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Interactions in Aqueous 3−1 Rare Earth Electrolyte Quaternary Systems and Their Ternary Subsystems to Very High Concentrations

Mei He,*[†] Ling Dong,[†] and Biao Li[‡]

[†]Department of Applied Chemistry, Shenyang University of Chemical Technology, Shenyang 110142, P. R. China

[‡]Department of Criminal Science and Technique, China Criminal Police College, Shenyang 110854, P. R. China

ABSTRACT: Ionic interactions have been investigated from isopiestic measurements on 3−1 rare earth electrolyte quaternary systems $H_2O-Er(NO_3)_3-La(NO_3)_3-Y(NO_3)_3$, $H_2O-Er(NO_3)_3-Pr(NO_3)_3-Y(NO_3)_3$, and $H_2O-Er(NO_3)_3-Nd(NO_3)_3-Y(NO_3)_3$ and their ternary subsystems $H_2O-Er(NO_3)_3-La(NO_3)_3$, $H_2O-Er(NO_3)_3-Pr(NO_3)_3$, $H_2O-Er(NO_3)_3-Nd(NO_3)_3$, and $H_2O-Er(NO_3)_3-Y(NO_3)_3$ at 298.15 K to near saturation. The isopiestic measurements can be represented by a modified Pitzer ion-interaction model extending to $C^{(3)}$ within the experimental uncertainty over a full concentration range. In addition, the Zdanovskii−Stokes−Robinson model or partial ideal solution model is obeyed by all systems within isopiestic accuracy, indicating zero exchange energy between the unlike salts, which is consistent with the nature of rare earth elements.

■ INTRODUCTION

Thermodynamic properties from infinite dilution to saturation (or supersaturation) of aqueous electrolytes and their mixtures are important for many biological, geological, and industrial systems and have theoretical interest. One of the major advances in this field over the last 30 years has been the Pitzer ion-interaction model.[1−3] Various modifications to the Pitzer ion-interaction model extending either to $F^{(0)}$, $\beta^{(2)}$, $C^{(2)}$, or to $D^{(2)}$ have been introduced for highly soluble 1−1, 2−1, and 2−2 electrolytes[4−7] and their mixtures.[8,9] However, all of them cannot fit the highly soluble and highly unsymmetrical electrolytes very well, particularly for rare earth nitrites, chlorides, and perchlorates, where their standard deviations are significantly higher than the experimental errors of the precise isopiestic measurements of Spedding et al.[10] and Rard et al.[11−17] We[18] found that this problem could simply be solved by introducing a $C^{(3)}$ parameter into the Pitzer ion-interaction model, which can quantitatively represent these literature isopiestic[10−17] measurements up to the maximum saturate or supersaturate concentrations available.

Ionic interactions in 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. Therefore, 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.

Besides, scientists studying different kinds of the solutions such as organic mixtures, aqueous and nonaqueous electrolyte and nonelectrolyte solutions, alloys, molten salt mixtures, slags, and nonstoichiometric solid solutions often use rather different 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 $0 \le x_j \le 1\{j \in (B, C, \cdots, Z)\}$), which was based on the Raoult law first discovered in pyridine solutions and which may be derived from a quasi-lattice treatment.[19] Similarly, based on the Zdanovskii−Stokes−Robinson (ZSR) rule[20−24] for unsaturated aqueous solutions at isopiestic conditions, Wang[25−30] developed a partial ideal solution (PIS) model for every kind of the 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 $0 \le [x_j/(x_B + x_C + \cdots + x_Z)] \le 1$ for the systems with zero interchange energies among B, C, ···, Z and which may be derived from a modified quasi-lattice treatment. The precise literature data for aqueous electrolyte mixtures at constant water activity, which could be used in the ZSR model testing, are normally available only to moderate ionic strengths.[20,22] It is therefore interesting to examine whether the new isopiestic measurements for the aqueous rare earth electrolyte quaternary systems and their ternary subsystems to very high concentrations still follow the ZSR model (or the partial ideal solution model).

To gain deeper insights into 3−1 rare earth electrolyte mixtures, we extend the isopiestic measurements to the quaternary systems $H_2O-Er(NO_3)_3-La(NO_3)_3-Y(NO_3)_3$, $H_2O-Er(NO_3)_3-Pr(NO_3)_3-Y(NO_3)_3$, $H_2O-Er(NO_3)_3-Nd(NO_3)_3-Y(NO_3)_3$, and their ternary subsystems $H_2O-Er(NO_3)_3-La(NO_3)_3$, $H_2O-Er(NO_3)_3-Pr(NO_3)_3$, $H_2O-Er(NO_3)_3-Nd(NO_3)_3$, and $H_2O-Er(NO_3)_3-Y(NO_3)_3$ to near-saturation and represent the new measurements by the new simple modified ion-interaction model, the ZSR model, and other empirical rules (or equations).

