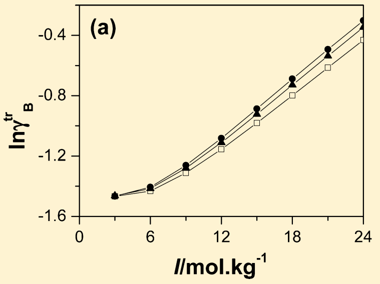
JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

Interactions in the Quaternary Systems $H_2O-Er(NO_3)_3-La(NO_3)_3-Pr(NO_3)_3$, $H_2O-Er(NO_3)_3-La(NO_3)_3-Nd(NO_3)_3$, and $H_2O-Er(NO_3)_3-Pr(NO_3)_3-Nd(NO_3)_3$ to Very High Concentrations

Biao Li[†] and Mei He*[,‡]

[†]Department of Criminal Science and Technique, China Criminal Police University, Shenyang 110854, P. R. China
[‡]Department of Applied Chemistry, Shenyang University of Chemical Technology, Shenyang 110142, P. R. China

ABSTRACT: The ionic interactions have been investigated from the isopiestic measurements on the quaternary systems $H_2O-Er(NO_3)_3-La(NO_3)_3-Pr(NO_3)_3$, $H_2O-Er(NO_3)_3-La(NO_3)_3-Nd(NO_3)_3$, and $H_2O-Er(NO_3)_3-Pr(NO_3)_3-Nd(NO_3)_3$ 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 of the systems within isopiestic accuracy, indicating zero exchange energy between the unlike salts, which is consistent with the nature of rare earth elements.



■ INTRODUCTION

The Pitzer ion-interaction model,[1−3]which contains a Debye−Hückel limiting law parameter and the empirically determined $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} parameters, has widely been used in the representation of thermodynamic properties of aqueous electrolyte solutions and their mixtures to moderate ionic strengths. Recently, various modifications to the Pitzer ion-interaction model extending either to $\beta^{(2)}$, $C^{(2)}$, or $D^{(2)}$ 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 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.

On the other hand, based on the Zdanovskii−Stokes−Robinson (ZSR) model[19−23] for aqueous solutions, we have developed a partial ideal solution model[24−29] for every kind of the multicomponent systems A−B−C−...−Z with zero interchange energies among B, C, ..., Z related to their binary subsystems A−B, A−C, ..., A−Z at constant activity of the common component A. The partial ideal solution model has been verified by the experiments of organic mixtures, aqueous and nonaqueous solutions, alloys, molten salt mixtures, slags, and nonstoichiometric solid solutions. However, for aqueous electrolyte mixtures, the model testing is normally available only to moderate ionic strengths. It is therefore interesting to examine whether the new isopiestic measurements for quaternary mixed rare earth electrolyte solutions to very high concentrations still follow the ZSR model (or the partial ideal solution model).

In this paper, we tried to extend the isopiestic measurements to the quaternary systems $H_2O-Er(NO_3)_3-La(NO_3)_3-Pr(NO_3)_3$, $H_2O-Er(NO_3)_3-La(NO_3)_3-Nd(NO_3)_3$, and $H_2O-Er(NO_3)_3-Pr(NO_3)_3-Nd(NO_3)_3$ to near saturation and to represent the new measurements by the new simple modified ion-interaction model, the ZSR or partial ideal solution model, and other empirical equations.

■ EQUATIONS

For highly soluble and highly unsymmetrical electrolytes (MX) such as aqueous rare earth nitrates, perchlorates, and chlorides and their mixtures (MX−NX−...) with the same

