JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Densities of the Ternary Systems $Y(NO_3)_3 + La(NO_3)_3 + H_2O$, $La(NO_3)_3 + Ce(NO_3)_3 + H_2O$, and $La(NO_3)_3 + Nd(NO_3)_3 + H_2O$ and Their Binary Subsystems at Different Temperatures

Yu-Feng Hu,* Chuan-Wei Jin, Shan Ling, and Jin-Zhu Zhang

State Key Laboratory of Heavy Oil Processing and High Pressure Fluid Phase Behavior & Property Research Laboratory, China University of Petroleum, Beijing 102249, China

ABSTRACT: Densities were measured for the ternary systems $Y(NO_3)_3 + La(NO_3)_3 + H_2O$, $La(NO_3)_3 + Ce(NO_3)_3 + H_2O$, and $La(NO_3)_3 + Nd(NO_3)_3 + H_2O$ and their binary subsystems at (293.15, 298.15, and 308.15) K. The results were used to test the applicability of simple equations for the density of the mixed solutions. The predictions of the simple equations agree well with measured values, indicating that the densities of the examined electrolyte solutions can be well predicted from those of their constituent binary solutions by the simple equations.

INTRODUCTION

The thermodynamic and transport properties of mixed aqueous electrolyte solutions play an important role in a variety of fields such as chemistry and chemical engineering, separation processes, wastewater treatment, pollution control, and oil recovery. While extensive data have been reported in the literature for the thermodynamic and transport properties of binary aqueous electrolyte solutions, relatively few measurements have been made on multicomponent electrolyte solutions, especially aqueous solutions of (1:3 + 1:3) electrolyte mixtures. At the same time, one of the objectives of the theory of electrolyte solutions is to calculate various properties of mixed electrolyte solutions in terms of the properties of binary solutions, and much effort has indeed been made in the literature to develop simple equations that can make full use of the available information on binary electrolyte solutions and provide sufficient accuracy to predict the properties of mixed solutions.[1−7] There are several simple approaches for prediction of densities of mixed solutions, such as the rule of Young and Smith,[8] the rule of Patwardhan and Kumar,[6] and the semi-ideal solution theory.[1,2] These approaches could yield predictions for the thermodynamic properties of the mixed solutions in terms of the properties of their binary subsystems. Their accuracy has been tested by systematic comparisons with the experimental data for the mixed nonelectrolyte solutions,[9a] the mixed electrolyte solutions,[9b] and the mixed solutions of electrolytes and nonelectrolytes.[10] However, because little effort has been made to measure the densities of aqueous solutions of (1:3 + 1:3) electrolyte mixtures, tests have been generally limited to aqueous solutions of (1:1 + 1:1), (1:1 + 1:2), and (1:1 + 1:3) electrolyte mixtures and limited to lower ionic strength. Therefore, in our previous study[11] the densities of the ternary systems $Y(NO_3)_3 + Ce(NO_3)_3 + H_2O$, $Y(NO_3)_3 + Nd(NO_3)_3 + H_2O$, and $Ce(NO_3)_3 + Nd(NO_3)_3 + H_2O$ and their binary subsystems at (293.15, 298.15, and 308.15) K were determined and were used to test the predictability of simple predictive equations. In this study, the densities were measured for the ternary systems $Y(NO_3)_3 + La(NO_3)_3 + H_2O$, $La(NO_3)_3 + Ce(NO_3)_3 + H_2O$, and $La(NO_3)_3 + Nd(NO_3)_3 + H_2O$ and their binary subsystems $Y(NO_3)_3 + H_2O$, $Ce(NO_3)_3 + H_2O$, $La(NO_3)_3 + H_2O$, and $Nd(NO_3)_3 + H_2O$ at different temperatures and up to $I_{max} \leq 24.4\ mol \cdot kg^{-1}$ (I is ionic strength). The results were used to check the predictability of the well-known approaches.

EXPERIMENTAL SECTION

$Y(NO_3)_3 \cdot 6H_2O$ (99.99 %), $Ce(NO_3)_3 \cdot 6H_2O$ (99.99 %), $La(NO_3)_3 \cdot 6H_2O$ (99.99 %), and $Nd(NO_3)_3 \cdot xH_2O$ (> 99 %) supplied by the Shanghai Aladdin Reagent Co. Ltd. were dissolved into double-distilled deionized water. The resulting rare earth nitrate solutions were adjusted to their equivalent concentrations with dilute HNO_3 solution and then reheated and readjusted until stabilized.[11,12] The molalities of the rare earth nitrate stock solutions were analyzed by both the EDTA[13] and sulfate methods.[12] The stock solution concentrations were determined with a precision of ≤ 0.10 %.[13]

The experimental procedures are similar to those used in our previous study[9,11] and are described briefly as follows. Dilute solutions were prepared by diluting a stock solution by mass. We prepared the ternary solutions by mixing the binary solutions. All solutions were prepared immediately before use, and the uncertainty was $\pm 5 \cdot 10^{-5}\ mol \cdot kg^{-1}$. Densities of solutions were measured with a KEM oscillating-tube digital densimeter (DA-505) thermostatted to better than ± 0.01 K. The temperature in the measuring cell was monitored with a digital thermometer. The densimeter was calibrated with double-distilled water and dry air.[9,14−17] The densities of water at different temperatures were obtained from the literature.[18] The densities of dry air at different temperatures were taken from ref 19. In all the measured variables, the uncertainty in densities was $\pm 5 \cdot 10^{-5}\ g \cdot cm^{-3}$.

