

# Viscosities and Volumetric Properties of Binary and Ternary Mixtures of Tris(2-hydroxyethyl) Methylammonium Methylsulfate + Water + Ethanol at 298.15 K

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In this work, we report the experimental values of densities, viscosities, and refractive indices at 298.15 K and atmospheric pressure for the ternary and associated binary mixtures of tris(2-hydroxyethyl) methylammonium methylsulfate + water + ethanol. Excess molar volumes and viscosity logarithm variations have been calculated from the density and viscosity of these mixtures. The excess properties have been fitted with two polynomial models that produced acceptable correlations.

## Introduction

Ionic liquids (ILs) are currently defined as salts which melt below 100 °C. Because of their structure and ionic interactions, they present unique properties as such low volatility, nonflammable, low melting temperature, high heat capacity, high thermal conductivity, etc. ILs can be customized for a great range of applications through varying the structures of cations or anions. These specific properties make them good solvents for a wide range of organic, inorganic, and polymeric materials, replacing the volatile organic compounds of some industrial processes. Many other applications<sup>1–4</sup> are under study at the present time for these compounds such as catalysts, lubricants, electrolytes, heat transfer fluids, additives, antistatics, etc.

To be able to use ILs efficiently on all these kinds of applications, it is very important to characterize their fundamental thermodynamic properties and phase behavior. Experimental measurements on physical properties of mixtures with ionic liquids are critical to processes design, obtaining more information about the behavior and interactions of these substances, and checking thermodynamic models for correlation and prediction of their properties.

In this work, densities, viscosities, and refractive indices for the tris(2-hydroxyethyl) methylammonium methylsulfate + water + ethanol ternary system and for the corresponding binary systems are determined at 298.15 K and atmospheric pressure. The ionic liquid, the possible separation agent of ethanol and water, has been selected according to its miscibility with these components, its low melting point (below room temperature), and its low cost. Using the determined experimental properties, excess molar volumes  $V^E$  and the viscosity logarithm variations  $\Delta \ln(\eta/\eta^\circ)$ , in order to work with a more sensitive property due to the large values of viscosity changes of mixing, are calculated. Finally, the excess properties are correlated with composition data using two polynomial equations, the Redlich–Kister<sup>5</sup> and “z equation”.<sup>6</sup> A literature review has not shown volumetric or viscosity studies for these binary and ternary mixtures.

## Experimental Section

**Materials.** Tris(2-hydroxyethyl) methylammonium methylsulfate, [MTEOA][MeOSO<sub>3</sub>], ionic liquid used in the experimental part of this work was provided by Fluka, with a commercial mass fraction purity of 95 %. To remove possible impurities, the ionic liquid was immersed for 48 h in an oil bath at 80 °C attached to a high vacuum line, being that its original properties changed considerably. The presence of water and other impurities has an important effect on physical properties of ILs, as was established in the work of Seddon.<sup>7</sup> Finally, the water mass fraction of ionic liquid was measured using Karl Fisher titration and resulted in  $195 \cdot 10^{-6}$ . The ionic liquid was analyzed by <sup>1</sup>H NMR spectroscopy and IR, and no detectable impurities were found.

Ethanol was of the highest commercial purity, with a nominal mass fraction purity of 0.998, and was supplied by Merck. Water was purified using a Mili-Q Plus System. Information about the pure components, experimental densities, refractive indices, and viscosities at 298.15 K is shown in Table 1 and compared with those found in the literature,<sup>8</sup> when available.

**Procedure.** All weighing was carried out in a Mettler Toledo AT 261 balance with an uncertainty of  $\pm 10^{-4}$  g. The uncertainty in the mole fractions of the prepared mixtures was estimated to be  $\pm 0.0002$ . Water contents were measured using a Karl Fischer titration method in a Metrohm 737 KF coulometer. Densities were measured with viscosity correction in an Anton Paar DMA 5000 densimeter. The uncertainty in the measurement is  $\pm 10^{-5}$  g·cm<sup>-3</sup>. Refractive indices were measured in an ATAGO RX-5000 refractometer with a Hero Therm thermostat to maintain the temperature. The uncertainty in the refractive index measurement is  $\pm 4 \cdot 10^{-5}$ .

