Physical Properties of Pure 1-Ethyl-3-methylimidazolium Ethylsulfate and Its Binary Mixtures with Ethanol and Water at Several Temperatures

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This paper reports on the synthesis and the physical properties of the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate (EMISE). Experimental densities, speeds of sound and refractive indices were determined from (288.15 to 343.15) K. Dynamic viscosities were measured from (298.15 to 343.15) K and surface tension were measured from (288.15 to 313.15) K for pure ionic liquid. Densities, dynamic viscosities, speeds of sound, and isentropic compressibilities have been determined over the whole composition range for ethanol (1) + EMISE (2) and water (1) + EMISE (2) binary systems at $T = (298.15, 313.15, \text{and } 328.15)$ K and atmospheric pressure. Excess molar volumes, viscosity deviations, and deviations in isentropic compressibility for the binary systems were fitted to a Redlich−Kister equation to determine the fitting parameters and the root mean square deviations. Refractive indices were measured at 298.15 K over the whole composition range for the ethanol (1) + EMISE (2) and water (1) + EMISE (2) binary systems. The results were used to calculate deviations in the refractive index.

Introduction

Room-temperature ionic liquids (RTILs) constitute a new class of substances that are considered as potential substitutes to many traditional organic solvents in reaction and separation processes.[1,2] In spite of their importance and interest, accurate values for many of the fundamental physical−chemical properties of this ionic liquid are either scarce or absent.[3]

To design any process involving ionic liquids on an industrial scale, it is necessary to know a range of physical properties including viscosity and density. Furthermore, the presence of water in the ionic liquid phase can dramatically affect the physical properties.[4−6] Since it is impossible to measure all the possible combinations of systems, it is necessary to make measurements on selective systems to provide results that can be used to develop correlations and predictive methods.

Experimental density, speed of sound, surface tension, dynamic viscosity, and refractive index data of pure EMISE have been measured at several temperatures. Experimental density, dynamic viscosity, speed of sound and isentropic compressibility data over whole composition range for ethanol (1) + EMISE (2) and water (1) + EMISE (2) have been determined at temperatures of (298.15, 313.15, and 328.15) K and atmospheric pressure. The refractive indices of the binary systems ethanol (1) + EMISE (2) and water (1) + EMISE (2) were determined at 298.15 K over the whole composition range. The coefficient of thermal expansion, excess molar volumes, viscosity deviations, deviations in the refractive index, and deviations in isentropic compressibility were calculated from experimental data.

Experimental Section

Chemicals. Ethanol was supplied by Merck with a purity higher than 99.8 %. It was degassed ultrasonically and dried over molecular sieves type 4 Å, supplied by Aldrich, and kept in an inert argon atmosphere. Water was double-distilled and deionized.

Synthesis of 1-Ethyl-3-methylimidazolium Ethylsulfate. 1-Ethyl-3-methylimidazolium ethylsulfate was prepared according to a slightly modified literature procedure;[7] 0.42 mol of diethylsulfate was added dropwise to 0.42 mol of 1-methylimidazole in toluene (150 mL) and cooled in an ice bath under argon at a rate to maintain the reaction temperature below 313.15 K due to the reaction being highly exothermic. The reaction mixture was stirred at room temperature for (1 to 4) h depending on the amount of starting materials (the progress of the reaction was monitored by thin-layer chromatography). The upper organic phase of the resulting mixture was decanted, and the lower IL phase was washed with ethyl acetate (4 × 70 mL per 0.4 mol of starting 1-methylimidazole). After the last washing, the remaining ethyl acetate was removed by heating under reduced pressure. The ionic liquid obtained was dried by heating to (343.15 to 353.15) K and stirring under high vacuum (2×10^{-1} Pa) for 48 h. ^{1}H NMR (400 MHz, D_2O, ppm): δ 8.75 [s, 1 H, H-2], 7.54 [s, 1 H, H-4], 7.47 [s, 1 H, H-5], 4.28 [q, $J = 7.37$ Hz, 2 H, NCH_2CH_3], 4.17 [q, $J = 7.12$ Hz, 2 H, OCH_2CH_3], 3.95 [s, 3 H, NCH_3], 1.56 [t, $J = 7.36$ Hz, 3 H, NCH_2CH$_3$], 1.39 [t, $J = 7.12$ Hz, 3 H, OCH_2CH$_3$]. Its purity is 99 % mass fraction.

The ionic liquid was kept in bottles with inert gas. To reduce the water content to negligible values (lower than 0.03 % mass fraction determined using a 756 Karl Fisher coulometer) vacuum (2×10^{-1} Pa) and moderate temperature (343.15 K) were applied to the IL for the several days, always immediately prior to their use.

