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Isopiestic Determination of Unsaturated and $NaNO_3$-Saturated H_2O + $NaNO_3$ + $Y(NO_3)_3$ + $La(NO_3)_3$ Systems and Representation with the Pitzer Model, Zdanovskii−Stokes−Robinson Rule, and Ideal−Like Solution Model

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S *Supporting Information*

ABSTRACT: Isopiestic osmotic coefficients were determined for the unsaturated and $NaNO_3$-saturated H_2O + $NaNO_3$ + $Y(NO_3)_3$ + $La(NO_3)_3$ system up to the maximum ionic strength I = 22 $mol \cdot kg^{-1}$ 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 $NaNO_3$-saturated quaternary system, respectively, which indicate that there is nonzero interchange energy between $NaNO_3$ 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 $NaNO_3$-saturated quaternary systems are in good agreement with the ideal−like solution model.

INTRODUCTION

Ionic interactions in the 3−1 electrolytes are more complicated than those in the 1−1, 2−1, and 2−2 electrolytes,[1,2] and the 3−1 actinide and lanthanide ions may follow a similar ion−interaction trend due to the similarity of actinides and lanthanides; however, the actinides can hardly be manipulated at high concentrations due to their radioactivity.[3] 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. Furthermore, the mixtures containing both the 3−1 rare earth electrolyte pairs such as $Y(NO_3)_3$ and $La(NO_3)_3$ and the biological metal ion electrolyte such as $NaNO_3$ are of great interest from both theoretical and practical points of view, and any theory being obeyed by these mixtures may also be suitable for the mixtures containing both the 3−1 actinide electrolyte pairs and biological metal ion electrolyte.

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 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 solutions 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 $0 \le x_j \le 1\{j \in (B, C, ..., Z)\}$), which was based on the Raoult law first discovered in pyridine solutions and which may be derived from a quasilattice treatment.[4] Similarly, based on the Zdanovskii−Stokes−Robinson (ZSR) rule[5,6] for unsaturated aqueous solutions at isopiestic conditions, Wang[7−12] developed a partial ideal solution (PIS) model for every kind of multicomponent system 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 $0 \le [x_j/(x_B + x_C + \cdots + x_Z)] \le 1$ for the systems with zero interchange energies among B, C, ..., Z and which may be derived from a modified quasilattice treatment. Recently, Wang[13] has extended it to the ideal−like solution (ILS) model for every kind of the multicomponent systems A1 + A2 + ... + Aq + B + C + ... + Z related to their subsystems A1 + A2 + ... + Aq + B, A1 + A2 + ... + Aq + C, ..., A1 + A2 + ... + Aq + Z at constant activities of the common component A1, A2, ..., Aq. 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, but the latter equations are difficult to be experimentally verified.

Osmotic and activity coefficients have been determined precisely for aqueous solutions at higher concentrations by isopiestic measurements[14] 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.[15] and Rard et al.[16−22] have made

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isopiestic measurements up to an ionic strength $I = 51\ \mathrm{mol\cdot kg^{-1}}$ (i.e., $23\ \mathrm{mol\cdot kg^{-1}}$ above saturation) for 14 pure rare earth nitrates, $I = 29\ \mathrm{mol\cdot kg^{-1}}$ for 12 pure rare earth perchlorates, and $I = 25\ \mathrm{mol\cdot kg^{-1}}$ for 14 pure rare earth chlorides, and Malatesta et al.[23] 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 $I = 0.001\ \mathrm{mol\cdot kg^{-1}}$. 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,[24] 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.[24−26] However, the ionic interaction analyses are still lacking for the aqueous solutions containing both the 3−1 rare earth electrolyte pairs and biological metal ion electrolyte to very high concentrations.[27] 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 $NaNO_3$-saturated $H_2O + NaNO_3 + Y(NO_3)_3 + La(NO_3)_3$.

