

# Modeling electrolyte solutions with the extended universal quasichemical (UNIQUAC) model\*

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*Abstract:* The extended universal quasichemical (UNIQUAC) model is a thermodynamic model for solutions containing electrolytes and nonelectrolytes. The model is a Gibbs excess function consisting of a Debye–Hückel term and a standard UNIQUAC term. The model only requires binary ion-specific interaction parameters. A unique choice of standard states makes the model able to reproduce solid–liquid, vapor–liquid, and liquid–liquid phase equilibria as well as thermal properties of electrolyte solutions using one set of parameters.

*Keywords:* extended UNIQUAC; electrolyte; salt; thermodynamic model; databank.

## INTRODUCTION

Most thermodynamic models for electrolyte solutions consist of a term for long-range, electrostatic interactions and a term for short-range interactions. The term for long-range, electrostatic interactions is usually derived from Debye–Hückel theory [1]. The theory of Debye and Hückel describes electrostatic interactions in an ideal solution of charged particles. In order to apply the Debye–Hückel theory to nonideal systems, it therefore has to be combined with a term for short-range interactions. The Pitzer model [2] combines a Debye–Hückel term with a virial expansion of terms in molality. The electrolyte nonrandom two-liquid (NRTL) model [3–5] combines a Debye–Hückel term with the NRTL local composition model. The local composition concept is modified for ions, and the model parameters are salt-specific. The extended universal quasichemical (UNIQUAC) model [6,7] combines a Debye–Hückel term with the UNIQUAC local composition model. The local composition term is identical for ions and other components, and the model parameters are ion-specific.

An alternative term for long-range electrostatic interactions has been derived from the mean spherical approximation (MSA) theory [8,9]. This term has mainly been applied in combination with short-range interactions derived from cubic equations of state [10,11].

## EXTENDED UNIQUAC MODEL

In this work, the extended UNIQUAC model is applied for modeling solutions containing electrolytes. In 1986, Sander et al. [12] first introduced an extended UNIQUAC model for electrolytes. This model was later modified by Nicolaisen et al. [13] by replacing the modified UNIQUAC term used by Sander et al. with a standard UNIQUAC term. The current version of the extended UNIQUAC model that is presented in this work was first presented by Thomsen et al. [6] and Thomsen and Rasmussen [7]. The

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model equations in the current version are identical to those presented by Nicolaisen et al. [13]. The main difference between these two versions is an improved method to determine model parameters that apparently has removed the upper limit for the number of ions and other solutes that can be accommodated by the model.

### Concentration units and standard states

The only concentration unit used in the extended UNIQUAC model is the mole fraction scale. Mole fractions are here defined on the basis of the speciation in the solution. Water is considered to be the only solvent. Ions, nonelectrolytes including alcohols, and dissolved gases are considered solutes. The chemical potential of water is calculated from:

$$\mu_w = \mu_w^0 + RT \ln(x_w \gamma_w) \quad (1)$$

In eq. 1,  $\mu_w^0$  is the standard-state chemical potential of water, identical to the chemical potential of pure water at the system temperature and pressure.  $R$  is the gas constant,  $T$  is the system temperature in Kelvin,  $x_w$  is the mole fraction of water, and  $\gamma_w$  is the activity coefficient of water. The activity coefficient for water follows the symmetric convention, where the activity coefficient is equal to one for the pure component. The chemical potential of solute  $i$  is calculated from:

$$\mu_i = \mu_i^* + RT \ln(x_i \gamma_i^*) \quad (2)$$

In eq. 2,  $\mu_i^*$  is the standard-state chemical potential corresponding to the unsymmetric convention, where the activity coefficient is equal to one at infinite dilution in water.  $\gamma_i^*$  is the unsymmetric activity coefficient for solute  $i$ . The unsymmetric activity coefficient is derived from the symmetric activity coefficient by division with the symmetric activity coefficient at infinite dilution:

$$\gamma_i^* = \gamma_i / \gamma_i^\infty \quad (3)$$

Experimental measurements of activity coefficients are usually reported on the molality scale. In order to compare calculated and experimental activity coefficients, it is necessary to convert between unsymmetric mole fraction activity coefficients and molal activity coefficients. The molal activity coefficient is derived from the unsymmetric mole fraction activity coefficient by multiplication with the water mole fraction:

$$\gamma_i^m = \gamma_i^* x_w \quad (4)$$

### Model equations

The Debye–Hückel contribution to the excess Gibbs energy of the extended UNIQUAC model is marked by superscript D–H, and given by the expression:

$$G^{E,D-H} / (RT) = -x_w M_w 4A \left[ \ln(1 + bI^{1/2}) - bI^{1/2} + 0.5b^2 I \right] / b^3 \quad (5)$$

