J. Chem. Eng. Data **2009,** *54,* 739–744

Viscosity and Density of the System NaCl + $LaCl_3$ + H_2O and Its Binary Subsystems at Different Temperatures

Yan-Sheng Liu, Yu-Feng Hu,* Qing-Cheng Hao, Xian-Ming Zhang, Zhi-Chang Liu, and Ji-Guang Li

State Key Laboratory of Heavy Oil, China University of Petroleum, Beijing 102249, China

Densities and viscosities were measured at (293.15, 298.15, and 303.15) K for the ternary system NaCl + $LaCl_3$ + H_2O and its binary subsystems NaCl + H_2O and $LaCl_3$ + H_2O. The results were used to test the applicability of simple equations for the densities and viscosities of the multicomponent solutions. The predictions agree well with measured values, implying that the densities and viscosities of the examined electrolyte solutions can be related to those of their constituent binary solutions using the simple equations.

Introduction

The thermodynamic and transport properties of multicomponent 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 ternary and multicomponent electrolyte solutions, especially on aqueous solutions of (1:1 + 1:3) electrolyte mixtures. Therefore, one of the objectives of the theory of electrolyte solutions is to calculate various properties of multicomponent 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 for predicting the properties of multicomponent solutions.[1−8] Up to now, such simple equations have been established for thermodynamic properties, including activity coefficients of either solute in the multicomponent solutions, volumetric properties, thermal properties, and surface tension. (For example, see refs 1 to 8a.) To extend the simple equations for thermodynamic properties to transport properties (viscosity), Patwardhan and Kumar's equation[5] has also been used together with Eyring's absolute rate theory[9] to establish simple equations for the viscosity of the multicomponent solutions.[8b] These simple equations could be used to predict the thermodynamic properties and viscosities of multicomponent solutions from the properties of their binary subsystems. Their accuracy has been tested by systematic comparison with experimental data for the multicomponent nonelectrolyte solutions[10] and the multicomponent electrolyte solutions (including strong electrolyte mixtures with and without common ions and electrolyte mixtures containing transition metal chlorides). However, because the densities and viscosities of aqueous solutions of (1:1 + 1:3) electrolyte mixtures are not available in the literature to our knowledge, tests were limited to aqueous solutions of (1:1 + 1:1) and (1:1 + 1:2) electrolyte mixtures. Therefore, in this study the densities and viscosities were measured for the ternary system NaCl + $LaCl_3$ + H_2O and its binary subsystems NaCl + H_2O and $LaCl_3$ + H_2O at different temperatures, and the results were used to check the applicability of the above-mentioned equations.

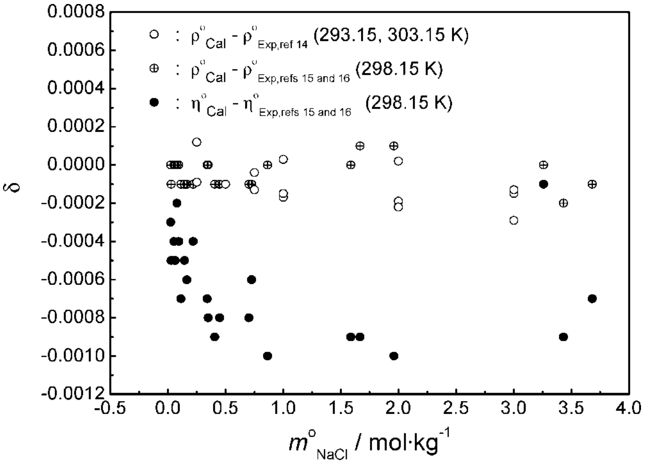

Figure 1. Variation of the δ value with the molality for the binary system NaCl + H_2O at different temperatures.

Experimental Section

Ultrapure NaCl was dried under vacuum over $CaCl_2$ for 7 days at 423 K immediately prior to use. Reagent grade $LaCl_3$ was dissolved into double-distilled deionized water and filtered twice. The molalities of $LaCl_3$ stock solutions were analyzed by EDTA and titration (of Cl^- with $AgNO_3$) methods.[3] The La^{3+} concentration was determined by EDTA titration with a precision of 0.05 % and an accuracy of 0.10 %. The Cl^- concentration was determined by the $AgNO_3$ titration with an accuracy of 0.10 % and a precision of 0.05 %.

The experimental procedures are similar to those used in our previous study[10] and are described briefly as follows. The NaCl solutions were prepared by mass using double-distilled deionized water and each of the solutes with a precision of $\pm 5 \cdot 10^{-5}$ g. All masses were corrected to vacuum. We made the $LaCl_3$ solutions by diluting a stock solution of $LaCl_3$ with its concentration determined above. We prepared the ternary solutions by mixing the binary solutions. All solutions were immediately prepared before use, and the uncertainty was $\pm 5 \cdot 10^{-5}$ mol·kg^{-1}. Densities

---

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

10.1021/je8004062 CCC: $40.75

Table 1. Parameters for the Binary System NaCl (B) + H_2O (A) at Different Temperatures

