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A Solvation Model for Vapor–Liquid Equilibria in the System H_2O–NaOH from 10 to 85 Wt%[1]

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Vapor–liquid equilibria in the electrolyte system water–sodium hydroxide are described by using a so-called solvation model. In such a model the formation of ion clusters is assumed, consisting of either of the ions Na^+ or OH^- being surrounded by water molecules, the number of which depends on the overall molar concentration of sodium hydroxide. Activities of the various components in the liquid phase are modeled by local composition models like the nonrandom two-liquid equation (NRTL) and the Wilson's equation. The vapor phase, assumed to consist of water only, is modeled by the equation of state (EOS) of Wagner and Saul. The models include seven parameters fitted to 230 experimental data points taken from the literature in the range 0.18 kPa to 8 MPa, 273 to 623 K, and 10 to 85 wt% NaOH. The system's pressure resulting from a $T, x \rightarrow p$ calculation procedure can be represented with a mean relative deviation of 1.3%.

KEY WORDS: electrolytes; local composition; sodium hydroxide; solvation model; vapor–liquid equilibria; water.

1. INTRODUCTION

A liquid mixture of sodium hydroxide and water is a fluid with the potential to be used in today's air-conditioning systems and in systems for reusing industrial waste heat such as absorption heat pumps and heat transformers [1,2].

To calculate and optimize absorption processes, accurate vapor–liquid equilibria (VLE)-data of the working fluid used especially at high NaOH-concentrations are needed. The models for VLE data available in today's

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open literature [3–5, 8] are always restricted to low NaOH concentrations, starting normally at zero concentration, i.e., pure water, and applying a modified Debye–Hückel theory [6–8]. We here present a so-called solvation model ranging from 10 to 85 wt% of sodium hydroxide in water. This model is based on the concept of ion–water clusters, originally introduced by Arrhenius et al. [9], and recently successfully used again by Engels [10, 11], and Engels and Bosen [12].

After presenting the experimental database we outline the solvation model, make a few remarks on the calculation procedure, and give a detailed comparison between experimental and calculated VLE data.

2. EXPERIMENTAL DATABASE

Measurements of vapor pressures of aqueous solutions of sodium hydroxide in the range 333–623 K, 0.01–8 MPa, and 10–85 wt% NaOH have been reported by Krey [13, 14]. Using these data plus VLE data in the range 273 to 353 K, Krey developed a semiempirical equation for the vapor pressure and provided tables including interpolations of these data in the range (273–573 K, 0.18 kPa–8 MPa, 10–85 wt% NaOH) [14]. These tables provide the base for our data correlation.

3. THEORETICAL MODEL

In this section, we formulate the basic assumptions and the related equations of a thermodynamic model to calculate VLE in the system $NaOH/H_2O$. For the liquid phase a so-called solvation model is applied. It is discussed in more detail in Ref. 15. The vapor phase is assumed to consist of water only, i.e., to include neither NaOH nor ionic complexes, possibly being formed by Na^+ and OH^- and water molecules. We also neglect the Poynting correction term for water, which ranges from 0.97 to 1.0 in the range of interest here (see Sect. 5). Also, the fugacity coefficient of pure water vapor above a mixture of $H_2O/NaOH$ at system pressure p is assumed to be equal to its value above pure water in its liquid boiling state at saturation pressure $p_{0,\,H_2O}$.

$$\varphi_{0,H_2O}(p_{0,H_2O}, T) = \varphi_{H_2O}(p, T) \tag{1}$$

This assumption is discussed in more detail in Section 5. The equilibrium conditions (Smith and van Ness [17]) are reduced to the single equation

$$p = x_{H_2O}\gamma_{H_2O}\,p_{0,H_2O}(T) \tag{2}$$

Aiming at a $T, x \to p$-type calculation we have to determine all quantities on the r.h.s. of Eq. (2). To achieve this, we proceed as follows: the vapor pressure of pure water p_{0,H_2O} has been calculated by means of the EOS of Saul and Wagner [16]. The activity coefficient of water γ_{H_2O} in an aqueous solution of sodium hydroxide has been determined by introducing a so-called solvation model and applying Wilson's equation [18], or the NRTL equation [19]. The basic idea underlying this model is that NaOH, after being dissolved in water, is dissociating in part. The ions Na^+ and OH^- immediately are coated with water molecules, forming ionic clusters or supermolecules which can be considered as new components in the sense of thermodynamics. The quasi-chemical equilibrium established in the liquid phase can be described by the stoichiometric equation

