Density and Viscosity of Binary Mixtures of {1-Butyl-3-methylimidazolium Thiocyanate + 1-Heptanol, 1-Octanol, 1-Nonanol, or 1-Decanol}

Urszula Domańska* and Marta Królikowska

Department of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

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Density and viscosity were determined for binary mixtures containing the ionic liquid 1-butyl-3-methylimidazolium thiocyanate ([BMIM][SCN]) and 1-alcohol (1-heptanol, 1-octanol, 1-nonanol, or 1-decanol) over the 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. These systems exhibit negative molar excess volumes. Volume expansivity and excess volume expansivity were described as functions of temperature and composition. The polynomial correlations describe the variation of density and viscosity with composition. For each system and for a chosen number of the Redlich−Kister parameters, A_r, the partial excess molar volumes, V_1^E and V_2^E, are presented. The Prigogine−Flory−Paterson (PFP) and the Flory−Benson−Treszczanowicz (FBT) models were used for the prediction of V_m^E and H_m^E of the measured systems. A comparison of the results for the four binary systems elucidates the influence of 1-alcohol carbon chain length on their physical properties.

Introduction

Ionic liquids (ILs) with a thiocyanate anion are novel solvents with interesting properties, which can be used in separation processes for several mixtures.[1–5] From the measurements of activity coefficients at infinite dilution we know that ILs as 1-ethyl-3-methylimidazolium thiocyanate ([EMIM][SCN]) and 1-butyl-3-methylimidazolium thiocyanate ([BMIM][SCN]) are very attractive for the separation of different organic compounds and especially aromatic hydrocarbons from aliphatic hydrocarbons or thiophene from aliphatic hydrocarbons with the highest selectivity in comparison with other ILs.[1,2] For ILs to be effectively used as solvents in liquid−liquid extraction, knowledge of the temperature and composition dependence of the density and viscosity is fundamental. Until recently, we presented the density and viscosity for binary mixtures containing [BMIM][SCN] and an alcohol (methanol, ethanol, and 1-propanol)[6] and those of [BMIM][SCN] with 1-alcohol (1-butanol, 1-pentanol, or 1-hexanol)[7] over a temperature range (298.15 to 348.15) K and ambient pressure.

The interactions in such liquid mixtures are influenced by dispersion forces, dipole−dipole interaction, hydrogen bonding, charge transfer, interstitial accommodation, and many others. Thus, the characteristic investigated here includes the effect of the alkyl chain length of an alcohol on density, viscosity, molar excess volumes, the partial molar volumes, molar excess enthalpies (predicted), volume expansivity, and excess volume expansivity.

This paper is a continuation of our wide range of investigation into the ILs containing the thiocyanate anion. We extend this study for [BMIM][SCN] with longer chain alcohols as 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol. The densities and viscosities of the binary systems with these alcohols are not known.

Table 1. Thermophysical Constants of Pure Alcohols and the IL: Measured Density, $\rho^{298.15}$, Density from Literature, ρ^{lit} (298.15 K), Dynamic Viscosity, η (298.15 K), and Dynamic Viscosity from Literature, η^{lit} (298.15 K)

compound	ρ (298.15 K) g·cm^{-3}	ρ^{lit} (298.15 K) g·cm^{-3}	η (298.15 K) mPa·s	η^{lit} (298.15 K) mPa·s
1-heptanol	0.81881	0.81946[a]	5.85	5.83[a]
1-octanol	0.82161	0.82302[a]	7.40	7.34[a]
1-nonanol	0.82427	0.82459[a]	9.34	9.02[a]
1-decanol	0.82638	0.82501[a]	11.09	11.32[a]
[BMIM][SCN]	1.06979		51.74	

[a] Ref 8.

Experimental Section

Materials. The IL 1-butyl-3-methylimidazolium thiocyanate, [BMIM][SCN], had a purity of mass fraction $w = 0.98$ and was supplied by Fluka. The structure of the investigated IL and its physicochemical properties were presented earlier.[3–7] The IL was further purified by subjecting the liquid to a very low pressure in a vacuum desiccator at temperature of about 300 K for approximately 5 h. This procedure removed any volatile chemicals and water from the IL. The alcohols and place of purchase are as follows: 1-heptanol (111-70-6, Aldrich, $w = > 0.99$), 1-octanol (111-87-5, Sigma-Aldrich, $w = > 0.99$), 1-nonanol (143-08-8, Aldrich, $w = > 0.99$), and 1-decanol (112-53-8, Aldrich, $w = > 0.99$); they were fractionally distilled over different drying reagents to the mass fraction purity $w = \geq 0.998$. They were also stored over freshly activated molecular sieves of type 4 Å (Union Carbide) and checked by gas−liquid chromatography (GLC). Basic volumetric properties of both IL and solvents are tabulated in Tables 1 to 5.

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* Corresponding author. Tel.: +48-22-6213115; fax: +48-22-6282741. E-mail address: ula@ch.pw.edu.pl.