	$\rho_{293.15}$	$\rho_{298.15}$	$\rho_{303.15}$		$\eta_{293.15}$	$\eta_{298.15}$	$\eta_{303.15}$
A_1	−0.006498	−0.005560	−0.007959	B_1	0.065500	0.058124	−0.045780
A_2	0.070243	0.065506	0.074340	B_2	−0.238449	−0.076081	0.344863
A_3	−0.044528	−0.038104	−0.052031	B_3	0.754023	0.223297	−0.421932
A_4	0.028552	0.024052	0.034227	B_4	−0.842095	−0.183737	0.316916
A_5	−0.009572	−0.007989	−0.011539	B_5	0.500564	0.091252	−0.129447
A_6	0.001217	0.000994	0.001473	B_6	−0.149160	−0.021838	0.030662
				B_7	0.017762	0.002264	−0.002871
Δ_ρ^o	$2.8\cdot10^{-5}$	$2.2\cdot10^{-5}$	$3.6\cdot10^{-5}$	Δ_η^o	$2.0\cdot10^{-5}$	$1.1\cdot10^{-5}$	$6.3\cdot10^{-5}$

Table 2. Parameters for the Binary System $LaCl_3$ (B) + H_2O (A) at Different Temperatures

	$\rho_{293.15}$	$\rho_{298.15}$	$\rho_{303.15}$		$\eta_{293.15}$	$\eta_{298.15}$	$\eta_{303.15}$
A_1	−0.028208	−0.036953	−0.024536	B_1	1.588309	1.320733	1.230570
A_2	0.440941	0.484173	0.395950	B_2	−10.904906	−9.079454	−8.550617
A_3	−0.550460	−0.669862	−0.438805	B_3	33.621577	27.980370	26.741411
A_4	0.647714	0.810238	0.515060	B_4	−52.172624	−43.072104	−42.062402
A_5	−0.394368	−0.499348	−0.315189	B_5	46.730069	38.298960	38.249766
A_6	0.097124	0.123238	0.078556	B_6	−22.605239	−18.416178	−18.806568
				B_7	4.573367	3.708666	3.869389
Δ_ρ^o	$8.5\cdot10^{-6}$	$1.2\cdot10^{-5}$	$1.4\cdot10^{-5}$	Δ_η^o	$1.7\cdot10^{-5}$	$1.5\cdot10^{-5}$	$2.3\cdot10^{-5}$

Table 3. Densities and Viscosities of the Binary System NaCl (B) + H_2O (A) at Different Temperatures

m_B	$\rho_{293.15}$	$\rho_{298.15}$	$\rho_{303.15}$	$\eta_{293.15}$	$\eta_{298.15}$	$\eta_{303.15}$
$mol\cdot kg^{-1}$	$g\cdot cm^{-3}$	$g\cdot cm^{-3}$	$g\cdot cm^{-3}$	$mPa\cdot s$	$mPa\cdot s$	$mPa\cdot s$
0.2076	1.0063	1.0057	1.0040	1.0120	0.9082	0.8115
0.3959	1.0140	1.0132	1.0117	1.0312	0.9237	0.8306
0.5997	1.0220	1.0212	1.0196	1.0536	0.9408	0.8489
0.7817	1.0290	1.0281	1.0264	1.0726	0.9565	0.8638
1.0102	1.0376	1.0366	1.0348	1.0977	0.9769	0.8825
1.1987	1.0445	1.0434	1.0414	1.1168	0.9944	0.8980
1.5018	1.0554	1.0543	1.0523	1.1508	1.0239	0.9236
1.7945	1.0657	1.0645	1.0625	1.1836	1.0541	0.9496
2.0038	1.0731	1.0718	1.0697	1.2082	1.0769	0.9695
2.4085	1.0869	1.0855	1.0834	1.2560	1.1240	1.0108
2.9996	1.1065	1.1050	1.1027	1.3316	1.2005	1.0802
3.5952	1.1255	1.1238	1.1214	1.4120	1.2878	1.1618
4.1858	1.1435	1.1417	1.1392	1.4962	1.3855	1.2562
4.8125	1.1621	1.1600	1.1575	1.5918	1.5021	1.3726

Table 4. Densities and Viscosities of the Binary Systems $LaCl_3$ (C) + H_2O (A) at Different Temperatures

m_C	$\rho_{293.15}$	$\rho_{298.15}$	$\rho_{303.15}$	$\eta_{293.15}$	$\eta_{298.15}$	$\eta_{303.15}$
$mol\cdot kg^{-1}$	$g\cdot cm^{-3}$	$g\cdot cm^{-3}$	$g\cdot cm^{-3}$	$mPa\cdot s$	$mPa\cdot s$	$mPa\cdot s$
0.0996	1.0208	1.0194	1.0180	1.0678	0.9503	0.8517
0.1997	1.0437	1.0421	1.0404	1.1089	0.9881	0.8863
0.2997	1.0656	1.0638	1.0620	1.1762	1.0488	0.9414
0.3994	1.0869	1.0850	1.0832	1.2552	1.1198	1.0056
0.4984	1.1077	1.1058	1.1039	1.3405	1.1963	1.0748
0.6000	1.1289	1.1269	1.1250	1.4325	1.2787	1.1493
0.6981	1.1491	1.1472	1.1453	1.5244	1.3609	1.2236
0.7983	1.1696	1.1677	1.1658	1.6205	1.4468	1.3012
0.9256	1.1955	1.1937	1.1918	1.7450	1.5580	1.4016
1.2011	1.2511	1.2495	1.2478	2.0204	1.8039	1.6236

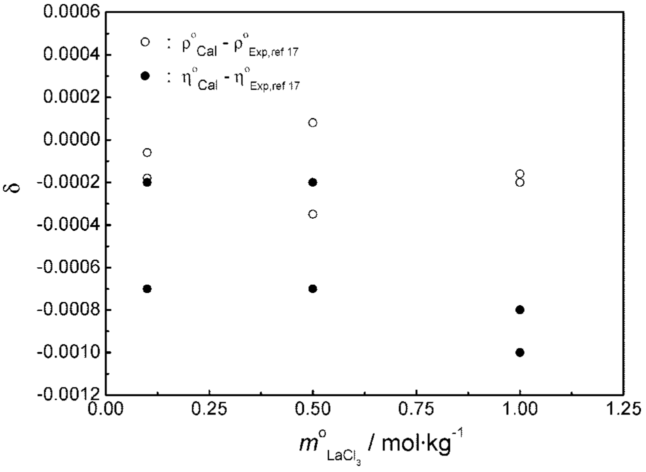

Figure 2. Variation of the δ value with the molality for the binary system $LaCl_3$ + H_2O at different temperatures.

