

Density and Viscosity Data for Binary Mixtures of 1-Alkyl-3-methylimidazolium Alkylsulfates + Water

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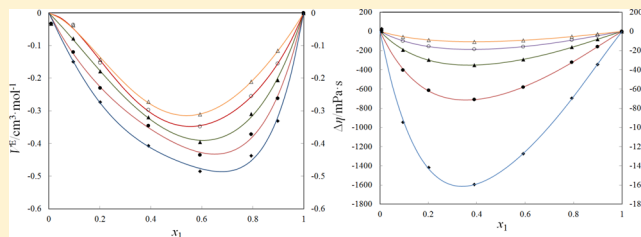
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ABSTRACT: Density and viscosity experimental data for binary mixtures of 1-alkyl-3-methylimidazolium alkylsulfates + water are reported using four ionic liquids: 1-butyl-3-methylimidazolium hydrogensulfate [C₄mim][HSO₄], 1-butyl-3-methylimidazolium methylsulfate [C₄mim][C₁SO₄], 1-ethyl-3-methylimidazolium methylsulfate [C₂mim][C₁SO₄], and 1-ethyl-3-methylimidazolium ethylsulfate [C₂mim][C₂SO₄]. The choice of the ionic liquids allows us to compare the effects of incrementing the alkyl chain length in the cation and the anion on the measured thermophysical properties behavior. The Gardas and Coutinho group contribution methods were applied to the description of the pure component densities and viscosities allowing the estimation of new group contribution parameters, to extend the applicability of these methods to new ILs. Excess molar volumes and viscosity deviations were calculated and correlated by Redlich–Kister polynomial expansions.



INTRODUCTION

In recent years, great attention has been focused on ionic liquids (ILs), which are organic salts that are liquid at temperatures below 100 °C. These unique solvents are generating interest as greener substitutes to traditional organic solvents with the aim of assisting environmentally acceptable chemistry practices. Room temperature ionic liquids are often referred to as “designer solvents”, due to the possibility of tuning their properties through a wise choice of cations and anions and/or the introduction of functional groups. The development of new ionic liquids for more efficient processes and products has been the focus of academics and industry in various fields^{1–5} since they can be applied for a wide range of different purposes such as solvents in catalytic reactions,⁶ separations and extractions,^{7–10} as electrolytic media in fuel cells,¹¹ heat transfer fluids,¹² and in biotechnological¹³ and engineering^{14–16} processes.

Industrial processes involving ionic liquids demand reliable thermo-physical data of pure components and mixtures. These reference data are required in the development of models for process design, energy efficiency, control of chemical processes, and evaluation of possible environmental impacts.¹⁷

Novel applications of ILs continue to be regularly proposed based on their uncommon combination of physical and chemical properties such as high thermal stability, lack of flammability, low volatility, chemical stability, and outstanding solubility of many organic compounds. The most common ionic liquids are

salts formed by imidazolium based cations combined with different ions such as [Cl][−], [BF₄][−], [PF₆][−], [CF₃–CO₂][−], [CF₃–SO₃][−], and alkyl sulfates or alkyl sulfonates.

ILs, based on alkyl sulfates anions (e.g., [HSO₄][−], [CH₃SO₄][−], and [C₂H₅SO₄][−]), are a cheap and interesting alternative for polar solvents in industrial applications. They are particularly tunable as the alkyl chain can be increased in both the cation and the anion allowing for a fine manipulation of their hydrophobic/hydrophilic balance and polarity. Yet, only a few pure ionic liquids of this type have been studied, and their behavior in mixtures with other solvents is even scarcer.

Among the most studied are 1-butyl-3-methylimidazolium methylsulfate [C₄mim][C₁SO₄] and 1-ethyl-3-methylimidazolium ethylsulfate [C₂mim][C₂SO₄], and some data is also available for 1-ethyl-3-methylimidazolium methylsulfate [C₂mim][C₁SO₄] for which pure thermo-physical properties and mixture data with several solvents are available.^{17–38} A complete study on the effect on the density and viscosity of increasing the alkyl chain length of 1-ethyl-3-methylimidazolium-based ionic liquids combined with alkylsulfate, [C_nSO₄][−] with *n* = 1, 4, 6, and 8, and hydrogensulfate, [HSO₄][−], at

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Table 1. Experimental Density ρ , Excess Molar Volume V^E , Dynamic Viscosity η , and Viscosity Deviation $\Delta\eta$ for the Binary System Water (1) + $C_4\text{mimHSO}_4$ (2)^a

x_1	T/K				
	303.15	313.15	323.15	333.15	343.15
	$\rho/\text{g}\cdot\text{cm}^{-3}$				
0.0083	1.2760	1.2699	1.2639	1.2580	1.2522
0.0950	1.2743	1.2680	1.2617	1.2555	1.2497
0.2013	1.2716	1.2652	1.2588	1.2527	1.2468
0.3903	1.2639	1.2573	1.2511	1.2450	1.2389
0.5924	1.2484	1.2419	1.2355	1.2290	1.2226
0.7934	1.2101	1.2032	1.1962	1.1893	1.1824
0.8988	1.1575	1.1504	1.1433	1.1362	1.1290
	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$				
0.0083	-0.0329	-0.0329	-0.0330	-0.0332	-0.0335
0.0950	-0.1523	-0.1228	-0.0806	-0.0390	-0.0391
0.2013	-0.2785	-0.2363	-0.1843	-0.1585	-0.1473
0.3903	-0.4179	-0.3571	-0.3300	-0.3078	-0.2804
0.5924	-0.5015	-0.4526	-0.4118	-0.3643	-0.3235
0.7934	-0.4600	-0.3943	-0.3306	-0.2767	-0.2275
0.8988	-0.3561	-0.2885	-0.2303	-0.1803	-0.1347
	$\eta/\text{mPa}\cdot\text{s}$				
0.0083	3464.8	1628.4	848.29	479.63	290.47
0.0950	2188.5	1070.2	574.42	333.16	206.27
0.2013	1351.0	686.70	380.33	226.51	143.38
0.3903	516.76	283.25	167.26	105.13	69.710
0.5924	138.81	83.980	53.969	36.546	25.786
0.7934	21.845	15.114	10.938	8.219	6.356
0.8988	5.838	4.375	3.401	2.724	2.234
	$\Delta\eta/\text{mPa}\cdot\text{s}$				
0.0083	28.696	13.485	7.023	3.969	2.402
0.0950	-947.235	-403.571	-193.338	-100.952	-56.652
0.2013	-1416.602	-614.084	-297.335	-156.679	-88.722
0.3903	-1596.009	-709.826	-350.148	-187.478	-107.570
0.5924	-1273.793	-580.086	-292.088	-159.211	-92.879
0.7934	-694.721	-321.881	-164.779	-91.257	-54.039
0.8988	-345.391	-160.947	-82.906	-46.217	-27.575

^aThe temperature uncertainty is ± 0.02 K from (288.15 to 343.15) K. The relative uncertainty of the dynamic viscosity is ± 0.35 %, and the absolute uncertainty of the density is ± 0.0005 $\text{g}\cdot\text{cm}^{-3}$.

atmospheric pressure in the temperature range $283 < T/\text{K} < 363$ was recently published.²⁵

In this work, viscosities and densities of pure 1-alkyl-3-methylimidazolium alkylsulfates and their binary mixtures with water were measured at atmospheric pressure and in the temperature range between (278.15 and 343.15) K. The Gardas and Coutinho³⁹ group contribution methods were applied to the description of the pure component densities and viscosities and new group contribution parameters were estimated whenever needed. Excess molar volumes and viscosity deviations were calculated for the aqueous mixtures and correlated by Redlich–Kister polynomial expansions.

