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Solubilities of Sodium Chloride and Potassium Chloride in Water + Ethanol Mixtures from (298 to 323) K

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The solubilities of sodium chloride in water + ethanol mixtures and of sodium and potassium chlorides in systems of NaCl + KCl + water + ethanol were determined from (298 to 323) K and up to 20 mass % alcohol in the solvent. An empirical fit of the measured data enabled the calculation of the solubility of NaCl in water + ethanol mixtures as a function of temperature and alcohol content with an average deviation of 0.1 mass %. Solubility data in the quaternary systems were correlated using an algorithm that makes use of the Pitzer mole fraction-based equations for the activity coefficients of the electrolytes. The parameters for the activity coefficient equations, taken from the literature, allowed fair agreement between calculated and experimental solubilities in the NaCl field. However, in the KCl domain the deviations were somewhat biased. A better fit of the entire set of solubilities was obtained by revising the value of the short-range interaction parameter $Q_{\text{ethanol,NaCl,KCl}}$. After this tuning, the algorithm reproduces the experimental solubility data of both salts with a standard deviation of $\pm 0.023\ \text{mol}\cdot\text{kg}_{\text{solvent}}^{-1}$. The maximum differences between the experimental and calculated contents of sodium and potassium chlorides in the invariant composition mixtures are 1.2% and 3.5%, respectively.

Introduction

Salt solubility data in mixed solvents are important as a tool for the design and simulation of unit operations such as drowning-out crystallization or liquid−liquid extraction. However, entire phase diagrams cannot be obtained in a reasonable period of time via experiment because of the degrees of freedom pertaining to multicomponent systems. Therefore, to predict the solubility of salts in aqueous brines several models have been proposed in the literature based on the thermodynamics of the electrolytes. The application of the Pitzer mole fraction-based equations[1,2] to describe the mean ionic activity coefficients in organic + water mixtures has been successful in the treatment of electromotive force data obtained in diluted solutions. This model was recently parametrized for the NaCl + KCl + water + ethanol system at low to moderate salt concentrations from emf data measured for each chloride in water and in water + ethanol mixtures[3,4] as well as in fairly dilute quaternary mixtures.[5]

The ability to predict the thermodynamic behavior of the electrolytes near saturation is, however, a severe test of the model parametrization because a large extrapolation far beyond the range of validity of the fitted parameters is usually required. The objective of this work was therefore to test and extend the use of the Pitzer−Simonson−Clegg model to represent the phase equilibrium of mixed-solvent electrolyte systems. The paucity of literature data concerning solid−liquid phase diagrams for the NaCl + KCl + water + ethanol system led us to measure the solubilities of both salts in these quaternary mixtures in order to evaluate the goodness of fit of the predicted values.

During the course of this study, solubilities of NaCl in water−ethanol solvents were also obtained. The agreement between the measured values and the literature data is excellent.

Experimental Section

Analytical-grade sodium and potassium chlorides were supplied by Riedel-de-Haën with minimum purities of 99.8% and 99.5%, respectively. Prior to measurements, the salts were dried in an oven at 120 °C for 24 h. Ethanol supplied by Merck was 99.8%+. All solutions were prepared using deionized water with a specific conductivity of 2 $\mu\text{S}\cdot\text{cm}^{-1}$.

Binary (water + ethanol) and ternary (water + ethanol + secondary electrolyte) mixtures were prepared by mass with an uncertainty of $\pm 1 \times 10^{-4}$ g.

The experiments were carried out in a tightly sealed 50-mL glass cell equipped with a Teflon-coated magnetic stirrer and a sampling port with a septum to allow the insertion of a 15-cm-long hypodermic syringe. The cell was first loaded with a weighed amount of dried salt (or of both salts in the double-saturation experiments) in small excess over the estimated equilibrium composition. Subsequently, a binary or ternary solution of known overall composition was added until only a small volume of the gas phase of (3 to 5) mL was left in the cell. The flask was then sealed to avoid evaporation and immersed in a thermostated bath Haake F3 equipped with an auxiliary cooler and controlled to ±0.1 K.

The temperature was measured in the thermostated fluid with a set of glass precision thermometers (Landsberger (+17 to +35) °C and (+34 to +52) °C certified by Glasmeβgeräte Darmstadt, calibrated to the ITS-90 scale

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Table 1. Solubility of Sodium Chloride S_{NaCl} in Water + Ethanol Mixtures with Various Ethanol Mass Fractions in the Solvent at Different Temperatures