This expression has been derived by simplifying the original expression by Debye and Hückel [1]. In eq. 5,  $G^E$  is the molar excess Gibbs energy,  $M_w$  is the molar mass of water ( $\text{kg mol}^{-1}$ ),  $b = 1.5 (\text{kg mol}^{-1})^{1/2}$  is a constant.  $A$  is the temperature- and pressure-dependent Debye–Hückel parameter. At the saturation pressure of water, the following equation gives the temperature dependence of  $A$  at temperatures up to 500 K ( $T_0$  is equal to 273.15 K):

$$A = \left[ 1.131 + 1.335 \cdot 10^{-3} \cdot (T - T_0) + 1.164 \cdot 10^{-5} \cdot (T - T_0)^2 \right] (\text{kg mol}^{-1})^{1/2} \quad (6)$$

One of the functions of the Debye–Hückel parameter  $A$  is to account for the temperature dependence of the relative permittivity of water. Although solutes, such as ions or alcohols, also have a strong influence on the relative permittivity of solutions, the relative permittivity is in this work considered independent of composition.  $I$  is the ionic strength calculated as a function of concentrations and the ionic charges  $z_i$ :

$$I = 0.5 \sum_i x_i z_i^2 / (x_w M_w) \quad (\text{mol kg}^{-1}) \quad (7)$$

By proper differentiation of eq. 5, the electrostatic contributions to the activity coefficients are obtained. For ions, this contribution is:

$$\ln \gamma_i^{\text{D-H}} = -z_i^2 A I^{1/2} / (1 + b I^{1/2}) \quad (8)$$

The corresponding term for water is:

$$\ln \gamma_w^{\text{D-H}} = M_w 2A \left[ 1 + b I^{1/2} - (1 + b I^{1/2})^{-1} - 2 \ln(1 + b I^{1/2}) \right] / b^3 \quad (9)$$

The UNIQUAC contribution to the excess Gibbs energy consists of a combinatorial part and a residual part. The combinatorial part is marked by superscript C and given by:

$$G^{\text{E,C}} / (RT) = \sum_i x_i \ln(\phi_i / x_i) - 5.0 \sum_i q_i x_i \ln(\phi_i / \theta_i) \quad (10)$$

In eq. 10,  $x_i$  is the mole fraction,  $\phi_i$  is the volume fraction, and  $\theta_i$  is the surface area fraction of component  $i$ . The volume and surface area fractions of component  $i$  are calculated as:

$$\phi_i = x_i r_i / \sum_j x_j r_j; \quad \theta_i = x_i q_i / \sum_j x_j q_j \quad (11)$$

The volume parameter  $r_i$  and the surface area parameter  $q_i$  are treated as adjustable parameters in this work. There is no known relation between these parameters and the density of a solution. The combinatorial contribution to the activity coefficient of component  $i$  is:

$$\ln \gamma_i^{\text{C}} = \ln(\phi_i / x_i) + 1 - \phi_i / x_i - 5.0 q_i \left[ \ln(\phi_i / \theta_i) + 1 - \phi_i / \theta_i \right] \quad (12)$$

The residual part of the excess Gibbs function is marked by superscript R and given by:

$$G^{\text{E,R}} / (RT) = - \sum_i x_i q_i \ln(\sum_j \theta_j \psi_{ji}) \quad (13)$$

$\psi_{ji}$  is defined by the equation:

$$\psi_{ji} = \exp \left[ - (u_{ji} - u_{ii}) / T \right] \quad (14)$$

The interaction energy parameters  $u_{ji}$  and  $u_{ii}$  are independent of composition, but are temperature-dependent:

$$u_{ji} = u_{ji}^0 + u_{ji}^t (T - 298.15) \quad (15)$$

The two parameters  $u_{ji}^0$  and  $u_{ji}^t$  in eq. 15 are adjustable parameters. The value of these parameters can be determined from experimental data. By differentiation of eq. 13, the residual contribution to the activity coefficients is obtained:

$$\ln \gamma_i^R = q_i [1 - \ln(\sum_l \theta_l \psi_{li}) - \sum_j (\theta_j \psi_{ij} / \sum_l \theta_l \psi_{lj})] \quad (16)$$

