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Physical Properties of Binary Mixtures of the Ionic Liquid 1-Ethyl-3-methylimidazolium Ethyl Sulfate with Several Alcohols at T = (298.15, 313.15, and 328.15) K and Atmospheric Pressure

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In this contribution, dynamic viscosities, densities, and speeds of sound of 1-ethyl-3-methylimidazolium ethyl sulfate (EMISE) with methanol, 1-propanol, and 2-propanol at T = (298.15, 313.15, and 328.15) K and refractive indices at T = 298.15 K and at atmospheric pressure have been measured over the whole composition range. Excess molar volumes, excess molar isentropic compressions, and viscosity deviations for the binary systems from T = 298.15 K to T = 328.15 K and refractive deviations at 298.15 K have been calculated and were satisfactorily fitted to a Redlich−Kister equation to give the fitting parameters and the root-mean-square deviations.

Introduction

Room-temperature ionic liquids (ILs) are organic salts with a low melting point (below 100 °C) which result from a combination of organic cations and various anions. As numerous combinations of cations and anions are possible, they have been considered as "designer solvents" due to their ability to vary the ions, thereby modifying and optimizing the ionic liquid physical properties for a specific application.

Due to their peculiar properties, such as very low vapor pressure[1−2] at normal temperature and pressure conditions, low melting point, ability to dissolve organic, inorganic, and polymeric materials, good thermal stability, and their wide liquid range, these novel solvents have been suggested as replacements for traditional volatile organic solvents (VOCs). They are easy to recycle and, in general, nonflammable.

Recently, there have been numerous publications about IL properties or their applications in catalytic reactions, separation processes, membrane technology, chemical analysis, batteries, solar cells, or as lubricants. Nevertheless, the information about physical and thermodynamic properties of ionic liquids[3−6] is limited because, in general, these new solvents are highly hygroscopic, and small quantities of water or other compounds in ionic liquids cause considerable changes in their physical properties.[7−9] For this reason, to ensure the purity of ILs, the samples should be prepared and stored in an inert atmosphere glovebox.

This paper is a continuation of our work about physical properties of ionic liquids with alcohols.[9,10] The physical properties of binary mixtures of some alcohols + 1-ethyl-3-methylimidazolium ethyl sulfate (EMISE) are determined. Dynamic viscosities, densities, and speeds of sound and their excess properties for the binary systems EMISE + methanol, or + 1-propanol, or + 2-propanol over the entire mole fraction composition range at T = (298.15 to 328.15) K and refractive indices and their deviations at T = 298.15 K and at atmospheric pressure have been studied. There are some experimental data of ionic liquids with alcohols in the literature,[6,11] but no experimental data about these binary systems were found.

Experimental

Chemicals. Methanol and 1-propanol used in this work were supplied by Sigma-Aldrich with a purity of > 99.9 %, and 2-propanol was supplied by Merck with a purity > 99.7 %. The alcohols were degassed ultrasonically and dried over molecular sieves (type 4 Å), supplied by Aldrich, and kept in an inert argon atmosphere. The maximum water mass fraction was $2\cdot10^{-6}$. EMISE was synthesized in our laboratory. It was dried by heating ((343.15 to 353.15) K) and stirring under high vacuum ($2\cdot10^{-1}$ Pa) for 48 h. To ensure its purity, an NMR was made, as described in the literature.[10] The water mass fraction was determined using a 787 Karl Fischer Titration Coulometer, and this mass fraction was lower than 0.05 %. Table 1 shows a comparison between experimental and literature data of pure components at 298.15 K.

***Apparatus and Procedure*.** Binary systems were prepared, in an inert atmosphere glovebox, by syringing known masses of the pure liquids into stoppered bottles, using a Mettler AX-205 Delta Range balance with an uncertainty of $\pm 10^{-5}$ g.

Densities and speeds of sound were measured using an Anton Paar DSA-48 digital vibrating tube densimeter. The uncertainty has been found to be $\pm 10^{-4}$ g·cm^{-3} for the density and ± 1 m·s^{-1} for the speed of sound. The apparatus was calibrated by measuring the density of Millipore quality water and ambient air according to the manual instruction. The calibration was checked with pure liquids shown in Table 1.

Refractive indices of the pure components and their mixtures at T = 298.15 K were determined using an automatic refractometer (ABBEMAT-WR, Dr. Kernchen) with an uncertainty of $\pm 4\cdot10^{-5}$.

Kinematic viscosities of the liquids and their mixtures were determined using an automatic viscosimeter (Lauda PVS1) with four Ubbelohde capillary microviscosimeters of $0.4\cdot10^{-3}$ m, $0.53\cdot10^{-3}$ m, and $0.70\cdot10^{-3}$ m diameter (the uncertainty in experimental measurement is ± 0.006 mPa·s) and $1.26\cdot10^{-3}$ m diameter (the uncertainty in experimental measurement is ± 0.01 mPa·s). The last capillary viscosimeter was used to measure the samples with higher viscosities, such as the pure ionic liquid. Gravity fall is the principle of measurement on which this viscosimeter is based. The capillary was maintained in a D20KP

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Table 1. Comparison of Density ρ, Viscosity η, Refractive Index n_D, and Speed of Sound u, with Literature Data for Pure Components at T = 298.15 K

	$\rho/(\text{g}\cdot\text{cm}^{-3})$		$\eta/(\text{mPa}\cdot\text{s})$		n_D		$u/(\text{m}\cdot\text{s}^{-1})$	
	exptl	lit.	exptl	lit.	exptl	lit.	exptl	lit.
EMISE	1.2376	1.23915[a] 1.23882[b] 1.2296[c] 1.23737[d]	97.6	100.77[a] 100.4[b] 95[d]	1.47940	1. 47889[a]	1679	1683[a]
methanol	0.7864	0.78637[e] 0.78664[f]	0.546	0.551[e] 0.543[f]	1.32687	1.32652[e] 1.32667[g]	1103	1103[h]
1-propanol	0.7996	0.79960[e]	2.017	1.951[i] 2.0074[h]	1.38309	1.38306[j] 1.38317[k]	1207	1207[i]
2-propanol	0.7807	0.7810[l] 0.7809[m,n]	2.082	2.081[m] 2.098[n]	1.37495	1.3752[e] 1.3745[o]	1138	1139[p]

[a] From ref 4. [b] From ref 6. [c] From ref 12. [d] From ref 13. [e] From ref 14. [f] From ref 15. [g] From ref 16. [h] From ref 17. [i] From ref 11. [j] From ref 18. [k] From ref 19. [l] From ref 20. [m] From ref 21. [n] From ref 22. [o] From ref 23. [p] From ref 24.

Table 2. Data of Heat Capacity, C_p, and Isobaric Expansibility, α

component	T/K	C_p/R	α
methanol	298.15	81.464[a]	0.001196[b]
	313.15	85.066[a]	
	328.15	89.158[a]	
1-propanol	298.15	140.684[a]	0.001004[b]
	313.15	147.023[a]	
	328.15	154.960[a]	
2-propanol	298.15	155.780[c]	0.001064[b]
	313.15	170.555[c]	
	328.15	192.440[c]	
EMISE	298.15	377.692[d]	0.0005[e]
	313.15	381.538[d]	
	328.15	385.220[d]	

[a] From ref 28. [b] From ref 14. [c] From ref 29. [d] From ref 30. [e] From ref 10.

