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Prediction of Solid−Liquid Phase Equilibrium in the System of Water (1) + Alcohols (2) + $MgSO_4 \cdot 7H_2O$ (3) + $MnSO_4 \cdot H_2O$ (4) by the Ion-Specific Electrolyte NRTL Model[†]

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The complex phase equilibria for the solubilities of $MnSO_4 \cdot H_2O$ and $MgSO_4 \cdot 7H_2O$ in three different organic solvents (methanol, ethanol, and 2-propanol) were predicted by the ion-specific electrolyte NRTL model. The salting-out effect of Mg^{2+}, solventing-out effects of alcohols, and their combined effects on the solubility of $MnSO_4 \cdot H_2O$ were represented in several thermodynamic figures as a function of temperature. We found that the solventing-out effect was stronger than the salting-out effect for the solubility of $MnSO_4 \cdot H_2O$ even though the solubility of $MnSO_4 \cdot H_2O$ decreased as temperature increased.

Introduction

The solubilities of inorganic salts are affected by changes in their activity coefficients in the presence of different solvents. Activity coefficient in the dilute electrolyte solution can be expressed by the Debye−Hückel equation,[1] which is a function of ion strength. In early studies, "Electrolyte Solution" by Robinson and Stokes[2] explained the theory of electrolyte solution and provided the activity data of many electrolytes. Pitzer[3,4] described the thermodynamic equation of the activity coefficient of electrolyte solution with the Debye−Hückel model. Cruz and Renon[5] first considered the NRTL model[6] combined with the Debye−Hückel model in 1978. Since the 1980s, Chen et al.[7,8] have also applied the electrolyte NRTL model to electrolyte solutions. Lu and Maurer[9] proposed the electrolyte UNIQUAC model[10] to be applied to mixed electrolyte systems. The electrolyte NRTL model is very useful because the limited ionic species can be applied for electrolyte solution. We have proposed the ion-specific NRTL parameters[11] by using published activity coefficient data.[12] As an industrial application of the electrolyte NRTL model, Safaeefar et al.[13−15] have also studied the solubility of manganese sulfate in mixed electrolyte and mixed solvent systems. Manganese sulfate monohydrate is mostly produced as a side product from the production of electrolytic manganese dioxide in the battery making industry. These byproducts consist of many impurities, mainly magnesium. Solventing-out crystallization is a good procedure to separate manganese from magnesium. The solubility of manganese sulfate monohydrate in aqueous alcohol solution is essential for solventing-out crystallization studies. Many separation processes such as solventing-out crystallization involve solutions of electrolytes dissolved in mixed liquid solvents. The main characteristic that distinguishes between electrolyte solution and molecular solution is the dissociation of the salts into cations and anions, and it has a strong nonideal effect on the thermodynamic properties of the solution.

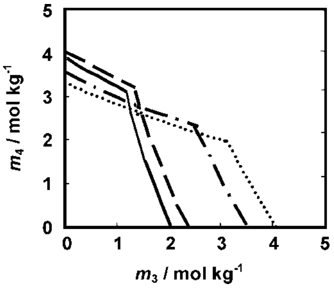

Figure 1. Solid−liquid equilibrium for the water (1) + $MgSO_4$ (3) + $MnSO_4$ (4) system at four different temperatures: —, 283 K; - -, 293 K, −•−, 323 K, •••, 333 K; m = molality.

In the previous works,[13−15] they could not consider the change of the eutectic points of two salts, $MnSO_4 \cdot H_2O$ and $MgSO_4 \cdot 7H_2O$, with mixed solvents as a function of temperature. In this study, the complete solubilities of $MnSO_4 \cdot H_2O$ and $MgSO_4 \cdot 7H_2O$ in water and aqueous alcohol solutions as a function of temperature were calculated by the electrolyte NRTL model, and the effects of solventing-out and salting-out effect on the solubility of manganese salts were explained.

