

Densities of the Ternary Systems $\text{Y}(\text{NO}_3)_3 + \text{Ce}(\text{NO}_3)_3 + \text{H}_2\text{O}$, $\text{Y}(\text{NO}_3)_3 + \text{Nd}(\text{NO}_3)_3 + \text{H}_2\text{O}$, and $\text{Ce}(\text{NO}_3)_3 + \text{Nd}(\text{NO}_3)_3 + \text{H}_2\text{O}$ and Their Binary Subsystems at Different Temperatures

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Densities were measured for the ternary systems $\text{Y}(\text{NO}_3)_3 + \text{Ce}(\text{NO}_3)_3 + \text{H}_2\text{O}$, $\text{Y}(\text{NO}_3)_3 + \text{Nd}(\text{NO}_3)_3 + \text{H}_2\text{O}$, and $\text{Ce}(\text{NO}_3)_3 + \text{Nd}(\text{NO}_3)_3 + \text{H}_2\text{O}$ 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 are in good agreement with measured values, implying 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. Up to now, extensive data have been reported in the literature for the thermodynamic and transport properties of binary aqueous electrolyte solutions, but 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} Up to now, such simple equations have been established for thermodynamic properties, including activity coefficients of either solute in the mixed solutions, volumetric properties, thermal properties, and surface tension.^{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 provide 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 the densities of aqueous solutions of (1:3 + 1:3) electrolyte mixtures are not available in the literature to our knowledge, tests were 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 this study the densities were measured for the ternary systems $\text{Y}(\text{NO}_3)_3 + \text{Ce}(\text{NO}_3)_3 + \text{H}_2\text{O}$, $\text{Y}(\text{NO}_3)_3 + \text{Nd}(\text{NO}_3)_3 + \text{H}_2\text{O}$, and $\text{Ce}(\text{NO}_3)_3 + \text{Nd}(\text{NO}_3)_3 + \text{H}_2\text{O}$ and their binary subsystems $\text{Y}(\text{NO}_3)_3 + \text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 + \text{H}_2\text{O}$, and $\text{Nd}(\text{NO}_3)_3 + \text{H}_2\text{O}$ at different temperatures and up to $I_{\text{max}} \leq 24.5 \text{ mol} \cdot \text{kg}^{-1}$ (I is ionic strength). The results were used to check the predictability of the well-known approaches.

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Experimental Section

$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99 %), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99 %), and $\text{Nd}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (> 99 %) supplied by 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 solutions and then reheated and readjusted until stabilized.¹¹ The molalities of rare earth nitrate stock solutions were analyzed by both EDTA¹² and sulfate methods.¹¹ The stock solution concentrations were determined with an accuracy of ≤ 0.10 %.¹²

The experimental procedures are similar to those used in our previous study^{9a,b} 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 $\pm 5 \cdot 10^{-5} \text{ mol} \cdot \text{kg}^{-1}$. 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.^{9,13–16} The densities of water at different temperatures were obtained from the literature.¹⁷ The densities of dry air at different temperatures were taken from ref 18. In all the measured variables, the uncertainty in densities was $\pm 5 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$.

Predictive Equations for Density of Mixed Electrolyte Solutions. In the following section, the variables with the superscript (*io*) together with the subscript M_iX_i were used to denote the quantities of component M_iX_i in the binary solution $M_iX_i + \text{H}_2\text{O}$ ($i = 1, 2, \dots, n$) 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^{1–3,19} can be expressed as

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$$\sum_i \frac{m_{M_iX_i}}{m_{M_iX_i}^{(io)}} = 1 \quad (1)$$

$$\left(a_w = \text{constant and } 0 \leq \frac{m_{M_iX_i}}{m_{M_iX_i}^{(io)}} \leq 1 \right)$$

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

According to the semi-ideal solution theory, the density of a multicomponent electrolyte solution is related to those of its constituent binary solutions of equal water activity by^{1,2}