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 by double-distilled water and dry air. The densities of water at different temperatures were obtained from the literature.[11] The densities of water and air at 298.15 K were taken as $0.99701\ g\cdot cm^{-3}$ and $1.18434\ kg\cdot m^{-3}$,[10] respectively. In all of the measured variables, the uncertainty in densities was $\pm\ 5\cdot10^{-5} g\cdot cm^{-3}$.

Viscosities were measured using a modified Cannon-Ubbelohde suspended level capillary viscometer. A thoroughly cleaned and perfectly dried viscometer filled with liquid was placed vertically in a glass-sided water thermostat. The temperature was maintained at (298.15 ± 0.01) K. After thermal equilibrium was attained, the efflux times of flow of the liquids were recorded with a digital stop watch with a precision of ± 0.01 s. Triplicate measurements were performed at each composition. At 298.15 K, the viscosity of water was $0.8903\ mPa\cdot s$,[11] and the uncertainty in viscosity was $\pm\ 2\cdot10^{-4} mPa\cdot s$. The viscosity of the solution is given by

$$\eta = \eta_o \frac{\rho\tau}{\rho_o\tau_o} \tag{1}$$

where η_o is the viscosity of water, ρ and ρ_o are the densities of the solution and water, respectively, and τ and τ_o are the flow times of the solution and water, respectively.

Predictive Equations for Density and Viscosity of Multicomponent 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 multicomponent solution, and those without the superscript o denote the corresponding quantities in the multicomponent solution.

The linear isopiestic relation[1−3,12] can be expressed as

$$\sum_i \frac{m_{\mathrm{M}_i\mathrm{X}_i}}{m^{(io)}_{\mathrm{M}_i\mathrm{X}_i}} = 1 \left(a_\mathrm{w} = \text{constant} \;\text{ and }\; 0 \le \frac{m_{\mathrm{M}_i\mathrm{X}_i}}{m^{(io)}_{\mathrm{M}_i\mathrm{X}_i}} \le 1 \right) \qquad (2)$$

where $m_{\mathrm{M}_i\mathrm{X}_i}$ and $m^{(io)}_{\mathrm{M}_i\mathrm{X}_i}$ are the molalities of $\mathrm{M}_i\mathrm{X}_i$ in multicomponent aqueous solution $\mathrm{M}_1\mathrm{X}_1 + ... + \mathrm{M}_i\mathrm{X}_i + \mathrm{H_2O}$ and its binary subsystems $\mathrm{M}_i\mathrm{X}_i + \mathrm{H_2O}$ ($i = 1, 2, ..., n$) 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[2,3]

$$\rho = \sum_i Y_{\mathrm{M}_i\mathrm{X}_i} \Big/ \sum_i \left(Y_{\mathrm{M}_i\mathrm{X}_i} / \rho^{(io)}_{\mathrm{M}_i\mathrm{X}_i} \right) \qquad (3)$$

with $Y_{\mathrm{M}_i\mathrm{X}_i} = m_{\mathrm{M}_i\mathrm{X}_i} / (m^{(io)}_{\mathrm{M}_i\mathrm{X}_i} + m_{\mathrm{M}_i\mathrm{X}_i} M_{\mathrm{M}_i\mathrm{X}_I})$, where m, ρ, and M denote molality, density, and molar mass. The density equation of Patwardhan and Kumar[6] is expressed as

$$\rho = \sum_i Y_{\mathrm{M}_i\mathrm{X}_i} \Big/ \sum_i \left(Y_{\mathrm{M}_i\mathrm{X}_i} / \rho^{\mathrm{o,I}}_{\mathrm{M}_i\mathrm{X}_i} \right) \qquad (4)$$

with $Y_{\mathrm{M}_i\mathrm{X}_i} = y_{\mathrm{M}_i\mathrm{X}_i} + m_{\mathrm{M}_i\mathrm{X}_i} M_{\mathrm{M}_i\mathrm{X}_i}$, where $y_{\mathrm{M}_i\mathrm{X}_i}$ is the ionic strength fraction and $\rho^{\mathrm{o,I}}_{\mathrm{M}_i\mathrm{X}_i}$ is the density of the binary solution having

Table 5. Comparisons of Measured and Predicted Densities of the Ternary Systems NaCl (B) + $LaCl_3$ (C) + H_2O (A) at Different Temperatures

