Isopiestic Determination of Unsaturated and NH_4NO_3-Saturated $H_2O + NH_4NO_3 + Y(NO_3)_3 + Nd(NO_3)_3$ System and Representation with the Pitzer Model, Zdanovskii−Stokes−Robinson Rule, and Ideal−Like Solution Model[†]

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Isopiestic osmotic coefficients were determined for the unsaturated and NH_4NO_3-saturated $H_2O + NH_4NO_3 + Y(NO_3)_3 + Nd(NO_3)_3$ system up to the maximum ionic strength $I = 30\ mol\cdot kg^{-1}$ at 298.15 K. The experimental results were represented by a modified Pitzer model (*J. Phys. Chem. B* **2007**, *111*, 3704). The isopiestic data were found to closely fit a modified Zdanovskii−Stokes−Robinson model for the unsaturated system and Wang's ideal−like solution model (*Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 1045) for the NH_4NO_3-saturated quaternary system, respectively, which indicate that there is nonzero interchange energy between NH_4NO_3 and each rare earth nitrate and a zero interchange energy between the unlike rare earth nitrates. The isopiestic osmotic coefficient measurements and the Pitzer model representations for the NH_4NO_3-saturated quaternary systems are in good agreement with the ideal−like solution model.

Introduction

Thermodynamic properties from infinite dilution to saturation (or supersaturation) are of fundamental importance for the pure and mixed aqueous solutions containing 3−1 rare earth electrolytes, since the ionic interactions in the 3−1 electrolytes are generally believed to be more complicated than those in the 1−1, 2−1, and 2−2 electrolytes[1,2] and since the 3−1 actinide and lanthanide ions may follow a similar ion interaction trend due to the similarity of actinides and lanthanides, but the actinides can hardly be manipulated at high concentrations due to their radioactivity.[3] Furthermore, the mixtures containing both the 3−1 rare earth electrolyte pairs such as $Y(NO_3)_3$ and $Nd(NO_3)_3$ and the salting-out agents such as NH_4NO_3 are of great interest from both theoretical and practical points of view, since the unlike rare earth electrolytes have closely similar physicochemical properties in being difficult to separate, but they may react with the salting-out agents to form complexes that may improve the rare earth extraction separation. Any theory being obeyed by these mixtures may also be suitable for the mixtures containing both the 3−1 actinide electrolyte pairs and salting-out agents.

Osmotic and activity coefficients have been determined precisely for aqueous solutions at higher concentrations by isopiestic measurements[4] and at lower concentrations by cell voltage measurements, particularly at 298.15 K. The results may be represented by the Pitzer ion interaction model and its various modifications. Spedding et al.[5] and Rard et al.[6−12] have made isopiestic measurements up to an ionic strength $I = 51\ mol\cdot kg^{-1}$ (i.e., 23 $mol\cdot kg^{-1}$ above saturation) for 14 pure rare earth nitrates, $I = 29\ mol\cdot kg^{-1}$ for 12 pure rare earth perchlorates, and $I = 25\ mol\cdot kg^{-1}$ for 14 pure rare earth chlorides, and Malatesta et al.[13] have reported the activity coefficients from cell voltage measurements for pure $LaCl_3$, $La(NO_3)_3$, and $La(ClO_4)_3$ down to about $I = 0.001\ mol\cdot kg^{-1}$. The Pitzer model and all the modifications cannot fit these rare earth electrolytes very well, for which their standard deviations are significantly higher than the experimental errors of the precise isopiestic measurements.[1,3] To overcome this problem, various new modified forms of the Pitzer model have been developed,[14] and surprisingly, it was found that one of the modifications only extending to $C^{(3)}$ could quantitatively represent the literature data from infinite dilution to saturation or supersaturation. This simple modification can also represent isopiestic measurements for ternary and quaternary aqueous rare earth nitrate solutions to near saturation.[14−16] However, the ionic interaction analyses are still lacking for the aqueous solutions containing both the 3−1 rare earth electrolyte pairs and the salting-out agents to very high concentrations.[17]

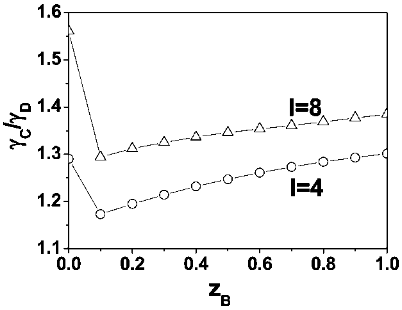

Figure 1. Dependence of activity coefficient ratios between the equal molality unlike rare earths on ionic strength fraction of NH_4NO_3 at $I = (4$ and $8)\ mol\cdot kg^{-1}$ calculated from the modified Pitzer model (eq 5) for the quaternary system $H_2O(A) + NH_4NO_3(B) + Y(NO_3)_3(C) + Nd(NO_3)_3(D)$.