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EQUATIONS

It is known that the complex formation is weak in the aqueous rare earth nitrates and very weak in the aqueous rare earth chlorides and perchlorates[31−33] and that the exchange energy is expected to be zero or near-zero between unlike rare earth ions in their aqueous mixtures. Hence, a simple modified ion-interaction model only containing the binary ($\beta^{(0)}, \beta^{(1)}, \cdots$) and third ($C^{(0)}, C^{(1)}, \cdots$) virials as well as the second (θ) and third mixing terms (ψ), both of which are dominated by pairwise and triplet interactions, would be desirable. Its complete expressions for the osmotic coefficient (ϕ) and activity coefficient (γ) may then be given by

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

$$\begin{aligned}\ln \gamma_{MX} = {} & -|z_M z_X| A_\phi [I^{1/2}/(1 + bI^{1/2}) \\ & + (2/b)\ln(1 + bI^{1/2})] \\ & + (\nu_M \nu_X/\nu_{MX}) m_T [2B_{MX} + (\nu_M \nu_X)^{1/2} m_T C^\gamma_{MX}] \\ & + \sum_c (\nu_c \nu_X/\nu_{cX}) m_{cX} m_T [(\nu_c \nu_X)^{1/2} C^\gamma_{cX}] \\ & + (\nu_M \nu_X/\nu_{MX}) m_{MX} m_T [(\nu_M \nu_X)^{1/2} C^\gamma_{MX}] \\ & + [(\nu_M/\nu_{MX}) \sum_c m_c (2\theta_{Mc} + m_X \psi_{McX}) \\ & + (\nu_X/\nu_{MX}) \sum_{c<c'} \sum m_c m_{c'} \psi_{cc'X}\end{aligned} \tag{2}$$

where A_ϕ is the Debye−Hückel limiting law parameter (0.3915 $\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$ at 298.15 K), $b = 1.2\ \text{kg}^{1/2}\cdot\text{mol}^{-1/2}$, $Z = \Sigma_i m_i |z_i|$, i denotes all ions, z is the charge number, ν is the stoichiometric coefficient, m is molality, and m_T is the total solute molality, and B and C are virial terms for pairwise and triplet interactions of the like salts given by

$$B_{cX} = \beta^{(0)}_{cX} + \beta^{(1)}_{cX} g(\alpha_{B1} I^{1/2}) + \beta^{(2)}_{cX} g(\alpha_{B2} I^{1/2}) \tag{3a}$$

$$C_{cX} = C^\phi_{cX}/2|z_c z_X|^{1/2} \tag{3b}$$

$$B^\phi_{cX} = \beta^{(0)}_{cX} + \beta^{(1)}_{cX} \exp(-\alpha_{B1} I^{1/2}) + \beta^{(2)}_{cX} \exp(-\alpha_{B2} I^{1/2}) \tag{3c}$$

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

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

where $g(x) = 2\{1 - [(1 + x)\exp(-x)/x^2]\}$, and θ and ψ are mixing terms for pairwise and triplet interactions of the unlike salts.

On the other hand, the modified ZSR equation at constant water activity and the McKay−Perring equation for aqueous mixtures may be given respectively by[22−24,34]

$$\Delta = \sum_j (m_j/m^\circ_j) - 1 \tag{4}$$

$$\nu_j \ln(m_T \gamma_j/m^\circ_j \gamma^\circ_j) = \int_0^{\ln a_w} \{\partial[\Delta/m_T(1 - y_j)]/\partial[1/(1 - y_j)]\} \mathrm{d} \ln a_w \tag{5}$$

and the Harned equation[35] at constant total ionic strength, which is often used for the aqueous electrolyte mixtures to moderate ionic strengths,[35−38] may be given by

$$\ln \gamma_j = \ln \gamma^\circ_j - \sum_k \alpha_{jk} y_k - \sum_k \beta_{jk} y_k{}^2 \tag{6}$$

where $y_j = m_j/m_T$, j and k denote different electrolytes, the superscript ° denotes the quantity of aqueous pure electrolytes, and α and β are the Harned coefficients. In one special case of $\Delta = 0$, eq 4 reduces to the ZSR model

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

and, if eq 7 holds from $a_w = 1$ to $a_w = a_w$, eq 5 reduces to the simplified McKay−Perring equation

$$m_T \gamma_j/m^\circ_j \gamma^\circ_j = 1 \tag{8}$$

In another special case of all $\beta = 0$, eq 6 reduces to the Harned rule[35]

$$\ln \gamma_j = \ln \gamma^\circ_j - \sum_k \alpha_{jk} y_k \tag{9}$$

EXPERIMENTAL SECTION

Er_2O_3, La_2O_3, Pr_6O_{11}, Nd_2O_3, and Y_2O_3 (99.99 % from Aldrich Chemical Co.) were used to prepare stock solutions of $Er(NO_3)_3$, $La(NO_3)_3$, $Pr(NO_3)_3$, $Nd(NO_3)_3$, and $Y(NO_3)_3$ by Rard's method.[11−17] 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. The rare earth nitrate molalities were determined by the ethylenediaminetetraacetic acid titration and by the gravimetric sulfate method, after destroying the nitrate ions by evaporation with hydrochloric acid. The stock solution concentrations were known to be 0.1 % or better. NaCl and $CaCl_2$ from the same source were recrystallized from water several times and dried over P_2O_5. The concentrations of aqueous NaCl and $CaCl_2$ were determined by the $AgNO_3$ titration. All of the solutions were prepared by weight in triple-distilled water and converted into mass. The aqueous NaCl and $CaCl_2$ were used as isopiestic standards for the dilute and concentrated rare earth nitrate solutions, respectively, and their osmotic coefficients were taken from the recent literature sources.[39,40] At isopiestic equilibrium, every samples have the same water activity, so that the osmotic coefficients of the rare earth nitrate solutions may be calculated by the equation[10]

