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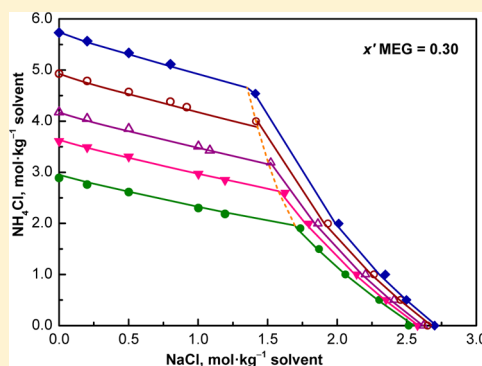
Solubility Measurement and Modeling for the NaCl–NH₄Cl–Monoethylene Glycol–H₂O System from (278 to 353) K

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Supporting Information

ABSTRACT: The solubilities of NH₄Cl and NaCl in the mixtures of monoethylene glycol (MEG) and water were determined, respectively, in the temperature range of (278 to 353) K by a dynamic method. The NaCl–NH₄Cl–MEG–H₂O system with MEG mole fraction of 0.30 on a salt-free basis was also investigated from (278 to 353) K to determine its phase equilibrium as a function of temperature and the concentration of electrolytes. The solubilities of both NH₄Cl and NaCl in the MEG–H₂O mixtures were found to decrease with the addition of MEG and the increasing concentration of the secondary electrolyte. The results show that the increment of temperature causes a marked increase in the solubility of NH₄Cl but only has a slight impact on the solubility of NaCl. The mixed-solvent electrolyte (MSE) model was applied to model solid–liquid equilibrium for the system containing NaCl, NH₄Cl, MEG, and H₂O. Binary interaction parameters for MEG–NH₄⁺, MEG–Na⁺, and Na⁺–NH₄⁺ were newly determined by regressing the experimental data. The MSE model with new parameters presented very high accuracy to calculate solubilities for the NaCl–NH₄Cl–MEG–H₂O system. The average absolute relative deviations (AARD) between the prediction and the experimental solubility are 0.75 and 0.88% for NH₄Cl and NaCl, respectively.



1. INTRODUCTION

The NaCl–NH₄Cl–H₂O system has been extensively investigated due to its importance in areas of atmosphere aerosols, wastewater treatment, and especially the manufacturing of soda.^{1–8} In the soda combination process,⁹ the byproduct NH₄Cl is recovered by a salting-out crystallization with the addition of NaCl as feed. It is known that monoethylene glycol (MEG) is widely used as an effective antisolvent in crystallization separation processes because MEG is almost nonvolatile (has a boiling point of 470.4 K) and can be fully miscible with many inorganic electrolyte solutions, such as NaCl,¹⁰ NH₄Cl,¹¹ Na₂CO₃,¹² MgCl₂,¹³ and CaSO₄.¹⁴ It is of considerable interest to investigate the effect of MEG on the solid–liquid equilibrium of the NaCl–NH₄Cl–H₂O system.

The effect of MEG on the solubility behavior of NaCl in aqueous solutions with or without a secondary salt has been investigated in many studies. The literature data cover a temperature range of (288 to 323) K in MEG–H₂O mixtures from pure water to pure MEG,^{10,15–18} from which the solubility of NaCl were found to decrease with the addition of MEG but is very weakly affected by temperature. Unlike the study on NaCl, there is scarce information on the solubility of NH₄Cl in MEG–H₂O mixtures except for that in pure water or pure MEG.¹¹ Because the solubility of salts in mixed solvents is of more practical and theoretical importance than those in pure solvents, additional measurements on the solubility of NH₄Cl in MEG–H₂O mixtures are required.

Thermodynamic modeling is a useful tool for understanding the solubility behavior of the NaCl–NH₄Cl–MEG–H₂O system and even further for designing and optimizing separation processes that are relevant to this system. A number of models have been developed for calculating solid–liquid equilibria of mixed-solvent electrolyte systems. Some examples are the electrolyte NRTL model,^{19,20} the extended UNIQUAC model,^{21,22} the LIQUAC model,²³ the Pitzer–Simonson–Clegg (PSC) model,²⁴ and the mixed-solvent electrolyte (MSE) model.^{25,26} Recently, Wang et al. developed a comprehensive thermodynamic model based on the MSE framework for calculating thermodynamic and transport properties of a variety of MEG-containing systems.²⁷ The MSE model was shown to accurately represent solubilities for aqueous MEG solutions with single or double salts and thus was used in the present work to model the phase equilibrium of the NaCl–NH₄Cl–MEG–H₂O system.

The objective of this study was to establish a thermodynamic model for the mixed-solvent electrolyte system containing NaCl, NH₄Cl, MEG, and H₂O. Solubilities of solid compounds in the ternary NaCl–MEG–H₂O, NH₄Cl–MEG–H₂O, NaCl–NH₄Cl–H₂O, and the quaternary NaCl–NH₄Cl–MEG–H₂O systems were measured at temperatures from

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(278 to 353) K. The experimental data of ternary systems were correlated by the MSE model to determine binary interaction parameters of the UNIQUAC and the middle-range terms. Using the newly obtained parameters, the solubility of the NaCl–NH₄Cl–MEG–H₂O system was calculated to evaluate the prediction capacity of the modified MSE model.

