J. Chem. Eng. Data **2007,** *52,* 2359−2364 **2359**

Viscosity, Density, Speed of Sound, and Refractive Index of Binary Mixtures of Organic Solvent + Ionic Liquid, 1-Butyl-3-methylimidazolium Hexafluorophosphate at 298.15 K

Mohammed Taghi Zafarani-Moattar* and Roghayeh Majdan-Cegincara

Physical Chemistry Department, Faculty of Chemistry (Excellence of Science for New Materials and Clean Chemistry)
University of Tabriz, Tabriz, Iran

The viscosity and refractive index of the solutions of room-temperature ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF_6] in tetrahydrofuran, dimethylsulfoxide, methanol, and acetonitrile have been measured at 298.15 K. The density and speed of sound for solutions of [BMIM][PF_6] + tetrahydrofuran or dimethylsulfoxide have also been measured. The changes in viscosity and molar refraction, the excess molar volume, and deviation in isentropic compressibility have been adequately fitted to the Redlich−Kister polynomial.

Introduction

Ionic liquids (ILs) are a group of organic salts that result from the combination of several organic cations and inorganic or organic anions, and they may be liquid at room temperature. Ils have been called designer solvents due to their ability to vary the ions, thereby modifying and optimizing the ionic liquid physical properties for a specific task. For this reason, a great number of applications are now being demonstrated for ionic liquids as catalysts, reactions media, and electrolytes in electrochemistry; in fuel and solar cells; as a stationary phase for chromatography; as matrices for mass spectrometry; as support for the immobilization of enzymes in separation technologies; as liquid crystals or templates for the synthesis of mesoporous, nanomaterials and ordered films; etc. The most commonly studied ILs contain the imidazolium cation with varying heteroatom functionality. The 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) is historically the important and the most commonly investigated ionic liquid. Thermodynamic functions such as heat capacity, enthalpy changes, and densities for [BMIM][PF_6] have been reported at different temperatures.[1,2] Its solubility in aromatic hydrocarbons and alkanes have been performed by a dynamic method.[3] Density and excess volumes of binary mixtures of [BMIM][PF_6] with benzyl alcohol or benzaldehyde have been determined at different temperatures.[4] Pereiro and Rodriguez[5] have determined densities, speed of sounds, and refractive index of the binary mixtures of [BMIM][PF_6] with 2-butanone, ethylacetate, and 2-propanol. Recently, we reported the volumetric and speed of sound of [BMIM][PF_6] with acetonitrile and methanol.[6] Also, we presented the density and speed of sound data for [BMIM]-[PF_6] in some organic solvents (methanol (MeOH), acetonitrile (MeCN), tetrahydrofuran (THF), *N*,*N*-dimethylacetamide, and dimethylsulfoxide (DMSO) in a dilute region.[7]

In the present work, the viscosity and refractive index of the solutions of [BMIM][PF_6] in MeOH, MeCN, THF, and DMSO have been measured over the entire composition range at 298.15 K from which the deviation in viscosity and deviation in molar refraction values have been calculated. We also report the density and speed of sound measurements on mixtures of [BMIM][PF_6] with THF and DMSO over the entire composition range at 298.15 K from which the excess molar volume and deviation in isentropic compressibility values have been calculated. These values have been fitted to the Redlich−Kister polynomial.

Table 1. Density, *d*, Speed of Sound, *u*, Dynamic Viscosity, *η*, and Refractive Index, n_D for Pure Components at T = 298.15 K

component	$10^{-3}\cdot d$ ($kg\cdot m^{-3}$)	u ($m\cdot s^{-1}$)	η (mPa·s)	n_D
THF	0.882008	1278.24	0.449	1.4050
	0.881996[7]	1278.49[7]	0.460[24]	1.40496[25]
	0.88072[26]	1277.9[27]		
	0.88201[28]			
	0.88198[29]			
DMSO	1.095295	1484.98	1.961	1.4769
	1.095271[7]	1485.12[7]	1.974[30]	1.4773[31]
	1.0972[32]	1489.2[33]		
MeOH	0.786654	1102.92	0.540	1.3269
	0.786531[6]	1102.68[6]	0.553[34]	1.3266[35]
MeCN	0.776565	1278.70	0.339	1.3419
	0.776533[6]	1278.62[6]	0.345[36]	1.34110[37]
[BMIM][PF_6]	1.366066	1443.54	212.10	1.4095
	1.366657[6]	1442.41[6]	207 ± 11.12[38]	1.40937[5]
	1.36595[2]	1443[5]		
	1.36600[39]			

Experimental Section

Materials. [BMIM][PF_6] was obtained from Solvent Innovation Co. (Köln, Germany) with minimum mass fraction purity of 0.98. It was used after being vacuum desiccated for at least 24 h to remove trace amounts of water. The sample was analyzed by Karl Fisher titration and showed a mass % of water lower than 10^{-4} using a titrator (751 GPD Titrino, Metrohm, Switzerland). MeOH (minimum mass fraction purity 0.999), MeCN (minimum mass fraction purity 0.999), THF (minimum mass fraction purity 0.995), and DMSO (minimum mass fraction purity 0.998) were obtained from Merck and used without further purification. During the course of the experiments, the purity of the ionic liquid and solvents was monitored by comparison of density measurements of pure components with the literature data.

---

* Corresponding author. E-mail: zafarani47@yahoo.com. Fax: +98 411 3340191.