Table 1 shows a comparison between experimental and literature data of the pure components at 298.15 K. The differences between experimental and literature data for pure EMISE can be explained because physical properties of ionic liquids depend on the water content and other impurities.

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Table 1. Comparison of Measured Pure Component Properties Data with Literature Values at T = 298.15 K

	ρ/g·cm^{-3}		$10^3\eta$/Pa·s	
compound	exptl	lit	exptl	lit
ethanol	0.78546	0.7854[a]	1.082	1.082[a]
water	0.99705	0.99705[b]	0.890	0.890[b]
EMISE	1.23763	1.23915[c] 1.2296[d]	97.58	100.77[c]

[a] Ref 8. [b] Ref 9. [c] Ref 10. [d] Ref 11.

Table 2. Density ρ, Speed of Sound u, Refractive Index n_D, Dynamic Viscosity η, and Surface Tension σ of EMISE at Several Temperatures

T	ρ	u		$10^3\eta$	σ
K	g·cm^{-3}	m·s^{-1}	n_D	Pa·s	mN·m^{-1}
288.15	1.24446	1703.9	1.48197		47.91
293.15	1.24100	1691.4	1.48072		47.39
298.15	1.23763	1679.0	1.47940	97.58	46.96
303.15	1.23425	1666.6	1.47803	76.67	46.58
308.15	1.23088	1654.0	1.47669	61.71	46.23
313.15	1.22751	1641.6	1.47535	50.01	45.84
318.15	1.22415	1629.2	1.47397	41.37	
323.15	1.22080	1616.8	1.47259	34.463	
328.15	1.21747	1604.5	1.47124	29.176	
333.15	1.21431	1591.3	1.46989	24.955	
338.15	1.21082	1578.9	1.46851	21.446	
343.15	1.20751	1566.4	1.46718	18.723	

Table 3. Fitting Parameters of Equation 1 and Standard Deviations, SD, of the Density, Refractive Index, Speed of Sound, and Surface Tension of EMISE

physical properties	a	b	SD
ρ/g·cm^{-3}	1.4375	-6.7·10^{-4}	6·10^{-5}
n_D	1.5603	-2.7·10^{-4}	2·10^{-4}
u/m·s^{-1}	2424	-2.499	2.4·10^{-1}
σ/mN·m^{-1}	71.23	-0.081	4·10^{-2}

Table 4. Adjustable Parameters of the Arrhenius Equation (n_∞, E_a) and of the VFT Equation (k, A, and T_0) with the Deviations of the Fit (srd) for the Viscosity of EMISE

	A	k	T_0	n_∞	E_a	
equation	mPa·s·K	K	K	mPa·s	kJ·mol^{-1}	srd
VFT	5.5·10^{-3}	945	162			0.0038
Arrhenius				3.1·10^{-4}	−31.3	0.0388

Apparatus and Procedure. Samples were prepared by syringing known masses of the pure liquids, into stoppered bottles, in a inert-atmosphere glove box, using a Mettler AX-205 Delta Range balance with a precision of ± 10^{-5} g. A glovebox was used because the ionic liquid is moisture sensitive.

Densities and speeds of sounds were measured using an Anton Paar DSA-5000 digital vibrating-tube densimeter. The repeatability and the uncertainty in experimental measurement have been found to be lower than (± 2·10^{-6} and ± 1·10^{-5}) g·cm^{-3} for the density and (± 0.01 and ± 0.1) m·s^{-1} for the speed of sound. The DSA 5000 automatically corrects the influence of viscosity on the measured density.

Refractive indices were determined using an automatic refractometer ABBEMAT-WR Dr. Kernchen with a resolution of ± 10^{-6} and an uncertainty in the experimental measurements of ± 4·10^{-5}.

Kinematic viscosities were determined using an automatic viscosimeter Lauda PVS1 with four Ubbelhode capillary microviscosimeters of 0.4·10^{-3} m, 0.53·10^{-3} m, 0.70·10^{-3} m diameter (the uncertainty in experimental measurement is ± 0.006 mPa·s), and 1.26·10^{-3} m diameter (the uncertainty in experimental measurement is ± 0.01 mPa·s). The last capillary viscosimeter is 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 is maintained in a D20KP 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.