2. EXPERIMENTAL SECTION

Chemicals. Sodium chloride (NaCl, 0.995 purity), ammonium chloride (NH₄Cl, 0.995 purity), and anhydrous monoethylene glycol (MEG, 0.998 purity) were supplied by Xilong Chemical Plant. All chemical reagents were used without further purification. The sample description is provided in Table 1. Deionized water with a conductivity less than 0.1 $\mu\text{S}\cdot\text{cm}^{-1}$ produced in local laboratory was used in all experiments.

Table 1. Chemical Samples

chemical name	formula	abbreviation	source	initial mass fraction purity ^a
sodium chloride	NaCl		Xilong Chemical Plant	0.995
ammonium chloride	NH ₄ Cl		Xilong Chemical Plant	0.995
ethane-1,2-diol	C ₂ H ₆ O ₂	MEG	Xilong Chemical Plant	0.998

^aAll chemical reagents were used without further purification.

Experimental Procedure. Solubilities for the NaCl(s)–NH₄Cl(s)–MEG–H₂O system were determined by a dynamic method.²⁸ The experiments were carried out in a tightly sealed 250 mL jacketed quartz vessel equipped with a magnetic stirrer. A circulating water bath, which was well-controlled to within ± 0.1 K, afforded thermostatic water through the jacket of the vessel. The investigated temperature range was from (278 to 353) K. All the chemical reagents were weighed with an electronic balance with an uncertainty of ± 0.001 g. In a typical experiment, a mixed MEG–water solvent with a known composition was prepared by weighing and placed in the vessel and then stirred. For the system containing double salts, one salt with a weighed amount was dissolved in the mixed solvent to prepare a solution with a certain concentration. The salt under investigation was then added to the solution with an initial amount equal to 50 wt % of the expected solubility. After it was entirely dissolved, more salt was added little by little until the last trace of solid remained undissolved for 6 h. When the solid was dissolved quite slowly in the solution, roughly 0.010 g of salt was added for each interval to ensure that the relative uncertainty was less than 0.002. The total mass of the salt added prior to the final addition is its solubility for a given condition. When the solubility measurements were completed, excess salt was added to the saturated solution. After 6 h of equilibration, the solid was filtered, washed, dried, and then characterized by the X-ray diffraction (XRD) analysis. Each experiment was replicated three times, and the data reported are the averages of the replicates.

Error Analysis for the measurements was performed based on calculations of the standard deviation (SD) for each experimental point as

$$\text{SD} = \sqrt{\frac{\sum_{i=1}^n (X_i - M)^2}{n - 1}} \quad (1)$$

where X_i represents the individual data point, M is the average value of replicates, and n is the replicate time. Standard deviations of all of the experimental solubility points were calculated. The maximum standard deviation (SD) for the solubility of NH₄Cl in aqueous MEG solution with single salt is 0.026 mol·kg^{−1} (moles of salt dissolved in per kilogram of solvent) and that for the solubility of NaCl is 0.015 mol·kg^{−1}. For the solubility in aqueous MEG solution with double salts, the standard deviation is below 0.007 and 0.012 mol·kg^{−1}, respectively, for NH₄Cl and NaCl.

3. THERMODYNAMIC MODEL

The equilibrium constant is calculated from the standard-state partial molal Gibbs free energy of reaction $\Delta_R \bar{G}^\circ$, as

$$\ln K = -\frac{\Delta_R \bar{G}^\circ}{RT} = -\frac{\sum_i \nu_i \Delta_f \bar{G}_i^\circ}{RT} \quad (2)$$

where ν_i is the stoichiometric coefficient and $\Delta_f \bar{G}_i^\circ$ is the standard-state partial molal Gibbs free energy of formation for species i . For solid species, the values of $\Delta_f \bar{G}_i^\circ$ are calculated from the Gibbs energy of formation and the entropy at the reference state and the heat capacity. For aqueous species, the Helgeson–Kirkham–Flowers (HKF) equation of state^{29–31} is used to calculate the standard-state properties including $\Delta_f \bar{G}_i^\circ$. The parameters of the HKF model are available for a large number of aqueous species in the literature. In OLI systems, the molality-based standard-state properties are converted to corresponding mole-fraction-based quantities.²⁵

In the MSE model, the excess Gibbs energy (G^E), which represents the nonideality of an electrolyte solution, is expressed as²⁵

$$\frac{G^E}{RT} = \frac{G_{LR}^E}{RT} + \frac{G_{MR}^E}{RT} + \frac{G_{SR}^E}{RT} \quad (3)$$

where G_{LR}^E stands for the long-range electrostatic interactions, G_{MR}^E represents the middle-range interactions for specific ionic interactions (ion–ion and ion–molecule) that are not included in the long-range term, and G_{SR}^E is the short-range contribution that takes into account the local interactions between ion–ion, ion–molecule, and molecule–molecule. For all the three terms of G^E , the activity coefficients are converted from symmetrical normalization to those based on the unsymmetrical reference state so that they are consistent with the HKF model for standard-state properties.²⁵ The long-range term is calculated from the Pitzer–Debye–Hückel expression.³² The middle-range term is represented by a symmetrical second virial coefficient-type expression

$$\frac{G_{MR}^E}{RT} = -\left(\sum_i n_i\right) \sum_i \sum_j x_i x_j B_{ij}(I_x) \quad (4)$$

where x is the mole fraction of a given species, and $B_{ij}(I_x)$ is a binary interaction parameter between the species i and j (ion or molecule), which is a function of ionic strength expressed by

