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

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S Supporting Information

ABSTRACT: Conductivities were measured for 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 $Y(NO_3)_3 + H_2O$, $Ce(NO_3)_3 + H_2O$, and $Nd(NO_3)_3 + H_2O$ at (293.15, 298.15, and 308.15) K. The measured conductivities were used to test the generalized Young's rule and the semi-ideal solution theory. The comparison results show that the generalized Young's rule and the semi-ideal solution theory can yield good predictions for the conductivities of the ternary electrolyte solutions, implying that the conductivities of aqueous solutions of (1:3 + 1:3) electrolyte mixtures can be well predicted from those of their constituent binary solutions by the simple equations.

INTRODUCTION

The thermodynamic properties and the transport properties of mixed aqueous solutions play an important role in a variety of fields, including chemistry and chemical engineering, separation process, wastewater treatment, pollution control, and oil recovery. Electrical conductivity is one of the principal transport properties of aqueous electrolyte solutions, not only for its intrinsic interest but also for technical and industrial applications such as batteries and plating. In addition, conductivity measurements are usually used to verify electrolyte theories.[1] However, whereas the thermodynamic and the transport properties of binary electrolyte solutions are extensively reported in the literature, relatively few data are available for mixed solutions, especially for aqueous solutions of (1:3 + 1:3) electrolyte mixtures. Therefore, it is very important to develop simple predictive equations to predict the properties of multicomponent solutions from the available properties of their binary solutions.[2−5]

The semi-ideality model has been extensively used to interpret deviations of the osmotic coefficient of aqueous solutions from ideal behavior,[6−9] which means that the solute−solute interactions can be neglected and the solute−solvent interactions can be simply described by a series of hydration equilibria. In 1966, Stokes and Robinson proposed a semi-ideality concept for aqueous solutions of several nonelectrolyte solutes under isopiestic condition.[10] Recently, a semi-ideal solution theory has been proposed to describe the process of mixing the binary nonideal solutions at constant water activity.[11,12] Both the Young's rule[13] and the semi-ideal solution theory[11,12] provide good predictions for the thermodynamic properties (including activity coefficient of each solute in multicomponent solutions, volumetric properties,[14] and thermal properties[15]) of mixed electrolyte solutions from the properties of their binary subsystems. They have also been extended to conductivity of mixed electrolyte solutions.[16,17] However, because the conductivities 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 conductivities were measured for 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 $Y(NO_3)_3 + H_2O$, $Ce(NO_3)_3 + H_2O$, and $Nd(NO_3)_3 + H_2O$ at different temperatures and up to $I_{max} \leq 24.4\ mol \cdot kg^{-1}$. The results were used to verify the applicability of the generalized Young's rule and the semi-ideal solution theory.

MATERIALS AND METHODS

$Y(NO_3)_3 \cdot 6H_2O$ (99.99 %), $Ce(NO_3)_3 \cdot 6H_2O$ (99.99 %), and $Nd(NO_3)_3 \cdot xH_2O$ (> 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.[18] The molalities of rare earth nitrate stock solutions were analyzed by both EDTA[19] and sulfate methods.[18] The stock solution concentrations were determined with an accuracy of ≤ 0.10 %.[19] Low-conductivity water was double-distilled, passed by a reverse osmosis system, and finally treated with a water purification system. The conductivity of the water was less than $0.050\ \mu S \cdot cm^{-1}$.

The experimental procedures are similar to those used in our previous study[17] and are described briefly as follows. Dilute solutions were prepared by diluting a stock solution by mass with water. We prepared the ternary solutions by mixing the binary solutions with known concentrations by mass. All solutions were prepared immediately before use, and the uncertainty