Received: October 6, 2011
Accepted: December 14, 2011
Published: January 6, 2012

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

m_{ref}	m_B	m_C	m_D				
mol·kg^{-1}	mol·kg^{-1}	mol·kg^{-1}	mol·kg^{-1}	Δ	ϕ_{exp}	ϕ_{calc}	$\Delta\phi^a$
(1) $H_2O(A)-Er(NO_3)_3(B)-La(NO_3)_3(C)-Pr(NO_3)_3(D)$							
2.1019	1.0019	0	0		1.041	1.040	0.001
$\{H_2O-NaCl\}$	0	1.1692	0		0.892	0.891	0.001
	0	0	1.1497		0.907	0.906	0.001
	0.3358	0.3895	0.3811	−0.0002	0.943	0.944	−0.001
	0.5819	0.2453	0.2402	−0.0005	0.977	0.978	−0.001
	0.1535	0.3432	0.6362	0.0001	0.921	0.921	0.000
4.1889	1.8338	0	0		1.292	1.291	0.001
$\{H_2O-NaCl\}$	0	2.2094	0		1.072	1.072	0.000
	0	0	2.1484		1.103	1.102	0.001
	0.6462	0.7107	0.6989	−0.0006	1.153	1.153	0.000
	0.9025	0.5565	0.5502	0.0001	1.179	1.181	−0.002
	0.5121	0.5508	1.0125	−0.0002	1.142	1.142	0.000
2.9589	2.6019	0	0		1.498	1.497	0.001
$\{H_2O-CaCl_2\}$	0	3.1453	0		1.239	1.238	0.001
	0	0	3.0438		1.280	1.280	0.000
	0.9117	1.0065	1.0033	0.0000	1.334	1.335	−0.001
	1.3125	0.7722	0.7596	−0.0005	1.370	1.371	−0.001
	0.7054	0.7421	1.4995	−0.0003	1.323	1.323	0.000
3.7112	3.4031	0	0		1.687	1.687	0.000
$\{H_2O-CaCl_2\}$	0	4.1019	0		1.400	1.399	0.001
	0	0	3.9650		1.448	1.448	0.000
	1.2234	1.2979	1.2854	0.0001	1.509	1.511	−0.002
	1.7735	0.9678	0.9621	−0.0003	1.551	1.552	−0.001
	0.8626	0.9931	1.9996	−0.0001	1.490	1.491	−0.001
(2) $H_2O(A)-Er(NO_3)_3(B)-La(NO_3)_3(C)-Nd(NO_3)_3(D)$							
2.1073	1.0039	0	0		1.042	1.041	0.001
$\{H_2O-NaCl\}$	0	1.1717	0		0.893	0.892	0.001
	0	0	1.1415		0.916	0.915	0.001
	0.3355	0.3891	0.3806	−0.0003	0.947	0.947	0.000
	0.5821	0.2458	0.2401	0.0000	0.980	0.980	0.000
	0.1522	0.3427	0.6348	0.0002	0.926	0.926	0.000
4.1038	1.8002	0	0		1.282	1.282	0.000
$\{H_2O-NaCl\}$	0	2.1680	0		1.065	1.064	0.001
	0	0	2.0743		1.113	1.112	0.001
	0.6383	0.6895	0.6793	0.0001	1.150	1.151	−0.001
	0.8932	0.5377	0.5308	0.0001	1.177	1.178	−0.001
	0.4952	0.5252	1.0001	−0.0005	1.143	1.142	0.001
2.9893	2.6337	0	0		1.506	1.505	0.001
$\{H_2O-CaCl_2\}$	0	2.1837	0		1.246	1.245	0.001
	0	0	3.0241		1.311	1.311	0.000
	0.9202	1.0108	1.0074	0.0000	1.350	1.351	−0.001
	1.3205	0.7840	0.7617	−0.0005	1.384	1.384	0.000
	0.7096	0.7468	1.5005	0.0002	1.341	1.342	−0.001
3.6343	3.3179	0	0		1.669	1.668	0.001
$\{H_2O-CaCl_2\}$	0	4.0013	0		1.384	1.383	0.001
	0	0	3.7985		1.458	1.457	0.001
	1.1971	1.2518	1.2401	0.0001	1.501	1.503	−0.002
	1.6994	0.9521	0.9493	0.0001	1.538	1.539	−0.001
	0.8078	0.9625	1.9601	0.0000	1.485	1.485	0.000
(3) $H_2O(A)-Er(NO_3)_3(B)-Pr(NO_3)_3(C)-Nd(NO_3)_3(D)$							
2.1176	1.0082	0	0		1.043	1.042	0.001
$\{H_2O-NaCl\}$	0	1.1574	0		0.909	0.908	0.001
	0	0	1.1466		0.917	0.916	0.001
	0.3367	0.3853	0.3816	−0.0003	0.953	0.953	0.000
	0.5832	0.2441	0.2415	0.0000	0.984	0.985	−0.001
	0.1539	0.3387	0.6363	0.0002	0.932	0.932	0.000
4.1181	1.8053	0	0		1.284	1.283	0.001

