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Temperature and Composition Dependence of the Density and Viscosity of Binary Mixtures of {1-Butyl-3-methylimidazolium Thiocyanate + 1-Alcohols}

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Density and viscosity were determined for binary mixtures containing ionic liquid 1-butyl-3-methylimidazolium thiocyanate ([BMIM][SCN]) and 1-alcohol (methanol, ethanol, and 1-propanol) in a temperature range (298.15 to 348.15) K and ambient pressure. The temperature dependence of density and viscosity for these systems can be described by an empirical second-order polynomial and by the Vogel−Fucher−Tammann equation, respectively. Excess molar volumes and viscosity deviations were calculated and correlated by the Redlich−Kister polynomial expansions. Volume expansivity and excess volume expansivity were described in function of temperature and composition. The polynomial correlations describe the variation of density and viscosity with composition. Comparison of the results for three binary systems elucidates the influence of 1-alcohol carbon chain length on their physical properties.

Introduction

Ionic liquids (ILs) are a novel class of chemical compounds with interesting properties that are driving a lot of research in several fields.[1,2] For ILs to be effectively used as solvents in liquid−liquid extraction, the knowledge of the viscosity and density is fundamental.

Until recently, the most important extraction ILs of popular imidazolium, tetraalkylammonium, and phosphonium ionic liquids with cation structures by alkyl, or hydroxyl, or alkoxyalkyl, or aromatic substituents and bis(trifluoromethylsulfonyl)imide $[NTf_2]^-$, alkylsulfate $[RSO_4]^-$, trifluoroacetate $[CF_3COO]^-$, and thiocyanate $[SCN]^-$ anions have attracted our attention. From the measurements of activity coefficients at infinite dilution we know that ionic liquids with thiocyanate anion are very attractive for the separation of different organic compounds and especially aromatic hydrocarbons from aliphatic hydrocarbons with the highest selectivity in comparison with other ionic liquids.[2,3]

This paper is a continuation of our wide ranging of investigation into the ILs containing thiocyanate anion, becausse to our best knowledge the data of density and viscosity of pure IL and binary systems with alcohol are not known.

The purpose of this work is to present densities, dynamic viscosities, excess molar volumes, volumes expansivity, viscosity deviation, and their dependence on temperature and composition. It seems to be important information to allow the making of plans of new separation technologies. The new information will be present for two associated compounds and their mixtures. The interactions in such a liquid mixtures are influenced by dispersion forces, dipole−dipole interaction, hydrogen bonding, charge transfer, interstitial accommodation, and many others.

Experimental procedures and result for pure compounds and binary systems of IL with methanol, ethanol, and 1-propanol have been in detail tabulated and then briefly discussed and interpreted below. Thus, the characteristic investigated here includes the effect of the alkyl chain length of an alcohol on density and viscosity.

Experimental Section

Materials. The ionic liquid 1-butyl-3-methylimidazolium thiocyanate, [BMIM][SCN] had a purity of > 0.98 mass fraction and was supplied by Fluka. The structure of the investigated ionic liquid is presented in Table 1. The ionic liquid was further purified by subjecting the liquid to a very low pressure in a vacuum desiccator at a temperature of about 300 K for approximately 5 h. This procedure removed any volatile chemicals and water from the ionic liquid. The alcohols purchased from Aldrich were fractionally distilled over different drying reagents to the mass fraction purity ≥ 0.998 mass fractions. They were also stored over freshly activated molecular sieves of type 4 Å (Union Carbide) and checked by gas−liquid chromatography (GLC). The full set of basic information concerning investigated IL, including determined physicochemical properties (glass transition temperature and heat capacity at glass transition temperature) is presented in Table 1. Basic volumetric properties of both the ionic liquid and solvents are tabulated in Tables 2 to 5.

Water Content. Water content was analyzed by using the Karl Fischer titration technique (method TitroLine KF). Samples of [BMIM][SCN] were dissolved in methanol and titrated with steps 2.5 μL. The analysis showed that the water mass fraction in the IL, alcohols, and the mixtures with the ionic liquid was $< 2.2 \cdot 10^{-4}$.

Differential Scanning Calorimetry (DSC). The temperature of glass transition was measured by DSC (Perkin-Elmer Pyris 1). Measurements were carried out at a scan rate of $10\ K \cdot min^{-1}$ with a power sensitivity of $16\ mJ \cdot s^{-1}$ and with a recorder sensitivity of 5 mV. The DSC was calibrated with a 99.9999 % purity indium sample. The uncertainty of the calorimetric measurements was estimated to be ± 2 %.The uncertainty of measured glass transition temperatures $T_{tr,(g)}$ and that of C_p at glass transition was $\pm\ 3\ J \cdot K^{-1} \cdot mol^{-1}$. The results are shown in Table 1.

Density measurements. The densities of all the chemicals were measured using an Anton Paar GmbH 4500 vibrating-

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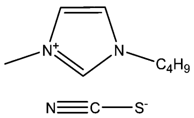
Table 1. Investigated Ionic Liquid: Chemical Structure, Name, Abbreviation, CAS Number, Molecular Weight and Measured Thermophysical Properties[a]

structure	name			
	1-butyl-3-methylimidazolium thiocyanate			
		abbreviation	$M/g\cdot mol^{-1}$	$V_{m,1}(298.15\ K)/cm^3\cdot mol^{-1}$
		[BMIM][SCN]	197.3	184.43
	CAS	$\eta^{298.15}/mPa\cdot s$	$T_{g,1}/K$	$\Delta C_{p(g),1}/J\cdot K^{-1}\cdot mol^{-1}$
	344790-87-0	51.7	181.6	97.7

[a] Molar volume ($V_{m,1}$) at $T = 298.15$ K, dynamic viscosity (η) at $T = 298.15$ K, glass transition temperature ($T_{g,1}$), and heat capacity change at $T_{g,1}$ ($\Delta C_{p(g),1}$).