EXPERIMENTAL SECTION

Materials. Four ionic liquids were used based on the 1-butyl-3-methylimidazolium cation and 1-ethyl-3-methylimidazolium cation: 1-butyl-3-methylimidazolium hydrogensulfate $[\text{C}_4\text{mim}][\text{HSO}_4]$, 1-butyl-3-methylimidazolium methylsulfate $[\text{C}_4\text{mim}][\text{C}_1\text{SO}_4]$, 1-ethyl-3-methylimidazolium methylsulfate $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]$, and 1-ethyl-3-methylimidazolium ethylsulfate $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$. The ionic liquids were acquired at IoLiTec

Table 2. Experimental Density ρ , Excess Molar Volume V^E , Dynamic Viscosity η , and Viscosity Deviation $\Delta\eta$ for the Binary System Water (1) + $C_4\text{mimC}_1\text{SO}_4$ (2)^a

x_1	T/K						
	283.15	293.15	303.15	313.15	323.15	333.15	343.15
	$\rho/\text{g}\cdot\text{cm}^{-3}$						
0.0004	1.225	1.2179	1.2111	1.2045	1.198	1.1916	1.1852
0.0999	1.2237	1.2167	1.2099	1.2033	1.1968	1.1903	1.1839
0.1940	1.2219	1.215	1.2082	1.2017	1.1952	1.1889	1.1825
0.3979	1.2168	1.2099	1.2032	1.1965	1.1898	1.1832	1.1763
0.6025	1.2052	1.1982	1.1913	1.1844	1.1776	1.1708	1.164
0.8005	1.1763	1.1691	1.162	1.1549	1.1477	1.1405	1.1332
0.8993	1.1343	1.1295	1.1226	1.1157	1.1086	1.1014	1.0942
	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$						
0.0004	-0.0013	-0.0013	-0.0013	-0.0013	-0.0013	-0.0013	-0.0013
0.0999	-0.1340	-0.1412	-0.1354	-0.1315	-0.1290	-0.1118	-0.1116
0.1940	-0.2180	-0.2294	-0.2178	-0.2239	-0.2187	-0.2306	-0.2302
0.3979	-0.4503	-0.4383	-0.4250	-0.3969	-0.3633	-0.3344	-0.2751
0.6025	-0.5164	-0.4713	-0.4246	-0.3727	-0.3291	-0.2848	-0.2464
0.8005	-0.4780	-0.4004	-0.3314	-0.2669	-0.2036	-0.1452	-0.0894
0.8993	-0.2777	-0.2669	-0.1995	-0.1417	-0.0864	-0.0358	0.0058
	$\eta/\text{mPa}\cdot\text{s}$						
0.0004	526.53	273.81	153.47	93.11	60.24	41.067	29.299
0.0999	432.08	229.28	132.83	82.621	54.527	37.805	27.725
0.1940	356.22	193.65	114.53	72.553	48.653	34.25	25.135
0.3979	182.06	104.30	64.514	42.474	29.476	21.442	16.875
0.6025	63.13	38.932	25.652	17.835	12.970	9.806	8.289
0.8005	19.722	13.006	9.056	6.609	5.006	3.929	3.175
0.8993	8.179	5.646	4.113	3.137	2.483	2.029	1.707
	$\Delta\eta/\text{mPa}\cdot\text{s}$						
0.0004	0.206	0.107	0.060	0.036	0.023	0.016	0.011
0.0999	-41.998	-17.286	-5.393	-1.256	0.248	0.793	1.312
0.1940	-68.394	-27.223	-9.315	-2.616	-0.004	1.061	1.443
0.3979	-135.461	-60.948	-28.201	-13.843	-7.010	-3.468	-0.925
0.6025	-146.970	-70.520	-35.838	-19.573	-11.309	-6.800	-3.602
0.8005	-86.350	-42.412	-22.195	-12.486	-7.448	-4.635	-2.992
0.8993	-46.008	-22.823	-12.056	-6.825	-4.074	-2.525	-1.606

^aThe temperature uncertainty is ± 0.02 K from (288.15 to 343.15) K. The relative uncertainty of the dynamic viscosity is ± 0.35 %, and the absolute uncertainty of the density is ± 0.0005 $\text{g}\cdot\text{cm}^{-3}$.

with mass fraction purities higher than 98 %. In the present work the purity of each studied ionic liquid was checked by ¹H NMR and ¹³C NMR, which were also used to confirm that no degradation due to the contact between the IL and water occurred during the measurements.

The water content plays an important role in the IL properties, such as density and viscosity and significant deviations can be found. In order to reduce to negligible values the water content, vacuum (1×10^{-4} Pa), stirring, and moderate temperature (343 K) for a period of at least 48 h were applied. The final IL water content was determined with a Mettler Toledo DL32 Karl Fischer coulometer (using the Hydranal-Coulomat E from Riedel-de Haën as analyte), indicating 640 ppm, 28 ppm, 80 ppm, and 170 ppm for $[\text{C}_4\text{mim}][\text{HSO}_4]$, $[\text{C}_4\text{mim}][\text{C}_1\text{SO}_4]$, $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]$, and $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$, respectively.

Ultrapure water that was doubly distilled, passed through a reverse-osmosis system, and further treated with a Milli-Q plus 185 water purification apparatus was used. It has a resistivity of 18.2 $\text{M}\Omega\cdot\text{cm}$ and a total organic carbon (TOC) smaller than 5 $\mu\text{g}\cdot\text{L}^{-1}$, and it is free of particles greater than 0.22 μm .