Table 1. continued

m_{ref} mol·kg^{-1}	m_B mol·kg^{-1}	m_C mol·kg^{-1}	m_D mol·kg^{-1}	Δ	ϕ_{exp}	ϕ_{calc}	$\Delta\phi^a$
(3) $H_2O(A)–Er(NO_3)_3(B)–Pr(NO_3)_3(C)–Nd(NO_3)_3(D)$							
{H_2O–NaCl}	0	2.1148	0		1.096	1.095	0.001
	0	0	2.0802		1.115	1.114	0.001
	0.6405	0.6722	0.6802	−0.0004	1.164	1.163	0.001
	0.8957	0.5214	0.5355	0.0001	1.188	1.188	0.000
	0.4976	0.5125	1.0032	0.0002	1.152	1.152	0.000
2.9966	2.6405	0	0		1.508	1.507	0.001
{H_2O–$CaCl_2$}	0	3.0884	0		1.289	1.288	0.001
	0	0	3.0317		1.313	1.312	0.001
	0.9231	0.9953	0.9952	0.0001	1.367	1.367	0.000
	1.3247	0.7610	0.7643	0.0002	1.397	1.398	−0.001
	0.7126	0.7191	1.5069	−0.0002	1.355	1.354	0.001
3.7391	3.4341	0	0		1.694	1.693	0.001
{H_2O–$CaCl_2$}	0	4.0004	0		1.454	1.454	0.000
	0	0	3.9295		1.480	1.480	0.000
	1.2322	1.2796	1.2619	−0.0002	1.542	1.543	−0.001
	1.7676	0.9628	0.9584	−0.0007	1.577	1.577	0.000
	0.8487	0.9881	1.9885	0.0002	1.521	1.523	−0.002

[a] $\Delta\phi = \phi_{exp} - \phi_{calc}$.

Table 2. 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

[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 3. Mixing Parameters and Standard Deviations of the New Modified Pitzer Model for Fitting Osmotic Coefficients of the Aqueous Mixtures $H_2O–Er(NO_3)_3–La(NO_3)_3$, $H_2O–Er(NO_3)_3–Pr(NO_3)_3$, $H_2O–Er(NO_3)_3–Nd(NO_3)_3$, $H_2O–La(NO_3)_3–Pr(NO_3)_3$, $H_2O–La(NO_3)_3–Nd(NO_3)_3$, and $H_2O–Pr(NO_3)_3–Nd(NO_3)_3$ at 298.15 K

mixtures	$\theta_{cc'}{}^a$	$\psi_{cc'a}{}^b$	σ (with θ and ψ)	σ (without θ and ψ)
$H_2O–Er(NO_3)_3–La(NO_3)_3$	−0.02225	0.002170	0.0016	0.0027
$H_2O–Er(NO_3)_3–Pr(NO_3)_3$	−0.01475	0.001618	0.0010	0.0018
$H_2O–Er(NO_3)_3–Nd(NO_3)_3$	−0.01371	0.001397	0.0009	0.0017
$H_2O–La(NO_3)_3–Pr(NO_3)_3$	−0.001929	0.0000824	0.0011	0.0013
$H_2O–La(NO_3)_3–Nd(NO_3)_3$	−0.007020	0.0006041	0.0013	0.0015
$H_2O–Pr(NO_3)_3–Nd(NO_3)_3$	−0.005430	0.0005768	0.0008	0.0010

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

anion X, the new simple modified ion-interaction model for the osmotic coefficient (ϕ) and activity coefficient (γ) may simply be given by[18]

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

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

where A_ϕ is the Debye–Hückel limiting law parameter (0.3915 kg$^{1/2}$·mol$^{-1/2}$ at 298.15 K), b = 1.2 kg$^{1/2}$·mol$^{-1/2}$, $Z = \sum_i m_i|z_i|$,

Table 4. Harned Coefficients for Calculating Activity Coefficients of Quaternary Systems H_2O−$Er(NO_3)_3$−$La(NO_3)_3$−$Pr(NO_3)_3$, H_2O−$Er(NO_3)_3$−$La(NO_3)_3$−$Nd(NO_3)_3$, and H_2O−$Er(NO_3)_3$−$Pr(NO_3)_3$−$Nd(NO_3)_3$ at 298.15 K with $\sigma \leq 0.001$