4.83% ethanol		9.94% ethanol		15.05% ethanol		20.10% ethanol	
T	S_{NaCl}	T	S_{NaCl}	T	S_{NaCl}	T	S_{NaCl}
K	mol·kg^{-1}	K	mol·kg^{-1}	K	mol·kg^{-1}	K	mol·kg^{-1}
298.15	5.521	298.05	4.939	298.15	4.411	298.10	3.950
300.85	5.536	300.75	4.955	298.35	4.410	298.45	3.953
303.15	5.551	303.15	4.975	300.35	4.436	300.65	3.971
303.35	5.552	305.75	5.002	303.15	4.453	303.15	3.987
305.75	5.578	308.25	5.016	305.75	4.473	305.75	4.015
308.15	5.587	310.60	5.040	308.25	4.506	308.25	4.037
310.55	5.607	313.15	5.055	313.15	4.543	310.65	4.062
313.15	5.621	315.75	5.079	318.05	4.590	313.05	4.077
315.55	5.642	318.05	5.095	320.45	4.597	313.35	4.085
320.45	5.678	320.75	5.120	322.85	4.626	315.60	4.101
323.05	5.694	322.85	5.137			317.80	4.128
323.15	5.696	323.25	5.145			320.85	4.157
						323.25	4.183

and read with a precision of ±0.02 K). The temperature difference outside and inside the equilibrium cell never exceeded ±0.05 K after 15 min of equilibration. The uncertainty of the temperature readings was ±0.05 K.

During the experiments, the slurry was stirred for (3 to 48) h at constant temperature. At the end of a settling period of (2 to 7) h, at least three liquid samples of about 4 mL each were collected using a syringe equipped with a 0.40-μm filter and transferred to capped vials. Prior to sampling, syringes and filters were thermostated at a temperature slightly above the equilibrium value to prevent precipitation. The liquid samples were weighed and allowed to evaporate slowly to dryness at 343 K, followed by a period of at least 72 h in an oven at 393 K. The solid dehydration was considered complete when its mass was constant.

For the invariant points' determination, another three liquid samples were withdrawn and quickly injected into capped vials containing a known amount of distilled water to prevent precipitation. The diluted samples were analyzed by ionic chromatography for the mass ratio of sodium and potassium ions (relative combined standard uncertainty of 5%) as well as for the chloride content as a cross check of the accuracy of the cations' determination.

For both fields of the phase diagram, the invariant points excluded, the solubility of the main salt was calculated from the total mass of the anhydrous solid, the mass of solvent evaporated, and the concentration of the secondary electrolyte in the solvent. The solubilities reported here (molalities) are the average values of triplicate measurements with a standard uncertainty of better than ±0.003 mol·kg^{-1}. The concentrations of both electrolytes in the double-saturated solutions were obtained from the mass of the solid residue, the Na/K ratio, and the mass of the evaporated solvent. Taking into account the uncertainties of the ionic chromatography technique and of the experimental procedure, the maximum overall uncertainty values of the NaCl and KCl molalities at the invariant points are (±0.17 and ±0.14) mol·kg^{-1}, respectively.

Results and Discussion

Solubility Measurements. NaCl solubility data were obtained in aqueous solutions of (5, 10, 15 and 20) mass % ethanol in the salt-free solvent at temperatures ranging from (298 to 325) K. The solubilities of both chlorides in the quaternary systems were measured at four temperatures (298, 303, 313, and 323) K for (10 and 20) mass % ethanol in the salt-free solvent. The content of the secondary salt extended over the whole range of concentration up to the double saturation.

NaCl Solubility Data. The experimental results for sodium chloride solubility at several temperatures and different ethanol contents in the solutions are reported in Table 1.

The solubility of NaCl, S_{NaCl} (mol·kg^{-1}), was described as a function of the absolute temperature, T/K, and ethanol mass fraction in the alcohol solvent, X, by adjusting the following empirical equation to the experimental data:

$$S_{\mathrm{NaCl}}/(\mathrm{mol{\cdot}kg^{-1}}) = \frac{C(1-X)}{C+X} S_{\mathrm{NaCl}}^{\mathrm{water}}/(\mathrm{mol{\cdot}kg^{-1}}) \quad (1)$$

where

$$C = 0.0956424 \exp(0.0072512T/\mathrm{K}) \quad (2)$$

and $S_{\mathrm{NaCl}}^{\mathrm{water}}$ is the equilibrium molality in pure water. In the temperature range studied, a simple polynomial equation such as

$$S_{\mathrm{NaCl}}^{\mathrm{water}}/(\mathrm{mol{\cdot}kg^{-1}}) = 7.78461 - 0.01566T/\mathrm{K} + 0.000034(T/\mathrm{K})^2 \quad (3)$$

describes the literature data[6] with a standard deviation of ±0.003 mol·kg^{-1}.

The calculated NaCl solubilities are in good agreement with the measured values, as shown in Figure 1, for the different contents of ethanol in the solvent. The goodness of fit was calculated in terms of the root-mean-square deviation in salt content as ±0.004 mol·kg^{-1}, with a maximum absolute deviation of 0.011 mol·kg^{-1}.

