to mineral saturation and to 423.15 K, in the absence of any double salt.

5. Conclusion

In this study we proposed a new Pitzer parameterization for the binary NaOH-H_2O system and for ternary NaOH-NaCl-H_2O and NaOH-LiOH-H_2O systems. We represent the excess solution properties (osmotic coefficient, water activity, etc.) up to saturation and between 273.15 and 523.15 K (i.e., 30 mol·kgw^{-1} at 298.15 K and up to 250 mol·kgw^{-1} at 523.15 K). To do this, it is necessary to consider the partial dissociation of NaOH and add the neutral ion pair $NaOH^0$(aq), which has been considered by other authors. In this case, several parameters must be added to the Pitzer model (μ_{nnc}, λ_{nc}, $\lambda_{na}\cdots$ where n, c, a stand for neutral, cation and anion species respectively). After trial and error testing, we selected ζ_{nca} and λ_{nn}. The approach is fully consistent with the classical Pitzer model and can be easily applied to common geochemical calculation codes. We also determined the solubility products of anhydrous NaOH(cr) and five hydrated NaOH.$n$$H_2O$(cr) salts (where n = 1, 2, 3.11, 3.5, 4α) that we compared to values obtain by Christov and Møller [16]. For NaOH.H_2O, our equilibrium constant is roughly consistent with thermodynamic data. These new parameter values were successfully tested on the boiling point elevation, which was accurately predicted, and on the prediction of salt solubility in two ternary systems (NaOH-NaCl-H_2O and NaOH-LiOH-H_2O), which was improved at high molalities.

This study is part of on-going work to redefine basic binary systems by extending them to high salinities and temperatures in order to ensure the consistency of an extension to complex systems similar to real and industrial brines.

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Online Resource 1: Description of Pitzer's equations

Pitzer's model is described in detail elsewhere [6, 11, 18, 19, 69, 70]. We give here the equations for the osmotic coefficient (ϕ) and activity coefficient for aqueous (γ_M and γ_X) and neutral species (γ_N). These are developed for a system that contains c cations, a anions and n neutral species [30]

$$(\phi - 1) =$$

$$\left(\frac{2}{\sum_i m_i}\right)\left\{\begin{array}{ll}
\frac{-A_\phi I^{3/2}}{1+1.2I^{1/2}} + \sum_c \sum_a m_c m_a \left(B_{ca}^{\phi} + zC_{ca}\right) & \text{(i)}\geq 1 \text{ salt} \\
+\sum_c \sum_{<c'} m_c m_{c'} \left(\Phi_{cc'}^{\phi} + \sum_a m_a \psi_{cc'a}\right) & \text{(ii)}\geq 2 \text{ cations} \\
+\sum_a \sum_{<a'} m_a m_{a'} \left(\Phi_{aa'}^{\phi} + \sum_c m_c \psi_{aa'c}\right) & \text{(iii)}\geq 2 \text{ anions} \\
+\frac{1}{2}\sum_n m_n^2 \lambda_{nn} + \sum_n m_n^3 \mu_{nnn} & \text{(iv)}\geq 1 \text{ neutral} \\
+\sum_n \sum_{<n'} m_n m_{n'} \lambda_{nn'} + 3\sum_n \sum_{<n'} m_n^2 m_{n'} \mu_{nnn'} & \text{(v)}\geq 2 \text{ neutral} \\
+6\sum_{n<} \sum_{n'<} \sum_{n''} m_n m_{n'} m_{n''} \mu_{nn'n''} & \text{(vi)}\geq 3 \text{ neutral} \\
+\sum_n \sum_c m_n m_c \lambda_{nc} + 3\sum_n \sum_c m_n^2 m_c \mu_{nnc} & \text{(vii)}\geq 1 \text{ cation, }\geq 1 \text{ neutral} \\
+\sum_n \sum_a m_n m_a \lambda_{na} + 3\sum_n \sum_a m_n^2 m_a \mu_{nna} & \text{(viii)}\geq 1 \text{ anion, }\geq 1 \text{ neutral} \\
+\sum_n \sum_c \sum_a m_n m_c m_a \zeta_{nca} & \text{(ix)}\geq 1 \text{ cation, }\geq 1 \text{ anion, }\geq 1 \text{ neutral} \\
+\sum_n \sum_c \sum_{<c'} m_n m_c m_{c'} \eta_{ncc'} & \text{(x)}\geq 2 \text{ cations, }\geq 1 \text{ neutral} \\
+\sum_n \sum_a \sum_{<a'} m_n m_c m_{a'} \eta_{naa'} & \text{(xi)}\geq 2 \text{ anions, }\geq 1 \text{ neutral} \\
+6\sum_c \sum_n \sum_{<n'} m_c m_n m_{n'} \mu_{cnn'} & \text{(xii)}\geq 1 \text{ cation, }\geq 2 \text{ neutral} \\
+6\sum_a \sum_n \sum_{<n'} m_a m_n m_{n'} \mu_{ann'} & \text{(xii)}\geq 1 \text{ anion, }\geq 2 \text{ neutral}
\end{array}\right\} \qquad \text{(A-1)}$$

$$ln\,\gamma_M =$$

$$\left[\begin{array}{ll}
z_M^2 F + \sum_a m_a (2B_{Ma} + zC_{Ma}) + |z_M| \sum_c \sum_a m_a C_{ca} & \text{(i)}\geq 1 \text{ sel} \\
+\sum_c m_c (2\Phi_{MC} + \sum_a m_a \psi_{Mca}) & \text{(ii)}\geq 2 \text{ cations} \\
+\sum_a \sum_{<a'} m_a m_{a'} \psi_{Maa'} & \text{(iii)}\geq 2 \text{ anions} \\
+2\sum_n m_n \lambda_{Mn} + 3\sum_n m_n^2 \mu_{Mnn} & \text{(iv)}\geq 1 \text{ neutral} \\
+6\sum_{n<} \sum_{n'} m_n m_{n'} \mu_{Mnn'} & \text{(v)}\geq 2 \text{ neutral} \\
+\sum_n \sum_a m_n m_a \zeta_{Mna} & \text{(vi)}\geq 1 \text{ anion, }\geq 1 \text{ neutral} \\
+6\sum_n \sum_c m_n m_c \eta_{Mnc} & \text{(vii)}\geq 2 \text{ cations, }\geq 1 \text{ neutral} \\
 &
\end{array}\right] \qquad \text{(A-2)}$$

$$ln\,\gamma_X = \qquad \text{(A-3)}$$

$$\left[\begin{array}{ll} z_X^2 F + \sum_c m_c (2B_{cX} + zC_{cX}) + |z_X| \sum_c \sum_a m_c C_{ca} & \text{(i)}\geq 1 \text{ salt} \\ + \sum_a m_a (2\Phi_{Xa} + \sum_c m_c \psi_{cXa}) & \text{(ii)}\geq 2 \text{ anions} \\ + \sum_c \sum_{<c'} m_c m_{c'} \psi_{cc'X} & \text{(iii)}\geq 2 \text{ cations} \\ +2 \sum_n m_n \lambda_{Xn} + 3 \sum_n m_n^2 \mu_{Xnn} & \text{(iv)}\geq 1 \text{ neutral} \\ +6 \sum_{n<} \sum_{n'} m_n m_{n'} \mu_{Xnn'} & \text{(v)}\geq 2 \text{ neutral} \\ + \sum_n \sum_c m_n m_c \zeta_{ncX} & \text{(vi)}\geq 1 \text{ cation, } \geq 1 \text{ neutral} \\ +6 \sum_n \sum_a m_n m_a \eta_{Xna} & \text{(vii)}\geq 2 \text{ anions, } \geq 1 \text{ neutral} \\ & \end{array}\right]$$

$$ln\, \gamma_N = \left[\begin{array}{ll} 2 \sum_n m_n \lambda_{Nn} + 3 \sum_n m_n^2 \mu_{Nnn} & \text{(i)}\geq 1 \text{ neutral} \\ +6 \sum_n m_N m_n \mu_{NNn} & \text{(ii)}\geq 2 \text{ neutral} \\ +6 \sum_{n<} \sum_{n'} m_n m_{n'} \mu_{Nnn'} & \text{(iii)}\geq 3 \text{ neutral} \\ +2 \sum_c m_c \lambda_{Nc} + 2 \sum_a m_a \lambda_{Na} + \sum_c \sum_a m_c m_a \zeta_{Nca} & \text{(iv)}\geq 1 \text{ cation, } \geq 1 \text{ anion} \\ + \sum_{c<} \sum_{c'} m_c m_{c'} \eta_{Ncc'} & \text{(v)}\geq 2 \text{ cations} \\ + \sum_{a<} \sum_{a'} m_a m_{a'} \eta_{Naa'} & \text{(vi)}\geq 2 \text{ anions} \\ +6 \sum_n \sum_c m_n m_c \mu_{Nnc} + 6 \sum_n \sum_a m_n m_a \mu_{Nna} & \text{(vii)}\geq 1 \text{ cation, } \geq 1 \text{ anion, } \geq 1 \text{ neutral} \\ & \end{array}\right] \qquad \text{(A-4)}$$

Functions f^{Φ} (extended form of the Debye-Hückel equation) and B_{ca}^{ϕ} (form of the ionic strength dependence) are determined empirically. In his first paper, Pitzer [6] tried several forms for these functions and the best results for type 1-1, 2-1 and 1-2 electrolytes at 298.15 K were obtained with:

$$f^{\Phi} = -A_{\phi} I^{1/2} / \left(1 + bI^{\frac{1}{2}}\right) \qquad \text{(A-5)}$$

$$B_{ca}^{\Phi} = \beta_{ca}^{(0)} + \beta_{ca}^{(1)} \exp(-\alpha I^{1/2}) \qquad \text{(A-6)}$$

where I is the ionic strength defined by:

$$I = 1/2 \sum_i m_i z_i^2 \qquad \text{(A-7)}$$

In these equations, b and α are universal parameters whose values are 1.2 $kg^{1/2}\cdot mol^{-1/2}$ and 2.0 $kg^{1/2}\cdot mol^{-1/2}$, respectively.