$$B_{ij}(I_x) = b_{ij} + c_{ij} \exp(-\sqrt{I_x + 0.01}) \quad (5)$$

where $B_{ij}(I_x) = B_{ji}(I_x)$ and $B_{ii}(I_x) = B_{jj}(I_x) = 0$. b_{ij} and c_{ij} are temperature-dependent coefficients calculated by

$$b_{ij} = b_{0,ij} + b_{1,ij}T + b_{2,ij}/T + b_{3,ij}T^2 + b_{4,ij}\ln T \quad (6)$$

$$c_{ij} = c_{0,ij} + c_{1,ij}T + c_{2,ij}/T + c_{3,ij}T^2 + c_{4,ij}\ln T \quad (7)$$

where T is the temperature in Kelvin, $b_{0,ij}$, $b_{1,ij}$, $c_{0,ij}$, $c_{1,ij}$ and so forth are adjustable parameters between species i and j that can be obtained by the regression of experimental data.

The short-range term is calculated by the UNIQUAC equation.³³ The Gibbs free energy calculated from the UNIQUAC equation is a combination of a combinatorial term G^C and a residual term G^R . In the MSE model, parameters a_{ij} and a_{ji} in the UNIQUAC equation are expressed using a quadratic function of the temperature²⁵

$$a_{ij} = a_{0,ij} + a_{1,ij}T + a_{2,ij}T^2 \quad (8)$$

$$a_{ji} = a_{0,ji} + a_{1,ji}T + a_{2,ji}T^2 \quad (9)$$

where T is the temperature in Kelvin, $a_{0,ij}$, $a_{0,ji}$ and so forth are adjustable parameters between species i and j that can be obtained by the regression of experimental data such as the solubility.

4. RESULTS AND DISCUSSION

Solubilities of NH_4Cl and NaCl in the MEG– H_2O Mixtures. The solubility measurements for NH_4Cl and NaCl in aqueous MEG solutions were carried out by the dynamic method as described above. To verify the validity and accuracy of this experimental procedure, the solubilities of salts in pure MEG determined in this work were compared with those in the literature^{11,15,16} as provided in Table 2 and Figure 1. It indicates

Table 2. Comparison of the Experimental and Literature Values for the Solubilities of NaCl and NH_4Cl in Pure MEG at the Pressure $p = 0.1$ MPa^a

T , K	NaCl , mol·kg ⁻¹ solvent			NH_4Cl , mol·kg ⁻¹ solvent		
	this work	literature value	relative deviation	this work	literature value	relative deviation
298	1.201	1.198 ^b	0.25%	1.895		
313	1.191			2.062	2.008 ^d	2.69%
323	1.164	1.170 ^c	−0.51%	2.185		
353	1.173			2.551	2.525 ^d	1.03%

^aStandard uncertainties u are $u(T) = 0.10$ K, $u_r(p) = 0.05$, and $u_r(m) = 0.02$. Data taken from the literature: ^bref 15, ^cref 16, and ^dref 11.

that the solubility values obtained in this study are in good agreement with the data reported in the literature within the temperature range of (298 to 353) K, for which the maximum relative deviation is less than 2.7%.

The solubility of NH_4Cl in the MEG– H_2O mixtures containing (0 to 1) mole fraction of MEG was measured at (278, 288, 298, 313, 333, and 353) K. The solubility data are compiled in Table 3 and depicted in Figure 2 (symbols) in terms of moles of NH_4Cl dissolved in 1 kg of mixed solvent (mol·kg⁻¹ solvent). Figure 2 demonstrates that the composition of the mixed solvent has a significant effect on the NH_4Cl solubility. As would be expected, the addition of MEG to water decreases the solubility of NH_4Cl . It is also shown in Figure 2 that the solubility of NH_4Cl increases with increasing temperature. In pure water, the solubility of NH_4Cl increases

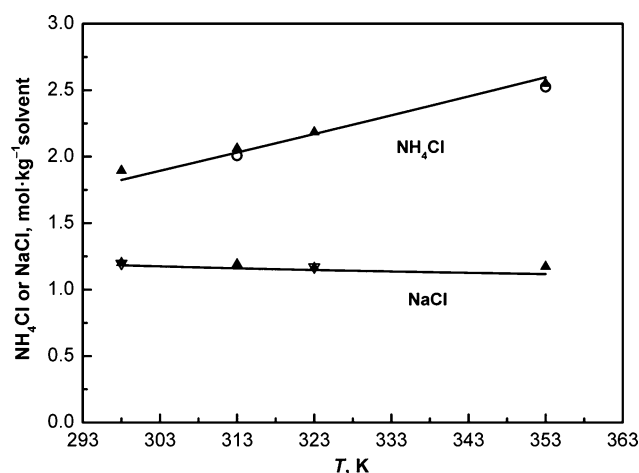


Figure 1. Comparison of the experimental and literature values for the solubilities of NaCl and NH_4Cl in pure MEG at different temperatures. \blacktriangle , this work; \circ , Pownceby et al.;¹¹ ∇ , Kraus et al.¹⁵ and Baldwin et al.;¹⁶ solid lines (—), OLI MSE model calculation.

from 5.835 mol·kg⁻¹ at 278 K to 11.906 mol·kg⁻¹ at 353 K. In pure MEG, the increment in solubility is relatively less in the same temperature range; that is, it increases from 1.489 to 2.551 mol·kg⁻¹.