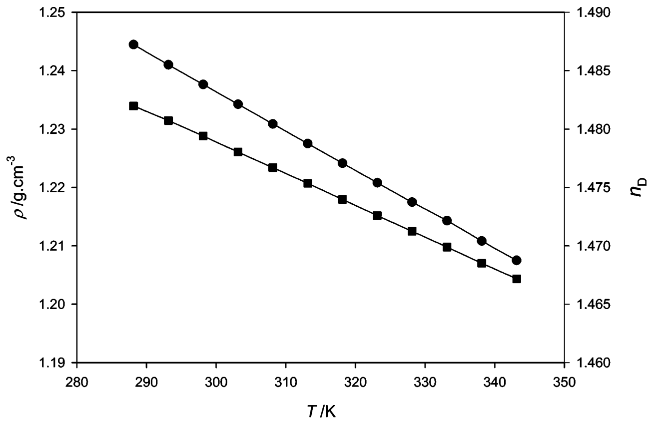

Figure 1. Plot of experimental values of densities (●, ρ) and refractive indices (■, n_D) against temperature and fitted curves for EMISE.

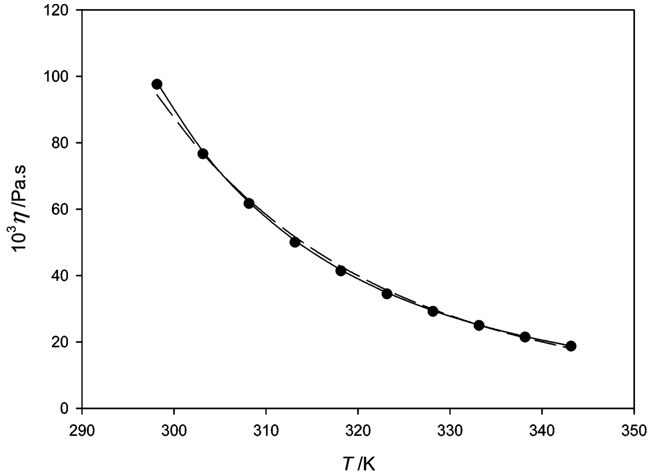

Figure 2. Experimental dynamic viscosities of EMISE as a function of temperature. Lines correspond to the fit of the data —, by eq 4; - - -, by eq 3.

The surface tension of pure liquid was measured with the tensiometer Lauda TVT2 by the hanging drop tensiometer method. The measured tank was thermostatized in a Polyscience controller temperature with a temperature stability of ± 0.01 K, which is regulated in a D20KP Lauda thermostat with a resolution of ± 0.01 K. The equipment has both a control unit and a mechanical one that are connected to a PC-controlled instrument for the precise measurement of surface tension with an uncertainty of ± 0.1 mN·m^{-1}. The radiuses of the needles were calibrated and were credited by the supplier company. The calibration was checked with pure liquids with know surface tension.

Results and Discussion

Pure Components. The physical properties of EMISE were measured experimentally from (288.15 to 343.15) K for the density, speed of sound, and refractive index; from (298.15 to 343.15) K for the dynamic viscosity; and from (288.15 to 313.15) K for the surface tension. The values are summarized in Table 2.

Table 5. Densities ρ, Dynamic Viscosities η, Refractive Indices n_D, Speeds of Sound u, Isentropic Compressibilities k_s, Excess Molar Volumes V^E, Viscosity Deviations $\Delta\eta$, Deviations in the Refractive Index Δn_D, and Deviations in Isentropic Compressibility Δk_s of the Binary Mixture Ethanol (1) + EMISE (2) at Several Temperatures