Solubility Model

Crystallization of $MnSO_4 \cdot H_2O$ and $MgSO_4 \cdot 7H_2O$ is based on the solubility product defined by activity coefficient and molality of aqueous ions as follows.

$$K_s = a_+^{\nu+} a_-^{\nu-} = (\gamma_+^* x_+)^{\nu+} (\gamma_-^* x_-)^{\nu-} \tag{1}$$

where a and x denote activity and mole fraction of solubility, respectively. The subscripts + and − refer to cation and anion,

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Table 1. Predictive NRTL Parameters g_{ij} of the Binary Pair of $i-j$ Species[a]

	water	methanol	ethanol	2-propanol	Mg^{2+}	Mn^{2+}	SO$_4^{2}$
	g_{ij}/J·mol^{-1}	g_{ij}/J·mol^{-1}	g_{ij}/J·mol^{-1}	g_{ij}/J·mol^{-1}	g_{ij}/J·mol^{-1}	g_{ij}/J·mol^{-1}	g_{ij}/J·mol^{-1}
water	0	2717	5427	7825	8170	2820	−7990
methanol	−1430	0	–	–	−3160	−13100	−84200
ethanol	−527	–	0	–	−24900	14400	78200
2-propanol	−54	–	–	0	−27500	−6900	400
Mg^{2+}	−13600	−6530	−23000	−28600	0	−27200	5400
Mn^{2+}	−13500	15000	11800	14300	47700	0	7750
SO$_4^{2}$	−5100	15000	14000	14200	−18500	−24700	0

[a] 0, ideal interaction; -, not used.

Table 2. Pure Parameters of Solubility Product for Pure Salts

	A/J·mol^{-1}	B/J·mol^{-1}·K^{-1}
MnSO$_4$·H$_2$O	−246	46500
MgSO$_4$·7H$_2$O	−83.2	−5090

respectively. The temperature dependence can be expressed by the van't Hoff type equation.

$$R \ln K_s = A + \frac{B}{T} \tag{2}$$

R is the universal gas constant. The constants A and B denote the thermal parameters of pure salt and are independent of concentration of salt in the aqueous solution. The relationship of solubility unit between mole fraction of ion species, x, and molality of salt, m, is given by

$$x_+ = \frac{v_+ m}{\frac{1000}{M_s} + m(v_+ + v_-)}, \quad x_- = \frac{v_- m}{\frac{1000}{M_s} + m(v_+ + v_-)} \tag{3}$$

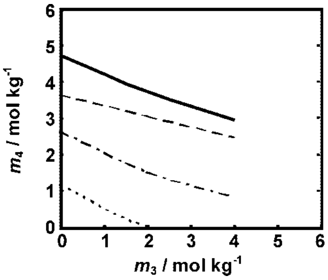

Figure 2. Solubility of MnSO$_4$ (4) in three aqueous alcohol solutions with MgSO$_4$ (3) at 293 K: —, nonantisolvent; - -, methanol, $x_2 = 0.07$; —·—, ethanol, $x_2 = 0.07$; ···, 2-propanol, $x_2 = 0.07$; m = molality.

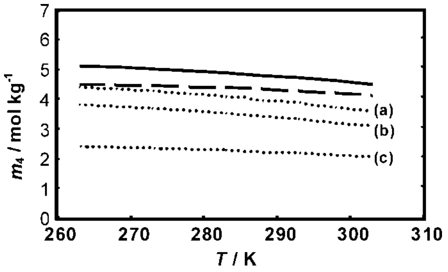

Figure 3. Solubility of MnSO$_4$ (4) as a function of temperature in three different aqueous alcohol solutions at constant content of MgSO$_4$ (3): –, normal solubility ($m_3 = 0$, $x_2 = 0$); - -, MgSO$_4$ salting-out effect ($m_3 = 0.81$); ···, alcohol antisolvent effect ($x_2 = 0.06$). (a) Aqueous methanol solution; (b) aqueous ethanol solution; (c) aqueous 2-propanol solution; m = molality.