Besides, scientists studying different kinds of solutions such as organic mixtures, aqueous and nonaqueous electrolyte and nonelectrolyte solutions, alloys, molten salt mixtures, slags, and nonstoichiometric solid solutions often use different concentration units, equations, and formalisms, which make it difficult

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for scientists in one of the fields to understand or benefit from advances in other fields. One of the primary goals of physical chemistry is to understand all of them in a unified way. The first success in this direction would be the classically ideal solution model for every kind of solution B + C + ... + Z with zero interchange energies among B, C, ..., Z related to their pure components B, C, ..., Z within the whole concentration range (i.e., mole fraction $0 \le x_j \le 1\{j \in (\mathrm{B, C,\ldots, Z})\}$), which was based on the Raoult law first discovered in pyridine solutions and which may be derived from a quasi-lattice treatment.[18] Similarly, based on the Zdanovskii−Stokes−Robinson (ZSR) rule[19,20] for unsaturated aqueous solutions at isopiestic conditions, Wang[21−26] developed a partial ideal solution (PIS) model for every kind of multicomponent systems A + B + C + ... + Z related to their binary subsystems A + B, A + C, ..., A + Z at constant activity of the common component A, which is valid within $0 \le [x_j/(x_\mathrm{B} + x_\mathrm{C} + \ldots + x_\mathrm{Z})] \le 1$ for the systems with zero interchange energies among B, C, ..., Z and which may be derived from a modified quasi-lattice treatment. Recently, Wang[27] has extended it to the ideal−like solution (ILS) model for every kind of multicomponent system A1 + A2 + ... + A*q* + B + C + ... + Z related to their subsystems A1 + A2 + ... + A*q* + B, A1 + A2 + ... + A*q* + C, ..., A1 + A2 + ... + A*q* + Z at constant activities of the common components A1, A2, ..., A*q*. When the ILS model is applied to aqueous electrolyte solutions, for example, the linear concentration equations (see eqs 9 and 10 below) and the activity coefficient equations of B, C, ..., Z (see eq 11 below) are of the same importance; however, the latter equations are difficult to be experimentally verified. Nevertheless, quantitative verifications may be performed by the Pitzer model representations for the quaternary system data at constant activities of two components such as the isopiestic data of the NH_4NO_3-saturated H_2O + NH_4NO_3 + $Y(NO_3)_3$ + $Nd(NO_3)_3$.

To gain deeper insight into the ionic interactions and solute−solute interactions in the mixed aqueous solutions containing both the 3−1 rare earth electrolytes and salting-out agents to very high concentrations, this work reports the isopiestic determinations of the unsaturated and NH_4NO_3-saturated quaternary system H_2O + NH_4NO_3 + $Y(NO_3)_3$ + $Nd(NO_3)_3$, where NH_4NO_3 and $Ln(NO_3)_3$ (Ln = Y and Nd) may form complexes. A newly modified Pitzer model[17] is used for analyzing quantitatively the ionic interactions in these complicated systems. We aim to analyze their ionic interactions and solute−solute interactions by the Pitzer model, ZSR rule, and ILS model or their modifications, respectively. We also aim to examine the applicability of the ILS model for the NH_4NO_3-saturated solutions by the isopiestic determinations and the Pitzer model calculations.

Equations. When aqueous solutions are at isopiestic equilibrium, the water activity (a_w) in the vapor phase is equal to that in each of the solutions. Osmotic coefficients (ϕ) of the unknown solutions may then be determined from the known ϕ, m relationship of a reference solution by[4]

$$\phi = \nu^* m^* \phi^* / \sum_\mathrm{s} \nu_\mathrm{s} m_\mathrm{s} \tag{1}$$

where ν is the stoichiometric coefficient; s denotes all solutes in the unknown aqueous solutions; and the asterisk denotes the properties of the isopiestic reference solutions.

Ionic interactions in the aqueous pure and mixed electrolytes may be determined by using the Pitzer model or its modifications. A newly modified Pitzer model[17] has been developed for the aqueous complex solutions H_2O + MX + NX + ... containing both the 3−1 rare earth electrolyte pairs and salting-out agents having the same anion X, for which the complete expressions for the osmotic coefficient and activity coefficient (γ) from infinite dilution to saturation or supersaturation may be given by

$$\begin{aligned}\phi - 1 = \Big(2/\sum_i m_i\Big)\Big\{&-A_\phi I^{3/2}/(1 + bI^{1/2}) + \sum_\mathrm{c} m_\mathrm{c} m_\mathrm{X}(B^\phi_\mathrm{cX} + \\ &ZC_\mathrm{cX}) + \sum_{\mathrm{c<c'}}\sum m_\mathrm{c} m_\mathrm{c'}(\Phi^\phi_\mathrm{cc'} + m_\mathrm{X}\psi_\mathrm{cc'X} + m_\mathrm{X}^2\Omega_\mathrm{cc'2X} + \\ &m_\mathrm{X}^3\Omega_\mathrm{cc'3X} + m_\mathrm{X}^4\Omega_\mathrm{cc'4X} + m_\mathrm{X}^5\Omega_\mathrm{cc'5X})\Big\}\end{aligned} \tag{2}$$

$$\begin{aligned}\ln \gamma_\mathrm{M} = z_\mathrm{M}^2 F + m_\mathrm{X}(2B_\mathrm{MX} + ZC_\mathrm{MX}) + |z_\mathrm{M}|\sum_\mathrm{c} m_\mathrm{c} m_\mathrm{X} C_\mathrm{cX} + \\ \sum_\mathrm{c} m_\mathrm{c}\{2\Phi_\mathrm{Mc} + m_\mathrm{X}\psi_\mathrm{McX} + (2/3)m_\mathrm{X}^2\Omega_\mathrm{Mc2X} + \\ (1/2)m_\mathrm{X}^3\Omega_\mathrm{Mc3X} + (2/5)m_\mathrm{X}^4\Omega_\mathrm{Mc4X} + (1/3)m_\mathrm{X}^5\Omega_\mathrm{Mc5X}\}\end{aligned} \tag{3}$$