Predictive Equations for the Density of Mixed Electrolyte Solutions. In this study, the variables with the superscript (io) together with the subscript M_iX_i were used to denote the

Received: August 24, 2010
Accepted: February 4, 2011
Published: February 23, 2011

Table 1. Parameters for the Binary Solutions $Y(NO_3)_3 + H_2O$, $La(NO_3)_3 + H_2O$, $Ce(NO_3)_3 + H_2O$, and $Nd(NO_3)_3 + H_2O$ at Different Temperatures

T/K	293.15	298.15	308.15		293.15	298.15	308.15
		$\rho^o_{Y(NO_3)_3+H_2O}$				$\rho^o_{La(NO_3)_3+H_2O}$	
A_0	0.997384	0.995502	0.992848	A_0	0.996292	0.996226	0.997470
A_1	0.229023	0.229400	0.225443	A_1	0.277932	0.272716	0.254035
A_2	−0.0263047	−0.0278444	−0.0263024	A_2	−0.0369772	−0.0325625	−0.0153379
10^3A_3	3.623389	4.365811	3.850967	10^3A_3	6.639391	4.534001	−3.104635
10^4A_4	−5.751668	−7.222839	−6.270300	10^4A_4	−11.277461	−6.544596	9.042222
10^5A_5	4.293403	5.350563	4.681642	10^5A_5	8.702432	4.784853	−7.055529
δ^o_ρ	$3.0\cdot10^{-5}$	$4.9\cdot10^{-5}$	$4.2\cdot10^{-5}$	δ^o_ρ	$5.9\cdot10^{-5}$	$7.4\cdot10^{-5}$	$1.6\cdot10^{-5}$
		$\rho^o_{Ce(NO_3)_3+H_2O}$				$\rho^o_{Nd(NO_3)_3+H_2O}$	
A_0	0.993492	0.994296	0.991069	A_0	0.997386	0.995387	0.993223
A_1	0.292139	0.283609	0.280844	A_1	0.281981	0.283925	0.277342
A_2	−0.0506119	−0.0424636	−0.0424357	A_2	−0.0335038	−0.0382564	−0.0335567
10^3A_3	13.181371	9.345383	9.647246	10^3A_3	5.050950	8.053080	5.875711
10^4A_4	−25.136345	−16.867863	−17.778089	10^4A_4	−7.660146	−15.685357	−10.844769
10^5A_5	19.340987	12.774323	13.603820	10^5A_5	5.254163	12.933185	8.940584
δ^o_ρ	$9.0\cdot10^{-6}$	$5.2\cdot10^{-5}$	$5.9\cdot10^{-5}$	δ^o_ρ	$4.1\cdot10^{-5}$	$1.7\cdot10^{-5}$	$3.1\cdot10^{-5}$
	$\varphi^{o,298.15}_{Y(NO_3)_3+H_2O}$	$\varphi^{o,298.15}_{La(NO_3)_3+H_2O}$	$\varphi^{o,298.15}_{Ce(NO_3)_3+H_2O}$	$\varphi^{o,298.15}_{Nd(NO_3)_3+H_2O}$			
B_0	0.816929	0.754000	−3.299233	0.760181			
B_1	−0.343762	−0.067401	14.079971	−0.131740			
B_2	0.722643	0.113989	−19.061765	0.132389			
B_3	−0.164927	0.083768	12.696013	0.207792			
B_4	0.010871	−0.022761	−4.046712	−0.102828			
B_5	−0.000546	0.000447	0.499920	0.014000			
δ^o_φ	$9.7\cdot10^{-4}$	$8.2\cdot10^{-4}$	$4.0\cdot10^{-3}$	$6.5\cdot10^{-4}$			

quantities of component M_iX_i in the binary solution $M_iX_i + H_2O$ ($i = 1, 2, ..., n$) having the same water activity as that of a mixed solution, and those without the superscript (io) denote the corresponding quantities in the mixed solution.

The linear isopiestic relation can be expressed as[1−3,20]

$$\sum_i \frac{m_{M_iX_i}}{m^{(io)}_{M_iX_i}} = 1$$
$$\left(a_w = \text{constant and } 0 \le \frac{m_{M_iX_i}}{m^{(io)}_{M_iX_i}} \le 1\right) \quad (1)$$

where $m_{M_iX_i}$ and $m_{M_iX_i}{}^{(io)}$ are the molalities of M_iX_i in the mixed aqueous solution $M_1X_1 + ... + M_iX_i + H_2O$ and its binary subsystems $M_iX_i + H_2O$ ($i = 1, 2, ..., n$) of equal water activity.

According to the semi-ideal solution theory, the density of a mixed electrolyte solution is related to those of its constituent binary solutions of equal water activity by[1,2]

$$\rho = \sum_i Y_{M_iX_i} / \sum_i (Y_{M_iX_i}/\rho^{(io)}_{M_iX_i}) \quad (2)$$

with $Y_{M_iX_i} = m_{M_iX_i}/m_{M_iX_i}{}^{(io)} + m_{M_iX_i}M_{M_iX_i}$, where m, ρ, and M denote molality, density, and molar mass, respectively. The density equation of Patwardhan and Kumar[6] can be expressed as

$$\rho = \sum_i Y_{M_iX_i} / \sum_i (Y_{M_iX_i}/\rho^{o,I}_{M_iX_i}) \quad (3)$$

with $Y_{M_iX_i} = y_{M_iX_i} + m_{M_iX_i}M_{M_iX_i}$ where $y_{M_iX_i}$ is the ionic strength fraction and $\rho_{M_iX_i}{}^{o,I}$ is the density of the binary solutions having the same ionic strength fraction as that of the mixed solution.