x_1	ρ / $g \cdot cm^{-3}$	$10^3\eta$ / Pa·s	n_D	u / $m \cdot s^{-1}$	k_s / $T \cdot Pa^{-1}$	V^E / $cm^3 \cdot mol^{-1}$	$10^3\Delta\eta$ / Pa·s	Δn_D	Δk_s / $T \cdot Pa^{-1}$
$T = 298.15$ K									
0.0000	1.23763	97.58	1.47940	1679.0	286.61	0.000	0.000	0.000	0.00
0.0623	1.22890	79.12	1.47717	1669.8	291.85	−0.049	−12.44	0.005	−37.30
0.2300	1.20126	44.93	1.47031	1626.6	314.62	−0.219	−30.45	0.018	−128.95
0.4113	1.16168	22.965	1.46017	1564.0	351.48	−0.464	−34.93	0.030	−215.77
0.5393	1.12363	13.580	1.45018	1506.5	392.16	−0.595	−31.96	0.035	−262.43
0.6788	1.06670	7.224	1.43532	1428.8	459.23	−0.672	−24.85	0.037	−290.59
0.7662	1.01790	4.598	1.42247	1367.2	525.59	−0.629	−19.04	0.034	−283.87
0.8303	0.97300	3.178	1.41052	1315.6	593.79	−0.574	−14.28	0.030	−259.37
0.9554	0.84860	1.573	1.37687	1195.9	823.98	−0.267	−3.811	0.011	−114.57
0.9640	0.83740	1.427	1.37373	1186.2	848.67	−0.218	−3.133	0.009	−95.71
0.9863	0.80610	1.271	1.36514	1160.7	920.86	−0.081	−1.133	0.003	−38.76
1.0000	0.78546	1.082	1.36023	1146.3	968.90	0.000	0.000	0.000	−0.07
$T = 313.15$ K									
0.0000	1.22751	50.01		1641.6	302.29	0.000	0.000		0.00
0.0623	1.21887	42.18		1633.6	307.41	−0.085	−4.766		−43.65
0.2300	1.19117	26.189		1590.1	332.05	−0.308	−12.51		−150.18
0.4113	1.15132	14.716		1527.7	372.14	−0.587	−15.07		−251.88
0.5393	1.11300	8.577		1459.1	422.03	−0.735	−14.91		−302.13
0.6788	1.05570	5.208		1381.0	496.66	−0.825	−11.41		−336.67
0.7662	1.00660	3.413		1318.9	571.09	−0.782	−8.910		−330.62
0.8303	0.9613	2.398		1266.2	648.81	−0.710	−6.776		−303.00
0.9554	0.8362	1.200		1143.3	914.83	−0.361	−1.819		−134.87
0.9640	0.8247	1.095		1132.7	945.01	−0.287	−1.504		−111.37
0.9863	0.7934	0.971		1106.2	1030.08	−0.144	−0.529		−43.77
1.0000	0.7720	0.827		1092.8	1084.57	0.000	0.000		0.00
$T = 328.15$ K									
0.0000	1.21747	29.176		1604.5	319.04	0.000	0.000		0.00
0.0623	1.20877	25.355		1594.8	325.25	−0.101	−2.042		−49.43
0.2300	1.18101	16.839		1551.0	351.96	−0.385	−5.774		−172.34
0.4113	1.14094	10.140		1488.2	395.75	−0.707	−7.301		−290.31
0.5393	1.10230	6.204		1431.1	442.96	−0.871	−7.584		−357.34
0.6788	1.04470	3.934		1350.7	524.68	−0.984	−5.872		−400.16
0.7662	0.99520	2.642		1286.7	606.93	−0.934	−4.669		−395.91
0.8303	0.94960	1.874		1232.2	693.52	−0.854	−3.610		−366.47
0.9554	0.8235	0.941		1102.6	998.85	−0.437	−0.972		−172.81
0.9640	0.8120	0.862		1091.4	1033.95	−0.361	−0.808		−145.34
0.9863	0.7803	0.759		1063.1	1134.05	−0.180	−0.272		−65.18
1.0000	0.7586	0.641		1043.2	1211.45	0.000	0.000		0.00

The density ρ, speed of sound u, refractive index n_D, and surface tension σ values were fitted by the method of least-squares using the following linear equation:

$$z = a + b \cdot (T/K) \tag{1}$$

where z is ρ, u, n_D, or σ; T is the absolute temperature; and a and b are adjustable parameters. The units for a are $g \cdot cm^{-3}$, $m \cdot s^{-1}$, or $mN \cdot m^{-1}$, and the unit of b is K^{-1}. The characteristic parameters a and b are given in Table 3 together with the standard deviation, σ. These properties, density, refractive index, speed of sound, and surface tension decrease as the temperature increases. Figure 1 shows experimental values of densities and refractive indices against temperature.

The variation of the molar volume with temperature can be expressed by the coefficient of thermal expansion, defined as

$$\alpha = 1/V(\partial V/\partial T)_p = -(\partial \ln \rho/\partial T)_p \tag{2}$$

where α is the coefficient of thermal expansion, V is the molar volume of the ionic liquid, and ρ is the density of ionic liquid. The α value is obtained from the slope of the representation of ln ρ against temperature. A value $\alpha = 5 \cdot 10^{-4}$ was obtained.

The viscosity values were fitted using Arrhenius-like law and the Vogel−Fulcher−Tamman (VFT) equations. The most commonly used equation to correlate the variation of viscosity with temperature is the Arrhenius-like law:

$$\eta = \eta_\infty \exp\left(\frac{-E_a}{RT}\right) \tag{3}$$

Viscosity at infinite temperature (η) and the activation energy (E_a) are characteristics parameters generally adjusted from experimental data. According to Seddon et al.,[11] the Arrhenius law can generally be applied when the cation presents only a limited symmetry. If it is not the case, and especially in the presence of symmetrical cations, the VFT equation, an empirical extension of eq 6, is recommended:[12−14]