10.1021/je700338t CCC: $37.00

Table 2. Dynamic Viscosities, η, Deviations in Viscosity, $\Delta\eta$, Refractive Indexes, n_D, Molar Refractions, R_m, and Deviations in Molar Refractions, ΔR, of Binary Mixtures Containing Organic Solvents + [BMIM][PF$_6$] at 298.15 K

x_2	η (mPa·s)	$\Delta\eta$ (mPa·s)	n_D	R_m ($m^3·mol^{-1}$)	$10^6·\Delta R$ ($m^3·mol^{-1}$)	x_2	η (mPa·s)	$\Delta\eta$ (mPa·s)	n_D	R_m ($m^3·mol^{-1}$)	$10^6·\Delta R$ ($m^3·mol^{-1}$)
		THF(1) + [BMIM][PF$_6$](2)						MeOH(1) + [BMIM][PF$_6$](2)			
0.0502	0.750	−10.332	1.4084	21.468	−2.302	0.0503	0.913	−10.258	1.3480	10.389	−7.051
0.0967	1.140	−19.784	1.4117	22.930	−3.844	0.0993	1.483	−20.058	1.3636	12.580	−11.234
0.1524	1.732	−30.971	1.4125	24.593	−5.317	0.1517	2.331	−30.312	1.3710	14.766	−14.120
0.1999	2.476	−40.294	1.4126	26.039	−6.224	0.1969	3.059	−39.138	1.3768	16.690	−15.592
0.2969	4.937	−58.344	1.4130	29.079	−7.246	0.3024	6.057	−58.462	1.3872	21.253	−16.775
0.3484	6.979	−67.219	1.4128	30.703	−7.462	0.3531	8.072	−67.170	1.3892	23.373	−16.696
0.3994	10.065	−74.917	1.4127	32.315	−7.489	0.4106	11.027	−76.381	1.3941	25.955	−16.044
0.4484	14.539	−80.813	1.4126	33.869	−7.371	0.4510	13.523	−82.424	1.3961	27.707	−15.454
0.5028	18.503	−88.364	1.4117	35.532	−7.153	0.5020	17.293	−89.450	1.3986	29.943	−14.508
0.6047	33.632	−94.796	1.4115	38.797	−6.260	0.6015	27.411	−100.388	1.4015	34.225	−12.296
0.7016	52.844	−96.107	1.4110	41.928	−5.054	0.7082	45.953	−104.410	1.4045	38.861	−9.396
0.8050	90.817	−80.019	1.4105	45.281	−3.473	0.7989	66.789	−102.766	1.4066	42.809	−6.646
0.9595	186.856	−16.674	1.4095	50.183	−0.790	0.8889	107.939	−80.655	1.4078	46.668	−3.785
		DMSO(1) + [BMIM][PF$_6$](2)						MeCN(1) + [BMIM][PF$_6$](2)			
0.0500	2.749	−9.721	1.4676	21.707	−2.616	0.0496	0.556	−10.281	1.3575	13.085	−4.923
0.0997	3.698	−19.211	1.4606	23.284	−4.515	0.1016	0.864	−20.989	1.3687	15.187	−8.375
0.1477	4.962	−28.046	1.4546	24.798	−5.874	0.1470	1.187	−30.292	1.3754	16.993	−10.451
0.1977	6.489	−37.010	1.4491	26.366	−6.887	0.2022	1.866	−41.282	1.3819	19.223	−12.06
0.2995	11.954	−52.939	1.4396	29.536	−8.004	0.2995	3.792	−59.979	1.3902	23.190	−13.255
0.3524	15.998	−60.007	1.4361	31.221	−8.151	0.3524	5.308	−69.649	1.3934	25.333	−13.308
0.3997	21.172	−64.793	1.4331	32.719	−8.117	0.4036	7.674	−78.136	1.3959	27.402	−13.070
0.4328	24.610	−68.293	1.4309	33.745	−8.027	0.4337	9.153	−83.023	1.3974	28.631	−12.804
0.5018	36.976	−70.444	1.4278	35.957	−7.572	0.4955	14.443	−90.834	1.3998	31.128	−12.065
0.5980	56.306	−71.317	1.4226	38.915	−6.701	0.5892	23.841	−101.269	1.4024	34.892	−10.522
0.7043	83.729	−66.229	1.4182	42.222	−5.319	0.6857	40.692	−104.855	1.4048	38.799	−8.480
0.7812	117.542	−48.582	1.4158	44.655	−4.086	0.8046	81.532	−89.185	1.4068	43.576	−5.565
0.8930	173.317	−16.298	1.4125	48.150	−2.099	0.8055	86.271	−84.650	1.4069	43.622	−5.532
						0.9176	154.061	−40.601	1.4084	48.137	−2.448

Table 3. Density, d, Excess Molar Volume, V_m^E, Speed of Sound, u, Isentropic Compressibility, κ_s, and Isentropic Compressibility Deviation, $\Delta\kappa_s$, of Binary Mixtures Containing Organic Solvents + [BMIM][PF$_6$] at 298.15 K

