Densities and Excess Molar Volumes for Binary Mixtures of Ionic Liquid 1-Ethyl-3-methylimidazolium Ethylsulfate with Solvents

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In this work density data for binary mixtures of the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM][EtSO$_4$]) with acetone, acetonitrile, propylene carbonate, dichloromethane, methanol, ethanol, and water are presented. Measurements were performed in dependence on composition for temperatures from (278.15 to 308.15) K using the vibrating-tube method with an expanded relative uncertainty ($k = 2$) of less than ± 0.02 %. All calculated excess molar volumes are negative, indicating denser molecular packing than in the pure liquids. The size and the structure of the solvent molecules as well as the nature of interaction between all mixture components seem to affect the extent of the observed compression effect.

Introduction

Ionic liquids (ILs) have attracted a rapidly increasing interest during the last 10 years. Because of the almost unlimited number of potential combinations of cations and anions, ILs can be tailored to a specific application. Nowadays potential applications extend from energy[1,2] over process engineering,[3−6] biotechnology,[7,8] and material engineering[9−12] to sensor technology.[13] ILs offer many possibilities as solvents for catalytic reactions, chemical synthesis, and separation technology or as electrolytes in batteries, capacitors, fuel cells, solar cells, and chemical sensors. The potential use of ILs in a wide range of applications is mainly founded by their unique properties. They are liquid over a wide temperature range, nearly nonvolatile, nonflammable, and thermally and electrically stable to a considerable degree, and they possess an excellent dissolving power for a wide range of inorganic and organic materials.

The increasing interest in IL technology is represented by the yearly increase in the number of publications. Today, a literature search using Web of Science (ISI Web of Knowledge) reveals about six publications per day for the topic “ionic liquid.” About 2 to 3 % of these publications are more or less concerned with thermophysical properties of pure ILs and mixtures of ILs with solvents. It is evident that the properties of every conceivable IL and its mixture with solvents cannot be obtained by carrying out appropriate measurements, which is a more substantial investment. In this context, it would be helpful to predict the desired properties of an IL and its mixtures with dissolved substances in dependence on composition and temperature. For this, however, knowledge on the origins of the fundamental properties of ILs and their mixtures with solvents is necessary.

Present research activities at SAOT and LTT in Erlangen are aimed at a fundamental understanding of the structure property relationships in pure ILs as well as in IL solvent mixtures. Thermophysical properties of interest are, for example, viscosity, surface tension, thermal conductivity, and mutual diffusion.[14−18] For their experimental determination, beside conventional methods, light scattering techniques are used extensively, where density data are often needed for data evaluation. Moreover, the analysis of the volumetric behavior can directly be used to investigate the molecular interactions between IL and molecular solute.

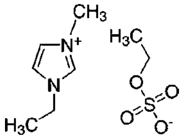

Figure 1. Molecular structure of [EMIM][EtSO$_4$].

This work summarizes our density measurements for binary mixtures of 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM][EtSO$_4$]; CAS Registry No. 342573-75-5; see Figure 1 for the molecular structure) with acetone, acetonitrile, propylene carbonate, dichloromethane, methanol, ethanol, and water, respectively, for the whole composition range and temperatures from (278.15 to 308.15) K. While density data for the mixtures with water and ethanol at 293.15 K were already published within our former work,[14] the present one summarizes the data for these mixtures over the entire temperature range.

The following experimental section gives some information on the vibrating-tube method. After a description of the sample preparation procedure, experimental conditions, and achieved uncertainty, the results for the excess molar volume of [EMIM][EtSO$_4$] solvent mixtures are compared with literature. Finally, our data for the excess molar volume are discussed concerning possible influences of structural variation and molecular interaction.

Experimental Section

Three batches of [EMIM][EtSO$_4$] were obtained by the synthesis procedure described by Maier and co-workers.[19] Their purity was higher than 99 % according to the total peak integral in the ^{1}H NMR spectrum (JEOL, ECX +400 spectrometer,

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Table 1. Suppliers and Purity Data for Purchased Solvents

solvent	supplier	nominal purity	water mass fraction
propylene carbonate	Sigma Aldrich, Germany	> 99.7 %	$< 5.0 \cdot 10^{-4}$
ethanol	Merck KGaA, Germany	> 99.9 %	$< 1.0 \cdot 10^{-3}$
methanol	Merck KGaA, Germany	> 99.9 %	$< 5.0 \cdot 10^{-4}$
acetone	Merck KGaA, Germany	> 99.8 %	$< 5.0 \cdot 10^{-4}$
acetonitrile	Merck KGaA, Germany	> 99.9 %	$< 5.0 \cdot 10^{-4}$
dichloromethane	Merck KGaA, Germany	> 99.9 %	$< 5.0 \cdot 10^{-4}$