$$\phi = \nu^* m^* \phi^* / \sum_j \nu_j m_j \tag{10}$$

Table 1. Isopiestic Results of Ternary Systems $H_2O-Er(NO_3)_3-La(NO_3)_3$, $H_2O-Er(NO_3)_3-Pr(NO_3)_3$, $H_2O-Er(NO_3)_3-Nd(NO_3)_3$, and $H_2O-Er(NO_3)_3-Y(NO_3)_3$ at 298.15 K

I_{NaCl}[a]	I[b]	y_C	ϕ_{exp}[c]	ϕ_{calc}[d]	I_{CaCl_2}[a]	I[b]	y_C	ϕ_{exp}[c]	ϕ_{calc}[d]
				(1) $H_2O(A)-Er(NO_3)_3(B)-La(NO_3)_3(C)$					
2.057	5.905	0	1.034	1.034	10.171	16.843	0	1.548	1.548
	6.098	0.2215	1.002	1.004		17.573	0.2390	1.484	1.487
	6.288	0.4302	0.972	0.974		18.238	0.4437	1.430	1.433
	6.479	0.6279	0.943	0.945		18.950	0.6478	1.376	1.378
	6.679	0.8174	0.915	0.916		19.660	0.8318	1.326	1.328
	6.881	1	0.888	0.888		20.342	1	1.282	1.281
4.132	10.874	0	1.285	1.285	12.307	20.421	0	1.687	1.687
	11.377	0.2611	1.228	1.230		21.244	0.2260	1.621	1.624
	11.855	0.4885	1.179	1.181		22.034	0.4308	1.563	1.566
	12.187	0.6365	1.147	1.149		22.892	0.6331	1.505	1.508
	12.624	0.8147	1.107	1.109		23.752	0.8227	1.450	1.453
	13.097	1	1.067	1.067		24.614	1	1.399	1.399
				(2) $H_2O(A)-Er(NO_3)_3(B)-Pr(NO_3)_3(C)$					
2.098	6.007	0	1.040	1.040	10.167	17.404	0	1.571	1.571
	6.180	0.2198	1.011	1.012		18.012	0.2333	1.518	1.519
	6.357	0.4269	0.983	0.985		18.569	0.4361	1.473	1.474
	6.530	0.6243	0.957	0.959		19.177	0.6405	1.426	1.428
	6.709	0.8149	0.931	0.932		19.763	0.8278	1.384	1.385
	6.893	1	0.906	0.906		20.333	1	1.345	1.345
4.214	11.067	0	1.294	1.294	12.005	20.611	0	1.694	1.694
	11.503	0.2573	1.245	1.247		21.289	0.2243	1.640	1.642
	11.915	0.4853	1.202	1.204		21.956	0.4317	1.590	1.593
	12.199	0.6348	1.174	1.175		22.648	0.6364	1.542	1.544
	12.574	0.8162	1.139	1.141		23.365	0.8322	1.494	1.496
	12.967	1	1.105	1.105		24.009	1	1.454	1.454
				(3) $H_2O(A)-Er(NO_3)_3(B)-Nd(NO_3)_3(C)$					
2.105	6.021	0	1.041	1.041	9.901	16.943	0	1.552	1.552
	6.186	0.2199	1.013	1.014		17.555	0.2409	1.500	1.498
	6.349	0.4271	0.987	0.989		18.092	0.4390	1.456	1.454
	6.510	0.6241	0.963	0.964		18.715	0.6568	1.407	1.405
	6.679	0.8180	0.938	0.939		19.265	0.8342	1.367	1.365
	6.846	1	0.916	0.915		19.801	1	1.328	1.328
4.436	11.596	0	1.319	1.319	11.999	20.601	0	1.693	1.693
	12.064	0.2655	1.268	1.269		21.280	0.2241	1.641	1.639
	12.467	0.4760	1.227	1.229		21.944	0.4318	1.592	1.590
	12.765	0.6256	1.198	1.199		22.638	0.6364	1.543	1.541
	13.154	0.8074	1.163	1.164		23.356	0.8324	1.496	1.494
	13.588	1	1.126	1.125		23.998	1	1.454	1.454
				(4) $H_2O(A)-Er(NO_3)_3(B)-Y(NO_3)_3(C)$					
2.109	6.034	0	1.041	1.041	8.418	17.039	0	1.556	1.556
	6.029	0.1987	1.042	1.042		16.993	0.2162	1.560	1.560
	6.022	0.3949	1.043	1.042		16.960	0.4019	1.563	1.563
	6.014	0.5927	1.045	1.043		16.915	0.6206	1.567	1.568
	6.009	0.7968	1.046	1.045		16.873	0.8114	1.571	1.571
	6.002	1	1.047	1.047		16.837	1	1.575	1.575
4.576	11.932	0	1.334	1.334	10.936	22.213	0	1.751	1.751
	11.907	0.2537	1.337	1.337		22.145	0.1871	1.756	1.757
	11.887	0.4493	1.339	1.338		22.090	0.3635	1.761	1.763
	11.869	0.5954	1.342	1.340		22.025	0.5582	1.766	1.768
	11.852	0.7822	1.343	1.343		21.941	0.7860	1.773	1.774
	11.829	1	1.346	1.346		21.872	1	1.778	1.778

[a] For isopiestic standards in mol·kg^{-1}. [b] For isopiestic samples in mol·kg^{-1}. [c] Equation 10. [d] Equation 1.

from the known properties of isopiestic reference solutions NaCl or $CaCl_2$ denoted by the asterisk.