The combinatorial and the residual parts of the activity coefficients calculated from eqs. 12 and 16 are symmetric activity coefficients. The electrostatic part of the solute activity coefficient, eq. 8, is an unsymmetric mole fraction activity coefficient. In order to calculate the unsymmetric mole fraction activity coefficient for a solute, it is necessary to convert the combinatorial and the residual parts of the activity coefficients to unsymmetric activity coefficients. This is done by dividing with the corresponding infinite dilution activity coefficients. An expression for the latter can be derived by setting the water mole fraction equal to one in eqs. 12 and 16. The expression for the solute activity coefficient is:

$$\ln \gamma_i^* = \ln(\gamma_i^C / \gamma_i^{C,\infty}) + \ln(\gamma_i^R / \gamma_i^{R,\infty}) + \ln \gamma_i^{D-H} \quad (17)$$

The expression for the solvent (water) activity coefficient is simply:

$$\ln \gamma_w = \ln \gamma_w^C + \ln \gamma_w^R + \ln \gamma_w^{D-H} \quad (18)$$

Thermal properties, such as excess enthalpy and excess heat capacity, are derived from the model by calculating the temperature derivatives of eqs. 17 and 18. It can be noticed from eq. 12 that the combinatorial part of the activity coefficient is independent of temperature. Equation 16 shows that the residual part of the activity coefficient is proportional to the surface area parameter  $q_i$ . The residual part of the excess enthalpy is, therefore, also proportional to the surface area parameter. Excess enthalpy data can, therefore, with advantage be used for determining the value of the surface area parameters.

### Gas-phase fugacities

In the temperature range up to 110 °C, aqueous solutions of gases like CO<sub>2</sub>, NH<sub>3</sub>, and SO<sub>2</sub> can have vapor pressures that exceed ideal gas behavior. In order to take such non-ideality into account in the extended UNIQUAC model, gas-phase fugacities are calculated with the Soave–Redlich–Kwong cubic equation of state. Gas-phase fugacities are only calculated for water and volatile solutes such as alcohols and gases, not for ions.

### Model parameters

The parameters needed in order to perform calculations with the extended UNIQUAC model are the Debye–Hückel  $A$  parameter, which is given in eq. 9 as a function of temperature. The Debye–Hückel  $b$  parameter is given the constant value 1.5 (kg mol<sup>-1</sup>)<sup>1/2</sup>. For calculation of gas-phase fugacities with the Soave–Redlich–Kwong cubic equation of state, the necessary parameters are derived from the critical properties of the volatile solutes.

The only unknown parameters in the model are:

- UNIQUAC volume and surface area parameters  $r_i$  and  $q_i$  for each species, and
- UNIQUAC interaction energy parameters  $u_{ji}^0$  and  $u_{ji}^t$  for each pair of interacting species.

The UNIQUAC volume and surface area parameters assigned to water by the authors of the UNIQUAC model [14] were retained. All other parameters were determined on the basis of experimental data from the IVC-SEP databank for electrolyte solutions [15]. The number of parameters needed to perform calculations with the extended UNIQUAC model is comparable to the number of parameters used in the electrolyte NRTL model, but is much lower than the number of parameters required for the Pitzer model.

Solutions of electrolytes necessarily contain more than one type of ion, it is, therefore, only possible to determine relative properties of ions. This is valid for experimental data [16] as well as for thermodynamic models. In this work, the parameter values were anchored by randomly fixing the values of the parameters of the hydrogen ion.

### *Electrolyte databank*

An extensive databank for aqueous electrolyte solutions has been compiled in the IVC-SEP research group at the Department of Chemical Engineering, Technical University of Denmark. The databank, which can be accessed on-line [15], currently contains more than 100 000 experimental datapoints concerning activity coefficients, enthalpy of mixing, heat capacity, degree of dissociation, gas solubility, salt solubility, liquid–liquid equilibrium, vapor–liquid equilibrium, density, and gas hydrate formation, all in binary, ternary, and quaternary solutions.

Data from this databank were retrieved, and a nonlinear, least-squares minimization was performed in order to minimize the difference between calculated and experimental data. The difference between calculated and experimental data was calculated in several different ways, depending on the type of data and the system in question. All data of the same type (e.g., osmotic coefficients) were weighted identically. An initial screening of data was performed in order to eliminate obvious discrepancies between data from different sources.