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 biological metal ion electrolytes to very high concentrations, this work reports the isopiestic determinations of the unsaturated and $NaNO_3$-saturated quaternary system $H_2O + NaNO_3 + Y(NO_3)_3 + La(NO_3)_3$. A newly modified Pitzer model[27] 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 $NaNO_3$-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[14]

$$\phi = \nu^* m^* \phi^* / \sum_s \nu_s m_s \tag{1}$$

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[27] has been developed for the aqueous complex solutions $H_2O + MX + NX + \ldots$ containing both the 3−1 rare earth electrolyte pairs and biological metal ion electrolyte 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

$$\begin{aligned}\phi - 1 = {} & (2/\sum_i m_i)\{-A_\phi I^{3/2}/(1 + bI^{1/2}) \\ & + \sum_c m_c m_X (B^\phi_{cX} + ZC_{cX}) + \sum\sum_{c<c'} m_c m_{c'} [\Phi^\phi_{cc'} + m_X \psi_{cc'X}]\}\end{aligned} \tag{2}$$

$$\begin{aligned}\ln \gamma_M = {} & z_M^2 F + m_X(2B_{MX} + ZC_{MX}) \\ & + |z_M| \sum_c m_c m_X C_{cX} + \sum_c m_c (2\Phi_{Mc} + m_X \psi_{McX})\end{aligned} \tag{3}$$

$$\begin{aligned}\ln \gamma_X = {} & z_X^2 F + \sum_c m_c (2B_{cX} + ZC_{cX}) + |z_X| \sum_c m_c m_X C_{cX} \\ & + \sum\sum_{c<c'} m_c m_{c'} \psi_{cc'X}\end{aligned} \tag{4}$$

$$\begin{aligned}\ln \gamma_{MX} = {} & |z_M z_X| F + (\nu_M/\nu_{MX}) m_X (2B_{MX} + ZC_{MX}) \\ & + (\nu_X/\nu_{MX}) \sum_c m_c (2B_{cX} + ZC_{cX}) \\ & + 2z_M (\nu_M/\nu_{MX}) \sum_c m_c m_X C_{cX} \\ & + (\nu_M/\nu_{MX}) \sum_c m_c (2\Phi_{Mc} + m_X \psi_{McX}) \\ & + (\nu_X/\nu_{MX}) \sum\sum_{c<c'} m_c m_{c'} \psi_{cc'X}\end{aligned} \tag{5}$$

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; and the F, B, C, and Φ terms may be given by

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

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

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

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

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

$$C_{cX} = C^\phi_{cX}/2|z_c z_X|^{1/2} \tag{6f}$$

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

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

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

Table 1. Parameters and Standard Deviations of the Modified Pitzer Model for Fitting Literature Osmotic and Activity Coefficients of Aqueous Pure Nitrates from Infinite Dilution to the Maximum Ionic Strengths Available at 298.15 K[a,b]

nitrates	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^{(0)}$	$C^{(1)}$	$C^{(2)}$	$C^{(3)}$	σ	maximum I
$NaNO_3$	−0.001139	0.1932	0	0.0000692	0.0005925	0	0	0.0006	11
$Y(NO_3)_3$	0.3188	5.47	−4.25	−0.00447	0.0679	−0.0522	0.2191	0.0024	43
$La(NO_3)_3$	0.2086	5.43	−3.42	−0.00198	0.0604	−0.0698	0.2282	0.0009	51

[a] Given $\alpha_{B1} = 1.8\ kg^{1/2}\cdot mol^{-1/2}$, $\alpha_{B2} = 6.0\ kg^{1/2}\cdot mol^{-1/2}$, $\alpha_{C1} = 0.15\ kg\cdot mol^{-1}$, $\alpha_{C2} = 0.25\ kg\cdot mol^{-1}$, and $\alpha_{C3} = 0.35\ kg\cdot mol^{-1}$. [b] Given β in $kg\cdot mol^{-1}$, C in $kg^2\cdot mol^{-2}$, and I in $mol\cdot kg^{-1}$.

Here $g(\alpha_B I^{1/2})$, $g'(\alpha_B I^{1/2})$, ${}^E\theta_{cc'}(I)$, and ${}^E\theta'_{cc'}(I)$ 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 Na^+ and one Ln^{3+} in the $\theta_{cc'}$, $\Phi_{cc'}$, and $\psi_{cc'X}$ parameters; the electrostatic terms ${}^E\theta_{cc'}(I)$ and ${}^E\theta'_{cc'}(I)$ 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 $\alpha_{B1} = 1.8\ kg^{1/2}\cdot mol^{-1/2}$, $\alpha_{B2} = 6.0\ kg^{1/2}\cdot mol^{-1/2}$, $\alpha_{C1} = 0.15\ kg\cdot mol^{-1}$, $\alpha_{C2} = 0.25\ kg\cdot mol^{-1}$, and $\alpha_{C3} = 0.35\ kg\cdot mol^{-1}$.