Table 2. Density ρ of Binary Mixtures of [EMIM][EtSO$_4$] (1) (Batch #3) + Acetone (2) at Temperature T at Atmospheric Pressure

	$\rho/(\mathrm{g \cdot cm^{-3}})$						
	T/K						
x_2	278.15	283.15	288.15	293.15	298.15	303.15	308.15
0	1.25104	1.24750	1.24404	1.24066	1.23727	1.23389	1.23051
0.0048	1.25035	1.24680	1.24335	1.23997	1.23657	1.23318	1.22980
0.0098	1.24971	1.24616	1.24272	1.23931	1.23593	1.23254	1.22915
0.0150	1.24899	1.24543	1.24200	1.23859	1.23520	1.23180	1.22841
0.0249	1.24795	1.24439	1.24097	1.23755	1.23416	1.23076	1.22737
0.0399	1.24549	1.24193	1.23851	1.23510	1.23167	1.22826	1.22486
0.0600	1.24252	1.23899	1.23556	1.23212	1.22869	1.22526	1.22185
0.0799	1.23964	1.23615	1.23270	1.22924	1.22579	1.22235	1.21892
0.1002	1.23648	1.23302	1.22954	1.22607	1.22261	1.21916	1.21571
0.1501	1.22875	1.22524	1.22172	1.21821	1.21471	1.21121	1.20773
0.2066	1.21826	1.21469	1.21111	1.20754	1.20400	1.20046	1.19693
0.2998	1.20004	1.19637	1.19271	1.18906	1.18543	1.18181	1.17819
0.3999	1.17643	1.17265	1.16888	1.16513	1.16139	1.15766	1.15394
0.5000	1.14624	1.14232	1.13842	1.13453	1.13065	1.12678	1.12292
0.6000	1.10944	1.10535	1.10127	1.09720	1.09315	1.08910	1.08507
0.7000	1.06254	1.05823	1.05392	1.04961	1.04532	1.04102	1.03674
0.8000	1.00165	0.99703	0.99240	0.98778	0.98315	0.97852	0.97388
0.9003	0.92034	0.91532	0.91028	0.90521	0.90015	0.89506	0.88995
0.9500	0.86949	0.86422	0.85892	0.85361	0.84826	0.84289	0.83749
1	0.80775	0.80215	0.79652	0.79086	0.78513	0.77938	0.77358

solvent dimethylsulfoxide-d_6). Before use, [EMIM][EtSO$_4$] was dried at about 333.15 K for a time period of approximately 4 h on a vacuum line with an oil-sealed vacuum pump and a liquid nitrogen trap. After that, water mass fractions of $4.35 \cdot 10^{-4}$ (batch #1), $1.05 \cdot 10^{-3}$ (batch #2), and $8.80 \cdot 10^{-4}$ (batch #3) were determined by Karl Fischer coulometric titration (Metrohm, 756 KF coulometer). The above three IL batches were used for the preparation of binary mixtures with ethanol, water, and the remaining solvents, respectively. The expanded relative uncertainty ($k = 2$) of the water content determinations is estimated to be between ± 20 % and ± 5 %, corresponding to water mass fractions ranging from $4.0 \cdot 10^{-4}$ to $5.0 \cdot 10^{-2}$. For higher mass fractions, the relative uncertainty was about ± 20 %. High purity water deionized by an ion-exchange water system (SG 2800 SK, SG Wasseraufbereitung und Regenerierstation, Germany) was used for the preparation of IL−water mixtures. Suppliers and purities for the solvents propylene carbonate, methanol, ethanol, acetone, acetonitrile, and dichloromethane are given in Table 1. Preparing binary mixtures of these solvents with [EMIM][EtSO$_4$], syringes containing the different substances were weighed (Satorius, BP 110 S, precision within $\pm 1 \cdot 10^{-4}$ g) before and after adding liquid to a mixing flask which finally contained a mixture volume of about 12 mL. For all substances, the expanded uncertainty ($k = 2$) of the weighing procedure is estimated to be $\pm 1 \cdot 10^{-3}$ g. After shaking the flask to ensure good mixing, a new syringe was used for transferring the mixture into the densimeter. The same procedure was applied for mixtures with water mole fractions of 0.9032 and higher. For smaller mole fractions, water was dosed stepwise into a vessel containing originally about 45 mL of pure IL using microliter syringes. Here, the resulting water mass fraction was measured after each step by Karl Fischer coulometric titration. It should be mentioned that the investigation of mixtures with water mole fractions up to 0.7408 was performed in connection with the evaluation of light scattering experiments,[14] where a relatively large uncertainty in density was sufficient. All sample contacted parts and glassware used during the experiments were cleaned, rinsed with deionized water, and oven-dried.