LAUDA thermostat with a resolution of 0.01 K. The capillaries are calibrated and credited by the company. The equipment has a control unit PVS1 (processor viscosity system) that is a PC-controlled instrument for the precise measurement of fall time, using standardized glass capillaries, with an uncertainty of 0.01 s. The calibration was checked with pure liquids shown in Table 1.

The kinematic viscosity was determined from the following equation

$$\nu = k(t - y) \tag{1}$$

where y is the kinetic energy correction, the Hagenbach–Couette correction, and this correction depends on the flow time of the mixture through the capillary; t is the flow time; and k is the Ubbelohde capillary microviscosimeter constant, supplied by the company. This constant depends on the diameter of the capillary (for $4\cdot10^{-3}$ m, $0.53\cdot10^{-3}$ m, $0.70\cdot10^{-3}$ m, and $1.26\cdot10^{-3}$ m diameters, the k values are 0.01, 0.03, 0.1, and 1, respectively). The dynamic viscosity is calculated from

$$\eta = \nu\rho \tag{2}$$

where η is the dynamic viscosity; ν is the kinematic viscosity; and ρ is the density.

Results and Discussion

The experimental data of density, speed of sound, dynamic viscosity, isentropic compression, excess molar volume, viscosity deviation, and excess molar isentropic compression for the binary systems methanol + EMISE, 1-propanol + EMISE, and 2-propanol + EMISE at T = (298.15, 313.15, and 328.15) K and at atmosphere pressure are determined. The refractive indices and their deviations for these mixtures at T = 298.15 K are also given.

The values of the excess molar volume V^E, viscosity deviation $\Delta\eta$, and refractive index deviation Δn_D are calculated by the following equations

$$V^E = \sum_{i=1}^{N} x_i M_i(\rho^{-1} - \rho_i^{-1}) \tag{3}$$

$$\Delta\eta = \eta - \sum_{i=1}^{N} x_i\eta_i \tag{4}$$

$$\Delta n_D = n_D - \sum_{i=1}^{N} x_i n_{Di} \tag{5}$$

where ρ and ρ_i are the density of the mixture and the density of the pure components, respectively; M_i is the molar mass of the pure components; x_i represents the mole fraction of the i component; η and η_i are the dynamic viscosity of the mixture and the pure component; and n_D and n_{Di} are the refractive index of the mixture and the pure component, respectively. The uncertainties for the excess molar volume and refractive index deviation are $4\cdot10^{-3}$ $\text{cm}^3\cdot\text{mol}^{-1}$ and $4\cdot10^{-5}$, respectively, and the uncertainties for the viscosity deviation are $6\cdot10^{-3}$ mPa·s (when Ubbelohde capillary microviscosimeters of $0.4\cdot10^{-3}$ m, $0.53\cdot10^{-3}$ m, and $0.70\cdot10^{-3}$ m diameter are used) and $1\cdot10^{-2}$ mPa·s (when an Ubbelohde capillary microviscosimeter of $1.26\cdot10^{-3}$ m is used).

The speed of sound u is related to the isentropic compression κ_S by the Laplace equation

$$\kappa_S = -V_m^{-1}\left(\frac{\partial V_m}{\partial \rho}\right)_S = \rho^{-1}u^{-2} = \frac{V_m}{M_m u^2} \tag{6}$$

where V_m is the molar volume and M_m is the molar mass of the mixture.

To achieve agreement with the other thermodynamic quantities, it is appropriate to shift from the volume-intensive κ_s to the mole-intensive quantity $K_{S,m}$[25,26]

$$K_{S,m} = -\left(\frac{\partial V_m}{\partial \rho}\right)_S = V_m\kappa_s = \frac{V_m^{\ 2}}{M_m u^2} \tag{7}$$

where $K_{S,m}$ is the molar isentropic compression.

The excess molar isentropic compression, $K_{S,m}^E$, is calculated by the following equation

$$K_{S,m}^E = K_{S,m} - K_{S,m}^{id} \tag{8}$$

Table 3. Density ρ, Speed of Sound u, Refractive Index n_D, Dynamic Viscosity η, Molar Isentropic Compression $K_{S,m}$, Excess Volume V^E, Excess Molar Isentropic Compression $K^E_{S,m}$, Refractive Index Deviation Δn_D, and Viscosity Deviation $\Delta\eta$ of Methanol (1) + EMISE (2)

Methanol (1) + EMISE (2)									
x_1	ρ / $g \cdot cm^{-3}$	u / $m \cdot s^{-1}$	η / $mPa \cdot s$	n_D	V^E / $cm^3 \cdot mol^{-1}$	$K_{S,m}$ / $m^3 \cdot TPa^{-1} \cdot mol^{-1}$	$K^E_{S,m}$ / $m^3 \cdot TPa^{-1} \cdot mol^{-1}$	Δn_D	$\Delta\eta$ / $mPa \cdot s$
$T = 298.15$ K									
0.0000	1.2376	1679	97.58	1.47940	0.000	0.05472	0.00000	0.0000	0.000
0.1346	1.2242	1663	60.93	1.47491	−0.148	0.05038	−0.00271	0.0160	−23.58
0.2595	1.2091	1640	39.32	1.47006	−0.368	0.04661	−0.00496	0.0302	−33.08
0.3267	1.1994	1624	30.59	1.46675	−0.486	0.04469	−0.00607	0.0372	−35.29
0.4741	1.1719	1583	16.38	1.45742	−0.725	0.04052	−0.00845	0.0503	−35.20
0.5701	1.1468	1547	10.12	1.44913	−0.802	0.03808	−0.00973	0.0567	−32.14
0.6664	1.1139	1500	6.450	1.43808	−0.910	0.03588	−0.01075	0.0603	−26.466
0.7757	1.0590	1423	3.232	1.42043	−0.912	0.03428	−0.01103	0.0593	−19.083
0.8294	1.0211	1371	2.351	1.40780	−0.859	0.03413	−0.01053	0.0549	−14.753
0.9230	0.9249	1251	1.639	1.37377	−0.662	0.03568	−0.00784	0.0352	−6.377
0.9626	0.8637	1187	1.263	1.35299	−0.418	0.03775	−0.00529	0.0204	−2.914
0.9917	0.8060	1123	1.039	1.33319	−0.132	0.04118	−0.00151	0.0051	−0.314
1.0000	0.7864	1103	0.546	1.32687	0.000	0.04259	0.00000	0.0000	0.000
$T = 313.15$ K									
0.0000	1.2275	1641	50.01		0.000	0.05824	0.00000		0.000
0.1346	1.2141	1627	33.83		−0.188	0.05351	−0.00338		−9.51
0.2595	1.1990	1603	23.40		−0.443	0.04962	−0.00603		−13.75
0.3267	1.1891	1587	18.94		−0.566	0.04761	−0.00736		−14.88
0.4741	1.1613	1546	11.02		−0.818	0.04326	−0.01024		−15.49
0.5701	1.1359	1509	7.173		−0.898	0.04079	−0.01176		−14.580
0.6664	1.1029	1461	4.776		−1.031	0.03858	−0.01301		−12.206
0.7757	1.0475	1382	2.508		−1.036	0.03715	−0.01335		−9.055
0.8294	1.0092	1330	1.860		−0.969	0.03713	−0.01284		−7.047
0.9230	0.9122	1207	0.901		−0.750	0.03941	−0.00963		−3.362
0.9626	0.8504	1137	0.660		−0.475	0.04244	−0.00620		−1.640
0.9917	0.7922	1076	0.516		−0.156	0.04643	−0.00192		−0.342
1.0000	0.7723	1055	0.446		0.000	0.04827	0.00000		0.000
$T = 328.15$ K									
0.0000	1.2175	1605	29.18		0.000	0.06188	0.00000		0.000
0.1346	1.2040	1588	20.92		−0.230	0.05712	−0.00385		−4.38
0.2595	1.1886	1564	15.25		−0.486	0.05304	−0.00709		−6.45
0.3267	1.1788	1549	12.65		−0.647	0.05092	−0.00875		−7.12
0.4741	1.1507	1506	7.887		−0.922	0.04644	−0.01225		−7.634
0.5701	1.1251	1469	5.387		−1.020	0.04387	−0.01416		−7.368
0.6664	1.0918	1420	3.661		−1.166	0.04168	−0.01571		−6.319
0.7757	1.0359	1340	2.020		−1.175	0.04041	−0.01624		−4.811
0.8294	0.9973	1287	1.501		−1.107	0.04060	−0.01568		−3.783
0.9230	0.8993	1162	0.666		−0.853	0.04374	−0.01191		−1.921
0.9626	0.8369	1090	0.551		−0.546	0.04768	−0.00770		−0.896
0.9917	0.7777	1029	0.430		−0.162	0.05268	−0.00251		−0.178
1.0000	0.7578	1006	0.369		0.000	0.05513	0.00000		0.000