$$\begin{aligned}\ln \gamma_\mathrm{X} = z_\mathrm{X}^2 F + \sum_\mathrm{c} m_\mathrm{c}(2B_\mathrm{cX} + ZC_\mathrm{cX}) + |z_\mathrm{X}|\sum_\mathrm{c} m_\mathrm{c} m_\mathrm{X} C_\mathrm{cX} + \\ \sum_{\mathrm{c<c'}}\sum m_\mathrm{c} m_\mathrm{c'}\{\psi_\mathrm{cc'X} + (4/3)m_\mathrm{X}\Omega_\mathrm{cc'2X} + (3/2)m_\mathrm{X}^2\Omega_\mathrm{cc'3X} + \\ (8/5)m_\mathrm{X}^3\Omega_\mathrm{cc'4X} + (5/3)m_\mathrm{X}^4\Omega_\mathrm{cc'5X}\}\end{aligned} \tag{4}$$

$$\begin{aligned}\ln \gamma_\mathrm{MX} = |z_\mathrm{M} z_\mathrm{X}|F + (\nu_\mathrm{M}/\nu_\mathrm{MX})m_\mathrm{X}(2B_\mathrm{MX} + ZC_\mathrm{MX}) + \\ (\nu_\mathrm{X}/\nu_\mathrm{MX})\sum_\mathrm{c} m_\mathrm{c}(2B_\mathrm{cX} + ZC_\mathrm{cX}) + \\ 2z_\mathrm{M}(\nu_\mathrm{M}/\nu_\mathrm{MX})\sum_\mathrm{c} m_\mathrm{c} m_\mathrm{X} C_\mathrm{cX} + (\nu_\mathrm{M}/\nu_\mathrm{MX})\sum_\mathrm{c} m_\mathrm{c}\{2\Phi_\mathrm{Mc} + \\ m_\mathrm{X}\psi_\mathrm{McX} + (2/3)m_\mathrm{X}^2\Omega_\mathrm{Mc2X} + (1/2)m_\mathrm{X}^3\Omega_\mathrm{Mc3X} + \\ (2/5)m_\mathrm{X}^4\Omega_\mathrm{Mc4X} + (1/3)m_\mathrm{X}^5\Omega_\mathrm{Mc5X}\} + (\nu_\mathrm{X}/\nu_\mathrm{MX})\sum_{\mathrm{c<c'}}\sum m_\mathrm{c} m_\mathrm{c'} \\ \{\psi_\mathrm{cc'X} + (4/3)m_\mathrm{X}\Omega_\mathrm{cc'2X} + (3/2)m_\mathrm{X}^2\Omega_\mathrm{cc'3X} + \\ (8/5)m_\mathrm{X}^3\Omega_\mathrm{cc'4X} + (5/3)m_\mathrm{X}^4\Omega_\mathrm{cc'5X}\}\end{aligned} \tag{5}$$

where A_ϕ is the Debye−Hückel parameter (0.3915 $\mathrm{kg^{1/2}\cdot mol^{-1/2}}$ at 298.15 K); $b = 1.2\ \mathrm{kg^{1/2}\cdot mol^{-1/2}}$; $Z = \sum_i m_i|z_i|$; i denotes all ions; c and c′ denote cations; z is charge number; B and C are second and third virials for pure electrolytes; Φ and ψ are second and third mixing terms; $\Omega_{\mathrm{cc'}n\mathrm{X}}$ ($n \ge 2$) are higher-order virial terms for mixed electrolytes; and the F, B, C, and Φ terms may be given by

$$\begin{aligned}F = -A_\phi\{I^{1/2}/(1 + bI^{1/2}) + (2/b)\ln(1 + bI^{1/2})\} + \\ \sum_\mathrm{c} m_\mathrm{c} m_\mathrm{X} B'_\mathrm{cx} + \sum_{\mathrm{c<c'}}\sum m_\mathrm{c} m_\mathrm{c'} \Phi'_\mathrm{cc'}\end{aligned} \tag{6a}$$

$$B^\phi_\mathrm{cX} = \beta^{(0)}_\mathrm{cX} + \beta^{(1)}_\mathrm{cX}\exp(-\alpha_{B1}I^{1/2}) + \beta^{(2)}_\mathrm{cX}\exp(-\alpha_{B2}I^{1/2}) \tag{6b}$$

$$B_\mathrm{cX} = \beta^{(0)}_\mathrm{cX} + \beta^{(1)}_\mathrm{cX} g(\alpha_{B1}I^{1/2}) + \beta^{(2)}_\mathrm{cX} g(\alpha_{B2}I^{1/2}) \tag{6c}$$

$$B'_\mathrm{cX} = \{\beta^{(1)}_\mathrm{cX} g'(\alpha_{B1}I^{1/2}) + \beta^{(2)}_\mathrm{cX} g'(\alpha_{B2}I^{1/2})\}/I \tag{6d}$$

$$\begin{aligned}C^\phi_\mathrm{cX} = 2\{C^{(0)}_\mathrm{cX} + C^{(1)}_\mathrm{cX}\exp(-\alpha_{C1}I) + C^{(2)}_\mathrm{cX}\exp(-\alpha_{C2}I) + \\ C^{(3)}_\mathrm{cX}\exp(-\alpha_{C3}I)\}\end{aligned} \tag{6e}$$