m_B / $\mathrm{mol \cdot kg^{-1}}$	m_C / $\mathrm{mol \cdot kg^{-1}}$	$\rho/\mathrm{g \cdot cm^{-3}}$ exptl	$\rho/\mathrm{g \cdot cm^{-3}}$ eq 4	$\Delta\rho$ / $\mathrm{g \cdot cm^{-3}}$
		293.15 K		
0.0306	0.0945	1.0203	1.0209	0.0006
0.0681	0.0883	1.0207	1.0209	0.0002
0.1325	0.0776	1.0207	1.0211	0.0004
0.2706	0.0547	1.0215	1.0214	−0.0001
0.1312	0.1780	1.0429	1.0438	0.0009
0.2661	0.1554	1.0429	1.0439	0.0010
0.0869	0.2852	1.0643	1.0656	0.0013
0.1901	0.2679	1.0646	1.0656	0.0010
0.3898	0.2346	1.0651	1.0656	0.0005
0.7867	0.1683	1.0657	1.0657	0.0000
0.1212	0.3793	1.0857	1.0869	0.0012
0.2613	0.3560	1.0859	1.0869	0.0010
0.5230	0.3126	1.0859	1.0869	0.0010
1.0507	0.2251	1.0870	1.0869	−0.0001
0.1391	0.4753	1.1069	1.1077	0.0008
0.6485	0.3907	1.1063	1.1075	0.0012
1.2936	0.2835	1.1078	1.1072	−0.0006
0.1672	0.5721	1.1275	1.1287	0.0012
0.3804	0.5365	1.1280	1.1285	0.0005
0.7709	0.4713	1.1276	1.1281	0.0005
1.5503	0.3413	1.1277	1.1274	−0.0003
0.1891	0.6666	1.1482	1.1488	0.0006
0.4483	0.6233	1.1476	1.1485	0.0009
0.8962	0.5486	1.1469	1.1479	0.0010
1.8036	0.3973	1.1477	1.1466	−0.0011
0.2226	0.7612	1.1687	1.1692	0.0005
0.5080	0.7137	1.1674	1.1687	0.0013
1.0150	0.6292	1.1667	1.1678	0.0011
			$\Delta_\rho^{\mathrm{eq4}a}$	$6.8 \cdot 10^{-4}$
		298.15 K		
0.0306	0.0945	1.0193	1.0195	0.0002
0.0681	0.0883	1.0200	1.0196	−0.0004
0.1325	0.0776	1.0198	1.0198	0.0000
0.2706	0.0547	1.0207	1.0202	−0.0005
0.0586	0.1900	1.0414	1.0422	0.0008
0.1312	0.1779	1.0420	1.0423	0.0003
0.2661	0.1554	1.0421	1.0424	0.0003
0.0869	0.2852	1.0634	1.0639	0.0005
0.1901	0.2679	1.0637	1.0639	0.0002
0.3898	0.2346	1.0639	1.0640	0.0001
0.7867	0.1683	1.0645	1.0641	−0.0004
0.1212	0.3793	1.0841	1.0850	0.0009
0.2613	0.3560	1.0840	1.0850	0.0010
0.5230	0.3126	1.0847	1.0851	0.0004
1.0507	0.2251	1.0857	1.0852	−0.0005
0.1391	0.4753	1.1043	1.1056	0.0013
0.3331	0.4431	1.1051	1.1056	0.0005
1.2936	0.2835	1.1062	1.1054	−0.0008
0.1672	0.5721	1.1263	1.1268	0.0005
0.3804	0.5365	1.1265	1.1266	0.0001
0.7709	0.4713	1.1259	1.1262	0.0003
1.5503	0.3413	1.1261	1.1255	−0.0006
0.4483	0.6233	1.1458	1.1465	0.0007
0.8962	0.5486	1.1447	1.1458	0.0011
1.8036	0.3972	1.1460	1.1449	−0.0011
0.2226	0.7612	1.1660	1.1670	0.0010
0.5080	0.7137	1.1661	1.1668	0.0007
1.0150	0.6292	1.1647	1.1659	0.0012
			$\Delta_\rho^{\mathrm{eq4}a}$	$6.2 \cdot 10^{-4}$
		303.15 K		
0.0306	0.0945	1.0176	1.0181	0.0005
0.0681	0.0883	1.0174	1.0182	0.0008
0.1325	0.0776	1.0179	1.0184	0.0005
0.2706	0.0547	1.0180	1.0187	0.0007
0.0586	0.1900	1.0397	1.0405	0.0008
0.1312	0.1780	1.0399	1.0405	0.0006
0.2661	0.1554	1.0399	1.0407	0.0008
0.0869	0.2852	1.0613	1.0620	0.0007
0.1901	0.2680	1.0615	1.0621	0.0006
0.3898	0.2346	1.0612	1.0621	0.0009
0.7867	0.1683	1.0614	1.0622	0.0008
0.1212	0.3793	1.0826	1.0832	0.0006
0.2613	0.3560	1.0823	1.0832	0.0009
0.5230	0.3126	1.0824	1.0832	0.0008
1.0507	0.2251	1.0825	1.0832	0.0007
0.1391	0.4753	1.1033	1.1039	0.0006
0.3331	0.4431	1.1031	1.1038	0.0007
0.6485	0.3907	1.1028	1.1036	0.0008
1.2936	0.2835	1.1025	1.1034	0.0009
0.1672	0.5721	1.1242	1.1248	0.0006
0.3804	0.5365	1.1238	1.1246	0.0008
0.7709	0.4713	1.1233	1.1242	0.0009
1.5503	0.3413	1.1225	1.1234	0.0009
0.1891	0.6666	1.1445	1.1450	0.0005
0.4483	0.6233	1.1439	1.1446	0.0007
0.8962	0.5486	1.1431	1.1439	0.0008
1.8036	0.3972	1.1415	1.1426	0.0011
0.2226	0.7612	1.1648	1.1654	0.0006
0.5080	0.7137	1.1638	1.1648	0.0010
1.0150	0.6292	1.1627	1.1638	0.0011
			$\Delta_\rho^{\mathrm{eq4}a}$	$6.9 \cdot 10^{-4}$