$$\eta = A \cdot T^{0.5} \exp\left(\frac{k}{(T - T_0)}\right) \tag{4}$$

where A, k, and T_0 are adjustable parameters. Table 4 lists the parameters for both equations with the standard relative deviation (srd):

$$\text{srd} = \left\{ \sum_{i}^{\eta_\infty} \left(\frac{z_{exp} - z_{cal}}{z_{cal}} \right)^2 / (n_{dat} - n_p) \right\}^{1/2} \tag{5}$$

where z_{exp} and z_{cal} are the values of the experimental and

Table 6. Densities ρ, Dynamic Viscosities η, Refractive Indices n_D, Speeds of Sound u, Isentropic Compressibilities k_s, Excess Molar Volumes V^E, Viscosity Deviations $\Delta\eta$, Deviations in the Refractive Index Δn_D, and Deviations in Isentropic Compressibility Δk_s of the Binary Mixture Water (1) + EMISE (2) at Several Temperatures

x_1	ρ / $g\cdot cm^{-3}$	$10^3\eta$ / $Pa\cdot s$	n_D	u / $m\cdot s^{-1}$	k_s / $T\cdot Pa^{-1}$	V^E / $cm^3\cdot mol^{-1}$	$10^3\Delta\eta$ / $Pa\cdot s$	Δn_D	Δk_s / $T\cdot Pa^{-1}$
				$T = 298.15$ K					
0.0000	1.23763	97.58	1.47940	1679.1	286.61	0.000	0.000	0.000	0.00
0.0715	1.23614	82.01	1.47827	1687.0	284.24	−0.037	−8.655	0.009	−13.88
0.2089	1.23272	57.84	1.47600	1696.7	281.78	−0.121	−19.54	0.027	−38.46
0.3227	1.2290	42.89	1.47344	1707.2	279.19	−0.188	−23.49	0.041	−59.38
0.5041	1.2200	24.739	1.46726	1729.0	274.19	−0.294	−24.10	0.062	−93.58
0.5975	1.2129	17.516	1.46243	1741.6	271.82	−0.352	−22.29	0.071	−111.00
0.7441	1.1922	10.576	1.44916	1773.0	266.83	−0.340	−15.05	0.079	−139.59
0.8540	1.1592	5.848	1.42825	1792.6	268.44	−0.273	−9.162	0.074	−155.66
0.9506	1.0844	2.316	1.38383	1709.2	315.66	−0.051	−3.349	0.044	−124.00
1.0000	0.9971	0.890	1.33251	1496.9	447.62	0.000	0.000	0.000	0.00
				$T = 313.15$ K					
0.0000	1.22751	50.01		1641.6	302.29	0.000	0.000		0.00
0.0715	1.22597	43.36		1640.1	303.22	−0.023	−3.122		−8.25
0.2089	1.22253	32.093		1660.8	296.56	−0.095	−7.607		−32.56
0.3227	1.21887	24.756		1671.0	293.82	−0.166	−9.325		−49.92
0.5041	1.20982	15.112		1692.6	288.51	−0.251	−10.02		−78.53
0.5975	1.20243	10.982		1703.9	286.44	−0.281	−9.536		−92.61
0.7441	1.18155	6.715		1734.5	281.32	−0.249	−6.567		−116.56
0.8540	1.14619	3.818		1749.2	285.15	−0.089	−4.042		−126.84
0.9506	1.07610	1.608		1693.1	324.19	−0.008	−1.482		−100.22
1.0000	0.9922	0.653		1529.6	430.75	0.000	0.000		0.00
				$T = 328.15$ K					
0.0000	1.21747	29.176		1604.5	319.04	0.000	0.000		0.00
0.0715	1.21587	25.800		1617.1	314.51	−0.011	−1.326		−12.09
0.2089	1.21240	19.817		1622.1	313.46	−0.072	−3.370		−27.67
0.3227	1.20882	15.800		1631.7	310.70	−0.148	−4.123		−42.47
0.5041	1.19954	10.024		1652.9	305.15	−0.204	−4.699		−67.21
0.5975	1.19202	7.450		1665.9	302.27	−0.223	−4.594		−79.97
0.7441	1.1708	4.622		1695.3	297.20	−0.168	−3.218		−100.55
0.8540	1.1353	2.596		1704.3	303.25	−0.006	−2.095		−106.12
0.9506	1.0669	1.189		1668.1	336.83	0.030	−0.731		−82.76
1.0000	0.9857	0.504		1545.4	424.82	0.000	0.000		0.00

Table 7. Fitting Parameters and Root Mean Square Deviations (smrd) for Ethanol (1) + EMISE (2) and Water (1) + EMISE (2)