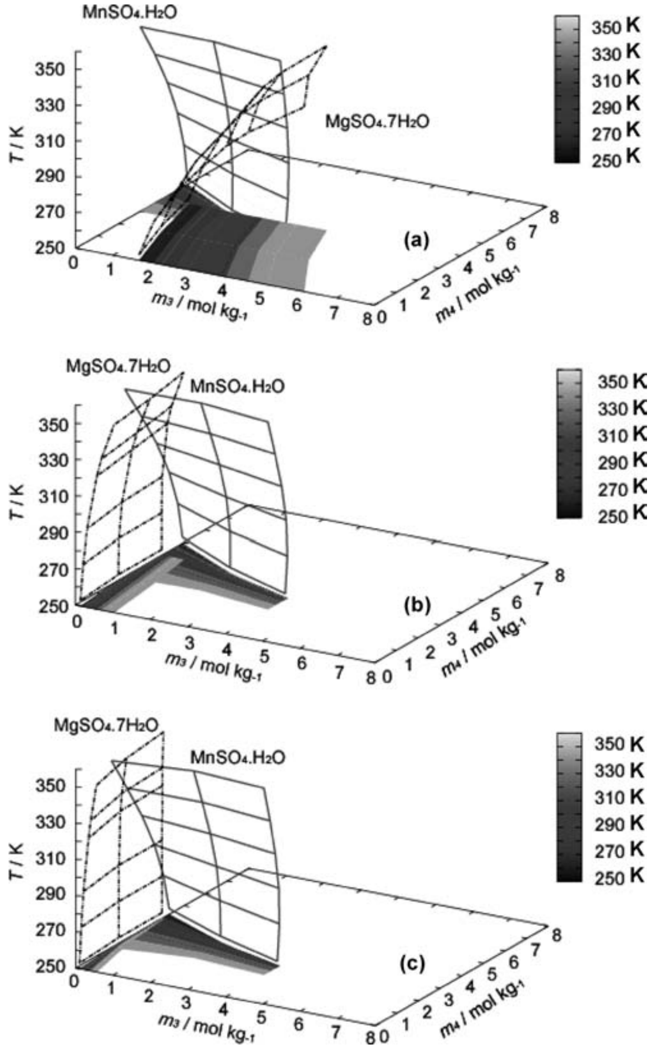

Figure 4. Complete solid−liquid equilibrium for the water (1) + methanol (2) + MnSO$_4$ (3) + MgSO$_4$ (4) system: (a) $x_2 = 0$, (b) $x_2 = 0.06$, (c) $x_2 = 0.12$, m = molality.

This complete dissociation assumption in the solution could be extended to aqueous mixed electrolyte systems. ν_- and ν_+ are the stoichiometric coefficients of the anion and cation, respectively, that is, the numbers of moles of the anion and cation produced during dissociation of one salt mole of ±. Since the activity coefficient of the individual ion i, γ_i^*, cannot be measured, the activity coefficients of aqueous ions are usually expressed as the mean ionic activity coefficient of neutral electrolyte. The mean activity coefficient, $\gamma_\pm^*$, is given by

$$\ln \gamma_\pm^* = \frac{\nu_+ \ln \gamma_+^* + \nu_- \ln \gamma_-^*}{\nu_{+-}} \tag{4}$$

ν_{ac} can be given by

$$\nu_{+-} = \nu_{+} + \nu_{-} \tag{5}$$

In the electrolyte NRTL model proposed by Chen et al.,[7,8] the activity coefficient of aqueous ion i is represented by the combination of the Pitzer−Debye−Hückel equation and the NRTL equation.

$$\ln \gamma_{\mathrm{i}}^{*} = \ln \gamma_{i,\mathrm{pdh}}^{*} + \ln \gamma_{i,\mathrm{NRTL}}^{*} \tag{6}$$

The Pitzer−Debye−Hückel equation is a function of ion strength, I_x, and electrostatic charge, z, that is given by

$$\ln \gamma_{i,\mathrm{pdh}}^{*} = -\left(\frac{1000}{M_{\mathrm{s}}}\right)^{1/2} A_{\phi}\left\{\left(\frac{2z_i^2}{\rho}\right)\ln(1+\rho I_x^{1/2}) + \left(\frac{z_i^2 I_x^{1/2} - 2I_x^{3/2}}{1+\rho I_x^{1/2}}\right)\right\} \tag{7}$$

where M_{s}, A_{ϕ}, and ρ refer to the molecular weight of solvent, the Pitzer−Debye−Hückel parameter, and the closest approach parameter (= 14.9/−), respectively. As for the mixed solvent systems, dielectric constant, $\varepsilon_{\mathrm{avg}}$, density, d_{avg}, and molecular weight, M_{s}, of the mixed solvents are calculated by mole fraction average. Consequently the Pitzer−Debye−Hückel parameter A_{ϕ} changes with the composition of the mixed solvent considerably.