The kinematic viscosity was determined by the micro Ubbelohde viscometer technique. Three micro Ubbelohde viscometers (capillaries I, II, and III) were used in the experiments according to the different viscosity values of the mixtures. The capillaries are calibrated and credited by the company and verified by ourselves, measuring the viscosity of different pure liquids (acetone, alcohols, and glycerol). Results were found to be in good agreement with published values. Flow time

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**Table 1. Water Content  $\omega$ , Density  $\rho$ , Dynamic Viscosity  $\eta$ , and Refractive Index  $n_D$  of the Pure Components at 298.15 K under Atmospheric Pressure**

component	CAS	$10^6\omega$	$\rho/\text{g}\cdot\text{cm}^{-3}$		$\eta/\text{mPa}\cdot\text{s}$		$n_D$	
			exptl	lit.	exptl	lit.	exptl	lit.
[MTEOA][MeOSO <sub>3</sub> ]	29463-06-7	195	1.34413	not found	1236	not found	1.48489	not found
water	7732-18-5		0.99705	0.99705 <sup>8</sup>	0.897	0.890 <sup>8</sup>	1.33305	1.33250 <sup>8</sup>
ethanol	64-17-5	7	0.78512	0.78493 <sup>8</sup>	1.076	1.083 <sup>8</sup>	1.35937	1.35941 <sup>8</sup>

measurements are performed by a Lauda Processor Viscosity system PVS1 with a resolution of 0.01 s. The temperature of the viscometer was kept constant using a Lauda clear view thermostat D 20 KP with a through-flow cooler DLK 10. Viscosity measurements were repeated at least three times for each sample and were found to be repeatable to within 0.03 s for times less than 100 s and  $\pm 0.5$  s for longer times. Kinematic viscosity of solution  $\nu$  is given by

$$\nu = K(t - y) \quad (1)$$

where  $\nu$  is the kinematic viscosity;  $t$  is the flow time;  $K$  is the capillary constant provided by the manufacturer; and  $y$  is the kinetic energy correction used if necessary. Dynamic viscosities are calculated from kinematic viscosities and densities. The uncertainty for the dynamic viscosity determination is estimated to be  $\pm 0.5$  %.

Temperatures of the densimeter, refractometer, and viscometer were measured with uncertainties of ( $\pm 0.01$ ,  $\pm 0.02$ , and  $\pm 0.005$ ) K, respectively.

## Results

Table 1 shows that the values of physical properties for ethanol and water pure components are in agreement with those reported in the literature. No comparable data were found in the literature for the [MTEOA][MeOSO<sub>3</sub>] ionic liquid.

The experimental values obtained for densities  $\rho$ , dynamic viscosities  $\eta$ , and refractive indices  $n_D$  of the binary and ternary mixtures of [MTEOA][MeOSO<sub>3</sub>] + water + ethanol at 298.15 K are listed in Table 2. From these data, excess molar volumes  $V^E$  and the viscosity logarithm variations  $\Delta\ln(\eta/\eta^\circ)$  are calculated as a function of mole fraction, using the following expressions

$$V^E = V_M - \sum_i x_i V_i \quad (2)$$

$$\Delta\ln(\eta/\eta^\circ) = \ln(\eta/\eta^\circ) - \sum_i x_i \ln(\eta_i/\eta_i^\circ) \quad (3)$$

where  $V_M$  is the molar volume;  $\eta$  is the dynamic viscosity of the mixture; and  $\eta^\circ = 1$  mPa·s.  $V_i$  and  $\eta_i$  are the molar volume and the viscosity for the component  $i$ , respectively. The values of these calculated properties are also shown in Table 2.

Figure 1 shows the excess properties for the two binary systems: [MTEOA][MeOSO<sub>3</sub>] + ethanol, Figure 1(a), and [MTEOA][MeOSO<sub>3</sub>] + water, Figure 1(b). The experimental values obtained for  $V^E$  and  $\Delta\ln(\eta/\eta^\circ)$  for the water + ethanol binary system were in good agreement with other literature data.<sup>9</sup> For the ternary system, Figures 2, 3, and 4 show density, refractive index, and dynamic viscosity isolines, respectively, and Figure 5 shows excess molar volume isolines.