[a] $\Delta_\rho^{\mathrm{eq\ 4}} = \sum_{i=1}^{N} (|\rho_{\mathrm{M}_i\mathrm{X}_i,(\mathrm{eq4})} - \rho_{\mathrm{M}_i\mathrm{X}_i,(\mathrm{Exptl})}| / \rho_{\mathrm{M}_i\mathrm{X}_i,(\mathrm{Exptl})})/N.$

Table 6. Comparisons of Measured and Predicted Viscosities of the Ternary Systems NaCl (B) + $LaCl_3$ (C) + H_2O (A) at Different Temperatures

m_B	m_C	η/mPa·s		$\Delta\eta$
mol·kg^{-1}	mol·kg^{-1}	exptl	eq 5	mPa·s
		293.15 K		
0.0306	0.0945	1.0610	1.0660	0.0050
0.0681	0.0883	1.0563	1.0642	0.0079
0.2706	0.0547	1.0585	1.0567	−0.0018
0.0586	0.1900	1.1095	1.1074	−0.0021
0.1312	0.1779	1.1096	1.1061	−0.0035
0.2661	0.1554	1.1119	1.1045	−0.0074
0.0869	0.2852	1.1784	1.1734	−0.0050
0.1901	0.2679	1.1808	1.1710	−0.0098
0.3898	0.2346	1.1822	1.1680	−0.0142
0.1212	0.3793	1.2561	1.2507	−0.0054
0.2613	0.3560	1.2597	1.2468	−0.0129
1.0507	0.2251	1.2515	1.2355	−0.0160
0.1391	0.4753	1.3419	1.3343	−0.0076
0.3331	0.4431	1.3435	1.3280	−0.0155
0.6485	0.3907	1.3380	1.3202	−0.0178
1.2936	0.2835	1.3236	1.3100	−0.0126
0.1672	0.5721	1.4245	1.4241	−0.0004
0.3804	0.5365	1.4228	1.4161	−0.0067
0.7709	0.4713	1.4176	1.4046	−0.0130
1.5503	0.3413	1.4056	1.3896	−0.0160
0.1891	0.6666	1.5125	1.5142	0.0017
0.4483	0.6233	1.5001	1.5037	0.0036
0.8962	0.5486	1.4911	1.4895	−0.0016
1.8036	0.3973	1.4778	1.4704	−0.0074
0.2226	0.7612	1.6097	1.6079	−0.0018
0.5080	0.7137	1.5890	1.5959	0.0069
1.0150	0.6292	1.5798	1.5791	−0.0007
			Δ_η^{eq5a}	$5.9\cdot10^{-3}$
		298.15 K		
0.0306	0.0945	0.9463	0.9489	0.0026
0.0681	0.0883	0.9436	0.9475	0.0039
0.1325	0.0776	0.9412	0.9454	0.0042
0.2706	0.0547	0.9408	0.9420	0.0012
0.0586	0.1900	0.9895	0.9867	−0.0028
0.1312	0.1779	0.9903	0.9854	−0.0049
0.2661	0.1554	0.9934	0.9839	−0.0095
0.0869	0.2852	1.0518	1.0462	−0.0056
0.1901	0.2679	1.0536	1.0441	−0.0095
0.3898	0.2346	1.0581	1.0412	−0.0169
0.1212	0.3793	1.1205	1.1159	−0.0046
0.2613	0.3560	1.1229	1.1127	−0.0102
0.5230	0.3126	1.1232	1.1083	−0.0149
1.0507	0.2251	1.1200	1.1035	−0.0165
0.1391	0.4753	1.1972	1.1913	−0.0059
0.3331	0.4431	1.1976	1.1866	−0.0110
0.6485	0.3907	1.1925	1.1808	−0.0117
1.2936	0.2835	1.1872	1.1743	−0.0129
0.1672	0.5721	1.2707	1.2725	0.0018
0.3804	0.5365	1.2677	1.2671	−0.0006
0.7709	0.4713	1.2640	1.2599	−0.0041
0.1891	0.6666	1.3483	1.3541	0.0058
0.4483	0.6233	1.3419	1.3480	0.0061
0.8962	0.5486	1.3293	1.3407	0.0114
1.8036	0.3973	1.3225	1.3342	0.0117
0.2226	0.7612	1.4355	1.4394	0.0039
0.5080	0.7137	1.4255	1.4337	0.0082
1.0150	0.6292	1.4118	1.4272	0.0154
			Δ_η^{eq5a}	$6.7\cdot10^{-3}$
		303.15 K		
0.0306	0.0945	0.8475	0.8507	0.0032
0.0681	0.0883	0.8440	0.8498	0.0058
0.1325	0.0776	0.8426	0.8486	0.0060
0.2706	0.0547	0.8444	0.8468	0.0024
0.0586	0.1900	0.8877	0.8853	−0.0024
0.1312	0.1779	0.8905	0.8846	−0.0059
0.2661	0.1554	0.8938	0.8839	−0.0099
0.0869	0.2852	0.9445	0.9392	−0.0053
0.1901	0.2679	0.9475	0.9375	−0.0100
0.1212	0.3793	1.0078	1.0022	−0.0056
0.2613	0.3560	1.0105	0.9994	−0.0111
0.5230	0.3126	1.0082	0.9956	−0.0126
1.0507	0.2251	1.0069	0.9917	−0.0152
0.1391	0.4753	1.0766	1.0704	−0.0062
0.3331	0.4431	1.0775	1.0662	−0.0113
0.6485	0.3907	1.0715	1.0612	−0.0103
1.2936	0.2835	1.0609	1.0557	−0.0052
0.1672	0.5721	1.1421	1.1439	0.0018
0.3804	0.5365	1.1399	1.1393	−0.0006
0.7709	0.4713	1.1366	1.1333	−0.0033
1.5503	0.3413	1.1282	1.1275	−0.0007
0.1891	0.6666	1.2127	1.2180	0.0053
0.4483	0.6233	1.2016	1.2131	0.0115
0.8962	0.5486	1.1945	1.2077	0.0132
1.8036	0.3973	1.1887	1.2041	0.0154
0.2226	0.7612	1.2919	1.2956	0.0037
0.5080	0.7137	1.2882	1.2917	0.0035
1.0150	0.6292	1.2681	1.2880	0.0099
			Δ_η^{eq5a}	$6.7\cdot10^{-3}$