$$A_{\phi\mathrm{avg}} = A_{\phi\mathrm{w}}\sqrt{d_{\mathrm{avg}}/d_{\mathrm{w}}}(\varepsilon_{\mathrm{avg}}/\varepsilon_{\mathrm{w}})^{2/3} \tag{8}$$

where the subscript, w, is for water. The ionic strength, I_x, based on mole fraction x, is defined by

$$I_x = \frac{1}{2}\sum_{i}^{N} z^2 x_i \tag{9}$$

The NRTL equation is expressed by

$$\ln \gamma_{i,\mathrm{NRTL}} = \frac{\sum_{j}^{N} x_j G_{ji}\tau_{ji}}{\sum_{k}^{N} x_k G_{ki}} + \sum_{j}^{N} \frac{x_j G_{ij}}{\sum_{k}^{N} x_k G_{kj}}\left(\tau_{ij} - \frac{\sum_{k}^{N} x_k G_{kj}\tau_{kj}}{\sum_{k}^{N} x_k G_{kj}}\right) \tag{10}$$

where

$$G_{ij} = \exp(-\alpha\tau_{ij})$$

$$\tau_{ij} = \frac{g_{ij}}{RT}$$

$$\alpha = \text{nonrandom factor } (= 0.2)$$

G_{ij}, τ_{ij}, and g_{ij} denote the NRTL binary interaction parameter of the $i-j$ combination for any species. The NRTL-derived

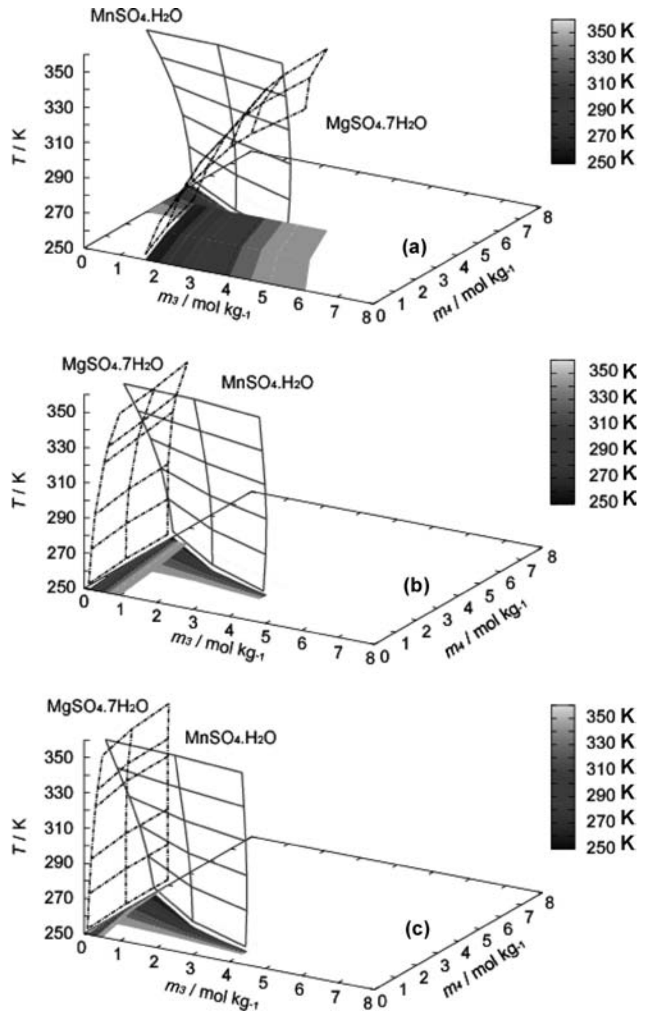

Figure 5. Complete solid−liquid equilibrium for the water (1) + ethanol (2) + $MnSO_4$ (3) + $MgSO_4$ (4) system: (a) $x_2 = 0$, (b) $x_2 = 0.04$, (c) $x_2 = 0.09$, m = molality.