For the density meter (Anton Paar, DMA 5000) used here, long-term drift is eliminated by an integrated reference oscillator. Only one adjustment at 293.15 K is sufficient to reach a high accuracy for the whole measuring temperature range. The temperature of the U-tube is controlled within ± 1 mK and measured by a high-precision platinum resistance probe with an uncertainty of ± 10 mK. For the automatic correction of viscosity-related errors, the integrated routine for viscosities < 100 mPa·s was chosen. Standard water and air were used for the density meter calibration. Corresponding to our former studies,[15] the calibration of the density meter was successfully checked by comparing measured liquid density data for toluene with those calculated by the equation of state by Lemmon and Span.[20] Taking into account the relative calibration error of the apparatus of 0.01 % and the error associated with the applied measurement procedure, the expanded relative uncertainty ($k = 2$) of the present density data is estimated to be less than ± 0.02 %. The relative precision or repeatability of the instrument was better than ± 0.001 %. The calibration of the density meter was controlled with deionized water and air after each sample. For each sample, densities were measured at atmospheric pressure starting from (278.15 up to 308.15) K in steps of 5 K. Before and after this temperature scan, further measurements for 293.15 K were performed to control the stability of the IL and the water mass fraction of the sample inside the densimeter. The mean value obtained for 293.15 K was used for data evaluation, whereas the maximum deviation of the single measurements was clearly within the precision of the instrument. For avoiding any influence of atmospheric moisture, the aperture of the densimeter was taped.

Table 3. Density ρ of Binary Mixtures of [EMIM][EtSO$_4$] (1) (Batch #3) + Acetonitrile (2) at Temperature T at Atmospheric Pressure

	$\rho/(\mathrm{g\cdot cm^{-3}})$						
	T/K						
x_2	278.15	283.15	288.15	293.15	298.15	303.15	308.15
0	1.25104	1.24750	1.24404	1.24066	1.23727	1.23389	1.23051
0.0051	1.25084	1.24729	1.24384	1.24044	1.23706	1.23368	1.23030
0.0099	1.25000	1.24645	1.24301	1.23961	1.23622	1.23283	1.22945
0.0202	1.24909	1.24554	1.24211	1.23869	1.23531	1.23191	1.22853
0.0499	1.24566	1.24209	1.23868	1.23526	1.23185	1.22844	1.22503
0.1001	1.23988	1.23638	1.23293	1.22948	1.22604	1.22260	1.21916
0.1426	1.23622	1.23277	1.22928	1.22581	1.22235	1.21890	1.21545
0.2507	1.21864	1.21507	1.21150	1.20795	1.20439	1.20086	1.19733
0.3434	1.20208	1.19844	1.19479	1.19115	1.18754	1.18393	1.18033
0.4592	1.17736	1.17360	1.16985	1.16612	1.16239	1.15868	1.15498
0.5799	1.14091	1.13700	1.13310	1.12922	1.12535	1.12149	1.11763
0.6790	1.10124	1.09717	1.09312	1.08908	1.08503	1.08100	1.07697
0.7423	1.06873	1.06452	1.06033	1.05615	1.05197	1.04780	1.04363
0.7865	1.04105	1.03674	1.03243	1.02813	1.02383	1.01953	1.01524
0.8539	0.98850	0.98397	0.97943	0.97491	0.97037	0.96584	0.96131
0.8970	0.94589	0.94118	0.93647	0.93176	0.92704	0.92231	0.91758
0.9342	0.90215	0.89728	0.89239	0.88747	0.88261	0.87789	0.87312
0.9567	0.87114	0.86613	0.86110	0.85607	0.85101	0.84595	0.84087
0.9707	0.84953	0.84443	0.83931	0.83419	0.82904	0.82387	0.81869
0.9803	0.83378	0.82862	0.82344	0.81824	0.81302	0.80778	0.80252
0.9872	0.82179	0.81657	0.81134	0.80609	0.80081	0.79552	0.79019
0.9925	0.81249	0.80723	0.80195	0.79667	0.79134	0.78600	0.78062
0.9967	0.80439	0.79909	0.79378	0.78844	0.78308	0.77769	0.77228
1	0.79801	0.79269	0.78733	0.78197	0.77656	0.77114	0.76568

Table 4. Density ρ of Binary Mixtures of [EMIM][EtSO$_4$] (1) (Batch #3) + Dichloromethane (2) at Temperature T at Atmospheric Pressure