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

T/K	293.15	298.15	308.15	T/K	293.15	298.15	308.15
	$\sigma^o_{Y(NO_3)_3 + H_2O}$				$\sigma^o_{Ce(NO_3)_3 + H_2O}$		
A_0	3.554291	2.946847	9.001244	A_0	8.110726	12.263023	14.187170
$10^{-2}A_1$	1.903583	2.245822	2.502971	$10^{-2}A_1$	1.674526	1.772205	2.110410
$10^{-2}A_2$	−1.208557	−1.446431	−1.579533	$10^{-2}A_2$	−1.229512	−1.284984	−1.530772
$10^{-1}A_3$	3.073794	3.774747	4.007953	$10^{-1}A_3$	3.716791	3.810032	4.590621
A_4	−3.650538	−4.634991	−4.736773	A_4	−5.381911	−5.389806	−6.595535
$10A_5$	1.675685	2.210391	2.139818	$10A_5$	3.071183	2.993848	3.718466
δ^o_σ	$7.5 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$	$8.5 \cdot 10^{-4}$	δ^o_σ	$7.0 \cdot 10^{-4}$	$6.1 \cdot 10^{-4}$	$6.5 \cdot 10^{-4}$
	$\sigma^o_{Nd(NO_3)_3 + H_2O}$				$\varphi^{o,298.15}_{Y(NO_3)_3 + H_2O}$	$\varphi^{o,298.15}_{Ce(NO_3)_3 + H_2O}$	$\varphi^{o,298.15}_{Nd(NO_3)_3 + H_2O}$
A_0	7.852768	9.167663	13.650377	B_0	0.816929	−3.299233	0.760181
$10^{-2}A_1$	1.672822	1.834471	2.120852	B_1	−0.343762	14.079971	−0.131740
$10^{-2}A_2$	−1.163168	−1.288338	−1.477699	B_2	0.722643	−19.061765	0.132389
$10^{-1}A_3$	3.283565	3.743737	4.254943	B_3	−0.164927	12.696013	0.207792
A_4	−4.393174	−5.280104	−5.906276	B_4	0.010871	−4.046712	−0.102828
$10A_5$	2.292078	2.986023	3.245291	B_5	−0.000546	0.499920	0.014000
δ^o_σ	$2.0 \cdot 10^{-4}$	$4.1 \cdot 10^{-4}$	$5.3 \cdot 10^{-4}$	δ^o_φ	$9.7 \cdot 10^{-4}$	$4.0 \cdot 10^{-3}$	$6.5 \cdot 10^{-4}$

was $\pm 5 \cdot 10^{-5}$ mol·kg^{-1}. The conductivity measurements were carried out with a METLER TOLEDO SevenEasy conductivity meter (cell constant = 0.57 cm^{-1}) calibrated with the standard aqueous potassium chloride solutions, and the uncertainty was ± 0.5 %.[17] During measurements, the cell was immersed in a model 501A thermostatic bath filled with silicone oil. The bath temperature was kept constant to within ± 0.05 K. The temperature was measured with a PT100 with an evaluating standard uncertainty of ± 0.006 K.

Predictive Equations for Conductivity 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 $M_iX_i + H_2O$ (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[20] can be expressed as

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

where $m_{M_iX_i}$ and $m^{(io)}_{M_iX_i}$ 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 conductivity of a mixed electrolyte solutions can be expressed as[17,21]

$$\ln \sigma = \sum_i x^{(io)}_{M_iX_i} \ln \sigma^{(io)}_{M_iX_i} \quad (2)$$

where

$$x^{(io)}_{M_iX_i} = \frac{m_{M_iX_i} + 55.51 \dfrac{m_{M_iX_i}}{m^{(io)}_{M_iX_i}}}{\sum_i m_{M_iX_i} + 55.51 \sum_i \dfrac{m_{M_iX_i}}{m^{(io)}_{M_iX_i}}}$$

is the mole fraction of the binary solution $M_iX_i + H_2O$ in the mixed solution $M_1X_1 + ... + M_iX_i + H_2O$ of equal water activity.

Table 2. Conductivities of the Binary Systems $Y(NO_3)_3 + H_2O$, $Ce(NO_3)_3 + H_2O$, $La(NO_3)_3 + H_2O$, and $Nd(NO_3)_3 + H_2O$ at Different Temperatures[a]