Table 2. Thermophysical Constants of Pure Alcohols[a]

compound	(ρ(298.15K)) ($g\cdot cm^{-3}$)	(ρ^{lit}(298.15K)) ($g\cdot cm^{-3}$)	(η(298.15K)) ($mPa\cdot s$)	(η^{lit}(298.15K)) ($mPa\cdot s$)
methanol	0.786 64	0.786 37[b]	0.577	0.5513[b]
ethanol	0.785 17	0.785 04[b]	1.09	1.0826[b]
1-propanol	0.799 52	0.799 60[b]	1.94	1.9430[b]

[a] Measured density, $\rho^{298.15}$; density from literature, ρ^{lit}(298.15 K); dynamic viscosity, η(298.15 K); dynamic viscosity from literature, η^{lit}(298.15 K). [b] Reference 4.

tube densimeter (Graz, Austria), thermostatted at different temperatures. Two integrated Pt 100 platinum thermometers provided good precision in temperature control internally ($T \pm 0.01$ K). Densimeter includes an automatic correction for the viscosity of the sample. The calibration for temperature and pressure was made by the producer. The apparatus is precise to within $1\cdot10^{-5}$ $g\cdot cm^{-3}$, and the uncertainty of the measurements was estimated to be better than $\pm\ 1\cdot10^{-4} g\cdot cm^{-3}$. The densimeter's calibration was performed at atmospheric pressure using doubly distilled and degassed water, specially purified benzene (CHEMIPAN, Poland 0.999), and dried air. Mixtures were prepared by weighing with the uncertainty in mole fraction being estimated as less than $5\cdot10^{-4}$. All weighing involved in the experimental work was carried out using a Mettler Toledo AB 204-S balance with a precision of $\pm\ 1\cdot10^{-4}$ g. The uncertainty of the excess molar volumes depend on the uncertainties od the density measurements and can be assumed as $\pm$ 0.0005 $cm^3\cdot mol^{-1}$. The densities of alcohols and IL are in satisfactory agreement with the literature values, which is shown with other physicochemical properties in Table 2.

Viscosity measurements. Viscosity measurements were carried out in an Anton Paar BmbH AMVn (Graz, Austria) programmable rheometer with a nominal uncertainty of $\eta_{dyn} = \pm\ 0.0014$ and reproducibility < 1 % for viscosities from 0.3 $mPa\cdot s$ to 2500 $mPa\cdot s$. Temperature was controlled internally with a precision of $\pm$ 0.01 K in a range from 283.15 to 373.15 K. The density, used to describe viscosity, is with uncertainty $\pm\ 1\cdot10^{-4}$ $g\cdot cm^{-3}$, thus the uncertainty of dynamic viscosity is from $\pm$ 0.003 $mPa\cdot s$ to $\pm$ 25 $mPa\cdot s$ (this depends on the range of measurements).

Results and Discussion

Effect of Temperature on Density and Viscosity. The experimental data of density, ρ, and dynamic viscosity, η, versus x_1, the mole fraction of the {[BMIM][SCN] (1) + methanol, ethanol, or 1-propanol (2)} at different temperatures are listed in Tables 3 to 5. The densities and viscosities are higher for IL than for 1-alcohol and decrease with increasing 1-alcohol content. As usual, both density and viscosity decrease with increasing temperature. We found no previous data as a function of temperature for these systems for comparison.

Table 3. Experimental Density, ρ; Excess Molar Volume, V_m^E; Dynamic Viscosity, η; and Viscosity Deviation, $\Delta\eta$, for the Binary Systems {[BMIM][SCN] (1) + Methanol (2)}

	T/K			
x_1	298.15	308.15	318.15	328.15
		$\rho/g\cdot cm^{-3}$		
1.0000	1.06979	1.06389	1.05802	1.05219
0.9046	1.06423	1.05822	1.05227	1.04637
0.8006	1.05746	1.05139	1.04536	1.03938
0.7114	1.05029	1.04413	1.03801	1.03194
0.6227	1.04188	1.03564	1.02943	1.02326
0.5083	1.02810	1.02168	1.01530	1.00899
0.3602	1.00145	0.99474	0.98806	0.98143
0.2076	0.95494	0.94769	0.94047	0.93323
0.1443	0.92463	0.91704	0.90943	0.90181
0.0964	0.89265	0.88464	0.87663	0.86859
0.0531	0.85466	0.84616	0.83763	0.82905
0.0154	0.81000	0.80087	0.79170	0.78241
0.0000	0.78664	0.77715	0.76759	0.75783
		$V_m^E/cm^3\cdot mol^{-1}$		
1.0000	0.0000	0.0000	0.0000	0.0000
0.9046	−0.1416	−0.1455	−0.1552	−0.1684
0.8006	−0.3578	−0.3785	−0.4029	−0.4328
0.7114	−0.5143	−0.5450	−0.5804	−0.6228
0.6227	−0.6878	−0.7319	−0.7803	−0.8361
0.5083	−0.9013	−0.9565	−1.0182	−1.0929
0.3602	−1.0557	−1.1255	−1.2023	−1.2924
0.2076	−1.0830	−1.1579	−1.2409	−1.3341
0.1443	−1.0237	−1.0966	−1.1745	−1.2644
0.0964	−0.8408	−0.9021	−0.9698	−1.0485
0.0531	−0.6038	−0.6494	−0.6990	−0.7586
0.0154	−0.2448	−0.2635	−0.2847	−0.3112
0.0000	0.0000	0.0000	0.0000	0.0000
		$\eta/mPa\cdot s$		
1.0000	51.7	34.9	24.2	16.7
0.9046	34.1	23.3	16.9	12.78
0.8006	25.4	18.0	13.4	10.32
0.7114	19.4	14.1	10.7	8.40
0.6227	14.5	10.8	8.40	6.68
0.5083	9.75	7.55	6.03	4.85
0.3602	5.15	4.13	3.33	2.82
0.2076	2.34	1.96	1.67	1.45
0.1443	1.62	1.39	1.20	1.06
0.0964	1.18	1.02	0.892	0.792
0.0531	0.871	0.765	0.681	0.613
0.0154	0.665	0.593	0.536	0.490
0.0000	0.577	0.525	0.481	0.443
		$\Delta\eta/mPa\cdot s$		
1.0000	0.00	0.00	0.00	0.00
0.9046	−12.72	−8.32	−5.04	−2.37
0.8006	−16.11	−10.05	−6.07	−3.14
0.7114	−17.55	−10.88	−6.65	−3.61
0.6227	−17.91	−11.13	−6.85	−3.89
0.5083	−16.81	−10.45	−6.51	−3.86
0.3602	−13.84	−8.78	−5.69	−3.48
0.2076	−8.85	−5.70	−3.74	−2.37
0.1443	−6.33	−4.10	−2.70	−1.73
0.0964	−4.33	−2.82	−1.88	−1.22
0.0531	−2.42	−1.59	−1.06	−0.69
0.0154	−0.70	−0.46	−0.31	−0.20
0.0000	0.00	0.00	0.00	0.00