Pitzer and Mayorga [18] studied the type 2-2 electrolyte and explained that for this electrolyte another form could be used for the second virial coefficient in order to reproduce the behaviour of this electrolyte below 0.1 mol·kgw^{-1}. They added $\beta_{ca}^{(2)}$ and α_2 parameters.

$$B_{ca}^{\phi} = \beta_{ca}^{(0)} + \beta_{ca}^{(1)} \exp\left(-\alpha_1 I^{1/2}\right) + \beta_{ca}^{(2)} \exp(-\alpha_2 I^{1/2}) \tag{A-8}$$

with values of 1.4 kg$^{1/2}$·mol$^{-1/2}$ and 12 kg$^{1/2}$·mol$^{-1/2}$ for α_1 and α_2, respectively.

The equation for the Debye-Hückel parameter A_{ϕ} is:

$$A_{\phi} = \frac{1}{3}(2\pi N_0 d_w/1000)^{1/2}(e^2/(\varepsilon kT))^{3/2} \tag{A-9}$$

The C_{ca} third virial coefficients are independent of ionic strength:

$$C_{ca} = C_{ca}^{\phi}/\left(2\sqrt{|z_C z_A|}\right) \tag{A-10}$$

But this term is coupled with the parameter z, which depends on the concentration:

$$z = \sum_i m_i |z_i| \tag{A-11}$$

C_{ca}^{ϕ} is the adjustable parameter.

The other parameters in the activity coefficient equation are defined by:

$$B_{ca} = \beta_{ca}^{(0)} + \beta_{ca}^{(1)} \mathrm{g}\left(\alpha_1 I^{1/2}\right) + \beta_{ca}^{(2)} \mathrm{g}(\alpha_2 I^{1/2}) \tag{A-12}$$

$$g(x) = 2\,[1 - (1 + x)\exp(-x)]/x^2 \tag{A-13}$$

$$F = f^{\gamma} + \sum_{c=1}^{nc}\sum_{a=1}^{na} m_c m_a B'_{ca} + \sum_{c=1}^{nc-1}\sum_{c\prime=2}^{nc} m_c m_{c\prime} \phi'_{cc\prime} + \sum_{a=1}^{na-1}\sum_{a\prime=2}^{na} m_a m_{a\prime} \phi'_{aa\prime} \tag{A-14}$$

where:

$$B'_{ca} = \left[\beta_{ca}^{(1)}\, g'\left(\alpha_1 I^{1/2}\right) + \beta_{ca}^{(2)} g'(\alpha_2 I^{1/2})\right]/I \quad \text{(A-15)}$$

$$g'(x) = -2[1 - (1 + x + x^2/2)\exp(-x)]/x^2 \quad \text{(A-16)}$$

$$f^{\gamma} = -A_{\phi}\left[I^{1/2}/\left(1 + bI^{1/2}\right) + 2/b \ln\left(1 + bI^{1/2}\right)\right] \quad \text{(I-17)}$$

The complete equation for Φ_{ij}, which takes into account the interaction between two ions of the same sign, is:

$$\Phi_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I) \quad \text{(A-18)}$$

$$\Phi'_{ij} = {}^{E}\theta'_{ij}(I) \quad \text{(A-19)}$$

$$\Phi_{ij}^{\phi} = \theta_{ij} + {}^{E}\theta_{ij}(I) + I^{E}\theta'_{ij}(I) \quad \text{(A-20)}$$

where ${}^{E}\theta_{ij}$ and ${}^{E}\theta'_{ij}$ take into account electrostatic unsymmetric mixing effects and only depend on ion charges, total ionic strength and solvent properties. θ_{ij} is an adjustable parameter. The third virial coefficient ψ_{ijk} is a mixed electrolyte parameter for each cation-cation-anion or anion-anion-cation triplet in a mixed electrolyte solution. This term is assumed to be independent of ionic strength.

Online Resource 2: Supplementary data

Table B-1. Thermodynamic properties of pure water at 1 Atm [53]

	Values	Units
Boiling point of water	373.15	K
Specific heat capacity, $C_p^S(273.15\ K)$	2.11	$J\cdot g^{-1}\cdot K^{-1}$
Specific heat capacity, $C_p^L(273.15\ K)$	4.2176	$J\cdot g^{-1}\cdot K^{-1}$
Specific heat capacity, $C_p^L(373.15\ K)$	4.2159	$J\cdot g^{-1}\cdot K^{-1}$
Specific heat capacity, $C_p^V(372.76\ K)$	2.0784	$J\cdot g^{-1}\cdot K^{-1}$
Enthalpy of vaporization, $\Delta H_0^{vap}(373.15\ K)$	40.657	$kJ\cdot mol^{-1}$
Enthalpy of fusion, $\Delta H_0^{fus}(273.15\ K)$	333.6	$J\cdot g^{-1}$

Table B-2. Boiling point raise (θ_B) of NaOH-H_2O system

Recommended values of :	θ_B Boiling point raise (°C)							
	0.98760 $mol\cdot kgw^{-1}$	1.90790 $mol\cdot kgw^{-1}$	3.50980 $mol\cdot kgw^{-1}$	6.25048 $mol\cdot kgw^{-1}$	9.76640 $mol\cdot kgw^{-1}$	13.46258 $mol\cdot kgw^{-1}$	16.66796 $mol\cdot kgw^{-1}$	20.45613 $mol\cdot kgw^{-1}$
This study	0.93	1.89	3.84	8.12	15.32	24.17	31.64	39.27
Christov and Møller [16]	0.96	2.09	4.66	10.81	-	-	-	-
Bialik *et al.* [55]	0.87	1.83	3.68	-	14.85	-	-	-
Kirschstein [54]	-	-	-	8	-	23.1	29.1	35.5

Recommended values of :	θ_B Boiling point raise (°C)							
	25.00194 mol·kgw^{-1}	30.55792 mol·kgw^{-1}	37.50291 mol·kgw^{-1}	46.43217 mol·kgw^{-1}	58.33785 mol·kgw^{-1}	75.00581 mol·kgw^{-1}	100.00775 mol·kgw^{-1}	141.67765 mol·kgw^{-1}
This study	46.93	54.95	63.88	74.43	86.96	100.65	114.19	127.76
Kirschstein [54]	42.5	50.1	58.8	69	81.5	97.1	117.5	144.9

Table B-3. Values of the fitting constants (Eq. (4)) for the interaction parameters of the LiOH-H_2O system

Parameters	*T range* (*K*)	*Constants (T in K)*						*Ref.*
		a_1 (-)	a_2 (T)	a_3 (T^2)	a_5 (1/T)	a_6 (ln(T))	a_7 (1/(T-263))	
$\beta^0_{Li+/OH-}$	273.15-473.15	0.121114	-3.45E-04	0	3.917769	0	0	[2]
$\beta^1_{Li+/OH-}$	273.15-473.15	1.235033	-3.984E-03	0	101.9411	0	0	[2]
$C^{\varphi}_{Li+/OH-}$	273.15-473.15	1.00E-10	2.51E-04	0	-0.51131	0	0	[2]

Figure captions

Fig. 1 Localization of the experimental data used in this study for the NaOH-H_2O system, as a function of temperature. The crosses represent water activity data according to molalities (given on the top x-axis). The circles represent osmotic coefficient data according to molalities (given on the bottom x-axis).

Fig. 2 Calculated (lines) and experimental (open diamonds) osmotic coefficient, Φ, for the NaOH-H_2O binary system as a function of fraction molar of total molality of NaOH. For convenience of representation, the curves were shifted 1.2 for 273.15 K, 1 for 298.15 K and so on. The osmotic coefficient data of Petrenko and Pitzer [15] are determined with their activity of water data. In the inset, it's a zoom at low molality.

Fig. 3 Evolution of concentration of $NaOH^0$(aq) as a function on a total molality of Na.