m_B	$\sigma^o_{293.15}$	$\sigma^o_{298.15}$/mS·cm^{-1}		$\sigma^o_{308.15}$
mol·kg^{-1}	mS·cm^{-1}	exp.	ref.	mS·cm^{-1}
		$Y(NO_3)_3$ (B) + H_2O (A)		
0.4989	72.02	83.39		99.22
0.9965	100.31	116.14		136.92
1.4972	103.55	119.96		141.72
1.9820	94.33	109.04		130.31
2.9475	63.49	74.21		90.84
3.9452	36.76	43.96		56.11
4.9575	18.88	22.84		30.78
		$Ce(NO_3)_3$ (B) + H_2O (A)		
0.5112	66.18	74.00		87.75
1.0313	85.13	94.46		112.42
1.5546	82.17	91.49		109.50
1.9969	72.44	81.03		97.79
3.1308	43.09	48.98		61.36
3.9676	26.73	30.99		40.18
4.4616	19.12	22.44		29.59
		$Nd(NO_3)_3$ (B) + H_2O (A)		
0.5220	67.83	74.76 (49.35)[b]	49.28[25]	89.71
1.0213	87.84	96.64 (33.68)	33.63	115.43
1.5554	86.55	95.45 (22.66)	22.64	114.44
2.0934	74.40	82.70 (15.14)	15.16	100.09
3.0857	47.08	53.29 (7.10)	7.11	66.51
4.1242	25.21	29.31 (3.14)	3.13	38.21
4.2972	22.19	26.23 (2.73)	2.73	34.22

[a] Standard uncertainties u are $u(m_B) = \pm 0.00005$ mol·kg^{-1}, $u(T) = \pm 0.05$ K, and the combined expanded uncertainty U_c is $U_c(\sigma) = \pm 0.5$ % (level of confidence = 0.95). [b] Values in parentheses are equivalent conductances, of which the unit is (absolute ohm)$^{-1}$ ·cm^2·equiv^{-1}.

Table 3. Comparisons of Measured and Predicted Conductivities of the Ternary System $Y(NO_3)_3$ (B) + $Ce(NO_3)_3$ (C) + H_2O (A) at Different Temperatures[a]

m_B	m_C	σ			$\Delta\sigma$	
		$mS\cdot cm^{-1}$			$mS\cdot cm^{-1}$	
$mol\cdot kg^{-1}$	$mol\cdot kg^{-1}$	exp	eq 2	eq 3	Δ_{eq} 2	Δ_{eq} 3
		293.15 K				
0.2545	0.7679	87.86	88.64	88.94	0.78	1.08
0.5027	0.5111	91.45	92.30	92.71	0.85	1.26
0.7527	0.2523	95.12	96.20	96.51	1.08	1.39
0.4944	1.4988	76.77	77.28	77.77	0.51	1.00
0.9897	0.9998	81.94	82.57	83.21	0.63	1.27
1.4843	0.5014	87.36	88.20	88.68	0.84	1.32
0.7655	2.3177	47.24	47.80	47.95	0.56	0.71
1.4879	1.5503	52.32	52.60	52.81	0.28	0.49
2.2402	0.7513	57.59	58.01	58.17	0.42	0.58
0.9855	2.9766	28.74	28.87	29.19	0.13	0.45
1.9734	1.9830	31.08	31.20	31.69	0.12	0.61
				$\delta_\sigma^{eq\,i\,b}$	$7.9\cdot 10^{-3}$	$1.4\cdot 10^{-2}$
		298.15 K				
0.2545	0.7679	98.69	99.55	99.92	0.86	1.23
0.5027	0.5111	103.80	104.81	105.32	1.01	1.52
0.7527	0.2523	109.17	110.39	110.77	1.22	1.60
0.4944	1.4988	86.48	87.35	87.89	0.87	1.41
0.9897	0.9998	93.50	94.16	94.89	0.66	1.39
1.4843	0.5014	100.42	101.37	101.91	0.95	1.49
0.7655	2.3177	54.24	54.77	54.98	0.53	0.74
1.4879	1.5503	60.22	60.68	60.98	0.46	0.76
2.2402	0.7513	66.84	67.38	67.61	0.54	0.77
0.9855	2.9766	33.73	33.79	34.18	0.06	0.45
1.9734	1.9830	36.68	36.81	37.42	0.13	0.74
				$\delta_\sigma^{eq\,i\,b}$	$7.9\cdot 10^{-3}$	$1.5\cdot 10^{-2}$
		308.15 K				
0.2545	0.7679	117.21	118.16	118.56	0.95	1.35
0.5027	0.5111	123.01	124.09	124.63	1.08	1.62
0.7527	0.2523	129.05	130.36	130.77	1.31	1.72
0.4944	1.4988	104.25	105.11	105.71	0.86	1.46
0.9897	0.9998	112.15	113.00	113.80	0.85	1.65
1.4843	0.5014	120.15	121.32	121.91	1.17	1.76
0.7655	2.3177	67.75	68.24	68.40	0.49	0.65
1.4879	1.5503	74.50	75.20	75.43	0.70	0.93
2.2402	0.7513	82.19	83.00	83.18	0.81	0.99
0.9855	2.9766	43.45	43.57	44.10	0.12	0.65
1.9734	1.9830	47.05	47.22	48.07	0.17	1.02
				$\delta_\sigma^{eq\,i\,b}$	$7.8\cdot 10^{-3}$	$1.4\cdot 10^{-2}$