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

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. The density equation of Patwardhan and Kumar⁶ can be expressed as

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

with $Y_{M_iX_i} = y_{M_iX_i} + m_{M_iX_i} M_{M_iX_i}$, where $y_{M_iX_i}$ is 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, and the test procedure is briefly summarized as follows:

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

$$\rho_{M_iX_i}^{o,(\text{calc})} = \sum_{l=0}^N A_l (m_{M_iX_i}^o)^l \quad (4)$$

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

(2) 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 $m_{M_iX_i}$ ($i = 1, 2, \dots, n$) using the osmotic coefficients of M_iX_i ($i = 1, 2, \dots, n$)²⁰⁻²² and eq 1. Note that the reported osmotic coefficient data²⁰⁻²² were represented by the polynomial equations $\varphi_{M_iX_i}^{o,(\text{calc})} = \sum_{l=0}^N B_l (m_{M_iX_i}^o)^{l/2}$. The values of B_l obtained for the binary solutions are shown in Table 1.

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

(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 predictions for the mixed solutions of given $m_{M_iX_i}$ ($i = 1, 2, \dots, n$), 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 by⁹

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

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

Results and Discussion

Table 2 shows the measured densities of the binary solutions $Y(\text{NO}_3)_3 + \text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 + \text{H}_2\text{O}$, and $\text{Nd}(\text{NO}_3)_3 + \text{H}_2\text{O}$ at different temperatures. Figure 1 shows the variations of the values of $\Delta\rho_{M_iX_i}$ ($= \rho_{M_iX_i}^{o,(\text{calc})} - \rho_{M_iX_i}^{o,(\text{exp})}$) with the molality in the binary solutions $Y(\text{NO}_3)_3 + \text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 + \text{H}_2\text{O}$, and $\text{Nd}(\text{NO}_3)_3 + \text{H}_2\text{O}$ at 298.15 K, where $\rho_{M_iX_i}^{o,(\text{exp})}$ is the density reported in the literature.²¹⁻²³ $\rho_{M_iX_i}^{o,(\text{calc})}$ is the density calculated from eq 4 together with the parameters shown in Table 1. It is seen that the agreements are good. It should be noted that the stock solution concentrations were determined with an accuracy of $\leq 0.10\%$,¹² which means that the density can be determined with an accuracy of $\leq 0.0004 \text{ g}\cdot\text{cm}^{-3}$. The fitted parameters were extrapolated to calculate the densities for the binary solution $Y(\text{NO}_3)_3 + \text{H}_2\text{O}$ in the molality range ($0.23521 \leq m_{M_iX_i}^o \leq 0.41718$) $\text{mol}\cdot\text{kg}^{-1}$. The calculated densities were then compared with the densities measured by Hakin et al.,²⁴ and the agreement is good, with $\delta_{\rho} = 1.8 \cdot 10^{-4}$.

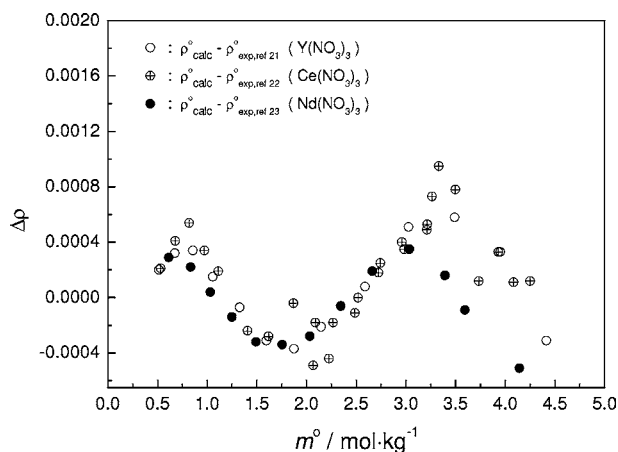
Table 3 compares the predicted and measured densities for the ternary solutions $Y(\text{NO}_3)_3 + \text{Ce}(\text{NO}_3)_3 + \text{H}_2\text{O}$ at different temperatures. It is notable that the osmotic coefficients of its binary subsystems at 298.15 K are used to calculate the compositions ($m_{M_iX_i}^{(io)}$) of the binary solutions at (293.15 and 308.15) K. It is clear from the third to seventh columns of Table