where $K^{id}_{S,m}$ is defined by the approach developed by Benson and Kiyohara[27]

$$K^{id}_{S,m} = \sum_i x_i \left[K^*_{S,i} + T\frac{(E^*_{p,i})^2}{C^*_{p,i}} \right] - T\left[\frac{(\sum_i x_i E^*_{p,i})^2}{\sum_i x_i C^*_{p,i}} \right] \qquad (9)$$

where $K^*_{S,i}$ is the product of the molar volume V^*_i and the isentropic compression $\kappa^*_{S,i}$ of the pure component i. The molar isobaric expansion of pure component i, $E^*_{p,i}$, is the product of the molar volume and the isobaric expansibility $\alpha^*_{p,i}$, and $C^*_{p,i}$ is the molar isobaric heat capacity of the pure component i. The uncertainty for this excess property is $1 \cdot 10^{-5}$ $m^3 \cdot TPa^{-1} \cdot mol^{-1}$. Values of C_p and α for the pure components are shown in Table 2.

The experimental data of density, speed of sound, dynamic viscosity, isentropic compression, and their derived properties for the studied systems are presented in Tables 3 to 5.

The excess or deviation properties at each temperature have been fitted to a Redlich−Kister[31] type equation

$$Z = x_1(1 - x_1) \sum_{p=0}^{M} B_p(2x_1 - 1)^p \qquad (10)$$

where Z is the excess or deviation property; x_1 is the mole fraction of the alcohol; B_P is the fitting parameter; and M is the degree of the polynomial expansion. The fitting parameters are calculated minimizing the following objective function

$$\mathrm{OF} = \{\sum_{1}^{n_{dat}} (z_{exptl} - z_{calcd})^2/n_{dat}\}^{1/2} \qquad (11)$$

The fitting parameters are given in Table 6 together with the root-mean-square deviations. These deviations were calculated from the values of the experimental and calculated properties represented by z_{exptl} and z_{calcd}, respectively. n_{dat} is the number of experimental data, where the points $x_1 = 0$ and $x_1 = 1$ are

Table 4. Density ρ, Speed of Sound u, Refractive Index n_D, Dynamic Viscosity η, Molar Isentropic Compression $K_{S,m}$, Excess Volume V^E, Excess Molar Isentropic Compression $K_{S,m}^E$, Refractive Index Deviation Δn_D, and Viscosity Deviation $\Delta\eta$ of 1-Propanol (1) + EMISE (2)

1-Propanol (1) + EMISE (2)									
x_1	ρ / $g\cdot cm^{-3}$	u / $m\cdot s^{-1}$	η / $mPa\cdot s$	n_D	V^E / $cm^3\cdot mol^{-1}$	$K_{S,m}$ / $m^3\cdot TPa^{-1}\cdot mol^{-1}$	$K_{S,m}^E$ / $m^3\cdot TPa^{-1}\cdot mol^{-1}$	Δn_D	$\Delta\eta$ / $mPa\cdot s$
				$T = 298.15$ K					
0.0000	1.2376	1679	97.58	1.47940	0.000	0.05472	0.00000	0.0000	0.000
0.1619	1.2081	1637	60.85	1.47317	−0.209	0.05319	−0.00314	0.0094	−21.25
0.2104	1.1979	1620	52.11	1.47102	−0.263	0.05290	−0.00391	0.0119	−25.36
0.3360	1.1674	1574	34.41	1.46449	−0.334	0.05245	−0.00560	0.0174	−31.06
0.5159	1.1116	1492	18.01	1.45240	−0.406	0.05286	−0.00698	0.0227	−30.27
0.7298	1.0155	1382	7.296	1.43139	−0.380	0.05468	−0.00727	0.0223	−20.540
0.8046	0.9700	1337	5.491	1.42139	−0.334	0.05620	−0.00649	0.0195	−15.196
0.8894	0.9077	1284	3.577	1.40743	−0.287	0.05859	−0.00494	0.0137	−9.008
0.9401	0.8625	1249	2.776	1.39739	−0.180	0.06088	−0.00315	0.0085	−4.964
0.9727	0.8298	1227	2.419	1.39003	−0.097	0.06261	−0.00175	0.0043	−2.209
1.0000	0.7996	1207	2.017	1.38310	0.000	0.06463	0.00000	0.0000	0.000
				$T = 313.15$ K					
0.0000	1.2275	1642	50.01		0.000	0.05816	0.00000		0.000
0.1619	1.1979	1600	33.73		−0.250	0.05656	−0.00395		−8.41
0.2104	1.1876	1584	29.56		−0.306	0.05637	−0.00485		−10.23
0.3360	1.1571	1537	20.72		−0.418	0.05599	−0.00705		−12.97
0.5159	1.1008	1456	11.73		−0.484	0.05660	−0.00905		−13.22
0.7298	1.0044	1340	5.125		−0.483	0.05946	−0.00929		−9.430
0.8046	0.9586	1294	3.918		−0.419	0.06143	−0.00840		−7.002
0.8894	0.8959	1238	2.580		−0.342	0.06470	−0.00636		−4.222
0.9401	0.8506	1201	1.997		−0.223	0.06770	−0.00409		−2.342
0.9727	0.8178	1178	1.729		−0.125	0.06994	−0.00233		−1.028
1.0000	0.7874	1155	1.430		0.000	0.07266	0.00000		0.000
				$T = 328.15$ K					
0.0000	1.2175	1605	29.18		0.000	0.06188	0.00000		0.000
0.1619	1.1876	1565	20.84		−0.271	0.06015	−0.00499		−3.78
0.2104	1.1773	1548	18.59		−0.348	0.05998	−0.00613		−4.66
0.3360	1.1467	1501	13.61		−0.497	0.05978	−0.00886		−6.11
0.5159	1.0902	1419	8.159		−0.606	0.06075	−0.01150		−6.502
0.7298	0.9932	1300	3.774		−0.606	0.06461	−0.01195		−4.869
0.8046	0.9472	1252	2.918		−0.540	0.06722	−0.01085		−3.620
0.8894	0.8840	1193	1.923		−0.425	0.07156	−0.00821		−2.229
0.9401	0.8385	1154	1.482		−0.286	0.07546	−0.00533		−1.244
0.9727	0.8055	1130	1.272		−0.163	0.07849	−0.00296		−0.538
1.0000	0.7748	1105	1.041		0.000	0.08199	0.00000		0.000