[a] Standard uncertainties u are $u(m_B) = \pm 0.00005\ mol\cdot kg^{-1}$, $u(m_C) = \pm 0.00005\ mol\cdot kg^{-1}$, $u(T) = \pm 0.05$ K, and the combined expanded uncertainty U_c is $U_c(\sigma) = \pm 0.5$ % (level of confidence = 0.95). [b] $\delta_\sigma^{eq\,i} = \sum_{j=1}^{N}(|\sigma_{j(eq\,i)} - \sigma_{j(exp)}|/\sigma_{j(exp)})/N$.

σ and $\sigma_{M_iX_i}^{(io)}$ are the conductivities of the mixed solution and its binary solution $M_iX_i + H_2O$ ($i = 1, 2, ..., n$) of equal water activity.

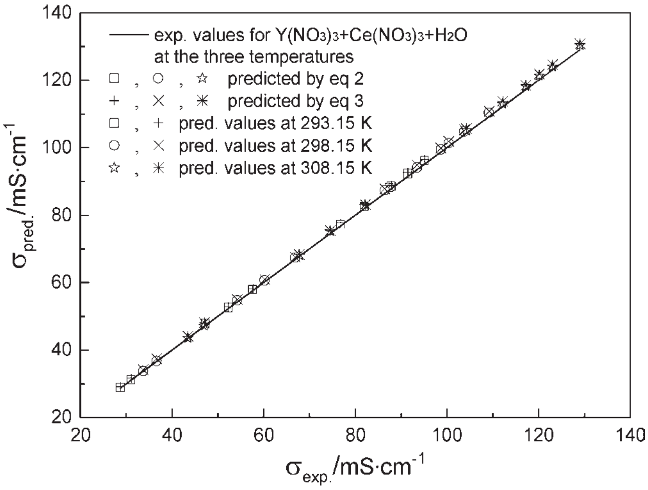

Figure 1. Comparisons of measured and predicted conductivities of the ternary system $Y(NO_3)_3 + Ce(NO_3)_3 + H_2O$ at different temperatures.

The generalized Young's rule for the conductivity of the mixed electrolyte solutions[1,16] can be expressed as

$$\sigma = \sum_i y_{M_iX_i}\sigma_{M_iX_i}^{o,I} \tag{3}$$

where $y_{M_iX_i} = I_{M_iX_i}/\sum_j I_{M_jX_j}$ is ionic strength fraction. $\sigma_{M_iX_i}^{o,I}$ is the conductivity of the binary solution $M_iX_i + H_2O$ of equal ionic strength.

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

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

$$\sigma_{M_iX_i(calc)}^{o} = \sum_{l=0}^{N} A_l(m_{M_iX_i}^{o})^l \tag{4}$$

where $\sigma_{M_iX_i(calc)}^{o}$ and $m_{M_iX_i}^{o}$ denote the conductivity and molality of the binary aqueous solution $M_iX_i + H_2O$ ($i = 1, 2, ..., n$). The optimum fit was obtained by variation of l until the values of $\delta_{\sigma,M_iX_i}^{o} = \sum_{j=1}^{N}(|\sigma_{M_iX_i(calc)}^{o} - \sigma_{M_iX_i(exp)}^{o}|/\sigma_{M_iX_i(exp)}^{o})/N$ is less than a few parts in 10^{-4}. The values of A_l and $\delta_{\sigma,M_iX_i}^{o}$ obtained for the three binary solutions are shown in Table 1. Note that seven molalities were studied for each binary solution, and $A_0 - A_5$ were used in each case to precisely reproduce the measured values. Therefore, eq 4 is not suitable for extrapolations to higher or lower molalities.