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Table 2. Experimental Density, ρ, Excess Molar Volume, V_m^E, Dynamic Viscosity, η, and Viscosity Deviation, $\Delta\eta$, for the Binary System {[BMIM][SCN] (1) + 1-Heptanol (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
0.9793	1.06613	1.06022	1.05436	1.04856	1.04280	1.03706
0.8852	1.04862	1.04269	1.03679	1.03094	1.02511	1.01934
0.7981	1.03104	1.02506	1.01911	1.01322	1.00736	1.00153
0.6949	1.00883	1.00279	0.99676	0.99079	0.98485	0.97895
0.5703	0.98045	0.97426	0.96812	0.96202	0.95592	0.94988
0.4903	0.96098	0.95470	0.94846	0.94226	0.93605	0.92989
0.3997	0.93773	0.93134	0.92497	0.91862	0.91228	0.90595
0.3006	0.91091	0.90436	0.89784	0.89132	0.88479	0.87824
0.2203	0.88814	0.88149	0.87482	0.86814	0.86143	0.85469
0.1400	0.86424	0.85745	0.85063	0.84379	0.83685	0.82985
0.0806	0.84564	0.83875	0.83182	0.82481	0.81769	0.81046
0.0000	0.81881	0.81173	0.80455	0.79722	0.78975	0.78208
V_m^E/cm^3·mol^{-1}						
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.9793	−0.0606	−0.0650	−0.0735	−0.0866	−0.0954	−0.1036
0.8852	−0.2730	−0.3093	−0.3323	−0.3705	−0.4053	−0.4518
0.7981	−0.3654	−0.4079	−0.4565	−0.5172	−0.5805	−0.6549
0.6949	−0.4106	−0.4687	−0.5324	−0.6125	−0.6999	−0.8056
0.5703	−0.4706	−0.5330	−0.6113	−0.7072	−0.8107	−0.9422
0.4903	−0.4606	−0.5255	−0.6063	−0.7077	−0.8184	−0.9590
0.3997	−0.4202	−0.4846	−0.5638	−0.6633	−0.7791	−0.9219
0.3006	−0.3634	−0.4188	−0.4927	−0.5867	−0.6971	−0.8333
0.2203	−0.3255	−0.3771	−0.4402	−0.5240	−0.6234	−0.7498
0.1400	−0.2729	−0.3118	−0.3617	−0.4328	−0.5093	−0.6099
0.0806	−0.2003	−0.2285	−0.2669	−0.3170	−0.3721	−0.4434
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
η/mPa·s						
1.0000	51.74	34.87	24.19	16.70	12.73	9.980
0.9793	47.21	31.20	21.90	16.16	12.38	9.802
0.8852	39.81	26.77	19.03	14.20	10.97	8.707
0.7981	34.60	23.67	17.02	12.79	9.943	7.930
0.6949	28.65	19.86	14.49	11.02	8.620	6.884
0.5703	22.22	15.73	11.67	8.926	7.057	5.663
0.4903	18.92	13.59	10.19	7.875	6.240	5.029
0.3997	15.50	11.31	8.550	6.634	5.262	4.222
0.3006	12.31	9.061	6.884	5.306	4.186	3.403
0.2203	10.16	7.479	5.654	4.369	3.470	2.837
0.1400	8.422	6.213	4.725	3.685	2.935	2.383
0.0806	7.319	5.395	4.085	3.166	2.508	2.022
0.0000	5.851	4.260	3.184	2.434	1.900	1.512
$\Delta\eta$/mPa·s						
1.0000	0.00	0.00	0.00	0.00	0.00	0.00
0.9793	−3.58	−3.04	−1.86	−0.24	−0.12	0.00
0.8852	−6.67	−4.58	−2.75	−0.86	−0.52	−0.30
0.7981	−7.87	−5.02	−2.93	−1.03	−0.60	−0.34
0.6949	−9.09	−5.67	−3.29	−1.33	−0.81	−0.51
0.5703	−9.80	−5.99	−3.49	−1.64	−1.02	−0.68
0.4903	−9.43	−5.68	−3.29	−1.55	−0.97	−0.64
0.3997	−8.69	−5.18	−3.03	−1.50	−0.97	−0.67
0.3006	−7.33	−4.40	−2.61	−1.42	−0.97	−0.65
0.2203	−5.80	−3.52	−2.16	−1.21	−0.82	−0.54
0.1400	−3.85	−2.33	−1.40	−0.75	−0.48	−0.31
0.0806	−2.23	−1.33	−0.79	−0.42	−0.27	−0.17
0.0000	0.00	0.00	0.00	0.00	0.00	0.00
$10^4\ \alpha$/K^{-1}						
1.0000	5.547	5.534	5.522	5.508	5.495	5.481
0.9793	5.559	5.551	5.543	5.535	5.527	5.518
0.8852	5.624	5.639	5.654	5.670	5.686	5.703
0.7981	5.709	5.746	5.783	5.822	5.862	5.903
0.6949	5.853	5.916	5.980	6.046	6.115	6.185
0.5703	6.091	6.186	6.284	6.385	6.489	6.596
0.4903	6.280	6.397	6.517	6.641	6.768	6.900
0.3997	6.529	6.671	6.817	6.968	7.122	7.282
0.3006	6.852	7.023	7.198	7.378	7.563	7.754
0.2203	7.168	7.362	7.561	7.765	7.975	8.191
0.1400	7.555	7.772	7.995	8.223	8.458	8.699
0.0806	7.908	8.142	8.382	8.627	8.879	9.138
0.0000	8.517	8.772	9.033	9.300	9.574	9.855
$10^4\ \alpha^E$/K^{-1}						
1.0000	0.000	0.000	0.000	0.000	0.000	0.000
0.9793	−0.036	−0.035	−0.035	−0.034	−0.034	−0.034
0.8852	−0.193	−0.190	−0.188	−0.186	−0.184	−0.181
0.7981	−0.321	−0.317	−0.314	−0.310	−0.306	−0.302
0.6949	−0.444	−0.438	−0.432	−0.427	−0.421	−0.415
0.5703	−0.546	−0.539	−0.531	−0.524	−0.516	−0.508
0.4903	−0.587	−0.579	−0.571	−0.562	−0.553	−0.545
0.3997	−0.610	−0.601	−0.592	−0.583	−0.574	−0.564
0.3006	−0.600	−0.591	−0.582	−0.572	−0.562	−0.552
0.2203	−0.551	−0.542	−0.533	−0.524	−0.515	−0.505
0.1400	−0.443	−0.435	−0.428	−0.420	−0.412	−0.404
0.0806	−0.305	−0.299	−0.294	−0.288	−0.282	−0.277
0.0000	0.000	0.000	0.000	0.000	0.000	0.000

Table 3. Experimental Density, ρ, Excess Molar Volume, V_m^E, Dynamic Viscosity, η, and Viscosity Deviation, $\Delta\eta$, for the Binary System {BMIM][SCN] (1) + 1-Octanol (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
0.9619	1.06227	1.05633	1.05045	1.04462	1.03882	1.03309
0.8721	1.04342	1.03747	1.03158	1.02572	1.01988	1.01414
0.7673	1.02012	1.01413	1.00817	1.00228	0.99640	0.99057
0.6750	0.99886	0.99279	0.98677	0.98077	0.97482	0.96889
0.5739	0.97482	0.96864	0.96250	0.95641	0.95033	0.94427
0.4693	0.94907	0.94278	0.93652	0.93028	0.92405	0.91785
0.3599	0.92124	0.91482	0.90842	0.90201	0.89562	0.88921
0.2208	0.88432	0.87772	0.87111	0.86448	0.85782	0.85113
0.1352	0.86064	0.85392	0.84719	0.84037	0.83353	0.82658
0.0874	0.84717	0.84037	0.83352	0.82665	0.81963	0.81255
0.0000	0.82161	0.81464	0.80757	0.80039	0.79309	0.78559
			V_m^E/cm^3·mol^{-1}			
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.9619	−0.1122	−0.1167	−0.1278	−0.1421	−0.1512	−0.1697
0.8721	−0.2434	−0.2715	−0.3092	−0.3501	−0.3882	−0.4467
0.7673	−0.2885	−0.3368	−0.3929	−0.4632	−0.5340	−0.6221
0.6750	−0.2997	−0.3565	−0.4274	−0.5069	−0.5981	−0.7064
0.5739	−0.3023	−0.3629	−0.4385	−0.5317	−0.6335	−0.7579
0.4693	−0.2897	−0.3527	−0.4318	−0.5263	−0.6336	−0.7707
0.3599	−0.2708	−0.3310	−0.4084	−0.4987	−0.6078	−0.7424
0.2208	−0.2158	−0.2650	−0.3288	−0.4072	−0.4994	−0.6211
0.1352	−0.1563	−0.1937	−0.2472	−0.3036	−0.3781	−0.4690
0.0874	−0.1280	−0.1551	−0.1914	−0.2450	−0.2919	−0.3665
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
			η/mPa·s			
1.0000	51.74	34.87	24.19	16.70	12.73	9.980
0.9619	45.09	29.99	21.14	15.59	11.94	9.462
0.8721	39.69	26.63	18.95	14.06	10.82	8.592
0.6750	29.44	20.38	14.79	11.14	8.648	6.874
0.5739	24.86	17.39	12.72	9.644	7.509	5.987
0.4693	20.44	14.47	10.67	8.141	6.379	5.100
0.3599	16.30	11.70	8.719	6.654	5.233	4.233
0.2208	12.08	8.726	6.516	5.003	3.928	3.171
0.1352	10.03	7.237	5.396	4.158	3.272	2.633
0.0874	9.062	6.504	4.842	3.691	2.884	2.306
0.0000	7.398	5.285	3.887	2.931	2.262	1.782
			$\Delta\eta$/mPa·s			
1.0000	0.00	0.00	0.00	0.00	0.00	0.00
0.9619	−4.96	−3.75	−2.27	−0.59	−0.39	−0.21
0.8721	−6.38	−4.45	−2.65	−0.88	−0.57	−0.34
0.6750	−7.89	−4.88	−2.80	−1.08	−0.68	−0.44
0.5739	−7.99	−4.87	−2.82	−1.19	−0.76	−0.50
0.4693	−7.77	−4.70	−2.74	−1.25	−0.80	−0.53
0.3599	−7.06	−4.23	−2.47	−1.23	−0.80	−0.50
0.2208	−5.11	−3.09	−1.85	−0.97	−0.65	−0.42
0.1352	−3.36	−2.05	−1.24	−0.64	−0.41	−0.26
0.0874	−2.21	−1.37	−0.82	−0.44	−0.29	−0.19
0.0000	0.00	0.00	0.00	0.00	0.00	0.00
			10^4 α/K^{-1}			
1.0000	5.547	5.534	5.522	5.508	5.495	5.481
0.9619	5.576	5.572	5.568	5.565	5.561	5.557
0.8721	5.660	5.678	5.696	5.715	5.734	5.754
0.7673	5.789	5.832	5.876	5.921	5.968	6.016
0.6750	5.932	5.997	6.064	6.133	6.204	6.278
0.5739	6.123	6.213	6.306	6.401	6.499	6.600
0.4693	6.366	6.482	6.601	6.724	6.850	6.980
0.3599	6.681	6.824	6.971	7.122	7.277	7.437
0.2208	7.195	7.373	7.555	7.741	7.933	8.130
0.1352	7.591	7.789	7.992	8.200	8.413	8.631
0.0874	7.844	8.053	8.267	8.486	8.710	8.941
0.0000	8.373	8.601	8.834	9.073	9.317	9.568
			10^4 α^E/K^{-1}			
1.0000	0.000	0.000	0.000	0.000	0.000	0.000
0.9619	−0.064	−0.064	−0.063	−0.062	−0.061	−0.061
0.8721	−0.203	−0.201	−0.198	−0.196	−0.194	−0.191
0.7673	−0.342	−0.338	−0.334	−0.329	−0.325	−0.321
0.6750	−0.442	−0.437	−0.431	−0.425	−0.420	−0.414
0.5739	−0.525	−0.518	−0.511	−0.504	−0.497	−0.490
0.4693	−0.574	−0.566	−0.558	−0.550	−0.542	−0.533
0.3599	−0.575	−0.566	−0.558	−0.549	−0.540	−0.531
0.2208	−0.477	−0.470	−0.462	−0.454	−0.446	−0.438
0.1352	−0.347	−0.341	−0.335	−0.329	−0.323	−0.317
0.0874	−0.246	−0.241	−0.237	−0.233	−0.228	−0.224
0.0000	0.000	0.000	0.000	0.000	0.000	0.000