Fig. 4 Comparison of thermodynamics solubility product of hydroxide sodium solids determined in this study. The solid lines are the constants determined in this study. The open symbols are the constants determined by Christov and Moller [16]. The grey symbols are determined using the standard thermodynamic properties of formation (Wagman *et al.* [51])

Fig. 5 Calculated (lines) and experimental (symbols) solubility of NaOH.nH_2O (n = 1, 2, 3.11, 3.5 or 4α) as a function of temperature in the NaOH-H_2O binary system. Experimental data are from Pickering [10]

Fig. 6 Calculated (lines) and experimental (open symbols) boiling point elevation as a function of a total molality of Na in the NaOH-H_2O binary system. The experimental data are from Kirschstein [54] (open diamonds) and Bialik *et al.* [55] (open circles)

Fig. 7 Calculated (lines) and axperimental (open symbols) solubility data for the NaOH-NaCl-H_2O systems. Experimental data are from Linke [42] and Zdanovskii et al. [41]

Fig. 8 Calculated (lines) and experimental (open diamonds) osmotic coefficient, Φ, for the NaOH-NaCl-H_2O ternary system as a function of total molality of NaOH. The open symbols are issued from Königsberger et al. [59]. The open circles are experimental data at 298.15 K. The open diamonds are experimental data at 323.15 K. The open triangles are experimental data at 373.15 K

Fig. 9 Calculated (lines) and experimental (open diamonds) activity coefficient for NaOH-NaCl-H_2O ternary system as a function of NaOH (a and b) or a function of NaCl (c)

Fig. 10 Calculated (lines) and experimental (symbols) solubility data for the NaOH-LiOH-H_2O mixed system a) at 303.15 K, b) at 323.15 K, c) at 373.15 K and 423.15 K. Experimental data are taken from Zdanovskii et al. [41][62]

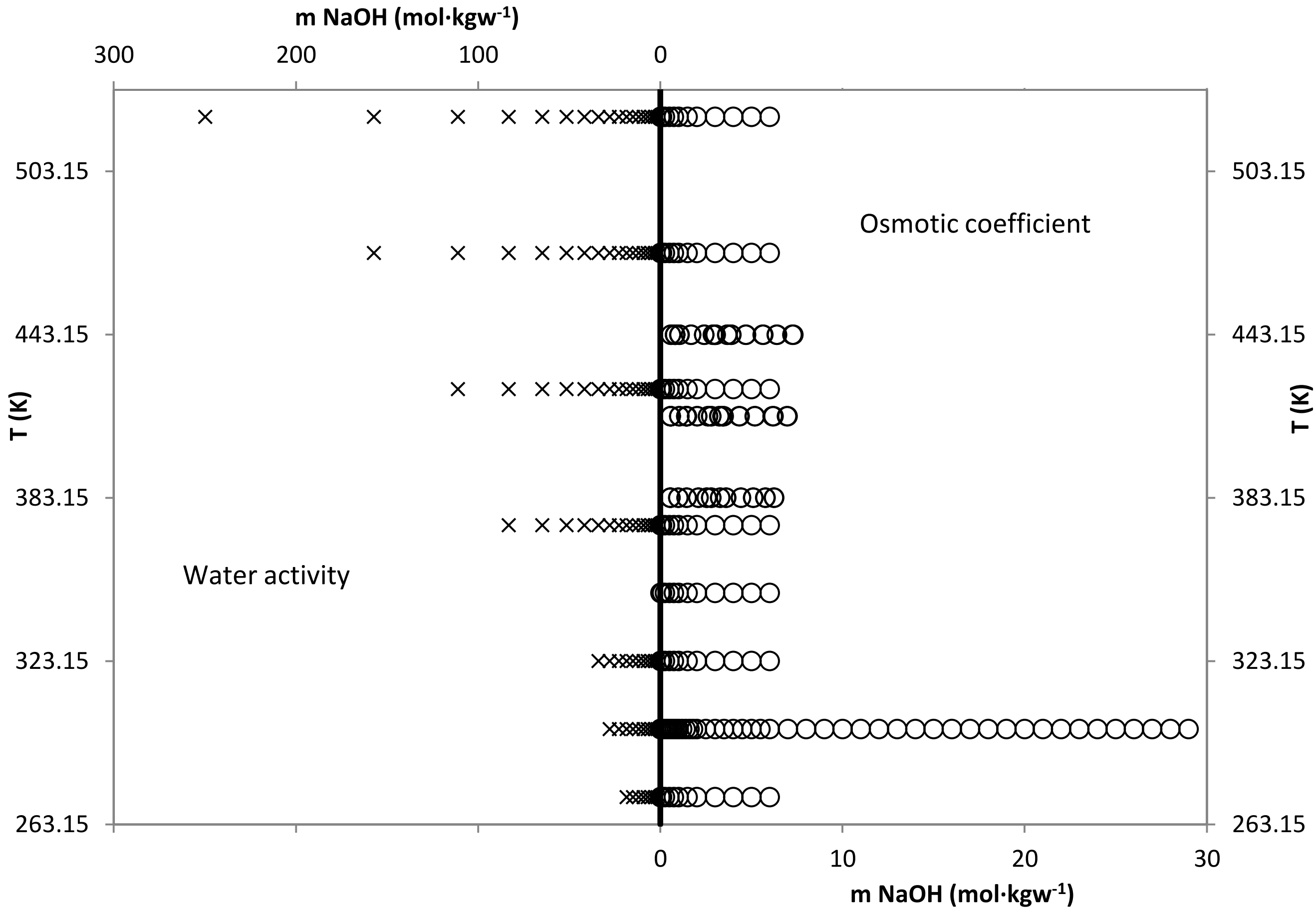

m NaOH (mol·kgw-1)
300
200
100
0
503.15
443.15
383.15
323.15
263.15
T (K)
Osmotic coefficient
Water activity
0
10
20
30
m NaOH (mol·kgw-1)

Figure 1

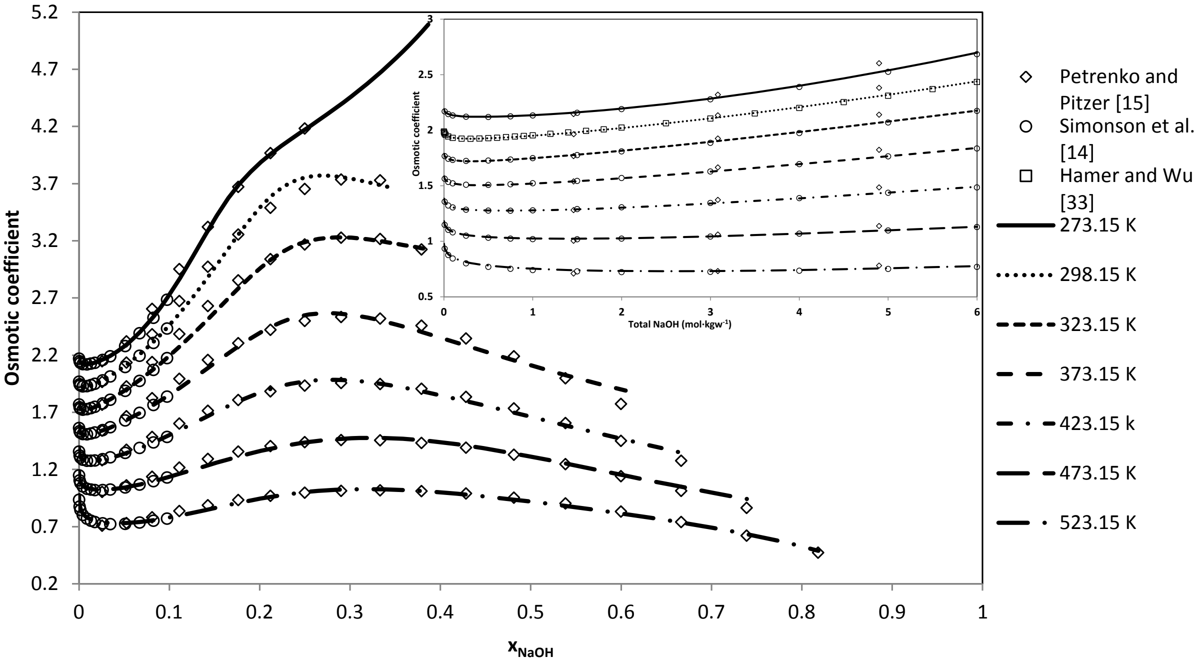

Osmotic coefficient
5.2
4.7
4.2
3.7
3.2
2.7
2.2
1.7
1.2
0.7
0.2
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
x_NaOH
Osmotic coefficient
3
2.5
2
1.5
1
0.5
0
1
2
3
4
5
6
Total NaOH (mol·kgw⁻¹)
Petrenko and Pitzer [15]
Simonson et al. [14]
Hamer and Wu [33]
273.15 K
298.15 K
323.15 K
373.15 K
423.15 k
473.15 K
523.15 K

Figure 2

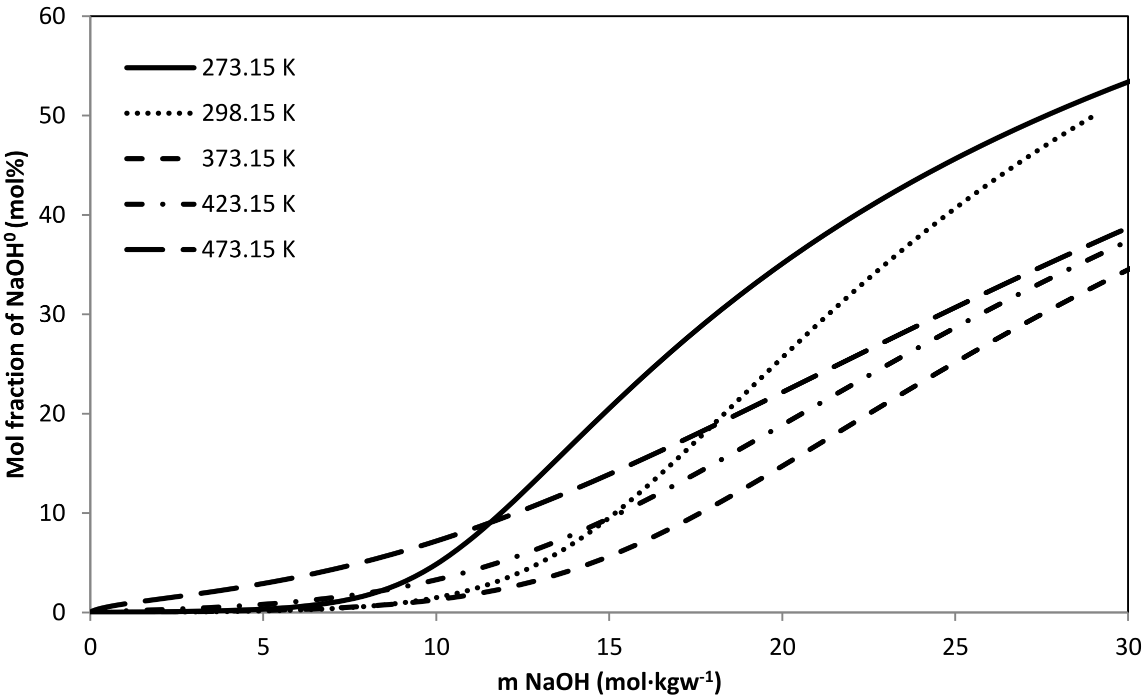

Mol fraction of NaOH⁰ (mol%)
60
50
40
30
20
10
0
273.15 K
298.15 K
373.15 K
423.15 K
473.15 K
0
5
10
15
20
25
30
m NaOH (mol·kgw⁻¹)