(2) The reported osmotic coefficient data[22−24] were represented by the equations $\varphi_{M_iX_i(calc)}^{o} = \sum_{l=0}^{N} B_l(m_{M_iX_i}^{o})^{l/2}$. The obtained values of B_l are shown in Table 1. Then, 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 $m_{M_iX_i}$ ($i = 1, 2, ..., n$) were determined using the osmotic coefficients of M_iX_i ($i = 1, 2, ..., n$)[22−24] 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 $\sigma_{M_iX_i}^{(io)}$ and $\sigma_{M_iX_i}^{o,I}$ calculated from eq 4 into eqs 2 and 3 to yield the predictions for the mixed solutions of given $m_{M_iX_i}$ ($i = 1, 2, ..., n$), which are then compared with the corresponding experimental data. Note that $m_{M_iX_i}^{(io)}$ and $m_{M_iX_i}^{o,I}$ are within the experimental molality ranges of the binary solutions and are close to

Table 4. Comparisons of Measured and Predicted Conductivities of the Ternary System $Y(NO_3)_3$ (B) + $Nd(NO_3)_3$ (C) + H_2O (A) at Different Temperatures[a]

m_B	m_C	σ			$\Delta\sigma$	
		$mS\cdot cm^{-1}$			$mS\cdot cm^{-1}$	
$mol\cdot kg^{-1}$	$mol\cdot kg^{-1}$	exp	eq 2	eq 3	Δ_{eq} 2	Δ_{eq} 3
		293.15 K				
0.2532	0.7618	89.85	90.78	90.97	0.93	1.12
0.5005	0.5083	93.01	93.78	94.04	0.77	1.03
0.7512	0.2514	95.92	96.97	97.16	1.05	1.24
0.5132	1.5514	78.42	79.03	79.32	0.61	0.90
1.0147	1.0217	83.09	83.88	84.27	0.79	1.18
1.5034	0.5055	87.98	88.93	89.23	0.95	1.25
0.7595	2.2906	50.58	50.90	51.06	0.32	0.48
1.5011	1.5142	54.48	54.89	55.11	0.41	0.63
2.2355	0.7454	58.76	59.13	59.29	0.37	0.53
1.0125	3.0658	27.45	27.54	27.99	0.09	0.54
				$\delta_\sigma^{eq\,i}$[b]	$8.1\cdot 10^{-3}$	$1.3\cdot 10^{-2}$
		298.15 K				
0.2532	0.7618	100.22	101.30	101.54	1.08	1.32
0.5005	0.5083	105.17	106.04	106.36	0.87	1.19
0.7512	0.2514	109.88	111.04	111.28	1.16	1.40
0.5132	1.5514	88.09	88.86	89.16	0.77	1.07
1.0147	1.0217	94.38	95.32	95.73	0.94	1.35
1.5034	0.5055	101.00	102.02	102.34	1.02	1.34
0.7595	2.2906	57.78	58.13	58.35	0.35	0.57
1.5011	1.5142	62.74	63.20	63.51	0.46	0.77
2.2355	0.7454	68.02	68.59	68.83	0.57	0.81
1.0125	3.0658	32.31	32.45	32.78	0.14	0.47
				$\delta_\sigma^{eq\,i}$[b]	$8.4\cdot 10^{-3}$	$1.3\cdot 10^{-2}$
		308.15 K				
0.2532	0.7618	119.36	120.53	120.79	1.17	1.43
0.5005	0.5083	124.80	125.73	126.09	0.93	1.29
0.7512	0.2514	130.22	131.21	131.48	0.99	1.26
0.5132	1.5514	106.27	107.14	107.47	0.87	1.20
1.0147	1.0217	113.57	114.52	114.98	0.95	1.41
1.5034	0.5055	121.08	122.17	122.52	1.09	1.44
0.7595	2.2906	71.65	72.24	72.42	0.59	0.77
1.5011	1.5142	77.51	78.17	78.43	0.66	0.92
2.2355	0.7454	83.62	84.43	84.63	0.81	1.01
1.0125	3.0658	41.78	41.92	42.51	0.14	0.73
				$\delta_\sigma^{eq\,i}$[b]	$8.0\cdot 10^{-3}$	$1.2\cdot 10^{-2}$

[a] Standard uncertainties u are $u(m_B) = \pm 0.00005\ mol\cdot kg^{-1}$, $u(m_C) = \pm 0.00005\ mol\cdot kg^{-1}$, $u(T) = \pm 0.05$ K, and the combined expanded uncertainty U_c is $U_c(\sigma) = \pm 0.5$ % (level of confidence = 0.95). [b] $\delta_\sigma^{eq\,i} = \sum_{j=1}^{N} (|\sigma_{j(eq\,i)} - \sigma_{j(exp)}|/\sigma_{j(exp)})/N$.