Table 4. Experimental Density, ρ, Excess Molar Volume V_m^E, Dynamic Viscosity, η, and Viscosity Deviation, $\Delta\eta$, for the Binary System {BMIM][SCN] (1) + 1-Nonanol (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
0.9651	1.06211	1.05618	1.05033	1.04450	1.03873	1.03299
0.8618	1.03846	1.03253	1.02662	1.02079	1.01499	1.00922
0.7658	1.01588	1.00989	1.00393	0.99803	0.99215	0.98631
0.6709	0.99314	0.98705	0.98102	0.97500	0.96904	0.96309
0.5697	0.96854	0.96240	0.95626	0.95015	0.94406	0.93798
0.3884	0.92366	0.91727	0.91089	0.90456	0.89820	0.89186
0.2814	0.89675	0.89024	0.88374	0.87725	0.87073	0.86418
0.2008	0.87627	0.86970	0.86296	0.85636	0.84977	0.84314
0.1203	0.85559	0.84888	0.84198	0.83540	0.82856	0.82164
0.0000	0.82427	0.81736	0.81040	0.80329	0.79610	0.78872
			V_m^E/cm^3·mol^{-1}			
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.9651	−0.0815	−0.0871	−0.1023	−0.1158	−0.1292	−0.1447
0.8618	−0.1942	−0.2295	−0.2665	−0.3179	−0.3681	−0.4271
0.7658	−0.2340	−0.2843	−0.3404	−0.4120	−0.4844	−0.5731
0.6709	−0.2437	−0.2995	−0.3687	−0.4485	−0.5403	−0.6482
0.5697	−0.2331	−0.3031	−0.3775	−0.4708	−0.5721	−0.6951
0.3884	−0.1835	−0.2423	−0.3101	−0.4085	−0.5108	−0.6462
0.2814	−0.1512	−0.2042	−0.2678	−0.3582	−0.4554	−0.5803
0.2008	−0.1201	−0.1725	−0.2201	−0.2825	−0.3831	−0.5131
0.1203	−0.0808	−0.1135	−0.1165	−0.2176	−0.2800	−0.3652
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
			η/mPa·s			
1.0000	51.74	34.87	24.19	16.70	12.73	9.980
0.9651	46.89	31.09	21.81	16.06	12.32	9.740
0.8618	41.61	27.80	19.67	14.55	11.22	8.890
0.6709	32.31	22.23	16.01	12.04	9.330	7.404
0.5697	28.04	19.35	14.03	10.61	8.260	6.512
0.3884	20.30	14.30	10.55	8.032	6.237	4.962
0.2814	16.58	11.81	8.739	6.629	5.139	4.102
0.2008	14.20	10.14	7.487	5.662	4.408	3.521
0.1203	12.19	8.664	6.378	4.782	3.695	2.971
0.0000	9.343	6.497	4.674	3.452	2.664	2.256
			$\Delta\eta$/mPa·s			
1.0000	0.00	0.00	0.00	0.00	0.00	0.00
0.9651	−3.37	−2.79	−1.70	−0.17	−0.06	0.03
0.8618	−4.27	−3.15	−1.83	−0.32	−0.12	−0.02
0.6709	−5.48	−3.30	−1.76	−0.30	−0.09	−0.03
0.5697	−5.45	−3.31	−1.76	−0.39	−0.14	−0.14
0.3884	−5.51	−3.22	−1.70	−0.57	−0.34	−0.29
0.2814	−4.69	−2.67	−1.43	−0.55	−0.36	−0.33
0.2008	−3.66	−2.05	−1.11	−0.45	−0.28	−0.29
0.1203	−2.25	−1.25	−0.64	−0.26	−0.18	−0.21
0.0000	0.00	0.00	0.00	0.00	0.00	0.00
			$10^4\ \alpha$/K^{-1}			
1.0000	5.547	5.534	5.522	5.508	5.495	5.481
0.9651	5.571	5.567	5.563	5.559	5.554	5.550
0.8618	5.674	5.695	5.716	5.738	5.761	5.784
0.7658	5.805	5.849	5.894	5.940	5.988	6.037
0.6709	5.966	6.032	6.100	6.170	6.242	6.316
0.5697	6.171	6.261	6.353	6.448	6.546	6.646
0.3884	6.634	6.766	6.901	7.040	7.183	7.329
0.2814	6.979	7.135	7.295	7.458	7.626	7.799
0.2008	7.284	7.457	7.634	7.816	8.002	8.194
0.1203	7.635	7.824	8.018	8.217	8.421	8.630
0.0000	8.264	8.477	8.694	8.916	9.144	9.377
			$10^4\ \alpha^E$/K^{-1}			
1.0000	0.000	0.000	0.000	0.000	0.000	0.000
0.9651	−0.066	−0.065	−0.064	−0.064	−0.063	−0.062
0.8618	−0.232	−0.229	−0.227	−0.224	−0.221	−0.219
0.7658	−0.353	−0.349	−0.345	−0.340	−0.336	−0.332
0.6709	−0.445	−0.439	−0.433	−0.428	−0.422	−0.416
0.5697	−0.511	−0.504	−0.497	−0.491	−0.484	−0.477
0.3884	−0.541	−0.533	−0.525	−0.517	−0.509	−0.501
0.2814	−0.491	−0.484	−0.477	−0.469	−0.461	−0.453
0.2008	−0.412	−0.405	−0.399	−0.392	−0.385	−0.378
0.1203	−0.287	−0.283	−0.278	−0.273	−0.268	−0.263
0.0000	0.000	0.000	0.000	0.000	0.000	0.000

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 of 2.5 μL. The analysis showed that the water mass fraction in the IL, alcohols, and the mixtures with the IL was $< 2.6 \cdot 10^{-4}$.

Density Measurements. The densities of all of the chemicals were measured using an Anton Paar GmbH 4500 vibrating-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). The 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 $1 \cdot 10^{-5}$ g·cm^{-3}, and the uncertainty of the measurements was estimated to be better than $\pm\ 1 \cdot 10^{-4}$ g·cm^{-3}. The densimeter's calibration was performed at atmospheric pressure using doubly distilled and degassed water, especially purified benzene (Chemipan, Poland, $w = > 0.99$) and dried air. Mixtures were prepared by weighing, with the uncertainty in mole fraction estimated as less than $5 \cdot 10^{-4}$. All weighing involved in the experimental work was carried out using a Mettler Toledo AB 204-S balance, with a precision of $\pm\ 1 \cdot 10^{-4}$ g. The uncertainty of the excess molar volumes depends on the uncertainties of the density measurements and can be assumed as $\pm$ 0.0005 cm^3·mol^{-1}. The densities of alcohols and IL are in satisfactory agreement with the literature values, which are shown with other physicochemical properties in Table 1.