	$\rho/(\mathrm{g\cdot cm^{-3}})$						
	T/K						
x_2	278.15	283.15	288.15	293.15	298.15	303.15	308.15
0	1.25104	1.24750	1.24404	1.24066	1.23727	1.23389	1.23051
0.0375	1.25239	1.24882	1.24538	1.24196	1.23855	1.23513	1.23172
0.0731	1.25422	1.25064	1.24719	1.24372	1.24027	1.23681	1.23336
0.1117	1.25578	1.25222	1.24872	1.24522	1.24173	1.23824	1.23476
0.1664	1.25885	1.25531	1.25175	1.24814	1.24463	1.24108	1.23755
0.2488	1.26374	1.26006	1.25638	1.25270	1.24903	1.24537	1.24171
0.3308	1.26890	1.26509	1.26128	1.25748	1.25369	1.24990	1.24613
0.4023	1.27469	1.27074	1.26678	1.26282	1.25890	1.25497	1.25105
0.4624	1.27933	1.27526	1.27118	1.26711	1.26305	1.25900	1.25496
0.5776	1.29069	1.28628	1.28187	1.27747	1.27307	1.26869	1.26432
0.6593	1.29995	1.29523	1.29051	1.28580	1.28109	1.27639	1.27169
0.7684	1.31591	1.31052	1.30514	1.29977	1.29438	1.28900	1.28361
0.8377	1.32728	1.32128	1.31526	1.30925	1.30321	1.29716	1.29111
0.8856	1.33558	1.32897	1.32235	1.31572	1.30905	1.30236	1.29565
0.9207	1.34130	1.33416	1.32699	1.31981	1.31258	1.30532	1.29803
0.9475	1.34571	1.33805	1.33035	1.32264	1.31487	1.30706	1.29921
0.9687	1.34906	1.34091	1.33271	1.32448	1.31618	1.30785	1.29946
0.9858	1.35132	1.34272	1.33407	1.32538	1.31661	1.30780	1.29892
1	1.35284	1.34380	1.33471	1.32558	1.31634	1.30706	1.29769

Results and Discussion

The experimental density data obtained at atmospheric pressure and temperatures in the range from (278.15 to 308.15) K are summarized in Tables 2 to 8. The densities of the three different batches of [EMIM][EtSO$_4$] show a maximum relative deviation of 0.08 %, which is outside the combined expanded uncertainties of the measurements. The differences among the batches can be attributed to different mass fractions of water as well as of impurities. Several authors have also studied the density of pure [EMIM][EtSO$_4$]. Here, for a detailed comparison the reader is referred to our previous work, where we have studied different pure ILs.[15] For the IL−water mixtures listed in Table 8, the densities for $x_{\mathrm{water}} = 0$ were extrapolated from fourth-order polynomial correlations describing the densities in dependence on the water mass fraction. For the other IL−solvent mixtures, the influence of the water mass fraction of the pure IL was neglected.

The excess molar volume $V_{\mathrm{m}}^{\mathrm{E}}$ for a given temperature is determined from the measured densities according to

$$V_{\mathrm{m}}^{\mathrm{E}} = \frac{x_{\mathrm{IL}}M_{\mathrm{IL}} + x_{\mathrm{solvent}}M_{\mathrm{solvent}}}{\rho} - \frac{x_{\mathrm{IL}}M_{\mathrm{IL}}}{\rho_{\mathrm{IL}}} - \frac{x_{\mathrm{solvent}}M_{\mathrm{solvent}}}{\rho_{\mathrm{solvent}}} \tag{1}$$

where ρ is the density of the mixture, x_{IL} and x_{solvent} are the mole fractions, M_{IL} and M_{solvent} denote the molar masses, and ρ_{IL} and ρ_{solvent} are the densities of the pure IL and the pure solvent, respectively. $V_{\mathrm{m}}^{\mathrm{E}}$ represents the difference between real and ideal mixing behavior. The expanded uncertainties of $V_{\mathrm{m}}^{\mathrm{E}}$ ($k = 2$) were determined by combining in quadrature the errors for x_{solvent} and for the measured densities of the IL−solvent mixtures as well as the pure components. Because of the precise temperature control of the densimeter, uncertainties caused by temperature differences could be neglected. For the IL mixtures with all solvents except water, the largest uncertainties of $V_{\mathrm{m}}^{\mathrm{E}}$

Table 5. Density ρ of Binary Mixtures of [EMIM][EtSO$_4$] (1) (Batch #1) + Ethanol (2) at Temperature T at Atmospheric Pressure