$$mH_2O + NaOH \Leftrightarrow C^+ + C^- \tag{3}$$

where $C^{\pm}$ indicate the ionic complexes, $C^+ = Na^+(H_2O)_{m^+}$, and $C^- = OH^-(H_2O)_{m^-}$.

The parameters m, $m^{\pm} \geqslant 0$ are so-called solvation numbers of the reaction, Eq.(3). They are related by $m = m^+ + m^-$ and have been discussed in more detail in Ref. 8. If we assume for the sake of simplicity the activity coefficients of the complexes to be equal, $\gamma_{C^+} = \gamma_{C^-} = \gamma_C$, the law of mass action related to Eq. (3) reads as

$$K_C = \frac{(\gamma_C x_C)^2}{(\gamma_{H_2O} x_{H_2O})^m \, (\gamma_{NaOH} x_{NaOH})} \tag{4}$$

where $x_C = x_{C^+} = x_{C^-}$ indicates the molar fractions of the complexes C^+, C^-, which according to (3) always have to be equal, and K_C the equilibrium constant. The temperature dependence of K_C can be described by the van 't Hoff relation

$$K_C = K_{C\infty} \exp\left[-\frac{\Delta H^0}{RT}\right] \tag{5}$$

ΔH^0 being the standard enthalpy of formation of the complexes $C^{\pm}$.

During formation of the ionic clusters, the initial molar fractions of water $x^0_{H_2O}$ and sodium hydroxide x^0_{NaOH} in the liquid phase are changed. Denoting by x_{H_2O}, x_{NaOH}, and x_C the molar fractions of the respective components after solvation, from the balance equations of mole numbers the following relations can be derived:

$$x_{NaOH} = x^0_{NaOH} + x_C(x^0_{NaOH}(m-1) - 1) \tag{6}$$

$$x_{H_2O} = x^0_{H_2O} + x_C(x^0_{H_2O}(m-1) - m) \tag{7}$$

In the literature the solvation number m in Eqs. (6) and (7) has been considered a constant [12]. However, there are physicochemical indications that m strongly depends on the concentration of sodium hydroxide brought into solution [20]. Therefore, we have considered m to be a function of x^0_{NaOH}. In principle, the solvation number m may also depend on other thermodynamic parameters of the system like its temperature, density, or pressure. However, since a clear picture of the molecular structure of water–base solutions is still lacking, we refrained from doing so, aiming always for a model which is as simple as possible. Interpolating numerical values of m gained by optimization procedures in fitting analytic and experimental VLE data over a wide range of temperature and concentration, we found a linear relation

$$m = a - bx^0_{\mathrm{NaOH}} \tag{8}$$

to be most adequate. Numerical values of the empirical parameters a and b are given in Table I. The linear relations given by Eq. (8) and specified in Table I include the solvation numbers proposed by Ulich ($m = 2$–4 [21]), but not those suggested by Riesenfeld and Reinhold ($m = 71$ [22]), the latter leading, via the data correlation procedure, to thermodynamically inconsistent results [23].

Table I. Statistical Parameter $f_{\mathrm{m}} = (1/M)\sum_{i=1}^{M}((|p_{\mathrm{calc.}} - p_{\mathrm{meas.}}|)/p_{\mathrm{meas.}})_i$ Resulting from a Correlation of the Database [14] by a Solvation Model[a]

Solvation model $m = a - bx^0_{\mathrm{NaOH}}$		Percentage		
a	b	Ideal liquid phase	Wilson's equation	NRTL equation
1	0	62.59	3.06	
2	0	18.93	2.63	1.63
3	0	26.99	2.40	1.15
4	0	37.34		
5	0	45.92		
4	5	10.31	3.11	2.62
3	2.5	10.51	2.77	1.90
4	2.5	19.84	1.75	1.30
5	7.5	15.46	3.72	

[a] $= 230$, number of VLE data; $p_{\mathrm{calc.}}$, pressure calculated by Eq. (1); $p_{\mathrm{meas.}}$, measured value of pressure.