	B_0	B_1	B_2	B_3	B_4	smrd
			Ethanol (1) + EMISE (2)			
			$T = 298.15$ K			
$V^E/cm^3\cdot mol^{-1}$	−2.2696	−1.8707	0.0953	−1.1140	−1.8363	0.008
$10^3\ \Delta\eta/Pa\cdot s$	−133.096	57.328	−18.008	14.396	−8.954	0.059
$\Delta k_s/T\cdot Pa^{-1}$	−1002.52	−660.54	−414.12	−525.21	−447.01	1.19
Δn_D	0.1348	0.0756	0.0467	0.0252	0.0013	$1.5\cdot 10^{-4}$
			$T = 313.15$ K			
$V^E/cm^3\cdot mol^{-1}$	−2.8298	−2.0184	0.1575	−1.7835	−3.1552	0.014
$10^3\ \Delta\eta/Pa\cdot s$	−60.173	17.188	4.171	6.150	−10.543	0.135
$\Delta k_s/T\cdot Pa^{-1}$	−1155.32	−790.02	−472.63	−603.30	−561.33	2.19
			$T = 328.15$ K			
$V^E/cm^3\cdot mol^{-1}$	−3.3739	−2.2260	−0.0167	−2.5308	−3.7024	0.018
$10^3\ \Delta\eta/Pa\cdot s$	−30.068	5.010	4.800	2.388	−5.401	0.098
$\Delta k_s/T\cdot Pa^{-1}$	−1363.46	−905.35	−507.88	−957.39	−969.08	3.25
			Water (1) + EMISE (2)			
			$T = 298.15$ K			
$V^E/cm^3\cdot mol^{-1}$	−1.1585	−1.3068	−1.1589	0.8021	1.6604	0.013
$10^3\ \Delta\eta/Pa\cdot s$	−97.494	31.556	7.923	7.091	−17.981	0.203
$\Delta k_s/T\cdot Pa^{-1}$	−389.44	−214.04	4.69	−1177.90	−1486.92	5.57
Δn_D	0.2491	0.1774	0.1139	0.2931	0.2864	$8.8\cdot 10^{-4}$
			$T = 313.15$ K			
$V^E/cm^3\cdot mol^{-1}$	−1.0102	−0.9247	−0.1085	1.3694	1.5530	0.008
$10^3\ \Delta\eta/Pa\cdot s$	−40.582	8.572	4.801	2.636	−4.705	0.118
$\Delta k_s/T\cdot Pa^{-1}$	−325.12	−176.05	−38.71	−975.66	−1084.71	4.82
			$T = 328.15$ K			
$V^E/cm^3\cdot mol^{-1}$	−0.8428	−0.5899	0.3040	1.3915	1.6254	0.011
$10^3\ \Delta\eta/Pa\cdot s$	−18.968	1.495	2.599	2.219	−2.363	0.079
$\Delta k_s/T\cdot Pa^{-1}$	−278.34	−185.73	−26.33	−699.74	−954.66	3.82

calculated property, n_{dat} is the number of experimental data, and n_p is the number of parameters.

Figure 2 shows the viscosity against temperature. As it can be observed in, the viscosity decreases as the temperature increases, and the viscosity of pure EMISE is 1 or 2 orders of magnitude greater than that of traditional organic solvents. As it can be observed in Table 4, for viscosity the better fitting is given by VFT, where the correlated values are in good agreement with the experimental data.

Binary Systems. Densities, dynamic viscosities, speeds of sound, isentropic compressibilities, excess molar volumes, viscosity deviations, and deviations in isentropic compressibility of the binary mixtures ethanol (1) + EMISE (2) and water (1) + EMISE (2) at temperatures of (298.15, 313.15, and 328.15) K and refractive indices and deviations in the refractive indices at 298.15 K and atmospheric pressure are listed in Tables 5 and 6.

From speed of sound experimental data, the volume-intensive k_s and the mole-intensive $k_{s,m}$ can be calculated. [15−17] This mole-intensive quantity $k_{s,m}$ depends on the heat capacities C_p of the pure components. Since, to our knowledge, no heat capacity of EMISE has been published earlier, we have determined the k_s by means of the Laplace equation, $k_s = \rho^{-1} \cdot u^{-2}$.