Comparisons with the Experimental Data. The measured densities were used to test eqs 2 and 3. The test procedure is briefly summarized as follows:

(1) Represent the measured densities of the binary solutions by the equations

$$\rho^o_{M_iX_i(calc)} = \sum_{l=0}^{N} A_l (m^o_{M_iX_i})^l \quad (4)$$

where $\rho^o_{M_iX_i(calc)}$ and $m_{M_iX_i}{}^o$ are the density and the molality of the binary solution $M_iX_i + H_2O$ ($i = 1, 2, ..., n$). The optimum fit was obtained by variation of $l \le 5$ until the value of $\delta_{\rho,M_iX_i}{}^o = \sum_{j=1}^{N}(|\rho^o_{M_iX_i(calc)} - \rho^o_{M_iX_i(exp)}|/\rho^o_{M_iX_i(exp)})/N$ is less than a few parts in 10^{-5}. The values of A_l and $\delta_{\rho,M_iX_i}{}^o$ obtained for the four binary solutions are shown in Table 1.

(2) The reported osmotic coefficient data[21−23] were represented by the equations $\varphi^o_{M_iX_i(calc)} = \sum_{l=0}^{N} B_l (m_{M_iX_i}{}^o)^{l/2}$. The obtained values of B_l are shown in Table 1. Then, determine the compositions ($m_{M_iX_i}{}^{(io)}$) of the binary solutions having the same water activity as that of the mixed solution of given molalities $m_{M_iX_i}$ ($i = 1, 2, ..., n$) using the osmotic coefficients of M_iX_i ($i = 1, 2, ..., n$)[21−23] and eq 1.

(3) Determine the compositions ($m_{M_iX_i}{}^{o,I}$) of the binary solutions having the same ionic strength as that of the mixed solution of given molalities $m_{M_iX_i}$ ($i = 1, 2, ..., n$).

(4) Insert the values of $\rho_{M_iX_i}{}^{(io)}$ and $\rho_{M_iX_i}{}^{o,I}$ calculated from eq 4 into eqs 2 and 3 to yield the predicted densities for

Table 2. Densities of the Binary Solutions $Y(NO_3)_3 + H_2O$, $Ce(NO_3)_3 + H_2O$, $La(NO_3)_3 + H_2O$, and $Nd(NO_3)_3 + H_2O$ at Different Temperatures

m_B	$\rho^o_{293.15}$	$(\rho^o_{298.15})/(g \cdot cm^{-3})$		$\rho^o_{308.15}$
$mol \cdot kg^{-1}$	$g \cdot cm^{-3}$	exp	ref.	$g \cdot cm^{-3}$
		$Y(NO_3)_3$ (B) + H_2O (A)		
0.23521		1.0484[a]	1.0480[25]	
0.27747		1.0574	1.0571[25]	
0.32132		1.0666	1.0665[25]	
0.37064		1.0769	1.0769[25]	
0.41718		1.0865	1.0867[25]	
0.4989	1.1055	1.1035	1.1033[22]	1.0992
0.9965	1.2026	1.2002	1.1999[22]	1.1947
1.4972	1.2908	1.2878	1.2882[22]	1.2814
1.9820	1.3687	1.3654	1.3656[22]	1.3582
2.9475	1.5028	1.4989	1.4985[22]	1.4905
3.9452	1.6157	1.6114	1.6111[22]	1.6022
4.9575	1.7089	1.7043	1.7048[22]	1.6947
		$Ce(NO_3)_3$ (B) + H_2O (A)		
0.5112	1.1312	1.1293	1.1291[23]	1.1247
1.0313	1.2528	1.2502	1.2498[23]	1.2444
1.5546	1.3619	1.3588	1.3593[23]	1.3520
1.9969	1.4462	1.4431	1.4434[23]	1.4357
3.1308	1.6332	1.6291	1.6286[23]	1.6205
3.9676	1.7464	1.7424	1.7421[23]	1.7331
4.4616	1.8060	1.8018	1.8014[23]	1.7922
		$La(NO_3)_3$ (B) + H_2O (A)		
0.4953	1.1256	1.1238	1.1237[24]	1.1192
0.9893	1.2406	1.2381	1.2377[24]	1.2316
1.4797	1.3431	1.3401	1.3403[24]	1.3335
1.9704	1.4369	1.4336	1.4335[24]	1.4263
2.9299	1.5958	1.5918	1.5919[24]	1.5834
3.9001	1.7293	1.7253	1.7255[24]	1.7163
4.3846	1.7879	1.7838	1.7841[24]	1.7746
		$Nd(NO_3)_3$ (B) + H_2O (A)		
0.5220	1.1361	1.1342	1.1340[24]	1.1296
1.0213	1.2551	1.2525	1.2524[24]	1.2467
1.5554	1.3698	1.3667	1.3671[24]	1.3599
2.0934	1.4747	1.4711	1.4713[24]	1.4635
3.0857	1.6421	1.6378	1.6375[24]	1.6288
4.1242	1.7859	1.7811	1.7816[24]	1.7714
4.2972	1.8070	1.8027	1.8031[24]	1.7928

[a] Extrapolated values.

the mixed solutions of given molalities $m_{M_iX_i}$ (i = 1, 2, ..., n), which are then compared with the corresponding experimental data.