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 of < 1 % for viscosities from (0.3 to 2500) mPa·s. The temperature was controlled internally with a precision of ± 0.01 K in a range from (283.15 to 373.15) K. The density used to describe viscosity is with the uncertainty of $\pm\ 1 \cdot 10^{-4}$ g·cm^{-3}; thus the uncertainty of dynamic viscosity is from (± 0.1 to ± 23) mPa·s {it depends on the range of measurements, and it is for the first capillary [ranging from (0.3 to 10) mPa·s; diameter 1.6, ball 1.5] for the maximum values of viscosity ± 0.1 mPa·s; for the second capillary [ranging from (2.5 to 70) mPa·s, diameter 1.8, ball 1.6] for the maximum values of viscosity ± 7 mPa·s; for the third capillary [ranging from (20 to 230) mPa·s, diameter 3.0, ball 2.5] for the maximum values of viscosity ± 23 mPa·s}.

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) + 1-heptanol, 1-octanol, 1-nonanol, or 1-decanol (2)} at different temperatures, are listed in Tables 2 to 5. The densities and viscosities are higher for the IL than for the 1-alcohol and decrease with increasing 1-alcohol content. As usual, both density and viscosity decrease with an increasing temperature. We found no previous data as a function of temperature for these systems for comparison.

Experimental densities at ambient pressure investigated in this work are shown as an example for the {[BMIM][SCN] (1) + 1-heptanol (2)} binary system in Figure 1 (three other systems are shown in Figures 1S to 3S in the Supporting Information (SI)). A second-order polynomial was found to satisfactorily correlate the change of density with temperature:

$$\rho = a_2 T^2 + a_1 T + a_0 \qquad (1)$$

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 6 for the pure substances and in Table 1S in the SI for the mixtures.

Table 5. Experimental Density, ρ, Excess Molar Volume V_m^E, Dynamic Viscosity, η, and Viscosity Deviation, $\Delta\eta$, for the Binary System {BMIM][SCN] (1) + 1-Decanol (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
0.9587	1.05980	1.05386	1.04802	1.04220	1.03643	1.03070
0.8692	1.03762	1.03169	1.02580	1.01998	1.01418	1.00843
0.7576	1.00983	1.00383	0.99787	0.99196	0.98605	0.98021
0.6659	0.98705	0.98101	0.97494	0.96892	0.96291	0.95695
0.5922	0.96881	0.96263	0.95650	0.95040	0.94432	0.93826
0.4924	0.94430	0.93802	0.93178	0.92554	0.91935	0.91313
0.3512	0.91003	0.90351	0.89708	0.89079	0.88437	0.87797
0.2537	0.88657	0.87995	0.87342	0.86689	0.86036	0.85379
0.1621	0.86467	0.85799	0.85135	0.84470	0.83800	0.83123
0.0747	0.84395	0.83719	0.83040	0.82359	0.81670	0.80976
0.0000	0.82638	0.81953	0.81262	0.80561	0.79848	0.79121
V_m^E/cm^3·mol^{-1}						
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.9587	−0.0763	−0.0822	−0.1017	−0.1196	−0.1363	−0.1571
0.8692	−0.1298	−0.1635	−0.2030	−0.2537	−0.3027	−0.3627
0.7576	−0.1403	−0.1911	−0.2510	−0.3232	−0.3955	−0.4885
0.6659	−0.1225	−0.1891	−0.2535	−0.3336	−0.4201	−0.5281
0.5922	−0.1021	−0.1588	−0.2303	−0.3162	−0.4142	−0.5312
0.4924	−0.0744	−0.1323	−0.2054	−0.2903	−0.3979	−0.5185
0.3512	−0.0502	−0.0842	−0.1467	−0.2555	−0.3546	−0.4833
0.2537	−0.0348	−0.0620	−0.1197	−0.1963	−0.2950	−0.4135
0.1621	−0.0135	−0.0385	−0.0851	−0.1500	−0.2298	−0.3244
0.0747	−0.0046	−0.0200	−0.0423	−0.0827	−0.1320	−0.2033
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
η/mPa·s						
1.0000	51.74	34.87	24.19	16.70	12.73	9.980
0.9587	49.31	33.30	23.30	16.10	12.18	9.624
0.8692	45.01	30.46	21.56	15.15	11.46	9.047
0.7576	40.00	27.12	19.40	14.04	10.76	8.487
0.6659	36.09	24.50	17.59	12.98	9.998	7.875
0.5922	32.87	22.29	16.04	11.98	9.243	7.278
0.4924	28.36	19.52	14.06	10.62	8.183	6.455
0.3512	22.48	15.62	11.39	8.553	6.586	5.195
0.2537	18.67	13.08	9.541	7.162	5.526	4.411
0.1621	15.50	10.96	7.964	5.959	4.567	3.578
0.0747	13.07	9.168	6.582	4.880	3.741	2.909
0.0000	11.09	7.632	5.375	3.928	2.964	2.399
$\Delta\eta$/mPa·s						
1.0000	0.00	0.00	0.00	0.00	0.00	0.00
0.9587	−0.75	−0.44	−0.11	−0.07	−0.15	−0.04
0.8692	−1.41	−0.85	−0.17	0.12	0.01	0.06
0.7576	−1.89	−1.15	−0.23	0.44	0.39	0.34
0.6659	−2.07	−1.27	−0.31	0.55	0.53	0.43
0.5922	−2.29	−1.47	−0.48	0.49	0.50	0.39
0.4924	−2.74	−1.52	−0.58	0.40	0.41	0.32
0.3512	−2.89	−1.58	−0.59	0.14	0.19	0.13
0.2537	−2.73	−1.46	−0.61	−0.01	0.08	0.09
0.1621	−2.18	−1.09	−0.46	−0.04	0.02	−0.05
0.0747	−1.06	−0.50	−0.20	0.00	0.05	−0.06
0.0000	0.00	0.00	0.00	0.00	0.00	0.00
$10^4\ \alpha$/K^{-1}						
1.0000	5.547	5.534	5.522	5.508	5.495	5.481
0.9587	5.572	5.570	5.568	5.565	5.563	5.560
0.8692	5.666	5.685	5.705	5.726	5.747	5.769
0.7576	5.842	5.888	5.935	5.983	6.033	6.084
0.6659	6.023	6.090	6.158	6.229	6.301	6.375
0.5922	6.187	6.270	6.355	6.443	6.533	6.625
0.4924	6.430	6.535	6.642	6.753	6.866	6.982
0.3512	6.816	6.950	7.087	7.228	7.373	7.521
0.2537	7.118	7.272	7.429	7.591	7.756	7.925
0.1621	7.445	7.616	7.790	7.970	8.153	8.341
0.0747	7.811	7.997	8.188	8.383	8.582	8.787
0.0000	8.184	8.382	8.584	8.791	9.003	9.220
$10^4\ \alpha^E$/K^{-1}						
1.0000	0.000	0.000	0.000	0.000	0.000	0.000
0.9587	−0.088	−0.087	−0.086	−0.085	−0.084	−0.083
0.8692	−0.238	−0.235	−0.232	−0.229	−0.227	−0.224
0.7576	−0.363	−0.359	−0.354	−0.350	−0.345	−0.341
0.6659	−0.427	−0.422	−0.416	−0.411	−0.405	−0.400
0.5922	−0.459	−0.453	−0.447	−0.441	−0.435	−0.429
0.4924	−0.480	−0.473	−0.467	−0.460	−0.454	−0.447
0.3512	−0.465	−0.458	−0.451	−0.445	−0.438	−0.431
0.2537	−0.415	−0.409	−0.403	−0.396	−0.390	−0.383
0.1621	−0.325	−0.320	−0.315	−0.310	−0.305	−0.299
0.0747	−0.183	−0.180	−0.177	−0.174	−0.171	−0.167
0.0000	0.000	0.000	0.000	0.000	0.000	0.000

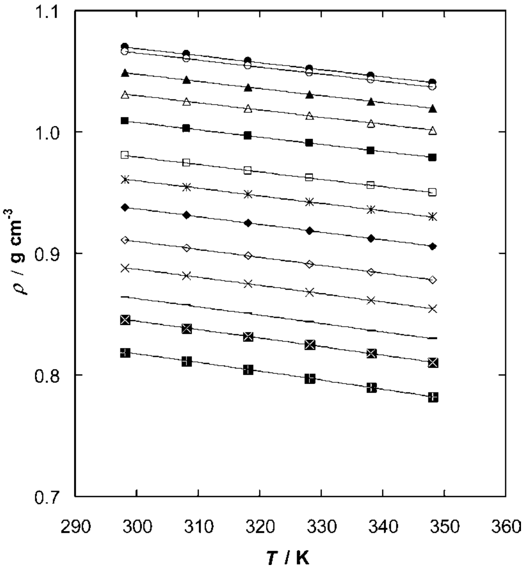

Figure 1. Density ρ for the {[BMIM][SCN] (1) + 1-heptanol (2)} binary system as a function of temperature at different mole fractions of the IL. ●, 1.0000; ○, 0.9793; ▲, 0.8852; △, 0.7981; ■, 0.6949; □, 0.5703; *, 0.4903; ♦, 0.3997; ◊, 0.3006; black ×, 0.2203; –, 0.1400; white ×, 0.0806; white +, 0.0000. Solid lines represent the polynomial.