not taken into consideration, and m is the number of parameters adjusted to the data

$$\sigma = \{\sum_{1}^{n_{\text{dat}}} (z_{\text{exptl}} - z_{\text{calcd}})^2/(n_{\text{dat}} - m)\}^{1/2} \tag{12}$$

Figures 1 to 4 show the fitted curves, as well as excess and deviation experimental values against the mole fraction of binary systems for methanol + EMISE, 1-propanol + EMISE, and 2-propanol + EMISE at $T = (298.15, 313.15, \text{and } 328.15)$ K. In Figure 1, we can observe that the excess molar volumes are negative, and they decrease as the temperature increases for all binary systems. This behavior can be explained because hydrogen bonding is certainly more T-dependent (becoming negligible at high temperatures) than Coulombic interactions. This result agrees with the work of Rebelo et al.[32] The V^E for the binary system methanol + EMISE presents a minimum at an alcohol mole fraction of approximately 0.8 for the three studied temperatures. In the binary systems formed by EMISE and 1- and 2-propanol, the minimum of V^E is present at approximately 0.6 mole fractions of alcohol. The values of V^E are smaller in the binary system containing methanol than 1- or 2-propanol. This behavior can be explained in terms of more efficient packing in the mixtures than in the pure liquid[33] and is due to the ion−dipole interactions between alcohol and ionic liquid.[34] As can be seen in Figure 1, the 2-propanol + EMISE excess volumes are more negative than 1-propanol + EMISE. It can be caused because the packing is stronger for primary than for secondary alcohols. We compare these excess molar volumes with the ones published previously (ethanol + EMISE, water + EMISE).[10] They all have negative values over the whole composition range. We can observe that as the hydrocarbon chain of alcohols decreases, the excess molar volume minimum is present at a higher molar fraction of alcohol. The binary system methanol + EMISE presents the smaller values of V^E, and the binary system water + EMISE presents the higher values in this excess property.

In Figure 2, the viscosity deviations are negative over the whole composition range and approach the minimum at $x_1 \approx 0.4$ for the three binary systems studied. It can be observed that the behavior of the viscosity deviation in the binary systems EMISE + 1-propanol and 2-propanol is similar. The viscosity deviations are less negative as the temperature increases in all systems.

The excess molar isentropic compressions are plotted in Figure 3. This property reaches a minimum at a mole composition of $x_1 \approx 0.8$ for the binary system methanol (1) + EMISE (2) and of $x_1 \approx 0.7$ for the binary systems 1-propanol (1) + EMISE (2) and 2-propanol (1) + EMISE (2).

Figure 4 shows the refractive index deviations at 298.15 K for the three studied binary mixtures. The deviation is positive over the whole composition range with a maximum over $x_1 \approx 0.65$ for the binary systems 1-propanol (1) + EMISE (2) and 2-propanol (1) + EMISE (2) and over $x_1 \approx 0.7$ for methanol

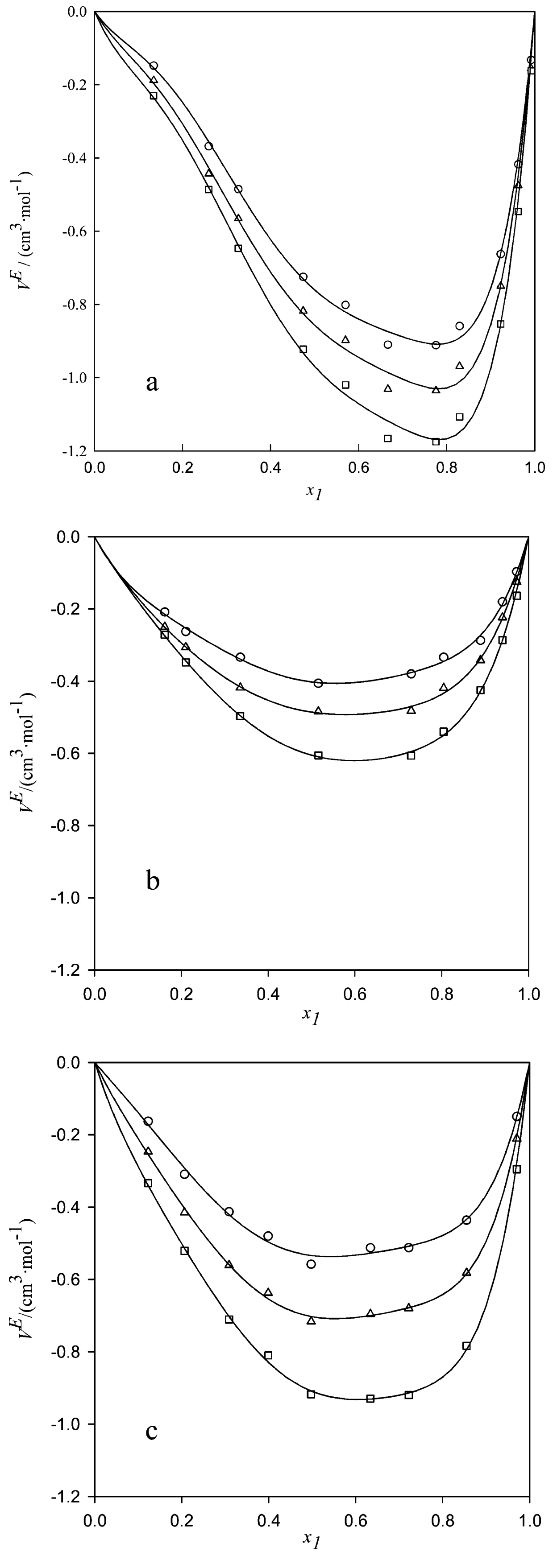

Figure 1. Excess molar volume, V^E, from the Redlich−Kister equation (−) plotted against mole fraction. Experimental points at ○, T = 298.15 K; △, T = 313.15 K; and □, T = 328.15 K for the binary mixtures (a) methanol (1) + EMISE (2), (b) 1-propanol (1) + EMISE (2), and (c) 2-propanol (1) + EMISE (2).