Experimental densities at ambient pressure, investigated in this work, are shown as an example for the {[BMIM][SCN] (1) + methanol (2)} binary system in Figure 1 (two other

Table 4. Experimental Density, ρ; Excess Molar Volume, V_m^E; Dynamic Viscosity, η; and Viscosity Deviation, $\Delta\eta$, for the Binary Systems {BMIM][SCN] (1) + Ethanol (2)}

	T/K					
x_1	298.15	308.15	318.15	328.15	338.15	348.15
			ρ/g·cm^{-3}			
1.0000	1.06979	1.06389	1.05088	1.05219	1.04643	1.04070
0.9174	1.06278	1.05682	1.05088	1.04499	1.03915	1.03334
0.8114	1.05290	1.04684	1.04084	1.03486	1.02895	1.02305
0.6960	1.03972	1.03357	1.02747	1.02140	1.01536	1.00940
0.5306	1.01459	1.00822	1.00190	0.99561	0.98936	0.98314
0.3637	0.97805	0.97137	0.96472	0.95811	0.95147	0.94488
0.2943	0.95741	0.95056	0.94372	0.93687	0.93003	0.92318
0.1877	0.91669	0.90946	0.90220	0.89491	0.88757	0.88022
0.1129	0.87641	0.86874	0.86106	0.85327	0.84544	0.83747
0.0473	0.82974	0.82161	0.81339	0.80505	0.79653	0.78785
0.0000	0.78517	0.77649	0.76767	0.75865	0.74935	0.73975
			V_m^E/cm^3·mol^{-1}			
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.9174	−0.1508	−0.1626	−0.1744	−0.1900	−0.2053	−0.2237
0.8114	−0.4140	−0.4397	−0.4737	−0.5097	−0.5526	−0.5994
0.6960	−0.6545	−0.6997	−0.7539	−0.8146	−0.8808	−0.9659
0.5306	−0.9028	−0.9668	−1.0424	−1.1290	−1.2290	−1.3465
0.3637	−1.0706	−1.1492	−1.2399	−1.3469	−1.4657	−1.6100
0.2943	−1.0789	−1.1610	−1.2542	−1.3601	−1.4847	−1.6306
0.1877	−1.0563	−1.1353	−1.2234	−1.3246	−1.4425	−1.5850
0.1129	−0.8230	−0.8842	−0.9567	−1.0368	−1.1365	−1.2507
0.0473	−0.4779	−0.5164	−0.5599	−0.6106	−0.6703	−0.7433
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
			η/mPa·s			
1.0000	51.7	34.9	24.2	16.7	12.73	9.98
0.9174	36.2	24.7	17.8	13.4	10.5	8.39
0.8114	27.4	19.2	14.2	10.9	8.64	7.01
0.6960	19.7	14.3	10.9	8.54	6.84	5.58
0.5306	11.7	8.89	7.00	5.97	4.56	3.80
0.3637	6.36	4.95	3.94	3.24	2.75	1.18
0.2943	4.70	3.77	3.10	2.59	2.20	1.90
0.1877	2.95	2.41	2.01	1.71	1.47	1.28
0.1129	2.07	1.71	1.44	1.23	1.06	0.926
0.0473	1.48	1.23	1.05	0.896	0.780	0.344
0.0000	1.09	0.912	0.774	0.664	0.589	0.512
			$\Delta\eta$/mPa·s			
1.0000	0.00	0.00	0.00	0.00	0.00	0.00
0.9174	−11.32	−7.36	−4.46	−1.98	−1.27	−0.80
0.8114	−14.77	−9.24	−5.57	−2.76	−1.80	−1.19
0.6960	−16.64	−10.20	−6.17	−3.29	−2.21	−1.51
0.5306	−16.26	−10.04	−6.23	−3.21	−2.47	−1.73
0.3637	−13.15	−8.31	−5.35	−3.26	−2.25	−1.46
0.2943	−11.29	−7.14	−4.57	−2.79	−1.96	−1.40
0.1877	−7.65	−4.87	−3.16	−1.97	−1.40	−1.01
0.1129	−4.74	−3.03	−1.98	−1.25	−0.90	−0.65
0.0473	−2.01	−1.28	−0.84	−0.53	−0.38	−0.32
0.0000	0.00	0.00	0.00	0.00	0.00	0.00

systems are shown in Figures 1S and 2S in Supporting Information). For the IL in this work, the temperature dependence becomes distinctly nonlinear, especially at high alcohol content. A second-order polynomial was found to satisfactorily correlate the change of density with temperature

$$\rho = a_2T^2 + a_1T + a_0 \tag{1}$$

where T is for the absolute temperature and a_2, a_1, and a_0 refer to the fit coefficients. Fit parameters are listed in Table 1S in Supporting Information. The polynomial correlations are plotted with solid lines in Figure 1, along with the experimental data.