Table 1. Parameters for the Binary Solutions $Y(\text{NO}_3)_3 + \text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 + \text{H}_2\text{O}$, and $\text{Nd}(\text{NO}_3)_3 + \text{H}_2\text{O}$ at Different Temperatures

T/K	293.15	298.15	308.15	293.15	298.15	308.15
		$\rho_{Y(\text{NO}_3)_3+\text{H}_2\text{O}}^o$			$\rho_{\text{Ce}(\text{NO}_3)_3+\text{H}_2\text{O}}^o$	
A_0	0.997384	0.995502	0.992848	A_0	0.993492	0.991069
A_1	0.229023	0.229400	0.225443	A_1	0.292139	0.280844
A_2	-0.0263047	-0.0278444	-0.0263024	A_2	-0.0506119	-0.0424357
$10^3 A_3$	3.623389	4.365811	3.850967	$10^3 A_3$	13.181371	9.345383
$10^4 A_4$	-5.751668	-7.222839	-6.270300	$10^4 A_4$	-25.136345	-16.867863
$10^5 A_5$	4.293403	5.350563	4.681642	$10^5 A_5$	19.340987	12.774323
δ_{ρ}^o	$3.0 \cdot 10^{-5}$	$4.9 \cdot 10^{-5}$	$4.2 \cdot 10^{-5}$	δ_{ρ}^o	$9.0 \cdot 10^{-6}$	$5.9 \cdot 10^{-5}$
		$\rho_{\text{Nd}(\text{NO}_3)_3+\text{H}_2\text{O}}^o$		$\varphi_{Y(\text{NO}_3)_3+\text{H}_2\text{O}}^{o,298.15}$	$\varphi_{\text{Ce}(\text{NO}_3)_3+\text{H}_2\text{O}}^{o,298.15}$	$\varphi_{\text{Nd}(\text{NO}_3)_3+\text{H}_2\text{O}}^{o,298.15}$
A_0	0.997386	0.995387	0.993223	B_0	0.816929	0.760181
A_1	0.281981	0.283925	0.277342	B_1	-0.343762	-0.131740
A_2	-0.0335038	-0.0382564	-0.0335567	B_2	0.722643	-19.061765
$10^3 A_3$	5.050950	8.053080	5.875711	B_3	-0.164927	12.696013
$10^4 A_4$	-7.660146	-15.685357	-10.844769	B_4	0.010871	-4.046712
$10^5 A_5$	5.254163	12.933185	8.940584	B_5	-0.000546	0.499920
δ_{ρ}^o	$4.1 \cdot 10^{-5}$	$1.7 \cdot 10^{-5}$	$3.1 \cdot 10^{-5}$	δ_{ρ}^o	$9.7 \cdot 10^{-4}$	$4.0 \cdot 10^{-3}$