Methods and Procedures. Mixtures of water and IL were prepared by mass using a high-precision analytical balance

Table 3. Experimental Density ρ , Excess Molar Volume V^E , Dynamic Viscosity η , and Viscosity Deviation $\Delta\eta$ for the Binary System Water (1) + $C_2mimC_1SO_4$ (2)^a

x_1	T/K						
	278.15	288.15	298.15	308.15	318.15	328.15	338.15
	$\rho/\text{g}\cdot\text{cm}^{-3}$						
0.0023	1.3014	1.2942	1.2873	1.2804	1.2736	1.2669	1.2603
0.0887	1.2992	1.2921	1.2852	1.2783	1.2715	1.2648	1.2583
0.2235	1.2949	1.2879	1.2809	1.2741	1.2673	1.2606	1.2541
0.4163	1.2851	1.2780	1.2710	1.2641	1.2572	1.2505	1.2438
0.6106	1.2658	1.2587	1.2517	1.2447	1.2378	1.2309	1.2240
0.7999	1.2195	1.2125	1.2056	1.1986	1.1916	1.1845	1.1774
0.8948	1.1648	1.1585	1.1522	1.1457	1.1391	1.1323	1.1254
	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$						
0.0023	-0.0096	-0.0094	-0.0093	-0.0093	-0.0093	-0.0093	-0.0093
0.0887	-0.1045	-0.1084	-0.1023	-0.0976	-0.0944	-0.0923	-0.1043
0.2235	-0.2513	-0.2512	-0.2249	-0.2237	-0.2152	-0.2098	-0.2185
0.4163	-0.3993	-0.3672	-0.3286	-0.3051	-0.2793	-0.2678	-0.2528
0.6106	-0.4392	-0.3841	-0.3318	-0.2893	-0.2559	-0.2244	-0.1939
0.7999	-0.2990	-0.2229	-0.1589	-0.1036	-0.0562	-0.0114	0.0279
0.8948	-0.1739	-0.1034	-0.0472	0.0005	0.0404	0.0769	0.1084
	$\eta/\text{mPa}\cdot\text{s}$						
0.0023	246.26	137.67	83.885	54.766	37.809	27.336	20.533
0.0887	225.97	129.24	80.206	53.071	37.008	26.982	20.417
0.2235	164.56	97.731	62.406	42.265	30.097	22.428	17.928
0.4163	81.878	51.528	34.537	24.358	17.941	13.716	10.890
0.6106	36.748	24.284	16.966	12.399	9.4039	7.3624	5.9236
0.7999	14.468	9.971	7.210	5.427	4.222	3.378	2.767
0.8948	6.791	4.861	3.635	2.817	2.247	1.836	1.534
	$\Delta\eta/\text{mPa}\cdot\text{s}$						
0.0023	0.560	0.313	0.190	0.124	0.085	0.061	0.046
0.0887	1.422	3.683	3.684	3.100	2.500	2.026	1.667
0.2235	-27.003	-9.426	-2.931	-0.422	0.605	1.089	1.887
0.4163	-62.501	-29.306	-14.799	-7.910	-4.377	-2.450	-1.276
0.6106	-60.083	-30.025	-16.246	-9.368	-5.684	-3.591	-2.337
0.7999	-36.020	-18.485	-10.286	-6.106	-3.820	-2.495	-1.688
0.8948	-20.466	-10.636	-5.983	-3.587	-2.263	-1.490	-1.013

^aThe temperature uncertainty is ± 0.02 K from (288.15 to 343.15) K. The relative uncertainty of the dynamic viscosity is ± 0.35 %, and the absolute uncertainty of the density is ± 0.0005 $\text{g}\cdot\text{cm}^{-3}$.

(Sartorius MC210P) with an uncertainty of $\pm 1 \times 10^{-4}$ g. All of the samples were prepared immediately before density and viscosity measurements to avoid variations in composition due to evaporation of water or absorption of water by the IL.

Measurements of viscosity and density of IL + water binary mixtures were carried out in the temperature range of (278.15 to 343.15) K at atmospheric pressure using an Anton Paar (model SVM 3000) automated rotational Stabinger viscometer-densimeter. However, it should be mentioned that the Stabinger is unable to correctly measure densities and viscosities of compounds such as water and diluted aqueous solutions. Hence, we did not measure the density and viscosity of pure water with the Stabinger and consequently referred to the corresponding data at various temperatures from NIST recommended values of density⁴⁰ and viscosity.⁴¹ The temperature uncertainty is ± 0.02 K from (278.15 to 343.15) K. The relative uncertainty of the dynamic viscosity is ± 0.35 %, and the absolute uncertainty of the density is ± 0.0005 $\text{g}\cdot\text{cm}^{-3}$. Further details about the equipment and method can be found elsewhere.⁴²

Table 4. Experimental Density ρ , Excess Molar Volume V^E , Dynamic Viscosity η , and Viscosity Deviation $\Delta\eta$ for the Binary System Water (1) + $C_2mimC_2SO_4$ (2)^a

x_1	T/K						
	283.15	293.15	303.15	313.15	323.15	333.15	343.15
	$\rho/\text{g}\cdot\text{cm}^{-3}$						
0.0023	1.2503	1.2432	1.2364	1.2296	1.2228	1.2162	1.2096
0.1225	1.2478	1.2408	1.2340	1.2271	1.2204	1.2137	1.2072
0.1966	1.2462	1.2392	1.2323	1.2254	1.2186	1.2120	1.2053
0.4270	1.2379	1.2308	1.2238	1.2169	1.2100	1.2032	1.1965
0.6124	1.2246	1.2175	1.2104	1.2033	1.1963	1.1894	1.1824
0.7980	1.1929	1.1857	1.1785	1.1712	1.1640	1.1567	1.1494
0.8983	1.1458	1.1392	1.1325	1.1256	1.1186	1.1116	1.1043
	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$						
0.0023	-0.0083	-0.0081	-0.0081	-0.0080	-0.0080	-0.0080	-0.0081
0.1225	-0.1068	-0.1098	-0.1021	-0.0823	-0.0919	-0.0752	-0.0883
0.1966	-0.2011	-0.1970	-0.1722	-0.1500	-0.1430	-0.1389	-0.1237
0.4270	-0.3957	-0.3590	-0.3128	-0.2821	-0.2567	-0.2274	-0.2124
0.6124	-0.4891	-0.4353	-0.3745	-0.3222	-0.2843	-0.2480	-0.2104
0.7980	-0.4918	-0.4153	-0.3434	-0.2783	-0.2273	-0.1739	-0.1282
0.8983	-0.3113	-0.2420	-0.1812	-0.1272	-0.0811	-0.0419	-0.0019
	$\eta/\text{mPa}\cdot\text{s}$						
0.0023	242.32	133.92	80.978	52.623	36.240	26.161	19.634
0.1225	171.28	99.101	62.109	41.507	29.171	21.464	16.366
0.1966	136.87	81.341	52.094	35.415	25.295	18.814	14.469
0.4270	62.49	40.028	27.263	19.525	14.566	11.24	8.918
0.6124	32.646	21.816	15.378	11.335	8.663	6.824	5.518
0.7980	14.523	10.006	7.240	5.453	4.246	3.402	2.791
0.8983	6.801	4.853	3.618	2.793	2.221	1.813	1.518
	$\Delta\eta/\text{mPa}\cdot\text{s}$						
0.0023	0.551	0.304	0.183	0.119	0.082	0.059	0.044
0.1225	-41.504	-18.530	-9.043	-4.747	-2.695	-1.548	-0.911
0.1966	-58.072	-26.450	-13.122	-6.992	-3.929	-2.296	-1.385
0.4270	-76.919	-37.137	-19.479	-10.907	-6.433	-3.950	-2.505
0.6124	-62.082	-30.707	-16.499	-9.463	-5.720	-3.602	-2.340
0.7980	-35.470	-17.846	-9.755	-5.698	-3.511	-2.255	-1.497
0.8983	-19.012	-9.664	-5.333	-3.144	-1.955	-1.267	-0.841

^aThe temperature uncertainty is ± 0.02 K from (288.15 to 343.15) K. The relative uncertainty of the dynamic viscosity is ± 0.35 %, and the absolute uncertainty of the density is ± 0.0005 $\text{g}\cdot\text{cm}^{-3}$.

