

Physical Properties of Binary Mixtures of the Ionic Liquid 1-Methyl-3-octylimidazolium Chloride with Methanol, Ethanol, and 1-Propanol at $T = (298.15, 313.15, \text{ and } 328.15) \text{ K}$ and at $P = 0.1 \text{ MPa}$

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In this work, dynamic viscosities, densities, and speed of sound of 1-methyl-3-octylimidazolium chloride, $[\text{C}_8\text{mim}][\text{Cl}]$, with methanol, ethanol, and 1-propanol at $T = (298.15, 313.15, \text{ and } 328.15) \text{ K}$ and refractive index at $T = 298.15 \text{ K}$ and $P = 0.1 \text{ MPa}$ have been measured over the whole composition range. Excess molar volumes, isentropic compressibility deviations, and viscosity deviations for the binary systems from $T = (298.15 \text{ to } 328.15) \text{ K}$ were calculated. These results were fitted to a Redlich–Kister equation to determine the fitting parameters and the root mean square deviations.

Introduction

Room temperature ionic liquids [RTILs] is a term that has been introduced to describe a class of organic salts that are liquids at or near room temperature in their pure state, and they are comprised entirely of ions. Since numerous combinations of the cationic and anionic structures are possible, they have been considered as “designer solvents”, and their physical and chemical properties could be adjusted by a careful choice of the cation and the anion.

They have unique physicochemical properties, such as negligible vapor pressure^{1,2} in normal temperature and pressure conditions (Earle et al.³ get to distillate ionic liquid in extreme T and P conditions), noninflammable, high ionic conductivity, and high thermal, chemical, and electrochemical stabilities. Due to their nonvolatile nature and favorable solvent properties, RTILs have been suggested replacements for traditional volatile organic solvents (VOCs).

The applications of ILs in catalytic reactions as solvents, separation processes, membrane technology, chemical analysis, and batteries have been studied recently by different authors.^{4–11} Despite their importance, there is limited information on physical and thermodynamic properties of these compounds. Values of their properties are very important to the design and control of chemical processes involving the ILs.

Because of that, the aim of this work is to measure physical properties in binary systems where 1-methyl-3-octylimidazolium chloride is present. The systems $[\text{C}_8\text{mim}][\text{Cl}]$ with methanol, or ethanol, or 1-propanol over the entire mole fraction composition range at $T = (298.15 \text{ to } 328.15) \text{ K}$ and at 0.1 MPa were studied.

For the technical application of IL at each binary system, the regeneration and subsequent recycling of the IL is essential. Direct distillation¹² and extraction with supercritical CO_2 ¹³ or organic solvents¹⁴ are possible methods in the purification and regeneration of the ILs.

Experimental Section

Chemicals. Ethanol and 1-propanol were supplied by Merck, and methanol was supplied by Fluka. The components were

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Table 1. Comparison of Density ρ , Viscosity η , and Refractive Index n_D with Literature Data for Pure Components at $T = 298.15 \text{ K}$

	$\rho/\text{g}\cdot\text{cm}^3$		$10^3\eta/\text{Pa}\cdot\text{s}$		n_D	
	exptl	lit.	expt	lit.	expt	lit.
$[\text{C}_8\text{mim}][\text{Cl}]$	1.00882	1.00882 ^a 1.00 ^b 1.0104 ^c	20868	20883 ^a	1.51051	1.50987 ^a 1.505 ^b
methanol	0.78664	0.78664 ^d	0.543	0.543 ^d	1.32687	1.32652 ^e
ethanol	0.78511	0.78522 ^f	1.085	1.085 ^d	1.35960	1.35941 ^e
1-propanol	0.79948	0.79940 ^g	1.951	1.951 ^g	1.38302	1.38294 ^d

^a Ref 15. ^b Ref 19. ^c Ref 20. ^d Ref 21. ^e Ref 22. ^f Ref 23. ^g Ref 24.

degassed ultrasonically and dried over molecular sieves type 4 Å, supplied by Aldrich, and kept in inert argon with a maximum water contents of $2 \cdot 10^{-6}$ mass fraction. Their mass fraction purities were >99 % for methanol and >99.8 % for ethanol and 1-propanol. The ionic liquid used in this work, $[\text{C}_8\text{mim}][\text{Cl}]$, was synthesized in our laboratory¹⁵ and submitted to NMR to ensure its purity. The water content was determined using a 787 Karl Fischer titration coulometer, and the obtained value was lower than 0.05 % mass fraction.