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

	$10^7 \cdot a_2$	$10^4 \cdot a_1$	a_0
	$g \cdot cm^{-3} \cdot K^{-2}$	$g \cdot cm^{-3} \cdot K^{-1}$	$g \cdot cm^{-3}$
[BMIM][SCN]	2.300	−7.308	1.267
1-heptanol	−7.34	−2.60	0.961
1-octanol	−6.38	−3.10	0.970
1-nonanol	−5.84	−3.3	0.975
1-decanol	−5.32	−3.6	0.981

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

The polynomial correlations are plotted with solid lines in Figure 1 and in Figures 1S to 3S in the SI 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.[9–11] This equation has been used to correlate variations of viscosity with temperature in a measured system:

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

The fit parameters, determined empirically, are in general A, B, and T_0 when the linear relation is observed between the logarithmic value of $\eta T^{0.5}$ and $(T - T_0)^{-1}$ according to 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, and T_0 is lower than the glass transition temperature. The difference between T_0 and $T_{tr(g)}$ is approximately (50 to 60) K.[9] For [BMIM][SCN] the temperature of glass transition determined by differential scanning calorimetry was 181.6 K.[3] For the best correlation of the experimental curves the value of T_0 equal to 127 K was used in the calculations. One value of parameter T_0 was used for all of the solutions with different alcohols and for different concentrations, as it is known that ΔT_0 discussed by many authors may be 10 K.[10,11] The values of A and B parameters together with the standard deviations are presented in Tables 2S and 3S in the SI.

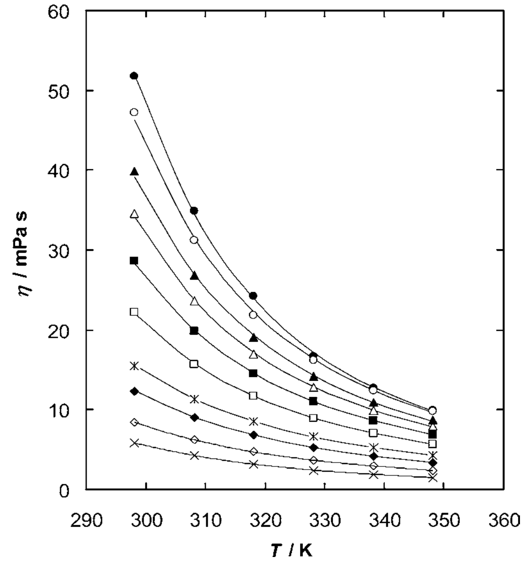

Figure 2. Dynamic viscosity η for the {[BMIM][SCN] (1) + 1-heptanol (2)} binary system as a function of temperature at different approximated mole fractions of the IL. ●, 1.0000; ○, 0.9793; ▲, 0.8852; △, 0.7981; ■, 0.6949; □, 0.5703; *, 0.3997; ♦, 0.3006; ◊, 0.1400; ×, 0.0000. Solid lines represent the VFT equation.

The VFT equation suitably correlates, as a function of the temperature, not only the viscosities of the pure IL but also the viscosities of the mixtures for the binary systems through the composition range (see Figure 2 and Figures 4S to 6S in the SI). The parameters A and B in eq 2 change smoothly with composition for all four systems. These parameters are strongly sensitive to the choice of T_0. The standard deviations are listed in Table 3S.

The viscosity decreases rapidly with an increase of temperature, which can be a result of the disruption of intramolecular hydrogen bonding between the IL molecules as well as the hydrogen bonding with the small impurities of water with the IL. Water in an alcohol or in the IL could change the density and viscosity by about 1 %. Water may be accommodated in the IL structure in the IL-rich region.

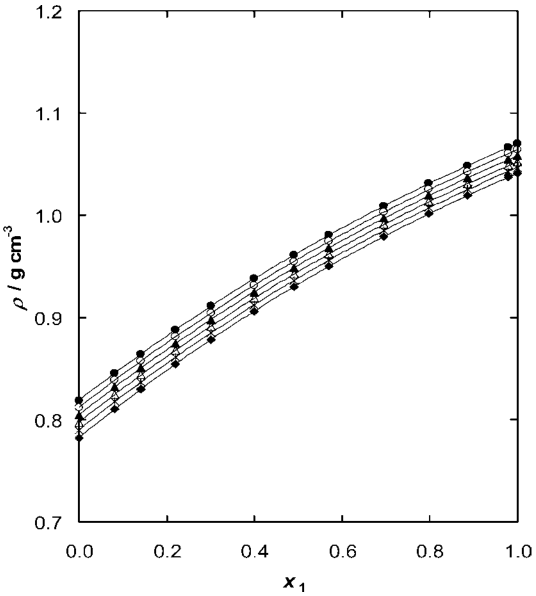

Figure 3. Density ρ for the {[BMIM][SCN] (1) + 1-heptanol (2)} system, as a function of mole fraction of the IL, at different temperatures. ●, 298.15 K; ○, 308.15 K; ▲, 318.15 K; △, 328.15 K; *, 338.15 K; ♦, 348.15 K. Solid lines represent the polynomial correlation.

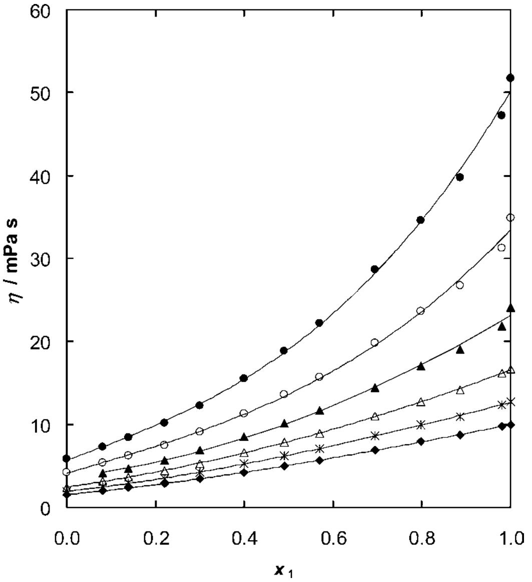

Figure 4. Dynamic viscosity, η, for the {[BMIM][SCN] (1) + 1-heptanol (2)} binary system as a function of mole fractions of the IL, at a different temperatures. ●, 298.15 K; ○, 308.15 K; ▲, 318.15 K; △, 328.15 K; *, 338.15 K; ♦, 348.15 K. Solid lines represent the polynomial correlation.

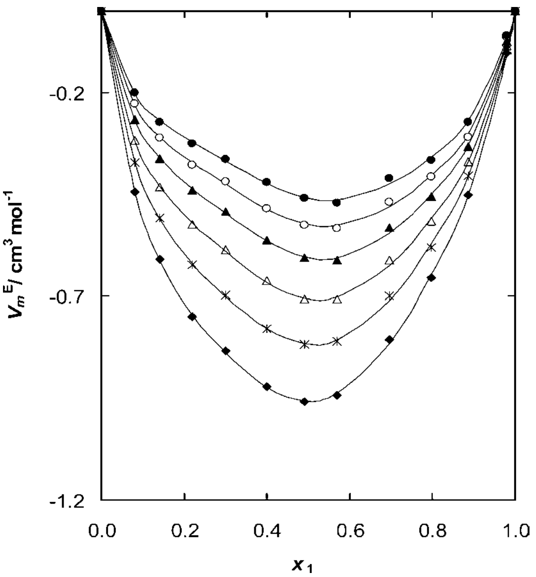

Figure 5. Excess molar volume, V_m^E, versus x_1 for the {[BMIM][SCN] (1) + 1-heptanol (2)} binary system at different temperatures. ●, 298.15 K; ○, 308.15 K; ▲, 318.15 K; △, 328.15 K; *, 338.15 K; ♦, 348.15 K. Solid lines represent the Redlich−Kister equation.