x_2	$10^{-3}·d$ ($kg·m^{-3}$)	$10^6 V_m^E$ ($m^3·mol^{-1}$)	u ($m·s^{-1}$)	$10^{12}·\kappa_s$ (Pa^{-1})	$10^{12}·\Delta\kappa_s$ (Pa^{-1})
		THF(1) + [BMIM][PF$_6$](2)			
0.0199	0.911565	−0.537	1279.16	670.444	−16.656
0.0376	0.936570	−0.994	1279.92	651.770	−29.249
0.0737	0.979097	−1.447	1287.89	615.767	−52.879
0.1500	1.055633	−2.257	1312.64	549.789	−92.744
0.2003	1.095843	−2.485	1329.15	516.540	−108.754
0.2486	1.129411	−2.618	1343.72	490.377	−118.343
0.3004	1.159966	−2.605	1357.31	467.947	−123.057
0.3491	1.185700	−2.585	1368.62	450.256	−124.058
0.4634	1.235907	−2.410	1390.52	418.466	−116.675
0.5808	1.276688	−2.137	1406.94	395.698	−99.223
0.6941	1.306088	−1.491	1418.73	380.389	−75.725
0.7996	1.329247	−0.906	1427.83	369.013	−50.948
0.8991	1.348144	−0.367	1435.73	359.847	−26.031
		DMSO(1) + [BMIM][PF$_6$](2)			
0.0011	1.096211	−0.003	1484.84	413.758	−0.199
0.0024	1.097258	−0.006	1484.88	413.341	−0.536
0.0187	1.109730	−0.011	1483.45	409.484	−3.368
0.0321	1.119442	−0.017	1482.37	406.523	−5.488
0.0552	1.135088	−0.027	1480.53	401.917	−8.648
0.0635	1.140411	−0.028	1479.89	400.387	−9.654
0.0996	1.161891	−0.041	1477.26	394.385	−13.393
0.1530	1.189469	−0.058	1473.65	387.131	−17.297
0.2381	1.225522	−0.094	1469.37	377.935	−21.154
0.3372	1.258279	−0.115	1464.46	370.568	−22.303
0.5586	1.309441	−0.125	1454.94	360.765	−18.222
0.7791	1.342894	−0.108	1448.17	355.074	−10.075
0.9250	1.359297	−0.081	1444.74	352.457	−3.541

Apparatus and Procedure. The viscosity was determined by Setavis Kinematic Viscometer-83541−3, England. Six Ubbelohde viscometers were used in the experiments according to the different viscosity values for the mixtures. Flow time measurements were made with a Setavis six-channel quartz timer-83550-3 with a resolution of 0.01 s. The bath temperature is controlled at any chosen temperature with uncertainty of 0.01 K by a solid-state device with digital temperature display. The viscosity measurements were repeated at least three times for each sample. The dynamic viscosity of solution, η, was calculated with the equation

$$\eta = dK(t - \gamma) \tag{1}$$

where t is the flow time, K is the viscometer constants, γ is the Hagenbach correction factor, and d is the density. The uncertainty for the dynamic viscosity determination was estimated to be ± 0.5 % (mPa·s). The necessary density values were calculated from the fitted polynomial equations using the experimental d values of the Table 3 and ref 6.

Refractive index measurements were made by using a refractometer (Quartz RS-232, Ceti, Belgium) with an uncertainty of ± 0.0001. The temperature of the refractometer was controlled with water from a large well-regulated water bath to within ± 0.01 K using a thermostat (Hetotherm PF, Heto Lab Equipment, Denmark).

Density and speed of sound data were continuously measured using a commercial density and speed of sound measurement apparatus (Anton Paar DSA 5000 densimeter and speed of sound analyzer). Details of the experimental setup and measuring procedure have been given elsewhere.[8] The temperature was automatically kept constant within uncertainty ± 0.001 K. In each measurement, the uncertainty of density and speed of sound were ± $3.0·10^{-6}$ $g·cm^{-3}$ and ± 0.5 $m·s^{-1}$, respectively.

The solutions were prepared by mass using an analytical balance (Shimatzu, 321−34553, Shimatzu Co., Japan) with an uncertainty of ± $1·10^{-7}$ kg. Solutions of [BMIM][PF$_6$] for measurements were prepared by weighing the ionic liquid in sealed vials. All the solutions were kept tightly sealed to minimize adsorption of atmospheric moisture. The sample is

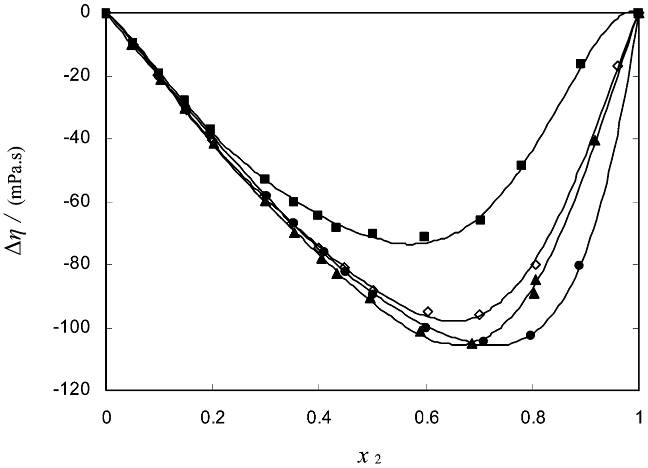

Figure 1. Experimental and calculated viscosity deviation data, $\Delta\eta$, plotted against mole fraction of [BMIM][PF$_6$], x_2, for the organic solvent + [BMIM][PF$_6$] systems: ◇, THF; ■, DMSO; ●, MeOH; ▲, MeCN; —, Redlich−Kister equation.

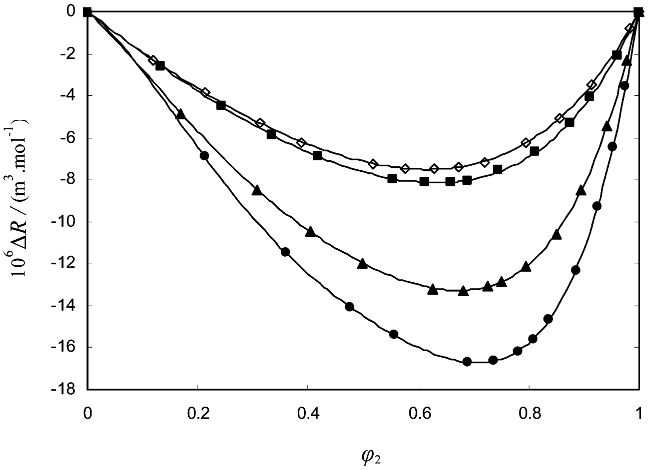

Figure 2. Experimental and calculated deviation in molar refraction, ΔR, plotted against volume fraction of [BMIM][PF$_6$], φ_2, for the organic solvent + [BMIM][PF$_6$] systems: ◇, THF; ■, DMSO; ●, MeOH; ▲, MeCN; —, Redlich−Kister equation.

taken from the vial with the syringe through a silicon septum and is immediately put into the apparatus.