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

(m_B) (mol·kg ⁻¹)	$(\rho_{293.15}^o)$ (g·cm ⁻³)	$(\rho_{298.15}^o)/(g·cm^{-3})$		$(\rho_{308.15}^o)$ (g·cm ⁻³)
		exp	ref	
Y(NO ₃) ₃ (B) + H ₂ O (A)				
0.23521		1.0484 ^a	1.0480 ²⁴	
0.27747		1.0574	1.0571 ²⁴	
0.32132		1.0666	1.0665 ²⁴	
0.37064		1.0769	1.0769 ²⁴	
0.41718		1.0865	1.0867 ²⁴	
0.4989	1.1055	1.1035	1.1033 ²¹	1.0992
0.9965	1.2026	1.2002	1.1999 ²¹	1.1947
1.4972	1.2908	1.2878	1.2882 ²¹	1.2814
1.9820	1.3687	1.3654	1.3656 ²¹	1.3582
2.9475	1.5028	1.4989	1.4985 ²¹	1.4905
3.9452	1.6157	1.6114	1.6111 ²¹	1.6022
4.9575	1.7089	1.7043	1.7048 ²¹	1.6947
Ce(NO ₃) ₃ (B) + H ₂ O (A)				
0.5112	1.1312	1.1293	1.1291 ²²	1.1247
1.0313	1.2528	1.2502	1.2498 ²²	1.2444
1.5546	1.3619	1.3588	1.3593 ²²	1.3520
1.9969	1.4462	1.4431	1.4434 ²²	1.4357
3.1308	1.6332	1.6291	1.6286 ²²	1.6205
3.9676	1.7464	1.7424	1.7421 ²²	1.7331
4.4616	1.8060	1.8018	1.8014 ²²	1.7922
Nd(NO ₃) ₃ (B) + H ₂ O (A)				
0.5220	1.1361	1.1342	1.1340 ²³	1.1296
1.0213	1.2551	1.2525	1.2524 ²³	1.2467
1.5554	1.3698	1.3667	1.3671 ²³	1.3599
2.0934	1.4747	1.4711	1.4713 ²³	1.4635
3.0857	1.6421	1.6378	1.6375 ²³	1.6288
4.1242	1.7859	1.7811	1.7816 ²³	1.7714
4.2972	1.8070	1.8027	1.8031 ²³	1.7928

^a Extrapolated values.**Figure 1.** Variations of the $\Delta\rho$ values with the molalities for the binary solutions $Y(NO_3)_3 + H_2O$, $Ce(NO_3)_3 + H_2O$, and $Nd(NO_3)_3 + H_2O$ at 298.15 K.

3 that the agreements are good: the $\delta_\rho^{eq, 2}$ values at (293.15, 298.15, and 308.15) K are $2.7 \cdot 10^{-4}$, $3.1 \cdot 10^{-4}$, and $3.4 \cdot 10^{-4}$, respectively. The values of $\delta_\rho^{eq, 3}$ at (293.15, 298.15, and 308.15) K are $2.6 \cdot 10^{-4}$, $3.1 \cdot 10^{-4}$, and $3.6 \cdot 10^{-4}$, respectively.

Table 4 compares the predicted and measured densities for the ternary solutions $Y(NO_3)_3 + Nd(NO_3)_3 + H_2O$ at different temperatures. The $\delta_\rho^{eq, 2}$ values at (293.15, 298.15, and 308.15) K are $4.4 \cdot 10^{-4}$, $4.8 \cdot 10^{-4}$, and $4.4 \cdot 10^{-4}$, respectively. The values of $\delta_\rho^{eq, 3}$ at (293.15, 298.15, and 308.15) K are $4.2 \cdot 10^{-4}$, $5.0 \cdot 10^{-4}$, and $4.6 \cdot 10^{-4}$, respectively.

Table 5 compares the predicted and measured densities for the ternary solutions $Ce(NO_3)_3 + Nd(NO_3)_3 + H_2O$ at different temperatures. The $\delta_\rho^{eq, 2}$ values at (293.15, 298.15, and 308.15) K are $2.1 \cdot 10^{-4}$, $2.9 \cdot 10^{-4}$, and $2.4 \cdot 10^{-4}$, respectively. The values