$m^{o}_{M_iX_i}$ and, therefore, eq 4 can yield accurate predictions for $\sigma^{(io)}_{M_iX_i}$ and $\sigma^{o,I}_{M_iX_i}$.

In this paper, the differences between predicted and measured conductivities are defined by[17]

$$\Delta_{eqi} = \sigma_{eqi} - \sigma_{exp} \qquad (5)$$

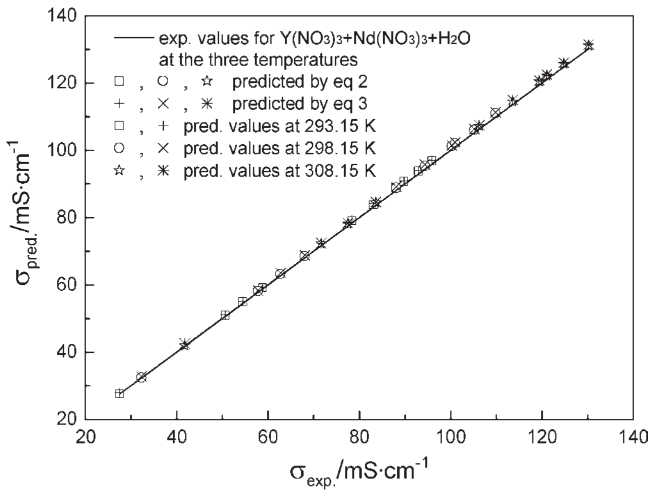

Figure 2. Comparisons of measured and predicted conductivities of the ternary system $Y(NO_3)_3 + Nd(NO_3)_3 + H_2O$ at different temperatures.

The average relative differences between the predicted and measured conductivities over the entire experimental composition range of the ternary solution are defined by[17]

$$\delta_\sigma = \sum_{i=1}^{N} |\delta_{\sigma,i}|/N \qquad (6)$$

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

RESULTS AND DISCUSSION

Table 2 shows the measured conductivities 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. Only the measured conductivities for binary solution $Nd(NO_3)_3 + H_2O$ at 298.15 K are compared with the values reported in ref 25. It can be seen that the agreements are good.

Table 3 and Figure 1 compare measured and predicted conductivities for the ternary solutions $Y(NO_3)_3 + Ce(NO_3)_3 + H_2O$ at different temperatures. It is notable that the osmotic coefficients of its binary subsystems at 298.15 K are used to calculate the compositions $(m^{(io)}_{M_iX_i})$ 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 $\delta_\sigma^{eq\,2}$ values at (293.15, 298.15, and 308.15) K are $7.9\cdot 10^{-3}$, $7.9\cdot 10^{-3}$, and $7.8\cdot 10^{-3}$, respectively. The values of $\delta_\sigma^{eq\,3}$ at (293.15, 298.15, and 308.15) K are $1.4\cdot 10^{-2}$, $1.5\cdot 10^{-2}$, and $1.4\cdot 10^{-2}$, respectively.

Table 4 and Figure 2 compare measured and predicted conductivities for the ternary solutions $Y(NO_3)_3 + Nd(NO_3)_3 + H_2O$ at different temperatures. The $\delta_\sigma^{eq\,2}$ values at (293.15, 298.15, and 308.15) K are $8.1\cdot 10^{-3}$, $8.4\cdot 10^{-3}$, and $8.0\cdot 10^{-3}$, respectively. The values of $\delta_\sigma^{eq\,3}$ at (293.15, 298.15, and 308.15) K are $1.3\cdot 10^{-2}$, $1.3\cdot 10^{-2}$, and $1.2\cdot 10^{-2}$, respectively.