■ THERMODYNAMIC MODELS

Pure Liquid Density Correlation. Gardas and Coutinho⁴³ extended the Ye and Shreeve⁴⁴ approach to the estimation of ionic liquid densities for a wide range of temperature, (273.15 to 343.15) K, and pressures, (0.10 to 100) MPa, according to the equation

$$\rho = \frac{M}{NV(a + bT + cp)} \quad (1)$$

where ρ is the density in $\text{kg}\cdot\text{m}^{-3}$, M the molecular weight in $\text{kg}\cdot\text{mol}^{-1}$, N the Avogadro constant, V the molecular volume in \AA^3 , T the temperature in K, and p the pressure in MPa. The universal coefficients a , b and c are 0.8005 ± 0.0002 , $6.652 \cdot 10^{-4} \pm 0.007 \cdot 10^{-4} \text{ K}^{-1}$ and $-5.919 \cdot 10^{-4} \pm 0.024 \cdot 10^{-4} \text{ MPa}^{-1}$, respectively, at 95 % confidence level. The accuracy of this model will be tested using the measured density data.

Pure Liquid Viscosity Correlation. The description of viscosities for the pure ILs studied was carried out using the group contribution method, based on the Vogel–Fulcher–Tammann correlation, proposed by Gardas and Coutinho³⁹ and represented by eq 2

$$\ln \eta = A_\eta + \frac{B_\eta}{(T/K - T_{0\eta})} \quad (2)$$

where η is viscosity, T is temperature, and A_η , B_η , and $T_{0\eta}$ are adjustable parameters. As proposed by the authors,³⁹ $T_{0\eta}$ is fixed to 165.06 K for ILs while A_η and B_η can be obtained by a group contribution method according to

$$A_\eta = \sum_{i=1}^k n_i a_{i,\eta} \quad (3)$$

$$B_\eta = \sum_{i=1}^k n_i b_{i,\eta} \quad (4)$$

where n_i is the number of groups of type i , k is the total number of different groups in the molecule, and the parameters $a_{i,\eta}$ and $b_{i,\eta}$ are adjusted to experimental data. The parameters $a_{i,\eta}$ and $b_{i,\eta}$ were reported for the studied ILs and were here estimated for the HSO_4^- anion.

Mixture Properties. The excess thermodynamic properties, which depend on the composition, temperature, or both, are of great importance in understanding the nature of the molecular interactions present in the binary mixtures. The excess molar volume, V^E , and viscosity deviation, $\Delta\eta$, were calculated from the experimental data for all the water + IL mixtures according to eqs 5 and 6

$$V^E = \sum x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \quad (5)$$

$$\Delta\eta = \eta - \sum x_i \eta_i \quad (6)$$

where ρ and η are the density and viscosity of the solution and ρ_i and η_i refer to the density and viscosity of the pure component i .

The excess volumes and viscosity deviations were correlated at each temperature with a Redlich–Kister polynomial as shown in eq 7

$$Q = x_w x_{\text{IL}} \sum_{i=0}^m A_i (x_w - x_{\text{IL}})^i \quad (7)$$

where Q represents either the excess molar volume V^E or the viscosity deviation $\Delta\eta$, A_i are the correlation parameters, and m is the degree of the polynomial expansion. A third-order polynomial was found to be the adequate level for both properties considering the number of experimental data points.

RESULTS AND DISCUSSION

The density and viscosity measurements for the pure ILs and their mixtures with water were carried out in the temperature range of (278.15 to 343.15) K at atmospheric pressure and are reported in Tables 1–4. In the case of $[\text{C}_4\text{mim}][\text{HSO}_4]$ measurements were only performed from 303.15 K onward, due to the high viscosity of this IL. The relative deviations between the density data measured on this work of pure ILs and that in the literature results^{18,21,22,24–30,36–38} are displayed in Figure 1. The average deviations are smaller than 0.5 %, with the exception of two sets of data for $\text{C}_2\text{mimC}_1\text{SO}_4$ ^{18,27} that present larger deviations, +1.91 % and –3.85 %. However, they are clear outliers and have not been plotted in the figure. The density values are highest for pure ILs and the values decrease with increasing mole-fraction of water. Also the data of pure ILs and their aqueous binary mixtures exhibits a systematic

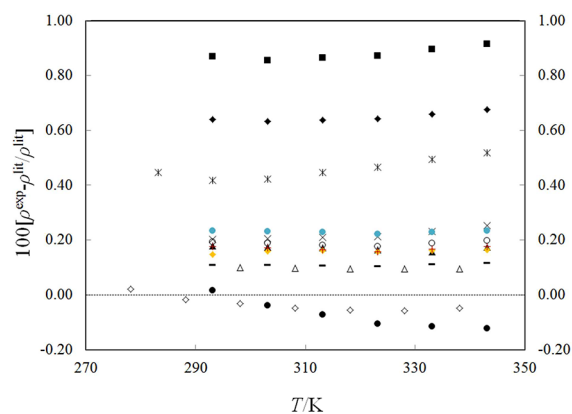


Figure 1. Relative deviations between this work's experimental data and density data available in the literature as a function of temperature for the ILs: \blacklozenge , $[\text{C}_4\text{mim}][\text{C}_1\text{SO}_4]$ from Fernandez et al.;²¹ \blacksquare , $[\text{C}_4\text{mim}][\text{C}_1\text{SO}_4]$ from Sanchez et al.;²² $*$, $[\text{C}_4\text{mim}][\text{C}_1\text{SO}_4]$ from Pereiro et al.;²⁴ \diamond , $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]$ from Ficke et al.;²⁶ Δ , $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]$ from Costa et al.;²⁵ \blacktriangle , $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ from Gomez et al.;²⁸ \bullet , $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ from Jacquemin et al.;³⁰ \circ , $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ from Rodríguez et al.;²⁹ yellow \blacklozenge , $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ from Costa et al.;²⁵ \times , $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ from Lehman et al.;³⁶ $-$, $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ from Larriba et al.;³⁷ blue \bullet , $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ from Fernandez et al.;²¹ red $+$, $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ from Schimdt et al.³⁸ (\ddagger Interpolated values.)