The isopiestic measurements were made by the method described previously.[41−46] Fourteen gold-plated silver cups were placed in an isopiestic apparatus made of copper. Each sample was run in duplicate. One glass ball and (1.5 to 3.0) g of reference solution or investigated system were placed in each of the cups. After evacuating air, the apparatus was rocked once every 5 s in the thermostat controlled at 298.15 ± 0.01 K during the whole experimental process. The isopiestic measurements were carried out from $I \approx 6$ mol·kg^{-1} to $I \approx 24$ mol·kg^{-1} (i.e., near to saturation) for the investigated systems. The isopiestic equilibrium may be reached within (5 to 7) days.

After each run, the isopiestic molalities were determined by weighing only as usual.[41−46] The individual equilibrium molalities of each nitrate were always reproducible to ± 0.06 % and mostly to ± 0.04 % between the duplicate samples.

RESULTS AND DISCUSSION

First, we discuss the solute−solute interchange energies in the ternary and quaternary mixed rare earth electrolyte solutions. Table 1 lists the isopiestic results for the ternary systems $H_2O-Er(NO_3)_3-La(NO_3)_3$, $H_2O-Er(NO_3)_3-Pr(NO_3)_3$, $H_2O-Er(NO_3)_3-Nd(NO_3)_3$, and $H_2O-Er(NO_3)_3-Y(NO_3)_3$ at 298.15 K, where ϕ_{exp} was determined by eq 10 and ϕ_{calc} was determined by eq 1. In Figure 1, the isopiestic molalities of these mixtures are compared with the modified ZSR model, eq 4. Table 2 lists the isopiestic results for the quaternary systems $H_2O-Er(NO_3)_3-La(NO_3)_3-Y(NO_3)_3$, $H_2O-Er(NO_3)_3-Pr(NO_3)_3-Y(NO_3)_3$, and $H_2O-Er(NO_3)_3-Nd(NO_3)_3-Y(NO_3)_3$ at 298.15 K. The isopiestic molalities of all of these systems are compared with the ZSR or partial ideal solution model. The results show that the Δ function defined by eq 4 is given by $|\Delta| \leq 0.001$ for all of the systems over entire concentration range, which is within the isopiestic experimental accuracy.[47] This means that all of the systems obey the ZSR or partial ideal solution model within experimental error. It has been earlier noted that the physical meaning of the ZSR or partial ideal solution model is zero interchange energy between the unlike solutes in the mixtures. This behavior is consistent with the nature of the rare earth mixtures. Thus, the solute activity coefficients of the mixtures may be calculated very easily from the data of pure electrolytes by eq 8.

Second, we discuss the ionic interactions in the ternary and quaternary mixed rare earth electrolyte solutions. The new simple modified Pitzer model, eq 1, with the seven parameters ($\beta^{(0)}, \beta^{(1)}, \beta^{(2)}, C^{(0)}, C^{(1)}, C^{(2)}$, and $C^{(3)}$) listed in Table 3 was used to represent our experimental ϕ_{exp} data of aqueous pure $Er(NO_3)_3$, $La(NO_3)_3$, $Pr(NO_3)_3$, $Nd(NO_3)_3$, and $Y(NO_3)_3$ and their mixtures. Our experimental ϕ_{exp} data for the aqueous pure $Er(NO_3)_3$, $La(NO_3)_3$, $Pr(NO_3)_3$, $Nd(NO_3)_3$, and $Y(NO_3)_3$ are in excellent agreement with the calculation results of eq 1.

Table 2. Isopiestic Results of Quaternary Systems $H_2O-Er(NO_3)_3-La(NO_3)_3-Y(NO_3)$, $H_2O-Er(NO_3)_3-Pr(NO_3)_3-Y(NO_3)$, and $H_2O-Er(NO_3)_3-Nd(NO_3)_3-Y(NO_3)_3$ at 298.15 K