Experimental results for the solubility of NaCl in the MEG– H_2O mixtures at (278, 298, 313, 323, and 353) K over the entire solvent composition range are given in Table 4 and depicted in Figure 3 (symbols). The solubilities at 298 and 323 K taken from the literature^{15,16} are also plotted in Figure 3 for comparison. Similar to NH_4Cl , the solubility of NaCl decreases considerably with increasing mole fraction of MEG. However, the increase of temperature only results in a negligible variation in the solubility of NaCl from (278 to 353) K in the mixed solvent. The solubility of NaCl at 353 K is slightly higher (5.6%) than that at 278 K in pure water while less (7.3%) than that at 278 K in pure MEG.

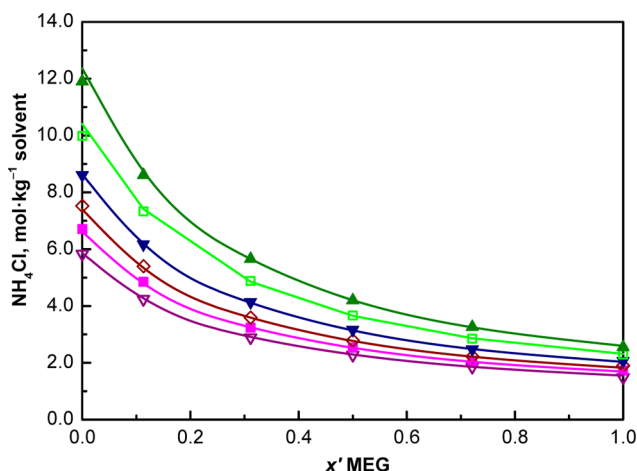
Phase Equilibria in the NaCl – NH_4Cl –MEG– H_2O System. The measured solubility data in the temperature range of (278 to 353) K for NH_4Cl and NaCl in the NaCl – NH_4Cl –MEG– H_2O system are summarized in Table 5 and depicted in Figure 4. The solvent composition of all the investigated solutions was kept constant at 0.3 mole fraction for MEG on a salt-free basis, that is, 60 wt % when converted to mass fraction. As can be seen in Figure 4, addition of NaCl results in a decrease in the solubility of NH_4Cl over the investigated temperature and concentration ranges. The same effect can be found for NH_4Cl on the solubility of NaCl due to the common ion effect of the chloride ion. As also illustrated in Figure 4, temperature has a very different effect on the solubility of NH_4Cl and that of NaCl . At a constant concentration of NaCl , the solubility of NH_4Cl increases obviously with increasing temperature from 278 to 353 K. For example, in an aqueous MEG solution containing 0.501 mol·kg⁻¹ of NaCl , the solubility of NH_4Cl increases almost 2-fold from 2.612 to 5.335 mol·kg⁻¹ when the temperature increases from 278 to 353 K. As with the solubility of NaCl , however, the impact of temperature is relatively weak.

Additionally, solubilities of NH_4Cl and NaCl in the NaCl – NH_4Cl – H_2O system (without MEG) at 353 K were also determined. The experimental results are depicted in Figure 5 and listed in Table 5. Table 5 also provides the density values of

Table 3. Experimental Solubility of NH_4Cl in the MEG– H_2O Mixtures at Temperatures from (278 to 353) K and at the Pressure $p = 0.1 \text{ MPa}$ ^a

$x'(\text{MEG})^b$	MEG, wt %	$m(\text{NH}_4\text{Cl}), \text{mol}\cdot\text{kg}^{-1} \text{ solvent}$					
		278 K	288 K	298 K	313 K	333 K	353 K
0.00	0	5.835	6.708	7.526	8.610	9.987	11.906
0.11	30.5	4.241	4.851	5.402	6.168	7.327	8.611
0.31	60.9	2.888	3.237	3.586	4.134	4.880	5.660
0.50	77.5	2.274	2.539	2.788	3.160	3.660	4.199
0.72	89.9	1.855	2.045	2.220	2.474	2.845	3.260
1.00	100	1.489	1.724	1.895	2.062	2.288	2.551

^aStandard uncertainties u are $u(T) = 0.10 \text{ K}$, $u_r(p) = 0.05$, $u(x') = 0.01$, and $u_r(m) = 0.02$. ^b x' represents the salt-free-based mole fraction of MEG.

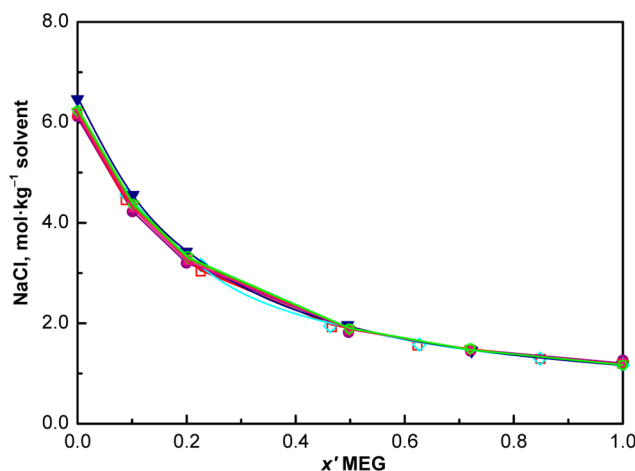
**Figure 2.** Experimental solubility of NH_4Cl in the MEG– H_2O mixtures. ▽, 278 K; ■, 288 K; ◇, 298 K; ▼, 313 K; □, 333 K; ▲, 353 K; solid lines (—), new model calculation.**Table 4.** Experimental Solubility of NaCl in the MEG– H_2O Mixtures at Temperatures from (278 to 353) K and at the Pressure $p = 0.1 \text{ MPa}$ ^a