The parameters and various thermodynamic properties necessary for performing calculations with the extended UNIQUAC model have been published in a number of papers [6,7,17–21].

## **EQUILIBRIUM CALCULATIONS**

Simultaneously with phase equilibrium calculations, speciation equilibrium calculations have to be performed. In the simplest case, only the auto protolysis of water has to be considered. In more complex cases, a number of speciation equilibria must be considered. The speciation equilibria can be formulated as a mathematical equation in terms of activity coefficients, concentrations, and standard chemical potentials. This mathematical formulation is similar to the way solid–liquid equilibria and vapor–liquid equilibria are formulated mathematically.

The condition for equilibrium between two phases is that the chemical potential is identical in the two phases. The chemical potentials of water and solutes are given by eqs. 1 and 2.

### **Standard-state properties**

In order to evaluate the chemical potentials of water and solutes according to eqs. 1 and 2, the standard-state chemical potentials need to be known. The standard-state chemical potentials of solutes at 298.15 K can be found in tables like “The NBS Tables of Chemical Thermodynamic Properties” [22]. These standard-state properties are reported with reference to the molality standard state and, therefore, need to be converted to the unsymmetric mole fraction scale. This conversion is achieved with the relation:

$$\mu_i^m = \mu_i^* + RT \ln M_w \quad (19)$$

The molality standard state is marked with superscript m. The standard-state chemical potentials at temperatures different from 298.15 K are evaluated using the Gibbs–Helmholtz equation:

$$d(\mu_i^* / RT) / dT = -\Delta_f H_i / (RT^2) \quad (20)$$

The standard-state heat capacity of ionic solutes was found to be described well by the three-parameter correlation [6]:

$$C_{p,i}^* = a_i + b_i T + c_i / (T - 200) \quad (21)$$

This standard-state heat capacity is used for evaluating the temperature dependence of the standard-state enthalpy of formation  $\Delta_f H_i$  in eq. 20, and for calculating the heat capacity of electrolyte solutions.

In solid–liquid equilibrium calculations, it is necessary to know the standard thermodynamic properties of the various solid phases. Such properties are listed in the NBS tables [22] for many salts. For salts not found in these tables, such properties were fitted to experimental solid–liquid equilibrium data.

### Solid–liquid equilibrium

For equilibrium between crystalline glauher salt [ $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  (c)] and an aqueous solution containing sodium sulfate, it is required that the chemical potential of 2 mol sodium ions plus the chemical potential of 1 mol sulfate ions and 10 mol water is identical to the chemical potential of 1 mol crystalline glauher salt. The equilibrium condition for this solid–liquid equilibrium can be expressed as:

$$\mu_{\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}}^0 = 2\mu_{\text{Na}^+} + \mu_{\text{SO}_4^{2-}} + 10\mu_{\text{H}_2\text{O}} \quad (22)$$

Superscript 0 on the chemical potential of glauher salt indicates that this is the chemical potential of a pure, crystalline phase. By using eqs. 1 and 2, eq. 22 can be written as:

$$\ln \left[ \left( x_{\text{Na}^+} \gamma_{\text{Na}^+}^* \right)^2 x_{\text{SO}_4^{2-}} \gamma_{\text{SO}_4^{2-}}^* \left( x_w \gamma_w \right)^{10} \right] = \left( \mu_{\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}}^0 - 2\mu_{\text{Na}^+}^* - \mu_{\text{SO}_4^{2-}}^* - 10\mu_w^0 \right) / RT \quad (23)$$

The right-hand side of eq. 23 can be calculated from the tabulated values [22] of the standard-state chemical potentials. The concentrations on the left-hand side of eq. 23 can then be adjusted by iteration until the activity product yields the desired value.

### Vapor–liquid equilibrium

Vapor–liquid equilibrium calculations follow a similar pattern. Equilibrium between volatile components in the gas phase and in the liquid phase requires that the chemical potentials of these volatile components are identical in the two phases. For equilibrium to exist between sulfur dioxide in the gas phase and in an aqueous phase, it is required that the chemical potential of sulfur dioxide is identical in the two phases:

$$\mu_{\text{SO}_2(\text{g})} = \mu_{\text{SO}_2(\text{aq})} \quad (24)$$

The chemical potential of  $\text{SO}_2$  in the gas phase can be expressed as an ideal gas chemical potential (superscript *ig*) plus a term that varies with fugacity. Similarly, the chemical potential of  $\text{SO}_2$  in the aqueous phase can be expressed in terms of the standard-state chemical potential of solutes and the activity coefficient according to eq. 2:

$$\mu_{\text{SO}_2}^{\text{ig}} + RT \ln \left( y_{\text{SO}_2} \hat{\phi}_{\text{SO}_2} P \right) = \mu_{\text{SO}_2}^* + RT \ln \left( x_{\text{SO}_2} \gamma_{\text{SO}_2}^* \right) \quad (25)$$