Figure 3

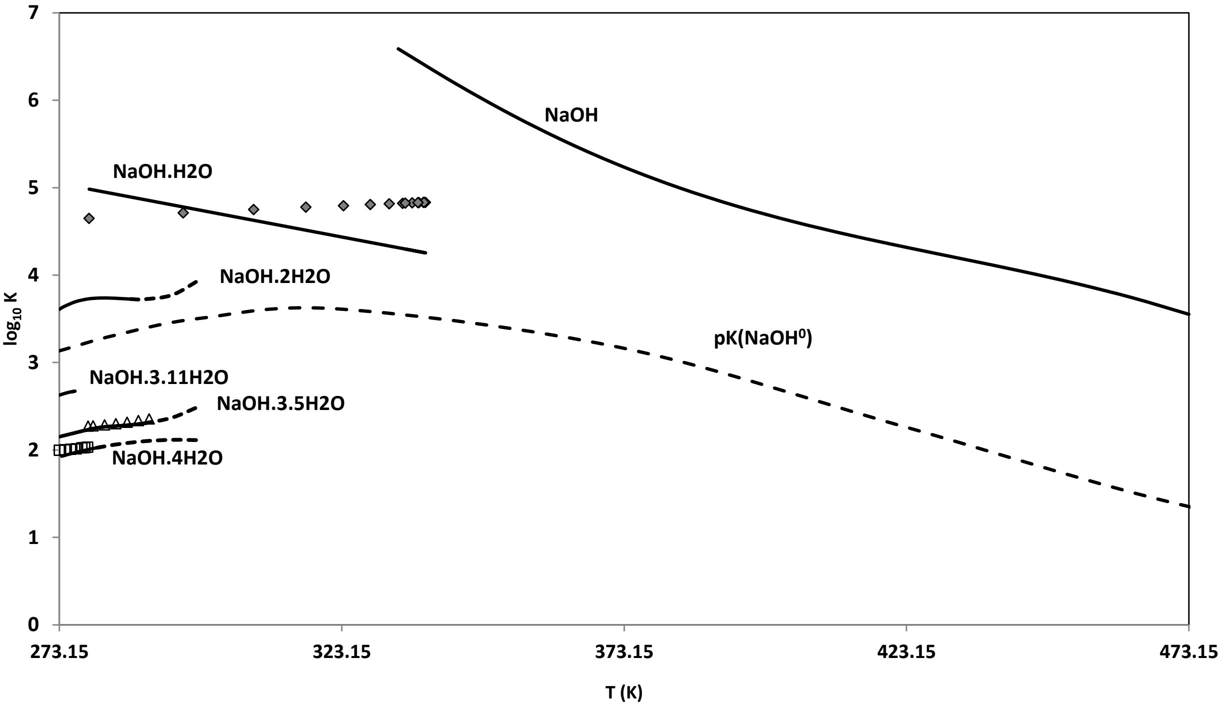

7
6
5
4
3
2
1
0
log10 K
NaOH
NaOH.H2O
NaOH.2H2O
pK(NaOH0)
NaOH.3.11H2O
NaOH.3.5H2O
NaOH.4H2O
273.15
323.15
373.15
423.15
473.15
T (K)

Figure 4

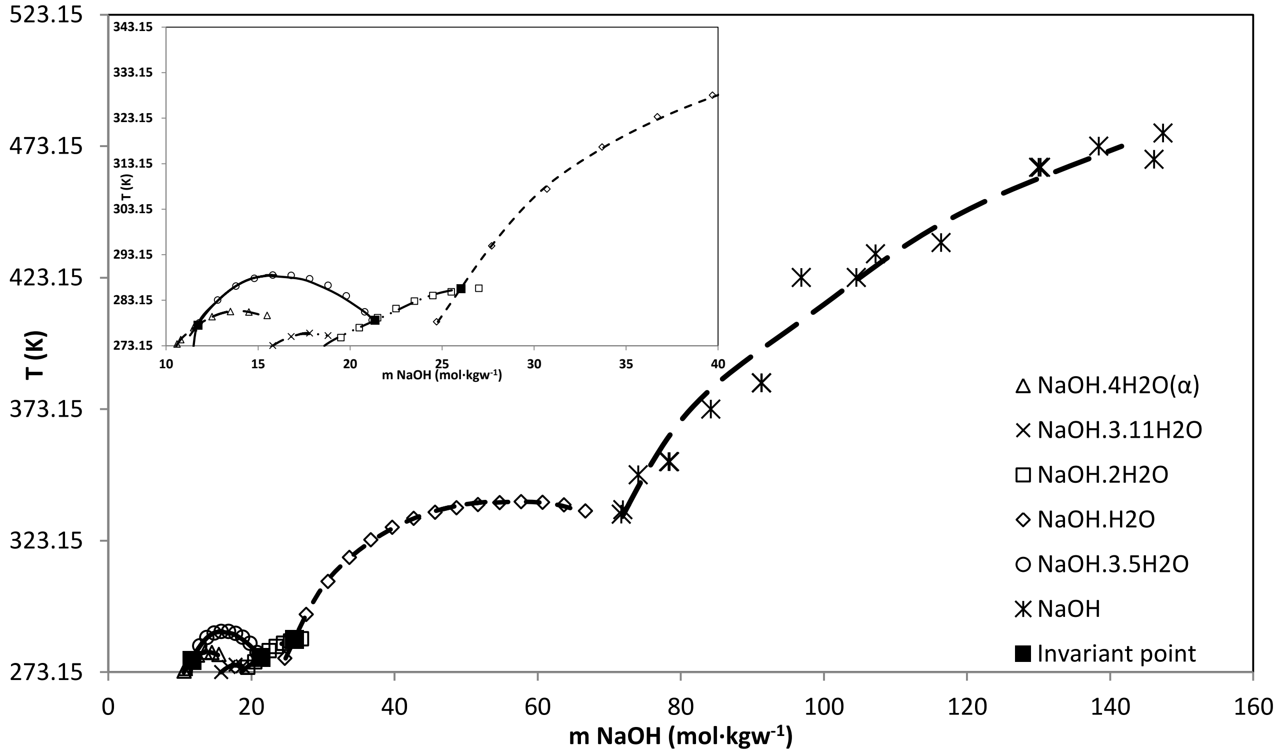

523.15
473.15
423.15
373.15
323.15
273.15
T (K)
0
20
40
60
80
100
120
140
160
m NaOH (mol·kgw⁻¹)
△ NaOH.4H2O(α)
× NaOH.3.11H2O
□ NaOH.2H2O
◇ NaOH.H2O
○ NaOH.3.5H2O
⋇ NaOH
■ Invariant point
343.15
333.15
323.15
313.15
303.15
293.15
283.15
273.15
T (K)
10
15
20
25
30
35
40
m NaOH (mol·kgw⁻¹)

Figure 5

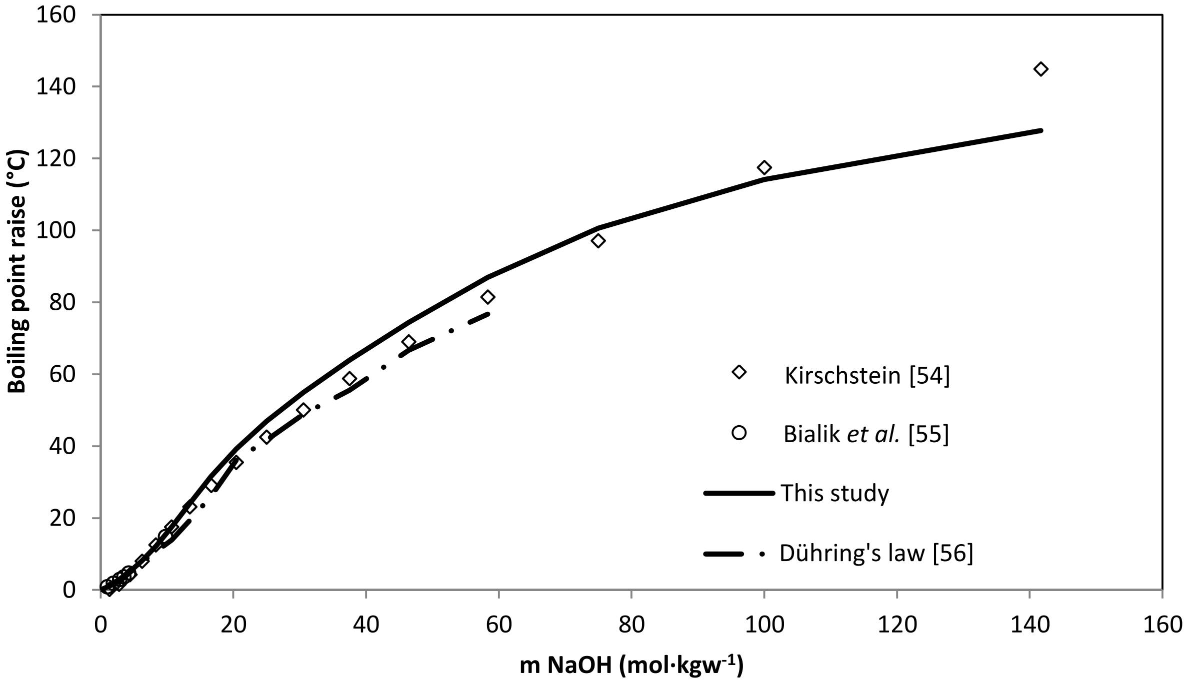

Boiling point raise (°C)
0
20
40
60
80
100
120
140
160
m NaOH (mol·kgw-1)
0
20
40
60
80
100
120
140
160
Kirschstein [54]
Bialik et al. [55]
This study
Dühring's law [56]