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-canceled or negligible solute−solute interactions as compared to solute−solvent interactions (or with zero interchange energy among the solutes) may be given by[5−10,12]

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

$$(\sum_k \nu_k m_k)\gamma_i = \nu_i m_i\circ \gamma_i\circ \tag{8}$$

at constant activities of the common components A and within $0 \le y_j \le 1$, where $j, k \in (B, C, \cdots, Z)$ are all solutes; y is the molality fraction defined by $y_j = m_j/\Sigma_k m_k$; 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[13]

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

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

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

at constant activities of the common components A1, A2, ..., Aq within $0 \le y_j \le 1$, where $\beta \in (A2, A3, \cdots, Aq)$, 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[13,26]

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

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

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

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[11] or PIS model[5−10] 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 that MX is saturated but by H_2O(A) + MX(B) + NX(C) + LX(D) in another case that none of solutes is saturated.

EXPERIMENTAL SECTION

Y_2O_3 and La_2O_3 (99.99% from Aldrich Chemical Co.) were used to prepare stock solutions of $Y(NO_3)_3$ and $La(NO_3)_3$ by Rard's method,[16−22] 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 $NaNO_3$, 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.[13,24−27] 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 investigated system were placed. The isopiestic measurements were carried out from $I \approx 2\ mol\cdot kg^{-1}$ to $I \approx 16\ mol\cdot kg^{-1}$ for the unsaturated solutions and from $I \approx 13\ mol\cdot kg^{-1}$ to $I \approx 22\ mol\cdot kg^{-1}$ for the $NaNO_3$-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 9. The $NaNO_3$-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 $NaNO_3$ 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 $NaNO_3$ crystals dissolved into the near-saturated solutions to form the $NaNO_3$-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 (26 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 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 % and mostly to ± 0.04 % between the duplicates. The isopiestic solubilities of $NaNO_3$ were determined by the EDTA titration of the total amount of rare earths after some of the saturated solution in the liquid phase was 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 $NaNO_3$ were calculated by $(1000 + m_{A2}M_{A2} + m_BM_B + m_CM_C)/(m_B + m_C) = W/n_{Ln}$, where A2 denotes $NaNO_3$; 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 $NaNO_3$.

Table 2. Mixing Terms and Higher-Order Virial Terms in the Modified Pitzer Model (Equations 2 to 5) for the Aqueous Solutions $H_2O-NaNO_3-Y(NO_3)_3$, $H_2O-NaNO_3-La(NO_3)_3$, and $H_2O-Y(NO_3)_3-La(NO_3)_3$ at 298.15 K

systems	$\theta_{cc'}$	$\psi_{cc'X}$	σ
$H_2O-NaNO_3-Y(NO_3)_3$	0.01606	−0.01149	0.0032
$H_2O-NaNO_3-La(NO_3)_3$	−0.01407	0.003071	0.0024
$H_2O-Y(NO_3)_3-La(NO_3)_3$	−0.02190	0.001294	0.0021

RESULTS AND DISCUSSION

First, the ionic interactions in the unsaturated quaternary system $H_2O + NaNO_3 + Y(NO_3)_3 + La(NO_3)_3$ and $NaNO_3$-saturated quaternary system $H_2O + NaNO_3(sat) + Y(NO_3)_3 + La(NO_3)_3$ were analyzed using the modified Pitzed model. Before doing so, we recalculated the osmotic coefficients of pure $NaNO_3$ in the whole concentrations from the literature isopiestic determinations[31] by eq 1 based on the recent critically assessed and consistent literature sources of the isopiestic reference standards of pure KCl[31] and NaCl.[32] We found that the newly calculated osmotic coefficient values may be quantitatively fitted by the Pitzer model containing the four parameters $\beta^{(0)}$, $\beta^{(1)}$, $C^{(0)}$, and $C^{(1)}$. Table 1 lists the Pitzer parameter values and fitting standard deviations of eq 2 for pure $NaNO_3$, $Y(NO_3)_3$, and $La(NO_3)_3$ with $\sigma = 0.0006$, 0.0024, and 0.0009, respectively. Table 2 lists the values of two mixing parameters θ and ψ for the aqueous solutions $H_2O + NaNO_3 + Y(NO_3)_3$, $H_2O + NaNO_3 + La(NO_3)_3$, and $H_2O + Y(NO_3)_3 + La(NO_3)_3$ with $\sigma = 0.0032$, 0.0024, and 0.0021, respectively. Table S1 (Supporting Information) lists the high-order electrostatic functions in the Pitzer model for the interaction between aqueous Na^+ and Ln^{3+} (Ln = Y and La) with $I = (0.5 \text{ to } 30)$ mol·kg^{-1}. All these parameters will be used in the ion-interaction analysis in this study.