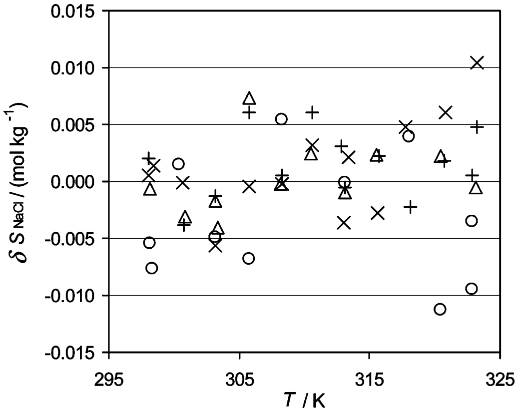

Figure 1. Deviations between experimental and calculated NaCl solubilities for various contents of ethanol in the solvent. △, 5% +, 10%; ○, 15%; ×, 20%.

Table 2. Solubility of Sodium Chloride in (10 and 20)% Mass Fraction Ethanol + Water Mixtures for Different Temperatures and Contents of KCl

10.0% ethanol				20.0% ethanol			
T	m_{NaCl}	T	m_{NaCl}	T	m_{NaCl}	T	m_{NaCl}
K	mol·kg^{-1}	K	mol·kg^{-1}	K	mol·kg^{-1}	K	mol·kg^{-1}
m_{KCl} = 0.1000 mol kg^{-1}		m_{KCl} = 0.9989 mol·kg^{-1}		m_{KCl} = 0.1000 mol·kg^{-1}		m_{KCl} = 0.9814 mol·kg^{-1}	
298.15	4.907	313.15	4.561	298.05	3.897	298.15	3.521
303.15	4.927	323.15	4.708	302.60	4.000	303.15	3.564
313.15	5.040	m_{KCl} = 1.0024 mol·kg^{-1}		313.25	4.079	313.65	3.685
323.15	5.112	298.15	4.402	323.05	4.110	323.15	3.749
m_{KCl} = 0.2500 mol·kg^{-1}		303.15	4.462	m_{KCl} = 0.2500 mol·kg^{-1}		m_{KCl} = 1.2499 mol·kg^{-1}	
298.15	4.821	m_{KCl} = 1.2499 mol·kg^{-1}		298.15	3.827	303.15	3.466
303.25	4.838	298.15	4.339	303.15	3.849	313.15	3.533
313.15	4.926	303.15	4.332	313.15	3.961	323.15	3.631
323.15	5.021	313.15	4.510	323.15	4.051	m_{KCl} = 1.4865 mol·kg^{-1}	
m_{KCl} = 0.5000 mol·kg^{-1}		323.15	4.532	m_{KCl} = 0.4979 mol·kg^{-1}		303.20	3.304
298.15	4.654	m_{KCl} = 1.5000 mol·kg^{-1}		298.25	3.731	313.15	3.459
303.25	4.746	298.15	4.199	303.05	3.788	323.15	3.535
313.15	4.767	303.15	4.245	312.45	3.849	m_{KCl} = 1.7501 mol·kg^{-1}	
323.15	4.885	313.15	4.332	322.65	3.903	323.15	3.430
m_{KCl} = 0.7500 mol·kg^{-1}		323.15	4.448	m_{KCl} = 0.7500 mol·kg^{-1}			
298.15	4.553	m_{KCl} = 2.0001 mol·kg^{-1}		298.15	3.610		
303.15	4.594	313.15	4.178	303.15	3.663		
313.15	4.684	323.15	4.281	313.15	3.774		
323.15	4.794			323.15	3.848		

In Figures 2 and 3, the calculated solubilities of sodium chloride in water + ethanol mixtures are compared with data available in the literature.[6−9] Within its range of applicability as well as up to 345 K and 40% mass ethanol in the mixed solvent, eq 1 represents, within ±4% mass salt, most of the literature data. For higher ethanol contents, extrapolating eq 1 produces NaCl solubilities in excess of up to 14% mass salt over the data of two literature sources,[8,9] although they are almost always lower than the recent values of Galleguillos et al.[7] (uncertainties not stated).

Solubility of NaCl and KCl in Quaternary Mixtures. The experimental solubilities obtained in the fields of NaCl and KCl at (298, 303, 313, and 323) K and (10 and 20)% mass ethanol in the solvent are reported in Tables 2 and 3, respectively. The invariant point data are listed in Table 4.

The correlation of the solubilities measured in the quaternary systems was carried out using a simple algorithm that makes use of the mole fraction-based model developed by Pitzer and co-workers[1,2] to describe the activity coefficients of the electrolytes. The solid−liquid equilibrium between a solution of a salt MX and the anhydrous solid is represented by

$$\mu_{\text{MX,anhydrous solid}} = \mu_{\text{MX,solution}} \qquad (4)$$

For the aqueous solution, the chemical potential of the dissolved salt is given as

$$\mu_{\text{MX,solution}} = \sum_i \nu_i[\mu_i^0(T, p) + RT\ln(\gamma_i m_i)] \qquad (5)$$

where γ_i is the activity coefficient on the molality scale, ν_i is the stoichiometric coefficient of ion i in one molecule, m_i is the equilibrium molality of the ith species, and $\mu_i^0(T, p)$ is the reference chemical potential at an arbitrarily standard state, chosen so that all γ_i become unity at infinite dilution. If the solid phase exhibits zero-solid solubility, then the chemical potential of the solid is independent of the species in the solution. Therefore, by combining all terms, which depend only on pressure and temperature,