Figure 2 shows the experimental dynamic viscosities for one binary system studied, as a function of temperature, for different compositions together with the well-known Vogel−Fulcher−Tammann, VFT equation.[5−7] This equation has been used to correlate variations of viscosity with temperature in a measured systems:

$$\eta = AT^{0.5}\exp\left(\frac{B}{T - T_0}\right) \tag{2}$$

The fit parameters, determined empirically are in general A, B, and T_0 when the linear relation is observed between logarithmic value of $\eta T^{0.5}$ and $(T - T_0)^{-1}$ according to the eq 2 with three adjustable parameters. However, for the glass-forming liquids, the refined value for T_0 (called the ideal transition temperature) can be found from the glass transition temperature. The difference between T_0 and $T_{tr(g)}$ is approximately 50 to 60 K.[7] It is known that T_0 is lower than that observed from DSC glass transition temperature. For the IL under study, the temperature of glass transition, determined by DSC (see Table 1) was 181.6 K. For the best correlation of the experimental curves the value of T_0 equals to 127 K was used in the calculations. One value of parameter T_0 was used for all the solutions with different alcohols and for different concentrations,

Table 5. Experimental Density, ρ; Excess Molar Volume V_m^E; Dynamic Viscosity, η; and Viscosity Deviation, $\Delta\eta$ for the Binary Systems {BMIM][SCN] (1) + 1-Propanol (2)}

	T/K					
x_1	298.15	308.15	318.15	328.15	338.15	348.15
			ρ/g·cm^{-3}			
1.0000	1.06979	1.06389	1.05802	1.05219	1.04643	1.04070
0.9342	1.06297	1.05702	1.05109	1.04522	1.03940	1.03361
0.8050	1.04814	1.04209	1.03608	1.03011	1.02420	1.01832
0.6791	1.03055	1.02439	1.01827	1.01218	1.00614	1.00013
0.5868	1.01547	1.00921	1.00301	0.99684	0.99070	0.98460
0.4577	0.98894	0.98250	0.97607	0.96967	0.96330	0.95697
0.3429	0.95902	0.95234	0.94566	0.93900	0.93234	0.92571
0.2538	0.93041	0.92349	0.91658	0.90963	0.90270	0.89573
0.1849	0.90316	0.89599	0.88881	0.88157	0.87427	0.86694
0.0833	0.85416	0.84663	0.83900	0.83126	0.82339	0.81539
0.0267	0.81906	0.81118	0.80318	0.79500	0.78660	0.77798
0.0000	0.79952	0.79141	0.78315	0.77466	0.76591	0.75684
			V_m^E/cm^3·mol^{-1}			
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.9342	−0.1198	−0.1290	−0.1380	−0.1526	−0.1666	−0.1836
0.8050	−0.4094	−0.4383	−0.4734	−0.5152	−0.5635	−0.6210
0.6791	−0.6391	−0.6865	−0.7430	−0.8089	−0.8853	−0.9766
0.5868	−0.8171	−0.8767	−0.9502	−1.0364	−1.1341	−1.2526
0.4577	−0.9069	−0.9783	−1.0595	−1.1575	−1.2725	−1.4137
0.3429	−0.9114	−0.9846	−1.0690	−1.1724	−1.2937	−1.4445
0.2538	−0.8799	−0.9499	−1.0338	−1.1324	−1.2547	−1.4017
0.1849	−0.7391	−0.7988	−0.8713	−0.9582	−1.0620	−1.1938
0.0833	−0.5275	−0.5740	−0.6255	−0.6887	−0.7647	−0.8608
0.0267	−0.2365	−0.2573	−0.2814	−0.3107	−0.3443	−0.3891
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
			η/mPa·s			
1.0000	51.7	34.9	24.2	16.7	12.7	9.98
0.9342	38.6	26.2	18.7	14.0	10.9	8.69
0.8050	25.8	18.1	13.4	10.4	8.19	6.62
0.6791	20.5	14.8	11.2	8.7	6.97	5.64
0.5868	16.7	12.3	9.37	7.3	5.89	4.81
0.4577	10.9	8.22	6.43	5.1	4.18	3.46
0.3429	7.42	5.71	4.49	3.6	3.01	2.56
0.2538	5.34	4.21	3.40	2.8	2.35	2.00
0.1849	4.27	3.39	2.75	2.27	1.90	1.62
0.0833	2.87	2.30	1.87	1.55	1.30	1.10
0.0267	2.26	1.80	1.46	1.20	1.00	0.848
0.0000	1.94	1.54	1.24	1.02	0.842	0.710
			$\Delta\eta$/mPa·s			
1.0000	0.00	0.00	0.00	0.00	0.00	0.00
0.9342	−9.91	−6.50	−3.97	−1.64	−1.06	−0.67
0.8050	−16.24	−10.26	−6.27	−3.29	−2.22	−1.55
0.6791	−15.22	−9.36	−5.65	−2.95	−1.95	−1.36
0.5868	−14.48	−8.83	−5.34	−2.88	−1.93	−1.34
0.4577	−13.88	−8.57	−5.31	−3.07	−2.11	−1.49
0.3429	−11.60	−7.27	−4.63	−2.78	−1.91	−1.33
0.2538	−9.24	−5.79	−3.67	−2.20	−1.51	−1.06
0.1849	−6.88	−4.32	−2.74	−1.65	−1.14	−0.81
0.0833	−3.22	−2.02	−1.28	−0.78	−0.54	−0.38
0.0267	−1.01	−0.63	−0.39	−0.24	−0.16	−0.11
0.0000	0.00	0.00	0.00	0.00	0.00	0.00