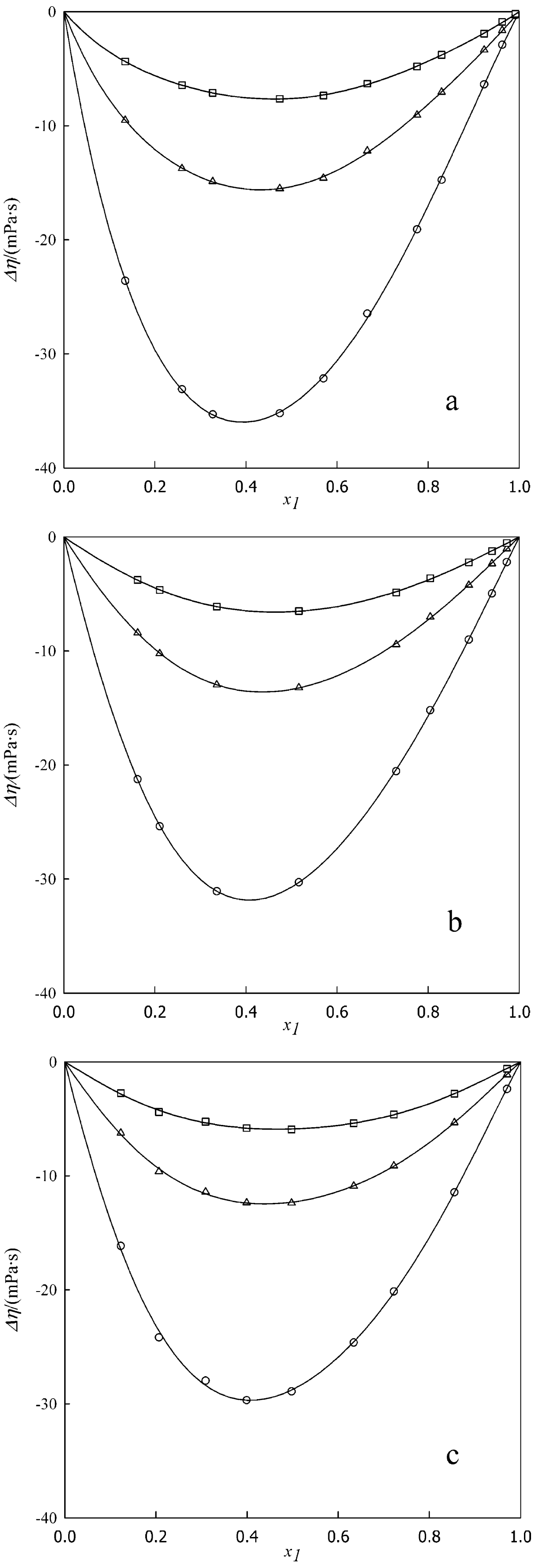

Figure 2. Viscosity deviations, $\Delta\eta$, from the Redlich−Kister equation (−) plotted against mole fraction. Experimental points at ○, T = 298.15 K; △, T = 313.15 K; and □, T = 328.15 K for the binary mixtures (a) methanol (1) + EMISE (2), (b) 1-propanol (1) + EMISE (2), and (c) 2-propanol (1) + EMISE (2).

Table 5. Density ρ, Speed of Sound u, Refractive Index n_D, Dynamic Viscosity η, Molar Isentropic Compression $K_{S,m}$, Excess Volume V^E, Excess Molar Isentropic Compression $K_{S,m}^E$, Refractive Index Deviation Δn_D, and Viscosity Deviation $\Delta\eta$ of 2-Propanol (1) + EMISE (2)

2-Propanol (1) + EMISE (2)									
	ρ	u	η		V^E	$K_{S,m}$	$K_{S,m}^E$		$\Delta\eta$
x_1	$g\cdot cm^{-3}$	$m\cdot s^{-1}$	mPa·s	n_D	$cm^3\cdot mol^{-1}$	$m^3\cdot TPa^{-1}\cdot mol^{-1}$	$m^3\cdot TPa^{-1}\cdot mol^{-1}$	Δn_D	mPa·s
T = 298.15 K									
0.0000	1.2376	1679	97.58	1.47940	0.000	0.05472	0.00000	0.0000	0.000
0.1228	1.2143	1644	69.71	1.47434	−0.163	0.05386	−0.00349	0.0078	−16.15
0.2066	1.1964	1611	53.67	1.47057	−0.309	0.05381	−0.00534	0.0127	−24.18
0.3090	1.1709	1570	40.10	1.46502	−0.413	0.05381	−0.00753	0.0179	−27.97
0.3990	1.1449	1529	29.79	1.45926	−0.480	0.05417	−0.00910	0.0215	−29.68
0.4977	1.1118	1475	21.14	1.45177	−0.558	0.05526	−0.01013	0.0244	−28.91
0.6341	1.0542	1399	12.40	1.43881	−0.512	0.05727	−0.01104	0.0256	−24.62
0.7223	1.0085	1342	8.462	1.42818	−0.512	0.05952	−0.01067	0.0242	−20.145
0.8551	0.9202	1251	4.475	1.40784	−0.436	0.06462	−0.00842	0.0178	−11.446
0.9706	0.8141	1164	2.499	1.38306	−0.149	0.07270	−0.00281	0.0050	−2.387
1.0000	0.7807	1138	2.082	1.37495	0.000	0.07614	0.00000	0.0000	0.000
T = 313.15 K									
0.0000	1.2275	1643	50.01		0.000	0.05809	0.00000		0.000
0.1228	1.2044	1608	37.79		−0.247	0.05723	−0.00436		−6.25
0.2066	1.1864	1576	30.34		−0.415	0.05718	−0.00681		−9.61
0.3090	1.1609	1534	23.56		−0.561	0.05734	−0.00956		−11.42
0.3990	1.1347	1491	18.23		−0.637	0.05799	−0.01148		−12.37
0.4977	1.1013	1439	13.41		−0.716	0.05917	−0.01311		−12.38
0.6341	1.0435	1360	8.274		−0.696	0.06194	−0.01423		−10.882
0.7223	0.9974	1302	5.753		−0.680	0.06465	−0.01403		−9.116
0.8551	0.9086	1207	3.081		−0.582	0.07120	−0.01127		−5.324
0.9706	0.8017	1113	1.658		−0.211	0.08199	−0.00377		−1.125
1.0000	0.7678	1085	1.354		0.000	0.08660	0.00000		0.000
T = 328.15 K									
0.0000	1.2175	1605	29.18		0.000	0.06188	0.00000		0.000
0.1228	1.1945	1569	22.97		−0.334	0.06111	−0.00539		−2.74
0.2066	1.1763	1537	18.93		−0.521	0.06115	−0.00850		−4.41
0.3090	1.1507	1494	15.20		−0.711	0.06153	−0.01197		−5.25
0.3990	1.1243	1451	12.10		−0.810	0.06237	−0.01451		−5.80
0.4977	1.0907	1399	9.184		−0.918	0.06382	−0.01677		−5.929
0.6341	1.0326	1318	5.878		−0.929	0.06725	−0.01847		−5.380
0.7223	0.9862	1259	4.150		−0.920	0.07072	−0.01832		−4.617
0.8551	0.8966	1161	2.225		−0.784	0.07902	−0.01501		−2.789
0.9706	0.7885	1063	1.147		−0.295	0.09292	−0.00545		−0.602
1.0000	0.7539	1031	0.919		0.000	0.09948	0.00000		0.000