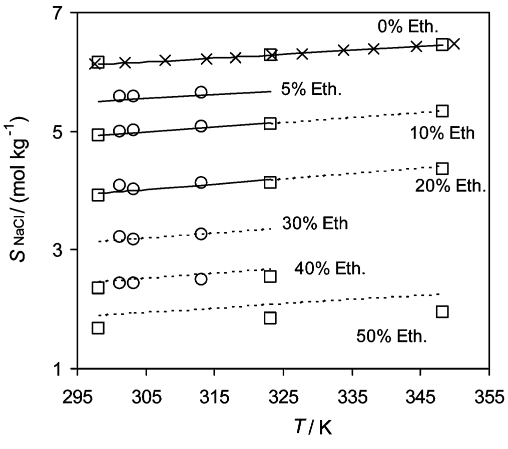

Figure 2. Literature (symbols) and calculated (lines) solubilities of NaCl in water + ethanol mixtures with different alcohol contents in the solvent. ×, Farelo et al.;[6] □, Pinho and Macedo;[8] ○, Linke and Seidell.[9] Solid lines, calculated within the range of validity of eq 1; broken lines, extrapolation of eq 1.

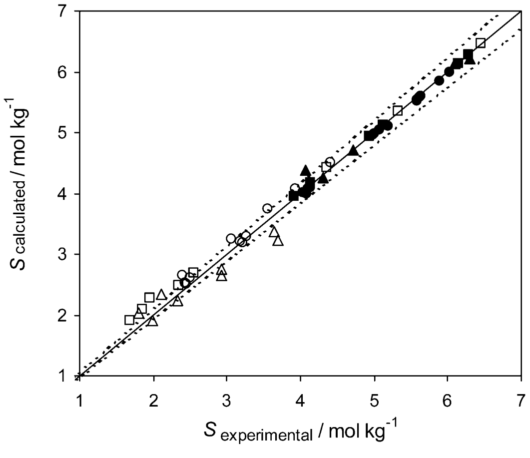

Figure 3. Literature vs calculated solubilities of NaCl in water + ethanol mixtures with various alcohol contents in the solvent and at different temperatures. △, Galleguillos et al.;[7] □, Pinho and Macedo;[8] ○, Linke and Seidell.[9] Filled symbols, within the range of validity of eq 1; open symbols, extrapolation of eq 1.

Table 3. Solubility of Potassium Chloride in (10 and 20)% Mass Fraction Ethanol + Water Mixtures for Different Temperatures and Contents of NaCl