Viscosity, refractive index, density, and speed of sound values of the pure components are given in Table 1 at 298.15 K and compared with the literature values.

Results and Discussion

The experimental dynamic viscosity, η, deviation in viscosity, $\Delta\eta$, refractive index, n_D, molar refraction, R_m, and deviation in molar refraction, ΔR, values for the organic solvents (1) + [BMIM][PF$_6$] (2) of the studied systems, as a function of [BMIM][PF$_6$] mole fraction, x_2, at 298.15 K are presented in Table 2.

The viscosity deviation, $\Delta\eta$, was calculated from the definition

$$\Delta\eta = \eta - \sum_{i=1}^{2} x_i\eta_i \qquad (2)$$

where η, x_i, and η_i are the viscosity of the mixture, mole fraction, and viscosities of pure component i, respectively; subscript i = 1 is for THF, DMSO, MeOH, and MeCN, and i = 2 is for the [BMIM][PF$_6$].

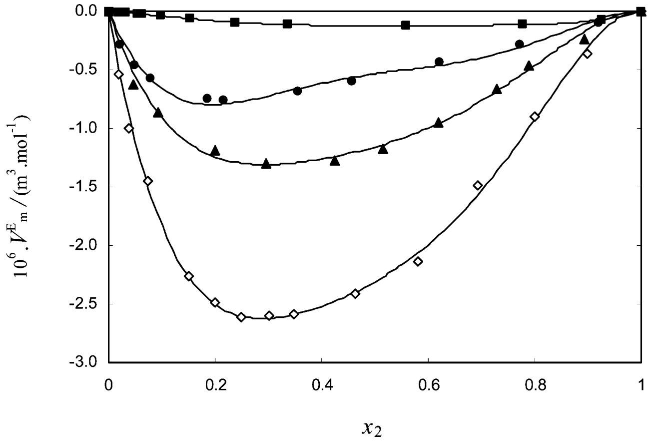

Figure 3. Experimental and calculated excess molar volume, V^E_m, plotted against the mole fraction of [BMIM][PF$_6$], x_2, for the organic solvent + [BMIM][PF$_6$] systems: ◇, THF; ■, DMSO; ●, MeOH taken from ref 6; ▲, MeCN taken from ref 6; —, Redlich−Kister equation.

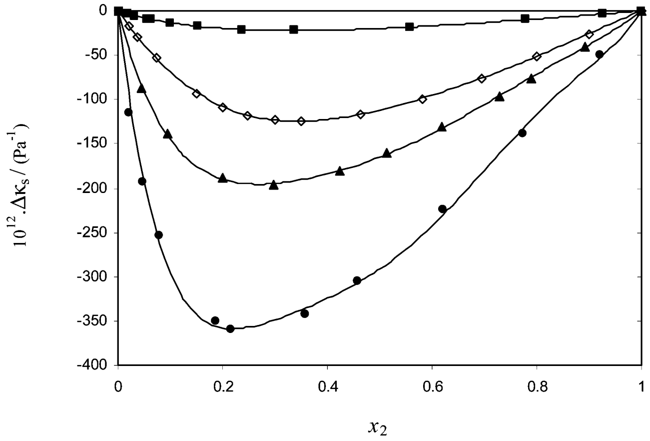

Figure 4. Experimental and calculated isentropic compressibility deviation, $\Delta\kappa_s$, plotted against mole fraction of [BMIM][PF$_6$], x_2, for the organic solvent + [BMIM][PF$_6$] systems: ◇, THF; ■, DMSO; ●, MeOH taken from ref 6; ▲, MeCN taken from ref 6; —, Redlich−Kister equation.

The deviations in viscosity for the studied mixtures have been plotted versus the mole fraction of [BMIM][PF$_6$] in Figure 1. It can be seen that $\Delta\eta$ has negative and large values. The negative values of viscosity deviations for the binary systems investigated suggest that the viscosities of associates formed between unlike molecules are relatively less than those of the pure component. The relation between $\Delta\eta$ values and both the energy and the extent of H-bonds in liquid mixtures has been reported.[9] It was shown that $\Delta\eta$ decreases as the number and strength of H-bonds are decreased.[9] Poole[10] indicated greater H-bond in the ionic liquids than typical polar nonionic solvents. The negative $\Delta\eta$ values obtained for the investigated organic solvents + [BMIM][PF$_6$] suggest that there may be reduction in the number and strength of H-bonds upon mixing. It should be noted that the negative viscosity deviation may also occur where dispersion forces are dominated particularly for the systems having different molecular sizes.[11]

The deviation in molar refraction, ΔR, was calculated from the equation

$$\Delta R = R_m - \sum_{i=1}^{2} R_i\varphi_i \qquad (3)$$

Table 4. Parameters of Redlich−Kister Polynomial, Eq 10, along with Standard Deviations, $\sigma(Q_{ij})$, of Binary Mixtures Containing Organic Solvents + [BMIM][PF$_6$] at 298.15 K

