1472 *J. Chem. Eng. Data* **2002,** *47,* 1472−1475

Solubility of Two Salts Containing Sulfate and Chloride Ions in Water for Ternary Systems at 313 K

Kouji Maeda,*,[†] Hidetoshi Kuramochi,[‡] Tomonori Shinkawa,[†] and Keisuke Fukui[†]

Department of Chemical Engineering, Himeji Institute of Technology, 2167 Shosha, Himeji, Hyogo 671-2201, Japan, and National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba-shi, Ibaraki 305-8506, Japan

The solubilities of three sulfate salts (Na_2SO_4, K_2SO_4, $MgSO_4$) and two chloride salts (NaCl, KCl) with a second salt in water were measured at 313 K. The ternary systems studied were water + NaCl + KCl, water + NaCl + Na_2SO_4, water + KCl + K_2SO_4, water + Na_2SO_4 + K_2SO_4, water + K_2SO_4 + $MgSO_4$, and water + Na_2SO_4 + $MgSO_4$. The solubilities of two salts in the ternary systems were obtained, and the data were used to obtain the eutectic concentrations of the ternary systems. The solubility data were also predicted by the electrolyte−NRTL model, in which parameters were obtained from the binary data. The qualitative effect of the second salt on the solubility of the first salt in water is discussed.

Introduction

The solubility of sulfate and chloride salts in aqueous solutions is of fundamental importance in the inorganic chemicals industry. The salts of highly concentrated electrolytes in aqueous solutions need to be crystallized out even though the saturated solution is not sufficiently concentrated to make it supersaturated. Kim and Myerson[1] described the different driving forces of crystallization on the basis of general concentration and activity. Activity coefficients of electrolytes in aqueous metastable solutions are required. In early studies, Pitzer[2−5] derived the thermodynamic equations for the activity coefficient of an electrolyte solution using the Debye−Hückel model, and co-workers[6] have applied several modified models to electrolyte solutions. The local composition model is an alternative for reproducing the activity coefficients of many electrolytes in practice. Cruz and Renon[7] first considered the NRTL model combined with the Debye−Hückel model in 1978. Since the 1980s, Chen and Evans[8,9] have also applied the electrolyte−NRTL model to electrolyte solutions; they took both the short-range and long-range interactions into consideration and obtained good reproducibility of activity coefficients of electrolytes for relatively high concentrations of salts in aqueous solutions. In this study, we measured the mutual solubilities of two salts in water and discussed the prediction of those solubilities by the electrolyte−NRTL model.

Experimental Section

All crystal salts used for the study were purchased from Sigma-Aldrich Corporation and were of extrapure grade. The solvent water was distilled and used to dissolve the salts for the solubility experiments. With reference to binary solubility data,[10] an adequate amount of the second salt that should be unsaturated in water was first dissolved completely at (313 ± 0.5 K). Several solutions having the same concentration of the second salt were prepared. These solutions having different concentrations of the first salt were then prepared and were left with agitation at (313 ± 0.5) K in a thermostat bath for several days. Some unsaturated solutions and one saturated solution were obtained. To determine the saturated concentration of the first salt, we constructed a calibration curve of a refractometer by using the unsaturated solutions and determined the concentration of one saturated solution. We continued to measure the solubility of the first salt for different contents of the second salt to obtain one solubility curve of the first salt. By changing the first salt to the second salt, another solubility curve of the second salt could be obtained for the same ternary system. The solubility data obtained from the experiments were expressed in units of molality. The temperature uncertainty and salt concentrations were ±0.5 K and 0.001 mol/kg of H_2O, respectively.