In this paper, the average relative differences between the predicted and measured densities (δ_ρ) over the entire experimental composition range of the mixed solution are defined by[9]

$$\delta_\rho = \sum_{i=1}^{N} |\delta_{\rho,i}|/N \quad (5)$$

with $\delta_{\rho,i} = (\rho_{i,(calc)} - \rho_{i,(exp)})/\rho_{i,(exp)}$, where N is the number of experimental data.

Table 3. Comparisons of Measured and Predicted Densities of the Ternary System $Y(NO_3)_3$ (B) + $La(NO_3)_3$ (C) + H_2O (A) at Different Temperatures and with $I_{max} \le 23.6\ mol \cdot kg^{-1}$

m_B		$\rho\ (g \cdot cm^{-3})$			$\Delta\rho\ (g \cdot cm^{-3})$	
$(mol \cdot kg^{-1})$	m_C	exp	eq 2	eq 3	Δ_{eq} 2	Δ_{eq} 3
			293.15 K			
0.2468	0.7443	1.2310	1.2311	1.2311	0.0001	0.0001
0.4914	0.5015	1.2216	1.2218	1.2218	0.0002	0.0002
0.7454	0.2493	1.2120	1.2121	1.2121	0.0001	0.0001
0.4943	1.4790	1.4203	1.4198	1.4199	−0.0005	−0.0004
0.9888	0.9874	1.4030	1.4028	1.4030	−0.0002	0.0000
1.4851	0.4940	1.3863	1.3857	1.3858	−0.0006	−0.0005
0.7308	2.2034	1.5735	1.5729	1.5730	−0.0006	−0.0005
1.4577	1.4809	1.5509	1.5500	1.5502	−0.0009	−0.0007
2.2043	0.7388	1.5275	1.5264	1.5266	−0.0011	−0.0009
0.9762	2.9351	1.7035	1.7017	1.7015	−0.0018	−0.0020
1.9589	1.9636	1.6749	1.6737	1.6734	−0.0012	−0.0015
2.9485	0.9853	1.6461	1.6451	1.6448	−0.0010	−0.0013
				$\delta_\rho^{eq\ i}$ [a]	$4.4 \cdot 10^{-4}$	$4.3 \cdot 10^{-4}$
			298.15 K			
0.2468	0.7443	1.2288	1.2285	1.2286	−0.0003	−0.0002
0.4914	0.5015	1.2191	1.2193	1.2194	0.0002	0.0003
0.7454	0.2493	1.2093	1.2096	1.2097	0.0003	0.0004
0.4943	1.4790	1.4168	1.4164	1.4166	−0.0004	−0.0002
0.9888	0.9874	1.3990	1.3994	1.3996	0.0004	0.0006
1.4851	0.4940	1.3828	1.3824	1.3825	−0.0004	−0.0003
0.7308	2.2034	1.5696	1.5689	1.5691	−0.0007	−0.0005
1.4577	1.4809	1.5466	1.5461	1.5463	−0.0005	−0.0003
2.2043	0.7388	1.5232	1.5225	1.5226	−0.0007	−0.0006
0.9762	2.9351	1.6985	1.6977	1.6975	−0.0008	−0.0010
1.9589	1.9636	1.6704	1.6696	1.6692	−0.0008	−0.0012
2.9485	0.9853	1.6419	1.6409	1.6405	−0.0010	−0.0014
				$\delta_\rho^{eq\ i}$ [a]	$3.6 \cdot 10^{-4}$	$3.8 \cdot 10^{-4}$
			308.15 K			
0.2468	0.7443	1.2228	1.2224	1.2225	−0.0004	−0.0003
0.4914	0.5015	1.2140	1.2134	1.2134	−0.0006	−0.0006
0.7454	0.2493	1.2037	1.2040	1.2040	0.0003	0.0003
0.4943	1.4790	1.4098	1.4093	1.4094	−0.0005	−0.0004
0.9888	0.9874	1.3929	1.3923	1.3924	−0.0006	−0.0005
1.4851	0.4940	1.3755	1.3752	1.3753	−0.0003	−0.0002
0.7308	2.2034	1.5611	1.5605	1.5606	−0.0006	−0.0005
1.4577	1.4809	1.5384	1.5377	1.5378	−0.0007	−0.0006
2.2043	0.7388	1.5149	1.5141	1.5142	−0.0008	−0.0007
0.9762	2.9351	1.6899	1.6887	1.6884	−0.0012	−0.0015
1.9589	1.9636	1.6615	1.6605	1.6601	−0.0010	−0.0014
2.9485	0.9853	1.6323	1.6316	1.6315	−0.0007	−0.0008
				$\delta_\rho^{eq\ i}$ [a]	$4.3 \cdot 10^{-4}$	$4.4 \cdot 10^{-4}$

[a] $\delta_\rho^{eq\ i} = \sum_{j=1}^{N}(|\rho_{j(eq\ i)} - \rho_{j(exp)}|/\rho_{j(exp)})/N$.