$$C_\mathrm{cX} = C^\phi_\mathrm{cX}/2|z_\mathrm{c} z_\mathrm{X}|^{1/2} \tag{6f}$$

$$\Phi^\phi_\mathrm{cc'} = \theta_\mathrm{cc'} + {}^E\theta_\mathrm{cc'}(I) + I\,{}^E\theta'_\mathrm{cc'}(I) \tag{6g}$$

$$\Phi_\mathrm{cc'} = \theta_\mathrm{cc'} + {}^E\theta_\mathrm{cc'}(I) \tag{6h}$$

$$\Phi'_{\text{cc}'} = {}^{E}\Phi'_{\text{cc}'}(I) \tag{6i}$$

Here, $g(\alpha_B I^{1/2})$, $g'(\alpha_B I^{1/2})$, ${}^{E}\theta_{\text{cc}'}(I)$, and ${}^{E}\theta'_{\text{cc}'}(I)$ are given, respectively, by eqs 50, 52, B-15, and B-16 in ref 2. In this study, the cations c and c′ may be either the unlike rare earth ion pair (Ln^{3+} and Ln'^{3+}) or one NH_4^+ and one Ln^{3+} in the $\theta_{\text{cc}'}$, $\Phi_{\text{cc}'}$, and $\psi_{\text{cc}'\text{X}}$ parameters, but must be one NH_4^+ and one Ln^{3+} in the $\Omega_{\text{cc}'n\text{X}}$ parameters (the situation is the same for the cations M and c in the θ_{Mc}, Φ_{Mc}, ψ_{McX}, and $\Omega_{\text{Mc}n\text{X}}$ parameters); the electrostatic terms ${}^{E}\theta_{\text{cc}'}(I)$ and ${}^{E}\theta'_{\text{cc}'}(I)$ for unsymmetrical mixing depend only on the charges of the ions and the total ionic strength of the investigated solutions, and the α parameters are given by $\alpha_{B1} = 1.8\ \text{kg}^{1/2}\cdot\text{mol}^{-1/2}$, $\alpha_{B2} = 6.0\ \text{kg}^{1/2}\cdot\text{mol}^{-1/2}$, $\alpha_{C1} = 0.15\ \text{kg}\cdot\text{mol}^{-1}$, $\alpha_{C2} = 0.25\ \text{kg}\cdot\text{mol}^{-1}$, and $\alpha_{C3} = 0.35\ \text{kg}\cdot\text{mol}^{-1}$.

On the other hand, solute−solute interactions in the mixed aqueous solutions may be analyzed by using the ZSR rule and ILS model or its modifications. In the case of A = water, the ZSR rule and PIS model for a multicomponent system A + B + C + ... + Z with mutually self-cancelled or negligible solute−solute interactions as compared to solute−solvent interactions (or with zero interchange energy among the solutes) may be given by[19−24,26]

$$\sum_j (m_j/m\circ_j) = 1 \tag{7}$$

$$\left(\sum_k \nu_k m_k\right)\gamma_i = \nu_i m\circ_i \gamma\circ_i \tag{8}$$

at constant activity of the common component A and within $0 \le y_j \le 1$, where $j,k \in$ (B,C, ..., Z) are all solutes; y is the molality fraction defined by $y_j = m_j/\sum_k m_k$; and the superscript ° denotes the properties of the binary subsystem A + j with the same water activity value as the multicomponent system A + B + C + ... + Z. In the case of A1 = water, the ILS model for a multicomponent system A1 + A2 + ... + Aq + B + C + ... + Z with zero interchange energy among B, C, ..., Z may be given by[27]

$$\sum_j \left(m_j/m_j^{q^\circ}\right) = 1 \tag{9}$$

$$\sum_j \left\{(m_j/m_\beta)/\left(m_j^{q^\circ}/m_\beta^{q^\circ,j}\right)\right\} = 1 \tag{10}$$

$$\left(\sum_k \nu_k m_k\right)\gamma_j = \upsilon_j m_j^{q^\circ}\gamma_j^{q^\circ} \tag{11}$$

at constant activities of the common components A1, A2, ..., Aq within $0 \le y_j \le 1$, where $\beta \in$ (A2, A3, ..., Aq), and the superscript $q°,j$ (or a combination of the superscript $q°$ with the subscript j) denotes the properties of the (q + 1)-component subsystem A1 + A2 + ... + Aq + j with the same activity values of A1, A2, ..., Aq as the multicomponent system A1 + A2 + ... + Aq + B + C + ... + Z. Deviation from the ILS model may be given by[16,27]

$$\Delta_{\text{A1}} = \sum_j \left(m_j/m_j^{q^\circ}\right) - 1 \tag{12}$$

$$\Delta_\beta = \sum_j \left\{(m_j/m_\beta)/\left(m_j^{q^\circ}/m_\beta^{q^\circ,j}\right)\right\} - 1 \tag{13}$$

$$\nu_j \ln\left\{\left(\sum_k \nu_k m_k\right)\gamma_j/\nu_j m_j^{q^\circ}\gamma_j^{q^\circ}\right\} = \int_0^{\ln a_\text{w}} \left\{\partial\left[\Delta_{\text{A1}}/\left(\sum_k m_k\right)(1 - y_j)\right]/\partial[1/(1 - y_j)]\right\}\text{d}\ln a_\text{w} \tag{14}$$

when B, C, ..., Z have nonzero interchange energies according to the modified ILS model. In the simplest case of $q = 1$ (where $m_\beta = 0$), the ILS model and its modifications reduce to the ZSR[25] or PIS model[19−24] and their modifications. Thus, when applying eqs 7 to 14 to solute−solute interaction analysis (see below), it is necessary to mark an isopiestic quaternary system H_2O + MX + NX + LX separately by H_2O(A1) + MX(A2) + NX(B) + LX(C) in one case for which MX is saturated but by H_2O(A) + MX(B) + NX(C) + LX(D) in another case where none of solutes is saturated.