Table 3. Comparisons of Measured and Predicted Densities of the Ternary Systems $Y(NO_3)_3$ (B) + $Ce(NO_3)_3$ (C) + H_2O (A) at Different Temperatures and with $I_{max} \leq 23.8 \text{ mol} \cdot \text{kg}^{-1}$

m_B (mol·kg ⁻¹)	m_C	ρ (g·cm ⁻³)			$\Delta\rho$ (g·cm ⁻³)	
		exp	eq 2	eq 3	$\Delta_{eq, 2}$	$\Delta_{eq, 3}$
293.15 K						
0.2545	0.7679	1.2401	1.2399	1.2400	-0.0002	-0.0001
0.5027	0.5111	1.2272	1.2274	1.2276	0.0002	0.0004
0.7527	0.2523	1.2153	1.2148	1.2149	-0.0005	-0.0004
0.4944	1.4988	1.4265	1.4269	1.4270	0.0004	0.0005
0.9897	0.9998	1.4077	1.4075	1.4077	-0.0002	0.0000
1.4843	0.5014	1.3884	1.3882	1.3883	-0.0002	-0.0001
0.7655	2.3177	1.6003	1.5999	1.6000	-0.0004	-0.0003
1.4879	1.5503	1.5683	1.5681	1.5682	-0.0002	-0.0001
2.2402	0.7513	1.5355	1.5346	1.5347	-0.0009	-0.0008
0.9855	2.9766	1.7147	1.7142	1.7142	-0.0005	-0.0005
1.9734	1.9830	1.6823	1.6817	1.6816	-0.0006	-0.0007
2.9596	0.9912	1.6496	1.6490	1.6488	-0.0006	-0.0008
				$\delta_\rho^{eq, a}$	$2.7 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$
298.15 K						
0.2545	0.7679	1.2370	1.2373	1.2374	0.0003	0.0004
0.5027	0.5111	1.2245	1.2249	1.2250	0.0004	0.0005
0.7527	0.2523	1.2130	1.2123	1.2124	-0.0007	-0.0006
0.4944	1.4988	1.4235	1.4236	1.4237	0.0001	0.0002
0.9897	0.9998	1.4045	1.4042	1.4044	-0.0003	-0.0001
1.4843	0.5014	1.3853	1.3848	1.3849	-0.0005	-0.0004
0.7655	2.3177	1.5964	1.5959	1.5960	-0.0005	-0.0004
1.4879	1.5503	1.5643	1.5641	1.5643	-0.0002	0.0000
2.2402	0.7513	1.5315	1.5307	1.5308	-0.0008	-0.0007
0.9855	2.9766	1.7107	1.7101	1.7101	-0.0006	-0.0006
1.9734	1.9830	1.6781	1.6776	1.6774	-0.0005	-0.0007
2.9596	0.9912	1.6453	1.6448	1.6445	-0.0005	-0.0008
				$\delta_\rho^{eq, a}$	$3.1 \cdot 10^{-4}$	$3.1 \cdot 10^{-4}$
308.15 K						
0.2545	0.7679	1.2319	1.2316	1.2317	-0.0003	-0.0002
0.5027	0.5111	1.2189	1.2192	1.2194	0.0003	0.0005
0.7527	0.2523	1.2062	1.2068	1.2069	0.0006	0.0007
0.4944	1.4988	1.4162	1.4163	1.4164	0.0001	0.0002
0.9897	0.9998	1.3973	1.3970	1.3971	-0.0003	-0.0002
1.4843	0.5014	1.3781	1.3776	1.3777	-0.0005	-0.0004
0.7655	2.3177	1.5875	1.5873	1.5874	-0.0002	-0.0001
1.4879	1.5503	1.5562	1.5556	1.5557	-0.0006	-0.0005
2.2402	0.7513	1.5232	1.5223	1.5223	-0.0009	-0.0009
0.9855	2.9766	1.7015	1.7008	1.7008	-0.0007	-0.0007
1.9734	1.9830	1.6691	1.6683	1.6682	-0.0008	-0.0009
2.9596	0.9912	1.6363	1.6355	1.6353	-0.0008	-0.0010
				$\delta_\rho^{eq, a}$	$3.4 \cdot 10^{-4}$	$3.6 \cdot 10^{-4}$