Table 6. Fitting Parameters and Root-Mean-Square Deviations σ for Binary Mixtures at T = (298.15, 313.15, and 328.15) K

T/K	B_0	B_1	B_1	B_2	B_3	B_4	σ
Methanol (1) + EMISE (2)							
$V^E/cm^3\cdot mol^{-1}$	298.15	−3.0405	−2.1161	0.0081	−3.6345	−4.3987	0.018
	313.15	−3.4271	−2.2571	−0.4171	−4.1579	−4.5898	0.023
	328.15	−3.8769	−2.6370	−0.3710	−4.4694	−5.6886	0.023
$K_{S,m}^E/m^3\cdot TPa^{-1}\cdot mol^{-1}$	298.15	−0.0359	−0.0249	−0.0087	−0.0352	−0.0540	$1.88\cdot10^{-4}$
	313.15	−0.0434	−0.0303	−0.0123	−0.0419	−0.0641	$1.70\cdot10^{-4}$
	328.15	−0.0521	−0.0369	−0.0139	−0.0552	−0.0809	$2.21\cdot10^{-4}$
Δn_D	298.15	0.2091	0.1397	0.1010	0.1070	0.0660	$1.23\cdot10^{-4}$
$\Delta\eta$/mPa·s	298.15	−137.85	54.86	−20.22	30.19	−4.95	0.170
	313.15	−61.34	16.64	−0.59	11.17	−12.26	0.063
	328.15	−30.47	4.73	0.53	5.19	−6.60	0.038
1- Propanol (1) + EMISE (2)							
$V^E/cm^3\cdot mol^{-1}$	298.15	−1.6090	−0.3029	−0.1465	−0.6409	−1.4859	0.007
	313.15	−1.9437	−0.3636	−0.6190	−1.0509	−0.9115	0.006
	328.15	−2.4200	−0.6520	−0.5049	−1.4265	−1.2228	0.006
$K_{S,m}^E/m^3\cdot TPa^{-1}\cdot mol^{-1}$	298.15	−0.0277	−0.0110	−0.0112	−0.0110	−0.0053	$5.08\cdot10^{-5}$
	313.15	−0.0358	−0.0157	−0.0091	−0.0117	−0.0156	$6.20\cdot10^{-5}$
	328.15	−0.0455	−0.0214	−0.0129	−0.0139	−0.0199	$6.16\cdot10^{-5}$
Δn_D	298.15	0.0896	0.0393	0.0172	0.0118	0.0093	$2.9\cdot10^{-5}$
$\Delta\eta$/mPa·s	298.15	−122.81	47.16	−11.25	−3.39	8.83	0.077
	313.15	−53.46	14.06	−1.81	−1.79	4.82	0.052
	328.15	−26.23	3.83	0.34	−0.65	2.42	0.037
2-Propanol (1) + EMISE (2)							
$V^E/cm^3\cdot mol^{-1}$	298.15	−2.1355	−0.2885	−0.1942	−2.0258	−1.3439	0.012
	313.15	−2.8113	−0.4307	−0.4446	−2.4122	−2.0147	0.008
	328.15	−3.6375	−0.9567	−0.6919	−2.6832	−3.0770	0.009
$K_{S,m}^E/m^3\cdot TPa^{-1}\cdot mol^{-1}$	298.15	−0.0412	−0.0183	−0.0088	−0.0146	−0.0194	$7.97\cdot10^{-5}$
	313.15	−0.0527	−0.0254	−0.0144	−0.0211	−0.0248	$6.97\cdot10^{-5}$
	328.15	−0.0677	−0.0351	−0.0150	−0.0320	−0.0461	$1.71\cdot10^{-4}$
Δn_D	298.15	0.0977	0.0407	0.0163	0.0169	0.0112	$5.3\cdot10^{-5}$
$\Delta\eta$/mPa·s	298.15	−114.96	39.22	−22.07	3.19	18.26	0.238
	313.15	−49.20	10.61	−7.85	0.88	9.14	0.098
	328.15	−23.52	2.54	−4.97	0.04	6.60	0.064