10.0% ethanol				20.0% ethanol			
T/K	m_{KCl}/mol·kg^{-1}	T/K	m_{KCl}/mol·kg^{-1}	T/K	m_{KCl}/mol·kg^{-1}	T/K	m_{KCl}/mol·kg^{-1}
m_{NaCl} = 0 mol·kg^{-1}		m_{NaCl} = 1.5001 mol·kg^{-1}		m_{NaCl} = 0 mol·kg^{-1}		m_{NaCl} = 1.5015 mol·kg^{-1}	
298.15	3.629	298.15	2.805	298.15	2.665	298.20	1.954
303.15	3.821	303.15	2.929	303.15	2.833	303.40	2.103
313.15	4.186	313.15	3.291	313.15	3.122	312.75	2.377
323.15	4.509	323.15	3.671	323.15	3.395	323.05	2.662
m_{NaCl} = 0.1000 mol·kg^{-1}		m_{NaCl} = 2.0002 mol·kg^{-1}		m_{NaCl} = 0.0971 mol·kg^{-1}		m_{NaCl} = 2.0234 mol·kg^{-1}	
298.15	3.565	298.15	2.617	298.15	2.614	298.20	1.757
303.15	3.733	303.15	2.763	302.85	2.779	302.70	1.891
313.15	4.120	313.15	3.086	313.10	3.022	312.60	2.149
323.15	4.446	323.15	3.397	323.15	3.362	323.15	2.444
m_{NaCl} = 0.2500 mol·kg^{-1}		m_{NaCl} = 2.4999 mol·kg^{-1}		m_{NaCl} = 0.2500 mol·kg^{-1}		m_{NaCl} = 2.2499 mol·kg^{-1}	
298.15	3.493	298.15	2.339	298.15	2.544	298.10	1.656
303.25	3.679	303.15	2.495	303.15	2.681	303.15	1.813
313.15	4.045	313.15	2.858	313.15	2.992	313.10	2.055
323.15	4.299	323.15	3.145	323.15	3.290	323.25	2.300
m_{NaCl} = 0.5000 mol·kg^{-1}		m_{NaCl} = 3.0002 mol·kg^{-1}		m_{NaCl} = 0.4972 mol·kg^{-1}		m_{NaCl} = 2.4989 mol·kg^{-1}	
298.15	3.334	298.15	2.082	298.20	2.418	298.15	1.542
303.25	3.499	303.25	2.244	303.25	2.586	303.25	1.710
313.15	3.879	313.15	2.586	312.95	2.888	313.05	1.982
323.15	4.244	323.15	2.869	323.15	3.125	322.95	2.196
m_{NaCl} = 0.7499 mol·kg^{-1}		m_{NaCl} = 3.5002 mol·kg^{-1}		m_{NaCl} = 0.7499 mol·kg^{-1}		m_{NaCl} = 2.7463 mol·kg^{-1}	
298.15	3.168	298.15	1.902	298.15	2.251	298.15	1.494
303.25	3.365	303.25	2.039	303.15	2.475	302.85	1.628
313.15	3.737	313.15	2.377	313.15	2.751	312.85	1.867
323.15	4.083	323.05	2.641	323.15	3.015	323.25	2.153
m_{NaCl} = 1.0000 mol·kg^{-1}		m_{NaCl} = 3.7492 mol·kg^{-1}		m_{NaCl} = 0.9927 mol·kg^{-1}		m_{NaCl} = 2.9730 mol·kg^{-1}	
298.15	3.074	298.15	1.854	297.95	2.175	298.15	1.441
303.25	3.271	303.25	1.958	302.65	2.306	303.25	1.557
313.15	3.631	313.15	2.257	312.85	2.578	312.25	1.787
323.15	3.911	323.15	2.522	323.15	2.931	322.85	2.057
m_{NaCl} = 1.2498 mol·kg^{-1}		m_{NaCl} = 3.9989 mol·kg^{-1}		m_{NaCl} = 1.2498 mol·kg^{-1}		m_{NaCl} = 3.2493 mol·kg^{-1}	
298.15	2.890	298.15	1.750	298.15	2.064	298.10	1.341
303.25	3.105	303.25	1.890	303.15	2.217	303.20	1.481
313.15	3.425	313.15	2.159	313.15	2.504	312.85	1.710
323.15	3.778			323.15	2.776	323.45	1.969

into the standard free energy, $\Delta G°$, the condition of ionic equilibrium takes the form

$$\frac{\Delta G^0}{RT} = \sum_i \nu_i \ln(\gamma_i m_i) \tag{6}$$

For a 1:1-type electrolyte MX, $\nu_M = \nu_X = 1$, and independently of the number of electrolytes in the solution, eq 6 can be written as

$$\frac{\Delta G^0}{RT} = \ln[(\gamma_{MX})^2 m_M m_X] \tag{7}$$

For each electrolyte and each mixed solvent, the value of $\Delta G°$ can be obtained from thermodynamic and solubility data on single-salt solutions. Accordingly, in a system containing two 1:1-type electrolytes with a common anion, MX and NX, the equilibrium compositions can be calculated by solving the following equation

$$(S^2_{MX})_{\mathrm{ternary}}(\gamma^2_{MX})_{\mathrm{ternary}} = (\gamma^2_{MX})_{\mathrm{quaternary}}(m_{MX} + m_{NX})m_{MX} \tag{8}$$

for m_{MX}, the equilibrium molality of the main salt in the system.

The Pitzer mole fraction-based thermodynamic model[1,2] has proved to be particularly adequate to describe the mean activity coefficients of strong electrolytes in mixed solvents. According to this model, the rational activity coefficient of a 1:1-type electrolyte MX is described by the sum of an extended Debye−Hückel term, accounting for the long-range interactions, with a short-range forces contribution developed as a Margules expansion. In a quaternary system of two neutral species, 1 and 2, and two strong electrolytes with a common anion, MX and NX, the rational activity coefficient is given by[5]

$$\begin{aligned}\ln f_{\pm MX} = {} & \ln f^{\mathrm{DH}}_{\pm MX} + (1 - Fx_I)\Big\{x_1 W_{1,MX} + x_2 W_{2,MX} + \frac{2}{3}x_1\Big[1 - x_1 + \frac{x_I}{2}\Big]U_{1,MX} \\ & + \frac{2}{3}x_2\Big[1 - x_2 + \frac{x_I}{2}\Big]U_{2,MX}\Big\} + Fx_I\Big\{x_1\Big[x_1 + \frac{1}{3}x_2\Big]U_{1,MX} + x_2\Big[x_2 + \frac{1}{3}x_1\Big]U_{2,MX}\Big\} \\ & - x_1x_2[w_{1,2} + 2(x_1 - x_2)u_{1,2} - (1 - 2Fx_I)Z_{1,2,MX} + 2x_I(1 - F)Z_{1,2,NX}] \\ & + x_I(1 - F)\Big\{-x_1W_{1,NX} - x_2W_{2,NX} + (1 - 2\,x_I)(x_1U_{1,NX} + x_2U_{2,NX}) \\ & + (1 - 2Fx_I)(x_1Q_{1,MX,NX} + x_2Q_{2,MX,NX}) + (1 - Fx_I)\frac{W_{MX,NX}}{2} \\ & + x_I[3F - 1 + 2Fx_I(1 - 2F)]\frac{U_{MN}}{2} - \frac{4}{3}x_1x_2(U_{1,NX} + U_{2,NX})\Big\} - \ln f^{\infty}_{\pm MX}\end{aligned} \tag{9}$$