4. COMPUTER EXPERIMENTS

For the sake of simplicity we started our computer experiments by assuming the liquid phase to be an ideal mixture and the vapor phase to be an ideal gas. Then we improved this "model" by applying the solvation model combined with Wilson's equation or with the NRTL equation, respectively, for the activity coefficients in the liquid phase As already mentioned, the parameter K_C in the law of mass action, Eq. (5), and parameters of the local composition are unknown and, in a first step, have to be chosen (nearly) at random. Usually, the pressure $p_{\text{calc.}}$ resulting from $T, x^0_{\text{NaOH}} \rightarrow p$ calculations described in Table I, will differ from the respective experimental value $p_{\text{meas.}}$. The model parameters were those minimizing the mean square relative deviation between calculated and measured pressures.

$$\sum_{i=1}^{M} \left(\frac{p_{\text{calc.}} - p_{\text{meas.}}}{p_{\text{meas.}}} \right)_i^2 \rightarrow \text{Min.} \tag{9}$$

We used the algorithm of Brown and Dennis [24], which is the difference analog to the differential algorithm of Levenberg and Marquardt. Trying to fit our database, consisting of $M = 230$ data sets, to the solvation model, we found that the optimal parameters were insensitive to the choice of the energy parameters describing in both Wilson's and the NRTL equation interactions between ionic complexes and sodium hydroxide. Hence, we have chosen them to be zero ($g_{23} - g_{22} = g_{32} - g_{33}, = 0$, $\lambda_{23} - \lambda_{22}, = \lambda_{32} - \lambda_{33} = 0$; index: 1...$H_2O$, 2...NaOH, 3...$C^{\pm}$). Taking the consistency condition of Acree [18] into account, the number of parameters to be optimized could be reduced from 14 (cf. Refs. 10–12) to 7 [15]. They are, for Wilson's equation [18], K_{C_∞}, ΔH^0, v_{01}/v_{02}, v_{01}/v_{03}, $\lambda_{12} - \lambda_{11}$, $\lambda_{13} - \lambda_{11}$, $\lambda_{31} - \lambda_{33}$, and for the NRTL equation [19], $K_{C\infty}$, ΔH^0, α_{12}, α_{13}, $g_{12} - g_{11}$, $g_{13} - g_{11}$, $g_{31} - g_{33}$. The correlation of the VLE database with the solvation model only, i.e., with activities set equal to 1 for the liquid phase, resulted in mean relative deviations f_m and dispersions σ of the vapor pressure, Eqs. (23) and (24) in Ref. (15) and also Table I, being at least one order of magnitude larger than the respective quantities obtained with Wilson's equation. Results are given in Table I. In the upper part, the solvation number m is assumed to be constant. The lower part of the table gives results for solvation numbers assumed to depend on the initial sodium hydroxide concentration x^0_{NaOH}, i.e., the concentration of sodium hydroxide prior to ionization and solvation. For an ideal liquid phase the values $a = 4$, $b = 5$ chosen by us [Eq. (8)], yield the best fit of the data, which itself is poor, but much better than those resulting for constant solvation numbers $m = 1...5$; see lines 1–5 in Table I.

In view of these results we decided to introduce for the activity coefficients of the liquid phase in (2) Wilson's equation and the NRTL equation, respectively. By means of a model with constant solvation number $m = 3$, and Wilson's equation for the activity coefficients, our database including 230 data could be correlated with a mean relative deviation $f_m = 2.4\%$. Use of a concentration-dependent solvation number Eq. (8), allowed us to reduce this deviation to $f_m = 1.75\%$. Correlating the same database with NRTL and the solvation model, the mean relative deviations for a constant solvation number m are nearly equal to those for a concentration-dependent m; see the last column in Table I. This result reflects the flexibility of the NRTL equation. However, it is important to use a solvation model with a concentration dependent solvation number m if one assumes the liquid phase either to be ideal or to be described by Wilson's equation.