■ RESULTS AND DISCUSSION

Table 2 shows the measured densities of the binary solutions $Y(NO_3)_3 + H_2O$, $La(NO_3)_3 + H_2O$, $Ce(NO_3)_3 + H_2O$, and $Nd(NO_3)_3 + H_2O$ at different temperatures. The densities at 298.15 K are compared with the values calculated from the

Table 4. Comparisons of Measured and Predicted Densities of the Ternary System $La(NO_3)_3$ (B) + $Ce(NO_3)_3$ (C) + H_2O (A) at Different Temperatures and with $I_{max} \leq 23.7$ mol·kg^{-1}

m_B		ρ (g·cm^{-3})			$\Delta\rho$ (g·cm^{-3})	
(mol·kg^{-1})	m_C	exp	eq 2	eq 3	Δ_{eq} 2	Δ_{eq} 3
			293.15 K			
0.2553	0.7651	1.2495	1.2496	1.2496	0.0001	0.0001
0.5119	0.4977	1.2468	1.2464	1.2465	−0.0004	−0.0003
0.7491	0.2504	1.2431	1.2435	1.2435	0.0004	0.0004
0.4926	1.4977	1.4441	1.4438	1.4438	−0.0003	−0.0003
0.9855	0.9982	1.4421	1.4415	1.4415	−0.0006	−0.0006
1.4777	0.4994	1.4395	1.4391	1.4391	−0.0004	−0.0004
0.7679	2.3103	1.6240	1.6236	1.6235	−0.0004	−0.0005
1.5247	1.5015	1.6141	1.6139	1.6139	−0.0002	−0.0002
2.2352	0.7423	1.6057	1.6048	1.6048	−0.0009	−0.0009
0.9848	2.9658	1.7429	1.7421	1.7421	−0.0008	−0.0008
1.9656	1.9680	1.7386	1.7378	1.7378	−0.0008	−0.0008
2.9339	0.9830	1.7346	1.7336	1.7336	−0.0010	−0.0010
				$\delta_\rho^{eq\ i\ a}$	$3.4 \cdot 10^{-4}$	$3.4 \cdot 10^{-4}$
			298.15 K			
0.2553	0.7651	1.2472	1.2470	1.2470	−0.0002	−0.0002
0.5119	0.4977	1.2441	1.2438	1.2439	−0.0003	−0.0002
0.7491	0.2504	1.2413	1.2409	1.2409	−0.0004	−0.0004
0.4926	1.4977	1.4409	1.4406	1.4406	−0.0003	−0.0003
0.9855	0.9982	1.4389	1.4382	1.4382	−0.0007	−0.0007
1.4777	0.4994	1.4366	1.4358	1.4358	−0.0008	−0.0008
0.7679	2.3103	1.6200	1.6195	1.6195	−0.0005	−0.0005
1.5247	1.5015	1.6105	1.6099	1.6099	−0.0006	−0.0006
2.2352	0.7423	1.6015	1.6008	1.6008	−0.0007	−0.0007
0.9848	2.9658	1.7382	1.7381	1.7381	−0.0001	−0.0001
1.9656	1.9680	1.7345	1.7338	1.7338	−0.0007	−0.0007
2.9339	0.9830	1.7301	1.7296	1.7295	−0.0005	−0.0006
				$\delta_\rho^{eq\ i\ a}$	$3.2 \cdot 10^{-4}$	$3.2 \cdot 10^{-4}$
			308.15 K			
0.2553	0.7651	1.2409	1.2410	1.2410	0.0001	0.0001
0.5119	0.4977	1.2383	1.2377	1.2378	−0.0006	−0.0005
0.7491	0.2504	1.2353	1.2347	1.2347	−0.0006	−0.0006
0.4926	1.4977	1.4334	1.4332	1.4332	−0.0002	−0.0002
0.9855	0.9982	1.4312	1.4309	1.4309	−0.0003	−0.0003
1.4777	0.4994	1.4292	1.4286	1.4286	−0.0006	−0.0006
0.7679	2.3103	1.6119	1.6109	1.6109	−0.0010	−0.0010
1.5247	1.5015	1.6018	1.6013	1.6014	−0.0005	−0.0004
2.2352	0.7423	1.5932	1.5923	1.5923	−0.0009	−0.0009
0.9848	2.9658	1.7296	1.7289	1.7289	−0.0007	−0.0007
1.9656	1.9680	1.7248	1.7247	1.7247	−0.0001	−0.0001
2.9339	0.9830	1.7210	1.7205	1.7205	−0.0005	−0.0005
				$\delta_\rho^{eq\ i\ a}$	$3.4 \cdot 10^{-4}$	$3.3 \cdot 10^{-4}$

[a] $\delta_\rho^{eq\ i} = \sum_{j=1}^{N}(|\rho_{j(eq\ i)} - \rho_{j(exp)}|/\rho_{j(exp)})/N$.

Table 5. Comparisons of Measured and Predicted Densities of the Ternary System $La(NO_3)_3$ (B) + $Nd(NO_3)_3$ (C) + H_2O (A) at Different Temperatures and with $I_{max} \leq 24.4$ mol·kg^{-1}