Apparatus and Procedure. Binary mixtures were prepared by syringing known masses of the pure liquids into stoppered bottles in an inert atmosphere glovebox, using a Mettler AX-205 Delta Range balance with a precision of $\pm 10^{-5} \text{ g}$, covering the whole composition range of the mixture. A glovebox was used because the ionic liquids, particularly chlorides, are highly hygroscopic, and small quantities of water in the ionic liquid cause considerable changes in the physical properties.^{15–18}

Densities and speeds of sound were measured using an Anton Paar DSA-5000 digital vibrating-tube densimeter. The repeatability and the uncertainty in experimental measurements have been found to be lower than $(\pm 2 \cdot 10^{-6} \text{ and } 1 \cdot 10^{-5}) \text{ g}\cdot\text{cm}^{-3}$ for the density and $(\pm 0.01 \text{ and } \pm 0.1) \text{ m}\cdot\text{s}^{-1}$ for the speed of sound. The apparatus was calibrated by measuring the density of Millipore quality water and ambient air according to the manual instructions. The calibration was checked with the pure liquids shown in Table 1. The DSA-5000 automatically corrects the influence of viscosity on the measured density.

Table 2. Density ρ , Speed of Sound u , Refractive Index n_D , Dynamic Viscosity η , Isentropic Compressibility k_s , Excess Volume V^E , Deviation in Isentropic Compressibility Δk_s , and Viscosity Deviation $\Delta \eta$ of Methanol (1) + [C₈mim][Cl] (2)

x_1	ρ g·cm ⁻³	u m·s ⁻¹	$10^3 \eta$ Pa·s	n_D	V^E cm ³ ·mol ⁻¹	k_s TPa ⁻¹	Δk_s TPa ⁻¹	$\Delta \eta$ Pa·s
$T = 298.15\text{ K}$								
0.0000	1.00882	1721	20868	1.51051	0.000	335	0.00	0.000
0.0565	1.00693	1683	10353	1.50817	-0.098	351	-24.0	-9336
0.1686	1.00242	1638	3456	1.50362	-0.264	372	-83.0	-13894
0.2638	0.99772	1608	1489	1.49975	-0.400	388	-134	-13874
0.3525	0.99206	1581	534	1.49421	-0.471	403	-182	-12978
0.4395	0.98537	1559	237.23	1.48828	-0.559	418	-229	-11460
0.5589	0.97332	1526	64.10	1.47696	-0.686	441	-290	-9141
0.7536	0.93925	1447	8.427	1.44786	-0.812	508	-361	-5134
0.8231	0.91805	1397	4.193	1.43053	-0.798	558	-361	-3688
0.8713	0.89737	1348	2.390	1.41277	-0.723	613	-340	-2684
0.8813	0.89218	1335	2.205	1.40840	-0.696	629	-332	-2475
0.9236	0.86628	1274	1.416	1.38754	-0.583	711	-279	-1593
0.9436	0.85042	1237	1.135	1.37577	-0.479	768	-236	-1176
0.9803	0.81347	1157	0.729	1.34680	-0.235	918	-113	-410.9
1.0000	0.78664	1103	0.543	1.32687	0.000	1045	0.00	0.000
$T = 313.15\text{ K}$								
0.0000	1.00020	1624	4062	0.000	379	0	0.000	
0.0565	0.99827	1602	2450	-0.109	390	-33	-1382	
0.1686	0.99368	1578	1002	-0.299	404	-108	-2375	
0.2638	0.98889	1558	499.91	-0.453	417	-170	-2491	
0.3525	0.98319	1536	211.59	-0.551	431	-225	-2419	
0.4395	0.97646	1518	106.68	-0.666	444	-280	-2170	
0.5589	0.96407	1486	34.968	-0.796	470	-349	-1757	
0.7536	0.92918	1406	5.817	-0.930	544	-427	-995.3	
0.8231	0.9075	1354	3.580	-0.915	601	-425	-715.3	
0.8713	0.88632	1304	1.854	-0.831	664	-401	-521.3	
0.8813	0.88100	1292	1.722	-0.802	680	-392	-480.8	
0.9236	0.85444	1229	1.133	-0.673	775	-331	-309.6	
0.9436	0.83816	1192	0.914	-0.556	840	-281	-228.6	
0.9803	0.80013	1110	0.594	-0.274	1014	-136	-79.86	
1.0000	0.77238	1054	0.444	0.000	1165	0	0.000	
$T = 328.15\text{ K}$								
0.0000	0.99167	1560	1091	0.000	414	0	0.000	
0.0565	0.98971	1548	757	-0.125	422	-43	-272.6	
0.1686	0.98504	1531	364.92	-0.342	433	-130	-542.2	
0.2638	0.98025	1514	205.49	-0.535	445	-203	-597.8	
0.3525	0.97448	1496	98.97	-0.655	459	-268	-607.6	
0.4395	0.96751	1478	55.20	-0.770	473	-330	-556.5	
0.5589	0.95487	1447	21.442	-0.920	500	-408	-460.0	
0.7536	0.91917	1365	4.388	-1.069	584	-497	-264.7	
0.8231	0.89697	1313	2.496	-1.051	647	-496	-190.8	
0.8713	0.87526	1263	1.491	-0.958	716	-469	-139.2	
0.8813	0.86980	1250	1.388	-0.925	736	-458	-128.4	
0.9236	0.84252	1186	0.93	-0.777	844	-387	-82.76	
0.9436	0.82578	1147	0.754	-0.645	920	-328	-61.13	
0.9803	0.78658	1070	0.497	-0.319	1110	-171	-21.36	
1.0000	0.75785	1008	0.369	0.000	1299	0	0.000	