This is the so-called gamma-phi approach to vapor–liquid equilibrium calculation.  $\hat{\phi}_{\text{SO}_2}$  is the fugacity coefficient of  $\text{SO}_2$  in the vapor phase,  $y_{\text{SO}_2}$  is the corresponding mole fraction.

### Liquid–liquid equilibrium

For liquid–liquid equilibrium to occur, the chemical potential of each independent component must be the same in both phases. In this connection, an independent component is a neutral species. For liquid–liquid equilibrium in a system consisting of NaCl, water, and iso-propanol, NaCl has to be considered an independent component. One equation can be written for the equilibrium of each of the three independent components between liquid phase I and liquid phase II. The equation for NaCl can, by using eq. 2, be expressed as:

$$\mu_{\text{Na}^+}^* + \mu_{\text{Cl}^-}^* + RT \ln \left( x_{\text{Na}^+}^{\text{I}} \gamma_{\text{Na}^+}^{*,\text{I}} x_{\text{Cl}^-}^{\text{I}} \gamma_{\text{Cl}^-}^{*,\text{I}} \right) = \mu_{\text{Na}^+}^* + \mu_{\text{Cl}^-}^* + RT \ln \left( x_{\text{Na}^+}^{\text{II}} \gamma_{\text{Na}^+}^{*,\text{II}} x_{\text{Cl}^-}^{\text{II}} \gamma_{\text{Cl}^-}^{*,\text{II}} \right) \quad (26)$$

Owing to the choice of standard states, the standard chemical potentials cancel each other, and the condition for equilibrium between the two phases for NaCl is simplified to:

$$x_{\text{Na}^+}^{\text{I}} \gamma_{\text{Na}^+}^{*,\text{I}} x_{\text{Cl}^-}^{\text{I}} \gamma_{\text{Cl}^-}^{*,\text{I}} = x_{\text{Na}^+}^{\text{II}} \gamma_{\text{Na}^+}^{*,\text{II}} x_{\text{Cl}^-}^{\text{II}} \gamma_{\text{Cl}^-}^{*,\text{II}} \quad (27)$$

A similar equilibrium equation is written for each of the other two components.

If instead the ternary mixture of NaCl, water and iso-propanol had been considered a pseudo binary mixture of NaCl in a mixed solvent, the standard state chemical potentials of the ions had varied with solvent composition. This would have complicated liquid–liquid and solid–liquid equilibrium calculations considerably, requiring the calculation of Gibbs energies of transfer as described by Lorimer [23].