	I^a	3	6	9	12	15	18	21	24
				(1) $H_2O(A)$−$Er(NO_3)_3(B)$−$La(NO_3)_3(C)$−$Pr(NO_3)_3(D)$					
$\ln \gamma_B$	α_{BC}	0.09613	0.1890	0.2553	0.3107	0.3529	0.3826	0.4047	0.4180
	α_{BD}	0.09247	0.1718	0.2255	0.2685	0.3004	0.3217	0.3374	0.3469
	β_{BC}	0	0	0.01330	0.02078	0.02724	0.03516	0.04273	0.05231
	β_{BD}	0	0	0.01234	0.01797	0.02162	0.02694	0.03233	0.03942
	β_{BCD}	0	−0.00202	0.02700	0.04067	0.04900	0.06183	0.07439	0.09067
$\ln \gamma_C$	α_{CB}	−0.08700	−0.1630	−0.2255	−0.2923	−0.3378	−0.3744	−0.4052	−0.4327
	α_{CD}	0.005080	−0.01138	−0.02752	−0.03905	−0.04765	−0.05663	−0.06499	−0.07134
	β_{CB}	0	0	0	0.01683	0.02336	0.02882	0.03437	0.04172
	β_{CD}	0	0	0	0	0	0	0	0
	β_{CBD}	0	−0.005270	−0.02085	0.001992	0.006879	0.0006298	0.006893	0.007895
$\ln \gamma_D$	α_{DB}	−0.08410	−0.1504	−0.2043	−0.2595	−0.2935	−0.3212	−0.3451	−0.3656
	α_{DC}	−0.00488	0.01152	0.02819	0.04016	0.04919	0.05842	0.06710	0.07386
	β_{DB}	0	0	0	0.01481	0.01882	0.02302	0.02833	0.03336
	β_{DC}	0	0	0	0	0	0	0	0
	β_{DBC}	0	−0.01182	−0.01994	−0.002492	−0.004472	−0.005470	−0.008431	−0.01162
				(2) $H_2O(A)$−$Er(NO_3)_3(B)$−$La(NO_3)_3(C)$−$Nd(NO_3)_3(D)$					
$\ln \gamma_B$	α_{BC}	0.09613	0.1890	0.2553	0.3107	0.3529	0.3826	0.4047	0.4180
	α_{BD}	0.09583	0.1629	0.2188	0.2454	0.2707	0.2889	0.3036	0.3132
	β_{BC}	0	0	0.01330	0.02078	0.02724	0.03516	0.04273	0.05231
	β_{BD}	0	0	0	0.01298	0.01611	0.01959	0.02307	0.02942
	β_{BCD}	0	−0.03053	0.01418	0.03705	0.04390	0.05332	0.06281	0.07600
$\ln \gamma_C$	α_{CB}	−0.08700	−0.1630	−0.2255	−0.2923	−0.3378	−0.3744	−0.4052	−0.4327
	α_{CD}	0.000910	−0.02268	−0.04205	−0.06011	−0.07710	−0.09079	−0.1007	−0.1060
	β_{CB}	0	0	0	0.01683	0.02336	0.02882	0.03437	0.04172
	β_{CD}	0	0	0	0	0	0	0	0
	β_{CBD}	0	−0.008340	−0.01690	0.006637	0.01121	0.01332	0.01398	0.01643
$\ln \gamma_D$	α_{DB}	−0.08701	−0.1433	−0.1905	−0.2244	−0.2633	−0.2848	−0.3049	−0.3247
	α_{DC}	−0.00084	0.02311	0.04352	0.06266	0.08095	0.09557	0.1062	0.1117
	β_{DB}	0	0	0	0	0.01399	0.01576	0.01946	0.02573
	β_{DC}	0	0	0	0	0	0	0	0
	β_{DBC}	0	−0.007521	−0.01879	−0.02654	−0.007719	−0.01428	−0.02007	−0.02199
				(3) $H_2O(A)$−$Er(NO_3)_3(B)$−$Pr(NO_3)_3(C)$−$Nd(NO_3)_3(D)$					
$\ln \gamma_B$	α_{BC}	0.09247	0.1718	0.2255	0.2685	0.3004	0.3217	0.3374	0.3469
	α_{BD}	0.09583	0.1629	0.2188	0.2454	0.2707	0.2889	0.3036	0.3132
	β_{BC}	0	0	0.01234	0.01797	0.02162	0.02694	0.03233	0.03942
	β_{BD}	0	0	0	0.01298	0.01611	0.01959	0.02307	0.02942
	β_{BCD}	0	0.02854	0.01303	0.02974	0.03819	0.04553	0.05288	0.06323
$\ln \gamma_C$	α_{CB}	−0.08410	−0.1504	−0.2043	−0.2595	−0.2935	−0.3212	−0.3451	−0.3656
	α_{CD}	−0.003470	−0.01200	−0.01485	−0.02161	−0.03052	−0.03577	−0.03712	−0.03634
	β_{CB}	0	0	0	0.01481	0.01882	0.02302	0.02833	0.03336
	β_{CD}	0	0	0	0	0	0	0	0
	β_{CBD}	0	0	0	0.005267	0.004829	0.005283	0.007281	0.009024
$\ln \gamma_D$	α_{DB}	−0.08701	−0.1433	−0.1905	−0.2244	−0.2633	−0.2848	−0.3049	−0.3247
	α_{DC}	0.003630	0.01215	0.01502	0.02195	0.03107	0.03653	0.03782	0.03703
	β_{DB}	0	0	0	0	0.01399	0.01576	0.01946	0.02573
	β_{DC}	0	0	0	0	0	0	0	0
	β_{DBC}	0	0	0	−0.02552	0.003459	−0.007467	−0.01111	−0.01024