Table 5. Group Contribution Parameters for the Viscosity³⁹ and Density⁴¹ Models

viscosity model ³⁹		
cations/anions/groups	$a_{i,\eta}$	$b_{i,\eta}/\text{K}$
1,3-dimethylimidazolium (+)	-7.271 ⁴³	510.51 ⁴³
HSO_4^- (-)	-2.238	815.09
MeSO_4^- (-)	-1.204 ²⁵	248.39 ²⁵
EtSO_4^- (-)	-1.498 ⁴³	317.87 ⁴³
$-\text{CH}_2-$	$7.528 \cdot 10^{-2}$ ⁴³	40.92
density model ⁴³		
cations/anions	$V/\text{\AA}^3$	
1-butyl-3-methylimidazolium (+)	238 ⁴³	
1-ethyl-3-methylimidazolium (+)	182 ⁴³	
HSO_4^- (-)	69.9 ²⁵	
MeSO_4^- (-)	104 ²⁵	
EtSO_4^- (-)	135 ³⁷	

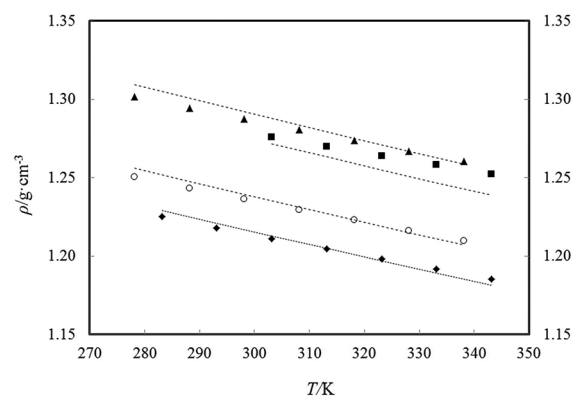


Figure 2. Density versus temperature for \blacksquare , $[\text{C}_4\text{mim}][\text{HSO}_4]$; \blacklozenge , $[\text{C}_4\text{mim}][\text{C}_1\text{SO}_4]$; \blacktriangle , $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]$; and \circ , $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$. The lines are calculated with the Gardas and Coutinho⁴³ model.

Table 6. Coefficients for Redlich–Kister Correlations for Excess Molar Volume and Calculated Root Mean Square Deviation (σ)

water (1) + C ₄ mimHSO ₄ (2)							
T/K							
coeff.	283.15	293.15	303.15	313.15	323.15	333.15	343.15
A ₀			−1.857	−1.654	−1.539	−1.420	−1.284
A ₁			−0.674	−0.780	−0.679	−0.409	−0.310
A ₂			−1.393	−0.936	−0.248	0.237	0.402
A ₃			−0.913	−0.321	−0.349	−0.685	−0.371
σ			0.012	0.011	0.011	0.012	0.012
water (1) + C ₄ mimC ₁ SO ₄ (2)							
T/K							
coeff.	283.15	293.15	303.15	313.15	323.15	333.15	343.15
A ₀	−2.002	−1.869	−1.764	−1.614	−1.465	−1.333	−1.133
A ₁	−1.027	−0.482	−0.217	0.056	0.182	0.460	0.387
A ₂	−0.486	−0.479	−0.038	0.160	0.388	0.603	0.600
A ₃	−0.248	−0.752	−0.558	−0.364	0.047	0.085	0.796
σ	0.015	0.009	0.011	0.009	0.007	0.009	0.012
water (1) + C ₂ mimC ₁ SO ₄ (2)							
T/K							
coeff.	278.15	288.15	298.15	308.15	318.15	328.15	338.15
A ₀	−1.743	−1.584	−1.409	−1.276	−1.180	−1.103	−1.015
A ₁	−0.498	−0.233	−0.132	0.102	0.222	0.416	0.600
A ₂	0.264	0.524	0.794	1.001	1.182	1.396	1.408
A ₃	0.288	0.669	1.008	1.067	1.323	1.376	1.566
σ	0.003	0.004	0.004	0.003	0.008	0.007	0.008
water (1) + C ₂ mimC ₂ SO ₄ (2)							
T/K							
coeff.	283.15	293.15	303.15	313.15	323.15	333.15	343.15
A ₀	−1.772	−1.605	−1.398	−1.248	−1.125	−1.009	−0.901
A ₁	−1.450	−1.235	−1.086	−0.855	−0.754	−0.540	−0.440
A ₂	−0.883	−0.626	−0.371	0.002	0.126	0.364	0.496
A ₃	0.043	0.490	0.801	0.781	1.202	1.168	1.508
σ	0.014	0.013	0.013	0.013	0.014	0.011	0.013

decrease of density as the alkyl side chain of the cation and anion of the IL is increased. The same trend for density is observed for all the systems with increasing temperatures.

The Gardas and Coutinho model⁴³ was applied to estimate the pure component density data. The molecular volumes, V , of ions and groups, listed in Table 5, were taken from the literature^{25,37,43} or calculated following the Jenkins⁴⁵ procedure. The predicted densities are in good agreement with the data as shown in Figure 2 with an overall relative average deviation of 0.71 %, 0.37 %, 0.29 %, and 0.21 % for the [C₄mim][HSO₄], [C₄mim][C₁SO₄], [C₂mim][C₁SO₄], and [C₂mim][C₂SO₄], respectively.

The values of excess molar volume, V^E , and viscosity deviation, $\Delta\eta$, of binary aqueous ILs mixtures, are also reported in Tables 1–4. Redlich–Kister coefficients along with obtained deviations are shown in Table 6 for V^E and Table 7 for $\Delta\eta$. The excess molar volumes of the binary mixtures studied as a function of compositions are shown in Figures 3–6. The graphs of V^E show that all mixtures exhibit negative deviations from ideality, implying increased densities compared with ideal mixing behavior. These results agree with the literature for many IL–water mixtures.^{19,29,46–48} They seem to indicate the trend of occupancy of interstitials formed by the IL network by the relatively small solvent molecules for the IL rich region. Concerning the water rich region the negative excess volume is typical for electrolytes aqueous solution due to the water

solvation of ions. Furthermore, a closer molecular packing might be attributed to stronger intermolecular bonds in the mixtures than in the pure liquids. The considerable large differences for the excess molar volumes of ILs mixtures with water may be attributed to various effects, e.g., the size and structure of the solvent molecules could hinder or promote the occupation of interstitials. In addition, the strength of the interactions of the solvent molecules among each other or with the IL could be important. The same effects might also be the reason for the different locations of the minima of the excess molar volume. All minima can be found in the water-rich region and could be construed as the optimum combination of strong interactions between the mixture components and a high degree of occupation of IL interstitials with solvent molecules.⁴⁶ These interactions can also be explained by the capability of each anion to form hydrogen bonds with water molecules. There is also an indication that the sulfate functional group presents three clearly accessible, negatively charged oxygen atoms to form a hydrogen bond. The temperature dependence of V^E is also explained for the binary mixtures. Figures 3–6 show that the magnitude of the negative excess molar volume, V^E , decreases with increasing temperature. This can be explained by the fact that for higher temperatures the increased thermal motion will decrease the effective occupation of interstitials in the mixture.