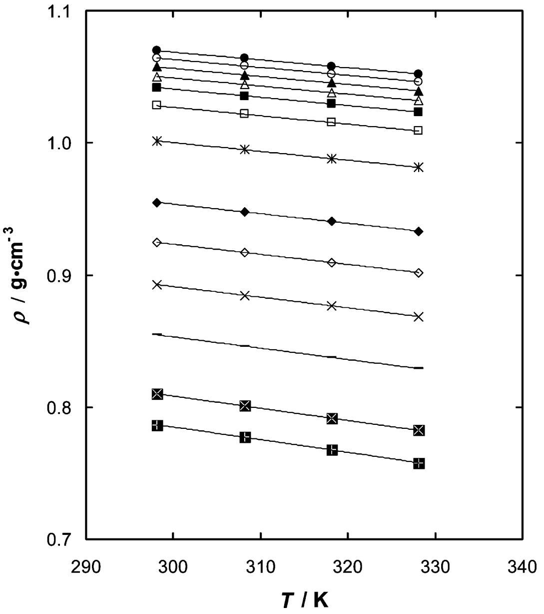


Figure 1. Density ρ for the {[BMIM][SCN] (1) + methanol (2)} binary system as a function of temperature at different mole fraction of the IL: ●, 1.0000; ○, 0.9046; ▲, 0.8006; Δ, 0.7114; ■, 0.6227; □, 0.5083; *, 0.3602; ♦, 0.2076; ◊, 0.1443; x, 0.0964; -, 0.0531; x in filled box, 0.0154; ⊞, 0.0000. Solid lines represent polynomial.

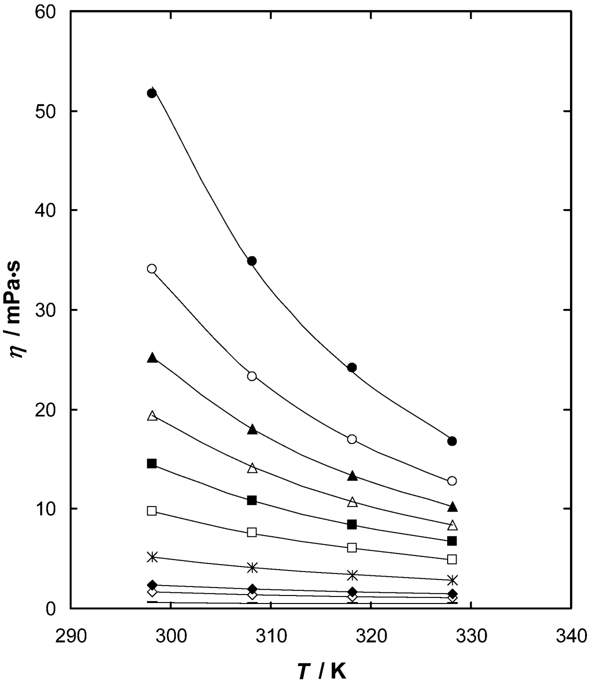


Figure 2. Dynamic viscosity η for the {[BMIM][SCN] (1) + methanol (2)} binary system as a function of temperature at different approximated mole fractions of the IL: ●, 1.0000; ○, 0.9046; ▲, 0.8006; Δ, 0.7114; ■, 0.6227; □, 0.5083; *, 0.3602; ♦, 0.2076; ◊, 0.1443; -, 0.0000. Solid lines represent the VFT equation.

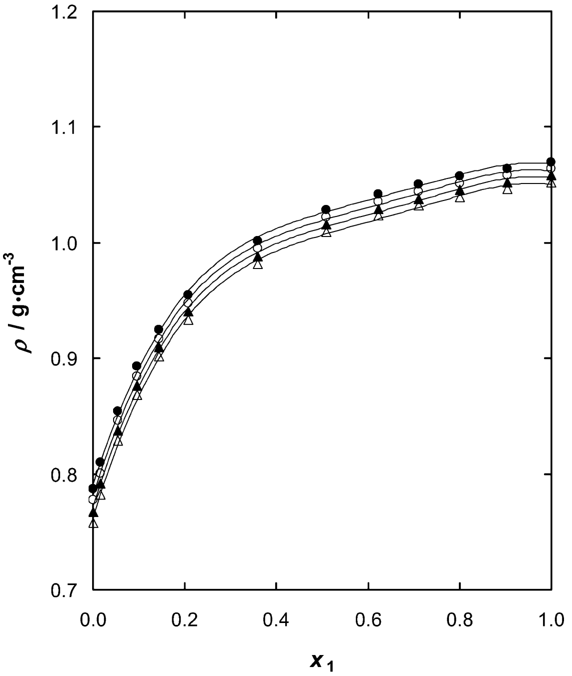


Figure 3. Density ρ for the {[BMIM][SCN] (1) + methanol (2)} binary system, as a function of mole fractions of the IL, at different temperatures: ●, 298.15 K; ○, 308.15 K; ▲, 318.15 K; Δ, 328.15 K. Solid lines represent the polynomial correlation.

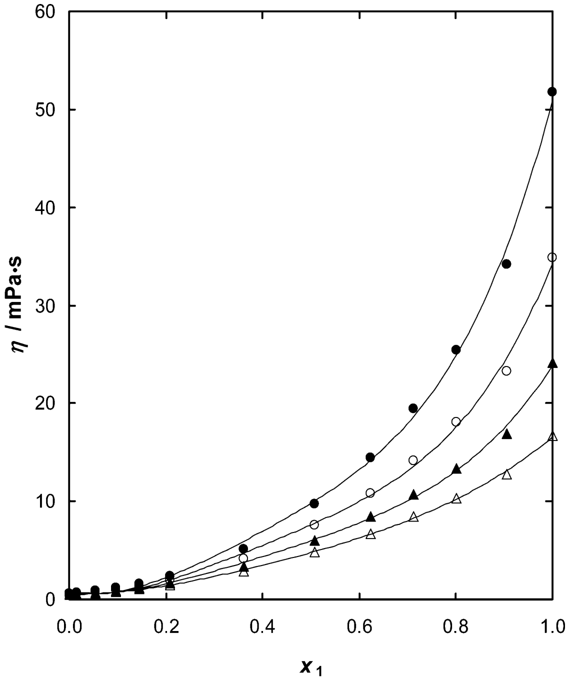


Figure 4. Dynamic viscosity, η for the {[BMIM][SCN] (1) + methanol (2)} binary system as a function of mole fractions of the IL at a different temperatures: ●, 298.15 K; ○, 308.15 K; ▲, 318.15 K; Δ, 328.15 K. Solid lines represent the polynomial correlation.

because the IL is here the most important and ΔT_0 discussed by many authors may be 10 K.[8,9] The values of A and B parameters together with standard deviations are presented in Table 2S in Supporting Information.