The excess molar volumes, viscosity deviations, deviations in the refractive index, and deviations in isentropic compressibility were calculated from experimental values as follows:

$$V^{E} = \sum_{i=1}^{N} x_i M_i(\rho^{-1} - \rho_i^{-1}) \tag{6}$$

$$\Delta\eta = \eta - \sum_{i}^{N} x_i \eta_i \tag{7}$$

$$\Delta n_D = n_D - \sum_{i}^{N} x_i n_{D,i} \tag{8}$$

$$\Delta k_s = k_s - \sum_{i}^{N} x_i k_{s,i} \tag{9}$$

where ρ and ρ_i are the density of the mixture and the density of the pure components, respectively; x_i represents the mole fraction of the i component; η and η_i are the dynamic viscosity of the mixture and the pure components, respectively, k_s is the isentropic compressibility of the mixture, and $k_{s,i}$ is the isentropic compressibility of the pure components, and n_D and $n_{D,i}$ are the refractive index of the mixture and the refractive index of the pure components, respectively.

The binary deviations at several temperatures were fitted to a Redlich−Kister[18] type equation:

$$\Delta Q_{ij} = x_i x_j \sum_{p=0}^{M} B_p (x_i - x_j)^p \tag{10}$$

where ΔQ_{ij} is the excess property, x is the mole fraction, B_p is the fitting parameter, and M is the degree of the polynomic expansion, which was optimized using the F-test.[19] The fitting parameters are given in Table 7 together with the root mean square deviations (rmsd). They are calculated from the values of the experimental and calculated property and the number of experimental data, represented by z_{exp}, z_{calc}, and n_{dat}, respectively:

$$\text{rmsd} = \{\sum_{i}^{n_\infty} (z_{exp} - z_{calc})^2 / n_{dat}\}^{1/2} \tag{11}$$

Figures 3 and 4 show the fitted curves as well as experimental excess molar volume and viscosity deviations values for binary mixtures: ethanol (1) + EMISE (2) and water (1) + EMISE (2) at T = (298.15, 313.15, and 328.15) K. In Figure 3 we can observe that the excess molar volumes present a minimum at $x \approx 0.7$ for the two systems and the water + EMISE system presents a maximum at $x \approx 0.95$. The minimum and the maximum increase when temperature increases; 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.[20] The minimum can be due to hydrogen bonds between water and ionic liquid. At higher concentration of water, in the water (1) + EMISE (2) system we can observe a maximum that can be due to the dissociation of the ion pairs forming the ionic liquids. This behavior agrees with the study made by Miki et al.[21] In Figure 4, for viscosity deviations, the sign is negative for the two binary systems, and the minima lie at a mole fraction of approximately 0.4 for ethanol (1) + EMISE (2) and at a 0.5 for water (1) + EMISE (2). The viscosity deviations decrease as the temperature increases; this behavior is similar for both systems.

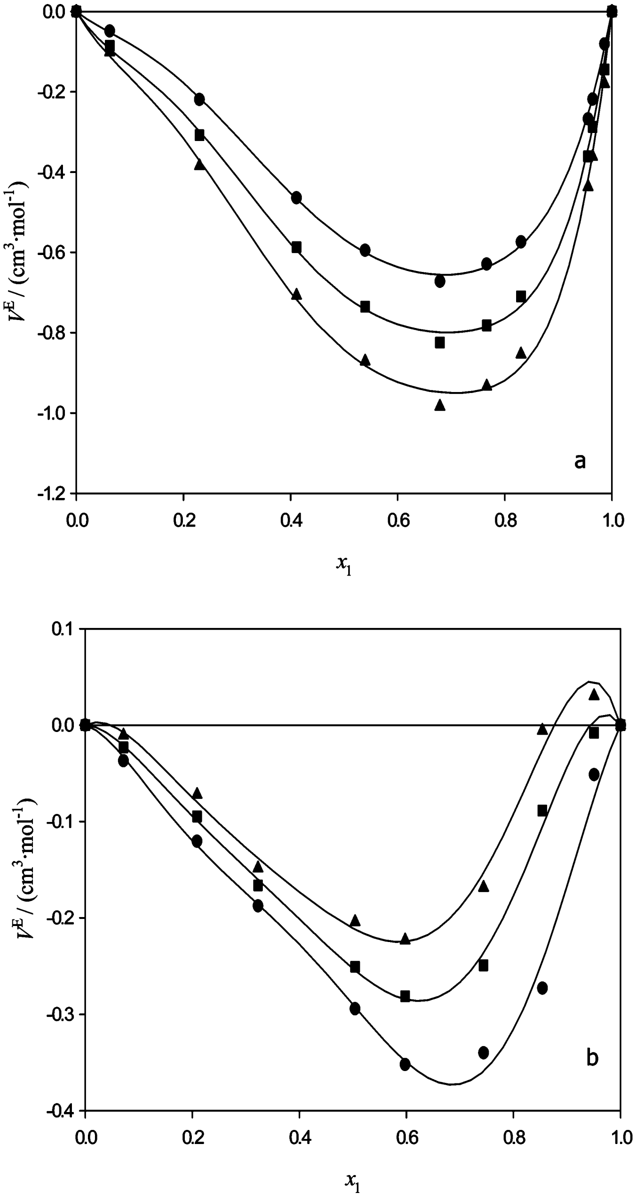

Figure 3. Excess molar volumes, V^E, from the Redlich−Kister equation plotted against mole fraction at ●, T = 298.15 K; ■, T = 313.15 K; and ▲, T = 328.15 K for the binary mixtures: (a) ethanol (1) + EMISE (2) and (b) water (1) + EMISE (2).