Refractive indices of the pure components and their mixtures at $T = 298.15\text{ K}$ were determined using an automatic refractometer, ABBEMAT-WR Dr. Kernchen, with an uncertainty of $\pm 4 \cdot 10^{-5}$.

Kinematic viscosities of the liquids and their mixtures were determined using an automatic viscosimeter Lauda PVS1 with four Ubbelohde capillary microviscosimeters of $0.4 \cdot 10^{-3}\text{ m}$, $0.53 \cdot 10^{-3}\text{ m}$, $0.70 \cdot 10^{-3}\text{ m}$, and $1.26 \cdot 10^{-3}\text{ m}$ diameter and two Ubbelohde capillary viscosimeters of $4.70 \cdot 10^{-3}\text{ m}$ and $3 \cdot 10^{-3}\text{ m}$ diameter. The uncertainty in the viscosity measurements depends on the diameter of different capillaries. It increases with the diameter and was $\pm 0.001\text{ mPa}\cdot\text{s}$, $\pm 0.001\text{ mPa}\cdot\text{s}$, $\pm 0.001\text{ mPa}\cdot\text{s}$, $\pm 0.01\text{ mPa}\cdot\text{s}$, $\pm 1\text{ mPa}\cdot\text{s}$, and $\pm 1\text{ mPa}\cdot\text{s}$, respectively. Gravity fall is the principle of measurement on which this viscosimeter is based. The capillary is maintained in a D20KP LAUDA thermostat with a resolution of 0.01 K. The capillaries are calibrated and credited by the company. The equipment has a control unit PVS1 (Processor Viscosity System) that is a PC-controlled instrument for the precise measurement of fall

time, using standardized glass capillaries, with an uncertainty of 0.01 s.

The kinematic viscosity was determined from the following equation:

$$\nu = k(t - y) \quad (1)$$

where y is the Hagenbach correction, t is the flow time, and k is the Ubbelohde capillary microviscosimeter constant that is supplied by the company. The dynamic viscosity is calculated from

$$\eta = \nu \rho \quad (2)$$

where η is the dynamic viscosity, ν is the kinematic viscosity, and ρ is the density. In Table 1, the experimental density, viscosity and refractive index of the pure components are compared with the literature data.

Results and Discussion

The experimental data of density, speed of sound, dynamic viscosity, isentropic compressibility, excess molar volume,

Table 3. Density ρ , Speed of Sound u , Refractive Index n_D , Dynamic Viscosity η , Isentropic Compressibility k_s , Excess Volume V^E , Deviation in Isentropic Compressibility Δk_s , and Viscosity Deviation $\Delta \eta$ of Ethanol (1) + [C₈mim][Cl] (2)