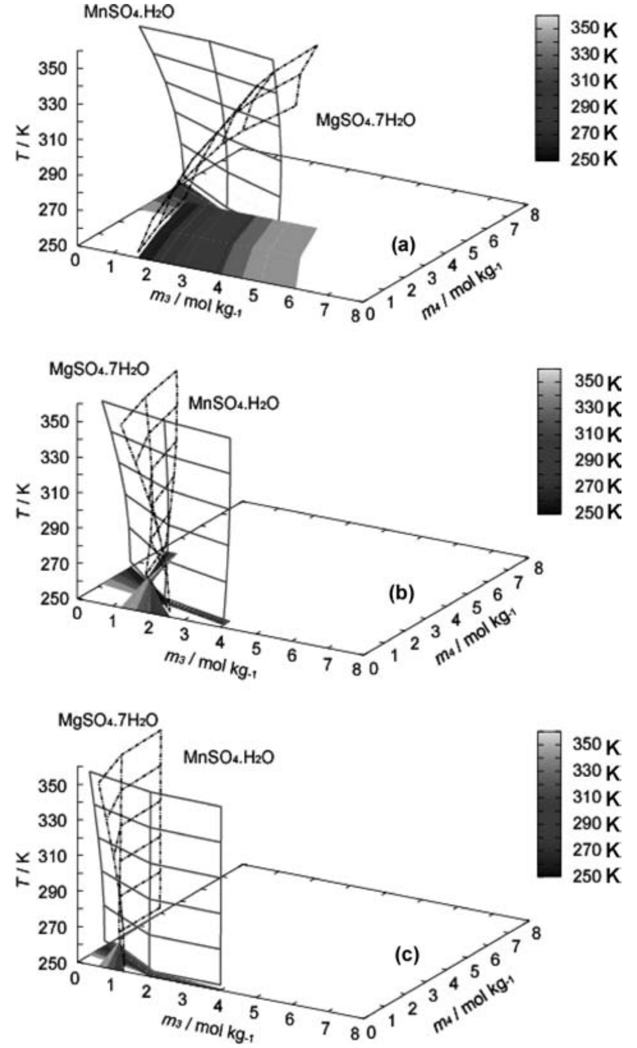

Figure 6. Complete solid−liquid equilibrium for the water (1) + 2-propanol (2) + $MnSO_4$ (3) + $MgSO_4$ (4) system: (a) $x_2 = 0$, (b) $x_2 = 0.03$, (c) $x_2 = 0.07$, m = molality.

activity coefficient, $\gamma_{i,\mathrm{NRTL}}$, is based on symmetric convention. This convention is different from that of the activity coefficient of aqueous salts. Therefore, the activity coefficient must be transformed to the unsymmetric activity coefficient, $\gamma^{*}_{i,\mathrm{NRTL}}$, using the NRTL-derived infinite dilution activity coefficient, $\gamma^{\infty}_{i,\mathrm{NRTL}}$, as the following equation.

$$\ln \gamma^{*}_{i,\mathrm{NRTL}} = \ln \gamma_{i,\mathrm{NRTL}} - \ln \gamma^{\infty}_{i,\mathrm{NRTL}} \qquad (11)$$

Ion-Specific NRTL parameters

We defined apparent components as water (1), alcohol (2), magnesium sulfate (3), and manganese sulfate (4). In the ion-specific electrolyte solution model, five species (water, alcohol, Mg^{2+}, Mn^{2+}, and SO_4^{2-}) exist in the solution of four substances. According to the previous papers,[11−13,16] the ion-specific NRTL parameters of possible binary pairs of five species are listed in Table 1. The parameters of solubility product of $MnSO_4 \cdot H_2O$ were determined by using the electrolyte NRTL model with the universal parameters, and they are shown in Table 2. All phase diagrams in this paper were calculated by using those parameters.