Table 3 and Table 4 list the measured isopiestic osmotic coefficients for the unsaturated quaternary system $H_2O + NaNO_3 + Y(NO_3)_3 + La(NO_3)_3$ to $I = 16$ mol·kg^{-1} and for the $NaNO_3$-saturated quaternary system $H_2O + NaNO_3(sat) + Y(NO_3)_3 + La(NO_3)_3$ to $I = 22$ mol·kg^{-1}, respectively, at 298.15 K. Our experimental osmotic coefficients for aqueous $NaNO_3$, $Y(NO_3)_3$, and $La(NO_3)_3$ solutions listed in Tables 3 and 4 are in excellent agreement with those calculated by the modified Pitzer model with the virial parameters listed in Table 1. 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 $C^{(3)}$ (eq 2) was found to be suitable for fitting the isopiestic osmotic coefficients of the unsaturated quaternary system

Table 3. Experimental Isopiestic Osmotic Coefficients, ϕ, of the Unsaturated Aqueous Solution $H_2O(A) + NaNO_3(B) + Y(NO_3)_3(C) + La(NO_3)_3(D)$ at 298.15 K

m_{NaCl}[a]	m					m_{NaCl}[a]	m				
mol·kg^{-1}	mol·kg^{-1}	y_C[b]	y_D[b]	Δ_A (eq 12)	ϕ	mol·kg^{-1}	mol·kg^{-1}	y_C[b]	y_D[b]	Δ_A (eq 12)	ϕ
1.415	0.812	0	1		0.832	4.165	2.199	0	1		1.070
	0.712	1	0		0.949		1.811	1	0		1.299
	1.622	0	0		0.833		5.983	0	0		0.786
	1.069	0.222	0.257	0.015	0.855		3.353	0.189	0.220	0.017	0.995
	0.974	0.368	0.215	0.012	0.877		2.972	0.306	0.194	0.013	1.055
	1.205	0.156	0.168	0.016	0.847		4.026	0.118	0.141	0.019	0.929
2.762	1.505	0	1		0.948	5.151	2.680	0	1		1.156
	1.261	1	0		1.132		2.197	1	0		1.410
	3.550	0	0		0.804		7.942	0	0		0.780
	2.141	0.198	0.237	0.014	0.929		4.275	0.177	0.222	0.022	1.036
	1.909	0.334	0.202	0.012	0.973		3.777	0.297	0.192	0.024	1.102
	2.521	0.121	0.153	0.014	0.889		5.199	0.108	0.143	0.024	0.953

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

Table 4. Experimental Isopiestic Osmotic Coefficients of the $NaNO_3$-Saturated Aqueous Solutions $H_2O(A1) + NaNO_3(A2)(sat) + Y(NO_3)_3(B) + La(NO_3)_3(C)$ at 298.15 K