Results and Discussion

The experimental and predicted data are listed in Table 1. Solubility data were obtained for six ternary systems, with two individual solubility curves of two salts for each system. The values of the first column show the molality (m_1) of the first salt, and they were unsaturated. The values of the second column show the saturated molality (m_2) of the second salt. The predictive saturated molality ($m_{2\text{cal}}$) mentioned later was also listed in Table 1. When analyzing the effect of the second salt on the solubility of the first salt in water, the thermodynamic equations should be considered for our data. The electrolyte solutions are more difficult to be modeled than molecular solutions. In a previous study, Pitzer[2] described the electrolyte solution model with the Debye−Hückel theory and successfully derived the activity coefficient of the dilute electrolyte solution. In fact, the activity coefficients of dilute electrolytes in aqueous solution depend only on ion length. However, a requirement of a practical model is that it can be applied to highly concentrated electrolyte solutions. The electrolyte−NRTL model is most convenient and useful because of its simplicity and its extensive use. Here, we use Chen's electrolyte−NTRL model[8, 9] to predict the solubilities of two salts for ternary systems. Unfortunately, the electrolyte-specific parameters and local electric neutralization defined in their paper are unsuccessful for predicting the activity coefficients of mixed salts on the

---

* Corresponding author. E-mail: maeda@cheng.eng.himeji-tech.ac.jp.
[†] Himeji Institute of Technology.
[‡] National Institute for Environmental Studies.

10.1021/je0255426 CCC: $22.00

Table 1. Experimental and Predicted Data of Solubilities of Two Salts in Water for Ternary Systems at 313.15 K

m_1/ mol·kg^{-1}	m_2, m_{2cal}/ mol·kg^{-1}	m_1/ mol·kg^{-1}	m_2, m_{2cal}/ mol·kg^{-1}
K_2SO_4 (1) + $MgSO_4$ (2)		$MgSO_4$ (1) + K_2SO_4 (2)	
0.000	3.722, 3.548	0.000	0.855, 0.778
0.043	3.675, 3.537	0.372	0.868, 0.801
0.086	3.598, 3.526	0.744	0.873, 0.799
0.171	3.592, 3.504	1.489	0.880, 0.770
		1.861	0.881, 0.752
KCl (1) + K_2SO_4 (2)		K_2SO_4 (1) + KCl (2)	
0.000	0.855, 0.778	0.000	5.366, 5.265
0.537	0.578, 0.600	0.043	5.316, 5.246
1.073	0.413, 0.470	0.086	5.312, 5.226
1.610	0.365, 0.379	0.171	5.167, 5.186
2.146	0.264, 0.316		
Na_2SO_4 (1) + K_2SO_4 (2)		K_2SO_4 (1) + Na_2SO_4 (2)	
0.000	0.855, 0.778	0.000	3.435, 3.670
0.344	0.813, 0.865	0.086	3.426, 3.678
0.687	0.737, 0.940	0.171	3.416, 3.686
1.031	0.692, 1.002	0.257	3.348, 3.692
1.374	0.595, 1.051	0.342	3.275, 3.698
1.718	0.552, 1.091		
Na_2SO_4 (1) + $MgSO_4$ (2)		$MgSO_4$ (1) + Na_2SO_4 (2)	
0.000	3.722, 3.548	0.000	3.435, 3.670
0.172	3.685, 3.522	0.372	3.407, 3.576
0.344	3.681, 3.493	0.744	3.296, 3.401
0.687	3.526, 3.426	1.117	3.140, 3.387
1.031	3.508, 3.350	1.489	3.114, 3.294
1.374	3.343, 3.269		
NaCl (1) + KCl (2)		KCl (1) + NaCl (2)	
0.000	5.366, 5.265	0.000	6.229, 6.293
0.537	4.941, 4.830	0.623	5.780, 5.875
1.073	4.789, 4.428	1.246	5.295, 5.483
1.610	4.407, 4.057	1.869	4.776, 5.116
2.146	4.132, 3.714	2.492	4.540, 4.772
NaCl (1) + Na_2SO_4 (2)		Na_2SO_4 (1) + NaCl (2)	
0.000	3.435, 3.670	0.000	6.229, 6.293
0.311	2.873, 3.440	0.172	5.948, 6.148
0.623	2.792, 3.220	0.687	5.618, 5.724
1.246	2.334, 2.807	1.031	5.112, 5.450
1.869	2.131, 2.432	1.374	4.444, 5.184
2.491	2.135, 2.094		

basis of the binary parameters alone. Their model requires additional parameters such as interaction energy parameters between an electrolyte and another electrolyte for multicomponent prediction. Therefore, the NRTL parameters used in this study were treated as ion-specific parameters. In addition, the local electric neutralization for anions and cations was not considered. These corrections enable one to predict the activity coefficient of any ion species in a multicomponent system without any additional parameters. The calculation procedure and explanation of the used equations are described immediately below.