[a] Given in mol·kg^{-1}.

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

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

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

$$B_{cX}^{\phi} = \beta_{cX}^{(0)} + \beta_{cX}^{(1)} \exp(-\alpha_{B1} I^{1/2}) + \beta_{cX}^{(2)} \exp(-\alpha_{B2} I^{1/2}) \tag{3c}$$

$$C_{cX}^{\phi} = 2[C_{cX}^{(0)} + C_{cX}^{(1)} \exp(-\alpha_{C1} I) + C_{cX}^{(2)} \exp(-\alpha_{C2} I) + C_{cX}^{(3)} \exp(-\alpha_{C3} I)] \tag{3d}$$

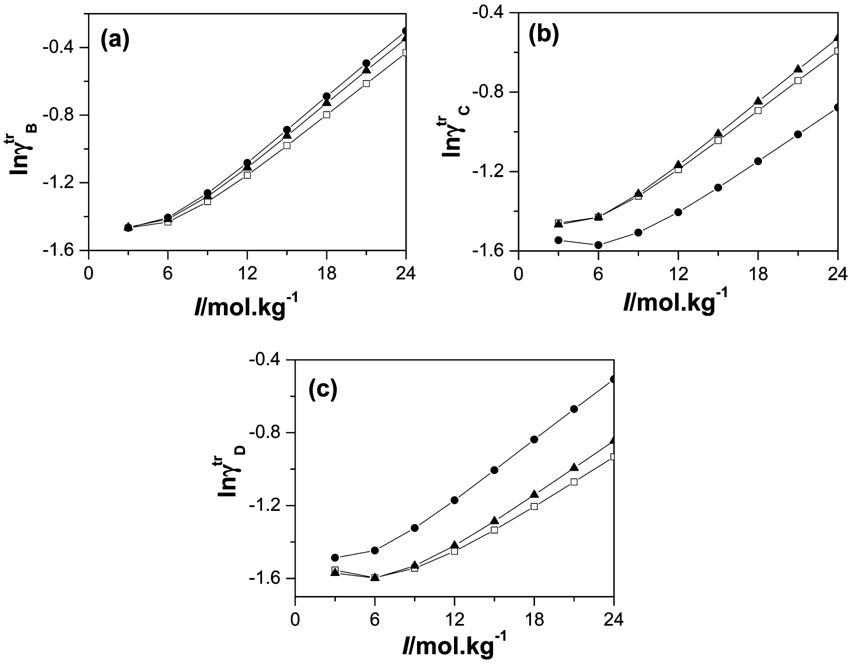


Figure 1. Dependence of (a) ln γ_B^{tr} on I, (b) ln γ_C^{tr} on I, and (c) ln γ_D^{tr} on I for the quaternary systems □, H_2O−$Er(NO_3)_3$(B)−$La(NO_3)_3$(C)−$Pr(NO_3)_3$(D); ●, H_2O−$Er(NO_3)_3$(B)−$La(NO_3)_3$(C)−$Nd(NO_3)_3$(D); and ▲, H_2O−$Er(NO_3)_3$(B)−$Pr(NO_3)_3$(C)−$Nd(NO_3)_3$(D).