a

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

of $\delta_\rho^{eq, 3}$ at the three temperatures are $2.0 \cdot 10^{-4}$, $2.8 \cdot 10^{-4}$, and $2.4 \cdot 10^{-4}$, respectively. Further comparisons using the reported densities²⁵⁻²⁸ at 298.15 K show that the average relative differences ($\delta_\rho^{eq, 2} / \delta_\rho^{eq, 3}$) between the predicted and measured densities are $3.5 \cdot 10^{-4} / 3.5 \cdot 10^{-4}$ for NaCl + KCl + H₂O ($I_{max} = 4.4 \text{ mol} \cdot \text{kg}^{-1}$), $2.2 \cdot 10^{-4} / 2.2 \cdot 10^{-4}$ for KCl + CaCl₂ + H₂O ($I_{max} = 3.6 \text{ mol} \cdot \text{kg}^{-1}$), $3.5 \cdot 10^{-4} / 3.8 \cdot 10^{-4}$ for HCl + KCl + NaCl + H₂O ($I_{max} = 2.2 \text{ mol} \cdot \text{kg}^{-1}$), and $3.6 \cdot 10^{-4} / 5.9 \cdot 10^{-4}$ for Na₂SO₄ + NaCl + H₂O ($I_{max} = 1.9 \text{ mol} \cdot \text{kg}^{-1}$), in which I_{max} is the maximum ionic strength. 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} By comparison, the equation of Patwardhan and Kumar is not applicable to the mixtures involving nonelectrolyte solutes, as they are based on the ionic strength fraction, which is not defined for nonelectrolyte solutes.

Table 4. Comparisons of Measured and Predicted Densities of the Ternary Systems Y(NO₃)₃ (B) + Nd(NO₃)₃ (C) + H₂O (A) at Different Temperatures and with $I_{\max} \leq 24.5 \text{ mol}\cdot\text{kg}^{-1}$

m_B (mol·kg ⁻¹)		ρ (g·cm ⁻³)			$\Delta\rho$ (g·cm ⁻³)	
m_C	exp	eq 2	eq 3	$\Delta_{\text{eq} 2}$	$\Delta_{\text{eq} 3}$	
293.15 K						
0.2532	0.7618	1.2416	1.2417	1.2418	0.0001	0.0002
0.5005	0.5083	1.2282	1.2287	1.2287	0.0005	0.0005
0.7512	0.2514	1.2163	1.2155	1.2155	-0.0008	-0.0008
0.5132	1.5514	1.4477	1.4474	1.4475	-0.0003	-0.0002
1.0147	1.0217	1.4211	1.4207	1.4208	-0.0004	-0.0003