$x'(\text{MEG})^b$	MEG, wt %	$m(\text{NaCl}), \text{mol}\cdot\text{kg}^{-1} \text{ solvent}$				
		278 K	298 K	313 K	323 K	353 K
0.00	0	6.115	6.164	6.212	6.236	6.460
0.10	27.8	4.224	4.298	4.359	4.375	4.554
0.20	46.2	3.200	3.247	3.306	3.333	3.428
0.50	77.3	1.818	1.857	1.886	1.894	1.962
0.72	90.0	1.449	1.467	1.494	1.500	1.451
1.00	100	1.265	1.201	1.191	1.164	1.173

^aStandard uncertainties u are $u(T) = 0.10 \text{ K}$, $u_r(p) = 0.05$, $u(x') = 0.01$, and $u_r(m) = 0.02$. ^b x' represents the salt-free-based mole fraction of MEG.

saturated solutions with different temperatures and concentrations that were calculated by OLI Stream Analyzer 9.1.³⁴

Model Parameterization. To calculate the solubility of NH_4Cl in the MEG– H_2O mixtures by the MSE model, interaction parameters for the MEG– NH_4^+ molecule–ion pair are required, and these are also essential to further model the NaCl – NH_4Cl –MEG– H_2O system. However, parameters for the MEG– NH_4^+ interaction are not available either in the literature or in the OLI's databank due to the lack of experimental data for aqueous systems containing NH_4Cl and MEG. Therefore, new parameters for the MEG– NH_4^+ interaction were determined via the regression of the NH_4Cl solubility in the MEG– H_2O mixtures obtained in this work

**Figure 3.** Solubility of NaCl in the MEG– H_2O mixtures. In this work: ●, 278 K; ■, 298 K; ▽, 313 K; ○, 323 K; ▼, 353 K. In the literature: □, 298 K, Kraus et al.;¹⁵ ◇, 323 K, Baldwin et al.;¹⁶ solid lines (—), new model calculation.

from (278 to 353) K. The determined parameters are listed in Table 6, including those for the UNIQUAC and the middle-range terms. The comparison between the regressed (solid lines) and the experimental solubilities (symbols) for the NH_4Cl –MEG– H_2O system was shown in Figure 2. The relative deviation (RD) and the average absolute relative deviation (AARD) were calculated by the following equations.

$$\text{RD}_i = \frac{X_{i,\text{calc}} - X_{i,\text{exp}}}{X_{i,\text{exp}}} \times 100\% \quad (10)$$

$$\text{AARD} = 1/n \sum_{i=1}^n \frac{|X_{i,\text{calc}} - X_{i,\text{exp}}|}{X_{i,\text{exp}}} \times 100\% \quad (11)$$

where $X_{i,\text{calc}}$, $X_{i,\text{exp}}$ refer to the calculated and experimental values for the individual point i , respectively, and n denotes the number of data points. The relative deviation for each point is plotted in Figure 6. It is obviously shown in Figures 2 and 6 that all the regressed solubility data are in agreement with the experimental values with 1.09% AARD.

Model parameters for the NaCl –MEG– H_2O system including interactions for the Na^+ – Cl^- , MEG– Na^+ , MEG– Cl^- , and MEG– H_2O pairs were determined by Kosinski et al.²⁶ and Wang et al.²⁷ and now are also available in the OLI's databank as summarized in Table 6. Of these parameters, binary interaction parameters for MEG– Na^+ were newly regressed in order to improve the calculation ability of the MSE model for multicomponent systems investigated in this

Table 5. Experimental Solubilities of NH_4Cl and NaCl in the NaCl – NH_4Cl –MEG– H_2O System for $(x' \text{ MEG} = 0.30)^a$ at Temperatures from (278 to 353) K and at the Pressure $p = 0.1 \text{ MPa}^b$