By using activities from a local composition model without a solvation model, we obtain for the main relative deviation $f_m = 11.54\%$ using Wilson's equation and $f_m = 2.76\%$ using NRTL, results much poorer than for the solvation model.

5. MODELS FOR THE VAPOR PHASE

We now discuss the assumption of Eq. (1) regarding the fugacities of water vapor above pure water and a sodium hydroxide–water solution. For the water component, the exact condition for VLE is [17]

$$\begin{aligned}\varphi_{H_2O}(p, T, y_{H_2O} = 1)p \\ = a_{H_2O}\varphi_{0,H_2O}(p_{0,H_2O}, T)\, p_{0,H_2O} \exp\left(\frac{v_{0,H_2O}(p - p_{0,H_2O})}{RT}\right) \quad (10)\end{aligned}$$

Here a_{H_2O} indicates the activity of water in the liquid mixture, φ_{H_2O} is the fugacity coefficient of water vapor at system pressure p, φ_{0,H_2O} the fugacity coefficient of pure water at saturation pressure p_{0,H_2O}, and v_{0,H_2O} the molar volume of pure water in its liquid boiling state at temperature T of the system.

Using the EOS of Saul and Wagner [16], we calculated the Poynting correction term in (10). As expected, its numerical value is always ~ 1.

To calculate the fugacities in (10) we have chosen both the three-parameter EOS of Ishikawa et al. [26], and that of Iwai et al. [27]. It turned out that the ratio of the fugacities $\varphi_{0,H_2O}(p_{0,H_2O}, T)/\varphi_{H_2O}(p, T, y_{H_2O} = 1)$ may assume values between 0.75 and 1, i.e., deviate from 1 considerably!

Taking these fugacities into account, and using the solvation model, Section 3 with liquid phase activities according to the NRTL equation, we correlated the data. We obtained a fit with mean relative deviation (Table I) $f_m = 2.49\%$ by using Ishikawa's EOS, and $f_m = 2.74\%$ for Iwai's EOS. These fits are not quite as good as that resulting from the solvation model including assumption (1); see Section 7. Nevertheless, they are of the same statistical quality as other more sophisticated VLE models for this system proposed in the literature. As an example, we mention the model of Sako et al. [28], which correlates VLE data in the range 293–433 K with mean relative deviation $f_m = 2.77\%$.

The somewhat poorer fits with the EOSs for the vapor phase may be due partly to the fact that actually water vapor data cannot be described precisely by either of the three-parameter EOSs used. It also may be due to inaccuracies in the database, especially as far as pressure data in the very high and very low region are concerned, [13]. As already mentioned, we are aiming here at a model as simple as possible serving predominantly engineering needs, i.e., to correlate the given database as accurately as possible. Therefore, we propose the model described in Section 3, being aware of the fact that it would be highly desirable to extend the experimental database in order to develop and test more accurate and reliable models for both the vapor and the liquid phase of the system.

6. MOLECULAR STRUCTURE

To elucidate the role of the "complexes" $C^{\pm}$, in this model, we sketch in Fig. 1 a triangular diagram referring to the concentrations of the three (hypothetical) components water, sodium hydroxide, and complexes $(C^+ + C^-)$ and indicate the isotherms of the liquid's concentrations. To find the concentrations of the components one has to start at a given concentration of sodium hydroxide prior to solvation x^0_{NaOH}, i.e., at any point on the baseline connecting H_2O and NaOH. Then one has to calculate from Eq. (8) with $a = 4$, $b = 2.5$, the respective value of the solvation number m and, by interpolation, to sketch the straight line of all states belonging to this value. The lines referring to the special values $m = 2$, 2.5, 3, 3.5 are depicted in the diagram. The intersections of the respective line (m = const.) with the isotherms corresponding to the (given) temperature of the system yield the concentrations of all components of the liquid phase. The isotherms clearly indicate that sodium hydroxide in water is forming clusters including 2–4 water molecules up to a maximum of 30% complexes $(C^+ + C^-)$ at 293.15 K. With increasing temperature the number of complex molecules decreases. Also, the isotherms of the liquid