1.5034	0.5055	1.3949	1.3945	1.3945	-0.0004	-0.0004
0.7595	2.2906	1.6075	1.6067	1.6068	-0.0008	-0.0007
1.5011	1.5142	1.5723	1.5718	1.5719	-0.0005	-0.0004
2.2355	0.7454	1.5382	1.5370	1.5370	-0.0012	-0.0012
1.0125	3.0658	1.7442	1.7429	1.7430	-0.0013	-0.0012
2.0077	2.0254	1.7011	1.7002	1.7003	-0.0009	-0.0008
2.9764	1.0127	1.6591	1.6582	1.6582	-0.0009	-0.0009
			$\delta_{\rho}^{\text{eqi} a}$	$4.4\cdot 10^{-4}$	$4.2\cdot 10^{-4}$	
298.15 K						
0.2532	0.7618	1.2391	1.2392	1.2392	0.0001	0.0001
0.5005	0.5083	1.2255	1.2262	1.2262	0.0007	0.0007
0.7512	0.2514	1.2137	1.2130	1.2131	-0.0007	-0.0006
0.5132	1.5514	1.4443	1.4439	1.4440	-0.0004	-0.0003
1.0147	1.0217	1.4178	1.4173	1.4173	-0.0005	-0.0005
1.5034	0.5055	1.3916	1.3911	1.3911	-0.0005	-0.0005
0.7595	2.2906	1.6029	1.6025	1.6026	-0.0004	-0.0003
1.5011	1.5142	1.5690	1.5677	1.5678	-0.0013	-0.0012
2.2355	0.7454	1.5339	1.5329	1.5330	-0.0010	-0.0009
1.0125	3.0658	1.7398	1.7385	1.7382	-0.0013	-0.0016
2.0077	2.0254	1.6970	1.6960	1.6956	-0.0010	-0.0014
2.9764	1.0127	1.6548	1.6541	1.6537	-0.0007	-0.0011
			$\delta_{\rho}^{\text{eqi} a}$	$4.8\cdot 10^{-4}$	$5.0\cdot 10^{-4}$	
308.15 K						
0.2532	0.7618	1.2336	1.2334	1.2335	-0.0002	-0.0001
0.5005	0.5083	1.2202	1.2205	1.2206	0.0003	0.0004
0.7512	0.2514	1.2079	1.2075	1.2075	-0.0004	-0.0004
0.5132	1.5514	1.4368	1.4364	1.4365	-0.0004	-0.0003
1.0147	1.0217	1.4105	1.4099	1.4099	-0.0006	-0.0006
1.5034	0.5055	1.3840	1.3838	1.3838	-0.0002	-0.0002
0.7595	2.2906	1.5942	1.5936	1.5937	-0.0006	-0.0005
1.5011	1.5142	1.5599	1.5590	1.5591	-0.0009	-0.0008
2.2355	0.7454	1.5255	1.5244	1.5245	-0.0011	-0.0010
1.0125	3.0658	1.7298	1.7289	1.7286	-0.0009	-0.0012
2.0077	2.0254	1.6876	1.6865	1.6862	-0.0011	-0.0014
2.9764	1.0127	1.6460	1.6447	1.6444	-0.0013	-0.0016
			$\delta_{\rho}^{\text{eqi} a}$	$4.4\cdot 10^{-4}$	$4.6\cdot 10^{-4}$	