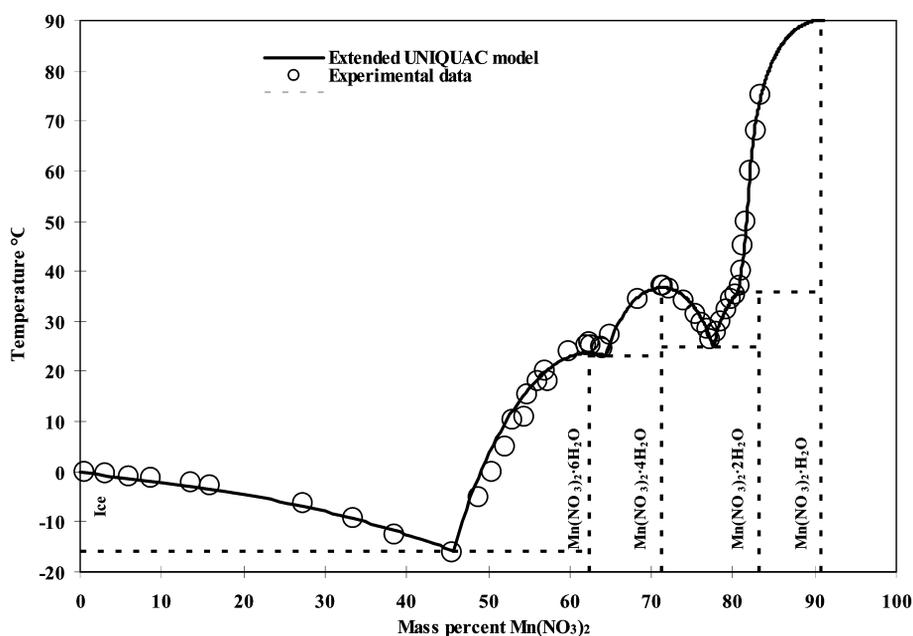
## RESULTS

The ability of the extended UNIQUAC model to describe the solubility of a salt as a function of temperature is illustrated in Fig. 1. The solubility of  $\text{Mn}(\text{NO}_3)_2$  as a function of temperature from  $-16$  to  $90$  °C is shown. Experimental data from several sources are plotted along with the calculated curve. The solubility line consists of five parts, one for ice, and one for each of the four salt hydrates of manganous nitrate: the hexahydrate, the tetrahydrate, the dihydrate, and the monohydrate. The very particular shape of this solubility diagram is reproduced quite accurately by the model. Decomposition of manganous nitrate starts at  $75$  °C [24], which explains why there are no experimental data above this temperature. As a result of this decomposition, anhydrous manganous nitrate can not precipitate from a binary aqueous solution.

The parameters needed to describe the phase behavior of  $\text{Mn}(\text{NO}_3)_2$  (Fig. 1) were determined simultaneously with the parameters for  $\text{MnCl}_2$  and  $\text{MnSO}_4$ . Parameters were already available for the anions. The only parameters needed were thus a volume parameter and a surface area parameter for the manganese ion in addition to the interaction parameters (eq. 15) for the interaction of the manganese ion with water and with each of the three anions. Each of these four interaction parameters consists of two parts, a constant  $u^0$  and a temperature gradient  $u^t$  (eq. 15).

The reason why the parameters were determined simultaneously was in order to be able to distinguish between the interaction of manganese with water on one side and with each of the anions on the other side. Also, the simultaneous parameter estimation enables us to distinguish between the contribution from the combinatorial part (eq. 10) and the contribution from the residual part (eq. 13) of the UNIQUAC equation to the activity coefficients.

As the interaction parameters for the anions were already known, the parameters determined for the three binary systems,  $\text{Mn}(\text{NO}_3)_2\text{-H}_2\text{O}$ ,  $\text{MnCl}_2\text{-H}_2\text{O}$ , and  $\text{MnSO}_4\text{-H}_2\text{O}$  are at the same time the



**Fig. 1** The solubility of manganese nitrate as a function of temperature calculated with the extended UNIQUAC model and plotted along with experimental data from various sources.

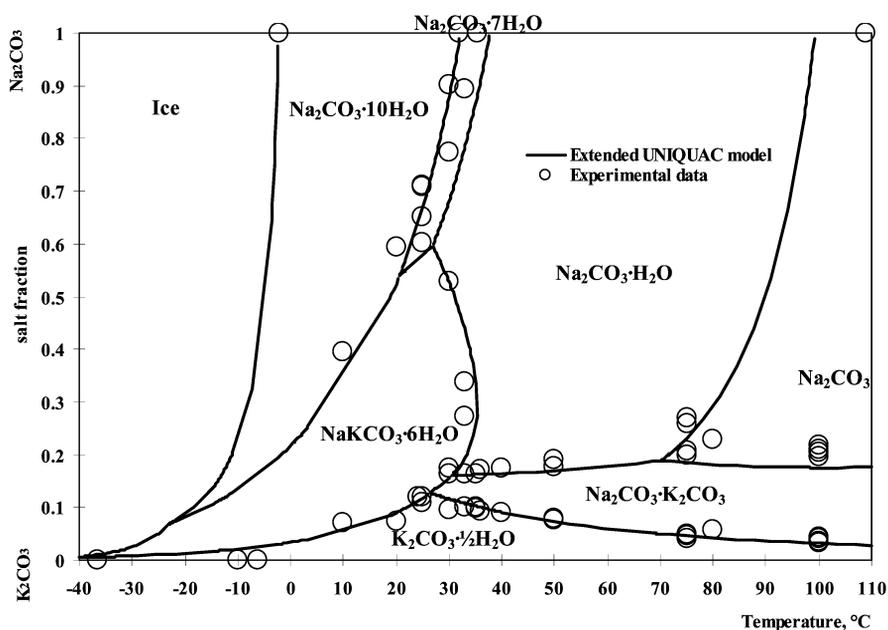
only parameters necessary for the ternary systems  $\text{Mn}(\text{NO}_3)_2\text{-MnCl}_2\text{-H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2\text{-MnSO}_4\text{-H}_2\text{O}$ , and  $\text{MnCl}_2\text{-MnSO}_4\text{-H}_2\text{O}$ . Therefore, binary as well as ternary data could be used to determine the six parameters required for these systems.