Table 7. Coefficients for Redlich–Kister Correlations for Viscosity Deviation and Calculated Root Mean Square Deviation (σ)

water (1) + C ₄ mimHSO ₄ (2)							
coeff.	T/K						
	283.15	293.15	303.15	313.15	323.15	333.15	343.15
A ₀			−5836.901	−2632.876	−1313.969	−710.641	−411.535
A ₁			3449.220	1406.325	636.257	313.124	165.186
A ₂			−2050.954	−771.415	−338.578	−164.326	−87.021
A ₃			1245.520	485.930	230.292	119.010	66.186
σ			47.875	20.616	10.014	5.308	3.025
water (1) + C ₄ mimC ₁ SO ₄ (2)							
coeff.	T/K						
	283.15	293.15	303.15	313.15	323.15	333.15	343.15
A ₀	−594.544	−276.840	−135.591	−71.092	−39.167	−22.081	−9.975
A ₁	−134.835	−108.519	−83.142	−61.667	−46.131	−35.679	−27.413
A ₂	226.352	119.729	79.401	52.413	35.370	24.514	13.548
A ₃	160.238	104.813	55.562	34.613	24.205	19.027	11.629
σ	2.556	1.481	0.792	0.479	0.309	0.212	0.024
water (1) + C ₂ mimC ₁ SO ₄ (2)							
coeff.	T/K						
	278.15	288.15	298.15	308.15	318.15	328.15	338.15
A ₀	−263.805	−127.886	−67.088	−37.434	−21.844	−13.122	−7.644
A ₁	4.308	−19.994	−22.462	−19.862	−16.898	−14.691	−16.494
A ₂	238.962	138.748	85.735	55.510	37.594	26.845	21.794
A ₃	−221.158	−115.018	−66.014	−40.023	−24.903	−15.541	−5.440
σ	0.178	0.090	0.051	0.035	0.031	0.044	0.175
water (1) + C ₂ mimC ₂ SO ₄ (2)							
coeff.	T/K						
	283.15	293.15	303.15	313.15	323.15	333.15	343.15
A ₀	−293.000	−142.971	−75.758	−42.842	−25.490	−15.816	−10.136
A ₁	142.177	59.182	25.995	11.771	5.050	2.025	0.602
A ₂	−4.881	8.650	9.314	7.228	4.893	3.571	2.636
A ₃	−48.597	−29.563	−17.494	−10.397	−5.455	−3.449	−2.245
σ	0.553	0.275	0.155	0.094	0.071	0.046	0.029

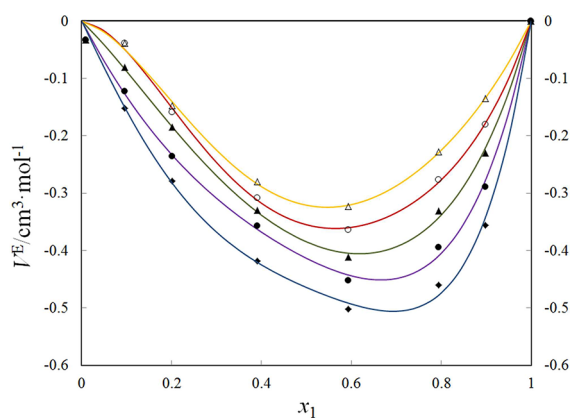


Figure 3. Excess molar volume, V^E , dependence with molar fraction of water for the binary system H₂O + [C₄mim][HSO₄] at different temperatures. The symbols represent experimental values, and the solid lines represent the corresponding correlation by the Redlich–Kister equation. (◆) 303.15 K, (●) 313.15 K, (▲) 323.15 K, (○) 333.15 K, and (Δ) 343.15 K.

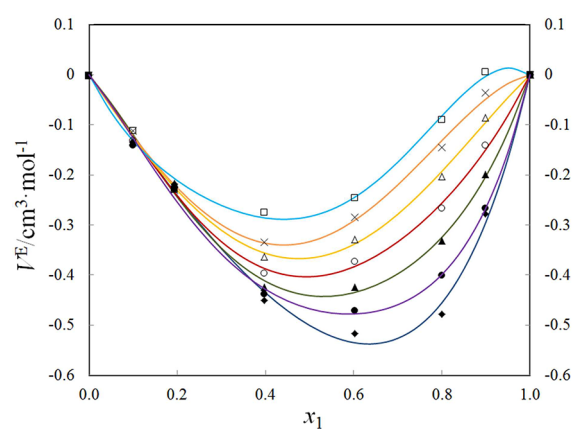


Figure 4. Excess molar volume, V^E , dependence with molar fraction of water for the binary system H₂O + [C₄mim][C₁SO₄] at different temperatures. The symbols represent experimental values, and the solid lines represent the corresponding correlation by the Redlich–Kister equation. (◆) 283.15 K, (●) 293.15 K, (▲) 303.15 K, (○) 313.15 K, (Δ) 323.15 K, (×) 333.15 K, and (□) 343.15 K.

The relative deviations in viscosity between the data measured in this work and those reported in literature is depicted in Figure 7.^{21,24,25,28–30,37,38} Larger differences are observed in the viscosity data compared to relative deviations in

density among different authors. Viscosity measurements are more sensitive to the presence of impurities than densities. In particular, small amounts of water have a tremendous effect in the viscosity of ionic liquids in the lower temperature range.

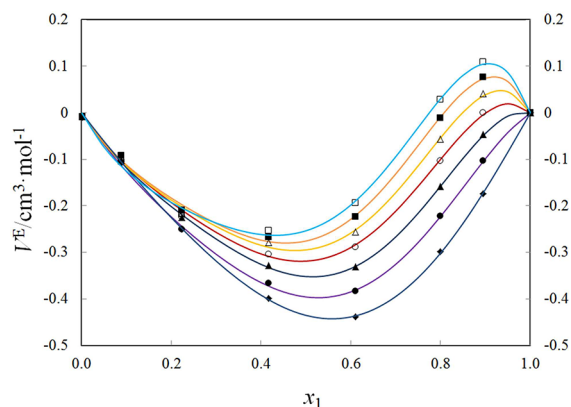


Figure 5. Excess molar volume, V^E , dependence with molar fraction of water for the binary system $\text{H}_2\text{O} + [\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]$ at different temperatures. The symbols represent experimental values, and the solid lines represent the corresponding correlation by the Redlich–Kister equation. (◆) 278.15 K, (●) 288.15 K, (▲) 298.15 K, (○) 308.15 K, (△) 318.15 K, (■) 338.15 K, and (□) 338.15 K.