## Correlation

It is well-known that working with ionic liquid solutions presents some difficulties because of certain characteristics of these components. This is the case for the determination of property changes of mixing. It is usual to find in bibliography

dispersed data due to IL purity or miscibility problems. It is very important to have a suitable model to check these properties and to estimate them when experimental values are not available. In this work, two different correlations have been performed with the  $V^E$  and  $\Delta\ln(\eta/\eta^\circ)$  calculated data: the Redlich–Kister<sup>5</sup> and  $z$  equation.<sup>6</sup> The general expressions of these equations for binary systems are, respectively

$$Y_{ij}^{\text{RK}} = x_i x_j \sum_0^n A_n (x_i - x_j)^n \quad (4)$$

$$Y_{ij}^z = z_i z_j \sum_0^n B_n z_i^n \quad (5)$$

where  $Y$  represents the property changes of mixing,  $V^E$  or  $\Delta\ln(\eta/\eta^\circ)$  in this work;  $i$  and  $j$  are the components;  $A_n$  and  $B_n$  are the polynomial coefficients and  $n$  is the grade of the polynomial;  $x$  is the molar fraction; and  $z$  is the active fraction.

For binary systems of components 1 and 2, eqs 4 and 5 become, respectively

$$Y_{12}^{\text{RK}} = x(1 - x)(A_0 + A_1(2x - 1) + A_2(2x - 1)^2 + \dots) \quad (6)$$

$$Y_{12}^z = z(1 - z)(B_0 + B_1z + B_2z^2 + \dots) \quad (7)$$

where  $z = x/(x + k(1 - x))$  is the active fraction of the compound in the binary mixture.

For ternary systems the Redlich–Kister and  $z$  equation are, respectively:

$$Y_{123}^{\text{RK}} = Y_{12} + Y_{23} + Y_{13} + x_1 x_2 x_3 \{A + B(x_1 - x_2) + C(x_2 - x_3) + D(x_1 - x_3) + E(x_1 - x_2)^2 + F(x_2 - x_3)^2 + G(x_1 - x_3)^2 + \dots\} \quad (8)$$

$$Y_{123}^z = Y_{12} + Y_{23} + Y_{13} + z_1 z_2 z_3 (C_0 + C_1 z_1 + C_2 z_2 + \dots) \quad (9)$$

where

$$z_1 = \frac{x_1}{x_1 + k_{21}x_2 + k_{31}x_3}; \quad z_2 = \frac{x_2 k_{21}}{x_1 + k_{21}x_2 + k_{31}x_3};$$

$$z_3 = \frac{x_3 k_{31}}{x_1 + k_{21}x_2 + k_{31}x_3}$$

In the last two equations, the  $Y_{ij}$  terms are the corresponding correlations for binary systems involved in the ternary, according to eqs 6 and 7.

In the case of excess molar volume, the  $z$  equation has been developed in a previous work<sup>6</sup> through theoretical foundation. The parameter  $k$  is identified with the quotient of molar volumes of the pure substances,  $k_{ij} = V_{M_i}^0/V_{M_j}^0$ . As the viscosity logarithm

**Table 2. Physical and Excess Properties for the Mixture [MTEOA][MeOSO<sub>3</sub>] (1) + Water (2) + Ethanol (3) at 298.15 K under Atmospheric Pressure**