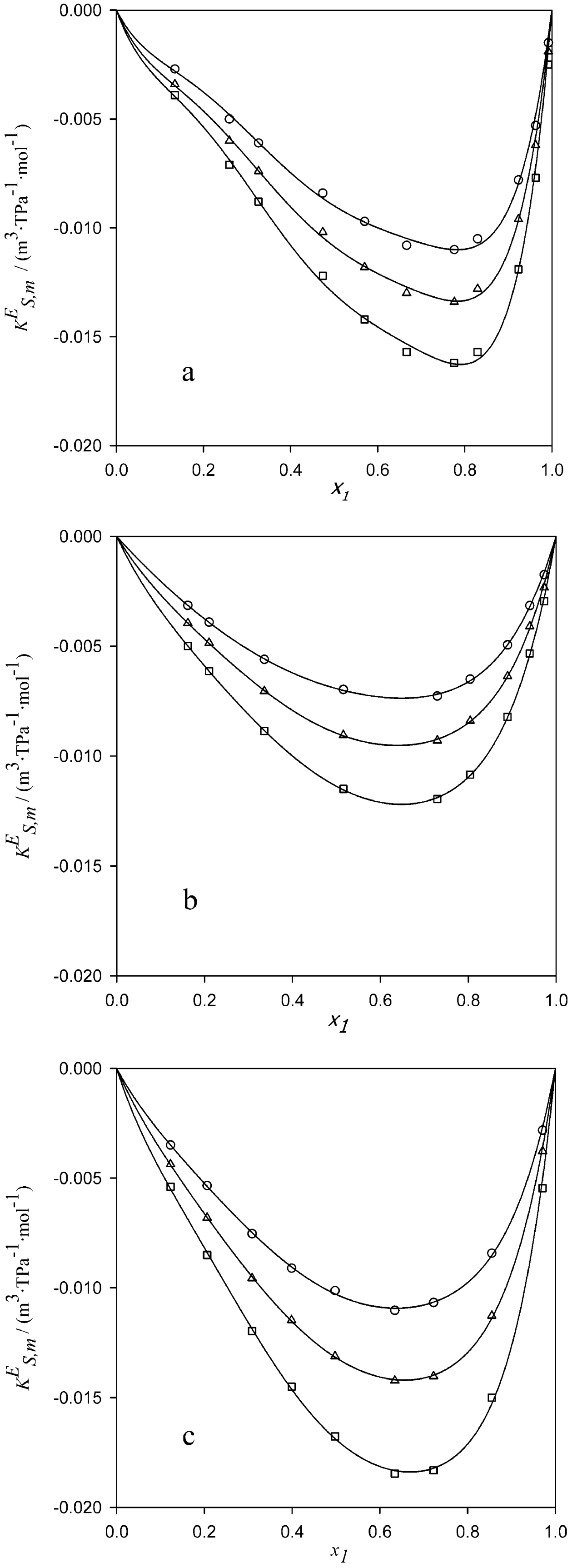

Figure 3. Excess molar isentropic compressions, $K^E_{S,m}$, from the Redlich−Kister equation (−) plotted against mole fraction. Experimental points at ○, T = 298.15 K; △, T = 313.15 K; and □, T = 328.15 K for the binary mixtures (a) methanol (1) + EMISE (2), (b) 1-propanol (1) + EMISE (2), (c) 2-propanol (1) + EMISE (2).

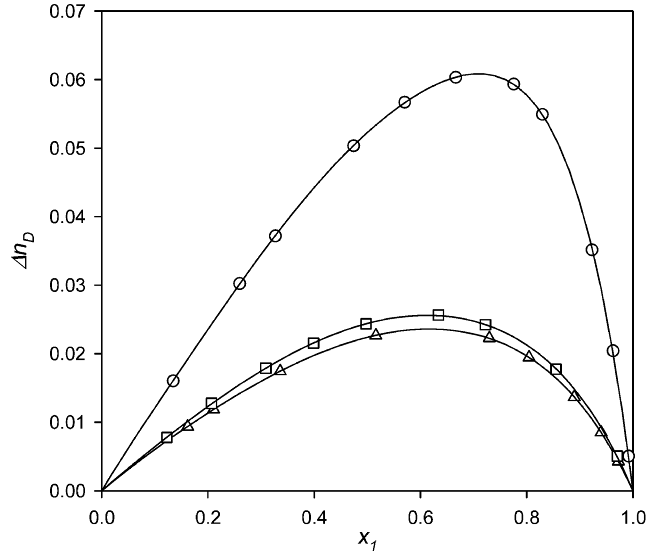

Figure 4. Refractive index deviations, Δn_D, from the Redlich−Kister equation (−) plotted against mole fraction. Experimental points at T = 298.15 K for the binary systems: ○, methanol (1) + EMISE (2); △, 1-propanol (1) + EMISE (2); and □, 2-propanol (1) + EMISE (2).

(1) + EMISE (2). For primary alcohols, the refractive index deviation decreases with the increase of the length of the chain of alcohol. Nevertheless, when the OH group is in secondary position on the chain of alcohol, the refractive index deviation is higher than when the OH group is in the last position on the chain of alcohol.

Conclusions

In this paper, densities, dynamic viscosities, and speeds of sound for the binary systems methanol (1), 1-propanol (1), and 2-propanol (1) + EMISE (2) at T = (298.15, 313.15, and 328.15) K and atmospheric pressure have been determined over the whole composition range. The refractive indices at T = 298.15 K have also been determined.

Excess molar volumes V^E and excess molar isentropic compressions $K^E_{S,m}$ for these binary systems have been calculated from the measured density and speed of sound data. The measured negative V^E values for these mixtures indicate that ion−dipole interactions and packing between alcohols and ILs are present.

The viscosity deviations are negative over the whole composition range, and their values are less negative as the temperature increases.

The refractive index deviations at T = 298.15 K have been determined. The three studied systems show positive values of the refractive index deviation over the whole composition range.

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Literature Cited

(1) Zaitsau, D. H.; Kabo, G. J.; Strechan, A. A.; Paulechka, Y. U.; Tschersich, A.; Verevkin, S. P.; Heintz, A. Experimental vapor pressures of 1-alkyl-2-methylimidazolium bis(trifluoromethylsulfonyl)-imides and a correlation scheme for estimation of vaporization enthalpies of ionic liquids. *J. Phys. Chem. A* **2006**, *110*, 7303−7306.

(2) Rebelo, L. P. N.; Lopes, J. N. C.; Esperança, J. M. S. S.; Filipe, E. On the critical temperature, normal boiling point and vapor pressure of ionic liquids. *J. Phys. Chem. B* **2005**, *109*, 6040 − 6043.

(3) Krummen, M.; Wasserscheid, P.; Gmehling, J. Measurement of activity coefficients at infinite dilution in ionic liquids using the dilutor technique. *J. Chem. Eng. Data* **2002**, *47*, 1411−1417.

(4) Jacquemin, J.; Husson, P.; Pádua, A. A. H.; Majer, V. Density and viscosity of several pure and water-saturated ionic liquids. *Green Chem.* **2006**, *8*, 172−180.

(5) Yang, J.; Lu, X.; Gui, J.; Xu, W.; Li, H. Volumetric properties of room temperature ionic liquid 2. The concentrated aqueous solutions of {1-methyl-3-ethylimidazolium ethyl sulfate} in a temperature range of 278.2 K to 338.2 K. *J. Chem. Thermodyn.* **2005**, *37*, 1250−1255.

(6) Arce, A.; Rodil, E.; Soto, A. Volumetric and viscosity study for the mixtures of 2-ethoxy-2-methylpropane, ethanol, and 1-ethyl-3-methylimidazolium ethyl sulfate ionic liquid. *J. Chem. Eng. Data* **2006**, *51*, 1453−1457.

(7) Seddon, K. R.; Stark, A.; Torres, M. J. Influence of chloride, water and organic solvents on the physical properties of ionic liquids. *Pure. Appl. Chem.* **2000**, *72*, 2275−2287.

(8) Calvar, N.; González, B.; Domínguez, A.; Tojo, J. Physical properties of the ternary mixtures ethanol + water + 1-butyl-3-methylimidazolium chloride at 298.15 K. *J. Chem. Eng. Data* **2006**, *51*, 696−701.

(9) González, E. J.; Alonso, L.; Domínguez, A. Physical properties of binary mixtures of the ionic liquid 1-methyl-3-octylimidazolium chloride with methanol, ethanol, and 1-propanol at T = (298.15, 313.15, and 328.15) K and at P = 0.1 MPa. *J. Chem. Eng. Data* **2006**, *51*, 1446−1452.

(10) Gómez, E.; González, B.; Calvar, N.; Tojo, E.; Domínguez, A. Physical properties of pure 1-ethyl-3-methylimidazolium ethylsulfate and its binary mixtures with ethanol and water at several temperatures. *J. Chem. Eng. Data* **2006**, *51*, 2096−2102.