x_1	ρ g·cm ⁻³	u m·s ⁻¹	$10^3 \eta$ Pa·s	n_D	V^E cm ³ ·mol ⁻¹	k_s TPa ⁻¹	Δk_s TPa ⁻¹	$\Delta \eta$ Pa·s
<i>T = 298.15 K</i>								
0.0000	1.00882	1721	20868	1.51051	0.000	335	0	0.000
0.0449	1.00627	1692	12571	1.50835	-0.025	347	-16	-7360
0.1305	1.00097	1646	5426	1.50474	-0.091	369	-49	-12719
0.2969	0.98854	1579	1127	1.49563	-0.285	406	-119	-13546
0.4753	0.96979	1518	185.58	1.48233	-0.480	447	-192	-10764
0.6858	0.93354	1437	21.263	1.45682	-0.602	519	-255	-6536
0.8809	0.86864	1304	3.501	1.41305	-0.574	677	-222	-2483
0.9170	0.84907	1264	2.551	1.40102	-0.481	737	-185	-1730
0.9550	0.82408	1215	1.754	1.38404	-0.342	822	-124	-938.3
0.9794	0.80461	1179	1.396	1.37207	-0.197	894	-68	-429.5
1.0000	0.78511	1143	1.085	1.35960	0.000	975	0	0.000
<i>T = 313.15 K</i>								
0.0000	1.00020	1624	4062		0.000	379	0	0.000
0.0449	0.99761	1606	2717		-0.034	389	-22	-1163
0.1305	0.99224	1578	1411		-0.118	405	-66	-2121
0.2969	0.97963	1530	393.63		-0.347	436	-152	-2463
0.4753	0.96076	1477	87.97		-0.600	477	-237	-2044
0.6858	0.92378	1395	14.598		-0.722	556	-306	-1262
0.8809	0.85766	1258	2.601		-0.678	737	-263	-481.9
0.9170	0.83768	1218	1.919		-0.570	-221	-221	-336.0
0.9550	0.81212	1169	1.341		-0.406	-151	-151	-182.2
0.9794	0.79215	1131	1.061		-0.233	-83	-83	-83.42
1.0000	0.77207	1093	0.826		0.000	0	0	0.000
<i>T = 328.15 K</i>								
0.0000	0.99167	1560	1091		0.000	414	0	0.000
0.0449	0.98905	1547	827		-0.047	422	-28	-214.9
0.1305	0.98362	1527	481.47		-0.157	436	-82	-467.2
0.2969	0.97096	1487	164.99		-0.453	466	-185	-602.3
0.4753	0.95169	1438	45.212		-0.726	508	-285	-527.5
0.6858	0.91405	1353	9.120		-0.873	598	-364	-334.1
0.8809	0.84668	1214	1.997		-0.818	801	-315	-128.5
0.9170	0.82615	1175	1.488		-0.683	877	-269	-89.65
0.9550	0.79994	1122	1.038		-0.486	993	-183	-48.67
0.9794	0.77938	1090	0.819		-0.279	1080	-115	-22.28
1.0000	0.75861	1043	0.641		0.000	1212	0	0.000

Table 4. Density ρ , Speed of Sound u , Refractive Index n_D , Dynamic Viscosity η , Isentropic Compressibility k_s , Excess Volume V^E , Deviation in Isentropic Compressibility Δk_s , and Viscosity Deviation $\Delta \eta$ of 1-Propanol (1) + [C₈mim][Cl] (2)

x_1	ρ g·cm ⁻³	u m·s ⁻¹	$10^3 \eta$ Pa·s	n_D	V^E cm ³ ·mol ⁻¹	k_s TPa ⁻¹	Δk_s TPa ⁻¹	$\Delta \eta$ Pa·s
<i>T = 298.15 K</i>								
0.0000	1.00882	1721	20868	1.51051	0.000	335	0	0.000
0.1071	1.0011	1659	7238	1.50524	-0.046	363	-28	-11395
0.2407	0.98968	1593	2056	1.49750	-0.118	398	-63	-13789
0.3036	0.98357	1566	912	1.49364	-0.182	415	-80	-13621
0.4070	0.97162	1531	385.53	1.48636	-0.227	439	-110	-11990
0.4887	0.9606	1504	178.51	1.47959	-0.290	460	-131	-10492
0.6209	0.93812	1456	50.81	1.46578	-0.362	502	-159	-7861
0.7248	0.91481	1413	19.246	1.45126	-0.399	548	-168	-5725
0.8516	0.87563	1342	6.342	1.42753	-0.404	634	-148	-3092
0.9024	0.85486	1304	4.597	1.41523	-0.374	688	-121	-2034
0.9400	0.83647	1271	3.238	1.40435	-0.297	740	-89	-1251
0.9729	0.8178	1238	2.648	1.39350	-0.190	798	-48	-564.7
1.0000	0.79948	1205	1.951	1.38302	0.000	861	0	0.000
<i>T = 313.15 K</i>								
0.0000	1.00020	1624	4062		0.000	379	0.00	0.000
0.1071	0.99242	1584	1720		-0.075	402	-39	-1907
0.2407	0.98087	1539	649		-0.174	430	-87	-2435
0.3036	0.9747	1517	334.46		-0.253	445	-108	-2494
0.4070	0.96254	1487	159.63		-0.304	470	-142	-2250
0.4887	0.9515	1461	84.10		-0.401	492	-167	-1993
0.6209	0.92861	1414	28.813		-0.470	538	-197	-1512
0.7248	0.90492	1369	12.215		-0.507	590	-205	-1107
0.8516	0.86508	1296	4.401		-0.498	688	-179	-599.6
0.9024	0.84394	1257	3.230		-0.455	750	-146	-394.5
0.9400	0.82519	1223	2.293		-0.361	811	-107	-242.7
0.9729	0.80609	1188	1.878		-0.227	879	-58	-109.5
1.0000	0.78728	1155	1.383		0.000	952	0.00	0.000