Figure 6

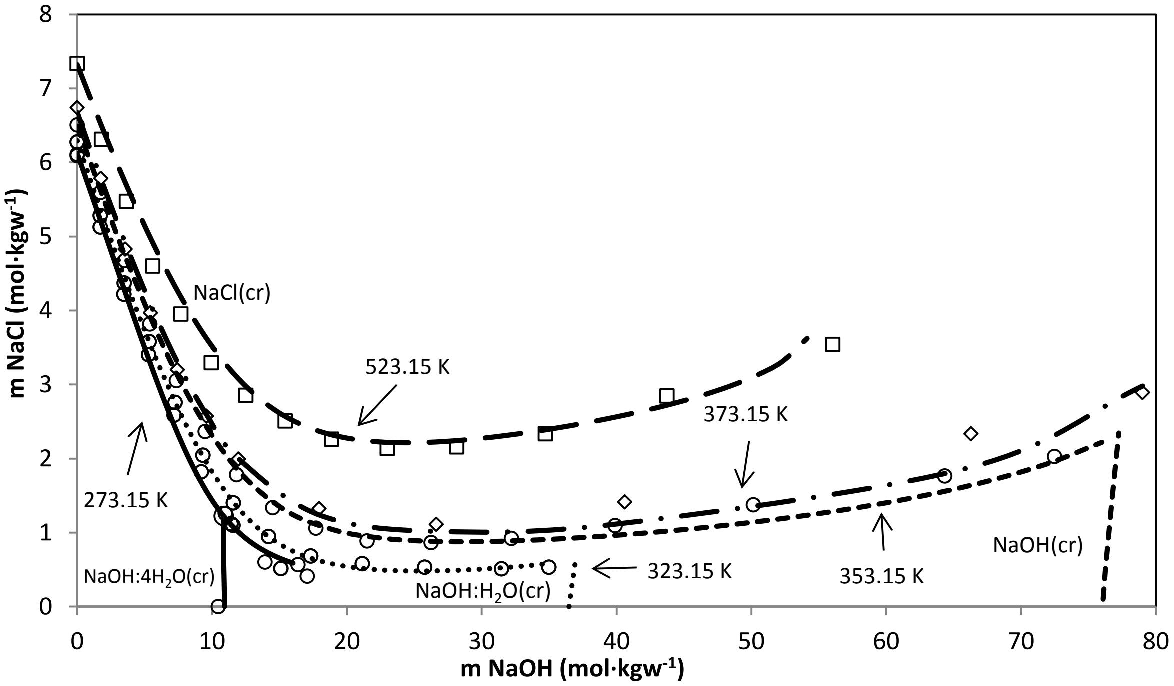

m NaCl (mol·kgw⁻¹)
m NaOH (mol·kgw⁻¹)
0
1
2
3
4
5
6
7
8
0
10
20
30
40
50
60
70
80
NaCl(cr)
523.15 K
373.15 K
273.15 K
353.15 K
323.15 K
NaOH(cr)
NaOH:4H2O(cr)
NaOH:H2O(cr)

Figure 7

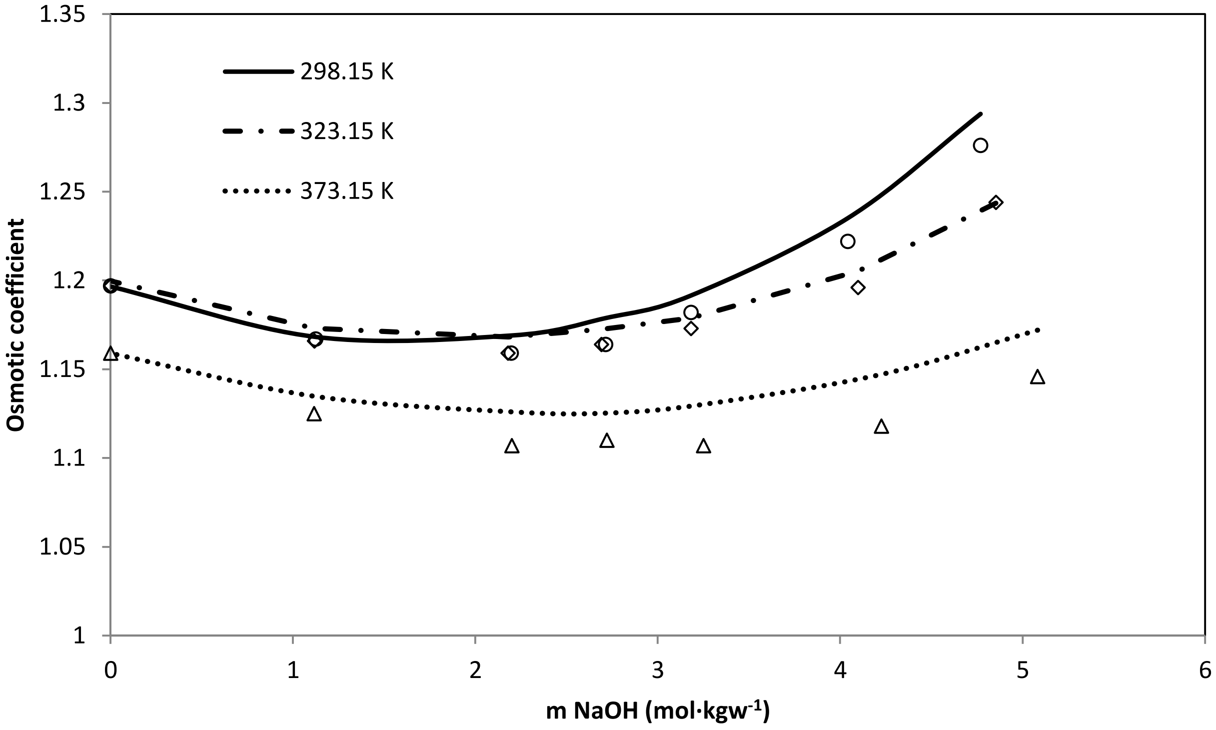
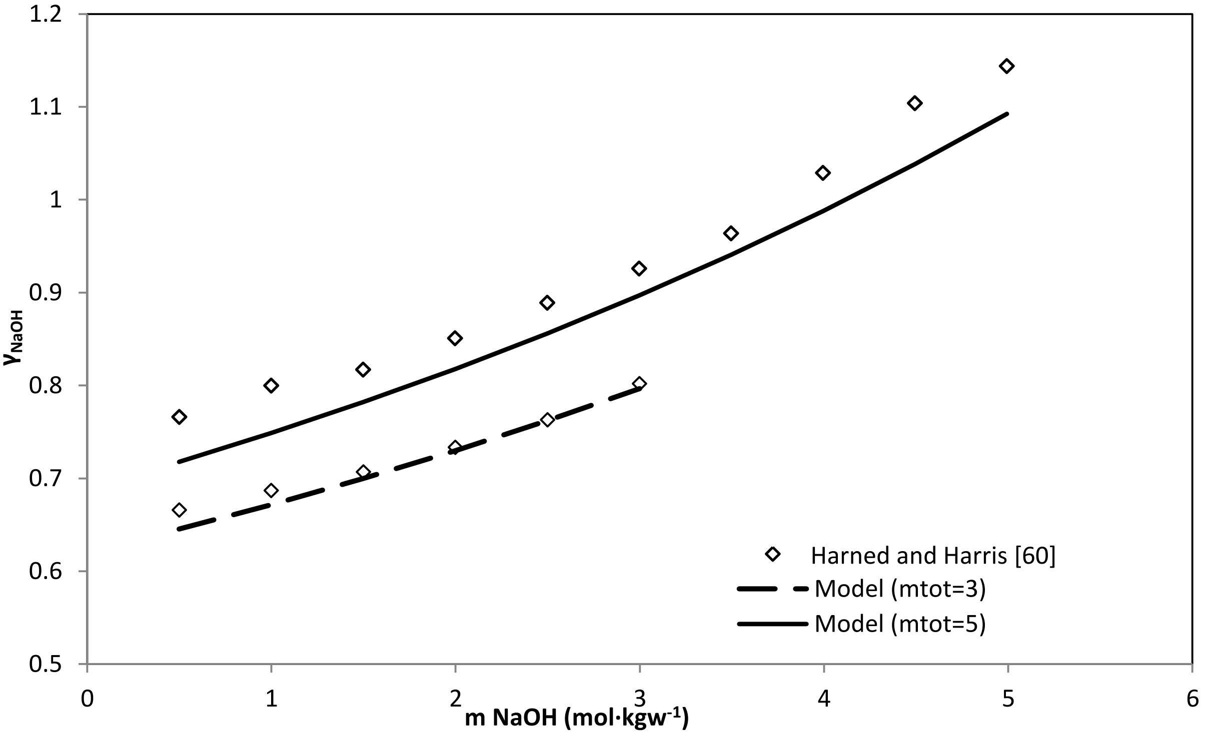
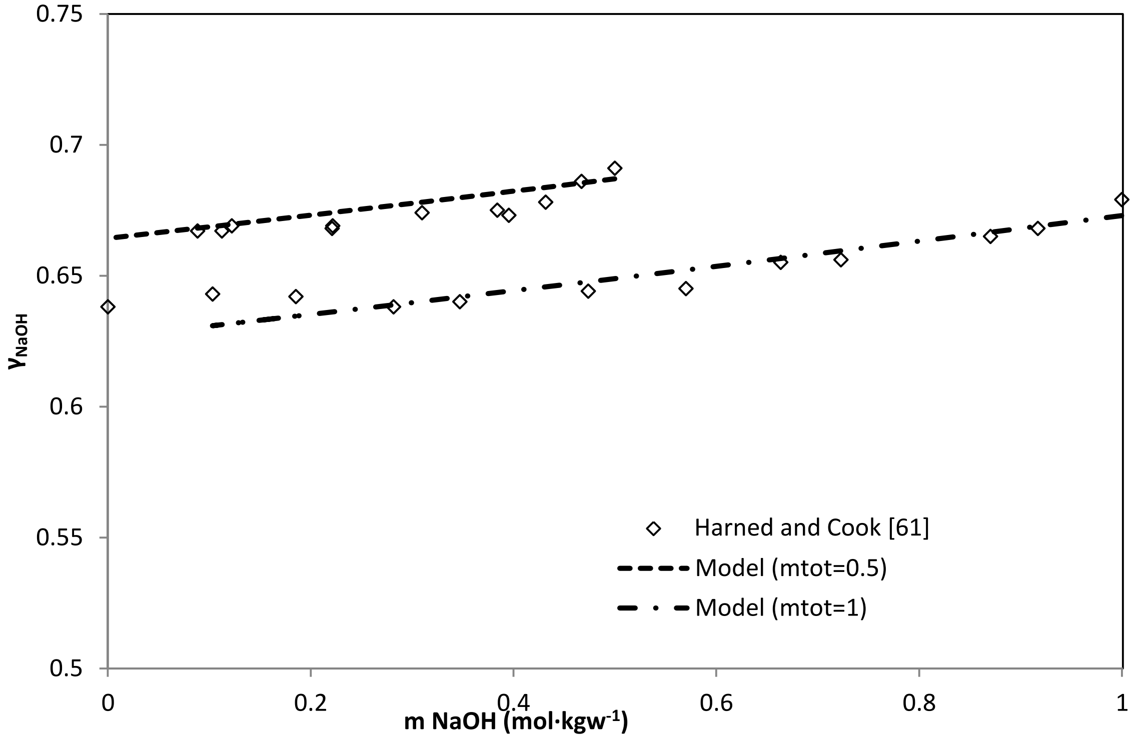