(11) Arce, A.; Rodil, E.; Soto, A. Physical and excess properties for binary mixtures of 1-methyl-3-octylimidazolium tetrafluoroborate, [Omim]-[BF$_4$], ionic liquid with different alcohols. *J. Solution Chem.* **2006**, *35*, 63−78.

(12) Yang, J. Z.; Lu, X. M.; Gui, J. S.; Wu, W. G. A new theory for ionic liquids- the Interstice Model. Part 1. The density and surface tension of ionic liquid EMISE. *Green Chem.* **2004**, *6*, 541−543.

(13) Rodríguez, H.; Brennecke, J. F. Temperature and composition dependence of the density and viscosity of binary mixtures of water + ionic liquid. *J. Chem. Eng. Data* **2006**, *51*, 2145−2155.

(14) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*; Wiley: New York, 1986.

(15) Chen, H. W.; Wen, C. C.; Tu, C. H. Excess molar volumes, viscosities, and refractive indexes for binary mixtures of 1-chlorobutane with four alcohols at T = (288.15, 298.15, and 308.15) K. *J. Chem. Eng. Data* **2004**, *49*, 347−351.

(16) Resa, J. M.; González, C.; Goenaga, J. M. Density, refractive index, speed of sound at 298.15 K, and vapor-liquid equilibria at 101.3 kPa for binary mixtures of methanol + 2-methyl-1-butanol and ethanol + 2-methyl-1-butanol. *J. Chem. Eng. Data* **2005**, *50*, 1570−1575.

(17) Pal, A.; Sharma, S. Excess Molar Volumes and Viscosities of 1-Propanol + Ethylene Glycol, + Ethylene Glycol Monomethyl, + Ethylene Glycol Dimethyl, + Diethylene Glycol Dimethyl, + Triethylene Glycol Dimethyl, + Diethylene Glycol Diethyl, and + Diethylene Glycol Dibutyl Ethers at 298.15 K. *J. Chem. Eng. Data* **1998**, *43*, 532−536.

(18) Das, M.; Roy, M. N. Volumetric, viscometric and acoustic studies of binary mixtures of 2-ethoxyethanol with 1-alkanols at 298.15 K. *Phys. Chem. Liq.* **2006**, *44*, 663−685.

(19) Tu, C. H.; Lee, S. L.; Peng, I. H. Excess volumes and viscosities of binary mixtures of aliphatic alcohols (C_1−C_4) with nitromethane. *J. Chem. Eng. Data* **2001**, *46*, 151−155.

(20) Mrityunjaya, I. A.; Jagadish, G. B. Physico-chemical and excess properties of the binary mixtures of methylcyclohexane + ethanol, + propan-1-ol, + propan-2-ol, + butan-1-ol, + 2-methyl-1-propanol, or 3-methyl-1-butanol at T = (298.15, 303.15, and 308.15) K. *J. Chem. Thermodyn.* **2006**, *38*, 434−442.

(21) Contreras, M. Densities and viscosities of binary mixtures of 1,4-dioxane with 1-propanol and 2-propanol at (25, 30, 35, and 40) °C. *J. Chem. Eng. Data* **2001**, *46*, 1149−1152.

(22) Rodríguez, A.; Canosa, J.; Domínguez, A.; Tojo, J. Viscosities of dimethyl carbonate with alcohols at several temperaturas UNIFAC-VISCO interaction parameters (-OCOO-/alcohol). *Fluid Phase Equilib.* **2004**, *216*, 167−174.

(23) Mutalik, V.; Manjeshwar, L. S.; Sairam, M.; Aminabhavi, T. M. Excess molar volumes, deviations in viscosity and refractive index of the binary mixtures of mesitylene with ethanol, propan-1-ol, propan-2-ol, butan-1-ol, pentan-1-ol and 3-methylbutan-1-ol at 298.15, 303.15, and 308.15 K. *J. Mol. Liq.* **2006**, *129*, 147−154.

(24) Rodríguez, A.; Canosa, J.; Tojo, J. Physical properties of binary mixtures (dimethyl carbonate + alcohols) at several temperatures. *J. Chem. Eng. Data* **2001**, *46*, 1506−1515.

(25) Douhéret, G.; Davis, M. I.; Reis, J. C. R.; Blandamer, M. J. Isentropic compressibilities-experimental origin and the quest for their rigorous estimation in thermodynamically ideal liquid mixtures. *Chem. Phys. Chem.* **2001**, *2*, 148−161.

(26) Douhéret, G.; Davis, M. I.; Reis, J. C. R.; Fjellanger, I. J.; Vaage, M. B.; Hoiland, H. Aggregative processes in aqueous solutions of isomeric 2-butoxyethanols at 298.15 K. *Phys. Chem. Chem. Phys.* **2002**, *4*, 6034−6042.

(27) Benson, G. C.; Kiyohara, O. Evaluation of excess isentropic compressibilities and isochoric heat capacities. *J. Chem. Thermodyn.* **1979**, *11*, 1061−164.

(28) Smith, J. M.; Van Ness, H. C.; Abbott, M. M. *Introducción a la Termodinámica en Ingeniería Química*; McGraw-Hill/Interamericana: México, 1999.

(29) Cerdeiriña, C. A.; Tovar, C. A.; Troncoso, J.; Carballo, E.; Romaní, L. Excess volumes and excess heat capacities of nitromethane + (1-propanol or 2-propanol). *Fluid Phase Equilib.* **1999**, *157*, 93−102.

(30) Zhang, Z. H.; Tan, Z. C.; Sun, L. X.; Yang, J. Z.; Lv, X. C.; Shi, Q. Thermodynamic investigation of room temperature ionic liquid: The heat capacity and standard enthalpy of formation of EMIES. *Themochim. Acta* **2006**, *447*, 141−146.

(31) Redlich, O.; Kister, A. T. Thermodynamics of Nonelectrolyte Solutions. Algebraic representation of thermodynamic properties and the classification of solutions. *Ing. Eng. Chem.* **1948**, *40*, 345−348.

(32) Rebelo, L. P. N.; Najdanovic-Visak, V.; Visak, Z. P.; Nunes da Ponte, M.; Szydlowski, J.; Cerdeiriña, C. A.; Troncoso, J.; Romani, L.; Esperança, J. M. S. S.; Guedes, Sousa, M. C. A detailed thermodynamic analysis of [C$_4$mim][BF$_4$] + water as a case study to model ionic liquid aqueous solutions. *Green Chem.* **2004**, *6*, 369−381.

(33) Wang, J.; Tian, Y.; Zhao, Y.; Zhuo, K. A volumetric and viscosity study for the mixtures of 1-n-butyl-3-methylimidazolium tetrafluoroborate ionic liquid with acetonitrile, dichloromethane, 2-butanone and N,N-dimethylformamide. *Green Chem.* **2003**, *5*, 618−622.

(34) Zafarani-Moattar, M. T.; Shekaari, H. Volumetric and speed of sound of ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate with acetonitrile and methanol at T = (298.15 to 318.15) K. *J. Chem. Eng. Data* **2005**, *50*, 1694−1699.

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