In addition to the model parameters, it was also necessary to fit the standard thermodynamic properties  $\Delta_f G$ ,  $\Delta_f H$ , and  $C_p$  for those solid phases appearing in these binary and ternary systems for which values could not be found in standard tables [22].

In Fig. 2, a temperature-composition diagram for the ternary system  $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-H}_2\text{O}$  is shown along with experimental data for this system. This type of diagram shows the solid phases that will be in equilibrium with saturated solutions in the whole temperature-composition area. This diagram covers temperatures from  $-40$  to  $110$  °C. The compositions of the saturated solutions are given on a dry basis, i.e., salt fraction is the sodium carbonate fraction of the total amount of salt on a molar basis. Lines in the diagram indicate compositions where two salts are in equilibrium with the same liquid.

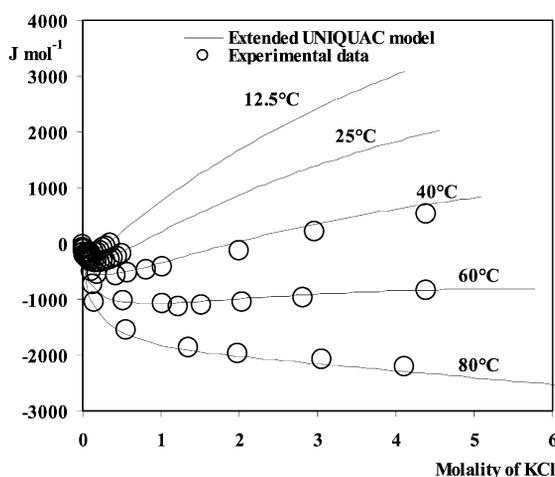
According to Fig. 2, eight different solid phases can precipitate from this ternary system in the temperature range considered. One of these,  $\text{NaKCO}_3\cdot 6\text{H}_2\text{O}$ , was considered to be a solid solution rather than a pure, crystalline salt by Hill and Miller [25], who investigated this system. As it appears from the diagram, the phase boundaries of this solid are relatively well described by assuming this solid to be a pure crystalline phase. At the conditions, where this solid appears, the solutions are very viscous and require a large degree of supersaturation before precipitation occurs, according to Hill and Miller [25], who seem to be the only ones who have investigated this system at low temperature in the last century.

A very unusual feature of the phase diagram shown in Fig. 2 is that at temperatures between  $30$  and  $35$  °C, solubility isotherms have two branches for the solubility of  $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$  interrupted by a branch for the solubility of  $\text{NaKCO}_3\cdot 6\text{H}_2\text{O}$ . This is caused by the curvature of the  $\text{NaKCO}_3\cdot 6\text{H}_2\text{O}\text{-Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$  two salt saturation line. This phenomenon seems to be unique to this ternary system.



**Fig. 2** Temperature-composition diagram for saturated solutions in the  $\text{Na}_2\text{CO}_3\text{--K}_2\text{CO}_3\text{--H}_2\text{O}$  system at temperatures from  $-40$  to  $110$  °C. The water contents of the solutions are not shown. The “salt fraction” unit on the ordinate is mol sodium carbonate per mol sodium carbonate plus potassium carbonate.

Thermal property data, such as heat of dilution data, were included in the data used to determine the parameters in the model. Data for the heat of dilution to infinite dilution corresponds to excess enthalpy with reference to the unsymmetric convention for activity coefficients. The excess enthalpy is calculated from the temperature derivative of the activity coefficients. Excess heat capacity is calculated from the second temperature derivative of the activity coefficients. By including such thermal properties in the parameter estimation, an improved temperature dependence of the activity coefficients is obtained. At the same time, the thermodynamic model is improved because it obtains the capability to calculate the thermal properties. An example of this is shown in Fig. 3, where calculated heat of dilution