m_B		ρ (g·cm^{-3})			$\Delta\rho$ (g·cm^{-3})	
(mol·kg^{-1})	m_C	exp	eq 2	eq 3	Δ_{eq} 2	Δ_{eq} 3
			293.15 K			
0.2529	0.7602	1.2512	1.2513	1.2513	0.0001	0.0001
0.5028	0.5023	1.2472	1.2476	1.2477	0.0004	0.0005
0.7480	0.2492	1.2450	1.2441	1.2441	−0.0009	−0.0009
0.5107	1.5508	1.4650	1.4648	1.4648	−0.0002	−0.0002
1.0105	1.0198	1.4557	1.4552	1.4552	−0.0005	−0.0005
1.4705	0.5311	1.4467	1.4464	1.4464	−0.0003	−0.0003
0.7598	2.2855	1.6311	1.6302	1.6302	−0.0009	−0.0009
1.4941	1.5122	1.6191	1.6186	1.6186	−0.0005	−0.0005
2.2268	0.7404	1.6079	1.6070	1.6070	−0.0009	−0.0009
1.0112	3.0548	1.7724	1.7715	1.7714	−0.0009	−0.0010
1.9959	2.0136	1.7584	1.7572	1.7572	−0.0012	−0.0012
2.9581	0.9962	1.7442	1.7432	1.7431	−0.0010	−0.0011
				$\delta_\rho^{eq\ i\ a}$	$4.2 \cdot 10^{-4}$	$4.3 \cdot 10^{-4}$
			298.15 K			
0.2529	0.7602	1.2493	1.2487	1.2488	−0.0006	−0.0005
0.5028	0.5023	1.2459	1.2451	1.2451	−0.0008	−0.0008
0.7480	0.2492	1.2418	1.2416	1.2415	−0.0002	−0.0003
0.5107	1.5508	1.4615	1.4613	1.4613	−0.0002	−0.0002
1.0105	1.0198	1.4531	1.4517	1.4518	−0.0014	−0.0013
1.4705	0.5311	1.4435	1.4430	1.4430	−0.0005	−0.0005
0.7598	2.2855	1.6268	1.6260	1.6260	−0.0008	−0.0008
1.4941	1.5122	1.6156	1.6145	1.6145	−0.0011	−0.0011
2.2268	0.7404	1.6043	1.6030	1.6030	−0.0013	−0.0013
1.0112	3.0548	1.7678	1.7668	1.7667	−0.0010	−0.0011
1.9959	2.0136	1.7544	1.7527	1.7527	−0.0017	−0.0017
2.9581	0.9962	1.7404	1.7389	1.7389	−0.0015	−0.0015
				$\delta_\rho^{eq\ i\ a}$	$5.9 \cdot 10^{-4}$	$5.9 \cdot 10^{-4}$
			308.15 K			
0.2529	0.7602	1.2425	1.2428	1.2428	0.0003	0.0003
0.5028	0.5023	1.2385	1.2390	1.2390	0.0005	0.0005
0.7480	0.2492	1.2359	1.2353	1.2353	−0.0006	−0.0006
0.5107	1.5508	1.4536	1.4538	1.4538	0.0002	0.0002
1.0105	1.0198	1.4452	1.4444	1.4444	−0.0008	−0.0008
1.4705	0.5311	1.4365	1.4357	1.4357	−0.0008	−0.0008
0.7598	2.2855	1.6175	1.6171	1.6171	−0.0004	−0.0004
1.4941	1.5122	1.6066	1.6058	1.6058	−0.0008	−0.0008
2.2268	0.7404	1.5955	1.5944	1.5944	−0.0011	−0.0011
1.0112	3.0548	1.7580	1.7573	1.7572	−0.0007	−0.0008
1.9959	2.0136	1.7449	1.7435	1.7434	−0.0014	−0.0015
2.9581	0.9962	1.7310	1.7298	1.7298	−0.0012	−0.0012
				$\delta_\rho^{eq\ i\ a}$	$4.8 \cdot 10^{-4}$	$4.9 \cdot 10^{-4}$

[a] $\delta_\rho^{eq\ i} = \sum_{j=1}^{N}(|\rho_{j(eq\ i)} - \rho_{j(exp)}|/\rho_{j(exp)})/N$.

density equations reported in the literature[22−24] and the molalities shown in Table 2. It can be seen that the agreements are good. Note that the stock solution concentrations were determined with a precision of ≤ 0.10 %,[13] which means that the density can be determined with a precision of ≤ 0.0004 g·cm^{-3} according to eq 4.

The fitted parameters were extrapolated to calculate the densities for the binary solution $Y(NO_3)_3 + H_2O$ in the molality range (0.23521 ≤ $m_{M_iX_i}^{o}$ ≤ 0.41718) mol·kg^{-1}. The calculated densities were then compared with the densities measured by Hakin et al.,[25] and the agreement is good, with $\delta_\rho = 1.8 \cdot 10^{-4}$.

Table 3 compares the predicted and measured densities for the ternary solutions $Y(NO_3)_3$ + $La(NO_3)_3$ + H_2O at different temperatures. It is notable that the osmotic coefficients of its binary subsystems at 298.15 K are used to calculate the compositions ($m_{M_iX_i}^{(io)}$) of the binary solutions at (293.15 and 308.15) K. It is clear from the third to seventh columns of Table 3 that the agreements are good: the $\delta_{\rho}^{eq\ 2}$ values at (293.15, 298.15, and 308.15) K are $4.4\cdot10^{-4}$, $3.6\cdot10^{-4}$, and $4.3\cdot10^{-4}$, respectively. The values of $\delta_{\rho}^{eq\ 3}$ at (293.15, 298.15, and 308.15) K are $4.3\cdot10^{-4}$, $3.8\cdot10^{-4}$, and $4.4\cdot10^{-4}$, respectively.

Table 4 compares the predicted and measured densities for the ternary solutions $La(NO_3)_3$ + $Ce(NO_3)_3$ + H_2O at different temperatures. The $\delta_{\rho}^{eq\ 2}$ values at (293.15, 298.15, and 308.15) K are $3.4\cdot10^{-4}$, $3.2\cdot10^{-4}$, and $3.4\cdot10^{-4}$, respectively. The values of $\delta_{\rho}^{eq\ 3}$ at (293.15, 298.15, and 308.15) K are $3.4\cdot10^{-4}$, $3.2\cdot10^{-4}$, and $3.3\cdot10^{-4}$, respectively.