Table 4 (Continued)

x_1	ρ g·cm ⁻³	u m·s ⁻¹	$10^3 \eta$ Pa·s	n_D	V^E cm ³ ·mol ⁻¹	k_s TPa ⁻¹	Δk_s TPa ⁻¹	$\Delta \eta$ Pa·s
<i>T = 328.15 K</i>								
0.0000	0.99167	1560	1091		0.000	414	0	0.000
0.1071	0.98383	1531	561		-0.111	433	-50	-413.4
0.2407	0.9721	1494	230.72		-0.236	461	-108	-597.9
0.3036	0.96591	1475	144.13		-0.342	476	-134	-616.1
0.4070	0.95364	1445	77.39		-0.424	502	-174	-570.0
0.4887	0.9424	1421	42.72		-0.529	525	-203	-515.6
0.6209	0.91912	1373	17.726		-0.609	577	-236	-396.5
0.7248	0.89505	1326	8.254		-0.651	635	-245	-292.7
0.8516	0.85446	1250	3.189		-0.626	748	-214	-159.6
0.9024	0.83287	1211	2.352		-0.564	819	-176	-105.0
0.9400	0.81368	1175	1.679		-0.445	890	-129	-64.73
0.9729	0.79406	1140	1.372		-0.277	970	-70	-29.17
1.0000	0.77464	1105	1.007		0.000	1057	0	0.000

Table 5. Fitting Parameters and Root Mean Square Deviations σ for Binary Mixtures at $T = (298.15, 313.15,$ and $328.15)$ K

	T/K	B_0	B_1	B_2	B_3	B_4	σ
Methanol (1) + [C ₈ mim][Cl] (2)							
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	298.15	-2.5027	-1.6445	-1.8057	-2.7568	-2.4284	0.015
	313.15	-2.9437	-1.8284	-1.6027	-3.3649	-3.3217	0.016
	328.15	-3.4124	-1.9510	-1.8366	-4.1844	-3.7726	0.019
$\Delta k_s/\text{TPa}^{-1}$	298.15	-1048.95	-834.81	-472.01	-1607.74	-1655.94	6.00
	313.15	-1270.59	-917.56	-514.06	-1931.17	-2056.45	7.74
	328.15	-1493.93	-1023.30	-521.04	-2295.74	-2594.86	10.94
$10^{-3} \Delta \eta/\text{Pa}\cdot\text{s}$	298.15	-41888.2	32160.6	-22948.5	61017.1	-58149.4	211.3
	313.15	-7944.2	6355.2	-4346.1	6782.8	-5750.1	19.3
	328.15	-2053.2	1583.5	-931.7	797.3	-562.9	3.2
Ethanol (1) + [C ₈ mim][Cl] (2)							
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	298.15	-2.0112	-1.3909	-0.2111	-2.9841	-2.9710	0.009
	313.15	-2.4982	-1.6394	0.2625	-3.4506	-4.1204	0.010
	328.15	-3.0225	-1.7734	-0.2156	-4.3337	-4.2548	0.012
$\Delta k_s/\text{TPa}^{-1}$	298.15	-806.30	-683.88	-446.49	-767.53	-646.63	2.30
	313.15	-995.80	-752.29	-468.12	-960.93	-882.27	3.62
	328.15	-1200.49	-834.95	-417.65	-1266.53	-1348.65	7.75
$10^{-3} \Delta \eta/\text{Pa}\cdot\text{s}$	298.15	-41671.6	34253.4	-22919.4	51211.5	-48574.9	153.5
	313.15	-7917.3	6282.5	-3617.4	6586.5	-6320.4	22.9
	328.15	-2032.6	1577.2	-970.1	675.2	-366.4	0.6
1-Propanol (1) + [C ₈ mim][Cl] (2)							
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	298.15	-1.2006	-0.9802	-0.1953	-2.0694	-2.5960	0.012
	313.15	-1.6127	-1.1865	-0.1021	-2.3346	-3.2676	0.015
	328.15	-2.1449	-1.4405	0.0001	-2.8001	-4.0937	0.016
$\Delta k_s/\text{T}\cdot\text{Pa}^{-1}$	298.15	-537.78	-470.86	-236.30	-316.40	-360.83	0.84
	313.15	-682.17	-512.60	-289.15	-413.18	-413.41	1.17
	328.15	-827.55	-584.80	-336.93	-508.42	-529.79	1.59
$10^{-3} \Delta \eta/\text{Pa}\cdot\text{s}$	298.15	-41196.0	37330.3	-32673.8	37784.8	-24943.2	70.1
	313.15	-7850.9	6697.4	-4915.1	4905.7	-3329.5	17.7
	328.15	-2020.8	1669.4	-1213.9	506.1	14.9	1.7

viscosity deviation, and isentropic compressibility deviation for the binary systems methanol + [C₈mim][Cl], ethanol + [C₈mim][Cl], and 1-propanol + [C₈mim][Cl]) at $T = (298.15, 313.15,$ and $328.15)$ K and at 0.1 MPa of pressure are presented respectively in Tables 2 to 4. The refractive index for these mixtures at $T = 298.15$ K is shown also.