The VFT equation suitably correlates, as a function of the temperature not only the viscosities of pure IL but also the viscosities of the mixtures for the binary systems through the composition range (see Figure 2 and Figures 3S and 4S in Supporting Information). The parameters A and B in eq 2 change smoothly with composition for all three systems. These parameters are strongly sensitive to the choice of T_0. The standard deviations are listed in Table 3S in Supporting Information.

The small impurities of water in the IL and/or in an alcohol could change the density and viscosity about 1 %. Water may be accommodated in the ionic liquid structure in the IL-rich region, possibly by forming hydrogen bonds with both the anion and the cation of the IL. This effect can influence the viscosity

Table 6. Fit Parameters a_0, a_1, and a_2 for Empirical Correlation of the Density in Function of Temperature for Pure Substances[a]

	$(10^7 \cdot a_2)$ $(\mathrm{g \cdot cm^{-3} \cdot K^{-2}})$	$(10^4 \cdot a_1)$ $(\mathrm{g \cdot cm^{-3} \cdot K^{-1}})$	(a_0) $(\mathrm{g \cdot cm^{-3}})$
[BMIM][SCN]	2.300	−7.308	1.267
methanol	−6.700	−5.372	1.007
ethanol	−11.600	−1.548	0.935
1-propanol	−12.100	−0.724	0.928

[a] $\rho/(\mathrm{g \cdot cm^{-3}}) = a_2(T/K)^2 + a_1(T/K) + a_0$.

Table 7. Coefficients of Redlich−Kister Equation for the Correlation of the Excess Molar Volume ($V_m^E/\mathrm{cm^3 \cdot mol^{-1}}$) of the System {[BMIM][SCN] (1) + Methanol, Ethanol, or 1-Propanol (2)}

i	b_i	$10^2 \cdot c_i$
	[BMIM][SCN] (1) + methanol (2)	
1	3.938	−2.486
2	−3.813	2.127
3	5.185	−2.789
4	−5.720	3.270
	[BMIM][SCN] (1) + ethanol (2)	
1	7.070	−3.602
2	−5.279	2.452
3	6.426	−2.996
4	−5.774	2.993
	[BMIM][SCN] (1) + 1-propanol (2)	
1	4.531	−2.745
2	−3.660	1.621
3	4.721	−1.896
4	−3.964	2.167

and density values of the pure IL. With increasing temperature, forming hydrogen bonds are broken, so viscosity decreases rapidly.

Effect of Composition on Density and Viscosity. The densities are highest for pure IL with decreasing values with increasing 1-alcohol content. The character of changes is presented in Figure 3 as an example for {[BMIM][SCN] (1) + methanol (2)} binary system together with solid lines calculated with polynomial (presentation for ethanol and 1-propanol are in Figures 5S and 6S in the Supporting Information). The parameters of correlation are shown in Table 4S in Supporting Information.

The character of changes of dynamic viscosities with composition is presented in Figure 4 for the same system together with solid lines calculated with polynomial (presentation for ethanol and 1-propanol are in Figures 7S and 8S in Supporting Information). The parameters of correlation are shown in Table 5S in Supporting Information. The observed decrease of viscosity with an increase of alcohol content is particularly strong in dilute solutions of an alcohol in the ionic liquid. As discussed above, ion-dipole interactions and/or hydrogen bonding between the cation of the IL and an alcohol will take place when an alcohol is added to the IL. This weakening of the strong hydrogen bonding interactions between cation and anion of the IL leads to a higher mobility of the ions and a lower viscosity of the mixture.

Experimental excess molar volumes V_m^E data of {[BMIM][SCN] (1) + methanol, ethanol, or 1-propanol (2)} are recorded in Tables 3 to 5. The data were calculated by the smoothing Redlich−Kister equation

$$V_m^E/(\mathrm{cm^3 \cdot mol^{-1}}) = x_1(1 - x_1)\sum_{i=1}^{4} A_i(T)(2x_1 - 1)^{i-1} \quad (3)$$

with temperature dependence parameters

$$A_i(T) = b_i + c_i T \quad (4)$$

where x_1 is the mole fraction of the IL, V_m^E is the molar excess volume, and i is the number of parameters. The values of the parameters (A_i), for V_m^E have been determined using a method of least-squares. The fit temperature dependence parameters for pure substances are summarized in Table 6 and the Redlich−Kister parameters in Table 7. The values of V_m^E as well as the Redlich−Kister fits are plotted in Figures 9Sa,b,c in Supporting Information for the concentration dependence of excess molar volume. The graphs of V_m^E indicate that all mixtures of {[BMIM][SCN] (1) + 1-alcohol (2)} exhibit negative deviations from ideality over the entire composition range. The minimum of V_m^E is -1.08 cm$^3 \cdot$mol^{-1}, -1.07 cm$^3 \cdot$mol^{-1}, and -0.91 cm$^3 \cdot$mol^{-1} at $x_1 = 0.20$, 0.29, and 0.34 (at $T = 298.15$ K) for methanol, ethanol, and 1-propanol, respectively. With the increasing temperature, the minimum of V_m^E shifts to the lower values of V_m^E. The excess molar volume data become less negative in the following order: methanol < ethanol <1-propanol. The high negative deviations from ideality, observed for these systems have to be a results of a strong interaction of IL with 1-alcohol. The strength of the intermolecular hydrogen bonding is not only one factor influencing the V_m^E. The molecular size