1.35
1.3
1.25
1.2
1.15
1.1
1.05
1
0
1
2
3
4
5
6
298.15 K
323.15 K
373.15 K
Osmotic coefficient
m NaOH (mol·kgw⁻¹)

Figure 8

a)


1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
γ NaOH
0
1
2
3
4
5
6
m NaOH (mol·kgw⁻¹)
Harned and Harris [60]
Model (mtot=3)
Model (mtot=5)

b)


0.75
0.7
0.65
0.6
0.55
0.5
γ NaOH
0
0.2
0.4
0.6
0.8
1
m NaOH (mol·kgw⁻¹)
Harned and Cook [61]
Model (mtot=0.5)
Model (mtot=1)

c)

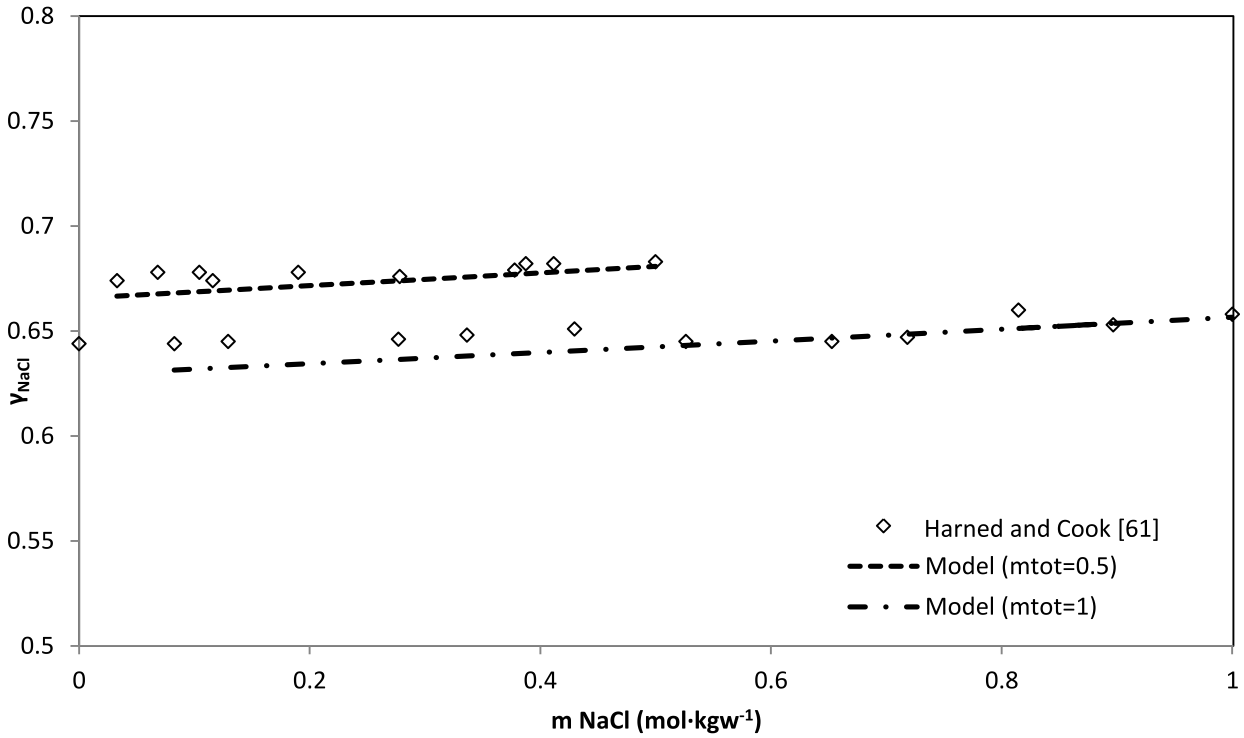
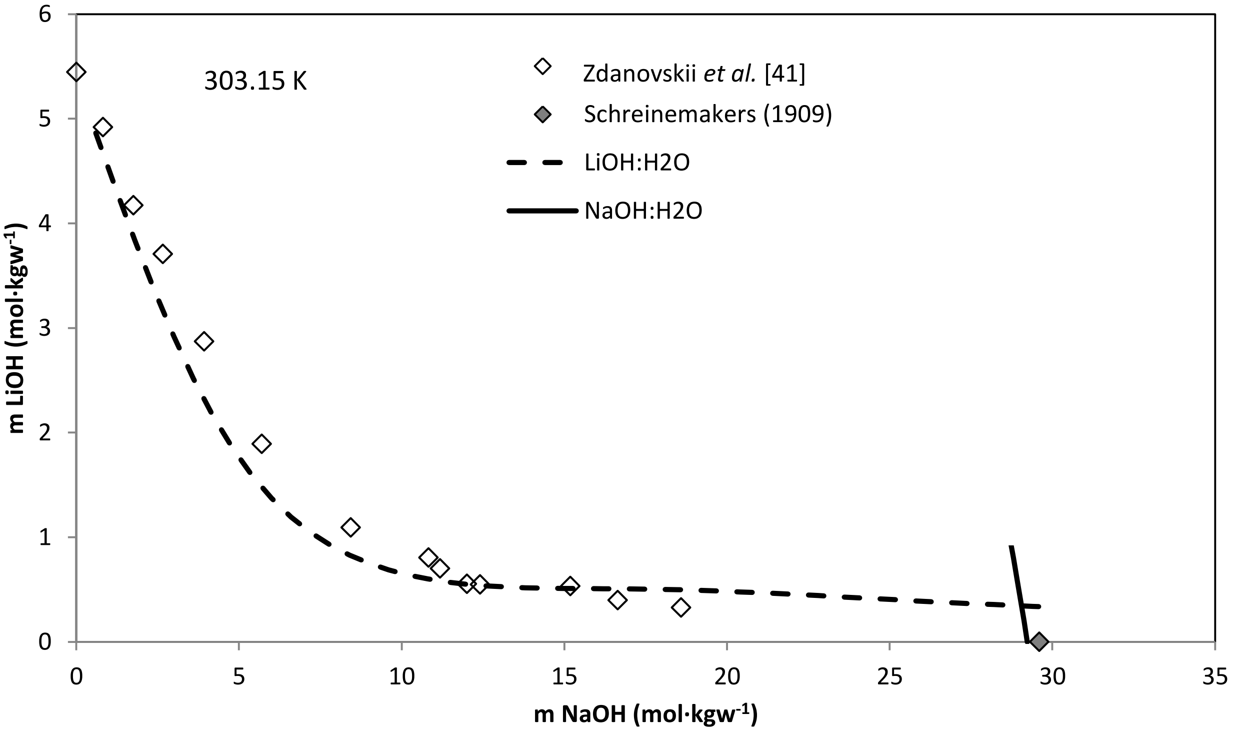
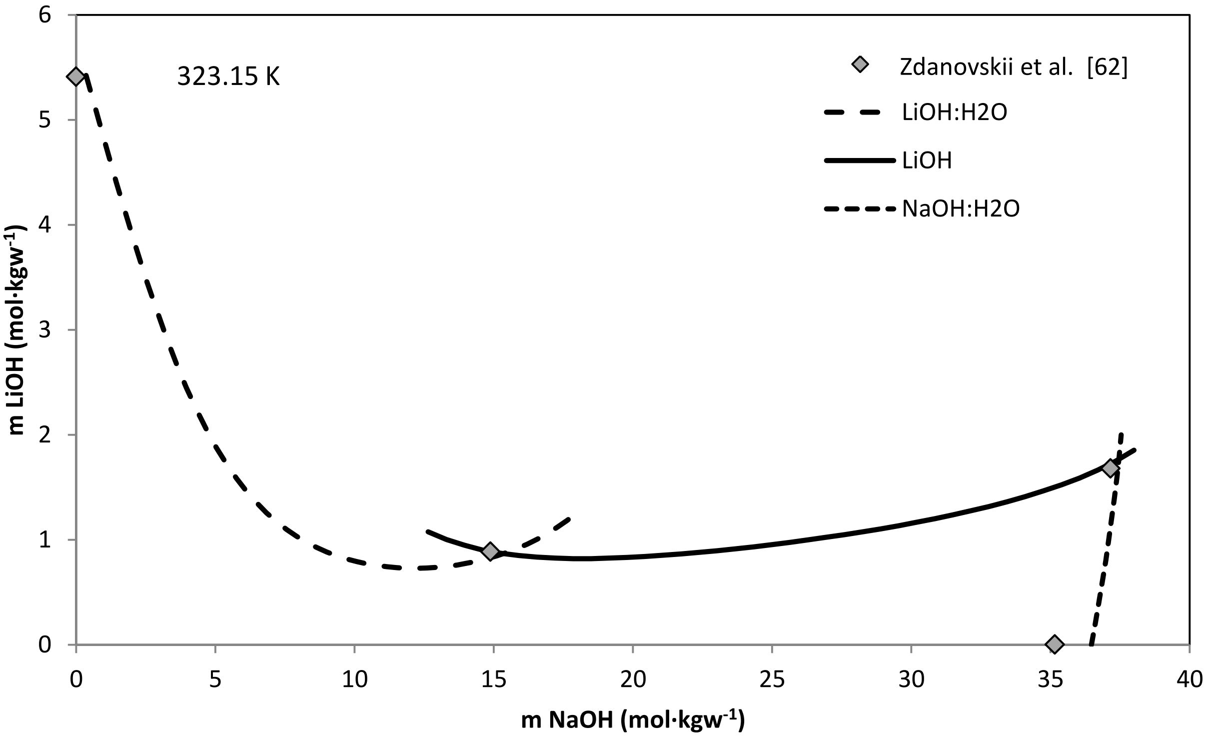