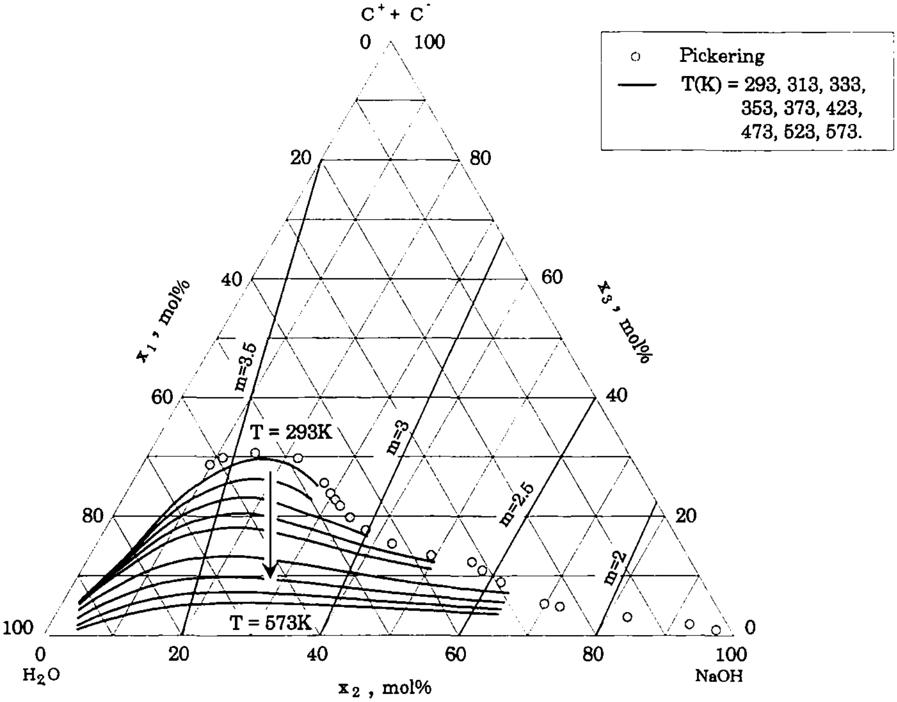

Fig. 1. Ternary diagram of the hypothetical mixture water–sodium hydroxide–ionic complexes ($C^+ + C^-$). The circles indicate data related to measurements of Pickering [29].

phase are limited by crystallization states as depicted in Fig. 1. These states have been calculated from data of Pickering [29], interpreted with the model proposed. Analyzing neighborhoods of molecules given by the NRTL equation, one can find that a group of molecules with a complex in the center is typical for the entire liquid phase.

7. RESULTS AND DISCUSSION

In this section, we compare the solvation model with the experimental and theoretical results of Krey [13, 14]. The fitting parameters as given in Table II describe the measured VLE data of our base [13], with a mean relative deviation of $f_m = 1.4\%$, and the reduced data set correlated by Krey [14], with $f_m = 1.3\%$. To elucidate the quality of the data correlation we provide diagrams of the respective residuals (Fig. 2.) Here the relative deviations of the experimental data are plotted as a function of pressure. As can be seen, the deviations are nearly uniformly scattered around the abscissa. For practical purposes a *p*, *T* diagram depicting boiling curves of

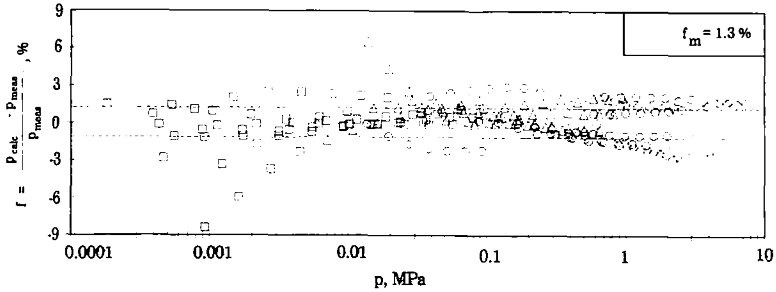

Fig. 2. Diagram of residuals, f_i, where $f_i = (p_{i,\text{calc.}} - p_{i,\text{meas}})/p_{i,\text{meas.}}$ (□) 273.15–373.15 K; (△) 383.15–453.15 K; (○) 463.15–523.15 K; (◇) 533.15–623.15 K.