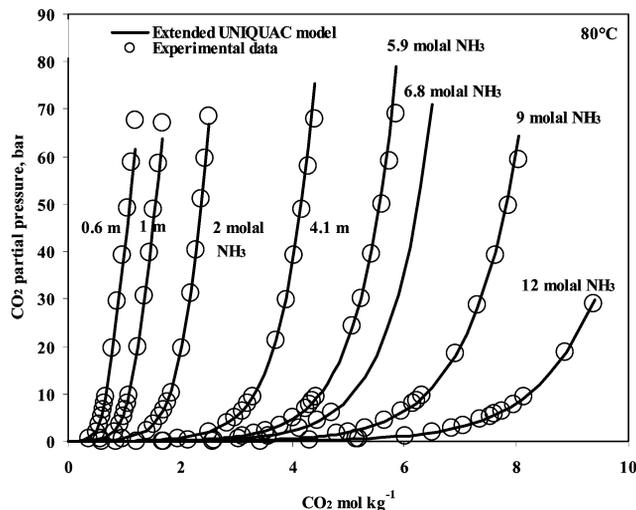
**Fig. 3** The heat of dilution to infinite dilution for KCl calculated at 5 different temperatures and plotted along with experimental data from various sources.

to infinite dilution data are compared with experimental data of the same type at five different temperatures.

A result of the modeling of gas solubility is shown in Fig. 4. Modeling of the aqueous  $\text{NH}_3\text{-CO}_2$  system requires that the formation of carbamate is taken into consideration:

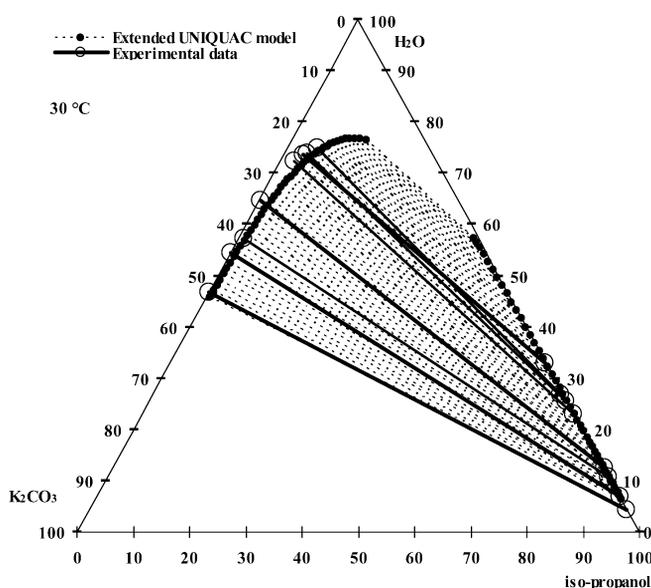


A significant amount of ammonia and carbon dioxide will be converted to carbamate, especially in a small pH range around  $\text{pH} = 9\text{--}11$ . The amounts of gases that are converted to carbamate do not contribute to the vapor pressure of the solution.



**Fig. 4** The partial pressure of carbon dioxide over aqueous solutions of carbon dioxide and ammonia. Model calculations are shown together with experimental data.

Liquid–liquid separation occurs in water–iso-propanol mixtures with the addition of certain salts. A result obtained for the potassium carbonate–water–iso-propanol system at 30 °C is shown in Fig. 5. The experimental data shown along with the calculated tie lines come from two different sources [26,27], which explains why some of the experimental tie lines cross each other. The result in Fig. 5 is very satisfactory in light of the quality and amount of experimental data. From the diagram in Fig. 5, an energy efficient method for the separation of water–iso-propanol mixtures can be suggested. By saturating such mixtures with potassium carbonate, an iso-propanol phase with a small amount of potassium carbonate and 8 mass % water will be obtained. The water phase in equilibrium with the iso-propanol phase will contain 53 mass % potassium carbonate and a small amount of iso-propanol. The iso-propanol phase obtained in this way will have an iso-propanol content that is higher than an azeotropic mixture of water and iso-propanol.



**Fig. 5** Liquid–liquid equilibrium in the potassium carbonate–water–iso-propanol system. Experimental tie lines are shown as full lines, while tie lines calculated with the extended UNIQUAC model are dashed. Concentrations are in mass %.

## CONCLUSION

The extended UNIQUAC model is a very simple thermodynamic model for electrolytes. Yet it is able to describe solid–liquid, liquid–liquid, and vapor–liquid equilibria using one set of parameters. In addition, thermal properties such as the heat of dilution and the heat capacities of electrolyte solutions are calculated quite accurately by the model.

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