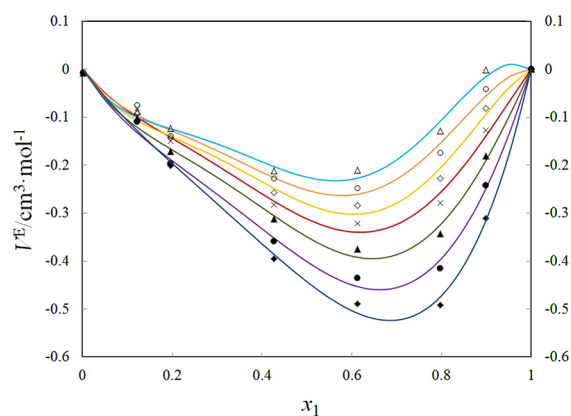


Figure 6. Excess molar volume, V^E , dependence with molar fraction of water for the binary system $\text{H}_2\text{O} + [\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ at different temperatures. The symbols represent experimental values, and the solid lines represent the corresponding correlation by the Redlich–Kister equation. (◆) 283.15 K, (●) 293.15 K, (▲) 303.15 K, (×) 313.15 K, (◇) 323.15 K, (○) 333.15 K, and (△) 343.15 K.

In this study the data show that viscosities are higher for the pure ILs, with decreasing values with increasing water content. This same trend is exhibited with increase in the alkyl chain length of cation and anion of the IL as well with increasing temperature.

The relative deviations of viscosity are within ± 5 –10 %, with the exception of the data for $[\text{C}_4\text{mim}][\text{C}_1\text{SO}_4]$, where significant differences were observed among different authors: at 293.15 K, although positive deviations of around 35 % were found from Fernandez et al.,²¹ -5 % deviations were obtained from Pereiro et al.²⁴ The data from Fernandez et al.²¹ is consistently smaller than the data reported in this work within the studied temperature range. It can be also observed that larger deviations were obtained for all the studied ILs in the low temperature region.

The prediction of viscosities for the studied ILs was carried out by the Gardas and Coutinho viscosity group contribution model based on the Vogel–Tammann–Fulcher equation.³⁹ The $a_{i,\eta}$ and $b_{i,\eta}$ parameters were taken from the literature and are listed in Table 5. The parameters for the HSO_4^- anion were derived using the data for $[\text{C}_4\text{mim}][\text{HSO}_4]$ measured in this

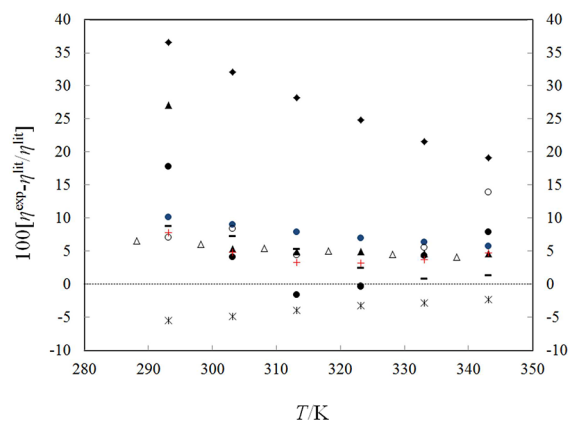


Figure 7. Relative deviations between the viscosity data measured in this work and those reported in literature as a function of temperature for the ILs: ◆, $[\text{C}_4\text{mim}][\text{C}_1\text{SO}_4]$ from Fernandez et al.;²¹ *, $[\text{C}_4\text{mim}][\text{C}_1\text{SO}_4]$ from Pereiro et al.;²⁴ △, $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]$ from Costa et al.;²⁵ ▲, $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]$ from Gomez et al.;²⁸ ●, $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ from Jacquemin et al.;³⁰ ‡ blue ●, $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ from Fernandez et al.;²¹ ○, $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ from Rodríguez et al.;²⁹ †, $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ from Larriba et al.;³⁷ red +, $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ from Schimdt et al.³⁸ (‡ Interpolated values.)

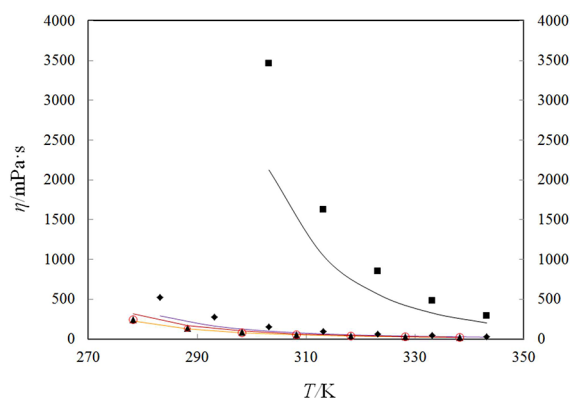


Figure 8. Viscosity versus temperature for ■, $[\text{C}_4\text{mim}][\text{HSO}_4]$; ◆, $[\text{C}_4\text{mim}][\text{C}_1\text{SO}_4]$; ▲, $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]$; red ○, $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$. The lines are calculated with the Vogel–Tammann–Fulcher³⁹ model.

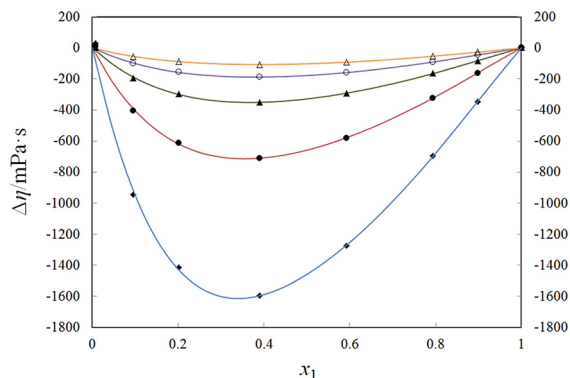


Figure 9. Viscosity deviation $\Delta\eta$ for the binary system $\text{H}_2\text{O} + [\text{C}_4\text{mim}][\text{HSO}_4]$ at different temperatures. The symbols represent experimental values, and the solid lines represent the corresponding correlation by the Redlich–Kister equation. (◆) 303.15 K, (●) 313.15 K, (▲) 323.15 K, (○) 333.15 K, and (△) 343.15 K.

work and were also compiled in Table 5. The description of the viscosity data group contribution model, taking into account