$x_1$	$x_2$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$n_D$	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\Delta \ln(\eta/\eta^0)$
0.7530	0.1124	1.31685	480.2	1.47880	-0.490	0.816
0.7090	0.1642	1.31501	413.4	1.47809	-0.500	0.985
0.6702	0.2100	1.31328	371.5	1.47704	-0.518	1.160
0.5789	0.3175	1.30843	234.3	1.47504	-0.560	1.362
0.5015	0.4088	1.30291	161.3	1.47232	-0.576	1.551
0.4078	0.5193	1.29373	94.11	1.46736	-0.580	1.692
0.2580	0.6959	1.26775	32.00	1.45477	-0.532	1.701
0.1627	0.8081	1.23350	12.53	1.43874	-0.431	1.455
0.0803	0.9053	1.17125	4.199	1.41007	-0.283	0.960
0.0400	0.9529	1.11016	2.096	1.38250	-0.152	0.559
0.6164	0.1078	1.28615	251.3	1.47296	-1.052	1.130
0.5506	0.2030	1.28278	188.9	1.47091	-1.033	1.325
0.4806	0.3043	1.27823	134.7	1.46847	-1.003	1.498
0.4007	0.4199	1.27113	86.95	1.46487	-0.945	1.645
0.3373	0.5118	1.26381	59.16	1.46074	-0.916	1.724
0.2909	0.5790	1.25691	41.83	1.45521	-0.896	1.716
0.2047	0.7037	1.23668	20.43	1.44641	-0.784	1.630
0.1345	0.8054	1.20571	9.752	1.43142	-0.588	1.403
0.0665	0.9037	1.14685	3.654	1.40282	-0.340	0.918
0.0340	0.9508	1.09502	2.005	1.37802	-0.207	0.556
0.4869	0.1100	1.24775	122.8	1.46471	-1.465	1.326
0.4378	0.1998	1.24478	96.36	1.46278	-1.414	1.446
0.3753	0.3140	1.23994	70.39	1.45992	-1.339	1.593
0.3207	0.4139	1.23427	50.07	1.45663	-1.260	1.656
0.2721	0.5027	1.22749	36.19	1.45274	-1.173	1.690
0.2148	0.6073	1.21660	23.07	1.44684	-1.069	1.662
0.1628	0.7025	1.20104	14.20	1.43775	-0.922	1.561
0.1061	0.8061	1.17178	7.224	1.42210	-0.677	1.304
0.0545	0.9004	1.12238	3.245	1.39600	-0.407	0.884
0.0274	0.9499	1.07604	1.870	1.37214	-0.222	0.532
0.3622	0.1012	1.19167	52.72	1.45272	-1.549	1.358
0.3173	0.2125	1.18885	42.59	1.45114	-1.498	1.481
0.2711	0.3273	1.18501	31.69	1.44763	-1.435	1.532
0.2303	0.4284	1.18030	24.28	1.44363	-1.357	1.571
0.1960	0.5137	1.17506	18.95	1.43994	-1.284	1.581
0.1601	0.6028	1.16721	14.07	1.43423	-1.174	1.553
0.1144	0.7160	1.15106	8.655	1.42353	-0.962	1.409
0.0784	0.8056	1.13036	5.410	1.41028	-0.762	1.210
0.0384	0.9046	1.08721	2.687	1.38445	-0.424	0.809
0.0185	0.9541	1.04948	1.646	1.36260	-0.203	0.469
0.1775	0.1042	1.06098	11.83	1.42317	-1.372	1.166
0.1578	0.2037	1.06187	10.89	1.42127	-1.401	1.240
0.1357	0.3151	1.06269	9.374	1.41909	-1.409	1.266
0.1183	0.4028	1.06336	8.428	1.41691	-1.408	1.298
0.0974	0.5081	1.06310	7.158	1.41295	-1.346	1.301
0.0771	0.6108	1.06169	5.957	1.40779	-1.241	1.279
0.0604	0.6951	1.05884	4.907	1.40102	-1.108	1.218
0.0385	0.8054	1.05105	3.530	1.38821	-0.863	1.063
0.0193	0.9025	1.03357	2.221	1.36833	-0.490	0.753
0.0096	0.9515	1.01773	1.522	1.35307	-0.240	0.452
0.0000	0.0480	0.79106	1.158	1.36013	-0.194	0.082
0.0000	0.1116	0.79908	1.261	1.36100	-0.411	0.179
0.0000	0.1599	0.80532	1.326	1.36150	-0.549	0.238
0.0000	0.1761	0.80744	1.360	1.36168	-0.589	0.266
0.0000	0.2668	0.82006	1.496	1.36247	-0.793	0.378
0.0000	0.3010	0.82506	1.556	1.36266	-0.852	0.424
0.0000	0.3994	0.84069	1.726	1.36295	-0.987	0.545
0.0000	0.4970	0.85826	1.932	1.36280	-1.063	0.676
0.0000	0.6122	0.88242	2.161	1.36176	-1.073	0.809
0.0000	0.7116	0.90785	2.385	1.35974	-1.025	0.926
0.0000	0.7774	0.92661	2.353	1.35727	-0.927	0.924
0.0000	0.8145	0.93762	2.366	1.35540	-0.837	0.936
0.0000	0.8529	0.94942	2.193	1.35243	-0.720	0.867
0.0000	0.8967	0.96095	1.920	1.34783	-0.500	0.742
0.0000	0.9481	0.97677	1.432	1.34063	-0.242	0.458
0.0478	0.9522	1.12913	2.341	1.38887	-0.150	0.614
0.0967	0.9033	1.19506	5.054	1.41769	-0.233	1.030
0.1939	0.8061	1.25848	16.79	1.44581	-0.323	1.528
0.2421	0.7579	1.27598	27.00	1.45390	-0.346	1.655
0.2894	0.7106	1.28849	41.22	1.45949	-0.344	1.736
0.3872	0.6128	1.30602	86.07	1.46758	-0.305	1.765
0.4858	0.5142	1.31749	159.5	1.47335	-0.248	1.670
0.6064	0.3936	1.32714	290.1	1.47587	-0.178	1.396