Table 7. Coefficients of the Redlich−Kister Equation for the Correlation of the Excess Molar Volume (V_m^E/cm^3·mol^{-1}) of the System {[BMIM][SCN] (1) + 1-Alcohol (2)}

i	b_i	$10^2 \cdot c_i$
	[BMIM][SCN] (1) + 1-Heptanol (2)	
1	9.989	−3.910
2	−3.110	0.876
3	2.832	−1.299
4	−2.523	1.015
	[BMIM][SCN] (1) + 1-Octanol (2)	
1	10.715	−3.932
2	−3.509	1.017
3	−0.001	−0.437
	[BMIM][SCN] (1) + 1-Nonanol (2)	
1	10.937	−3.906
2	−2.957	0.771
3	0.985	−0.594
	[BMIM][SCN] (1) + 1-Decanol (2)	
1	10.604	−3.614
2	−1.837	0.413
3	3.274	−1.303
4	−1.019	0.200

Effect of Composition on Density. The densities are highest for the pure IL, with decreasing values with increasing 1-alcohol content. The character of changes is presented in Figure 3 as an example for the {[BMIM][SCN] (1) + 1-heptanol (2)} binary system together with solid lines calculated with the polynomial (the presentation for the other 1-alcohols are in Figures 7S to 9S in the SI). The parameters of the correlation are shown in Table 4S in the SI.

The character of changes of dynamic viscosities with composition is presented in Figure 4 for the same system together with solid lines calculated with the polynomial (presentation for the other 1-alcohols is in Figures 10S to 12S in the SI). The parameters of correlation are shown in Table 5S in the SI. The observed decrease of viscosity with an increase of alcohol content is particularly strong in dilute solutions of an alcohol in the IL. The weakening of the strong hydrogen bonding interactions between the cation and the anion of the IL made by the addition of small amounts of an alcohol to 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) + 1-alcohol (2)} are recorded in Tables 2 to 5. The data were calculated by the smoothing Redlich−Kister equation:

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

with temperature dependence parameters

$$A_i(T) = b_i + c_iT \tag{4}$$

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 7. The values of V_m^E as well as the Redlich−Kister fits are plotted in Figure 5 for 1-heptanol and in Figures 13S to 15S in the SI for the other 1-alcohols 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 (−0.47, −0.30, −0.24, and −0.14) cm^3·mol^{-1} at x_1 = 0.57, 0.57, 0.67, and 0.75 (at T = 298.15 K) for 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol, respectively. In comparison with the alcohols with the shorter length of carbon chains,[6,7] the less negative values are observed, and the minimum of the V_m^E is shifted to the higher mole fraction of the IL. With increasing temperature the minimum of V_m^E shifts to lower values of V_m^E. The excess molar volume data become less negative in the following order: 1-heptanol < 1-octanol < 1-nonanol < 1-decanol. The small negative deviations from ideality observed for these systems have to be the results of a dipole−dipole interaction of the IL with the 1-alcohol. The molecular size and shape of the components and the packing effect are equally important factors. The values of the excess molar volumes, V_m^E, of mixtures formed from two self-associated (H-bonded) substances are a result of a number of effects which may

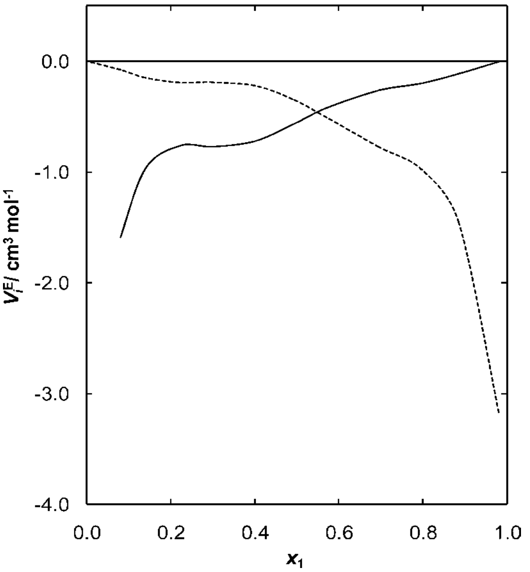

Figure 6. Excess partial molar volumes, V_1^E and V_2^E, versus x_1 for the {[BMIM][SCN] (1) + 1-heptanol (2)} binary system, calculated from the Redlich−Kister equation at T = 298.15 K. solid line, $-V_1^E$; dotted line, $-V_2^E$.

contribute to terms differing in sign. Disruption of the H-bonds makes a 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 a negative contribution. Packing effects or conformational changes of the molecules in the mixtures are more difficult to categorize.

For the given system and for chosen number of parameters A_r, the excess partial molar volumes V_1^E and V_2^E may be calculated according to the eqs:

$$V_1^E = V^E(x_1, A) - x\left(\frac{\partial V^E(x_1, A)}{\partial x_1}\right) \tag{5}$$

$$V_2^E = V^E(x_1, A) + (1 - x_1)\left(\frac{\partial V^E(x_1, A)}{\partial x_1}\right) \tag{6}$$

$$\left[\frac{\partial V^E(x_1, A)}{\partial x_1}\right] = \sum_{r=1}^{k} A_r[(1 - 2x_1)(2x_1 - 1)^{r-1} + 2(r - 1)(2x_1 - 1)^{r-2}(x_1 - x_1^2)] \tag{7}$$

Figure 6 shows the values of the excess partial molar volumes, V_1^E and V_2^E, calculated from the Redlich−Kister equation at 298.15 K for the IL (1) in 1-heptanol (2) as an example. In the system with 1-heptanol the excess partial molar volumes, V_1^E of the IL and V_2^E of an alcohol, showed negative values for the diluted solutions of IL and an alcohol (V_1^E of the IL is less negative than V_2^E for 1-heptanol). The positive effect of the disruption of the H-bond structure at a high dilution of an alcohol or an IL and negative effect in more concentrated solutions was observed as a result of partial H-bond disruption, as was found by us previously for the shorter-chain alcohols.[6,7] Usually, the negative contributions decrease in absolute values with an increase in the size of the alkyl chain of an alcohol. The discussed data are summarized in Tables 6S to 9S in the SI for all measured alcohols.

The small intermolecular interactions between the hydroxyl group and the IL lead to the small negative values of the excess molar volumes, V_m^E, in the measured systems. It was found for many ILs with organic solvent mixtures that the values of the H_m^E were positive.[12,13] In the present work we extend these thermodynamic studies to the excess molar enthalpies H_m^E for mixtures of {[BMIM][SCN] + 1-alcohol} using the Prigogine−Flory−Paterson (PFP) model or Flory−Benson−Treszczanowicz (FBT) model. These are very well-known, suitable theoretical models based on a statistical mechanical derivation, which accounts for the self-association in hydrogen-bonded liquid mixtures.[14,15]

Table 8. PFP and FBT Model Parameters of Pure Components at T/K = 298.15

component	10^4 α K^{-1}	10^4 κ_T GPa^{-1}	Δh^* kJ·mol^{-1}	Δv^* cm^3·mol^{-1}	K
[BMIM][SCN]	5.55[a]	0.3499[b]			
1-heptanol	8.47[c]	8.15[c]	−24.5	−5.6	24.2
1-octanol	8.27[c]	7.77[c]	−24.5	−5.6	22.2
1-nonanol	8.18[c]	7.40[c]	−24.5	−5.6	20.4
1-decanol	8.12[c]	7.33[c]	−24.5	−5.6	18.9

[a] This work. [b] Ref 20. [c] Ref 19.