$m(\text{NaCl})$	$m(\text{NH}_4\text{Cl})$	ρ^c	solid phase	$m(\text{NaCl})$	$m(\text{NH}_4\text{Cl})$	ρ^c	solid phase
mol·kg ⁻¹	mol·kg ⁻¹	g·mL ⁻¹		mol·kg ⁻¹	mol·kg ⁻¹	g·mL ⁻¹	
$T = 278 \text{ K}$				$T = 298 \text{ K}$			
0.000	2.889	1.1199	NH ₄ Cl	0.000	3.609	1.1166	NH ₄ Cl
0.202	2.759	1.1254	NH ₄ Cl	0.202	3.487	1.1215	NH ₄ Cl
0.501	2.612	1.1338	NH ₄ Cl	0.501	3.304	1.1286	NH ₄ Cl
1.002	2.300	1.1475	NH ₄ Cl	1.002	2.968	1.1404	NH ₄ Cl
1.194	2.185	1.1528	NH ₄ Cl	1.193	2.848	1.1449	NH ₄ Cl
1.696	1.957	1.1668	NH ₄ Cl + NaCl ^d	1.576	2.633	1.1542	NH ₄ Cl + NaCl ^d
2.514	0.000	1.1835	NaCl	2.577	0.000	1.1664	NaCl
2.302	0.503	1.1793	NaCl	2.352	0.503	1.1632	NaCl
2.059	1.001	1.1741	NaCl	2.139	1.001	1.1603	NaCl
1.869	1.498	1.1702	NaCl	1.797	1.996	1.1562	NaCl
1.736	1.904	1.1672	NaCl	1.626	2.602	1.1543	NaCl
$T = 313 \text{ K}$				$T = 333 \text{ K}$			
0.000	4.176	1.1121	NH ₄ Cl	0.000	4.928	1.1024	NH ₄ Cl
0.202	4.048	1.1166	NH ₄ Cl	0.202	4.788	1.1067	NH ₄ Cl
0.501	3.852	1.1233	NH ₄ Cl	0.501	4.571	1.1131	NH ₄ Cl
1.002	3.509	1.1345	NH ₄ Cl	0.800	4.381	1.1196	NH ₄ Cl
1.084	3.428	1.1362	NH ₄ Cl	0.918	4.275	1.1222	NH ₄ Cl
1.507	3.155	1.1458	NH ₄ Cl + NaCl ^d	1.427	3.882	1.1332	NH ₄ Cl + NaCl ^d
2.620	0.000	1.1558	NaCl	2.650	0.000	1.1408	NaCl
2.409	0.503	1.1527	NaCl	2.456	0.503	1.1391	NaCl
2.203	1.001	1.1505	NaCl	2.264	1.001	1.1373	NaCl
1.861	1.996	1.1478	NaCl	1.933	1.996	1.1353	NaCl
1.522	3.189	1.1458	NaCl	1.416	3.999	1.1330	NaCl
$T = 353 \text{ K}$				$T = 353 \text{ K } (x' \text{ MEG} = 0)$			
0.000	5.731	1.0895	NH ₄ Cl	0.000	11.906	1.0783	NH ₄ Cl
0.202	5.567	1.0938	NH ₄ Cl	1.004	11.029	1.0958	NH ₄ Cl
0.501	5.335	1.1002	NH ₄ Cl	1.997	10.256	1.1136	NH ₄ Cl
0.800	5.113	1.1068	NH ₄ Cl	2.525	9.830	1.1231	NH ₄ Cl
1.352	4.655	1.1188	NH ₄ Cl + NaCl ^d	3.007	9.581	1.1320	NH ₄ Cl
2.700	0.000	1.1268	NaCl	3.969	8.600	1.1502	NH ₄ Cl + NaCl ^d
2.498	0.503	1.1251	NaCl	6.460	0.000	1.1745	NaCl
2.346	1.001	1.1236	NaCl	5.589	2.001	1.1643	NaCl
2.010	1.996	1.1217	NaCl	4.920	3.956	1.1576	NaCl
1.412	4.540	1.1190	NaCl	4.295	5.998	1.1509	NaCl
				3.775	7.976	1.1450	NaCl

^a x' represents the salt-free-based mole fraction of MEG. ^bStandard uncertainties u are $u(T) = 0.10 \text{ K}$, $u_r(p) = 0.05$, $u_r(x') = 0.01$, and $u_r(m) = 0.02$. ^cDensity values were calculated by OLI Stream Analyzer 9.1. ^dMultiple saturation points were predicted by using newly obtained parameters of the MSE model.

study. A comparison of calculation results by using these parameters with the experimental solubility from this work and the literature is shown in Figure 3. As can be observed, the model calculated the solubility of NaCl in MEG – H_2O mixtures from (278 to 353) K with good accuracy. Relative deviations are plotted in Figure 6, for which the AARD is 1.16%.

Solubilities of NaCl and NH_4Cl in the NaCl – NH_4Cl – H_2O system reported in the literature^{35,36} at (273, 323, and 373) K were regressed by the MSE model to obtain parameters for the Na^+ – NH_4^+ interaction. Binary interaction parameters of the middle-range term for Na^+ – Cl^- and NH_4^+ – Cl^- were kept the same as those in the OLI default databank and are listed in Table 6. The calculated solubilities at (273, 323, and 373) K for both salts, as shown in Figure 5, are in good agreement with those from the literature. The AARD is 1.14% for NH_4Cl and 1.6% for NaCl .

Solubility Calculation. To test the predictive ability of the new model, calculations were performed for the multi-component NaCl – NH_4Cl – MEG – H_2O system by using parameters derived from the solubility data of simpler systems as mentioned above. To be specific, solubilities of NH_4Cl and NaCl in the mixed-solvent MEG – H_2O containing both salts were calculated from (278 to 353) K. The calculation results are depicted in Figure 4. It is obvious that all the calculated values agreed well with the experimental solubilities. The relative deviations were calculated and plotted in Figure 7. As can be observed from Figure 7, the relative deviations for the solubility of NH_4Cl are within the range of -2% to 2% with the AARD of 0.75%, whereas for the solubility of NaCl , they are within -2% to 3% with the AARD of 0.88%, indicating that the newly obtained parameters are capable of accurately calculating solubilities for the NaCl – NH_4Cl – MEG – H_2O system.