Table 2. Continued

$x_1$	$x_2$	$\rho$ $\text{g}\cdot\text{cm}^{-3}$	$\eta$ $\text{mPa}\cdot\text{s}$	$n_D$	$V^E$ $\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\ln(\eta/\eta^\circ)$
0.6698	0.3302	1.33096	390.7	1.47878	-0.140	1.235
0.7822	0.2178	1.33636	569.0	1.48130	-0.067	0.798
0.8670	0.1330	1.33964	756.2	1.48270	-0.019	0.470
0.9398	0.0602	1.34207	960.7	1.48341	0.015	0.183
0.0482	0.0000	0.87674	2.260	1.38180	-0.572	0.402
0.0981	0.0000	0.95117	4.523	1.39899	-0.939	0.745
0.1509	0.0000	1.01410	8.351	1.41373	-1.190	0.986
0.1994	0.0000	1.06107	13.32	1.42476	-1.325	1.111
0.2420	0.0000	1.09716	19.62	1.43322	-1.494	1.198
0.2922	0.0000	1.13275	29.16	1.44083	-1.578	1.241
0.3882	0.0000	1.18780	58.72	1.45307	-1.707	1.264
0.4841	0.0000	1.22934	110.8	1.46222	-1.678	1.223
0.5923	0.0000	1.26446	204.3	1.46950	-1.426	1.073
0.6288	0.0000	1.27393	247.6	1.47153	-1.262	1.008
0.6881	0.0000	1.28867	333.6	1.47511	-1.086	0.888
0.7379	0.0000	1.29919	430.4	1.47666	-0.859	0.792
0.7878	0.0000	1.30946	518.1	1.47867	-0.713	0.626
0.8379	0.0000	1.31878	657.1	1.48018	-0.550	0.511
0.8738	0.0000	1.32439	775.7	1.48134	-0.346	0.423
0.9203	0.0000	1.33187	902.1	1.48278	-0.184	0.247

variations  $\Delta\ln(\eta/\eta^\circ)$  do not represent an excess property, the  $z$  equation becomes empirical, and  $k$  is just one more correlation parameter in the data fitting process. This method of correlation can be used also for excess molar volumes. In this way, the correlation model fits better the experimental data (one more parameter is added), but the correlation parameters have no physical significance.

The Redlich–Kister coefficients for the binary and ternary systems and the standard deviations obtained in the correlations are listed in Tables 3 and 5, respectively. The  $z$  equation coefficients obtained for the binary and ternary systems and the standard deviations are listed in Tables 4 and 6, respectively. All these fitting coefficients were obtained by least-squares regression.