	$\rho/(\mathrm{g \cdot cm^{-3}})$						
	T/K						
x_2	278.15	283.15	288.15	293.15	298.15	303.15	308.15
0	1.25140	1.24784	1.24439	1.24101	1.23763	1.23424	1.23087
0.0160	1.24964	1.24608	1.24265	1.23925	1.23585	1.23245	1.22905
0.0254	1.24822	1.24465	1.24124	1.23784	1.23443	1.23103	1.22763
0.0425	1.24612	1.24258	1.23916	1.23576	1.23234	1.22894	1.22553
0.0877	1.24095	1.23747	1.23404	1.23059	1.22718	1.22375	1.22034
0.1178	1.23548	1.23205	1.22859	1.22514	1.22170	1.21826	1.21484
0.1420	1.23131	1.22785	1.22438	1.22092	1.21747	1.21402	1.21059
0.2344	1.21631	1.21279	1.20928	1.20578	1.20230	1.19883	1.19536
0.4236	1.17457	1.17096	1.16736	1.16379	1.16021	1.15665	1.15310
0.6005	1.11678	1.11306	1.10936	1.10567	1.10199	1.09832	1.09466
0.7305	1.05536	1.05154	1.04772	1.04392	1.04012	1.03636	1.03255
0.8330	0.98708	0.98314	0.97921	0.97530	0.97137	0.96746	0.96354
0.9022	0.92553	0.92155	0.91781	0.91345	0.91022	0.90622	0.90218
0.9567	0.86373	0.86074	0.85680	0.85132	0.84859	0.84444	0.84027
0.9846	0.82639	0.82221	0.81801	0.81381	0.80959	0.80536	0.80109
0.9924	0.81442	0.81028	0.80617	0.80175	0.79780	0.79353	0.78923
0.9963	0.80801	0.80379	0.79955	0.79530	0.79103	0.78674	0.78241
1	0.80212	0.79789	0.79363	0.78937	0.78508	0.78077	0.77642

Table 6. Density ρ of Binary Mixtures of [EMIM][EtSO$_4$] (1) (Batch #3) + Methanol (2) at Temperature T at Atmospheric Pressure

	$\rho/(\mathrm{g \cdot cm^{-3}})$						
	T/K						
x_2	278.15	283.15	288.15	293.15	298.15	303.15	308.15
0	1.25104	1.24750	1.24404	1.24066	1.23727	1.23389	1.23051
0.0050	1.25051	1.24696	1.24352	1.24013	1.23674	1.23336	1.22998
0.0097	1.25012	1.24657	1.24314	1.23975	1.23636	1.23297	1.22959
0.0150	1.24980	1.24624	1.24281	1.23942	1.23602	1.23263	1.22924
0.0252	1.24878	1.24523	1.24182	1.23842	1.23502	1.23163	1.22825
0.0403	1.24744	1.24388	1.24048	1.23707	1.23367	1.23027	1.22688
0.0598	1.24564	1.24213	1.23872	1.23531	1.23189	1.22849	1.22509
0.0800	1.24377	1.24029	1.23686	1.23344	1.23002	1.22661	1.22320
0.1001	1.24179	1.23835	1.23491	1.23147	1.22805	1.22463	1.22122
0.1500	1.23680	1.23334	1.22988	1.22642	1.22298	1.21954	1.21612
0.2000	1.23124	1.22775	1.22426	1.22078	1.21732	1.21387	1.21042
0.3000	1.21810	1.21456	1.21102	1.20750	1.20399	1.20050	1.19701
0.4000	1.20190	1.19830	1.19472	1.19115	1.18759	1.18405	1.18051
0.4999	1.18084	1.17718	1.17354	1.16991	1.16629	1.16269	1.15910
0.6000	1.15355	1.14982	1.14610	1.14240	1.13871	1.13503	1.13137
0.7000	1.11557	1.11173	1.10791	1.10411	1.10031	1.09653	1.09276
0.8000	1.05976	1.05579	1.05182	1.04787	1.04392	1.03998	1.03605
0.9000	0.97110	0.96689	0.96268	0.95849	0.95429	0.95010	0.94591
0.9500	0.90284	0.89844	0.89405	0.88967	0.88526	0.88086	0.87646
0.9800	0.84924	0.84469	0.84015	0.83563	0.83105	0.82649	0.82191
1	0.80553	0.80085	0.79616	0.79149	0.78677	0.78205	0.77730

ranging from (0.050 to 0.056) $\mathrm{cm^3 \cdot mol^{-1}}$ were found for the smallest mole fraction of the solvent. With increasing x_{solvent}, the uncertainty of $V_{\mathrm{m}}^{\mathrm{E}}$ gradually decreased until values ranging from (0.010 to 0.025) $\mathrm{cm^3 \cdot mol^{-1}}$ were reached for the largest solvent mole fractions. For the IL−water mixtures, the uncertainty of $V_{\mathrm{m}}^{\mathrm{E}}$ increased from (0.055 to 0.804) $\mathrm{cm^3 \cdot mol^{-1}}$ for water mole fractions ranging from 0.0057 to 0.7408. Here, the large uncertainties of $V_{\mathrm{m}}^{\mathrm{E}}$ are mainly caused by those of the water content originating from coulometric titration. For larger water mole fractions, the uncertainty of $V_{\mathrm{m}}^{\mathrm{E}}$ was smaller than 0.010 $\mathrm{cm^3 \cdot mol^{-1}}$.