Experimental Section

Y_2O_3 and Nd_2O_3 (99.99 % from Aldrich Chemical Co.) were used to prepare stock solutions of $\text{Y(NO}_3)_3$ and $\text{Nd(NO}_3)_3$ by Rard's method,[6−12] where, after reacting the rare earth oxides with analytical reagent HNO_3, the resulting rare earth nitrate solutions were adjusted to equivalent concentrations with dilute HNO_3 solutions and then reheated and readjusted until stabilized, and finally the rare earth nitrate molalities were determined by the EDTA titration. The stock solution concentrations were known to 0.1 % or better. AR grade NH_4NO_3, NaCl, and CaCl_2 from the same source were recrystallized from triple-distilled water several times and dried over P_2O_5. All the solutions were prepared by mass in triple-distilled water. The sample masses are always corrected for buoyancy.

The isopiestic measurements were made by the method described previously.[14−17,27] Fourteen gold-plated silver cups were placed in an isopiestic apparatus made of copper. Each sample was run in duplicate. In each of the cups, one glass ball and (1.5 to 3.0) g of reference solution or (2.0 to 3.0) g of the investigated system were placed. The isopiestic measurements were carried out from $I \approx 7\ \text{mol}\cdot\text{kg}^{-1}$ to $I \approx 23\ \text{mol}\cdot\text{kg}^{-1}$ for the unsaturated solutions and from $I \approx 23\ \text{mol}\cdot\text{kg}^{-1}$ to $I \approx 30\ \text{mol}\cdot\text{kg}^{-1}$ for the NH_4NO_3-saturated solutions of the investigated systems. To achieve isopiestic equilibrium more easily, the unsaturated pure electrolyte solutions with nearly equal water activities were prepared according to their known a_w, m relationship, and the unsaturated mixed solutions were approximately prepared by mixing them according to eq 7. The NH_4NO_3-saturated samples were prepared by placing (2.0 to 3.0) g of the near-saturated solutions with nearly equal water activities in each cup and then adding a small excess of NH_4NO_3 crystals into it. In this way, the initial mass of water and initial mole number of every solute were known for each sample.

After evacuation and degassing, the apparatus was placed into a thermostat controlled at (298.15 ± 0.01) K and then rocked in the thermostat once every 5 s. During the experimental process, some NH_4NO_3 crystals dissolved into the near-saturated solutions to form the NH_4NO_3-saturated solutions in each cup, and every one of the samples transferred water through the common vapor phase. The isopiestic equilibrium may be reached within (5 to 7) days for the unsaturated solutions and within (25 to 30) days for the saturated solutions. The aqueous NaCl and CaCl_2 were used as isopiestic standards for the dilute and concentrated nitrate solutions, respectively, and their osmotic coefficients were taken from the recent literature sources.[28,29]

The isopiestic molalities of unsaturated solutes were determined by weighing after each run. The individual equilibrium molalities of each nitrate were always reproducible to ± 0.06

Table 1. Experimental Isopiestic Osmotic Coefficients, ϕ, of the Unsaturated Aqueous Solution $H_2O(A) + NH_4NO_3(B) + Y(NO_3)_3(C) + Nd(NO_3)_3(D)$ at 298.15 K

m^{a}_{NaCl} $\mathrm{mol\cdot kg^{-1}}$	m $\mathrm{mol\cdot kg^{-1}}$	$y_C{}^{b}$	$y_D{}^{b}$	ϕ	$m^{a}_{\mathrm{CaCl_2}}$ $\mathrm{mol\cdot kg^{-1}}$	m $\mathrm{mol\cdot kg^{-1}}$	$y_C{}^{b}$	$y_D{}^{b}$	ϕ
2.134	1.155	0	1	0.919	2.892	2.909	0	1	1.289
	1.009	1	0	1.051		2.506	1	0	1.496
	2.828	0	0	0.750		12.700	0	0	0.590
	1.936	0.146	0.145	0.849		7.101	0.109	0.120	0.859
	1.646	0.207	0.249	0.886		5.556	0.173	0.194	0.988
	1.499	0.340	0.200	0.919		4.727	0.300	0.157	1.088
3.864	1.964	0	1	1.089	3.664	3.837	0	1	1.464
	1.690	1	0	1.266		3.303	1	0	1.700
	6.462	0	0	0.662		20.802	0	0	0.540
	4.053	0.119	0.128	0.847		10.510	0.104	0.116	0.876
	3.248	0.189	0.216	0.938		8.037	0.164	0.182	1.038
	2.833	0.319	0.182	1.006		6.521	0.298	0.157	1.184

[a] Isopiestic reference solutions. [b] Molality fractions $y_B + y_C + y_D = 1$.