function	A_0	A_1	A_2	A_3	A_4	$\sigma(Q_{ij})^a$
THF(1) + [BMIM][PF$_6$](2)						
$\Delta\eta/(\mathrm{mPa \cdot s})$	−349.522	−236.436	−161.046	98.145	221.416	0.919
$10^6 \cdot \Delta R/(\mathrm{m^3 \cdot mol^{-1}})$	−28.548	−12.360	−6.054	−2.016		0.021
$10^6 \cdot V_m^E/(\mathrm{m^3 \cdot mol^{-1}})$	−9.243	5.138	−4.108	8.525		0.047
$10^{12} \cdot \Delta k_s/(\mathrm{Pa^{-1}})$	−446.671	287.001	−172.252	24.579	80.961	0.531
DMSO(1) + [BMIM][PF$_6$](2)						
$\Delta\eta/(\mathrm{mPa.s})$	−286.013	−102.082	−13.434	204.087	262.244	0.967
$10^6 \cdot \Delta R/(\mathrm{m^3 \cdot mol^{-1}})$	−30.503	−14.604	−8.391	−4.775		0.025
$10^6 \cdot V_m^E/(\mathrm{m^3 \cdot mol^{-1}})$	−0.484	0.024	−0.361	−0.521		0.004
$10^{12} \cdot \Delta k_s/(\mathrm{Pa^{-1}})$	−79.806	49.743	−24.657	17.276	−13.880	0.093
MeOH(1) + [BMIM][PF$_6$](2)						
$\Delta\eta/(\mathrm{mPa.s})$	−355.907	−246.204	−184.066	−221.167	−150.880	0.434
$10^6 \cdot \Delta R/(\mathrm{m^3 \cdot mol^{-1}})$	−57.994	−35.186	−32.159	−37.022		0.143
MeCN(1) + [BMIM][PF$_6$](2)						
$\Delta\eta/(\mathrm{mPa.s})$	−368.252	−279.328	−183.343	113.155	230.313	1.020
$10^6 \cdot \Delta R/(\mathrm{m^3 \cdot mol^{-1}})$	−47.966	−26.505	−20.680	−18.023		0.066

[a] $\sigma(Q_{ij}) = \sqrt{\sum_{k=1}^{N}(Q_{ij\mathrm{cal}} - Q_{ij\mathrm{exp}})^2/N}$

where R_i and R_m are the molar refractions of pure components and of the mixture, respectively, and φ_i is the volume fraction of the ith component, given as

$$\varphi_i = x_i V_i \Big/ \sum_{i=1}^{2} x_i V_i \tag{4}$$

where $V_i = M_i/d_i$.

The molar refraction, R_i, was obtained from the Lorentz−Lorenz relation[12]

$$R_i = [(n_{D(i)}{}^2 - 1)/(n_{D(i)}{}^2 + 1)]V_i \tag{5}$$

where $n_{D(i)}$ is the refractive index for the pure ith component.

The equation for a binary mixture becomes

$$R_m = [(n_{D(m)}{}^2 - 1)/(n_{D(m)}{}^2 + 1)]V_m \tag{6}$$

where $n_{D(m)}$ is the refractive index of the mixture, $V_m = (x_1M_1 + x_2M_2)/d$.

The deviation in molar refraction for the systems investigated as a function of [BMIM][PF$_6$] volume fraction, φ_i, is shown in Figure 2. It can be seen that ΔR has negative and large values due to the big difference in sizes between ionic liquid and organic solvents investigated.

The experimental density, d, excess molar volume, V_m^E, speed of sound, u, isentropic compressibility, κ_s, and isentropic compressibility deviation, $\Delta\kappa_s$, data for THF + [BMIM][PF$_6$] and DMSO + [BMIM][PF$_6$] systems, as a function of [BMIM][PF$_6$] mole fraction, x_2, at 298.15 K are collected in Table 3.

Values of V_m^E were calculated by the following equation:

$$V_m^E = \sum_{j=1}^{2} x_j M_j \left[\frac{1}{d} - \frac{1}{d_j}\right] \tag{7}$$

where M_j, d_j, and d are molar mass of the components, densities of pure component, and densities of mixtures, respectively, and subscript $j = 1$ is for the THF or DMSO, and $j = 2$ is for the [BMIM][PF$_6$]. The V_m^E for THF + [BMIM][PF$_6$] and DMSO + [BMIM][PF$_6$] systems together with the V_m^E values for MeOH + [BMIM][PF$_6$] and MeCN + [BMIM][PF$_6$] systems taken from our previous work[6] have been plotted versus the mole fraction of [BMIM][PF$_6$], x_2, in Figure 3. As can be seen from Table 3 and Figure 3, the values of V_m^E are negative for all of these systems studied. A minimum in V_m^E is reached with mole fraction of this ionic liquid near to 0.25, 0.22, and 0.3 for THF + [BMIM][PF$_6$], MeOH + [BMIM][PF$_6$] and MeCN + [BMIM][PF$_6$] systems, respectively. The negative excess molar volumes indicate that a more efficient packing and/or attractive interaction occurred when the ionic liquid and organic molecular liquids were mixed. The similar phenomenon has been observed for [BMIM][PF$_6$] + benzyl alcohol and [BMIM][PF$_6$] + benzaldehyde systems by Zhong, et al.[4]

Table 5. Parameters of Eq 11 along with Standard Deviations, $\sigma(\eta)$, of Binary Mixtures Containing Organic Solvents + [BMIM][PF$_6$] at 298.15 K

systems	A	$\sigma(\eta)/(\mathrm{mPa \cdot s})$
THF + [BMIM][PF$_6$]	0.216	3.760
DMSO + [BMIM][PF$_6$]	0.299	9.582
MeOH + [BMIM][PF$_6$]	0.182	2.886
MeCN + [BMIM][PF$_6$]	0.203	4.304

On the other hand, Holbrey and Seddon[13] found that ionic liquid (including [BMIM][PF$_6$] and [BMIM][BF$_4$]) exhibited liquid clathrate formation in tricholoromethane with a ratio of ionic liquid/CHCl$_3$ = 1:3. Rogers and co-workers[14] reported the formation of liquid clathrates with various ratios in (ionic liquid + aromatic mixtures). Wang et al.[15] and Zhong et al.[4] suggested that quasiclathrates were probably formed in the mixtures of [BMIM][PF$_6$] + organic components. They addressed the issue that at least an unusual structure appeared in the vicinity of this particular composition of the mixtures ($x \approx 0.3$). The quasiclathrates are probably also formed in the mixtures of [BMIM][PF$_6$] + organic liquids studied in this work from which a minimum in V_m^E is reached with the mole fraction of this ionic liquid near to 0.3. However, in the case of DMSO solutions no minimum for excess molar volume is observed from Figure 3.