The viscosity of the pure ionic liquid [C₈mim][Cl] obtained in this work is larger than the values obtained by other authors (337 mPa·s).¹⁹ This difference can be explained because small quantities of water cause a great viscosity decrease, although the density is not affected as much.

From the speed of sound, u , and density data, ρ , of the studied mixtures, the isentropic compressibility, k_s , was determined using the Laplace–Newton equation:

$$k_s = \rho^{-1} u^{-2} \quad (3)$$

The values of the excess molar volume, V^E , the deviation in

isentropic compressibility, Δk_s , and viscosity deviation, $\Delta \eta$, are calculated by the following equations:

$$V^E = \sum_{i=1}^N x_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (4)$$

$$\Delta k_s = k_s - \sum_{i=1}^N x_i k_{s,i} \quad (5)$$

$$\Delta \eta = \eta - \sum_{i=1}^N x_i \eta_i \quad (6)$$

where ρ and ρ_i are the density of the mixture and the density of the pure components, respectively; M_i is the molar mass of the pure components; k_s is the isentropic compressibility of the mixture; $k_{s,i}$ is the isentropic compressibility of the pure components; x_i represents the mole fraction of the i component;

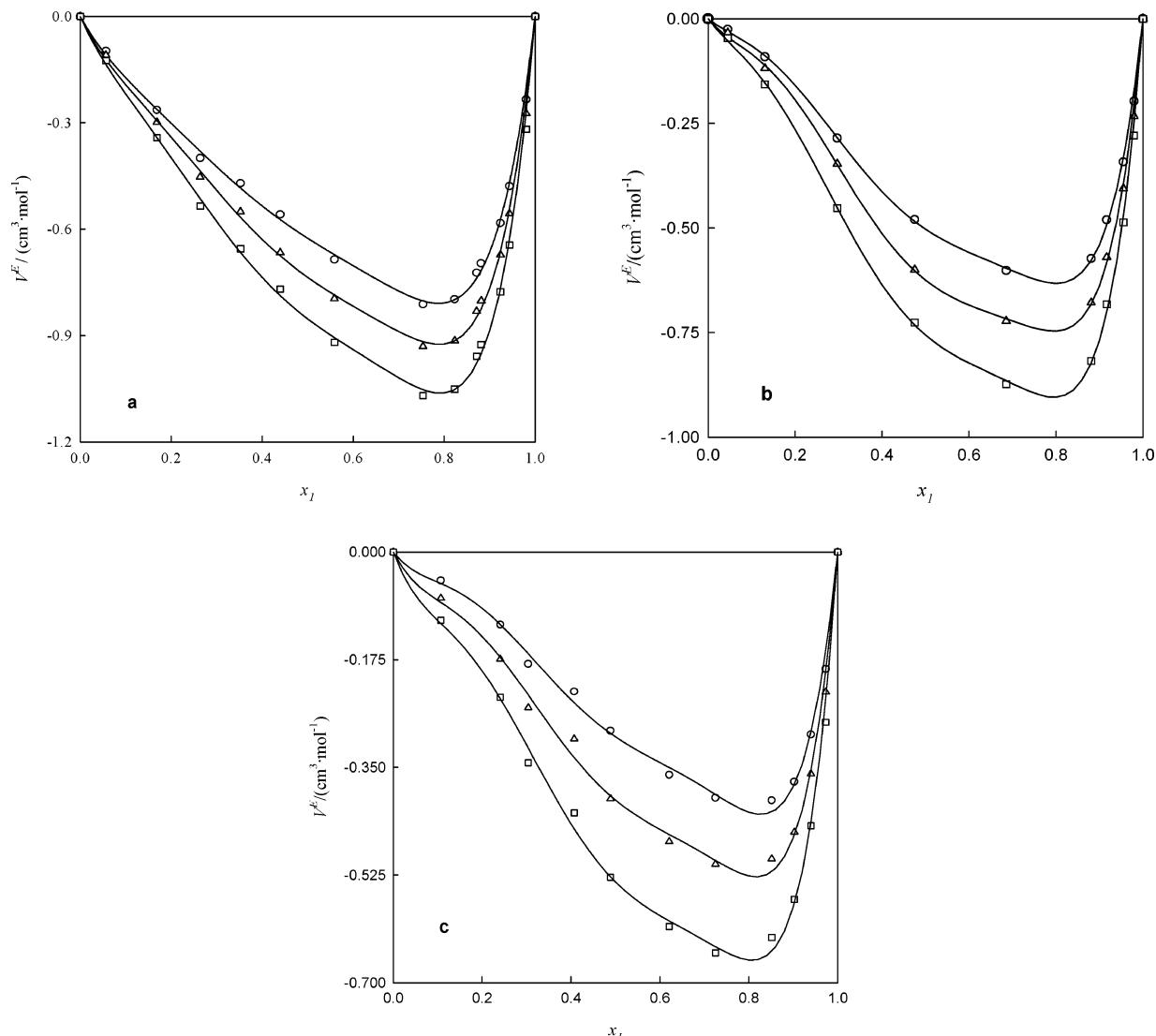


Figure 1. Excess molar volume, V^E , from the Redlich–Kister equation plotted against mole fraction at \circ , $T = 298.15\text{ K}$; \triangle , $T = 313.15\text{ K}$; and \square , $T = 328.15\text{ K}$ for the binary mixtures: (a) methanol (1) + $[\text{C}_8\text{mim}][\text{Cl}]$ (2), (b) ethanol (1) + $[\text{C}_8\text{mim}][\text{Cl}]$ (2), and (c) 1-propanol (1) + $[\text{C}_8\text{mim}][\text{Cl}]$ (2).

and η and η_i are the dynamic viscosity of the mixture and the pure component, respectively.

The binary deviations at several temperatures have been fitted to a Redlich–Kister²⁵ type equation:

$$\Delta Q_{ij} = x_i x_j \sum_{p=0}^M B_p (x_i - x_j)^p \quad (7)$$