Table 2. Experimental Isopiestic Osmotic Coefficients of the NH_4NO_3-Saturated Aqueous Solutions $H_2O(A1) + NH_4NO_3(A2)(sat) + Y(NO_3)_3(B) + Nd(NO_3)_3(C)$ at 298.15 K

$m^{a}_{\mathrm{CaCl_2}}$ $\mathrm{mol\cdot kg^{-1}}$	m $\mathrm{mol\cdot kg^{-1}}$	$y_B{}^{b}$	$y_C{}^{b}$	Δ_{A1} (eq 12)	Δ_{A2} (eq 13)	ϕ	$m^{a}_{\mathrm{CaCl_2}}$ $\mathrm{mol\cdot kg^{-1}}$	m $\mathrm{mol\cdot kg^{-1}}$	$y_B{}^{b}$	$y_C{}^{b}$	Δ_{A1} (eq 12)	Δ_{A2} (eq 13)	ϕ
3.822	18.755	0	0.0445			0.617	3.910	15.791	0	0.0029			0.715
	18.564	0.0082	0.0357	−0.0002	0.0004	0.624		15.646	0.0193	0.0920	0.0001	0.0001	0.723
	18.392	0.0163	0.0270	−0.0001	0.0002	0.630		15.487	0.0386	0.0710	−0.0008	0.0004	0.732
	18.226	0.0246	0.0180	0.0001	−0.0001	0.636		15.334	0.0590	0.0489	−0.0009	0.0006	0.740
	18.046	0.0330	0.0090	−0.0001	−0.0001	0.643		15.182	0.0804	0.0258	−0.0009	0.0007	0.749
	17.874	0.0414	0			0.649		15.039	0.1041	0			0.757
3.810	17.368	0	0.0669			0.649	4.186	14.960	0	0.1705			0.808
	17.197	0.0111	0.0551	0.0001	0.0000	0.656		14.793	0.0256	0.1433	0.0001	−0.0002	0.819
	16.996	0.0244	0.0410	−0.0001	0.0002	0.664		14.586	0.0548	0.1124	−0.0009	−0.0001	0.832
	16.829	0.0362	0.0285	0.0001	0.0002	0.671		14.365	0.0869	0.0787	−0.0009	0.0013	0.846
	16.620	0.0513	0.0124	0.0002	−0.0001	0.680		14.173	0.1211	0.0423	−0.0006	0.0001	0.859
	16.453	0.0630	0			0.687		13.943	0.1611	0			0.874

[a] Isopiestic reference solution. [b] Molality fractions $y_{A2} + y_B + y_C = 1$.

% and mostly to ± 0.04 % between the duplicates. The isopiestic solubilities of NH_4NO_3 were determined by the EDTA titration of the total amount of rare earths after some of the saturated solution in the liquid phase were transferred, weighed, and diluted. The transfer of the saturated solution was carried out by the method of Kelly et al.,[30] which was through a pipet fitted with a sintered-glass filter tip space preheated slightly above 298.15 K. The isopiestic solubilities of NH_4NO_3 were calculated by $(1000 + m_{A2}M_{A2} + m_BM_B + m_CM_C)/(m_B + m_C) = W/n_{Ln}$, where A2 denotes NH_4NO_3, B and C denote unlike rare earth nitrates, M denotes molar mass, W denotes the mass of the saturated solution transferred for EDTA titration, and $n_{Ln}(= n_B + n_C)$ denotes the total mole number of rare earth nitrates in W grams of the saturated solution. The transfer and EDTA titration of the saturated solution may result in an additional probable uncertainty of not more than ± 0.10 % for the isopiestic solubility of NH_4NO_3.

Results and Discussion

First, the ionic interactions in the unsaturated quaternary system $H_2O + NH_4NO_3 + Y(NO_3)_3 + Nd(NO_3)_3$ and NH_4NO_3-saturated quaternary system $H_2O + NH_4NO_3(sat) + Y(NO_3)_3 + Nd(NO_3)_3$ were analyzed using the modified Pitzed model. Table S1 (Supporting Information) lists the Pitzer parameter values and fitting standard deviations of eq 1 for pure NH_4NO_3, $Y(NO_3)_3$,and $Nd(NO_3)_3$ with $\sigma = 0.0011$, 0.0024, and 0.0018, respectively. Table S2 lists the values of two mixing parameters θ and ψ and higher-order virial terms up to $\Omega_{cc'5X}$ for the aqueous solutions $H_2O + Y(NO_3)_3 + Nd(NO_3)_3$, $H_2O + NH_4NO_3+Y(NO_3)_3$, and $H_2O + NH_4NO_3 + Nd(NO_3)_3$ with $\sigma = 0.0016$, 0.0030, and 0.0030, respectively. Table S3 lists the high-order electrostatic functions in the Pitzer model for the interaction between aqueous $NH_4{}^+$ and Ln^{3+} (Ln = Y and Nd) with $I = (0.5 \text{ to } 30)\ \mathrm{mol\cdot kg^{-1}}$. Both of these parameters were reported in refs 14 and 17. All these parameters will be used in the ion-interaction analysis in this study.

Table 1 and Table 2 list the measured isopiestic osmotic coefficients for the unsaturated quaternary system $H_2O + NH_4NO_3 + Y(NO_3)_3 + Nd(NO_3)_3$ to $I = 23\ \mathrm{mol\cdot kg^{-1}}$ and for the NH_4NO_3-saturated quaternary system $H_2O + NH_4NO_3(sat) + Y(NO_3)_3 + Nd(NO_3)_3$ to $I = 30\ \mathrm{mol\cdot kg^{-1}}$, respectively, at 298.15 K. Our experimental osmotic coefficients for aqueous NH_4NO_3, $Y(NO_3)_3$, and $Nd(NO_3)_3$ solutions listed in Tables 1 and 2 are in excellent agreement with those calculated by the modified Pitzer model with the virial parameters listed in Table S1 (Supporting Information). The largest differences in the ϕ values between them are only 0.003 for all the pure electrolytes.