Through the use of the speed of sound and density data, the isentropic compressibilities (κ_s) were calculated from the Laplace−Newton equation

$$\kappa_s = \frac{1}{du^2} \tag{8}$$

The experimental isentropic compressibility deviations ($\Delta\kappa_s$) are obtained using the relation

$$\Delta\kappa_s = \kappa_s - (\sum_j^2 x_j\kappa_{sj}) \tag{9}$$

where κ_{sj} is the value of isentropic compressibility of pure component j. The experimental $\Delta\kappa_s$ values for the THF + [BMIM][PF$_6$] and DMSO + [BMIM][PF$_6$] together with the $\Delta\kappa_s$ values for MeOH + [BMIM][PF$_6$] and MeCN + [BMIM][PF$_6$] systems[6] are represented in Figure 4. As can be seen from Table 3 and Figure 4, the values of $\Delta\kappa_s$ are negative for all of these systems. The behavior of isentropic compressibility deviation, $\Delta\kappa_s$, implies that these mixtures are less compressible than the ideal mixture. This is due to a closer approach of unlike molecules and a stronger interaction between components of mixtures[16,17] that leads to a decrease in compressibility.

In regard to the solvent properties of ionic liquid, Poole[10] applied an empirical scale of solvent polarity, E_T^N scale, and concluded that the ionic liquid [BMIM][PF$_6$] and dimethylsulfoxide have similar E_T^N values and therefore similar solvent polarities. IUPAC defines solvent polarity as "the sum of all possible, nonspecific and specific, intermolecular interactions between the solute ions or molecules and solvent molecules, excluding such interactions leading to definite chemical alterations of the ions or molecules of the solute".[18] Therefore, from the similar solvent polarities of the ionic liquid and DMSO, we expect that the excess molar volume (V_m^E), $\Delta\eta$, and $\Delta\kappa_s$ values for solutions containing DMSO should be close to their ideal values. This is indeed what we observe for the [BMIM][PF$_6$] + DMSO system. However, in the case of ΔR, larger deviations are observed for [BMIM][PF$_6$] + DMSO than the [BMIM][PF$_6$] + THF. The order observed in Figure 2 for deviation in molar refraction, THF < DMSO < MeCN < MeOH, is consistent with the order we have for molar volumes or sizes of these solvents, which are (81.76, 71.33, 52.86, 40.73) cm^3·mol^{-1} for THF, DMSO, MeCN, and MeOH, respectively.

Correlation

The $\Delta\eta$, ΔR, V_m^E , and $\Delta\kappa_s$ calculated data were correlated with the composition data by means of the Redlich−Kister polynomial, which for binary mixtures is

$$Q_{ij} = x_i x_j \sum_{k\geq 0} A_k(x_i - x_j)^k \tag{10}$$

where Q_{ij} is $\Delta\eta$, V_m^E, or $\Delta\kappa_s$, and x_i is the mole fraction of component i; Q_{ij} is ΔR, with x_i as the volume fraction of component i. A_k is the polynomial coefficient, and κ is the number of the polynomial coefficient. The adjustable parameters A_k determined by fitting the experimental values to eq 10 along with standard deviations of $\Delta\eta$, V_m^E, ΔR, and $\Delta\kappa_s$ are given in Table 4. The full lines in Figures 1−4 correspond to the Redlich−Kister polynomials.

In regard to the behavior of viscosity of the ionic liquid + solvent, Seddon et al.[19] stated that viscosities can be generally described by the exponential expression

$$\eta = \eta_{IL}\exp(- x_1/A) \tag{11}$$

where x_1 is the mole fraction of the solvent, A is a constant characteristic for the mixture, and η_{IL} is the viscosity of the pure ionic liquid. To see the performance of eq (11) in representing our viscosity data, we also fitted the viscosity data reported in Table 2 to eq 11. The results of fitting viscosity data to eq 11 are given in Table 5. The lines generated for the viscosity of the studied systems using eq 11 with the A values reported in Table 5 are also shown in Figure 5. As can be seen from Figure 5 and the reported standard deviations in Table 5, the quality of eq 11 is fairly good, except for the system DMSO + [BMIM][PF$_6$] for which the agreement between the experimental and calculated data by eq 11 is not satisfactory. However, better quality of fitting viscosity data is obtained with the Redlich−Kister equation for all the systems studied as can be seen from Figure 1 and the standard deviations reported in Table 4.

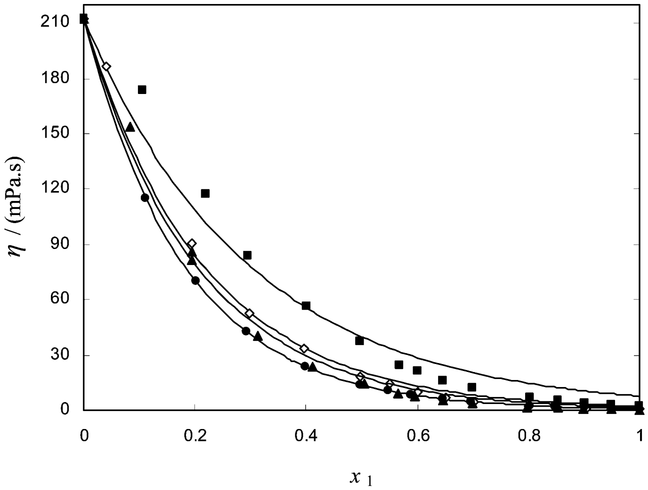

Figure 5. Experimental and calculated viscosity, η, plotted against mole fraction of organic solvent, x_1, for the organic solvent + [BMIM][PF$_6$] systems: ◇, THF; ■, DMSO; ●, MeOH; ▲, MeCN; —, eq 11.