Table 5 and Figure 3 compare measured and predicted conductivities for the ternary solutions $Ce(NO_3)_3 + Nd(NO_3)_3 + H_2O$ at different temperatures. The $\delta_\sigma^{eq\,2}$ values at (293.15, 298.15, and 308.15) K are $5.5\cdot 10^{-3}$, $5.8\cdot 10^{-3}$, and $6.0\cdot 10^{-3}$, respectively. The values of $\delta_\sigma^{eq\,3}$ at the three temperatures are $5.6\cdot 10^{-3}$, $5.9\cdot 10^{-3}$, and $6.1\cdot 10^{-3}$, respectively. The above results indicate that both eqs 2 and 3 can provide good predictions for the conductivities of the examined mixed solutions and

Table 5. Comparisons of Measured and Predicted Conductivities of the Ternary System $Ce(NO_3)_3$ (B) + $Nd(NO_3)_3$ (C) + H_2O (A) at Different Temperatures[a]

m_B	m_C	σ			$\Delta\sigma$	
		mS·cm^{-1}			mS·cm^{-1}	
mol·kg^{-1}	mol·kg^{-1}	exp	eq 2	eq 3	Δ_{eq} 2	Δ_{eq} 3
293.15 K						
0.2565	0.7673	86.45	87.14	87.15	0.69	0.70
0.5097	0.5165	86.14	86.46	86.47	0.32	0.33
0.7720	0.2568	85.30	85.76	85.77	0.46	0.47
0.5182	1.5501	73.35	73.89	73.91	0.54	0.56
1.0233	1.0207	73.03	73.38	73.41	0.35	0.38
1.5159	0.5042	72.61	72.87	72.90	0.26	0.29
0.7723	2.3246	45.75	46.08	46.08	0.33	0.33
1.5687	1.5396	44.78	45.07	45.06	0.29	0.28
2.3415	0.7779	43.90	44.10	44.09	0.20	0.19
1.0189	3.0651	25.78	25.65	25.64	−0.13	−0.14
2.0174	2.0272	25.91	26.05	26.03	0.14	0.12
3.0001	1.0057	26.51	26.40	26.39	−0.11	−0.12
				$\delta_\sigma^{eq\,i}$[b]	$5.5\cdot10^{-3}$	$5.6\cdot10^{-3}$
298.15 K						
0.2565	0.7673	95.30	96.06	96.07	0.76	0.77
0.5097	0.5165	94.95	95.52	95.52	0.57	0.57
0.7720	0.2568	94.56	94.95	94.96	0.39	0.40
0.5182	1.5501	81.72	82.23	82.26	0.51	0.54
1.0233	1.0207	81.45	81.79	81.84	0.34	0.39
1.5159	0.5042	80.95	81.37	81.40	0.42	0.45
0.7723	2.3246	51.79	52.22	52.22	0.43	0.43
1.5687	1.5396	50.87	51.12	51.11	0.25	0.24
2.3415	0.7779	49.70	50.07	50.06	0.37	0.36
1.0189	3.0651	29.95	29.74	29.74	−0.21	−0.21
2.0174	2.0272	30.28	30.18	30.18	−0.10	−0.10
3.0001	1.0057	30.74	30.59	30.59	−0.15	−0.15
				$\delta_\sigma^{eq\,i}$[b]	$5.8\cdot10^{-3}$	$5.9\cdot10^{-3}$
308.15 K						
0.2565	0.7673	113.76	114.63	114.63	0.87	0.87
0.5097	0.5165	113.37	113.88	113.89	0.51	0.52
0.7720	0.2568	112.48	113.10	113.12	0.62	0.64
0.5182	1.5501	98.69	99.44	99.47	0.75	0.78
1.0233	1.0207	98.39	98.85	98.89	0.46	0.50
1.5159	0.5042	97.63	98.27	98.30	0.64	0.67
0.7723	2.3246	64.70	65.24	65.23	0.54	0.53
1.5687	1.5396	63.67	63.92	63.92	0.25	0.25
2.3415	0.7779	62.25	62.67	62.66	0.42	0.41
1.0189	3.0651	38.89	38.74	38.74	−0.15	−0.15
2.0174	2.0272	38.99	39.26	39.25	0.27	0.26
3.0001	1.0057	39.96	39.73	39.73	−0.23	−0.23
				$\delta_\sigma^{eq\,i}$[b]	$6.0\cdot10^{-3}$	$6.1\cdot10^{-3}$

[a] Standard uncertainties u are $u(m_B) = \pm 0.00005$ mol·kg^{-1}, $u(m_C) = \pm 0.00005$ mol·kg^{-1}, $u(T) = \pm 0.05$ K, and the combined expanded uncertainty U_c is $U_c(\sigma) = \pm 0.5$ % (level of confidence = 0.95). [b] $\delta_\sigma^{eq\,i} = \sum_{j=1}^{N} (|\sigma_{j(eq\,i)} - \sigma_{j(exp)}|/\sigma_{j(exp)})/N$.