Table 9. Characteristic Parameters of Pure Components: Volume V^*, Temperature T^*, Pressure P^*, and Reduce Volume $\tilde{v}$ from the PFP and FBT Models at T/K = 298.15

component	V^* cm^3·mol^{-1}	T^* K	P^* J·cm^{-3}	$\tilde{v}$
[BMIM][SCN]	160.54	7579	624	1.149
1-heptanol	116.75	5754	457	1.215
1-octanol	130.88	5837	465	1.211
1-nonanol	144.74	5876	481	1.209
1-decanol	158.59	5902	481	1.208

Prigogine−Flory−Paterson (PFP) Model. [14] The theory of Flory and co-workers[16−18] has been useful in predicting and correlating the thermodynamic properties of binary mixtures of polar and nonpolar molecules. The PFP model has been applied to the chosen mixtures discussed here using the same procedure and formulas as published before.[19] The interchange parameter χ_{12} which minimized V_m^E experimental data was adjusted and then used to predict the H_m^E in the system {[BMIM][SCN] + 1-alcohol}, using the thermal expansivity, α, from this work and isobaric compressibility, κ_T of [BMIM][SCN], adjusted just now in our laboratory.[20] The pure substance parameters, thermal expansivity, α, the isothermal compressibility, κ_T, the enthalpy of hydrogen bonding, ΔH_i^*, the values of changing volumes, Δv_i^*/cm^3·mol^{-1}, and the association constant, $K_{298.15}$, for solvents are presented in Table 8. The value of $\Delta v_2^* = 0$, $K_2 = 0$, and $\Delta H_2^* = 0$ for the IL were assumed to be zero, which means that the IL is not a self-associating compound (no data).

Flory−Benson−Treszczanowicz (FBT) Model. [15] The FBT model has been applied first to the excess volumes of binary systems formed by mixing a polar substance base with an alkane or cycloalkane. In this work the excess volumes were described as sums of two contributions. One arises from the self-association of an alcohol base and is evaluated according to the Mecke−Kempter continuous association model.[21] The other comprises the equation of state and interaction effects, which are treated according to the Flory theory.[16] The chemical contribution arising from the self-association is:

$$V_m^E = \Delta v x_1\left(\frac{1}{\chi_1} - \frac{1}{\chi}\right) \tag{8}$$

where Δv is the increase in volume per mole of bonds formed between associating molecules and x_1 is the mole fraction of these molecules in the mixture. The values of χ and χ_1 represent the average degree of self-association of the associating molecule

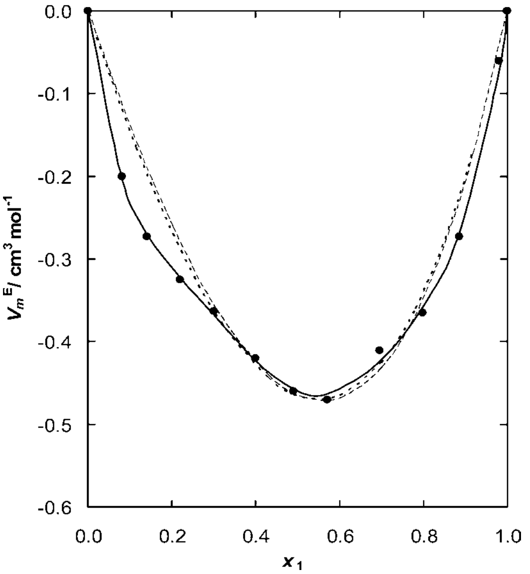

Figure 7. Values of V_m^E for the {[BMIM][SCN] (1) + 1-heptanol (2)} binary system at $T = 298.15$ K. ●, experimental results; solid line, the Redlich−Kister correlation; dotted line, the PFP model; dashed line, the FBT model.

Table 10. Interaction Parameters, χ_{12}, for the {[BMIM][SCN] (1) + 1-Alcohol (2)} Binary Systems at T/K = 298.15

χ_{12} / J·mol^{-1}	PFP	FBT
1-heptanol	30.9	31.3
1-octanol	36.7	37.1
1-nonanol	34.5	34.5
1-decanol	40.0	40.0

in the mixture and in the pure liquid, respectively. Application of the Flory theory requires equation-of-state parameters for the pure components. The pure component's characteristic parameters, volume V^*, temperature T^*, pressure P^*, and reduce volume $\tilde{v}$ at 298.15 K are presented in Table 9.

A comparison of the predicted and the experimental excess properties for {[BMIM][SCN] + 1-alcohol} binary mixtures shows that the PFP and FBT models are able to describe the excess functions. For the systems under study, the calculated V_m^E values are very similar to the experimental values (see Figure 7 and Figures 16S to 18S in the SI). The general agreement of the sign and character of the curves is good, but the symmetry of V_m^E especially for the longer chain 1-alcohols is not described properly. The predictive curves are shifted to the lower mole fraction of the IL.

The values of the predicted H_m^E by the FBT model at $T = 298.15$ K using the parameters listed in Tables 9 and 10 are plotted in Figure 8. Both models present the very similar data of H_m^E. For all alcohols the excess molar enthalpy is positive in these systems. The maximum values of $H_{m(max)}^E$ are as follows: 1002.12 J·mol^{-1} at $x_1 = 0.525$, 1294.88 J·mol^{-1} at $x_1 = 0.525$, 1286.44 J·mol^{-1} at $x_1 = 0.5$, and 1593.12 J·mol^{-1} at $x_1 = 0.5$ for 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol, respectively. Finally, it should be noted that estimates of excess molar volumes and enthalpies, based on the interchange energy parameters, obtained from the present analysis of excess molar volumes, generally exhibit relatively large deviations from the experimental results due to the importance of contributions from other structural effects, such as interstitial accommodation and conformational changes. The positive excess molar enthalpies demonstrate weak interactions between the IL and the alcohols under study.

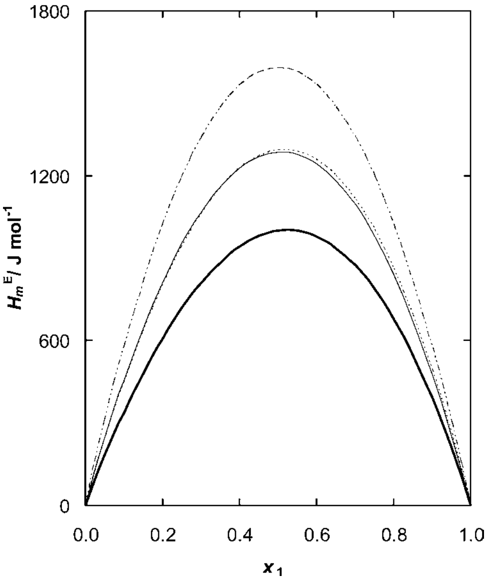

Figure 8. Predicted H_m^E values for the {[BMIM][SCN] (1) + 1-alcohol (2)} binary systems at $T = 298.15$ K by the FBT model. Bold solid line, 1-heptanol; solid line, 1-octanol; dotted line, 1-nonanol; dashed line, 1-decanol.

Volume Expansivity and the Excess Volume Expansivity. From the density−temperature dependence the volume expansivity (coefficient of thermal expansion), α, defined by the eq 9 was calculated

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \qquad (9)$$

where the subscript p indicates constant pressure. The volume expansivity can be presented in a function of the composition and temperature as it is shown for pure substances and their mixtures in Tables 2 to 5 for 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol, 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 {[BMIM][SCN] (1) + 1-heptanol (2)} binary system against mole fraction x_1 at different temperatures are shown in Figure 9 and for three other alcohols in Figures 19S to 21S in the SI. The trends of the volume expansivity with the composition of the mixtures is the same for all alcohols, for which the parameter α decreases with an increase of the mole fraction of the IL. The volume expansivity of these mixtures is considerably less dependent on temperature than that observed for typical organic mixtures.[22] Moving along the concentration scale, the expansivity for an alcohol system falls from a high value for a pure alcohol to the considerably lower one for the IL. This decrease is nonlinear, being less regular at a low mole fraction of the IL. Thus, these solutions reveal the volumetric properties typical for mixtures of the two compounds.