For the correlation of the excess molar volume, the Redlich−Kister equation,

$$V_{\mathrm{m,fit}}^{\mathrm{E}} = x_{\mathrm{solvent}}(x_{\mathrm{solvent}} - 1)\sum_{i=0}^{N} A_i(1 - 2x_{\mathrm{solvent}})^i \qquad (2)$$

is used.[21−23] In eq 2, A_i are the polynomial coefficients, and N is the degree of the polynomial. For our data, which were all considered with the same statistical weight, the polynomial coefficients of the third-order Redlich−Kister correlations are listed in Table 9. Here, also the standard deviations of the calculated excess molar volumes to the correlation,

$$\mathrm{rms} = \sqrt{\frac{\sum_{i=1}^{B}(V_{\mathrm{m}}^{\mathrm{E}} - V_{\mathrm{m,fit}}^{\mathrm{E}})^2}{B - (N + 1)}} \qquad (3)$$

are given. In eq 3, B is the number of experimental data points. The standard deviations do not exceed a value of 0.04 $\mathrm{cm^3 \cdot mol^{-1}}$, except for IL mixtures with ethanol and acetonitrile. For these mixtures, maximum root-mean-square (rms) values of (0.122 and 0.079) $\mathrm{cm^3 \cdot mol^{-1}}$ can be found.

For data comparison, excess molar volume data for mixtures of [EMIM][EtSO$_4$] with ethanol[24−26] and water[24,27,28] are available in the literature. All of these data sets are based on the vibrating U-tube method and instruments of the same manufacturer. For the measurements of García-Miaja et al.,[26,28] even the same instrument as in this work was used. Gómez et al.,[24] Arce et al.,[25] Rodríguez and Brennecke,[27] and García-Miaja et al.[26,28] specify the uncertainty of their density measure-

Table 7. Density ρ of Binary Mixtures of [EMIM][EtSO$_4$] (1) (Batch #3) + Propylene Carbonate (2) at Temperature T at Atmospheric Pressure

	$\rho/(\mathrm{g \cdot cm^{-3}})$						
	T/K						
x_2	278.15	283.15	288.15	293.15	298.15	303.15	308.15
0	1.25104	1.24750	1.24404	1.24066	1.23727	1.23389	1.23051
0.0266	1.25069	1.24712	1.24368	1.24027	1.23686	1.23345	1.23006
0.0513	1.25041	1.24682	1.24339	1.23997	1.23653	1.23311	1.22969
0.0755	1.25013	1.24655	1.24310	1.23964	1.23619	1.23274	1.22930
0.1231	1.24960	1.24604	1.24254	1.23904	1.23555	1.23206	1.22858
0.1825	1.24889	1.24535	1.24179	1.23820	1.23468	1.23113	1.22760
0.2548	1.24805	1.24441	1.24076	1.23711	1.23349	1.22988	1.22627
0.3178	1.24717	1.24345	1.23973	1.23601	1.23232	1.22864	1.22496
0.3778	1.24640	1.24261	1.23881	1.23504	1.23127	1.22752	1.22378
0.4859	1.24438	1.24042	1.23647	1.23254	1.22862	1.22471	1.22083
0.5725	1.24260	1.23850	1.23440	1.23034	1.22628	1.22225	1.21822
0.6971	1.23908	1.23473	1.23040	1.22609	1.22179	1.21752	1.21325
0.7812	1.23590	1.23135	1.22682	1.22231	1.21781	1.21333	1.20886
0.8427	1.23295	1.22823	1.22351	1.21883	1.21415	1.20949	1.20484
0.8893	1.23036	1.22548	1.22062	1.21578	1.21095	1.20614	1.20134
0.9259	1.22781	1.22279	1.21779	1.21281	1.20784	1.20289	1.19794
0.9554	1.22535	1.22020	1.21507	1.20996	1.20485	1.19976	1.19468
0.9797	1.22322	1.21797	1.21273	1.20751	1.20230	1.19709	1.19190
1	1.22093	1.21557	1.21021	1.20488	1.19955	1.19423	1.18891

Table 8. Density ρ of Binary Mixtures of [EMIM][EtSO$_4$] (1) (Batch #2) + Water (2) at Temperature T at Atmospheric Pressure[a]