Table 4. Experimental Invariant Points' Compositions m_{NaCl} and m_{KCl} in (10 and 20)% Mass Fraction Ethanol + Water Mixtures at Different Temperatures

10.0% ethanol			20.0% ethanol		
T / K	m_{NaCl} / mol·kg^{-1}	m_{KCl} / mol·kg^{-1}	T / K	m_{NaCl} / mol·kg^{-1}	m_{KCl} / mol·kg^{-1}
298.15	4.1_0	1.7_0	298.15	3.3_7	1.3_2
303.35	4.0_6	1.8_6	302.80	3.4_1	1.3_8
313.15	4.0_2	2.1_8	313.10	3.4_2	1.6_3
322.50	4.0_7	2.3_7	322.50	3.3_9	1.8_4

Table 5. Coefficients of Equation 13 for the Calculation of the Pitzer–Simonson–Clegg Parameters in Ethanol + Water Solvents

	q_1	q_2	q_3	q_4	q_5
$w_{1,2}$[3]	1.2051	112.7180	0.72716	0	0
$u_{1,2}$[3]	0.2583	438.6720	2.84530	0	0
B_{NaCl}[4]	11.6357	0	392.5222	−2.8291	2.50×10^{-3}
$W_{1,NaCl}$[4]	−6.5281	0	7.5015	0.0056	0
$U_{1,NaCl}$[4]	−4.9401	0	47.4266	−0.1056	0
$W_{2,NaCl}$[4]	−2.0974	0	0	−29.5414	0.0458
$U_{2,NaCl}$[4]	−23.2750	0	0	9.5467	−0.0156
$Z_{1,2,NaCl}$[4]	10.2047	0	0	15.8086	−0.0245
B_{KCl}[3]	4.7265	0	88.0505	−0.2151	0
$W_{1,KCl}$[3]	−3.0229	0	0.48470	0.0042	0
$U_{1,KCl}$[3]	−1.9981	0	28.6039	−0.0745	0
$W_{2,KCl}$[3]	16.8101	0	0	−2.8094	1.32×10^{-3}
$U_{2,KCl}$[3]	−55.3182	0	0	0.0180	-2.08×10^{-4}
$Z_{1,2,KCl}$[3]	3.2750	0	0	0.9283	3.82×10^{-4}
$W_{NaCl,KCl}$[5]	−4.9235	3.30×10^{-4}	23.8465	−0.0349	0
U_{NaK}[5]	0.0259	0.01342	12.2093	−0.0406	0
$Q_{1,NaCl,KCl}$[5]	2.4520	0.03844	−6.7937	7.04×10^{-3}	0
$Q_{2,NaCl,KCl}$[5]	10.2025	0	−0.1733	−21.4783	0.0338
$Q_{2,NaCl,KCl}$[a]	−3.1202	0	9.79×10^{-4}	−0.5599	-1.76×10^{-4}

[a] This work.

$\ln f^{DH}_{\pm MX}$ is the extended Debye–Hückel term

$$\ln f^{DH}_{\pm MX} = -A_x\left[\left(\frac{2}{\rho}\right)\ln(1 + \rho I_x^{1/2}) + \frac{(1 - 2I_x)I_x^{1/2}}{1 + \rho I_x^{1/2}}\right] + + I_x^2[FB_{MX} + (1 - F)B_{NX}]\left[\frac{1}{2I_x} - 1\right]\exp(-\alpha I_x^{1/2}) + \frac{1}{2}I_x g(\alpha I_x^{1/2})B_{MX} \quad (10)$$

where A_x is the Debye–Hückel parameter for the osmotic function on a molar fraction basis, ρ is equivalent to the distance of closest approach of the Debye–Hückel theory, and α is a fitting parameter. I_x is the ionic strength and F is the mole fraction of M in the mixture of the two cations. The total mole fraction of ions in the solution, x_I, is given as $x_I = 1 - x_1 - x_2$. B_{cX} (c = Na, K) is a specific constant for each salt. The Margules parameters $W_{s,cX}$, $U_{s,cX}$, $W_{cX,c'X}$, U_{MN}, $w_{1,2}$, and $u_{1,2}$ represent binary interactions, and $Z_{1,2,cX}$ and $Q_{s,MX,NX}$ account for the interactions between triplets (s = 1, 2).