Figure 5 shows that the viscosity of the studied organic solvent + [BMIM][PF$_6$] mixtures decreases exponentially when the mole fraction of solvent ($0 < x_1 < 0.6$) increases. This behavior agrees with previous studies of various ionic liquid + molecular solvent systems.[19−22] Figure 5 also shows that the viscosities decrease rapidly when each of the studied solvents is added to the ionic liquid. This decrease is particularly strong in dilute solutions of solvent in the ionic liquid. This result has been interpreted[23] by the fact that the strong columb interaction between the ions is weakened upon mixing with the neutral solvent leading to a higher mobility of the ions.

Conclusion

Experimental viscosity and refractive index data were obtained for the [BMIM][PF$_6$] + THF, + DMSO, + MeOH, or + MeCN systems over the whole range of composition at T = 298.15 K. Experimental density and sound velocity measurements were presented for the systems of [BMIM][PF$_6$] + THF and [BMIM][PF$_6$] + DMSO over the entire range of composition at T = 298.15 K. From the experimental viscosity, refractive index, density, and speed of sound values, viscosity deviation, refractive index deviation, excess molar volume, and deviation in isentropic compressibility were calculated, respectively. It was found that all of these calculated quantities are negative. The Redlich−Kister equation was applied successfully for the correlation of $\Delta\eta$, V_m^E, ΔR, and $\Delta\kappa_s$ values.

Literature Cited

(1) Kabo, G. J.; Blokhin, A. V.; Paulechka, Y. U.; Kabo, A. G.; Shymanovich, M. P.; Magee, J. W. Thermodynamic properties of 1-Butyl-3-methylimidazolium hexafluorophosphate in the condensed state. *J. Chem. Eng. Data* **2004**, *49*, 453−461.

(2) Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. Thermodynamical properties of imidazolium-based ionic liquids. *J. Chem. Eng. Data* **2004**, *49*, 954−961.

(3) Domanska, U.; Marciniak, A. Solubility of 1-alkyl-3-methylimidazolium hexafluorophosphate in hydrocarbons. *J. Chem. Eng. Data* **2003**, *48*, 451−456.

(4) Zhong, Y.; Wang, H.; Diao, K. Densities and excess volumes of binary mixtures of the ionic liquid 1-Butyl-3-methylimidazolium hexafluorophosphate with aromatic compound at $T = (298.15$ to $313.15)$ K. *J. Chem. Thermodyn.* **2006**, *39*, 291−296.

(5) Pereiro, A. B.; Rodriguez, A. Thermodynamic properties of ionic liquids in organic solvents from (293.15 to 303.15) K. *J. Chem. Eng. Data* **2007**, *52*, 600−608.

(6) 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.

(7) Zafarani-Moattar, M. T.; Shekaari, H. Volumetric and compressibility behaviour of ionic liquid, 1-Butyl-3-methylimidazolium hexafluorophosphate and tetrabutylammonium hexafluorophosphate in organic solvents at $T = 298.15$ K. *J. Chem. Thermodyn.* **2006**, *38*, 624−633.

(8) Zafarani-Moattar, M. T.; Shekaari, H. Apparent Molar volume and isentropic compressibility of ionic liquid 1-butyl-3-methylimidazolium bromide in water, methanol, and ethanol at $T = (298.15$ to $318.15)$ K. *J. Chem. Thermodyn.* **2005**, *37*, 1029−1035.

(9) Jeffery, G. A.; Sanger, W. *Hydrogen bonding in biological structures*; Springer-Verlag: Berlin, 1991.

(10) Poole, Colin, F. Chromatographic and spectroscopic methods for the determination of solvent properties of room temperature ionic liquids. *J. Chromatogr., A*, **2004**, *1037*, 49−82.

(11) Aznarez, S.; de Ruiz Holgado, M. M. E. F.; Arancibia, E. L. Viscosity of mixtures of 2-alkanols with tetraethyleneglycol dimethyl ether at different temperatures. *J. Mol. Liq.* **2006**, *124*, 78−83.

(12) Gerecze, N. G. Ultrasonic studies in solution of poly (ethylene glycol). *Acoustica* **1977**, *38*, 51−58.

(13) Holbrey, J. D.; Seddon, K. R. The phase behavior of 1-alkyl-3-methylimidazolium tetrafluoroborates; ionic liquids and ionic liquid crystals. *J. Chem. Soc., Dalton Trans.* **1999**, 2133−2139.

(14) Holbrey, J. D.; Reichert, M.; Nieuwenhuyzen, M.; Sheppard, O.; Hardacre, C.; Rogers, R. D. Liquid clathrate formation in ionic liquid−aromatic mixtures. *Chem. Commun.* **2003**, *14*, 476−477.

(15) Wang, J.; Zhu, A.; Zhao, Y.; Zhuo, K. Excess molar volumes and excess logarithm viscosities for binary mixtures of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate with some organic compounds. *J. Solution Chem.* **2005**, *34*, 585−596.

(16) Victor, P. J.; Hazra, D. K.; Excess molar volumes, viscosity deviations, and isentropic compressibility changes in binary mixtures of *N*-methylacetamide + 2-methoxyethanol and *N*-methylacetamide + water at (308.15, 313.15, and 318.15) K. *J. Chem. Eng. Data* **2002**, *47*, 79−82.

(17) Saha, N.; Das, B.; Hazra, D. Viscosities and excess molar volumes for acetonitrile + methanol at 298.15, 308.15, and 318.15 K. *J. Chem. Eng. Data* **1995**, *40*, 1264−1266.