[a] $\Delta_\eta^{eq\ 5} = \sum_{i=1}^{N} (|\eta_{M_iX_i,(eq5)} - \eta_{M_iX_i,(Exptl)}|/\eta_{M_iX_i,(Exptl)})/N$.

the same ionic strength fraction as that of the multicomponent solution.

The viscosity of a multicomponent electrolyte solution is related to those of its constituent binary solutions of equal ionic strength by[8b]

$$\ln \eta = \sum_{i=1}^{n} \frac{x_{M_iX_i}}{x^{o,I}_{M_iX_i}} \ln \eta^{o,I}_{M_iX_i} + \sum_{i=1}^{n} \frac{c_{M_iX_i}\nu_{M_iX_i}m_{M_iX_i}}{\nu_{M_iX_i}m_{M_iX_i} + 55.51} \ln y_{M_iX_i} \tag{5}$$

where $x^{o,I}_{M_iX_i}$ and $\eta^{o,I}_{M_iX_i}$ are the mole fraction and viscosity of M_iX_i in the binary solution $M_iX_i + H_2O$ ($i = 1, 2, ..., n$) having the same ionic strength as that of the multicomponent solution $M_1X_1 + ... + M_iX_i + H_2O$. $c_{M_iX_i}$ is the electrolyte specific parameter.

Comparisons with the Experimental Data

The measured densities and viscosities were used to test eqs 3, 4, and 5, and the test procedure is briefly summarized as follows:

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

$$\rho^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Calcd})} = \rho_{\mathrm{H_2O}}(T) + \sum_{l} A_l \left(m^{o}_{\mathrm{M}_i\mathrm{X}_i}\right)^{l/2} \qquad (6)$$

$$\eta^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Calcd})} = \eta_{\mathrm{H_2O}}(T) + \sum_{l} B_l \left(m^{o}_{\mathrm{M}_i\mathrm{X}_i}\right)^{l/2} \qquad (7)$$

where $\rho_{\mathrm{H_2O}}(T)$ and $\eta_{\mathrm{H_2O}}(T)$ are the properties of water at T. $\rho^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Calcd})}$, $\eta^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Calcd})}$, and $m^{o}_{\mathrm{M}_i\mathrm{X}_i}$denote the density, viscosity, and molality of the binary aqueous solution $\mathrm{M}_i\mathrm{X}_i + \mathrm{H_2O}$ ($i = 1, 2, ..., n$). The optimum fit was obtained by variation of l until the values of $\Delta^{o}_{\rho,\mathrm{M}_i\mathrm{X}_i} = \sum_{j=1}^{N} (|\rho^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Calcd})} - \rho^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Exptl})}|/\rho^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Exptl})})/N$ and $\Delta^{o}_{\eta,\mathrm{M}_i\mathrm{X}_i} = \sum_{j=1}^{N} (|\eta^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Calcd})} - \eta^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Exptl})}|/\eta^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Exptl})})/N$ are less than a few parts in 10^{-4}. The values of A_l, B_l, $\Delta^{o}_{\rho,\mathrm{M}_i\mathrm{X}_i}$, and $\Delta^{o}_{\eta,\mathrm{M}_i\mathrm{X}_i}$ obtained for the two binary solutions are shown in Table 1.

(2) Determine the compositions ($m^{(io)}_{\mathrm{M}_i\mathrm{X}_i}$) of the binary solutions having the same water activity as that of the multicomponent solution of given molalities $m_{\mathrm{M}_i\mathrm{X}_i}$ ($i = 1, 2, ..., n$) using the osmotic coefficients of $\mathrm{M}_i\mathrm{X}_i$ ($i = 1, 2, ..., n$)[13] and eq 2.

(3) Determine the compositions ($m^{o,\mathrm{I}}_{\mathrm{M}_i\mathrm{X}_i}$) of the binary solutions having the same ionic strength as that of the multicomponent solution of given molalities $m_{\mathrm{M}_i\mathrm{X}_i}$ ($i = 1, 2, ..., n$).

(4) Insert the values of $\rho^{(io)}_{\mathrm{M}_i\mathrm{X}_i}$, $\eta^{(io)}_{\mathrm{M}_i\mathrm{X}_i}$, $\rho^{o,\mathrm{I}}_{\mathrm{M}_i\mathrm{X}_i}$, and $\eta^{o,\mathrm{I}}_{\mathrm{M}_i\mathrm{X}_i}$ calculated from eqs 6 or 7 into eqs 3 and 4 or 5 to yield the predictions for the multicomponent solutions of given $m_{\mathrm{M}_i\mathrm{X}_i}$ ($i = 1, 2, ..., n$), which are then compared with the corresponding experimental data. ($c_{\mathrm{NaCl}} = 0.15$ and $c_{\mathrm{LaCl_3}} = 1.28$ were determined from the measured viscosities of $\mathrm{NaCl} + \mathrm{LaCl_3} + \mathrm{H_2O}$ at 293.15 K and then were used to predict the viscosities of this ternary solution at (298.15 and 303.15) K.)