where ΔQ_{ij} is the excess property, x_i is the mole fraction of the component i , B_p is the fitting parameter, and M is the degree of the polynomial expansion that was optimized using the F -test.²⁶ The fitting parameters are given in Table 5 together with the root mean square deviations. They were calculated from the values of the experimental and calculated property and the number of experimental data, represented by z_{exp} , z_{calc} , and n_{dat} , respectively:

$$\sigma = \left\{ \sum_i^{n_{\text{dat}}} (z_{\text{exp}} - z_{\text{calc}})^2 / n_{\text{dat}} \right\}^{1/2} \quad (8)$$

Figures 1 and 2 show the fitted curves as well as excess and deviation experimental values against the mole fraction of binary systems for methanol + $[\text{C}_8\text{mim}][\text{Cl}]$, ethanol + $[\text{C}_8\text{mim}][\text{Cl}]$,

and 1-propanol + $[\text{C}_8\text{mim}][\text{Cl}]$ at $T = (298.15, 313.15,$ and $328.15)\text{ K}$. For V^E , the Redlich–Kister fitting curves present a minimum at alcohol mole fraction of approximately 0.8 for all binary systems. In Figure 1, we can observe how the excess molar volumes are negative over the entire composition range. In all systems, the excess molar volume decreases as the temperature increases and presents a minimum at alcohol mole fraction of approximately 0.80 for $T = (298.15, 313.15,$ and $328.15)\text{ K}$, which becomes more negative when the alcohol chain decreases. This behavior can be explained in terms of more efficient packing in the mixtures than in the pure liquid²⁷ and due to the ion–dipole interactions between alcohol and ionic liquid.²⁸

In Figure 2, the viscosity deviations are negative over the whole composition range and approach the minimum at $x_1 \approx 0.2$ for the system methanol (1) + $[\text{C}_8\text{mim}][\text{Cl}]$ (2) and ethanol (1) + $[\text{C}_8\text{mim}][\text{Cl}]$ (2) and at a mole fraction $x_1 \approx 0.25$ for the system 1-propanol (1) + $[\text{C}_8\text{mim}][\text{Cl}]$ (2). The viscosity deviations are less negative as the temperature increases, and this behavior is similar in all systems. The viscosity deviation is particularly strong in solutions with a few quantities of alcohol due to the high difference viscosity of pure compounds. The viscosity deviation at 298.15 K is greater than at 313.15 K or