m_{CaCl2}[a] $mol \cdot kg^{-1}$	m $mol \cdot kg^{-1}$	y_B[b]	y_C[b]	Δ_{A1} (eq 12)	Δ_{A2} (eq 13)	ϕ	m_{CaCl2}[a] $mol \cdot kg^{-1}$	m $mol \cdot kg^{-1}$	y_B[b]	y_C[b]	Δ_{A1} (eq 12)	Δ_{A2} (eq 13)	ϕ
3.123	9.262	0	0.0819			0.852	3.529	8.519	0	0.2442			0.994
	9.270	0.0148	0.0667	−0.0001	0.0008	0.852		8.615	0.0436	0.1929	−0.0009	0.0009	0.989
	9.287	0.0291	0.0519	0.0000	0.0006	0.851		8.716	0.0827	0.1469	−0.0004	0.0013	0.983
	9.305	0.0450	0.0356	0.0004	0.0008	0.850		8.836	0.1279	0.0937	−0.0002	0.0014	0.976
	9.332	0.0624	0.0175	0.0003	−0.0003	0.848		8.935	0.1668	0.0478	−0.0009	0.0013	0.970
	9.344	0.0794	0			0.847		9.064	0.2071	0			0.962
3.283	8.791	0	0.1589			0.913	3.820	8.502	0	0.3141			1.080
	8.819	0.0284	0.1283	0.0002	0.0002	0.912		8.667	0.0598	0.2441	−0.0002	0.0008	1.068
	8.849	0.0563	0.0982	0.0003	0.0001	0.911		8.804	0.1093	0.1861	−0.0008	0.0018	1.059
	8.874	0.0846	0.0677	0.0000	0.0002	0.910		8.985	0.1686	0.1165	−0.0009	0.0019	1.046
	8.913	0.1160	0.0337	0.0005	−0.0001	0.908		9.153	0.2183	0.0579	−0.0008	0.0008	1.033
	8.939	0.1473	0			0.907		9.330	0.2674	0			1.021

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

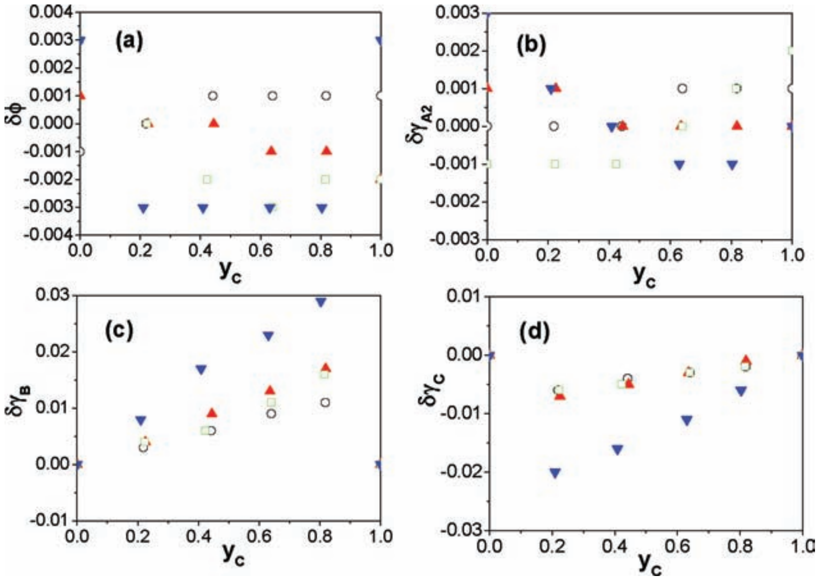

Figure 1. Deviations of (a) $\delta\phi = \phi(\text{expt}) - \phi(\text{calc})$, of (b) $\delta\gamma_{A2} = \gamma_{A2}(\text{expt}) - \gamma_{A2}(\text{calc})$, of (c) $\delta\gamma_B = \gamma_B(\text{expt}) - \gamma_B(\text{calc})$, and of (d) $\delta\gamma_C = \gamma_C(\text{expt}) - \gamma_C(\text{calc})$ obtained at water activity $a_w(= a_{A1})$ = □, 0.7351; ○, 0.7152; ▲, 0.6843; and ▼, 0.6473; for the $NaNO_3$-saturated aqueous solution $H_2O(A1) + NaNO_3(A2) + Y(NO_3)_3(B) + La(NO_3)_3(C)$.

$H_2O + NaNO_3 + Y(NO_3)_3 + La(NO_3)_3$ and $NaNO_3$-saturated quaternary system $H_2O + NaNO_3(sat) + Y(NO_3)_3 + La(NO_3)_3$. The standard deviations are within $\sigma_{max} \leq 0.003$. These results, together with those reported in ref 25, 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 $H_2O + NaNO_3 + Y(NO_3)_3 + La(NO_3)_3$ and $NaNO_3$-saturated quaternary system $H_2O + NaNO_3(sat) + Y(NO_3)_3 + La(NO_3)_3$. The values of high-order electrostatic functions listed in Table S1 (Supporting Information) were inserted in eqs 6g to 6i to give the mixing 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.