Table 8. Coefficients of Redlich−Kister Equation for the Correlation of the Viscosity Deviation ($\Delta\eta/\mathrm{mPa \cdot s}$) of the System {[BMIM][SCN] (1) + Methanol, Ethanol, or 1- Propanol (2)}, along with the Standard Deviations ($\sigma/\mathrm{mPa \cdot s}$)

T/K	D_1	D_2	D_3	D_4	D_5	D_6	σ/mPa·s
			[BMIM][SCN] (1) + methanol (2)				
298.15	−67.5313	31.0210	−5.8924	3.8176	−62.4279	61.0692	0.1666
308.15	−42.2340	17.8664	−2.3094	1.0656	−47.3748	47.6193	0.1474
318.15	−26.4786	8.5151	−1.7867	3.9149	−28.0032	26.3744	0.1159
328.15	−15.6323	1.4696	−0.9700	9.8604	−9.6019		0.0621
			[BMIM][SCN] (1) + ethanol (2)				
298.15	−64.1816	28.9940	−0.4132	−6.4896	−66.7694	75.6451	0.2509
308.15	−39.8278	15.4327	0.5392	1.1287	−47.9414	49.2041	0.1617
318.15	−24.8960	7.0759	1.4334	4.3714	−30.5758	27.4258	0.0997
328.15	−13.2247	−0.1159	−7.3678	11.7597			0.1151
338.15	−9.9306	−0.0294	1.2509	6.3931	−7.3939		0.0402
348.15	−6.8051	0.3495	0.6822	2.3183	−4.5901		0.0552
			[BMIM][SCN] (1) + 1- propanol (2)				
298.15	−55.8665	13.2116	−36.8182	105.7791	−32.6328	−41.7368	0.2161
308.15	−34.3271	6.1447	−24.4819	73.6662	−23.8614	−27.4482	0.1284
318.15	−20.5731	4.4085	−23.6818	32.7685			0.1815
328.15	−11.7693	−2.9036	−11.6229	41.7327	3.1320	−33.1465	0.0882
338.15	−7.9777	−2.7034	−8.0503	30.9482	2.8461	−25.6206	0.0772
348.15	−5.5553	−2.0197	−6.2625	22.6584	3.6847	−20.2147	0.0668

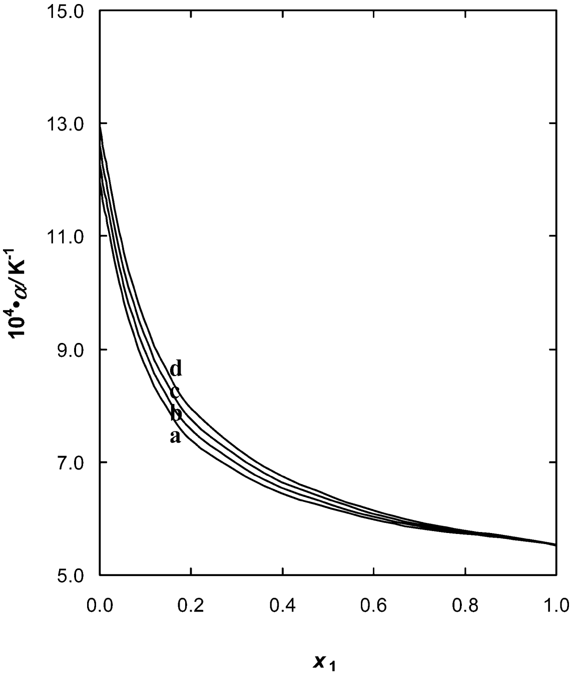


Figure 5. Plot of volume expansivity, α of the {[BMIM][SCN] (1) + methanol (2)} binary system against mole fraction x_1 at the following different temperatures: (a) 298.15 K; (b) 308.15 K; (c) 318.15 K; and (d) 328.15 K.

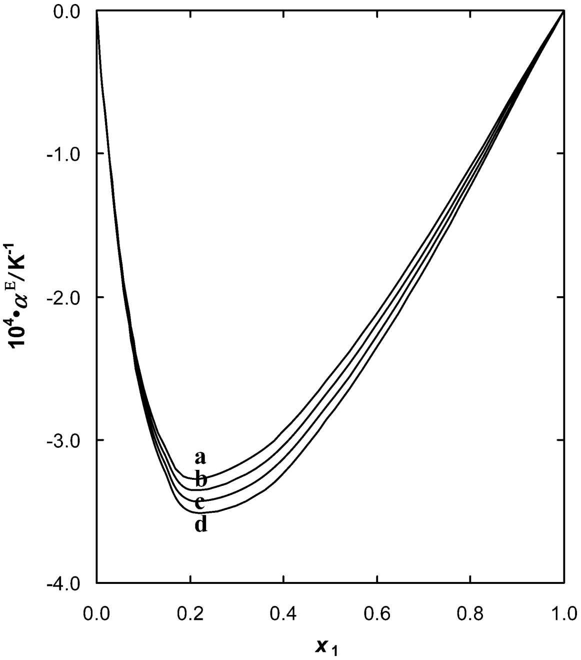


Figure 6. Plot of excess volume expansivity, α^E of the {[BMIM][SCN] (1) + methanol (2)} binary system against mole fraction x_1 at the following different temperatures: (a) 298.15 K; (b) 308.15 K; (c) 318.15 K; (d) 328.15 K.

and shape of the components and the packing effect are equally important factors. The values of V_m^E of a mixture formed from two self-associated (H-bonded) substances is a result of a number of effects that may contribute terms differing in sign. Disruption of H-bonds makes positive contribution, but specific interaction makes negative contributions to V_m^E. The free volume effect, which depends on differences in the characteristic pressures and temperatures of the components, makes negative contribution. Packing effects or conformational changes of the molecules in the mixtures are more difficult to categorize. However, interstitial accommodation and the effect of the condensation give further negative contributions. In our mixtures, the observed V_m^E values may be explained by four opposing sets of contributions: (1) expansion of an alcohol due to breaking of some of the hydrogen bonds of an alcohol during addition of the IL; (2) contraction due to specific interactions of an alcohol molecule with an IL; (3) size difference; and (4) expansion due to steric repulsion between alkyl chain of an alcohol (i.e., 1-propanol) and that of [BMIM][SCN] (van der Waals interactions between the alkane chains).