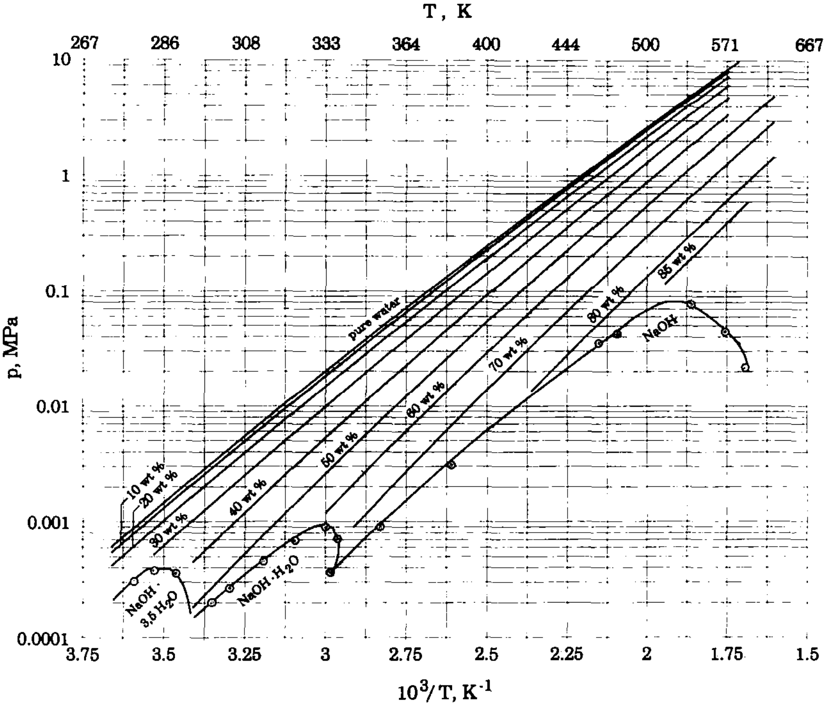

Fig. 3. Pressure–temperature diagram of H_2O–NaOH.

Table II. Optimal Parameters of the NRTL Equation [19] ($G_{ii} = G_{23} = G_{32} = 1$) and of K_C (3). Solvation Model: $a = 4$, $b = 2.5$, Eq. (7)

Parameters of NRTL equation

$$G_{12} = \exp\left[\frac{(-0.0916)(10097.29\ \mathrm{kJ \cdot kmol^{-1}})}{RT}\right] \quad G_{21} = \exp\left[\frac{(0.0916)(20389.13\ \mathrm{kJ \cdot kmol^{-1}})}{RT}\right]$$

$$G_{13} = \exp\left[\frac{(-0.6182)(31042.94\ \mathrm{kJ \cdot kmol^{-1}})}{RT}\right] \quad G_{31} = \exp\left[\frac{(-0.6182)(556.52\ \mathrm{kJ \cdot kmol^{-1}})}{RT}\right]$$

Constant in the law of mass action, Eq. (3)

$$K_C = 2.24 \times 10^{-5} \exp\left[\frac{49356.11\ \mathrm{kJ \cdot kmol^{-1}}}{RT}\right]$$

$NaOH/H_2O$ solutions for constant concentrations (weight-percentage) is enclosed (Fig. 3). In it lines of crystal states have been included.

8. SUMMARY

A solvation model has been developed for calculating VLE, i.e., the vapor pressure in the system $H_2O/NaOH$ in the range 273 to 623 K and near zero to the crystal state concentration of NaOH. The model includes seven parameters, which have been fitted to 230 data points, which are themselves reproduced with a mean relative deviation of 1.3%.

A solvation model with a concentration-dependent solvation number combined with the activity coefficients for the liquid phase should also be able to describe VLE in other water–single base systems like H_2O–KOH and H_2O–CsOH. However, it should be emphasized that presently it is not evident how such a model can be generalized to mixed electrolyte solutions, this interesting problem being left to future investigations.

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