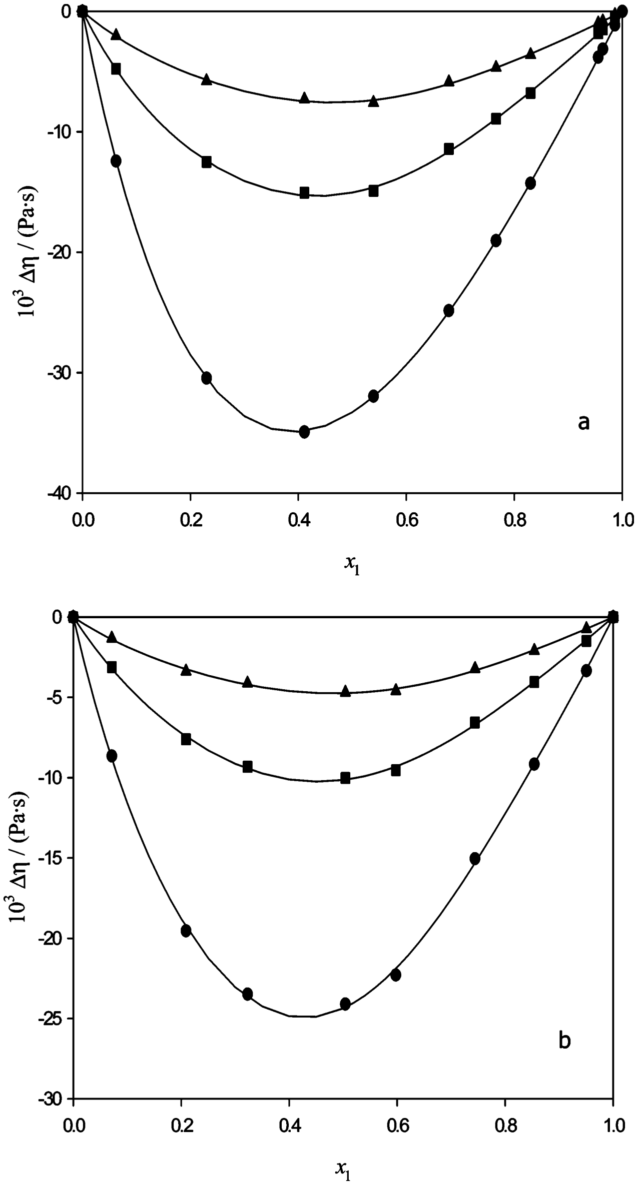

Figure 4. Viscosity deviations, $\Delta\eta$, from the Redlich−Kister equation plotted against mole fraction at ●, $T = 298.15$ K; ■, $T = 313.15$ K; and ▲, $T = 328.15$ K for the binary mixtures: (a) ethanol (1) + EMISE (2) and (b) water (1) + EMISE (2).

Conclusions

In this paper we present values of density, speed of sound, refractive index, dynamic viscosity, and surface tension at several temperatures of pure EMISE. It can be seen that the density and the refractive index decrease linearly with the temperature. The viscosity decreases as the temperature increases.

Density, dynamic viscosity, speed of sound, and isentropic compressibility of the binary systems ethanol (1) + EMISE (2) and water (1) + EMISE (2) at $T = (298.15, 313.15, \text{and } 328.15)$ K and atmospheric pressure, over the whole composition range, have been determined. The excess molar volumes, viscosity deviations, and deviations in isentropic compressibility for these binary systems were determined from experimental data. These data were fitted to Redlich−Kister equation to test the quality of the experimental values.

The calculated excess molar volumes are negative over the whole composition range for the ethanol (1) + EMISE (2) system and negative for the binary water (1) + EMISE (2) system except for large concentrations of water at 298.15 and 313.15 K. The viscosity deviations are negative, while deviations in the refractive index are positive for both binary systems over the whole composition range. Refractive indices were determined at 298.15 K for the two studied binary systems. Deviations in the refractive index were calculated from these experimental data.

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