From the density−temperature dependence, one can calculate the volume expansivity (coefficient of thermal expansion), α, defined as

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \tag{5}$$

where subscript p indicates constant pressure. If one considers a plot of ρ versus T to be linear, then the magnitude of α increases with increasing temperature. A more careful analysis reveals that the densities of the pure IL measured here actually do not increase linearly with temperature. Using eqs 3 to 7, the volume expansivity can be presented in a function of the composition and temperature. The results of our analysis for pure substances and their mixtures are listed in Table 6S to 8S in Supporting Information for methanol, ethanol, and 1-propanol, respectively. The errors of derived values of parameters calculated through the statistical analysis depend significantly on the form of an equation chosen to represent density as a function of temperature at constant pressure. As a result, the increasing volume expansivity with increasing temperature was observed. This is a typical behavior for fluids in general. Plots of volume expansivity α of the binary {[BMIM][SCN] (1) + methanol (2)} system against mole fraction x_1 at different temperatures (298.15, 308.15, 318.15, 328.15) K are shown in Figure 5 and for two other alcohols in Figures 10S and 11S in Supporting Information. The trends of the volume expansivity with the composition of the mixtures is the same for three alcohols, for which the parameter α decreases with an increase of the mole fraction of 1-alcohol. The volume expansivity of these mixtures are considerably less dependent on temperature than it was observed for typical organic mixtures.[10] Moving along the concentration scale, the expansivity for an alcohol systems fall from a high value for pure alcohol to the considerably lower one for the IL. This decrease is nonlinear due to being less regular at low mole fraction of the IL. Thus, these solutions reveal the volumetric properties typical for mixtures of two compounds.

Next the corresponding excess function was determined. The excess volume expansivity was calculated by the equation

$$\alpha^E = \alpha - \phi_1^{id}\alpha_1 - \phi_2^{id}\alpha_2 \tag{6}$$

where ϕ_i^{id} is an ideal volume fraction given by the following relation

$$\phi_i^{id} = \frac{x_i V_{mi}}{x_1 V_{m1} + x_2 V_{m2}} \tag{7}$$

in which V_{mi} stands for a molar volume for a pure component i.

Typical concentration dependencies of excess expansivity are given in Figure 6 for {[BMIM][SCN] (1) + methanol (2)} binary system as an example. This mixture reveal minimum of α^E with absolute minimum values much lower (about $-3.5\ K^{-1}$ at 328.15 K) as was usually observed in organic mixtures.[10]

The curves are asymmetrical, especially for methanol with the minimum for methanol located at the IL mole fraction about 0.2. The excess expansivity increases (is less negative) with an increase of an alcohol alkyl chain (see Tables 6S and 8S and Figures 12S and 13S in Supporting Information). Thus the same lowering of the specific interaction between two dissimilar molecules decreases for the longer chain alcohol, as was observed for the excess molar volumes.

For a viscosity deviation, the negative deviations were observed for all three systems. This effect is the highest for methanol. These data are reported in Figures 14Sa,b,c in Supporting Information. Viscosity deviation was correlated by the Redlich−Kister equation. The parameters are listed in Table 8. Viscosity deviation decreases with an increase of temperature. The influence of temperature is much stronger than for the density. This indicates the specific interaction between dissimilar molecules in the solution, which decreases with increasing temperature. The minimum of $\Delta\eta$ shifts to the higher mole fraction of IL.

Conclusions

New data on densities and viscosities of pure ionic liquid, [BMIM][SCN] and 1-alcohols and their binary mixtures were measured. From the density−temperature dependence the volume expansivities, α and the excess volume expansivities were described for the IL at different temperatures. In this work, the negative deviations were observed for excess molar volumes, the excess volume expansivity, and viscosity deviation, which are a result of the strong interaction between IL and 1-alcohols. The lower V_m^E of IL with methanol means also possible better packing effects.

The results of the correlations with the second order polynomial, Redlich−Kister equation, and VFT equation of density, excess molar volumes, viscosity, and viscosity deviation were with very low standard deviation.

Supporting Information Available:

Fit parameters and standard deviation for the empirical correlation of density in the systems {[BMIM][SCN] (1) + methanol, ethanol, or 1-propanol (2)}, (Table 1S, Figures 1S and 2S); fit parameters of the VFT equation and the relative standard deviations for the correlation of viscosity as a function of temperature in the systems {[BMIM][SCN] (1) + methanol, ethanol, or 1-propanol (2)} together with standard deviations, (Tables 2S and 3S, Figures 3S and 4S); coefficients of polynomial for the correlation of density and viscosity in function of the IL mole fraction in the systems {[BMIM][SCN] (1) + methanol, ethanol, or 1-propanol (2)}, (Tables 4S and 5S, Figures 5S to 8S). The excess molar volumes (Figure 9Sa,b,c); volume expansivity as a function of temperature and composition (Tables 6S to 8S and Figures 10S and 11S); excess volume expansivities (Figures 12S and 13S); viscosity deviation (Figure 14Sa,b,c). This material is available free of charge via the Internet at http://pubs.acs.org.

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