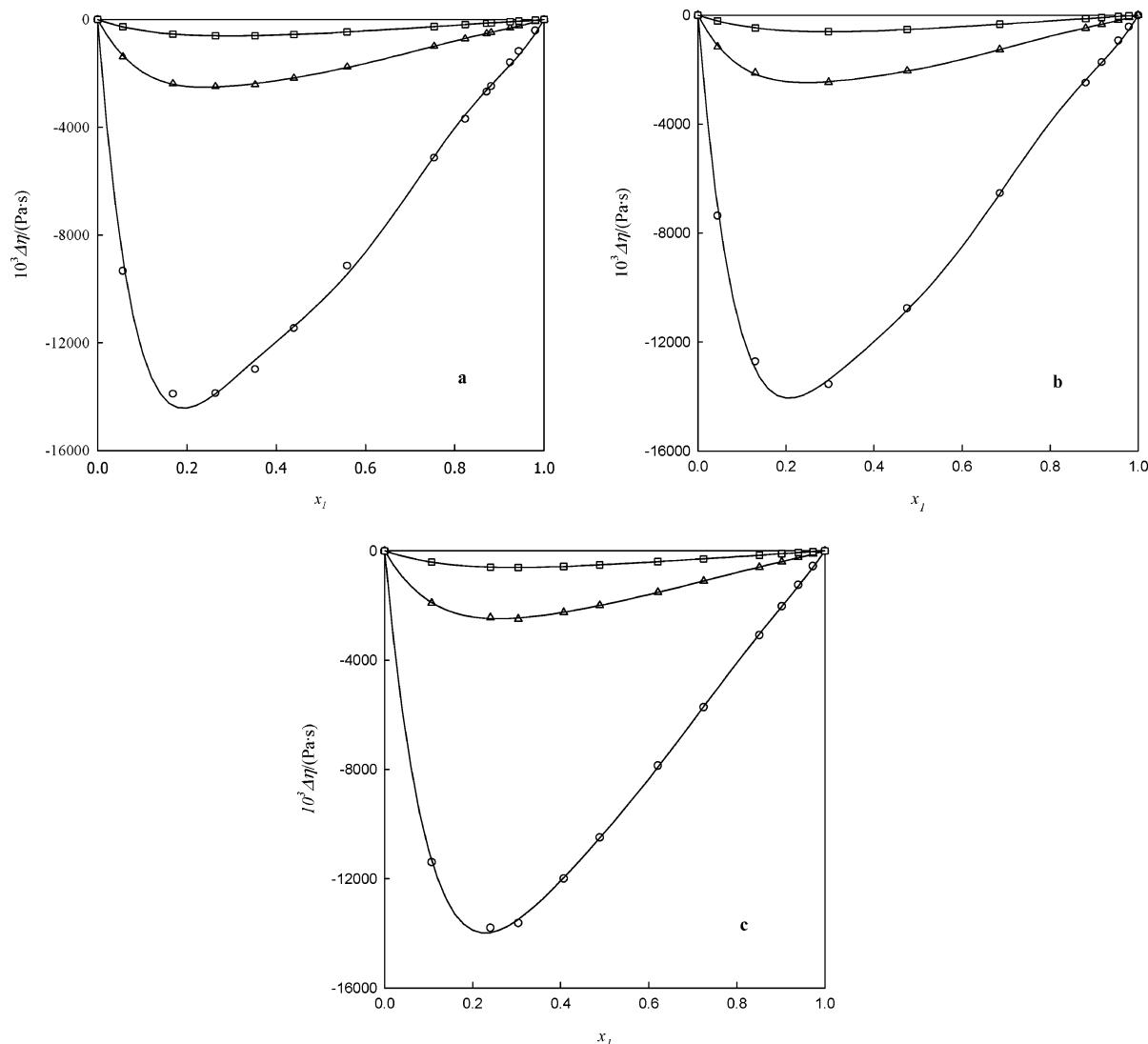


Figure 2. Viscosity deviations, $\Delta\eta$, from the Redlich–Kister equation plotted against mole fraction at \circ , $T = 298.15$ K; \triangle , $T = 313.15$ K; and \square , $T = 328.15$ K for the binary mixtures: (a) methanol (1) + $[C_8mim][Cl]$ (2), (b) ethanol (1) + $[C_8mim][Cl]$ (2), and (c) 1-propanol (1) + $[C_8mim][Cl]$ (2).

328.15 K due to the viscosity of the pure ionic liquid decrease quickly when the temperature increase.

Recycling of Ionic Liquid. Laali and Gettwert¹⁴ have pointed out that a major concern in the use of ionic liquids is their relatively high cost, which makes their recycling (i.e., recovery and reuse) an important issue for further study. As a large amount of ionic liquid was used in the measurements, its recovery and reuse should be possible. In this case, as the ionic liquid has a negligible vapor pressure, the ionic liquids recovering from binary systems ILs + alcohol was realized by removal of the alcohol components by vacuum at $T = 343.15$ K. Appreciable changes in the physical properties of the recovered ionic liquid have not been observed.

Conclusions

In this paper, density, dynamic viscosities, and speed of sound of the binary systems methanol + $[C_8mim][Cl]$, ethanol + $[C_8mim][Cl]$, and 1-propanol + $[C_8mim][Cl]$ at $T = (298.15$, 313.15 , and 328.15) K and at 0.1 MPa of pressure have been determined over the whole composition range.

Excess molar volumes, V^E , and isentropic compressibility deviation, Δk_s , values of these binary systems have been calculated from the measured density and speed of sound data. The measured negative V^E values for these mixtures indicate

that ion–dipole interactions and packing between alcohols and IL are present.

The viscosity deviations are negative over the whole composition range, and their values are less negative as the temperature increase. The viscosity deviation is particularly strong in dilute solutions of alcohol in the ionic liquid. The ionic liquid can be recovered and reused by vacuuming at each binary system at least three times with no loss in its purity.

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