(18) Muller, P. Glossary of terms used in physical organic chemistry (IUPAC Recommendation 1994) Commission on Physical Organic Chemistry. *Pure Appl. Chem*. **1994**, *66*, 1077−1184.

(19) 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.

(20) Comminges, C.; Barhdadi, R.; Laurent, M.; Troupel, M. Determination of viscosity, ionic conductivity, and diffusion coefficients in some binary systems: ionic liquid + molecular solvents. *J. Chem. Eng. Data* **2006**, *51*, 680−685.

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

(22) Xu, H.; Zhao, D.; Xu, P.; Liu, F.; Gao, G. Conductivity and viscosity of 1-allyl-3-methylimidazolium chloride + water and + ethanol from 293.13 K to 333.15 K. *J. Chem. Eng. Data* **2005**, *50*, 133−135.

(23) Kundu, A.; Kishore, N. Volumetric properties of nucleic acid bases and nucleosides in aqueous ethanol, 1, 2-ethanediol, 2-propanol, and 2-methyl-2-propanol at 25°C. *J. Solution Chem.* **2002**, *31*, 477−476.

(24) Bhattacharyya, D. N.; Lee, C. L.; Smid, J.; Szwarc, M. Studies of ions and ion pairs in tetrahydrofuran solution. Alkali metal salts of tetraphenylboride. *J. Phys. Chem*. **1965**, *69*, 608−611.

(25) Marsden, C.; Mann, S. *Solvents Guide*, 2nd ed.; Interscience: New York, 1963.

(26) Roy, M. N.; Dey, R.; Jha, A. Study of ion-solvent interactions of some alkali metal chlorides in tetrahydrofuran + water mixture at different temperatures. *J. Chem. Eng. Data* **2001**, *46*, 1327−1329.

(27) Afanasyef, V.; Zyatkova, L. Speed of sound, densities, and viscosities for solutions of lithium hexafluoroarsenate in tetrahydrofuran at 283.15, 298.15, and 313.15 K. *J. Chem. Eng. Data* **1996**, *41*, 1315−1318.

(28) Zhao; Y.; Wang, J.; Lu, H.; Lin, R. Standard partial molar volumes of some electrolytes in ethylene carbonate-based mixtures. *J. Chem. Thermodyn.* **2004**, *36*, 1−6.

(29) Brocos, P.; Pineiro, N.; Bravo, R.; Amigo, A.; Roux, A. H.; Roux-Desgranges, G. Thermodynamics of mixtures involving some linear or cyclic ketones and cyclic ethers. 1. Systems containing tetrahydrofuran. *J. Chem. Eng. Data* **2002**, *47*, 351−358.

(30) Wei, I-C.; Rowley, R. L. Binary liquid mixture viscosities and densities. *J. Chem. Eng. Data* **1984**, *29*, 332−335.

(31) *Dimethyl sulfoxide*; Technical bulletin and supplement, 1963, 1966; Crown Zellerbach Corp. Chemical Products: Camas, WA, 1963, 1966.

(32) Sylal, V. K.; Chauhan, S.; Gautam, R. Ultrasonic velocity measurements of carbohydrates in binary mixtures of DMSO + H_2O at 25°C. *Ultrasonics* **1998**, *36*, 619−623.

(33) Krakowiak, J.; Bobicz, D.; Grzybkowski, W. Partial molar volumes of tetrabuthylammonium perchlorate and tetraphenylborate in *N*, *N*-dimethylacetamide, triethylphosphate, acetonitrile and dimethyl sulphoxide. *J. Mol. Liq.* **2000**, *88*, 197−207.

(34) Rodriguez, A.; Pereiro, A. B.; Canosa, J.; Tojo, J. Dynamic viscosities of the ternary liquid mixtures (dimethyl carbonate + methanol + ethanol) and (dimethyl carbonate + methanol + hexane) at several temperatures. *J. Chem. Thermodyn.* **2006**, *38*, 505−519.

(35) Ritzoulis, G.; Fidantsi, A. Relative permittivities, refractive indices, and densities for the binary mixtures *N, N′*-dimethylacetamide with methanol, ethanol, 1-butanol, and 2-propanol at 298.15 K. *J. Chem. Eng. Data* **2000**, *45*, 207−209.

(36) Saha, N.; Das, B.; Hazra, D. K. Viscosities and Excess Molar Volumes for Acetonitrile + Methanol at 298.15 K, 308.15 K, and 318.15 K. *J. Chem. Eng. Data* **1995**, *40*, 1264−1266.

(37) Bakshi, M. S.; Singh, J.; Kaur, H.; Ahmad, S. T.; Kaur, G. Thermodynamic behavior of mixtures. 3. Mixtures of acetonitrile with dimethylacetamide, dimethyl sulfoxide, nitrobenzene, and methanol at 25 °C. *J. Chem. Eng. Data* **1996**, *41*, 1459−1461.

(38) Baker, Sh. N.; Baker, G. A.; Kane, M. A.; Bright, F. V. The cybotactic region surrounding fluorescent probes dissolved in 1-buthyl-3-methylimidazolium hexaflurophosphate: Effect of temperature and added carbon dioxide. *J. Phys. Chem. B* **2001**, *105*, 9663−9668.

(39) de Azevedo, R. G.; Esperanca, J. M. S. S.; Najdanovic-Visak, V.; Visak, Z. P.; Guedes, H. J. R.; da Ponte, M. N.; Rebelo, L. P. N. Thermophysical and thermodynamic properties of 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium hexafluorophosphate over an extended pressure range. *J. Chem. Eng. Data* **2005**, *50*, 997−1008.

Received for review June 13, 2007. Accepted July 28, 2007.

JE700338T