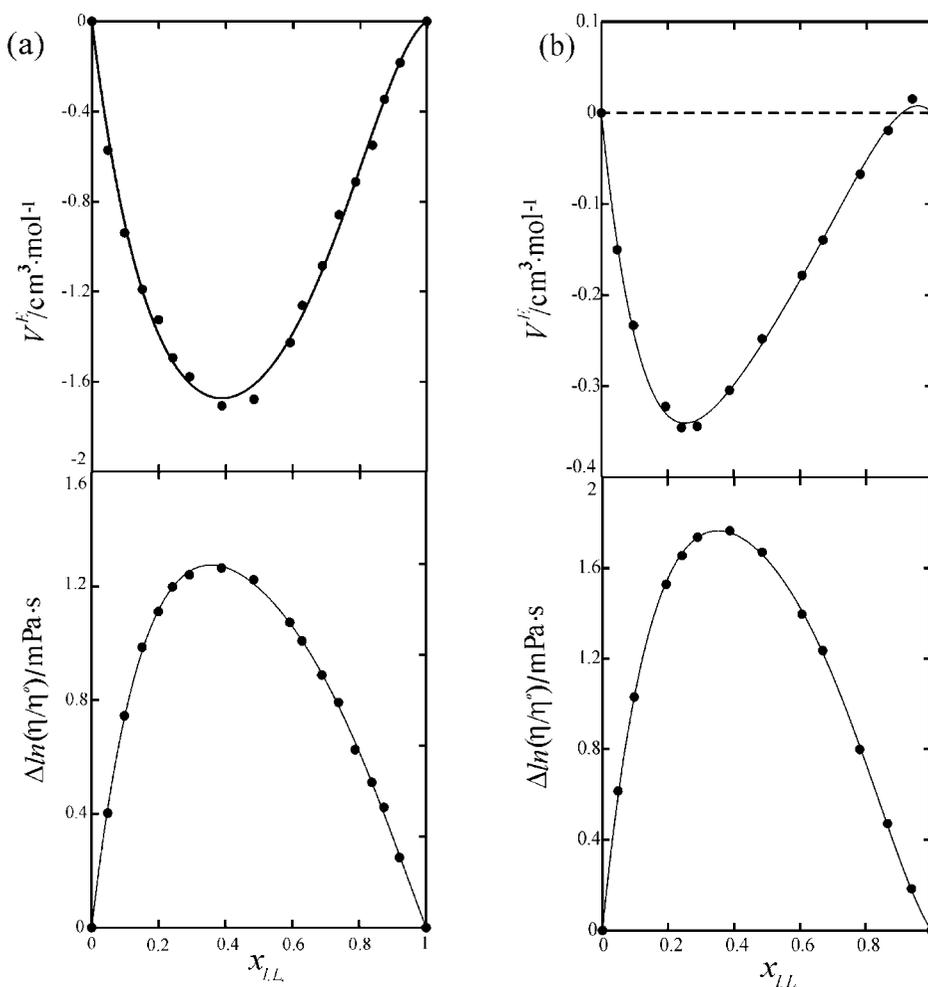
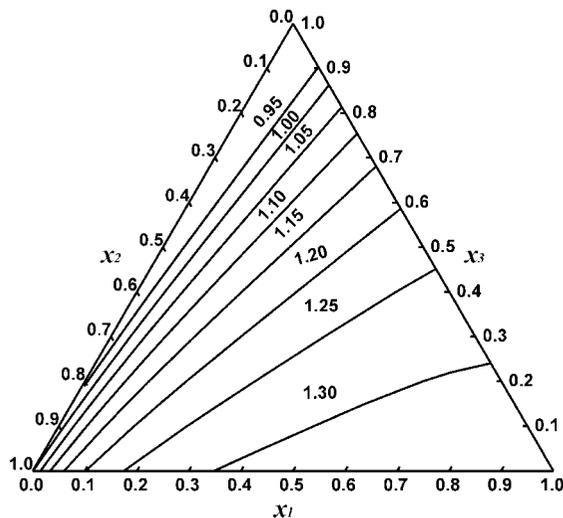
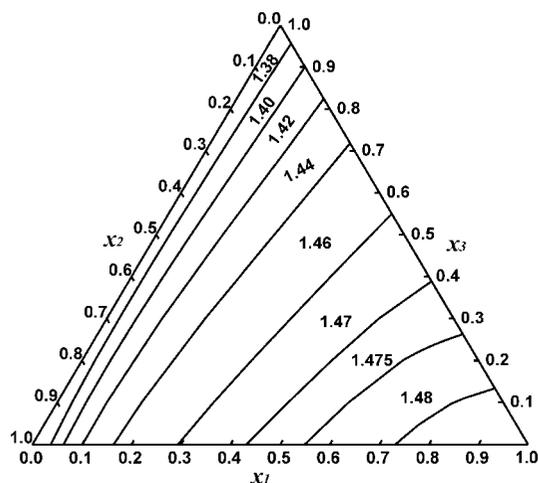


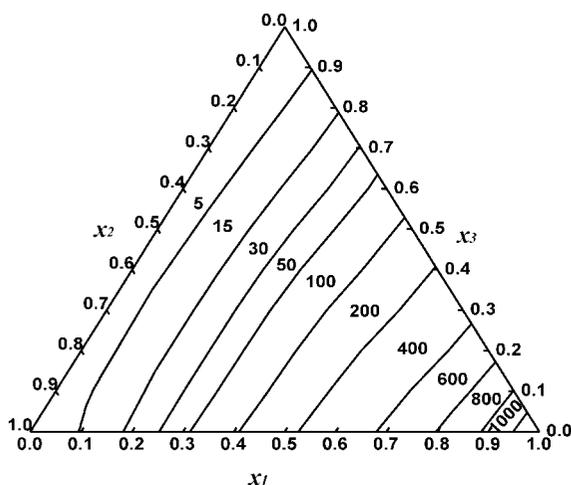
Figure 1. Excess properties for binary systems at 298.15 K under atmospheric pressure: (a) [MTEOA][MeOSO<sub>3</sub>] + ethanol and (b) [MTEOA][MeOSO<sub>3</sub>] + water. ●, Experimental values; —, Redlich–Kister correlation.