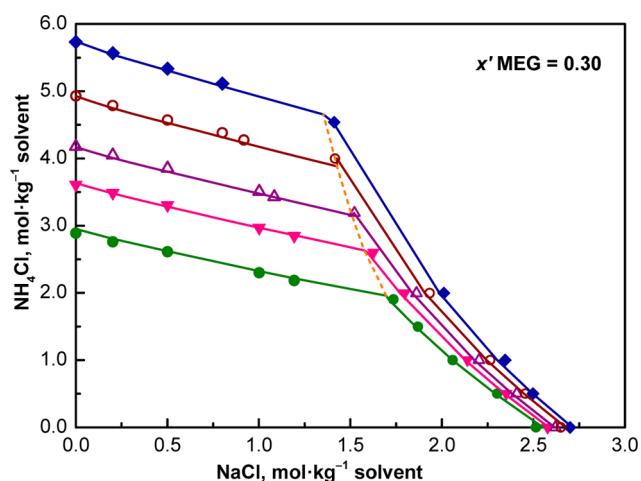


Figure 4. Experimental solubilities of NH_4Cl and NaCl in the NaCl – NH_4Cl – MEG – H_2O system. \bullet , 278 K; \blacktriangledown , 298 K; \triangle , 313 K; \circ , 333 K; \blacklozenge , 353 K; solid lines (—), new model calculation; dashed line (---), multiple saturation points predicted by the new model.

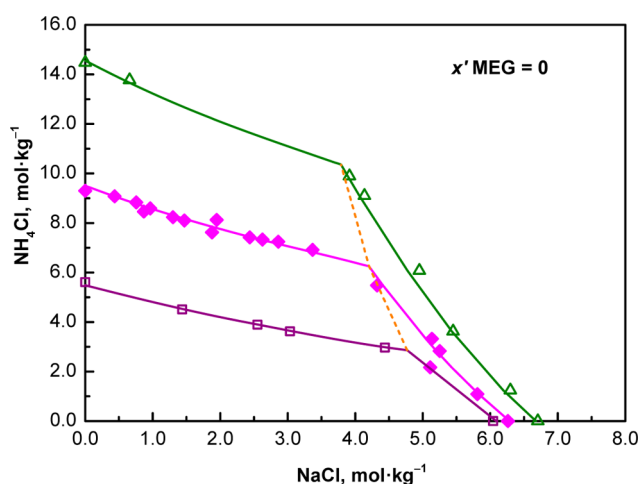


Figure 5. Solubilities of NH_4Cl and NaCl in the NaCl – NH_4Cl – H_2O system. \square , 273 K, Linke and Seidell;³⁵ \blacklozenge , 323 K, Silcock;³⁶ \triangle , 373 K, Silcock;³⁶ solid lines (—), new model calculation; dashed line (---), multiple saturation points predicted by new model.

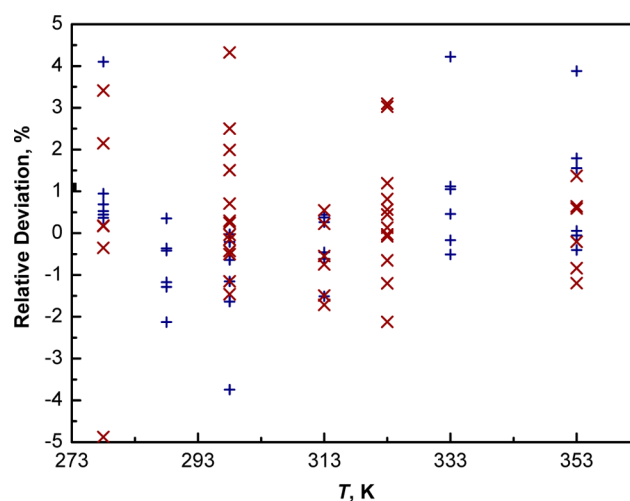


Figure 6. Relative deviations between the regressed values and the experimental data for the solubilities of NH_4Cl and NaCl , respectively, in the MEG – H_2O mixtures. +, NH_4Cl ; x, NaCl .

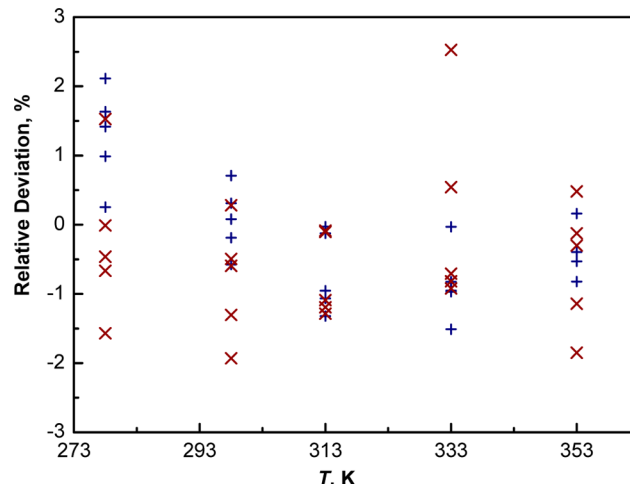


Figure 7. Relative deviations between the calculated values the experimental data for solubilities in the NaCl – NH_4Cl – MEG – H_2O system. +, NH_4Cl ; x, NaCl .