I_{NaCl}[a]	I[b]	y_C[c]	y_D[c]	ϕ_{exp}[d]	ϕ_{calc}[e]	I_{CaCl_2}[a]	I[b]	y_C[c]	y_D[c]	ϕ_{exp}[d]	ϕ_{calc}[e]
(1) $H_2O(A)-Er(NO_3)_3(B)-La(NO_3)_3(C)-Y(NO_3)_3(D)$											
1.997	5.758	0	0	1.026	1.026	8.873	15.602	0	0	1.498	1.497
	6.696	1	0	0.883	0.883		18.860	1	0	1.239	1.238
	5.728	0	1	1.032	1.032		15.431	0	1	1.514	1.513
	6.063	0.3749	0.3074	0.975	0.976		16.532	0.3462	0.3271	1.414	1.415
	5.938	0.2224	0.2030	0.995	0.997		16.268	0.2564	0.2637	1.436	1.436
	5.995	0.3018	0.5559	0.986	0.988		16.217	0.2539	0.4889	1.441	1.441
4.230	11.101	0	0	1.296	1.296	11.160	20.487	0	0	1.689	1.689
	13.378	1	0	1.076	1.075		24.692	1	0	1.402	1.401
	11.011	0	1	1.307	1.306		20.195	0	1	1.714	1.714
	11.770	0.3501	0.3209	1.223	1.224		21.578	0.3272	0.3310	1.604	1.605
	11.608	0.2689	0.2653	1.240	1.241		21.314	0.2506	0.2488	1.624	1.625
	11.587	0.2693	0.4663	1.242	1.243		21.251	0.2540	0.5161	1.629	1.630
(2) $H_2O(A)-Er(NO_3)_3(B)-Pr(NO_3)_3(C)-Y(NO_3)_3(D)$											
2.027	5.833	0	0	1.030	1.030	8.952	15.770	0	0	1.504	1.504
	6.681	1	0	0.900	0.900		18.446	1	0	1.286	1.286
	5.803	0	1	1.036	1.036		15.595	0	1	1.521	1.521
	6.079	0.3341	0.3362	0.989	0.990		16.523	0.3391	0.3331	1.436	1.437
	6.007	0.2420	0.2506	1.001	1.001		16.322	0.2556	0.2624	1.453	1.454
	6.043	0.2995	0.5516	0.995	0.996		16.282	0.2529	0.4872	1.457	1.458
4.313	11.300	0	0	1.306	1.305	11.190	20.539	0	0	1.692	1.691
	13.241	1	0	1.114	1.114		23.928	1	0	1.452	1.452
	11.208	0	1	1.316	1.316		20.246	0	1	1.716	1.716
	11.843	0.3303	0.3230	1.246	1.247		21.410	0.3259	0.3308	1.623	1.623
	11.719	0.2597	0.2587	1.259	1.259		21.218	0.2518	0.2500	1.638	1.639
	11.682	0.2523	0.5078	1.263	1.263		21.128	0.2526	0.5189	1.645	1.645
(3) $H_2O(A)-Er(NO_3)_3(B)-Nd(NO_3)_3(C)-Y(NO_3)_3(D)$											
2.013	5.795	0	0	1.029	1.028	9.160	16.202	0	0	1.522	1.522
	6.577	1	0	0.906	0.906		18.598	1	0	1.326	1.326
	5.765	0	1	1.034	1.034		16.018	0	1	1.540	1.539
	6.024	0.3342	0.3334	0.990	0.990		16.860	0.3310	0.3300	1.463	1.464
	5.958	0.2440	0.2515	1.001	1.001		16.688	0.2503	0.2567	1.478	1.478
	5.979	0.2809	0.5374	0.997	0.998		16.648	0.2509	0.4895	1.482	1.482
4.282	11.228	0	0	1.302	1.302	11.280	20.731	0	0	1.699	1.698
	12.937	1	0	1.130	1.130		23.720	1	0	1.485	1.484
	11.137	0	1	1.313	1.312		20.432	0	1	1.724	1.723
	11.707	0.3291	0.3283	1.249	1.249		21.519	0.3306	0.3297	1.637	1.638
	11.593	0.2573	0.2610	1.261	1.261		21.320	0.2508	0.2503	1.652	1.652
	11.562	0.2497	0.5131	1.264	1.265		21.247	0.2509	0.5160	1.658	1.660

[a] For isopiestic standards in $\text{mol}\cdot\text{kg}^{-1}$. [b] For isopiestic samples in $\text{mol}\cdot\text{kg}^{-1}$. [c] Molality fractions $y_B + y_C + y_D = 1$. [d] Equation 10. [e] Equation 1.

The mixing terms were then obtained by calculating the difference between the experimental ϕ_{exp} values of the ternary mixtures and the values calculated with the parameter values of the pure rare earth nitrates listed in Table 3 but with zero values for the mixing terms in eq 1. Table 4 lists the mixing parameters and fitting standard deviations of the new modified model for the aqueous mixtures $Er(NO_3)_3-La(NO_3)_3$, $Er(NO_3)_3-Pr(NO_3)_3$, $Er(NO_3)_3-Nd(NO_3)_3$, $Er(NO_3)_3-Y(NO_3)_3$, $Y(NO_3)_3-La(NO_3)_3$, $Y(NO_3)_3-Pr(NO_3)_3$, and $Y(NO_3)_3-Nd(NO_3)_3$. It can be seen that with the non-zero mixing terms the standard deviation values are given by $\sigma = 0.0006-0.0016$ for the aqueous mixtures $Er(NO_3)_3-La(NO_3)_3$, $Er(NO_3)_3-Pr(NO_3)_3$, $Er(NO_3)_3-Nd(NO_3)_3$, and $Er(NO_3)_3-Y(NO_3)_3$. Table 4 also shows the much smaller mixing parameter values of the $Er(NO_3)_3-Y(NO_3)_3$ mixtures than the $Er(NO_3)_3-La(NO_3)_3$, $Er(NO_3)_3-Pr(NO_3)_3$, and $Er(NO_3)_3-Nd(NO_3)_3$ mixtures and the zeroth increase, 0.0000, in root-mean-square average values when omitting the mixing terms for $Er(NO_3)_3-Y(NO_3)_3$. Thus, the solute activity coefficients of all mixtures may also be calculated from the parameters by eq 2.