In this Article, the average relative differences between the predicted and measured densities (Δ_ρ) and viscosities (Δ_η) over the entire experimental composition range of the multicomponent solution are defined by

$$\Delta_\rho = \sum_{i=1}^{N} \left|\Delta_{\rho,i}\right| / N \qquad (8)$$

$$\Delta_\eta = \sum_{i=1}^{N} \left|\Delta_{\eta,i}\right| / N \qquad (9)$$

with $\Delta_{\rho,i} = (\rho_{i,(\mathrm{Calcd})} - \rho_{i,(\mathrm{Exptl})})/\rho_{i,(\mathrm{Exptl})}$ and $\Delta_{\eta,i} = (\eta_{i,(\mathrm{Calcd})} - \eta_{i(\mathrm{Exptl})})/\eta_{i,(\mathrm{Exptl})}$, where N is the number of experimental data.

Results and Discussions

Table 2 shows the measured densities and viscosities of the binary solutions $\mathrm{NaCl} + \mathrm{H_2O}$ at different temperatures. Figure 1 shows the variations of the values of $\delta_{\rho,\mathrm{M}_i\mathrm{X}_i}$ ($= \rho^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Calcd})} - \rho^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Exptl})}$) and $\delta_{\eta,\mathrm{M}_i\mathrm{X}_i}$ ($= \eta^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Calcd})} - \eta^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Exptl})}$) with the molality in the binary solution $\mathrm{NaCl} + \mathrm{H_2O}$ at different temperatures, where $\rho^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Exptl})}$ and $\eta^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Exptl})}$ are the densities and viscosities reported in the literature[14−16] and $\rho^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Calcd})}$ and $\eta^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Calcd})}$ are those calculated from eqs 6 and 7 together with the parameters shown in Table 1. It is seen that the agreements are good. Table 3 shows the measured densities and viscosities of the binary solutions $\mathrm{LaCl_3} + \mathrm{H_2O}$ at different temperatures. Figure 2 shows the variations of the values of $\delta_{\rho,\mathrm{M}_i\mathrm{X}_i}$ ($= \rho^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Calcd})} - \rho^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Exptl})}$) and $\delta_{\eta,\mathrm{M}_i\mathrm{X}_i}$ ($= \eta^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Calcd})} - \eta^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Exptl})}$) with the molality in the binary solutions $\mathrm{LaCl_3} + \mathrm{H_2O}$ at different temperatures, where $\rho^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Exptl})}$ and $\eta^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Exptl})}$ are the densities and viscosities reported in the literature[17] and $\rho^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Calcd})}$ and $\eta^{o}_{\mathrm{M}_i\mathrm{X}_i(\mathrm{Calcd})}$ are those calculated from eqs 6 and 7 together with the parameters shown in Table 1. It is seen that the agreements are also good.

Table 5 compares the predicted and measured densities for the ternary solutions $\mathrm{NaCl} + \mathrm{LaCl_3} + \mathrm{H_2O}$ at different temperatures. The third to fifth columns show that the agreements are good; the $\Delta_\rho^{\mathrm{eq}\ 4}$ values at (293.15, 298.15, and 303.15) K are $6.8 \cdot 10^{-4}$, $6.2 \cdot 10^{-4}$, and $6.9 \cdot 10^{-4}$, respectively. The value of $\Delta_\rho^{\mathrm{eq}\ 3}$ at 298.15 K is $1.2 \cdot 10^{-3}$. Further comparisons using the reported densities[15,16,18,19] at 298.15 K show that the average relative difference ($\Delta_\rho^{\mathrm{eq}\ 3}/\Delta_\rho^{\mathrm{eq}\ 4}$) between the predicted and measured densities are $3.5 \cdot 10^{-4}/3.5 \cdot 10^{-4}$ for $\mathrm{NaCl} + \mathrm{KCl} + \mathrm{H_2O}$ ($I_{\max} = 4.4\ \mathrm{mol \cdot kg^{-1}}$), $2.2 \cdot 10^{-4}/2.2 \cdot 10^{-4}$ for $\mathrm{KCl} + \mathrm{CaCl_2} + \mathrm{H_2O}$ ($I_{\max} = 3.6\ \mathrm{mol \cdot kg^{-1}}$), $3.5 \cdot 10^{-4}/3.8 \cdot 10^{-4}$ for $\mathrm{HCl} + \mathrm{KCl} + \mathrm{NaCl} + \mathrm{H_2O}$ ($I_{\max} = 2.2\ \mathrm{mol \cdot kg^{-1}}$), and $3.6 \cdot 10^{-4}/5.9 \cdot 10^{-4}$ for $\mathrm{Na_2SO_4} + \mathrm{NaCl} + \mathrm{H_2O}$ ($I_{\max} = 1.9\ \mathrm{mol \cdot kg^{-1}}$), in which $I_{\max}$ is the maximum ionic strength.[1] The above results indicate that eqs 3 and 4 hold well for the multicomponent electrolyte solutions. Note that eq 3 also applies well to multicomponent nonelectrolyte solutions.[10]