Furthermore, the modified Pitzer model extending to $C^{(3)}$ and $\Omega_{cc'5X}$ (eq 2) was found to be suitable for fitting the isopiestic osmotic coefficients of the unsaturated quaternary system $H_2O + NH_4NO_3 + Y(NO_3)_3 + Nd(NO_3)_3$ and the NH_4NO_3-saturated quaternary system $H_2O + NH_4NO_3(sat) + Y(NO_3)_3 + Nd(NO_3)_3$. The standard deviations are within $\sigma_{max} \leq 0.003$. These results, together with those reported in ref 14, indicate that the modified Pitzer model (eq 2) instead of the original Pitzer model or its other modifications can well represent the ionic interactions in the unsaturated quaternary system $H_2O + NH_4NO_3 + Y(NO_3)_3 + Nd(NO_3)_3$ and NH_4NO_3-saturated quaternary system $H_2O + NH_4NO_3(sat) + Y(NO_3)_3 + Nd(NO_3)_3$. The values of high-order electrostatic functions listed in Table S3 (Supporting Information) were inserted in eqs 6g−i to give the mixing

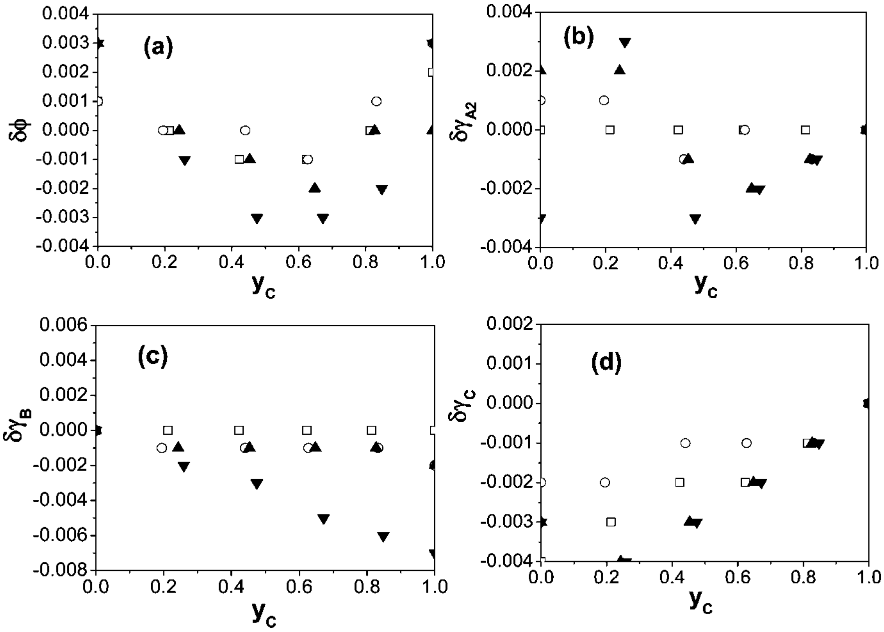

Figure 2. Deviations of (a) $\delta\phi = \phi(\text{expt}) - \phi$ (eq 2) and of (b) $\delta\gamma_{A2} = \gamma_{A2}(\text{expt}) - \gamma_{A2}$ (eq 5) calculated by the modified Pitzer model from the experimental values for ϕ and γ_{A2} as well as of (c) $\delta\gamma_B = \gamma_B$ (eq 11) $- \gamma_B$ (eq 5) and (d) $\delta\gamma_C = \gamma_C$ (eq 11) $- \gamma_C$ (eq 5) calculated by the modified Pitzer model from the like−ideal solution model values for γ_B and γ_C at water activity $a_w(= a_{A1})$ = □, 0.6471; ○, 0.6485; ▲, 0.6358; and ▼, 0.6005 for the NH_4NO_3-saturated aqueous solution $H_2O(A1) + NH_4NO_3(A2) + Y(NO_3)_3(B) + Nd(NO_3)_3(C)$.

terms of $\Phi^{\phi}_{cc'}$, $\Phi_{cc'}$, and $\Phi'_{cc'}$. Thus, the solute activity coefficients in the quaternary systems can quantitatively be calculated by eq 5.

Figure 1 demonstrates activity coefficient ratios of equal molality $Y(NO_3)_3$ and $Nd(NO_3)_3$ in $H_2O + NH_4NO_3 + Y(NO_3)_3 + Nd(NO_3)_3$ as functions of NH_4NO_3 ionic strength fraction at I = (4 and 8) mol·kg^{-1}. It would seem that the difference between the $(Ln^{3+})(NH_4^{+})(NO_3^{-})_5$ and $(Ln'^{3+})(NH_4^{+})(NO_3^{-})_5$ interactions yields the changes in activity coefficient ratios of the unlike rare earth nitrates, which may be the thermodynamic basis of the rare earth liquid−liquid extraction separation.