Eutectic Solubilities of the Water + $MgSO_4 \cdot 7H_2O$ + $MnSO_4 \cdot H_2O$ Basic System

Before considering the solventing-out effect and salting-out effect on manganese sulfates, the solubilities of binary electrolytes of magnesium sulfate and manganese sulfate in water should be well-known. Figure 1 shows two solubilities of $MgSO_4 \cdot 7H_2O$ and $MnSO_4 \cdot H_2O$ and eutectic points where both salts cocrystallize at different temperatures. The solubility of $MgSO_4 \cdot 7H_2O$ increased, but the solubility of $MnSO_4 \cdot H_2O$ decreased as the temperature increased. Therefore, the eutectic point shifted to the magnesium sulfate side as the temperature increased. Cooling crystallization may be a good alternative to obtain manganese sulfate selectively.

Solventing-Out Effect and Salting-Out Effect

Figure 2 shows solubilities of $MnSO_4 \cdot H_2O$ in water (solid line) and three aqueous alcohol (dashed lines) solutions with the same amount of $MgSO_4 \cdot 7H_2O$ as a function of temperature. In water and aqueous alcohol solutions, the solubility of $MnSO_4 \cdot H_2O$ decreased with temperature. Addition of $MgSO_4 \cdot 7H_2O$ lowered the solubilities of manganese sulfate slightly. The solventing-out effect of methanol was similar to the salting-out effect of $MgSO_4 \cdot 7H_2O$. The solventing-out effects of ethanol and 2-propanol was much stronger than the salting-out effect. The synergy of antisolvent and cosalt is shown in Figure 3. The solventing-out effect became stronger in the order: methanol < ethanol < 2-propanol. The salting-out effect of $MgSO_4 \cdot 7H_2O$ with alcohol became stronger in the order: methanol < ethanol < 2-propanol.

Three-Dimensional Phase Diagrams

Figures 4, 5, and 6 show the three-dimensional solubility diagrams for methanol, ethanol, and 2-propanol aqueous solution systems, respectively. There were two solubility surfaces for $MnSO_4 \cdot H_2O$ and $MgSO_4 \cdot 7H_2O$ as a function of temperature, T, molality of $MgSO_4 \cdot 7H_2O$, m_3, and molality of $MnSO_4 \cdot H_2O$, m_4, at different alcohol content, x_2. Those figures show that on the bottom faces one solution phase (white region near origin) against $MnSO_4 \cdot H_2O$ solubility's surfaces became smaller with alcohol in the following order, methanol > ethanol > propanol, but that against $MgSO_4 \cdot 7H_2O$, the order was reversed with 2-propanol larger than that for methanol or ethanol. These three-dimensional diagrams predicted by the electrolyte NRTL model with ion-specific NRTL parameters could provide useful information for comparing the effects of cooling, antisolvent, and salting-out in the crystallization of manganese sulfate hydrates. The eutectic point of two salts is the limitation of the crystallization process. The eutectic point of two salts changed to the magnesium sulfate region as temperature increased. However, the solubility of magnesium sulfate decreased very much even though the solubility of manganese sulfate did not decrease much as methanol or ethanol content increased in the solvent. Consequently, the eutectic point changed to the manganese sulfate region as methanol or ethanol content increased in the solvent. As for the mixed solvent with 2-propanol, the solubility of magnesium sulfate was not small, and the eutectic point did not change much.

For the separation process of two salts, the solventing-out crystallization for the magnesium sulfate should be first carried out, and the heating crystallization of manganese sulfate should be secondarily performed for selective separation.

Conclusion

The complete phase equilibrium for the quaternary water (1) + alcohol (2) + $MgSO_4$ (3) + $MnSO_4$ (4) systems were predicted by the electrolyte NRTL model with ion-specific NRTL parameters. It was found that the model could reasonably predict the eutectic behavior of two salts, solventing-out effect, salting-out effect, and synergy of antisolvent and cosalt. The complex phase diagrams could be depicted in three-dimensional figures.

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