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

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[21−23,30]

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

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

and the Harned equation[31] at constant total ionic strength, which is often used for the aqueous electrolyte mixtures to moderate ionic strengths,[31−34] may be given by

$$\ln\gamma_j = \ln\gamma_j^o - \sum_k \alpha_{jk}y_k - \sum_k \beta_{jk}y_k^2 - \sum_k\sum_l \beta_{jkl}y_k y_l \tag{6}$$

where $y_j = m_j/m_T$, $y_l = m_l/m_T$, j, k, and l 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

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

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

$$m_T\gamma_j/m_j^o\gamma_j^o = 1 \tag{8}$$

In another special case of all $\beta = 0$, eq 6 reduces to the Harned rule[31]

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

■ EXPERIMENTAL SECTION

Er_2O_3, La_2O_3, Pr_6O_{11}, and Nd_2O_3 (99.99 % from Aldrich Chemical Co.) were used to prepare stock solutions of $Er(NO_3)_3$, $La(NO_3)_3$, $Pr(NO_3)_3$, and $Nd(NO_3)_3$ by Rard's method.[11−17] After reacting the rare earth oxides with the 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 (EDTA) 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.[35,36] At isopiestic equilibrium, all samples have the same water activity, so that the osmotic coefficients of the rare earth nitrate solutions may be calculated by the equation

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

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.[37−42] 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 investigated system were placed. 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.[37−42] 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 quaternary mixed rare earth electrolyte solutions. Table 1 lists the isopiestic results for the quaternary systems $H_2O-Er(NO_3)_3-La(NO_3)_3-Pr(NO_3)_3$, $H_2O-Er(NO_3)_3-La(NO_3)_3-Nd(NO_3)_3$, and $H_2O-Er(NO_3)_3-Pr(NO_3)_3-Nd(NO_3)_3$ at 298.15 K, where ϕ_{exp} was determined by eq 10. The isopiestic molalities 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 the entire concentration range, which is within the isopiestic experimental accuracy.[43] 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 quaternary mixed rare earth electrolyte solutions based on the new simple modified Pitzer model, eqs 1 to 3. Table 2 lists seven parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $C^{(0)}$, $C^{(1)}$, $C^{(2)}$, and $C^{(3)}$) for each pure salt which were first reported in ref 18. Table 3 gives two mixing parameters ($\theta_{cc'}$ and $\psi_{cc'X}$) for each pair of salts, among which data of the last three mixtures were first reported in ref 18. Table 3 shows the much smaller mixing parameter values of the $La(NO_3)_3-Pr(NO_3)_3$, $La(NO_3)_3-Nd(NO_3)_3$, and $Pr(NO_3)_3-Nd(NO_3)_3$ 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 very small increase, 0.0002, in root-mean-square average values when omitting the mixing terms for $La(NO_3)_3-Pr(NO_3)_3$, $La(NO_3)_3-Nd(NO_3)_3$, and $Pr(NO_3)_3-Nd(NO_3)_3$. Therefore, two mixing parameters ($\theta_{cc'}$ and $\psi_{cc'X}$) for $La(NO_3)_3-Pr(NO_3)_3$, $La(NO_3)_3-Nd(NO_3)_3$, and $Pr(NO_3)_3-Nd(NO_3)_3$ mixtures can be omitted. The osmotic coefficients calculated by eq 1, ϕ_{calc}, are listed in the seventh column of Table 1. The values of $\Delta\phi$ ($\equiv \phi_{exp} - \phi_{calc}$) are listed in the eighth column of Table 1. The values of $|\Delta\phi| \leq 0.002$ indicate that the simple modification to the Pitzer ion-interaction model extending to the $C^{(3)}$ parameter can represent the new measurements within experimental uncertainty over the full concentration range. Thus, the solute activity coefficients of all of the mixtures may also be calculated from the parameters listed in Tables 2 and 3 by eq 2.

The calculated values of trace activity coefficient, $\ln \gamma_j^{tr}$, are generally sensitive to the method of representing experimental ϕ_{exp} data.[16] It is therefore interesting to compare the $\ln \gamma_j^{tr}$ 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 $\ln \gamma_j^{tr}$ values from the two calculation approaches are $\sigma_{max} \leq 0.020$ at $I = 9$ mol·kg^{-1} and to $\sigma_{max} = 0.042$ to 0.055 at $I = 24$ mol·kg^{-1} for the $H_2O-Er(NO_3)_3-La(NO_3)_3-Pr(NO_3)_3$, $H_2O-Er(NO_3)_3-La(NO_3)_3-Nd(NO_3)_3$, and $H_2O-Er(NO_3)_3-Pr(NO_3)_3-Nd(NO_3)_3$ systems. Figure 1 presents the similar ionic strength dependence trend of $\ln \gamma_B^{tr}$, $\ln \gamma_C^{tr}$, and $\ln \gamma_D^{tr}$ for the three quaternary systems. The plots show the regular increase in trace activity coefficients with increasing ionic strength at $I \geq 6$ mol·kg^{-1}.