The function $g(\alpha I_x^{1/2})$ is defined as

$$g(\alpha I_x^{1/2}) = \frac{2[1 - (1 + \alpha I_x^{1/2})\exp(-\alpha I_x^{1/2})]}{(\alpha I_x^{1/2})^2} \quad (11)$$

The last term in eq 9, $\ln f^{\infty}_{\pm MX}$, allows the shift to the infinitely dilute reference state. The mole fraction-based activity coefficients of each electrolyte are converted to the molal basis by

$$f_{\pm MX} = \gamma_{\pm MX}(1 + 0.002M_s m_{MX}) \quad (12)$$

where M_s is the mean molar mass of the mixed solvent in g·mol^{-1}.

The solubilities of both salts in the quaternary mixtures NaCl + KCl + water + ethanol were calculated for various temperatures and contents of the secondary solute in systems with (0, 10, and 20)% mass ethanol in the solvent by solving iteratively eqs 8 to 12. Additionally, the solubility of sodium chloride in the ternary systems was estimated from eq 1, whereas for potassium chloride a similar dependency on temperature and ethanol content in the aqueous solvent was obtained from the literature.[10] The parameters of the rational activity coefficients were also calculated according to the literature[3−5] as

$$p(T) = q_1 + q_2\left(\frac{1}{(T/K)} - \frac{1}{(T_R/K)}\right) + q_3\ln\left(\frac{T/K}{T_R/K}\right) + q_4(T/K - T_R/K) + q_5((T/K)^2 - (T_R/K)^2) \quad (13)$$

where T_R = 298.15 K using the coefficients listed in Table 5. The invariant point compositions were obtained by solving simultaneously the whole set of equations pertaining to both salts.

In the NaCl field, the solubilities produced by using the literature parameters for the activity coefficient equations are in fair agreement with experiment, with deviations always lower than ±3% mass salt. However, the solubilities of potassium chloride are poorly predicted when the content of NaCl exceeds 1.0 mol·kg^{-1}. Near double saturation in 20% mass ethanol systems, these values are in error by 14% or more.

Thermodynamic calculations concerning highly soluble electrolytes are extremely sensitive to the values of the empirical parameters because even small changes in those values have pronounced effects on the calculated activities. Therefore, for calculations carried out at elevated concentrations, the short-range interaction coefficients are usually parametrized from two-salt solubility data. The aforemen-

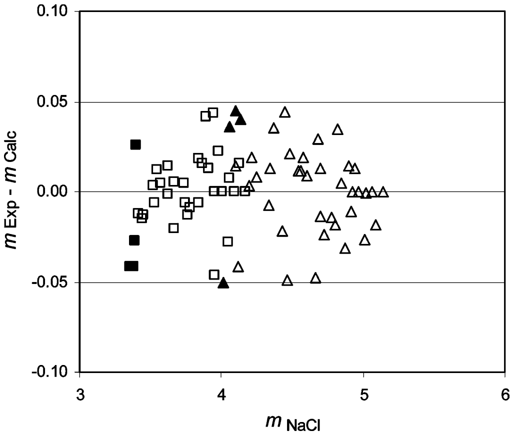

Figure 4. Deviations between experimental and calculated NaCl solubilities (mol kg^{-1}) in NaCl + KCl + water + ethanol mixtures. △, 10% mass ethanol; □, 20% mass ethanol; filled symbols, invariant points' data.

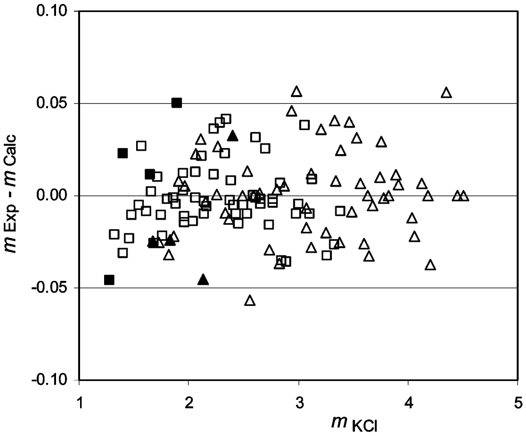

Figure 5. Deviations between experimental and calculated KCl solubilities (mol kg^{-1}) in NaCl + KCl + water + ethanol mixtures. △, 10% mass ethanol; □, 20% mass ethanol; filled symbols, invariant points' data.