Second, the solute−solute interactions in the unsaturated quaternary system $H_2O + NaNO_3 + Y(NO_3)_3 + La(NO_3)_3$ 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 3 shows that the isopiestic molalities for the unsaturated quaternary system $H_2O(A) + NaNO_3(B) + Y(NO_3)_3(C) + La(NO_3)_3(D)$ deviates from eq 7 or 9, the values of the $\Delta_A(= \Delta_{A1})$ function defined by eq 12 being high up to 0.024, which indicates the nonzero interchange energies between $NaNO_3$ and $Ln(NO_3)_3$.

Table 4 shows that the isopiestic molalities of the $NaNO_3$-saturated quaternary systems $H_2O(A1) + NaNO_3(A2) + Y(NO_3)_3(B) + La(NO_3)_3(C)$ 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 $NaNO_3$-saturated quaternary system over the entire concentration range. This means that the $NaNO_3$-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 $NaNO_3$-saturated quaternary system, the activity coefficients of the rare earth nitrates can also be calculated by using a very simple equation (eq 11). Figure 1 shows the deviations of (a) $\delta\phi = \phi(\mathrm{expt}) - \phi(\mathrm{calc})$, of (b) $\delta\gamma_{A2} = \gamma_{A2}(\mathrm{expt}) - \gamma_{A2}(\mathrm{calc})$, of (c) $\delta\gamma_B = \gamma_B(\mathrm{expt}) - \gamma_B(\mathrm{calc})$, and of (d) $\delta\gamma_C = \gamma_C(\mathrm{expt}) - \gamma_C(\mathrm{calc})$, where $\phi(\mathrm{expt})$ was obtained from the isopiestic experiments (eq 1); $\gamma_{A2}(\mathrm{expt})$ was obtained from both the isopiestic molalities of the $NaNO_3$-saturated quaternary system and the $NaNO_3$ activity value 12.27, which was calculated from the molality value ($10.83\ \mathrm{mol \cdot kg^{-1}}$) and activity coefficient value (0.3235) listed in Table S2 (Supporting Information) for aqueous pure $NaNO_3$ and which is invariant for the $NaNO_3$—-saturated solutions; and $\gamma_B(\mathrm{expt})$ and $\gamma_C(\mathrm{expt})$ were obtained from the ILS model (eq 11). Meanwhile, $\phi(\mathrm{calc})$, $\gamma_{A2}(\mathrm{calc})$, $\gamma_B(\mathrm{calc})$, and $\gamma_C(\mathrm{calc})$ were calculated by the modified Pitzer model equations (eqs 2 and 5) for the $NaNO_3$-saturated quaternary system. 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}, $\sigma_{\max} = 0.03$ for γ_B, and $\sigma_{\max} = 0.02$ for γ_C of $H_2O(A1) + NaNO_3(A2) + Y(NO_3)_3(B) + La(NO_3)_3(C)$. 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 systems 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 $NaNO_3$-saturated quaternary system $H_2O + NaNO_3 + Y(NO_3)_3 + La(NO_3)_3$. A modified Pitzer model extending to $C^{(3)}$ is used for quantitatively representing the ionic interactions in this system. This model can sufficiently describe the ionic interactions in the aqueous solutions containing both the 3−1 rare earth electrolyte pairs and sodium ion electrolyte from dilution to saturation.

The unsaturated quaternary system $H_2O + NaNO_3 + Y(NO_3)_3 + La(NO_3)_3$ obviously deviates from the ZSR rule or PIS model, which indicates the nonzero solute−solute interaction energy between $NaNO_3$ and each rare earth nitrate. On the other hand, the $NaNO_3$-saturated quaternary system $H_2O + NaNO_3(\mathrm{sat}) + Y(NO_3)_3 + La(NO_3)_3$ 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 biological metal ions electrolyte. Furthermore, the ILS model is verified completely both by the precise isopiestic determinations and by the quantitative Pitzer model calculations for the $NaNO_3$-saturated quaternary system $H_2O + NaNO_3(\mathrm{sat}) + Y(NO_3)_3 + La(NO_3)_3$.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Table S1 lists the high-order electrostatic functions in the Pitzer model for the interaction between aqueous Na^+ and Ln^{3+} (Ln = Y and La). Table S2 lists the osmotic coefficients and activity coefficients of pure $NaNO_3$ aqueous solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

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

(2) Pitzer, K. S. *Ion Interaction Approach: Theory and Data Correlation in Activity Coefficients in Electrolyte Solutions*, 2nd ed.; Pitzer, K. S., Ed.; CRC Press: Boca Raton, FL, 1991; Chapter 3.