	$\rho/(\mathrm{g \cdot cm^{-3}})$						
	T/K						
x_2	278.15	283.15	288.15	293.15	298.15	303.15	308.15
0	1.25063	1.24718	1.24379	1.24039	1.23700	1.23363	1.23027
0.0136	1.25046	1.24691	1.24347	1.24009	1.23670	1.23331	1.22993
0.0253	1.25019	1.24663	1.24321	1.23982	1.23642	1.23303	1.22965
0.0415	1.24980	1.24624	1.24285	1.23946	1.23606	1.23267	1.22929
0.0729	1.24917	1.24566	1.24227	1.23888	1.23548	1.23209	1.22870
0.1429	1.24767	1.24426	1.24085	1.23744	1.23404	1.23064	1.22725
0.2344	1.24553	1.24212	1.23869	1.23528	1.23186	1.22846	1.22506
0.3920	1.23994	1.23650	1.23306	1.22963	1.22620	1.22278	1.21936
0.5695	1.22884	1.22535	1.22187	1.21847	1.21498	1.21155	1.20812
0.7408	1.20789	1.20440	1.20090	1.19739	1.19386	1.19033	1.18678
0.9032	1.14937	1.14618	1.14295	1.13965	1.13637	1.13302	1.12961
0.9577	1.09419	1.09190	1.08950	1.08699	1.08440	1.08170	1.07889
0.9840	1.04511	1.04388	1.04243	1.04071	1.03874	1.03644	1.03381
0.9923	1.02367	1.02291	1.02188	1.02061	1.01912	1.01742	1.01554
0.9963	1.01218	1.01169	1.01085	1.00945	1.00824	1.00656	1.00439
1	0.99996	0.99969	0.99909	0.99820	0.99704	0.99564	0.99402

[a] The densities for $x_2 = 0$ represent extrapolated values.

ments to be ± 0.00001 $\mathrm{g \cdot cm^{-3}}$, ± 0.00001 $\mathrm{g \cdot cm^{-3}}$, ± 0.00005 $\mathrm{g \cdot cm^{-3}}$, and ± 0.0001 $\mathrm{g \cdot cm^{-3}}$, respectively. Taking into account both the error connected with the calibration and that of the subsequent measuring procedure, most of the above stated uncertainties for the vibrating U-tube method seem to be underestimated, that is, below the expected values. No uncertainties of V_m^E are given for the literature data. In general, our excess molar volume results for [EMIM][EtSO$_4$] mixtures with water and ethanol agree with those reported in literature. Except for the work of Gómez et al.,[24] the standard deviation (rms) of the Redlich−Kister correlations for our V_m^E data from corresponding correlations given in the literature is in the range from (0.065 to 0.091) $\mathrm{cm^3 \cdot mol^{-1}}$. In comparison with the results reported by Gómez et al.,[24] rms values of (0.096 and 0.168) $\mathrm{cm^3 \cdot mol^{-1}}$ can be found for the mixtures with water and ethanol. It should be noted that the V_m^E data given by Gómez et al.[24] also distinctly deviate from those reported by Arce et al.,[25] García-Miaja et al.,[26,28] and Rodríguez and Brennecke.[27]

The influence of the nature of different solvents on the excess molar volume at 293.15 K is exemplarily shown in Figure 2. For the other temperatures, likewise behavior can be found. In Figure 2, besides the calculated data of the excess molar volume, also their correlation in form of the Redlich−Kister equation, eq 2, is given. It can be seen that eq 2 for the IL−water mixture has several points of inflection. The reason for this behavior is mainly founded by the relatively large uncertainty of V_m^E indicated by the exemplarily depicted error bars. Figure 2 shows negative V_m^E values for all mixtures, implying increased densities compared with ideal mixing behavior. These results are in agreement with literature for many IL−solvent mixtures.[22−31] They seem to indicate that the relatively small solvent molecules tend to occupy interstitials formed by the IL network. Furthermore, stronger intermolecular bonds in the mixtures than in the pure liquids might contribute to a closer molecular packing. The quite large differences for the excess molar volumes of [EMIM][EtSO$_4$] mixtures with different solvents may be attributed to various effects. For example, 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 solvent-rich region and could be interpreted as the optimum combination of strong interactions

Table 9. Polynomial Coefficients of the Redlich−Kister Equation (eq 2) and Standard Deviations (eq 3) of the Measured Values from the Fit for All [EMIM][EtSO$_4$]−Solvent Mixtures at the Studied Temperatures *T*