Table 6. MSE Model Parameters of the UNIQUAC and the Middle-Range Interactions for the NaCl – NH_4Cl – MEG – H_2O System

species		UNIQUAC interaction parameters					
<i>i</i>	<i>j</i>	$a_{0,ij}$	$a_{0,ji}$	$a_{1,ij}$	$a_{1,ji}$	$a_{2,ij}$	$a_{2,ji}$
MEG	H_2O^a	1.956597×10^2	$-2.125369 \cdot 10^2$	$-1.772271 \cdot 10$	$3.150075 \cdot 10$	$2.244026 \cdot 10^{-2}$	$-5.463013 \cdot 10^{-2}$
MEG	NH_4^+	$8.859905 \cdot 10^3$	$8.738450 \cdot 10^2$	0	0	0	0
MEG	Na^+	$1.064302 \cdot 10^3$	$3.774311 \cdot 10^3$	0	0	0	0
MEG	Cl^-	$1.521117 \cdot 10^3$	$2.238015 \cdot 10^3$	0	0	0	0
species		middle-range interaction parameters					
<i>i</i>	<i>j</i>	$b_{0,ij}$	$b_{1,ij}$	$b_{2,ij}$	$c_{0,ij}$	$c_{1,ij}$	$c_{2,ij}$
MEG	NH_4^+	5.945064	0	$-8.292285 \cdot 10^2$	$-8.538574 \cdot 10^{-1}$	0	0
MEG	Na^+	2.157143	0	$-3.022264 \cdot 10^2$	$-2.711171 \cdot 10^{-1}$	0	0
MEG	Cl^-	-8.698285	0	$9.832170 \cdot 10^2$	8.841474	0	0
Na^+	NH_4^+	$5.538967 \cdot 10$	$-1.028922 \cdot 10^{-1}$	$-1.253665 \cdot 10^4$	$2.901004 \cdot 10$	0	0
NH_4^+	Cl^-	$4.369664 \cdot 10^3$	2.325859	$-9.627391 \cdot 10^4$	$-9.748479 \cdot 10^3$	-5.062129	$2.197460 \cdot 10^5$
Na^+	Cl^-	$-2.139990 \cdot 10^2$	1.863230	$1.603680 \cdot 10^4$	$2.02887 \cdot 10^2$	-2.153910	$-9.832110 \cdot 10^3$

^aParameters for MEG – H_2O , MEG – Cl^- , NH_4^+ – Cl^- , and Na^+ – Cl^- were taken from the default databank of OLI systems (version 9.1).

Moreover, multiple saturation points for the NaCl–NH₄Cl–MEG–H₂O system containing 0.3 mole fraction of MEG in the solvent at temperatures from (278 to 353) K were predicted by using new parameters. Calculation results are reported in Table 5 and illustrated in Figure 4. The prediction was carried out in OLI Stream Analyzer 9.1 by calculating the scaling tendency values (supersaturation) of the involved salts as a function of temperature and the solution composition. A detailed description of this method for calculating multiple saturation points has been presented in our previous study.²⁸

5. CONCLUSIONS

The solubilities of NH₄Cl and NaCl in the NH₄Cl–MEG–H₂O, NaCl–MEG–H₂O, and NaCl–NH₄Cl–MEG–H₂O solutions were measured at temperatures ranging from (278 to 353) K. Effects of temperature, MEG, and electrolyte concentration on the solubility of both salts were thereby investigated. The experimentally determined solubilities and those reported for the NH₄Cl–MEG–H₂O, NaCl–MEG–H₂O, and NaCl–NH₄Cl–H₂O systems were modeled by using the mixed-solvent electrolyte (MSE) framework, from which new parameters for the MEG–NH₄⁺, MEG–Na⁺, and Na⁺–NH₄⁺ interactions were obtained. The MSE model with new parameters is capable of calculating solid–liquid equilibrium for the mixed-solvent electrolyte solutions containing NH₄Cl, NaCl, MEG, and H₂O over the temperature range of (278 to 353) K up to the multiple saturation points.

■ ASSOCIATED CONTENT

Supporting Information

Two figures (Figures S1 and S2) presenting the XRD patterns of solid phases in the NaCl–NH₄Cl–MEG–H₂O at 298 and 333 K are shown. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.5b00053.

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Notes

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■ NOMENCLATURE

a = activity

a_{ij} = UNIQUAC interaction parameter between species i and j

a_{ji} = UNIQUAC interaction parameter between species j and i

A_x = Debye–Hückel parameter

b_{ij} = middle-range interaction parameter between species i and j

B_{ij} = middle-range interaction parameter between species i and j

$b_{0,ij}$, $b_{1,ij}$, $b_{2,ij}$, and $b_{3,ij}$ = middle-range adjustable parameters of the MSE model

c_{ij} = middle-range interaction parameter between species i and j

$c_{0,ij}$, $c_{1,ij}$, $c_{2,ij}$, and $c_{3,ij}$ = middle-range adjustable parameters of the MSE model

G^E = excess Gibbs free energy

I_x = ionic strength on the mole fraction basis

K = dissociation or dissolution equilibrium constant

m = molality (mol·kg^{−1} solvent)

n_i = number of moles of i

P = pressure, Pa

$a_{0,ij}$, $a_{1,ij}$, $a_{2,ij}$, $a_{0,ji}$, $a_{1,ji}$, and $a_{2,ji}$ = short-range adjustable parameters of the MSE model

R = gas constant (8.314 J·mol^{−1}·K^{−1})

T = absolute temperature (K)

x_i = mole fraction of species i

x' = mole fraction of solvent on a salt-free basis

γ_i = activity coefficient of species i

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