**Figure 2.** Density  $\rho/\text{g}\cdot\text{cm}^{-3}$  isolines for tris(2-hydroxyethyl) methylammonium methylsulfate (1) + water (2) + ethanol (3) at 298.15 K under atmospheric pressure.



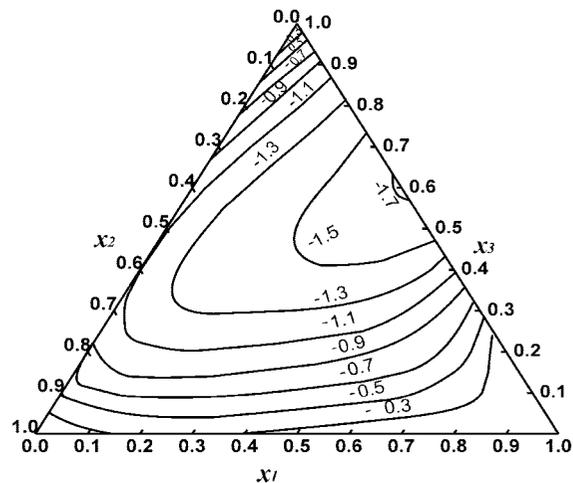
**Figure 3.** Refractive index  $n_D$  isolines for tris(2-hydroxyethyl) methylammonium methylsulfate (1) + water (2) + ethanol (3) at 298.15 K under atmospheric pressure.



**Figure 4.** Dynamic viscosity  $\eta/\text{mPa}\cdot\text{s}$  isolines for tris(2-hydroxyethyl) methylammonium methylsulfate (1) + water (2) + ethanol (3) at 298.15 K under atmospheric pressure.

## Conclusions

The density, refractive index, and viscosity data for the binary and ternary mixtures of tris(2-hydroxyethyl) methylammonium



**Figure 5.** Excess molar volume  $V^E/\text{cm}^3\cdot\text{mol}^{-1}$  isolines for tris(2-hydroxyethyl) methylammonium methylsulfate (1) + water (2) + ethanol (3) at 298.15 K under atmospheric pressure.

**Table 3.** Coefficients and Standard Deviations ( $\sigma$ ) Obtained Using the Redlich–Kister Polynomial, Equation 6, to Correlate  $V^E$  and  $\Delta\ln(\eta/\eta^\circ)$  for Binary Systems

property	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$\sigma$
[MTEOA][MeOSO <sub>3</sub> ] + Ethanol						
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-6.539	2.932	2.420	2.496	-4.444	0.028
$\Delta\ln(\eta/\eta^\circ)$	4.773	-2.107	1.800	-1.356		0.012
[MTEOA][MeOSO <sub>3</sub> ] + Water						
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-0.981	1.162	-0.616	0.813		0.005
$\Delta\ln(\eta/\eta^\circ)$	6.548	-3.247	1.761	-2.804		0.011
Water + Ethanol						
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	-4.298	-1.066	-1.073			0.020
$\Delta\ln(\eta/\eta^\circ)$	2.652	2.552	3.407	2.155		0.010

**Table 4.** Coefficients and Standard Deviations  $\sigma$  Obtained Using the  $z$  Equation, Equation 7, to Correlate  $V^E$  and  $\Delta\ln(\eta/\eta^\circ)$  for Binary Systems