It has been earlier noted that all of the rare earth nitrate mixtures obey the ZSR model due to zero interchange energies among unlike solutes at constant water activity. However, lanthanum, praseodymium, and neodymium are all light rare earths, while

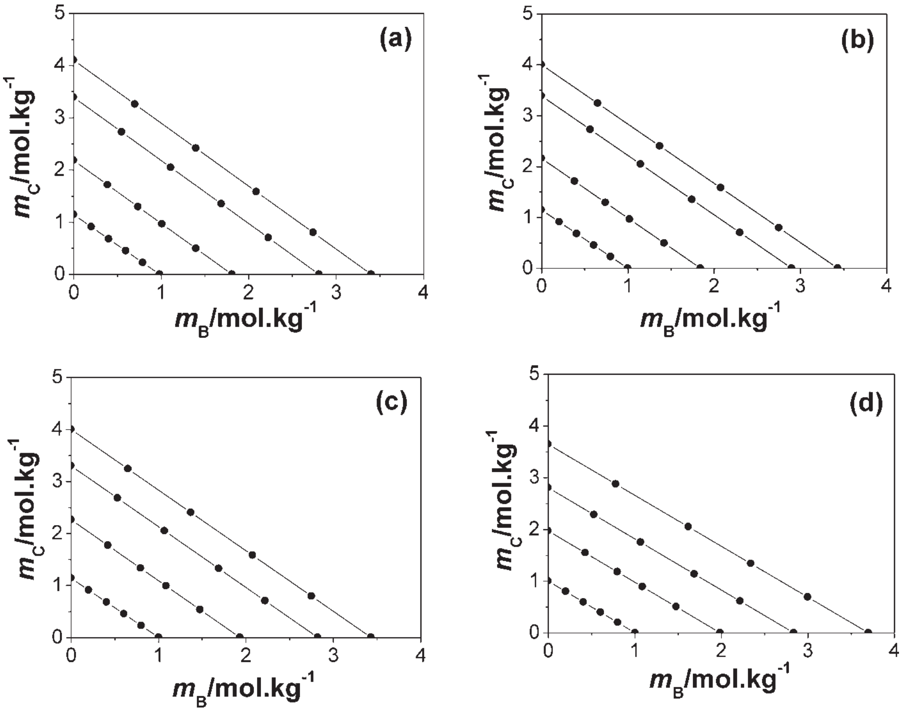

Figure 1. Isopiestic concentrations for the ternary systems (a) $H_2O-Er(NO_3)_3(B)-La(NO_3)_3(C)$, (b) $H_2O-Er(NO_3)_3(B)-Pr(NO_3)_3(C)$, (c) $H_2O-Er(NO_3)_3(B)-Nd(NO_3)_3(C)$, and (d) $H_2O-Er(NO_3)_3(B)-Y(NO_3)_3(C)$, determined in this study, as compared with the modified ZSR model.

Table 3. 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	$(3/2)\beta^{(0)}$	$(3/2)\beta^{(1)}$	$(3/2)\beta^{(2)}$	$(3^{3/2})C^{(0)}$	$(3^{3/2})C^{(1)}$	$(3^{3/2})C^{(2)}$	$(3^{3/2})C^{(3)}$	$10^3\ \sigma$	maximum I
$Er(NO_3)_3$	0.4597	8.41	−7.15	−0.02212	0.3805	−0.2866	1.1361	2.0	44
$La(NO_3)_3$	0.3129	8.15	−5.13	−0.01028	0.3138	−0.3629	1.1857	0.9	51
$Pr(NO_3)_3$	0.3342	7.80	−4.07	−0.01166	0.3420	−0.4790	1.2981	1.6	46
$Nd(NO_3)_3$	0.3436	7.32	−2.51	−0.01230	0.3763	−0.5732	1.3968	1.8	38
$Y(NO_3)_3$	0.4782	8.20	−6.38	−0.02325	0.3528	−0.2710	1.1385	2.4	43

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

Table 4. Mixing Parameters and Standard Deviations of the New Modified Pitzer Model for Fitting Osmotic Coefficients of the Aqueous Mixtures $Er(NO_3)_3-La(NO_3)_3$, $Er(NO_3)_3-Pr(NO_3)_3$, $Er(NO_3)_3-Nd(NO_3)_3$, $Er(NO_3)_3-Y(NO_3)_3$, $Y(NO_3)_3-La(NO_3)_3$, $Y(NO_3)_3-Pr(NO_3)_3$, and $Y(NO_3)_3-Nd(NO_3)_3$ at 298.15 K

mixtures	$\theta_{cc'}$[a]	$\psi_{cc'a}$[b]	σ (with θ and ψ)	σ (without θ and ψ)
$Er(NO_3)_3-La(NO_3)_3$	−0.02225	0.002170	0.0016	0.0027
$Er(NO_3)_3-Pr(NO_3)_3$	−0.01475	0.001618	0.0010	0.0018
$Er(NO_3)_3-Nd(NO_3)_3$	−0.01371	0.001397	0.0009	0.0017
$Er(NO_3)_3-Y(NO_3)_3$	−0.002065	0.0001614	0.0006	0.0006
$Y(NO_3)_3-La(NO_3)_3$	−0.02190	0.001294	0.0021	0.0043
$Y(NO_3)_3-Pr(NO_3)_3$	−0.01995	0.001922	0.0020	0.0030
$Y(NO_3)_3-Nd(NO_3)_3$	−0.02004	0.002167	0.0016	0.0026