Table 5 compares the predicted and measured densities for the ternary solutions $La(NO_3)_3$ + $Nd(NO_3)_3$ + H_2O at different temperatures. The $\delta_{\rho}^{eq\ 2}$ values at (293.15, 298.15, and 308.15) K are $4.2\cdot10^{-4}$, $5.9\cdot10^{-4}$, and $4.8\cdot10^{-4}$, respectively. The values of $\delta_{\rho}^{eq\ 3}$ at the three temperatures are $4.3\cdot10^{-4}$, $5.9\cdot10^{-4}$, and $4.9\cdot10^{-4}$, respectively. The above results indicate that eqs 2 and 3 hold well for the mixed electrolyte solutions. One of the advantages of the semi-ideal solution theory is that its simple equations are applicable to aqueous solutions of electrolyte mixtures, nonelectrolyte mixtures, and (electrolyte + nonelectrolyte) mixtures.[1,2,9] The advantage the equation of Patwardhan and Kumar has is that it does not require the osmotic coefficient data of the binary solutions. Equation 2 needs the osmotic coefficients of the binary solutions. However, as can be seen from the present results and the previous results,[26] the osmotic coefficients measured at 298.15 K can be used to determine the molalities $m_{M_iX_i}^{(io)}$ of the binary solutions at other temperatures, which can then be used to provide good predictions for the densities or the surface tensions of the mixed electrolyte solutions in the (293.15 to 308.15) K range and in the (283.15 to 343.15) K range, respectively. Because the osmotic coefficients of the binary electrolyte solutions at 298.15 K have been extensively reported in the literature, the use of the osmotic coefficients of the binary solutions makes the calculations more complicated but exerts little influence on the application of the corresponding equations.

CONCLUSIONS

In this study, the densities were measured for the ternary systems $Y(NO_3)_3$ + $La(NO_3)_3$ + H_2O, $La(NO_3)_3$ + $Ce(NO_3)_3$ + H_2O, and $La(NO_3)_3$ + $Nd(NO_3)_3$ + H_2O and their binary subsystems at (293.15, 298.15, and 308.15) K and then were used to test the predictability of predictive equations for the density of the mixed solutions. The comparison results show that eqs 2 and 3 can provide good predictions for the densities of the ternary electrolyte solutions in terms of the properties of the binary solutions. In addition, the compositions of the binary solutions having the same water activity as that of the mixed solutions at other temperatures can be determined from the osmotic coefficients of the binary solutions measured at 298.15 K and then can be used to yield good predictions for the densities of the mixed solutions at other temperatures.

AUTHOR INFORMATION

Corresponding Author

*E-mail: huyf3581@sina.com. Fax: +86-10-89733846. Tel.: +86-10-89733846.

Funding Sources

The authors thank the National Natural Science Foundation of China (20976189, 21076224, 21036008, and B060902) and the Program for New Century Excellent Talents in University of Ministry of Education of China (NCET-06-0088) for financial support.

REFERENCES

(1) Hu, Y. F. The Thermodynamics of Nonelectrolyte Systems at Constant Activities of any Number of Components. *J. Phys. Chem. B* **2003**, *107*, 13168–13177.

(2) Hu, Y. F.; Fan, S. S.; Liang, D. Q. The Semi-ideal Solution Theory for Mixed Ionic Solutions at Solid-Liquid-Vapor Equilibrium. *J. Phys. Chem. A* **2006**, *110*, 4276–4284.

(3) Hu, Y. F.; Zhang, X. M.; Li, J. G.; Liang, Q. Q. Semi-ideal Solution Theory. 2. Extension to Conductivity of Mixed Electrolyte Solutions. *J. Phys. Chem. B* **2008**, *112*, 15376–15381.

(4) Yang, J. Z.; Liu, J. G.; Tong, J.; Guan, W.; Fang, D. W.; Yan, C. W. Systematic Study of the Simple Predictive Approaches for Thermodynamic and Transport Properties of Multicomponent Solutions. *Ind. Eng. Chem. Res.* **2010**, *49*, 7671–7677.

(5) Patwardhan, V. S.; Kumar, A. A Unified Approach for Prediction of Thermodynamic Properties of Aqueous Mixed-Electrolyte Solutions. Part I: Vapor Pressure and Heat Vaporization. *AIChE J.* **1986**, *32*, 1419–1428.

(6) Patwardhan, V. S.; Kumar, A. A Unified Approach for Prediction of Thermodynamic Properties of Aqueous Mixed-Electrolyte Solutions. Part II: Volume, Thermal, and Other Properties. *AIChE J.* **1986**, *32*, 1429–1436.

(7) Hu, Y. F.; Lee, H. Prediction of the Surface Tension of Mixed Electrolyte Solutions Based on the Equation of Patwardhan and Kumar and the Fundamental Butler Equations. *J. Colloid Interface Sci.* **2004**, *269*, 442–448.

(8) Young, T. F.; Smith, M. B. Thermodynamic Properties of Mixtures of Electrolytes in Aqueous Solutions. *J. Phys. Chem.* **1954**, *58*, 716–724.