The molality unit (m) of our solubility data can be converted to true mole fraction unit (x) in an electrolyte aqueous solution as follows:

$$x_+ = \frac{\upsilon_+ m}{\dfrac{1000}{M_s} + m(\upsilon_+ + \upsilon_-)}, \quad x_- = \frac{\upsilon_- m}{\dfrac{1000}{M_s} + m(\upsilon_+ + \upsilon_-)} \tag{1}$$

M_s is the molecular weight of water. The rigorous solubility product (K_a) of the salt in the solution is given by activity (a) as follows:

$$K_a = a_+^{\upsilon_+} a_-^{\upsilon_-} = (\gamma_+^* x_+)^{\upsilon_+} (\gamma_-^* x_-)^{\upsilon_-} \tag{2}$$

which is a function of the unsymmetric activity coefficients (γ^*) and mole fractions of the ions in the solution. $\upsilon_\pm$ is the stoichiometric number when the salt is perfectly dissociated. We defined the solubility product as an Arrhenius function of temperature:

$$R \ln K_a = A + \frac{B}{T} \tag{3}$$

Here, R is the gas constant, and A and B are parameters of the solubility product for pure salts. These parameters are almost constant even though the salts are dissolved in various solutions. The activity coefficients of ions are significant variables which show the difference of solubility between the cases with or without the second salt. The unsymmetric activity coefficient is

$$\ln \gamma_i^* = \ln \gamma_{i,\mathrm{pdh}}^* + \ln \gamma_{i,\mathrm{NRTL}}^* \tag{4}$$

The first term of the right-hand side of eq 4 is the contribution of the long-range interaction of ions and is given by the Pitzer–Debye–Hückel equation:

$$\ln \gamma_{i,\mathrm{pdh}}^* = -(1000/M_s)^{1/2} A_\phi \{(2z_i^{\,2}/\rho) \ln(1 + \rho I_z^{1/2}) + (z_i^{\,2} I_z^{1/2} - 2I_z^{3/2})/(1 + \rho I_z^{1/2})\} \tag{5}$$

When the closest approach parameter (ρ) is constant, only ion strength (I) is the essential variable in eq 5. We used the value of the Pitzer–Debye–Hückel (A_ϕ) parameter given in Chen's paper.[8,9] Ion strength is given by

$$I = \frac{1}{2}\sum_i^N z^2 x_i \tag{6}$$

z is ion charge. The Pitzer–Debye–Hückel term alone is sufficient to predict the activity coefficients of dilute electrolytes. The second term of the right-hand side of eq 4 is the contribution due to the short-range interaction of any species in the solution and is given by the NRTL equation. The unsymmetric activity coefficient can be expressed by

$$\ln \gamma_{i,\mathrm{NRTL}}^* = \ln \gamma_{i,\mathrm{NRTL}} - \ln \gamma_{i,\mathrm{NRTL}}^\infty \tag{7}$$

The original NRTL equation[7] is given by

$$\ln \gamma_{i,\mathrm{NRTL}} = \frac{\sum_j^N x_j G_{ji} \tau_{ji}}{\sum_K^N x_k G_{ki}} + \sum_j^N \frac{x_j G_{ij}}{\sum_k^N x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_k^N x_k G_{kj} \tau_{kj}}{\sum_k^N x_k G_{kj}} \right)$$

$$G_{ij} = \exp(-\alpha\tau_{ij}), \quad \tau_{ij} = g_{ij}/RT \tag{8}$$

α is the nonrandomness parameter, and 0.2 is used in this study. g_{ij} is the most important parameter to present the interaction of the i–j combination for any species. By using the Marquart optimizing method, we have first obtained the binary NRTL parameters from the binary activity database,[10] as shown in Table 3. The NRTL parameters were given for anion and cation-specific parameters in order to be extended to any salts containing those anions and cations. Those ion-specific parameters for the NRTL model have not been available. Furthermore, we have second determined the pure parameters A and B of solubility products for five salts by using the electrolyte–NRTL model, as listed in Table 2. The pure parameters A and B,