(3) Oakes, C. S.; Rard, J. A.; Archer, D. G. Enthalpies of Dilution of $NdCl_3(aq)$ at Temperatures from 297.89 to 372.08 K and an Extended Pitzer Ion-Interaction Model for the $NdCl_3 + H_2O$ System. *J. Chem. Eng. Data* **2004**, *49*, 313–325.

(4) Guggenheim, E. A. *Mixtures*; Oxford University Press: Oxford, 1952.

(5) Zdanovskii, A. B. Regularities in the Property Variations of Mixed Solutions. *Tr. Solyanoi Lab. Akad. Nauk SSSR* No. 6, **1936**.

(6) Stokes, R. H.; Robinson, R. A. Interactions in Aqueous Nonelectrolyte Solutions. I. Solute-Solvent Equilibria. *J. Phys. Chem.* **1966**, *70*, 2126–2131.

(7) Wang, Z.-C. The Linear Concentration Rules at Constant Partial Molar Quantity Ψ_θ—Extension of Turkdogan's Rule and Zdanovskii's Rule. *Acta Metall. Sin.* **1980**, *16*, 195–206.

(8) Wang, Z.-C. Thermodynamics of Multicomponent Systems at Constant Partial Molar Quantity Ψ_θ — Thermodynamical Aspect of Iso-Ψ_θ Rules of Zdanovskii-Type and Turkdogan-Type. *Acta Metall. Sin.* **1981**, *17*, 168–176.

(9) Wang, Z.-C. *The Theory of Partial Simple Solutions for Multicomponent Systems in First China-USA Bilateral Metallurgical Conference*; The Metall. Ind. Press: Beijing, 1981; p 121.

(10) Wang, Z.-C. The Theory of Partial Simple Solutions for Multicomponent Systems. *Acta Metall. Sin.* **1982**, *18*, 141–152.

(11) Wang, Z.-C.; Zhang, X.-H.; He, Y.-Z.; Bao, Y.-H. High-Temperature Isopiestic Studies on $\{(1\text{-}y)Hg + y(1\text{-}t)Bi + ytSn\}(1)$ at 600 K. Comparison with the Partial Ideal Solution Model. *J. Chem. Thermodyn.* **1989**, *21*, 653–665.

(12) Wang, Z.-C.; Lück, R.; Predel, B. Pure Component A + Classically Ideal Solution (B + C + ...) = ? *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3641–3646.

(13) Wang, Z.-C. Novel General Linear Concentration Rules and Their Theoretical Aspects for Multicomponent Systems at Constant Chemical Potentials-Ideal-Like Solution Model and Dilute-Like Solution Model. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 1045–1058.

(14) Rard, J. A.; Platford, R. F. *Experimental Methods: Isopiestic in Activity Coefficients in Electrolyte Solutions*, 2nd ed.; Pitzer, K. S., Ed.; CRC Press: Boca Raton, FL, 1991; Chapter 5.

(15) Spedding, F. H.; Weber, H. O.; Saeger, V. W.; Petheram, H. H.; Rard, J. A.; Habenschuss, A. Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare Earth Electrolyte Solutions at 25 °C 1. The Rare Earth Chlorides. *J. Chem. Eng. Data* **1976**, *21*, 341–360.

(16) Rard, J. A.; Weber, H. O.; Spedding, F. H. Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare Earth Electrolyte Solutions at 25 °C. 1. The Rare Earth Perchlorates. *J. Chem. Eng. Data* **1977**, *22*, 187–201.

(17) Rard, J. A.; Shiers, L. E.; Heiser, D. J.; Spedding, F. H. Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare Earth Electrolyte Solutions at 25 °C. 3. The Rare Earth Nitrates. *J. Chem. Eng. Data* **1977**, *22*, 337–347.

(18) Rard, J. A.; Miller, D. G.; Spedding, F. H. Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare Earth Electrolyte Solutions at 25 °C. 4. $La(NO_3)_3$, $Pr(NO_3)_3$, and $Nd(NO_3)_3$. *J. Chem. Eng. Data* **1979**, *24*, 348–354.