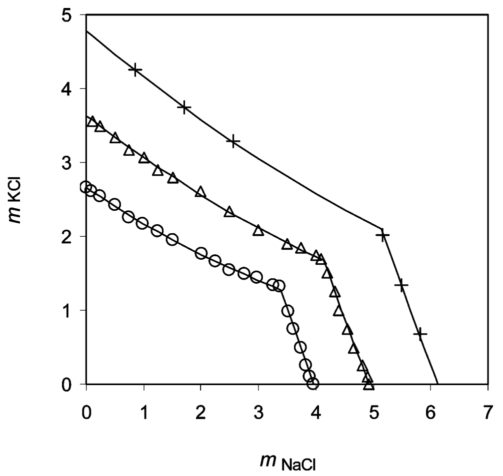

Figure 6. Literature and experimental (symbols) and calculated (lines) solubility of NaCl and KCl at 298 K in the system NaCl + KCl + water + ethanol with different ethanol contents in the solvent. +, 0% mass, Farelo et al.;[6] △, 10% mass, this work; ○, 20% mass, this work.

tioned deviations observed for the KCl field were, therefore, somewhat expected because the literature parameters pertaining to systems with ethanol were derived from electromotive force data obtained in quite dilute solutions.[5] The reliability of those parameters in the prediction of the thermodynamic quantities was asserted by comparison with the available literature data, the exception being $Q_{2,\mathrm{NaCl,KCl}}$, the parameter accounting for the interactions between both chlorides and ethanol. This ternary parameter is also likely to be responsible for large deviations because its domain of fitting for the quaternary KCl-rich mixtures extended only up to ionic strengths of about 2 mol·kg^{-1} at a constant sodium chloride content of 0.01 mol·kg^{-1}. Therefore, the value of $Q_{2,\mathrm{NaCl,KCl}}$ was here revised by fitting eqs 8 to 12 to the array of solubility data measured in NaCl + KCl + water + ethanol systems, and a new temperature was dependence proposed, as listed in Table 5. The differences between experimental and predicted solubilities thus calculated are shown in Figures 4 and 5. The experimental data pertaining to both salts are reproduced with a standard deviation of fit of ±0.023 mol·kg^{-1} over the whole range of concentration. The root-mean-square deviation for the invariant points' data is ±0.037 mol·kg^{-1}.

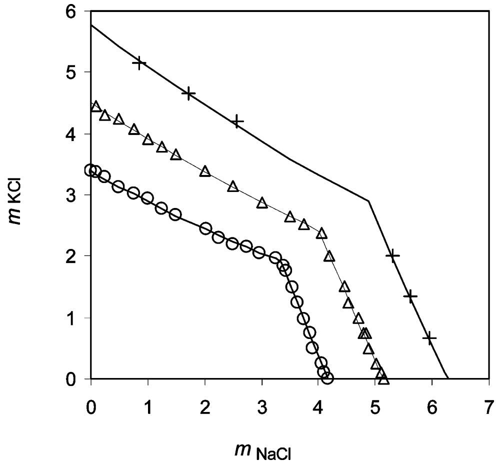

Figure 7. Literature and experimental (symbols) and calculated (lines) solubility of NaCl and KCl at 323 K in the system NaCl + KCl + water + ethanol with different ethanol contents in the solvent. +, 0% mass, Farelo et al.;[6] △, 10% mass, this work; ○, 20% mass, this work.

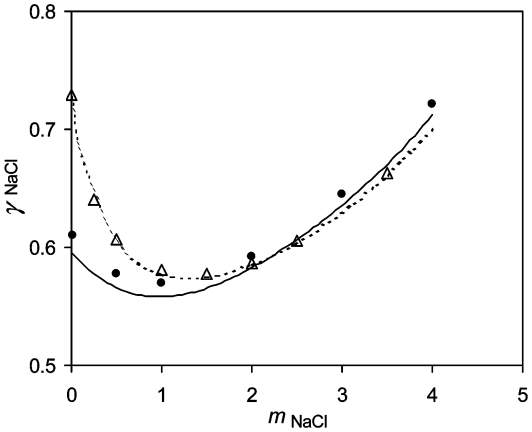

Figure 8. Literature[5] (symbols) and calculated (lines) activity coefficients of NaCl at 298.15 K in the system NaCl + KCl + water + ethanol for 20% mass ethanol in the solvent and two contents of the secondary electrolyte. Broken line, △, 0.1 mol kg^{-1} KCl; solid line, ●, 0.5 mol kg^{-1} KCl.

The excellent agreement of the model predictions with the measured data is well illustrated in Figures 6 and 7, where the isotherms at (298.15 and 323.15) K are depicted for systems containing (0, 10, and 20)% mass ethanol in the mixed solvent.

Literature solubility data for this quaternary system is available only for the invariant points at two temperatures (298.15 and 313.15) K and over the concentration range of (0 to 44)% mass ethanol in the solvent.[7] Within the range of validity of the parametrized model, the agreement between these data and the content of sodium chloride predicted by the model is fair, the deviations being of the same order of magnitude as the uncertainty of our own measurements. However, in what concerns the KCl content in the invariant mixtures, the differences between the two sets of data can randomly be higher than ±7% mass salt.

Although the values of the $Q_{2,\mathrm{NaCl,KCl}}$ parameter derived from electromotive force and solubility data are somewhat different, the loss of accuracy in the estimation of the activity coefficients of both chlorides in very dilute solutions is not significant because the contribution of the interaction parameter is minimal at low concentrations. The deviations increase slightly as the concentration of the secondary electrolyte increases, as shown in Figure 8.

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