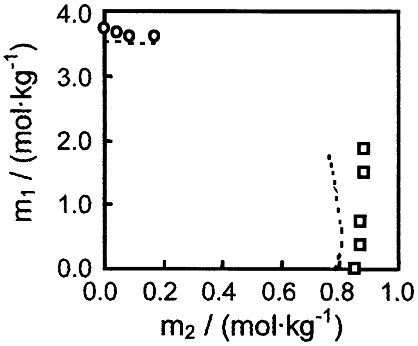

Figure 1. Two solubilities for the H_2O + K_2SO_4 (1) + $MgSO_4$ (2) + system: □, salt 1; ○, salt 2; the dashed line presents the predicted solubilities.

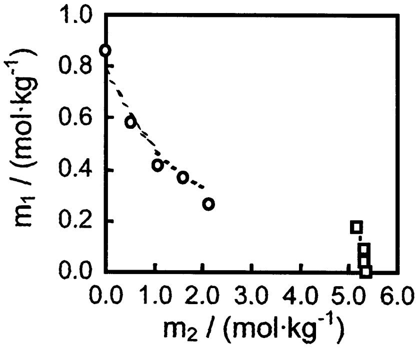

Figure 2. Two solubilities for the H_2O + KCl (1) + K_2SO_4 (2) system: □, salt 1; ○, salt 2; the dashed line presents the predicted solubilities.

Table 2. Parameters of Solubility Products for Pure Salts

	A/J·mol^{-1}	B/J·mol^{-1}·K^{-1}
$MgSO_4$	−82.82	−6129.35
K_2SO_4	−109.23	−7862.40
KCl	−21.27	−8603.35
Na_2SO_4	121.96	−71708.93
NaCl	−57.81	6130.40

Table 3. Predictive NRTL Parameters g_{ij}/J·mol^{-1} of the Binary Pair of i−j Species from Binary Data

	H_2O	Na^+	K^+	Mg^{2+}	Cl^-	SO_4^{2-}
H_2O	0	5270	6610	−16800	−21600	−18500
Na^+	−6640	0	0	0	8750	−1380
K^+	605	0	0	0	4440	−3690
Mg^{2+}	648	0	0	0	0	−3450
Cl^-	−7060	−11300	−2280	0	0	0
SO_4^{2-}	−4560	−1 000	−1700	851	0	0

which are determined by considering nonideality of electrolyte solutions, have also been not available. Figures 1−6 show the experimental data with the predicted values by the modified electrolyte−NRTL model for the solubilities of two salts for the ternary systems. As shown in Table 3, we cannot determine the binary interaction parameters between cation and cation and between anion and anion, because activity coefficient data for multiple salts are not available. However, the predictive NRTL parameters could qualitatively represent the experimental values of the solubilities of two salts reasonably well except for the H_2O + Na_2SO_4 + K_2SO_4 system. The interaction parameters of cation−cation and anion−anion are zero. It is thought that the interactions between anion and anion and between cation and cation do not vary for different ion species.

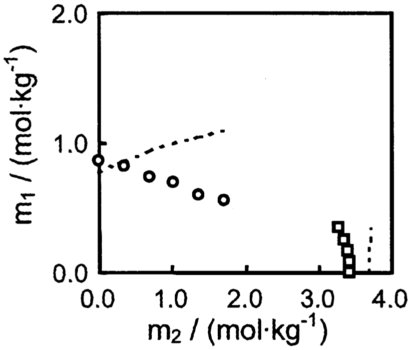

Figure 3. Two solubilities for the H_2O + Na_2SO_4 (1) + K_2SO_4 (2) system: □, salt 1; ○, salt 2; the dashed line presents the predicted solubilities.

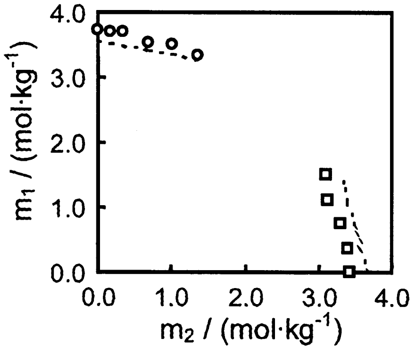

Figure 4. Two solubilities for the H_2O + Na_2SO_4 (1) + $MgSO_4$ (2) system: □, salt 1; ○, salt 2; the dashed line presents the predicted solubilities.