0.8
0.75
0.7
0.65
0.6
0.55
0.5
γ_{NaCl}
0
0.2
0.4
0.6
0.8
1
m NaCl ($mol \cdot kgw^{-1}$)
Harned and Cook [61]
Model (mtot=0.5)
Model (mtot=1)

Figure 9

a)


303.15 K
Zdanovskii et al. [41]
Schreinemakers (1909)
LiOH:H2O
NaOH:H2O
m LiOH (mol·kgw-1)
m NaOH (mol·kgw-1)
0
1
2
3
4
5
6
0
5
10
15
20
25
30
35

b)


323.15 K
Zdanovskii et al. [62]
LiOH:H2O
LiOH
NaOH:H2O
m LiOH (mol·kgw-1)
m NaOH (mol·kgw-1)
0
1
2
3
4
5
6
0
5
10
15
20
25
30
35
40

c)

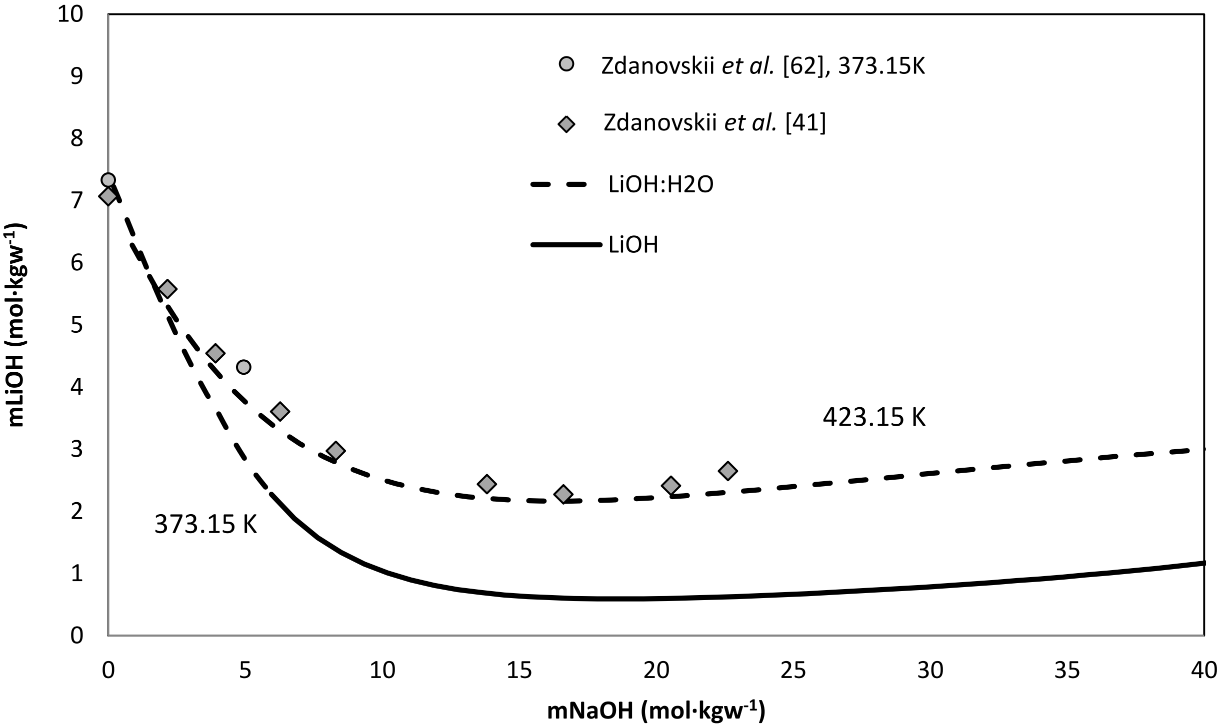

Zdanovskii *et al.* [62], 373.15K
Zdanovskii *et al.* [41]
LiOH:H2O
LiOH
423.15 K
373.15 K
mLiOH (mol·kgw-1)
mNaOH (mol·kgw-1)
0
1
2
3
4
5
6
7
8
9
10
0
5
10
15
20
25
30
35
40

Figure 10

TABLES

Table 1. Standard deviation (σ) values of osmotic coefficient in the NaOH-H_2O binary system (n is the number of experimental data points)

System	Method[a]	T/K	Molality Range	Reference	σ	n	Data used for parameterization
NaOH-H_2O	comp.	298.15	0.001-29	[33]	0.00973	52	✔
	iso	383.25-443.09	0.55-7.3	[39]	0.00915	79	**X**
	calo	273.15-523.15	0.01-6	[14]	0.00552	104	✔
	calo	273.15-523.15	1.46-249.78	[15]	0.04544	95	✔

[a] Experimental method: comp = compilation (including [34] and [35]) ; iso= isopiestic; calo = calorimetric

Table 2. Molality and temperature of invariant point in the NaOH-H_2O binary system

	m^S/ (mol.kg^{-1})		T/ °C	
	Calculated (this work)	Reference data	Calculated (this work)	Reference data
NaOH:4αH_2O + NaOH:3.5H_2O	11.728	11.75[a]	4.54	4.70[a]
		11.98[b]		5.10[b]
		11.87[c]		5[c]
NaOH:3.5H_2O + NaOH:2H_2O	21.35	21.21[a]	5.60	5.53[a]
		22.17[b]		6.20[b]
		20.87[c]		5[c]
NaOH:3.5H_2O + NaOH:H_2O	22.964	22.96[a]	-7.83	-6.63[a]
		23.545[b]		3[b]
NaOH:2H_2O + NaOH:H_2O	26.025	25.82[a]	12.47	12.04[a]
		25.5[b]		12.9[b]
		27.7[c]		12[c]

[a] Experimental values of Pickering [10]; [b] Experimental values of Cohen-Adad *et al.* [39]; [c] Experimental values of Linke [41]

Table 3. Mean activity coefficient ($\gamma_{\pm}$) of NaOH in binary solutions as a function of molality and temperature