property	$k$	$B_0$	$B_1$	$B_2$	$B_3$	$\sigma$
[MTEOA][MeOSO <sub>3</sub> ] + Ethanol						
$aV^E/\text{cm}^3\cdot\text{mol}^{-1}$	0.286	-6.898	19.833	-45.827	21.308	0.048
$bV^E/\text{cm}^3\cdot\text{mol}^{-1}$	0.560	-9.081	21.040	-49.834	34.082	0.022
$\Delta\ln(\eta/\eta^\circ)$	0.605	6.260	-4.060	3.541		0.013
[MTEOA][MeOSO <sub>3</sub> ] + Water						
$aV^E/\text{cm}^3\cdot\text{mol}^{-1}$	0.088	-1.0491	2.121	-1.618	-3.443	0.016
$bV^E/\text{cm}^3\cdot\text{mol}^{-1}$	1.190	-4.066	12.697	-17.062	8.947	0.005
$\Delta\ln(\eta/\eta^\circ)$	0.835	12.466	-22.504	31.763	-18.466	0.008
Water + Ethanol						
$aV^E/\text{cm}^3\cdot\text{mol}^{-1}$	3.247	-11.926	36.813	-57.632	33.589	0.021
$bV^E/\text{cm}^3\cdot\text{mol}^{-1}$	0.851	-3.917	2.317	-5.711		0.020
$\Delta\ln(\eta/\eta^\circ)$	1.537	2.667	-2.460	7.209		0.007

<sup>a</sup>  $k$  parameter is calculated as the quotient of molar volumes. <sup>b</sup>  $k$  is just one more parameter in the data fitting process.

methylsulfate + water + ethanol at 298.15 K under atmospheric pressure were determined. From these data, excess molar volumes and viscosity logarithm variations were calculated and correlated for all the systems.

For the two binary systems with [MTEOA] [MeOSO<sub>3</sub>], the excess molar volume is negative over the whole composition range except for mixtures with water at high mole fractions of ionic liquid. The system with water leads to a minimum around  $-0.35\text{ cm}^3\cdot\text{mol}^{-1}$ , and the system with ethanol leads to a minimum around  $-1.7\text{ cm}^3\cdot\text{mol}^{-1}$ .

Due to the large values of viscosity changes of mixing, viscosity logarithm variations  $\Delta\ln(\eta/\eta^\circ)$  were calculated to work with a more sensitive property. This calculated property is

**Table 5. Polynomial Coefficients and Standard Deviations  $\sigma$  Obtained Using the Redlich–Kister Polynomial, Equation 8, to Correlate  $V^E$  and  $\Delta \ln(\eta/\eta^0)$  for the [MTEOA][MeOSO<sub>3</sub>] (1) + Water (2) + Ethanol (3) Ternary System**

property	A	B	C	D	E	F	G	$\sigma$
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-1.462	3.592	-0.838	1.754	-5.383	7.286	-2.541	0.025
$\Delta \ln(\eta/\eta^0)$	1.469	0.063	-4.706	-5.644	-6.427	-20.112	13.003	0.019

**Table 6. Polynomial Coefficients and Standard Deviations ( $\sigma$ ) Obtained Using the  $z$  Equation, Equation 9, to Correlate  $V^E$  and  $\Delta \ln(\eta/\eta^0)$  for the [MTEOA][MeOSO<sub>3</sub>] (1) + Water (2) + Ethanol (3) Ternary System**

property	$C_0$	$C_1$	$C_2$	$k_{21}$	$k_{31}$	$\sigma$
${}^a V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-0.570	9.709	2.907	0.088	0.286	0.038
${}^b V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-1.920	16.616	-0.692	1.102	1.127	0.028
$\Delta \ln(\eta/\eta^0)$	-4.327	8.827	4.511	0.330	0.517	0.023

<sup>a</sup>  $k$  parameters are calculated as the quotient of molar volumes. <sup>b</sup>  $k$  is just one more parameter in the data fitting process.

positive with maxima around 1.8 for the system with water and 1.3 for the system with ethanol.

The ternary system [MTEOA][MeOSO<sub>3</sub>] + water + ethanol exhibits relatively large and negative excess molar volumes for the entire range of homogeneous mixtures. It reaches a minimum around  $-1.7 \text{ cm}^3 \cdot \text{mol}^{-1}$ , which corresponds to the binary system [MTEOA][MeOSO<sub>3</sub>] + ethanol. Viscosity logarithm variations for the ternary system are positive with a maximum corresponding to the binary system [MTEOA][MeOSO<sub>3</sub>] + water.

The Redlich–Kister and  $z$  equation were successfully applied to the correlation of excess properties of binary and ternary systems. When the same number of parameters are employed, both equations produce similar correlations with almost identical representation of data. Nonetheless, when parameter  $k$  in the  $z$  equation was fixed, the standard deviation of some correlations increased slightly, as was expected. This is especially observed on systems where active and molar fractions are not similar

due to volumetric differences of the components, which is the case of mixtures with ionic liquids.

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