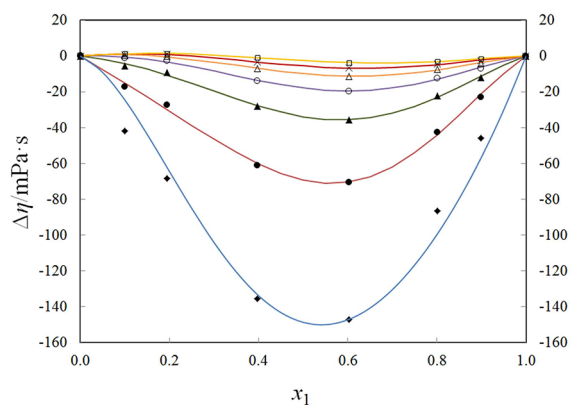


Figure 10. Viscosity deviation $\Delta\eta$ for the binary system $\text{H}_2\text{O} + [\text{C}_4\text{mim}][\text{C}_1\text{SO}_4]$ at different temperatures. The symbols represent experimental values, and the solid lines represent the corresponding correlation by the Redlich–Kister equation. (◆) 283.15 K, (●) 293.15 K, (▲) 303.15 K, (○) 313.15 K, (△) 323.15 K, (×) 333.15 K, and (□) 343.15 K.

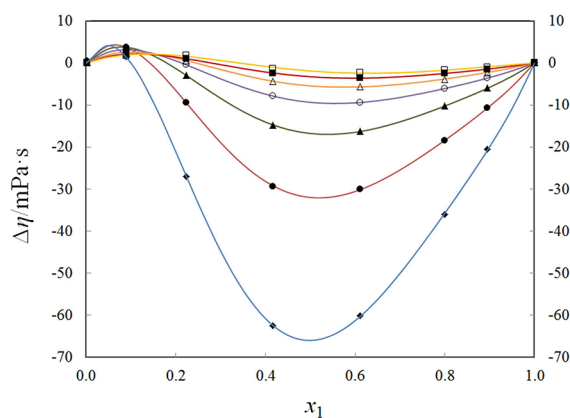


Figure 11. Viscosity deviation $\Delta\eta$ for the binary system $\text{H}_2\text{O} + [\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]$ at different temperatures. The symbols represent experimental values, and the solid lines represent the corresponding correlation by the Redlich–Kister equation. (◆) 278.15 K, (●) 288.15 K, (▲) 298.15 K, (○) 308.15 K, (△) 318.15 K, (■) 338.15 K, and (□) 338.15 K.

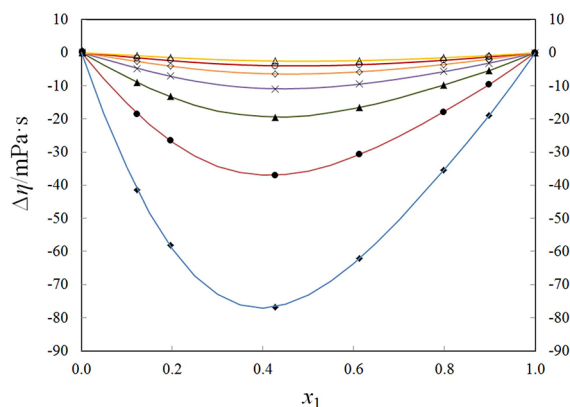


Figure 12. Viscosity deviation $\Delta\eta$ for the binary system $\text{H}_2\text{O} + [\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ at different temperatures. The symbols represent experimental values, and the solid lines represent the corresponding correlation by the Redlich–Kister equation. (◆) 283.15 K, (●) 293.15 K, (▲) 303.15 K, (×) 313.15 K, (◇) 323.15 K, (○) 333.15 K, and (△) 343.15 K.

eqs 3 and 4, along with the experimental measurements, is shown in Figure 8.

Viscosity deviations as a function of temperatures are plotted in Figures 9–12. All of the binary systems studied display strong negative viscosity deviations at low temperatures. As the temperature increases, the deviations are reduced and even reach some slightly positive values at the ionic liquid rich compositions (~ 0.1 water mole fraction). The viscosity deviations are very similar for the same temperature between the $\text{C}_2\text{mimC}_1\text{SO}_4$ and the $\text{C}_2\text{mimC}_2\text{SO}_4$, indicating a marginal effect of the alkyl size on the anion of this IL + water mixtures. The increase of the alkyl chain in the imidazolium seems to be more pronounced in the mixing viscosity properties. The viscosity deviation becomes larger (approximately doubly negative) for $\text{C}_4\text{mimC}_1\text{SO}_4$ than that observed for $\text{C}_2\text{mimC}_1\text{SO}_4$ and $\text{C}_2\text{mimC}_2\text{SO}_4$. In general, the Redlich–Kister polynomials fit provides a good description of the behavior of $\Delta\eta$ and V^E with composition for all four systems.

CONCLUSIONS

Experimental data for density and viscosity for pure and binary aqueous solutions of four ionic liquids, namely, 1-butyl-3-methylimidazolium hydrogensulfate $[\text{C}_4\text{mim}][\text{HSO}_4]$, 1-butyl-3-methylimidazolium methylsulfate $[\text{C}_4\text{mim}][\text{C}_1\text{SO}_4]$, 1-ethyl-3-methylimidazolium methylsulfate $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]$, and 1-ethyl-3-methylimidazolium ethylsulfate $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$, in the temperature range of (278 to 343) K at atmospheric pressure are presented. The density and the viscosity values are higher for the pure ILs. Both of these properties decrease with increasing mole-fraction of water. Also, the data of pure ILs and their aqueous binary mixtures exhibit a systematic decrease of density and viscosity as the alkyl side chain of the cation and anion of the IL is increased. The same trend is observed for all the systems with increasing temperatures.

Several methodologies were applied to the prediction of the experimental data here reported. An extension to the Ye and Shreeve⁴⁴ group contribution method shows a good agreement with the density data. The Gardas and Coutinho group contribution for the ionic liquid viscosity based on the Vogel–Tammann–Fulcher method³⁹ was used to predict the experimental viscosity data obtained.

The calculated values of excess molar volume of binary aqueous solution of the studied ILs, V^E , and viscosity deviation of those mixtures, $\Delta\eta$, are also reported. It could be observed that at all binary mixtures of water + IL systems exhibit negative V^E deviations from ideality indicating denser molecular packing than in the pure liquids. For all binary IL–water mixtures, the minimum of the excess molar volume lies in the water rich region. The position of the minimum and the absolute value of the excess molar volume in the water rich region (0.6–0.8) is an indication that the higher strength of the interaction in these mixtures is observed in the proportion 2:1 water/IL. It is also observed that the magnitude of the negative excess volume decreases with increasing temperature.

The binary IL–water mixtures show strong negative viscosity deviations at low temperatures, decreasing in magnitude as the temperature increases. The viscosity deviations increase with the cation alkyl chain length but only a marginal effect of the anion alkyl chain length was observed.

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Notes

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