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

$$\alpha^E = \alpha - \varphi_1^{id}\alpha_1 - \varphi_2^{id}\alpha_2 \qquad (10)$$

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

$$\varphi_1^{\mathrm{id}} = \frac{x_i V_{\mathrm{m}i}}{x_1 V_{\mathrm{m}1} + x_2 V_{\mathrm{m}2}} \qquad (11)$$

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

Typical concentration dependencies of excess expansivity are given in Figure 10 for the {[BMIM][SCN] (1) + 1-heptanol (2)} binary system as an example. The curves are asymmetrical, with the minimum for all 1-alcohols located at the IL mole fraction of about 0.4 to 0.5. The excess expansivity increases (is less negative) with an increase of an alcohol alkyl chain (see Figures 22S to 24S in the SI). 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.

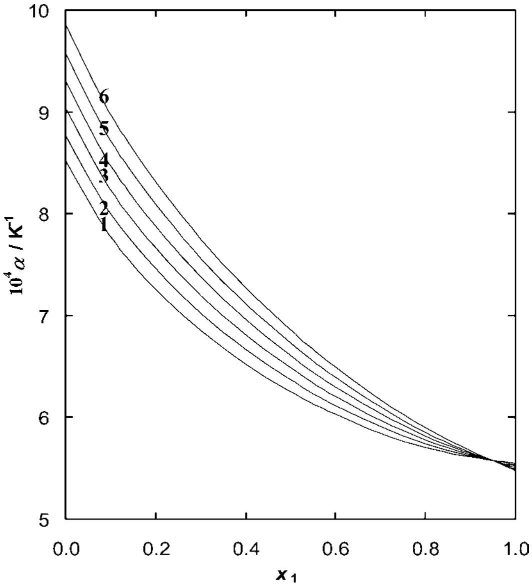

Figure 9. Plot of volume expansivity, α, of the {[BMIM][SCN] (1) + 1-heptanol (2)} binary system against mole fraction x_1 at different temperatures. **1**, 298.15 K; **2**, 308.15 K; **3**, 318.15 K; **4**, 328.15 K; **5**, 338.15 K; **6**, 348.15 K.

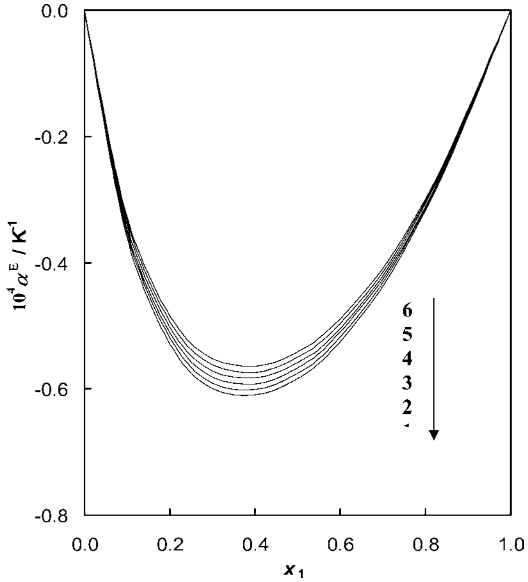

Figure 10. Plot of excess volume expansivity, α^E, of the {[BMIM][SCN] (1) + 1-heptanol (2)} binary system against mole fraction x_1 at different temperatures. **1**, 298.15 K; **2**, 308.15 K; **3**, 318.15 K; **4**, 328.15 K; **5**, 338.15 K; **6**, 348.15 K.

Table 11. Coefficients of the Redlich−Kister Equation for the Correlation of the Viscosity Deviation ($\Delta\eta$/mPa·s)[a] of the System {[BMIM][SCN] (1) + 1-Alcohol (2)}, along with the Standard Deviations (σ/mPa·s)

T/K	D_1	D_2	D_3	D_4	σ/mPa·s
		[BMIM][SCN] (1) + 1-Heptanol (2)			
298.15	−37.0665	3.6388	−17.6768	34.0226	0.77
308.15	−22.1026	1.5706	−15.7468	28.1768	0.74
318.15	−12.8216	0.1427	−10.2471	18.4875	0.45
328.15	−6.3293	−1.0930	−1.2669	3.7512	0.07
338.15	−4.0216	−1.3721	−0.6796	3.0414	0.05
348.15	−2.7163	−1.0528	0.2252	1.6425	0.05
		[BMIM][SCN] (1) + 1-Octanol (2)			
298.15	30.5745	0.9844	−28.3821	43.8108	0.87
308.15	−18.1744	0.2760	−23.654	35.2067	0.70
318.15	−10.4963	−0.4279	−14.7951	21.9630	0.43
328.15	−4.8310	−1.6302	−3.8989	6.7385	0.08
338.15	−3.0933	−1.2867	−2.6463	4.7456	0.06
348.15	−2.0300	−0.6491	−1.3436	2.3165	0.03
		[BMIM][SCN] (1) + 1-Nonanol (2)			
298.15	−21.8784	−3.8907	−17.8313	35.4062	0.75
308.15	−12.5663	−2.5949	−16.2285	31.9378	0.65
318.15	−6.5592	−1.8230	−10.3274	20.3096	0.16
328.15	−1.8402	−2.3700	−1.5031	4.7391	0.01
338.15	−0.9040	−2.1949	−0.8251	3.2059	0.01
348.15	−0.7930	−1.9330	−0.3235	1.0784	0.02
		[BMIM][SCN] (1) + 1-Decanol (2)			
298.15	−10.3506	−6.6026	−7.5355	8.5041	0.05
308.15	−6.1593	−2.5453	−2.9996	4.5517	0.04
318.15	−2.1877	−2.2716	−0.2920	2.0253	0.04
328.15	1.6569	−3.5861	−2.2469	5.0149	0.03
338.15	1.7796	−3.2306	−2.7355	6.2933	0.04
348.15	1.4218	−2.2116	−2.1846	2.6867	0.04

[a] Calculated with the equation: $\Delta\eta/(\mathrm{mPa\cdot s}) = x_1(1 - x_1)\sum_{i=1}^{4} D_i(2x_1 - 1)^{i-1}$.

Effect of Composition on Viscosity Deviation. The negative viscosity deviations were observed for all four systems (see Tables 2 to 5) with an exception of three higher temperatures for 1-decanol. This effect is the highest for 1-heptanol. These data are reported in Figures 25S to 28S in the SI. The viscosity deviation was correlated by the Redlich−Kister equation. The parameters are listed in Table 11. The viscosity deviation decreases with an increase of temperature. The influence of temperature is much stronger than that 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 the IL.

Conclusions

New data on densities and viscosities of binary systems {[BMIM][SCN] + 1-alcohols (C_7, C_8, C_9, or C_{10})} at five temperatures were measured. From the density−temperature dependence, the volume expansivities, α, and the excess volume expansivities, α^E, were described for the IL at different temperatures. In this work negative deviations were observed for excess molar volumes, the excess volume expansivity, and viscosity deviation, which is a result of the specific interaction between ILs and 1-alcohols.

The data were correlated with the second-order polynomial, the Redlich−Kister equation, and the VFT equation. The excess molar volumes and the excess molar enthalpies were predicted with the PFP and FBT theories.

Supporting Information Available:

Fit parameters and standard deviation for the empirical correlation of density in the systems {[BMIM][SCN] (1) + 1-octanol, 1-nonanol, and 1-decanol (2)} (Figures 1S, 2S, and 3S; Table 1S); 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) + 1-octanol, 1-nonanol, and 1-decanol (2)} (Figures 4S to 6S; Tables 2S and 3S); coefficients of the polynomial for the correlation of density and viscosity in function of the IL mole fraction in the systems {[BMIM][SCN] (1) + 1-octanol, 1-nonanol, and 1-decanol (2)}, (Figures 7S to 12S; Tables 4S and 5S); the excess molar volumes for different temperatures (Figures 13S to 15S); the excess partial molar volumes, V_1^E and V_2^E (Tables 4S to 7S); the excess molar volumes predicted by the PFP and FBT models (Figures 16S to 18S); the volume expansivity as a function of temperature and composition (Figures 19S to 21S); the excess volume expansivities (Figures 22S to 24S); viscosity deviation (Figures 25S to 28S). This material is available free of charge via the Internet at http://pubs.acs.org.

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