We also compared the solute activity coefficients of the quaternary systems $H_2O-Er(NO_3)_3-La(NO_3)_3-Pr(NO_3)_3$, $H_2O-Er(NO_3)_3-La(NO_3)_3-Nd(NO_3)_3$, and $H_2O-Er(NO_3)_3-Pr(NO_3)_3-Nd(NO_3)_3$ at I = (3, 6, 9, 12, 15, 18, 21, and 24) mol·kg^{-1} with the Harned rule, eq 9. The maximum deviation obtained at high ionic strengths is $\sigma_{max} = 0.0043$. Therefore, the solute activity coefficients of the quaternary systems $H_2O-Er(NO_3)_3-La(NO_3)_3-Pr(NO_3)_3$, $H_2O-Er(NO_3)_3-La(NO_3)_3-Nd(NO_3)_3$, and $H_2O-Er(NO_3)_3-Pr(NO_3)_3-Nd(NO_3)_3$ were refitted by the Harned equation, eq 6. Table 4 lists the Harned coefficients (α_{jk}, α_{jl}, β_{jk}, β_{jl}, and β_{jkl}) of the three quaternary systems with the fitting standard deviation $\sigma \leq 0.001$.

CONCLUSION

In this study, we have reported experimental isopiestic osmotic coefficient measurements on the quaternary systems $H_2O-Er(NO_3)_3-La(NO_3)_3-Pr(NO_3)_3$, $H_2O-Er(NO_3)_3-La(NO_3)_3-Nd(NO_3)_3$, and $H_2O-Er(NO_3)_3-Pr(NO_3)_3-Nd(NO_3)_3$ 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.

Funding

This work was supported by the Fund for the Key Laboratory Program of Universities of Liaoning Province under Contract

LS2010122 and by the Fund for the Doctoral Program of Shenyang University of Chemical Technology under Contract No. 200716.

■ 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.; Kim, J. J. Thermodynamics of Electrolytes. IV. Activity and Osmotic Coefficients for Mixed Electrolytes. *J. Am. Chem. Soc.* **1974**, *96*, 5701−5707.

(3) 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.

(4) Ananthaswamy, J.; Atkinson, G. Thermodynamics of Concentrated Electrolyte Mixtures. V. A Review of the Thermodynamic Properties of Aqueous Calcium Chloride in the Temperature Range 273.15−373.15 K. *J. Chem. Eng. Data* **1985**, *30*, 120−128.

(5) Archer, D. G. Thermodynamic Properties of the NaBr + H_2O System. *J. Phys. Chem. Ref. Data* **1991**, *20*, 509−555.

(6) Pitzer, K. S.; Wang, P.; Rard, J. A.; Clegg, S. L. Thermodynamics of Electrolytes. 13. Ionic Strength Dependence of Higher-Order Terms; Equations for $CaCl_2$ and $MgCl_2$. *J. Solution Chem.* **1999**, *28*, 265−282.

(7) Rard, J. A.; Wijesinghe, A. M. Conversion of Parameters Between Different Variants of Pitzer's Ion-Interaction Model, Both with and without Ionic Strength Dependent Higher-Order Terms. *J. Chem. Thermodyn.* **2003**, *35*, 439−473.

(8) Filippov, V. K.; Charykov, N. A.; Rumyantsev, V. Extension of the Pitzer Method to Aqueous Salt Systems with Solution Phase Complexing. *Dokl. Akad. Nauk. SSSR Fiz. Khim.* **1987**, *296*, 665−668.

(9) Anstiss, R. G.; Pitzer, K. S. Thermodynamics of Very Concentrated Aqueous Electrolytes: LiCl, $ZnCl_2$, and $ZnCl_2$-NaCl at 25 °C. *J. Solution Chem.* **1991**, *20*, 849−858.

(10) 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.

(11) 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.

(12) 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.

(13) 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.

(14) 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.

(15) 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.

(16) 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.

(17) 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.

(18) 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.