[a] Given in kg·mol^{-1}. [b] Given in kg^2·mol^{-2}.

yttrium, although not a lanthanide, has chemical and thermodynamic properties more similar to the heavy rare earth erbium than to the light ones. This would lead the $Er(NO_3)_3-La(NO_3)_3$, $Er(NO_3)_3-Pr(NO_3)_3$, and $Er(NO_3)_3-Nd(NO_3)_3$ mixtures as one group to be slightly different from the $Er(NO_3)_3-Y(NO_3)_3$ mixtures as another group.

We compared the solute activity coefficients of the ternary aqueous mixtures $Er(NO_3)_3-La(NO_3)_3$, $Er(NO_3)_3-Pr(NO_3)_3$,

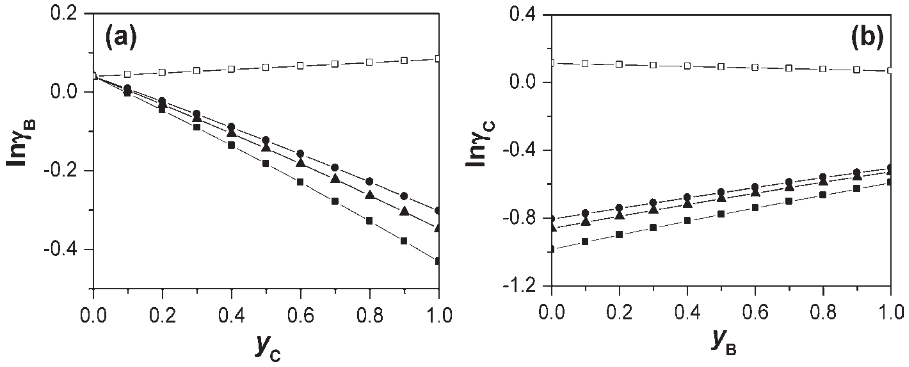

Figure 2. Variation of (a) ln γ_B with y_C and (b) ln γ_C with y_B at $I = 24\ \text{mol}\cdot\text{kg}^{-1}$ for the ternary systems ■, $H_2O-Er(NO_3)_3(B)-La(NO_3)_3(C)$; ▲, $H_2O-Er(NO_3)_3(B)-Pr(NO_3)_3(C)$; ●, $H_2O-Er(NO_3)_3(B)-Nd(NO_3)_3(C)$; and □, $H_2O-Er(NO_3)_3(B)-Y(NO_3)_3(C)$.