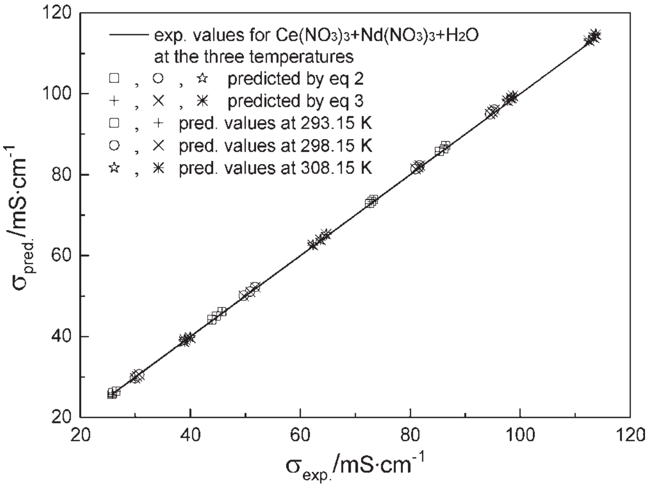

Figure 3. Comparisons of measured and predicted conductivities of the ternary system $Ce(NO_3)_3$ + $Nd(NO_3)_3$ + H_2O at different temperatures.

that the predictions of eq 2 are slightly better than those of eq 3. One of the advantages of the semi-ideal solution theory is that its simple equations are applicable to aqueous solutions of electrolyte mixtures and (electrolyte + nonelectrolyte) mixtures.[26] The advantage of the generalized Young's rule is that it does not require the osmotic coefficient data of the binary solutions. A limitation of the semi-ideal solution theory is that eq 2 needs the osmotic coefficients of the binary solutions. However, as can be seen from the present results and the previous results,[27,28] 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 or in the (283.15 to 343.15) K range, respectively. On the basis of these results, we are confident that the use of isopiestic data at 298.15 K can yield good predictions for the conductivities of mixed solutions in the (293.15 to 343.15) K range. 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. For systems in which isopiestic data are not available, a good activity coefficient model may be used to obtain the molalities of binary and ternary solutions with equal water activity.

The isopiestic results at 298.15 K have been reported[29] for the ternary system $Y(NO_3)_3$(B) + $Nd(NO_3)_3$(C) + H_2O and their binary subsystems. These results were used to calculate the values of z ($z = (m_B/m_B^o) + (m_C/m_C^o)$), see Table S1 of the Supporting Information). The thus-obtained relationship $(m_B/m_B^o) + (m_C/m_C^o) = z$ were used together with the reported osmotic coefficient data of the binary solutions[22,23] to determine the compositions ($m_{M_iX_i}^{(io)}$) of the binary solutions having the same water activity as that of the ternary solutions of given molalities $m_{M_iX_i}$ ($i = 1, 2, ..., n$). The values of $m_{M_iX_i}^{(io)}$ were used to calculate the values of $\sigma_{M_iX_i}^{(io)}$ and then to predict the conductivities for the mixed solutions. It is seen from Table S2 (Supporting Information) that the predictions agree well with the predictions based on eq 1, i.e., $(m_B/m_B^o) + (m_C/m_C^o) = 1$.

CONCLUSIONS

Conductivities were measured for 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 and then were used to verify the applicability of the generalized Young's rule and the semi-ideal solution theory for the conductivity of the mixed electrolyte solutions. The comparison results show that the two simple equations can yield good predictions for the conductivities of the ternary electrolyte solutions in terms of the properties of the binary solutions, but do not involve mixing parameters, avoiding much complexity in the calculation of conductivities 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.

ASSOCIATED CONTENT

Supporting Information. Calculated values of z for the ternary system $Y(NO_3)_3$ (B) + $Nd(NO_3)_3$ (C) + H_2O (A) (Table S1); comparisons of measured and predicted conductivities of the ternary system $Y(NO_3)_3$ (B) + $Nd(NO_3)_3$ (C) + H_2O (A) at 298.15 K (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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