a

$$\delta_{\rho}^{\text{eqi}} = \sum_{j=1}^N (|\rho_{j(\text{eqi})} - \rho_{j(\text{exp})}|/\rho_{j(\text{exp})})/N$$

The advantage the equation of Patwardhan and Kumar 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,²⁹ the osmotic coefficients measured at 298.15 K can be used to determine the molalities $m_{M_i X_i}^{(i)}$ 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

Densities were measured for the ternary systems Y(NO₃)₃ + Ce(NO₃)₃ + H₂O, Y(NO₃)₃ + Nd(NO₃)₃ + H₂O, and Ce(NO₃)₃

Table 5. Comparisons of Measured and Predicted Densities of the Ternary Systems Ce(NO₃)₃ (B) + Nd(NO₃)₃ (C) + H₂O (A) at Different Temperatures and with $I_{\max} \leq 24.5 \text{ mol}\cdot\text{kg}^{-1}$

m_B (mol·kg ⁻¹)		ρ (g·cm ⁻³)			$\Delta\rho$ (g·cm ⁻³)	
m_C	exp	eq 2	eq 3	$\Delta_{\text{eq} 2}$	$\Delta_{\text{eq} 3}$	
293.15 K						
0.2565	0.7673	1.2546	1.2545	1.2545	-0.0001	-0.0001
0.5097	0.5165	1.2534	1.2539	1.2539	0.0005	0.0005
0.7720	0.2568	1.2538	1.2534	1.2534	-0.0004	-0.0004
0.5182	1.5501	1.4672	1.4672	1.4672	0.0000	0.0000
1.0233	1.0207	1.4603	1.4601	1.4601	-0.0002	-0.0002
1.5159	0.5042	1.4528	1.4530	1.4530	0.0002	0.0002
0.7723	2.3246	1.6402	1.6399	1.6399	-0.0003	-0.0003
1.5687	1.5396	1.6377	1.6376	1.6377	-0.0001	0.0000
2.3415	0.7779	1.6362	1.6354	1.6354	-0.0008	-0.0008
1.0189	3.0651	1.7768	1.7758	1.7758	-0.0010	-0.0010
2.0174	2.0272	1.7659	1.7659	1.7659	0.0000	0.0000
3.0001	1.0057	1.7563	1.7561	1.7561	-0.0002	-0.0002
			$\delta_{\rho}^{\text{eqi} a}$	$2.1\cdot 10^{-4}$	$2.0\cdot 10^{-4}$	
298.15 K						
0.2565	0.7673	1.2517	1.2519	1.2519	0.0002	0.0002
0.5097	0.5165	1.2518	1.2513	1.2513	-0.0005	-0.0005
0.7720	0.2568	1.2511	1.2507	1.2507	-0.0004	-0.0004
0.5182	1.5501	1.4641	1.4638	1.4638	-0.0003	-0.0003
1.0233	1.0207	1.4570	1.4567	1.4567	-0.0003	-0.0003
1.5159	0.5042	1.4496	1.4497	1.4497	0.0001	0.0001
0.7723	2.3246	1.6362	1.6357	1.6357	-0.0005	-0.0005
1.5687	1.5396	1.6342	1.6335	1.6335	-0.0007	-0.0007
2.3415	0.7779	1.6319	1.6313	1.6313	-0.0006	-0.0006
1.0189	3.0651	1.7722	1.7712	1.7712	-0.0010	-0.0010
2.0174	2.0272	1.7618	1.7614	1.7615	-0.0004	-0.0003
3.0001	1.0057	1.7521	1.7518	1.7519	-0.0003	-0.0002
			$\delta_{\rho}^{\text{eqi} a}$	$2.9\cdot 10^{-4}$	$2.8\cdot 10^{-4}$	
308.15 K						
0.2565	0.7673	1.2457	1.2460	1.2461	0.0003	0.0004
0.5097	0.5165	1.2453	1.2455	1.2455	0.0002	0.0002
0.7720	0.2568	1.2445	1.2449	1.2449	0.0004	0.0004
0.5182	1.5501	1.4562	1.4562	1.4562	0.0000	0.0000
1.0233	1.0207	1.4495	1.4492	1.4492	-0.0003	-0.0003
1.5159	0.5042	1.4421	1.4423	1.4423	0.0002	0.0002
0.7723	2.3246	1.6276	1.6268	1.6268	-0.0008	-0.0008
1.5687	1.5396	1.6249	1.6247	1.6247	-0.0002	-0.0002
2.3415	0.7779	1.6235	1.6226	1.6226	-0.0009	-0.0009
1.0189	3.0651	1.7620	1.7616	1.7616	-0.0004	-0.0004
2.0174	2.0272	1.7522	1.7519	1.7520	-0.0003	-0.0002
3.0001	1.0057	1.7428	1.7424	1.7425	-0.0004	-0.0003
			$\delta_{\rho}^{\text{eqi} a}$	$2.4\cdot 10^{-4}$	$2.4\cdot 10^{-4}$	

a

$$\delta_{\rho}^{\text{eqi}} = \sum_{j=1}^N (|\rho_{j(\text{eqi})} - \rho_{j(\text{exp})}|/\rho_{j(\text{exp})})/N$$

+ Nd(NO₃)₃ + H₂O and their binary subsystems at (293.15, 298.15, and 308.15) K and then were used to test the predictability of the simple density equations. The comparison results show that eqs 2 and 3 can yield good predictions for the densities of the ternary electrolyte solutions in terms of the properties of the binary solutions that do not involve mixed parameters, which indicates that these equations can make use of the information on the binary solutions, avoiding much complexity in the calculation of densities of the mixed solutions, and provide good predictions for the densities of the mixed solutions. The comparison results also show that the extensively reported osmotic coefficients of the binary solutions measured at 298.15 K can be used to determine the compositions of the binary solutions having the same water activity as that of the mixed solutions at other temperatures.

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