(19) Zdanovskii, A. B. Regularities in The Property Variations of Mixed Solutions. *Tr. Solyanoi Lab. Akad. Nauk SSSR* **1936**, *6*, 5−70.

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

(21) Chen, H.; Sangster, J.; Teng, T. T.; Lenzi, F. A General Method of Predicting the Water Activity of Ternary Aqueous Solutions from Binary Data. *Can. J. Chem. Eng.* **1973**, *51*, 234−241.

(22) Clegg, S. L.; Seifeld, J. H.; Edney, E. O. Thermodynamic Modelling of Aqueous Aerosols Containing Electrolytes and Dissolved Organic Compounds. II. An Extended Zdanovskii-Stokes-Robinson Approach. *J. Aerosol Sci.* **2003**, *34*, 667−690.

(23) Clegg, S. L.; Seifeld, J. H. Improvement of the Zdanovskii-Stokes-Robinson Model for Mixtures Containing Solutes of Different Charge Types. *J. Phys. Chem. A* **2004**, *108*, 1008−1017.

(24) Wang, Z.-C. The Linear Concentration Rules at Constant Partial Molar Quantity $\bar{\Psi}_0$—Extension of Turkdogan's Rule and Zdanovskii's Rule. *Acta Metall. Sin.* **1980**, *16*, 195−206.

(25) Wang, Z.-C. Thermodynamics of Multicomponent Systems at Constant Partial Molar Quantity $\bar{\Psi}_0$—Thermodynamical Aspect of Iso-$\bar{\Psi}_0$ Rules of Zdanovskii-Type and Turkdogan-Type. *Acta Metall. Sin.* **1981**, *17*, 168−176.

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

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

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

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

(30) McKay, H. A. C.; Perring, J. K. Calculations of the Activity Coefficients of Mixed Aqueous Electrolytes from Vapour Pressures. *Trans. Faraday Soc.* **1953**, *49*, 163−165.

(31) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolyte Solutions*, 3rd ed.; Reinhold: New York, 1958; Chapter 14.

(32) Kumar, A. Ionic Interactions in Aqueous Mixtures of NaCl with Guanidinium Chloride: Osmotic Coefficients, Densities, Speeds of Sound, Surface Tensions, Viscosities, and the Derived Properties. *J. Phys. Chem. B* **2000**, *104*, 9505−9512.

(33) Kumar, A. The Mixing of K^+, $(nBu_4)N^+$, Mg^{2+}, and Ca^{2+} with Guanidinium Cation in Water: Ionic Interactions from a Thermodynamic Study. *J. Phys. Chem. B* **2001**, *105*, 9828−9833.

(34) Kumar, A. Ionic Interactions from the Mixing of NaCl with the Acetate, Nitrate, Perchlorate, and Sulfate Salts of Guanidinium in Water. *J. Phys. Chem. B* **2003**, *107*, 2808−2814.

(35) 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.

(36) 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.

(37) Wang, Z. C.; Yu, H. L.; Hu, Y. F. Isopiestic Studies on {Mannitol + Sorbitol + Sucrose}(aq) at the Temperature 298.15 K. Comparison with the Partial Ideal Solution Model. *J. Chem. Thermodyn.* **1994**, *26*, 171−176.

(38) Hu, Y. F.; Wang, Z.-C. Isopiestic Studies on {Mannitol + Sorbitol + D-Glucose}(aq) and the Subsystems at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1997**, *29*, 879−884.

(39) Wang, M.; Zhang, H.; Wang, Z.-C. Isopiestic Studies on the Saturated Quinary Systems (Water + Sodium Chloride(sat) + Glycine(sat) + Sorbitol + Sucrose) and (Water + Sodium Chloride(sat) + Barium Chloride(sat) + Sorbitol + Sucrose) at the

Temperature 298.15 K: Comparison with the Ideal-Like Solution Model. *J. Chem. Thermodyn.* **2001**, *33*, 711−717.

(40) Wang, J.; Wang, Z.-C. An Ideal-Like Quinary Aqueous Solution Equilibrated with a Solid Cadminm-Containing Complex. *Z. Phys. Chem.* **2004**, *218*, 881−885.

(41) 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.

(42) He, M.; Wang, Z.-C.; Gong, L.-D.; Xia, P.-M. 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 Pitzer Model, Zdanovskii−Stokes−Robinson Rule, and Ideal−Like Solution Model. *J. Chem. Eng. Data* **2009**, *54*, 511−516.

(43) 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.