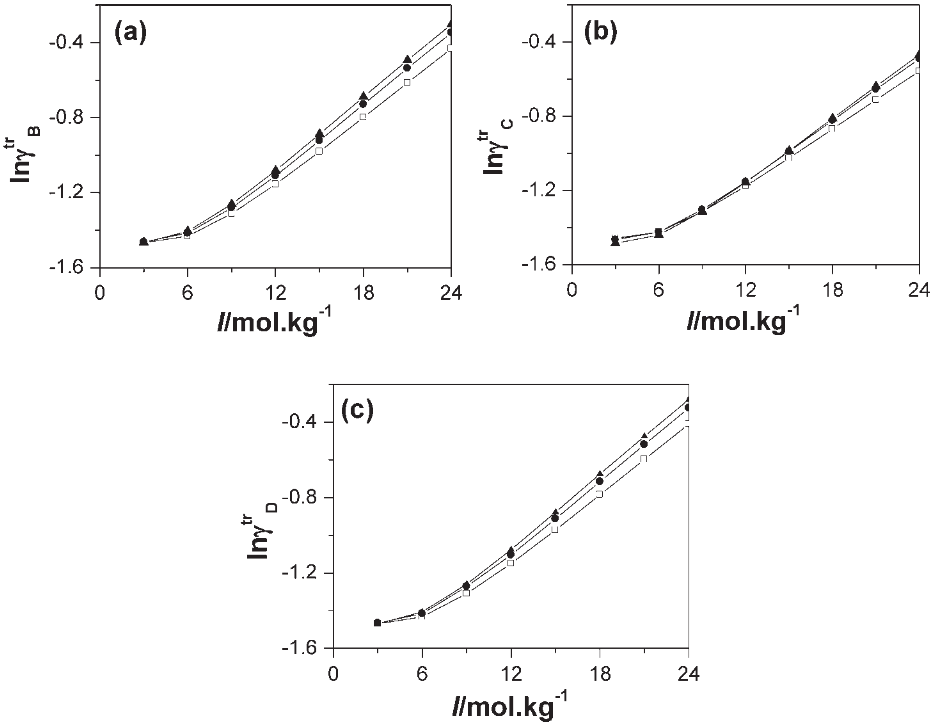

Figure 3. Dependence of (a) ln γ_B^{tr} on I, (b) ln γ_C^{tr} on I, and (c) ln γ_D^{tr} on I for the quaternary systems □, $H_2O-Er(NO_3)_3(B)-La(NO_3)_3(C)-Y(NO_3)_3(D)$; ●, $H_2O-Er(NO_3)_3(B)-Pr(NO_3)_3(C)-Y(NO_3)_3(D)$; and ▲, $H_2O-Er(NO_3)_3(B)-Nd(NO_3)_3(C)-Y(NO_3)_3(D)$.

$Er(NO_3)_3-Nd(NO_3)_3$, and $Er(NO_3)_3-Y(NO_3)_3$ at I = (3, 6, 9, 12, 15, 18, 21, and 24) $\text{mol}\cdot\text{kg}^{-1}$ with the Harned rule, eq 9. The maximum deviation obtained at high ionic strengths is only $\sigma_{\max} = 0.0003$ for $Er(NO_3)_3-Y(NO_3)_3$ but $\sigma_{\max} = 0.004$ for $Er(NO_3)_3-La(NO_3)_3$, $Er(NO_3)_3-Pr(NO_3)_3$, and $Er(NO_3)_3-Nd(NO_3)_3$. Figure 2 shows the variation of ln γ_B with respect to y_C and of ln γ_C with respect to y_B at $I = 24\ \text{mol}\cdot\text{kg}^{-1}$ for the four aqueous mixtures, which also shows a linear relationship for $Er(NO_3)_3-Y(NO_3)_3$ but slight deviation from the linearity for $Er(NO_3)_3-La(NO_3)_3$, $Er(NO_3)_3-Pr(NO_3)_3$, and $Er(NO_3)_3-Nd(NO_3)_3$. Therefore, the solute activity coefficients of the mixtures $Er(NO_3)_3-La(NO_3)_3$, $Er(NO_3)_3-Pr(NO_3)_3$, and $Er(NO_3)_3-Nd(NO_3)_3$ should be refitted by the Harned equation, eq 6.

The calculated values of trace activity coefficient, ln γ_j^{tr}, are generally sensitive to the method of representing experimental $\phi_{\exp}$ data.[16] It is therefore interesting to compare the ln γ_j^{tr} values of the rare earth nitrate mixtures calculated from the new simple modified ion-interaction model, eq 2, and from the simplified McKay–Perring equation, eq 8. Both of them show excellent agreement at lower ionic strengths but present some differences at higher ionic strengths. The largest differences in the ln γ_j^{tr} values from the two calculation approaches are $\sigma_{\max} \leq 0.019$ at $I = 9\ \text{mol}\cdot\text{kg}^{-1}$ and to $\sigma_{\max} = 0.041-0.053$ at $I = 24\ \text{mol}\cdot\text{kg}^{-1}$ for the $H_2O-Er(NO_3)_3-La(NO_3)_3-Y(NO_3)_3$, $H_2O-Er(NO_3)_3-Pr(NO_3)_3-Y(NO_3)_3$, and $H_2O-Er(NO_3)_3-Nd(NO_3)_3-Y(NO_3)_3$ systems. Figure 3 presents the similar ionic strength dependence trend of ln γ_B^{tr}, ln γ_C^{tr}, and ln γ_D^{tr} for the three quaternary systems. The plots show the regular increase in trace activity coefficients with increasing ionic strength at $I \geq 6\ \text{mol}\cdot\text{kg}^{-1}$.

CONCLUSION

In this study, we have reported experimental isopiestic osmotic coefficient measurements on the quaternary systems $H_2O-Er(NO_3)_3-La(NO_3)_3-Y(NO_3)_3$, $H_2O-Er(NO_3)_3-Pr(NO_3)_3-Y(NO_3)_3$, and $H_2O-Er(NO_3)_3-Nd(NO_3)_3-Y(NO_3)_3$ and their ternary subsystems $H_2O-Er(NO_3)_3-La(NO_3)_3$, $H_2O-Er(NO_3)_3-Pr(NO_3)_3$, $H_2O-Er(NO_3)_3-Nd(NO_3)_3$, and $H_2O-Er(NO_3)_3-Y(NO_3)_3$ at 298.15 K to near saturation. The new modified Pitzer ion-interaction model only extending to the $C^{(3)}$ parameter and the ZSR or partial ideal solution model are used to represent the experimental results. The agreement is excellent among the isopiestic measurements, the new simple modified Pitzer model, and the ZSR or partial ideal solution model. The calculated solute activity coefficients for the quaternary systems also show the consistence among the new simple modified Pitzer model, the McKay−Perring equation, and the Harned equation. All of the interaction analysis suggests the applicability of the new simple modified Pitzer model and the ZSR or partial ideal solution model for the rare earth electrolyte mixtures up to very high concentrations.

AUTHOR INFORMATION

Corresponding Author

*E-mail: hemeilibiao@126.com.

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