(9) (a) Hu, Y. F.; Zhang, Z. X.; Zhang, Y. H.; Fan, S. S.; Liang, D. Q. Viscosity and Density of the Non-Electrolyte System Mannitol + Sorbitol + Sucrose + H_2O and Its Binary and Ternary Subsystems at 298.15 K. *J. Chem. Eng. Data* **2006**, *51*, 438–442. (b) Liu, Y. S.; Hu, Y. F.; Hao, Q. C.; Zhang, X. M.; Liu, Z. C.; Li, J. G. Viscosity and Density of the System NaCl + $LaCl_3$ + H_2O and Its Binary Subsystems at Different Temperatures. *J. Chem. Eng. Data* **2009**, *54*, 739–744.

(10) Hu, Y. F.; Peng, X. M.; Jin, C. W.; Liang, Y. G.; Chu, H. D.; Zhang, X. M. The Semi-ideal Solution Theory. 4. Applications to the Densities and Electrical Conductivities of Mixed Electrolyte and Nonelectrolyte Solutions. *J. Solution Chem.* **2010**, *39*, 1597–1608.

(11) Hu, Y. F.; Jin, C. W.; Ling, S.; Zhang, J. Z. Densities of the Ternary Systems $Y(NO_3)_3$ + $Ce(NO_3)_3$ + H_2O, $Y(NO_3)_3$ + $Nd(NO_3)_3$ + H_2O, and $Ce(NO_3)_3$ + $Nd(NO_3)_3$ + H_2O and Their Binary Subsystems at Different Temperatures. *J. Chem. Eng. Data* **2010**, *55*, 5031–5035.

(12) Spedding, F. H.; Pikal, M. J.; Ayers, B. O. Apparent Molal Volumes of Some Aqueous Rare Earth Chloride and Nitrate Solutions at 25°C. *J. Phys. Chem.* **1966**, *70*, 2440–2449.

(13) Spedding, F. H.; Cullen, P. F.; Habenschuss, A. Apparent Molal Volumes of Some Dilute Aqueous Rare Earth Salt Solutions at 25°C. *J. Phys. Chem.* **1974**, *78*, 1106–1110.

(14) Weng, W. L.; Chen, J. T. Density and Viscosity Measurement of *n*-Butylamine with Hexyl Alcohol Isomer Binary Systems. *J. Chem. Eng. Data* **2004**, *49*, 1748–1751.

(15) Salabat, A.; Alinoori, M. Viscosity, Density, and Refractive Index of Poly(vinylpyrrolidone) + 1-Propanol and + 2-Propanol at 298.15 K. *J. Chem. Eng. Data* **2009**, *54*, 1073–1075.

(16) Vijande, J.; Piñeiro, M. M.; García, J.; Valencia, J. L.; Legido, J. L. Density and Surface Tension Variation with Temperature for Heptane + 1-Alkanol. *J. Chem. Eng. Data* **2006**, *51*, 1778–1782.

(17) Pan, H. P.; Bai, T. C.; Wang, X. D. Density, Viscosity, and Electric Conductance of a Ternary Solution of (Nicotinic Acid + Polyethanol + Water). *J. Chem. Eng. Data* **2010**, *55*, 2257–2262.

(18) (a) Stokes, R. H.; Mills, R. *Viscosity of Electrolytes and Related Properties*; Pergamon: New York, 1965. (b) George, J.; Sastry, N. V. Densities, Viscosities, Speeds of Sound, and Relative Permittivities for Water + Cyclic Amides (2-Pyrrolidinone, 1-Methyl-2-pyrrolidinone, and 1-Vinyl-2-pyrrolidinone) at Different Temperatures. *J. Chem. Eng. Data* **2004**, *49*, 235–242.

(19) Lemmon, E. W.; Jacobsen, R. T.; Penoncello, S. G.; Friend, D. G. Thermodynamic Properties of Air and Mixtures of Nitrogen, Argon, and Oxygen from 60 to 2000 K at Pressures to 2000 MPa. *J. Phys. Chem. Ref. Data* **2000**, *29*, 331–370.

(20) Zdanovskii, A. B. Regularities in the Property Variations of Mixed Solutions. *Trudy Solyanoi Laboratorii Akad. Nauk SSSR* **1936**, *No. 6*, 5–70.

(21) 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.

(22) 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.

(23) Ruas, A.; Simonin, J. P.; Turq, P.; Moisy, Ph. Experimental Determination of Water Activity for Binary Aqueous Cerium(III) Ionic Solutions: Application to an Assessment of the Predictive Capability of the Binding Mean Spherical Approximation Model. *J. Phys. Chem. B* **2005**, *109*, 23043–23050.

(24) Spedding, F. H.; Shiers, L. E.; Brown, M. A.; Baker, J. L.; Guitierrez, L.; McDowell, L. S.; Habenschuss, A. Densities and Apparent Molal Volumes of Some Aqueous Rare Earth Solutions at 25°C. III. Rare Earth Nitrates. *J. Phys. Chem.* **1975**, *79*, 1087–1096.

(25) Hakin, A. W.; Liu, J. L.; Erickson, K.; Munoz, J. V.; Rard, J. A. Apparent Molar Volumes and Apparent Molar Heat Capacities of $Pr(NO_3)_3$ (aq), $Gd(NO_3)_3$ (aq), $Ho(NO_3)_3$ (aq), and $Y(NO_3)_3$ (aq) at T = (288.15, 298.15, 313.15, and 328.15) K and p = 0.1 MPa. *J. Chem. Thermodyn.* **2005**, *37*, 153–167.

(26) Peng, X. M.; Hu, Y. F.; Ling, S.; Zhang, J. Z. A New Equation for Prediction of Surface Tension of Mixed Electrolyte Solutions. *Sci. China Chem.* **2010**, *40*, 1324–1331.