		$\gamma_{\pm}$ (NaOH)								
Recommended values of:	T/K	0.1	0.5	1	4	6	10	14	18	22
						mol·kgw^{-1}				
This study	273.15	0.784	0.686	0.662	0.884	1.363	4.289	11.232	22.927	42.836
Simonson *et al*. [14]		0.782	0.682	0.656	0.864	1.320	-	-	-	-
Holmes and Mesmer [39]		0.782	0.682	0.656	0.864	-	-	-	-	-
Petrenko and Pitzer [15]		-	-	-	-	1.514	4.520	11.694	24.332	41.517
Christov and Møller [16]		0.773	0.672	0.658	0.970	1.491	-	-	-	-
Pabalan et Pitzer [13]		0.778	0.675	0.652	0.877	1.312	4.084			
This study	298.15	0.778	0.687	0.673	0.918	1.315	3.234	8.208	15.792	22.989
Hamer and Wu [33]		0.775	0.685	0.674	0.911	1.302	3.258	8.083	15.570	23.030
Simonson *et al*. [14]		0.781	0.692	0.676	0.902	1.295	-	-	-	-
Holmes and Mesmer [39]		0.781	0.691	0.674	0.901	-	-	-	-	-
Petrenko and Pitzer [15]		-	-	-	-	1.463	3.683	8.064	14.648	22.565
Christov and Møller [16]		0.768	0.667	0.652	0.925	1.342	-	-	-	-
Pabalan et Pitzer [13]		0.777	0.684	0.668	0.900	1.287	3.293			
This study	323.15	0.769	0.676	0.661	0.875	1.185	2.399	4.848	8.251	11.560
Simonson *et al*. [14]		0.772	0.682	0.666	0.865	1.176	-	-	-	-
Holmes and Mesmer [39]		0.773	0.683	0.667	0.867	-	-	-	-	-
Petrenko and Pitzer [15]		-	-	-	-	1.319	2.855	5.430	8.822	12.506
Christov and Møller [16]		0.759	0.654	0.635	0.856	1.177	-	-	-	-
Pabalan et Pitzer [13]		0.772	0.682	0.668	0.887	1.219	2.666			
This study	373.15	0.743	0.633	0.604	0.700	0.865	1.422	2.308	3.310	4.112
Simonson *et al*. [14]		0.744	0.637	0.607	0.704	0.865	-	-	-	-
Holmes and Mesmer [39]		0.746	0.639	0.610	0.703	-	-	-	-	-
Petrenko and Pitzer [15]		-	-	-	-	0.944	1.587	2.419	3.310	4.139
Christov and Møller [16]		0.730	0.606	0.572	0.671	0.838	-	-	-	-

Pabalan et Pitzer [13]		0.749	0.648	0.621	0.715	0.877	1.447			
This study	423.15	0.707	0.575	0.528	0.522	0.587	0.803	1.086	1.353	1.550
Simonson *et al*. [14]		0.705	0.571	0.525	0.521	0.581	-	-	-	-
Holmes and Mesmer [39]		0.706	0.574	0.527	0.516	-	-	-	-	-
Petrenko and Pitzer [15]		-	-	-	-	0.613	0.841	1.088	1.315	1.504
Christov and Møller [16]		0.690	0.539	0.486	0.478	0.545	-	-	-	-
Pabalan et Pitzer [13]		0.717	0.597	0.554	0.536	0.59	0.778			
This study	473.15	0.659	0.502	0.441	0.365	0.373	0.422	0.486	0.546	0.594
Simonson *et al*. [14]		0.651	0.49	0.429	0.356	0.362	-	-	-	-
Holmes and Mesmer [39]		0.652	0.492	0.430	0.354	-	-	-	-	-
Petrenko and Pitzer [15]		-	-	-	-	0.371	0.432	0.493	0.544	0.582
Christov and Møller [16]		0.638	0.458	0.388	0.309	0.323	-	-	-	-
Pabalan et Pitzer [13]		0.673	0.533	0.477	0.401	0.407	0.457			
This study	523.15	0.594	0.412	0.341	0.234	0.219	0.219	0.229	0.240	0.246
Simonson *et al*. [14]		0.578	0.393	0.322	0.219	0.205	-	-	-	-
Holmes and Mesmer [39]		0.578	0.393	0.322	0.220	-	-	-	-	-
Petrenko and Pitzer [15]		-	-	-	-	0.208	0.211	0.219	0.225	0.229
Christov and Møller [16]		0.572	0.366	0.287	0.177	0.168	-	-	-	-
Pabalan et Pitzer [13]		0.610	0.445	0.380	0.279	0.265	0.264			

Table 4. Values of the fitting constants (Eq. 4) for the interaction parameters of the NaOH-H_2O system

Parameters	*T range (K)*	*Constants (T in Kelvins)*						
		$a_1.10^{-2}$ (-)	$a_2.10^{2}$ (T)	$a_3.10^{5}$ (T^2)	a_4 (T^3)	$a_5.10^{-3}$ (1/T)	a_6 (ln(T))	a_7 (1/(T-263))
$\beta^0_{Na+/OH-}$	273.15-523.15	1.76163458	7.45876059	-2.912616	0	-4.4350726	-31.74100105	0
$\beta^1_{Na+/OH-}$	273.15-523.15	-1.90826953	-7.24331884	2.49076378	0	5.015999075	33.98668662	0
$C^{\varphi}_{Na+/OH-}$	273.15-523.15	-0.30432318	-1.31691039	0.52162679	0	0.7611094636	5.501621124	0
$\zeta_{Na+/OH-/NaOH}$	273.15-523.15	-2.68090134	-18.57691692	14.88943	-5.968463E-08	5.3795557	51.5647202	-0.241033029
$\lambda_{NaOH/NaOH}$	273.15-523.15	20.46946424	145.164266	-117.09484	4.67468E-07	-39.9754	-395.60413	2.253727133

Table 5. Values of fitting constants (Eq. 5) for log K of formation of aqueous complex and dissolution of solid phases.

Compound	*T range (K)*	*Constants (T in K)*					*Ref.*
		A_1 (-)	A_2 (T)	A_3 (1/T)	A_4 (log T)	A_5 ($1/T^2$)	
$NaOH^0(aq)$	273.15-523.15	-3663.4088	-0.5287506	1.9340326E+05	1326.5866	-1.010544E+07	This study
NaOH	333.15-473.15	-17395.74	-2.361777	1020186.8	6221.183	-62919000	This study
$NaOH.H_2O$	278.15-338.15	8.389405425	-0.012234586	0.	0.	0.	This study
$NaOH.2H_2O$	273.15-286.15	-6791.770346	9.017375873	2.1146982E+06	-288.1361747	-2.020161E+08	This study
$NaOH.3.11H_2O$	273.15-276.15	397.6450437	-0.711283192	-5.4829635E+04	0.	0.	This study
$NaOH.3.5H_2O$	273.15-289.15	-3799.931206	4.471346177	1.07816176E+06	0.	-1.019490E+08	This study
$NaOH.4\alpha H_2O$	273.15-281.15	70.38429455	-0.115845089	-1.0057598E+04	0.	0.	This study
Halite	273.15-573.15	-7.522495E+02	-1.1904958E-01	4.1385703E+04	2.7417933E+02	-2.480911E+06	[58]

Table 6. Values of the constants (Eq. 4) for the interaction parameters of the NaCl-H_2O system

Parameters	*T range (K)*	*Constants (T in K)*							*Ref.*
		a_1 (-)	a_2 (T)	a_3 (T^2)	a_5 (1/T)	a_6 (ln(T))	a_8 (1/(680-T))	a_9 (1/(T-227))	
$\beta^{0}_{\mathrm{Na+/Cl-}}$	273.15-573.15	14.3783204	5.607674E-03	-2.617181E-06	-422.185236	-2.51226677	4.43854508	-1.70502337	[32]
$\beta^{1}_{\mathrm{Na+/Cl-}}$	273.15-573.15	-0.483060685	1.406775E-03	0	119.311989	0	0	-4.23433299	[32]
$C^{\varphi}_{\mathrm{Na+/Cl-}}$	273.15-573.15	-0.100588714	1.805294E-05	3.411721E-08	8.61185543	1.248809E-02	6.83041E-02	0.293922611	[32]

Table 7. Values of the fitting constants (Eq. (4)) for the interaction parameters of the NaOH-NaCl-H_2O system

Parameters	*T range (K)*	*Constants (T in K)*						*Ref.*
		a_1 (-)	a_2 (T)	a_3 (T^2)	a_5 (1/T)	a_6 (ln(T))	a_7 (1/(T-263))	
$\theta_{Cl-/OH-}$	273.15-523.15	0.110485703	0	0	-49.36134550	0	0	[16]
$\psi_{Na+/Cl-/OH-}$	273.15-423.15	208.2495564	0.109186283	-5.10064E-05	-4572.706051	-38.77759442	0.090538347	This study
$\zeta_{Na+/Cl-/NaOH}$	273.15-423.15	-84.73528452	-0.046364355	2.22369E-05	1787.028796	15.89833951	-0.03439274	This study

Table 8. Values of the fitting constants (Eq. 4) for the interaction parameters of the NaOH-LiOH-H_2O system

Parameters	*T range (K)*	*Constants (T in K)*					*Ref.*
		a_1 (-)	a_2 (T)	a_3 (T^2)	a_5 (1/T)	a_7 (1/(T-263))	
$\theta_{Li+/Na+}$	303.15-423.15	-2.304375225	9.185919E-3	-11.382562E-6	195.8054794	0	[16]
$\psi_{Na+/Li+/OH-}$	303.15-423.15	-4.254512E-2	9.112903E-5	0	0	0	This study
$\lambda_{Li+/NaOH}$	303.15-423.15	4.0637268125	-4.6714348E-03	0	-9.344074E+02	17.856540491	This study