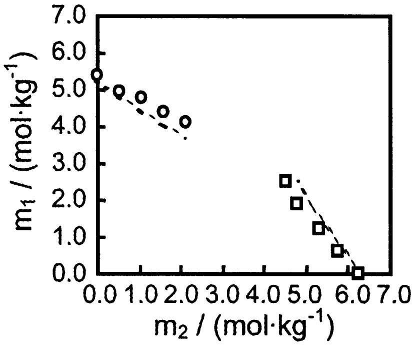

Figure 5. Two solubilities for the H_2O + NaCl (1) + KCl (2) system: □, salt 1; ○, salt 2; the dashed line presents the predicted solubilities.

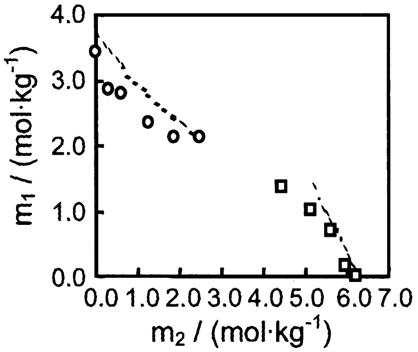

Figure 6. Two solubilities for the H_2O + NaCl (1) + Na_2SO_4 (2) system: □, salt 1; ○, salt 2; the dashed line presents the predicted solubilities.

Although data on the solubility of mixed salts are important for industrial inorganic processes, there is actually little useful data for considering thermodynamic solution models. Many solubility data measurements for multiple salts need to be made systematically in the future.

Conclusions

Solubility data for two salts for ternary systems have been measured at 313 K in aqueous solutions. The electrolyte−NRTL model was used to predict the solubilities of the two salts in water. The predicted values corresponded reasonably well with the experimental values. It was found that the NRTL parameters, which could be extended to any salts containing Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-}, were useful even though the parameters were obtained from binary data.

Literature Cited

(1) Kim, S.; Myerson, A. S. Metastable Solution Thermodynamics Properties and Crystal Growth Kinetics. *Ind. Eng. Chem. Res.* **1996**, *35*, 1078−1084.

(2) Pitzer, K. S.; Brewer, L. Revised edition of *Thermodynamics*, 2nd ed.; Lewis, G. N., Randall, M., Eds.; McGraw-Hill: New York, 1961.

(3) Pitzer, K. S. Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *J. Phys. Chem.* **1973**, *77*, 268−277.

(4) Pitzer, K. S.; Mayorga, G. Thermodynamics of Electrolytes. II. Activity Coefficients for Strong Electrolytes with One and Both Ions Univalent. *J. Phys. Chem.* **1973**, *77*, 2300−2308.

(5) Pitzer, K. S.; Kim, J. J. Thermodynamics of Electrolytes. IV. Activity and Osmotic Coefficients for Mixed Electrolytes. *J. Am. Chem. Soc.* **1974**, *96*, 5701−5707.

(6) Pitzer, K. S. Electrolytes. From Dilute Solution to Fused Salts. *J. Am. Chem. Soc.* **1980**, *102*, 2902−2906.

(7) Cruz, J.-L.; Renon, H. A New Thermodynamic Representation of Binary Electrolyte Solutions Nonideality in the Whole Range of Concentration. *AIChE J.* **1978**, *24*, 817−830.

(8) Chen, C.-C.; Britt, H. I.; Boston, J. F.; Evans, L. B. Local Composition Model for Excess Gibbs Energy of Electrolyte Systems Part I: Singe Solvent, Single Completely Dissociated Electrolyte System. *AIChE J.* **1982**, *28*, 588−596.

(9) Chen, C.-C.; Evans, L. B. A Local Composition Model for the Excess Gibbs Energy of Aqueous Electrolyte Systems. *AIChE J.* **1986**, *32*, 444−454.

(10) Mullin, J. M. *Crystallization*, 3rd ed.; Butterworth-Heinemann: Oxford, 1993.

Received for review May 1, 2002. Accepted September 5, 2002. The authors wish to thank the Grant-in-Aid for Scientific Research.

JE0255426