(19) Rard, J. A.; Spedding, F. H. Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare Earth Electrolyte Solutions at 25 °C. 5. $Dy(NO_3)_3$, $Ho(NO_3)_3$, and $Lu(NO_3)_3$. *J. Chem. Eng. Data* **1981**, *26*, 391–395.

(20) Rard, J. A.; Spedding, F. H. Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare Earth Electrolyte Solutions at 25 °C. 6. $Eu(NO_3)_3$, $Y(NO_3)_3$, and YCl_3. *J. Chem. Eng. Data* **1982**, *27*, 454–461.

(21) Rard, J. A. Osmotic and Activity Coefficients of Aqueous $La(NO_3)_3$ and Densities and Apparent Molar Volumes of Aqueous $Eu(NO_3)_3$ at 25 °C. *J. Chem. Eng. Data* **1987**, *32*, 92–98.

(22) Rard, J. A. Isopiestic Determination of the Osmotic and Activity Coefficients of Aqueous $NiCl_2$, $Pr(NO_3)_3$, and $Lu(NO_3)_3$ and Solubility of $NiCl_2$ at 25 °C. *J. Chem. Eng. Data* **1987**, *32*, 334–341.

(23) Malatesta, F.; Bruni, F.; Fanelli, N. Activity Coefficients of Lanthanum Salts at 298.15 K. *Phys. Chem. Chem. Phys.* **2002**, *4*, 121–126.

(24) Wang, Z.-C.; He, M.; Wang, J.; Li, J.-L. Modeling of Aqueous 3−1 Rare Earth Electrolytes and Their Mixtures to Very High Concentrations. *J. Solution Chem.* **2006**, *35*, 1137–1156.

(25) He, M.; Wang, Z.-C. Interactions in the Quaternary Systems H_2O-$Y(NO_3)_3$-$La(NO_3)_3$-$Pr(NO_3)_3$, H_2O-$Y(NO_3)_3$-$La(NO_3)_3$-$Nd(NO_3)_3$ and H_2O-$Y(NO_3)_3$-$Pr(NO_3)_3$-$Nd(NO_3)_3$ to Very High Concentrations. *J. Solution Chem.* **2006**, *35*, 1607–1619.

(26) He, M.; Wang, Z.-C. Interactions in the Quinary System H_2O-$Y(NO_3)_3$-$La(NO_3)_3$-$Pr(NO_3)_3$- $Nd(NO_3)_3$ to Very High Concentrations. *J. Solution Chem.* **2007**, *36*, 1547–1558.

(27) Wang, Z.-C.; He, M.; Gong, L.-D. Thermodynamics of Aqueous Complex Solutions Containing 3/1 Rare Earth Electrolyte Pairs and Salting-Out Agents to Very High Concentrations. *J. Phys. Chem. B* **2007**, *111*, 3704–3715.

(28) Archer, D. G. Thermodynamic Properties of the NaCl + H_2O System II. Thermodynamic Properties of NaCl(aq), $NaCl\cdot 2H_2O$(cr), and Phase Equilibria. *J. Phys. Chem. Ref. Data* **1992**, *21*, 793–829.

(29) Rard, J. A.; Clegg, S. L. Critical Evaluation of the Thermodynamic Properties of Aqueous Calcium Chloride. 1. Osmotic and Activity Coefficients of 0−10.77 $mol\cdot kg^{-1}$ Aqueous Calcium Chloride Solutions at 298.15 K and Correlation with Extended Pitzer Ion-Interaction Models. *J. Chem. Eng. Data* **1997**, *42*, 819–849.

(30) Kelly, F. J.; Robinson, R. A.; Stokes, R. H. The Thermodynamics of the Ternary System Mannitol-Sodium Chloride-Water at 25 oC from Solubility and Vapor Pressure Measurements. *J. Phys. Chem.* **1961**, *65*, 1958–1960.

(31) Wu, Y. C.; Hamer, W. J. Revised Values of the Osmotic Coefficients and Mean Activity Coefficients of Sodium Nitrate in Water at 25 °C. *J. Phys. Chem. Ref. Data* **1980**, *9*, 513–518.

(32) Guendouzi, M. E.; Marouani, M. Water Activities and Osmotic and Activity Coefficients of Aqueous Solutions of Nitrates at 25 °C by the Hygrometric Method. *J. Solution Chem.* **2003**, *32*, 535–546.