The tests using the reported viscosities[15,16,18] show that the average relative differences ($\Delta_\eta^{\mathrm{eq5}}$) between the predicted and measured viscosities at 298.15 K are $1.0 \cdot 10^{-3}$ for $\mathrm{NaCl} + \mathrm{KCl} + \mathrm{H_2O}$ ($I_{\max} = 4.4\ \mathrm{mol \cdot kg^{-1}}$), $0.5 \cdot 10^{-3}$ for $\mathrm{HCl} + \mathrm{NaCl} + \mathrm{H_2O}$ ($I_{\max} = 4.0\ \mathrm{mol \cdot kg^{-1}}$), $1.6 \cdot 10^{-3}$ for $\mathrm{KCl} + \mathrm{CaCl_2} + \mathrm{H_2O}$ ($I_{\max} = 6.0\ \mathrm{mol \cdot kg^{-1}}$), and $4.8 \cdot 10^{-3}$ for $\mathrm{KBr} + \mathrm{NaCl} + \mathrm{H_2O}$ ($I_{\max} = 4.0\ \mathrm{mol \cdot kg^{-1}}$),[8] indicating that eq 5 holds well for these multicomponent electrolyte solutions. The average relative differences ($\Delta_\eta^{\mathrm{eq}\ 5}$) between the predicted and measured viscosities of the ternary solution $\mathrm{NaCl} + \mathrm{LaCl_3} + \mathrm{H_2O}$ at (273.15, 298.15, and 303.15) K are $5.9 \cdot 10^{-3}$, $6.7 \cdot 10^{-3}$, and $6.7 \cdot 10^{-3}$, respectively, implying that the agreements are also reasonably good.

Conclusions

Densities and viscosities were measured for the ternary system $\mathrm{NaCl} + \mathrm{LaCl_3} + \mathrm{H_2O}$ and its binary subsystems $\mathrm{NaCl} + \mathrm{H_2O}$ and $\mathrm{LaCl_3} + \mathrm{H_2O}$ at different temperatures. The results were used to test the applicability of simple equations for the density and viscosity of multicomponent solutions. The comparison results show that eqs 3, 4, and 5 can yield good predictions for the densities and viscosities of the ternary electrolyte solutions from the data of the binary solutions that do not involve multicomponent parameters, which indicates that these equations can make use of the information on the binary solutions, avoid much complexity in the calculation of multicomponent viscosities, and provide good predictions for the multicomponent solutions.

Literature Cited

(1) Hu, Y. F. A New Equation for Predicting the Density of Multicomponent Aqueous Solutions Conforming to the Linear Isopiestic Relation. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2380–2382.

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

(3) 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.

(4) Li, Z. B.; Li, Y. G.; Lu, J. F. Surface Tension Model for Concentrated Electrolyte Aqueous Solutions by the Pitzer Equation. *Ind. Eng. Chem. Res.* **1999**, *38*, 1133–1139.

(5) Patwardhan, V. S.; Kumar, A. A United 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 United 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. New Predictive Equations for the Specific and Apparent Molar Heat Capacities of Multicomponent Aqueous Solutions Conforming to the Linear Isopiestic Relation. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 47–52.

(8) (a) 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. (b) Hu, Y. F. Prediction of Viscosity of Mixed Electrolyte Solutions Based on the Eyring's Absolute Rate Theory and the Equations of Patwardhan and Kumar. *Chem. Eng. Sci.* **2004**, *59*, 2457–2464.

(9) Glasstone, S.; Laidler, K. J.; Eyring, H. *The Theory of Rate Process*; McGraw-Hill: New York, 1941.

(10) 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.

(11) Stokes, R. H.; Mills, R. *Viscosity of Electrolytes and Related Properties*; Pergamon: New York, 1965.

(12) Zdanovskii, A. B. *Trudy Solyanoi Lab. Akad. Nauk SSSR* **1936**, *No. 6*.

(13) Stokes, R. H.; Mills, R. *Viscosity of Electrolytes and Related Properties*; Pergamon: New York, 1965.

(14) Pitzer, K. S.; Christopher, J. Thermodynamic Properties of Aqueous Sodium Chloride Solution. *J. Phys. Chem. Ref. Data* **1984**, *13*, 1–102.

(15) Zhang, H. L.; Han, S. J. Viscosity and Density of Water + Sodium Chloride + Potassium Chloride Solutions at 298.15 K. *J. Chem. Eng. Data* **1996**, *41*, 516–520.

(16) Zhang, H. L.; Chen, G. H.; Han, S. J. Viscosity and Density of NaCl + $CaCl_2$ + H_2O and KCl + $CaCl_2$ + H_2O at 298.15 K. *J. Chem. Eng. Data* **1997**, *42*, 526–530.

(17) Toshlakl, I. Density, Viscosity, and Electrolytic Conductivity of Concentrated Aqueous Electrolyte Solutions at Several Temperatures. Alkaline-Earth Chlorides, $LaCI_3$, Na_2SO_4, $NaNO_3$, NaBr, KNO_3, KBr, and $Cd(NO_3)_2$. *J. Chem. Eng. Data* **1984**, *29*, 45–52.

(18) Ruby, C. E.; Kawai, J. The Densities, Equivalent Conductances and Relative Viscosities at 25 °C, of Solutions of Hydrochloride Acid, Potassium Chloride and Sodium Chloride, and of Their Binary and Ternary Mixtures of Constant Chloride-Ion-Constituent Content. *J. Am. Chem. Soc.* **1926**, *48*, 1119–1126.

(19) Stakhanova, M. S.; Epikhin, A. Yu.; Karapet′yants, M. K. *Russ. J. Phys. Chem.* **1963**, *37*, 1389–1396.

Received for review June 8, 2008. Accepted November 29, 2008. We thank the National Natural Science Foundation of China (40673043 and 20576073), CNPC Innovation Fund (04E7031), and the Program for New Century Excellent Talents in University of Ministry of Education of China (NCET-06-0088) for financial support.

JE8004062