Second, the solute−solute interactions in the unsaturated quaternary system $H_2O + NH_4NO_3 + Y(NO_3)_3 + Nd(NO_3)_3$ were analyzed using the ILS model or its modifications. As mentioned above, the ILS model reduces to the ZSR or PIS model for the unsaturated solutions at isopiestic equilibrium. Table 1 shows that the isopiestic molalities for the unsaturated quaternary system $H_2O(A) + NH_4NO_3(B) + Y(NO_3)_3(C) + Nd(NO_3)_3(D)$ deviate from eq 7 or 9, the values of the $\Delta_A(= \Delta_{A1})$ function defined by eq 12 being high up to 0.042, which indicates the nonzero interchange energies between NH_4NO_3 and $Ln(NO_3)_3$.

Table 2 shows that the isopiestic molalities of the NH_4NO_3-saturated quaternary systems $H_2O(A1) + NH_4NO_3(A2) + Y(NO_3)_3(B) + Nd(NO_3)_3(C)$ closely fit eqs 9 and 10. The Δ_{A1} and Δ_{A2} functions defined by eqs 12 and 13 are given by $|\Delta_{A1}| \leq 0.001$ and $|\Delta_{A2}| \leq 0.002$, respectively, for the NH_4NO_3-saturated quaternary system over the entire concentration range. This means that the NH_4NO_3-saturated quaternary system obeys the ILS model within the experimental uncertainties due to zero interchange energies between the unlike rare earth nitrates, which is identical with the nature of the rare earth elements. Therefore, for the NH_4NO_3-saturated quaternary system, the activity coefficients of the rare earth nitrates can also be calculated by using a very simple equation (eq 11). Figure 2 shows the deviations of the thermodynamic values either obtained from the isopiestic experiments for ϕ and γ_{A2} or calculated from the ILS model for γ_B and γ_C (eq 11) from those calculated by the modified Pitzer model equations (eqs 2 and 5) for the NH_4NO_3-saturated quaternary system, where the experimental values for γ_{A2} were obtained from both the isopiestic molalities of the NH_4NO_3-saturated quaternary system and the NH_4NO_3 activity value 11.90, which was calculated from the molality value (25.954 mol·kg^{-1}) and activity coefficient value (0.1329) listed in Table S4 (Supporting Information) for aqueous pure NH_4NO_3 and which is invariant for the NH_4NO_3-saturated solutions. It can be seen that the agreement is excellent. The maximum deviations are only $\sigma_{max} = 0.003$ for ϕ, $\sigma_{max} = 0.003$ for γ_{A2}, $\sigma_{max} = 0.007$ for γ_B, and $\sigma_{max} = 0.004$ for γ_C of $H_2O(A1) + NH_4NO_3(A2) + Y(NO_3)_3(B) + Nd(NO_3)_3(C)$. Thus, the ILS model (eqs 9 to 11) at $q = 2$ is completely verified in this study by combining the precise isopiestic experiments with the quantitative Pitzer model calculations. As mentioned above, the ILS model is obeyed by every kind of the multicomponent system A1 + A2 + ... + Aq + B + C + ... + Z with zero interchange energies among B, C, ..., Z.

Conclusion

Studies in the present work provide a set of precise isopiestic data for the unsaturated and NH_4NO_3-saturated quaternary system $H_2O + NH_4NO_3 + Y(NO_3)_3 + Nd(NO_3)_3$. A modified Pitzer model extending to $C^{(3)}$ and $\Omega_{cc'5X}$ specific for the 3−1 rare earth electrolytes and the $(Ln^{3+})(NH_4^{+})(NO_3^{-})_5$ complexes is used for quantitatively representing the ionic interactions in this complicated system. This model can sufficiently describe the ionic interactions in the aqueous solutions containing both the 3−1 rare earth electrolyte pairs and the salting-out agents from infinite dilution to saturation or supersaturation.

The unsaturated quaternary system $H_2O + NH_4NO_3 + Y(NO_3)_3 + Nd(NO_3)_3$ obviously deviates from the ZSR rule or PIS model, which indicates the nonzero solute−solute interaction energy between NH_4NO_3 and each rare earth nitrate. On the other hand, the NH_4NO_3-saturated quaternary system $H_2O + NH_4NO_3(\text{sat}) + Y(NO_3)_3 + Nd(NO_3)_3$ obeys the ILS model very well, which indicates zero solute−solute interaction energy between the unlike rare earth nitrates. Thus, both the modified ionic interaction model and the ILS model would be the powerful tool for the aqueous complex solutions containing the 3−1 rare earth or actinide electrolyte pairs and salting-out agents. Furthermore, the ILS model is verified completely both by the precise isopiestic determinations and by the quantitative Pitzer model calculations for the NH_4NO_3-saturated quaternary system $H_2O + NH_4NO_3(sat) + Y(NO_3)_3 + Nd(NO_3)_3$.

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Supporting Information Available:

Table S1 listing the Pitzer parameter values of eq 2 for aqueous pure NH_4NO_3, $Y(NO_3)_3$, and $Nd(NO_3)_3$; Table S2 listing the Pitzer mixing parameter values and higher-order virial terms for the ternary systems $H_2O + NH_4NO_3 + Nd(NO_3)_3$, $H_2O + NH_4NO_3 + Y(NO_3)_3$ and $H_2O + NH_4NO_3 + Nd(NO_3)_3$. Table S3 lists the high-order electrostatic functions in the Pitzer model for the interaction between aqueous NH_4^+ and Ln^{3+} (Ln = Y and Nd). Table S4 lists the osmotic coefficients and activity coefficients of pure NH_4NO_3 aqueous solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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