T	A_0	A_1	A_2	A_3	rms
K	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$
			Acetone		
278.15	8.67604	−3.57082	2.32792	−2.50181	0.031
283.15	8.99737	−3.70609	2.57204	−2.56189	0.031
288.15	9.30938	−3.92427	2.79526	−2.54986	0.033
293.15	9.62218	−4.13188	2.93803	−2.69306	0.034
298.15	9.96426	−4.35730	3.13811	−2.83716	0.035
303.15	10.32477	−4.58636	3.33077	−3.00491	0.036
308.15	10.70976	−4.83592	3.55307	−3.14587	0.038
			Acetonitrile		
278.15	4.78611	−2.67039	3.26431	−3.14135	0.068
283.15	4.98873	−2.73458	3.47443	−3.30580	0.070
288.15	5.16810	−2.86535	3.72832	−3.36637	0.071
293.15	5.34664	−3.00473	3.88028	−3.56924	0.073
298.15	5.53603	−3.14125	4.09607	−3.76782	0.075
303.15	5.73731	−3.26882	4.32171	−4.04526	0.077
308.15	5.95209	−3.40334	4.56724	−4.31576	0.079
			Dichloromethane		
278.15	2.46914	−1.90842	2.11848	−2.53094	0.016
283.15	2.75005	−2.01028	2.33442	−2.67678	0.016
288.15	3.01091	−2.19188	2.58213	−2.70540	0.016
293.15	3.26617	−2.40123	2.73949	−2.84418	0.016
298.15	3.54397	−2.59904	2.96886	−2.97673	0.016
303.15	3.83683	−2.81419	3.17501	−3.13236	0.017
308.15	4.14905	−3.04031	3.40648	−3.28214	0.017
			Ethanol		
278.15	2.37484	−0.63643	1.81505	−1.16461	0.054
283.15	2.47000	−0.45858	2.23481	−1.77742	0.061
288.15	2.55352	−0.47248	2.49983	−2.02816	0.064
293.15	2.69130	−0.79902	2.20608	−1.28072	0.056
298.15	2.73615	−0.53993	2.82935	−2.58424	0.066
303.15	2.85260	−0.61261	2.94873	−2.74183	0.121
308.15	2.97710	−0.67205	3.05910	−2.92840	0.122
			Methanol		
278.15	2.81701	−1.74898	2.42897	−2.89763	0.018
283.15	2.93687	−1.77683	2.62829	−2.97019	0.019
288.15	3.03519	−1.87827	2.81838	−2.95111	0.020
293.15	3.12322	−1.96860	2.93097	−3.09389	0.021
298.15	3.22602	−2.06116	3.06902	−3.21643	0.022
303.15	3.33530	−2.15047	3.20413	−3.37101	0.023
308.15	3.45370	−2.24842	3.36427	−3.50163	0.025
			Propylene Carbonate		
278.15	1.02070	−0.74835	0.41425	−0.70448	0.006
283.15	1.08998	−0.68257	0.47558	−0.80266	0.006
288.15	1.12620	−0.71389	0.57340	−0.71699	0.006
293.15	1.15144	−0.75718	0.58982	−0.73691	0.006
298.15	1.18674	−0.77522	0.62767	−0.78088	0.007
303.15	1.22676	−0.80695	0.65244	−0.81869	0.007
308.15	1.27342	−0.83721	0.69209	−0.84170	0.007
			Water		
278.15	1.63806	−0.80363	2.76427	−3.66863	0.025
283.15	1.55653	−0.58802	2.45024	−3.73239	0.021
288.15	1.45529	−0.49481	2.24004	−3.53922	0.020
293.15	1.37642	−0.43223	2.02850	−3.29485	0.019
298.15	1.28966	−0.33593	1.85868	−3.18060	0.018
303.15	1.21802	−0.26405	1.66649	−3.03156	0.017
308.15	1.15147	−0.19911	1.46345	−2.89775	0.016

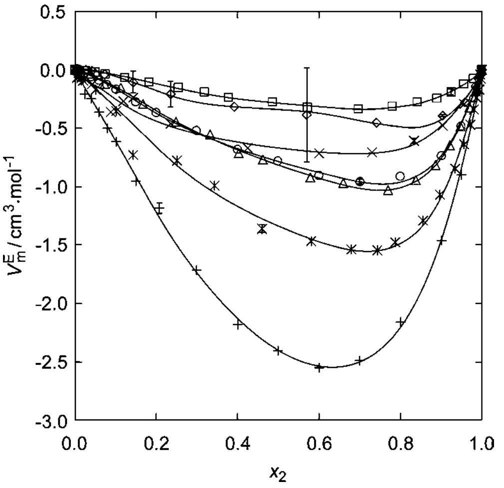

Figure 2. Excess molar volume V_m^E of binary mixtures of [EMIM][EtSO$_4$] (1) + solvents (2) as a function of the mole fraction x_2 at 293.15 K and atmospheric pressure: □, propylene carbonate; ◇, water; ×, ethanol; ○, methanol; △, dichloromethane; ∗, acetonitrile; +, acetone.

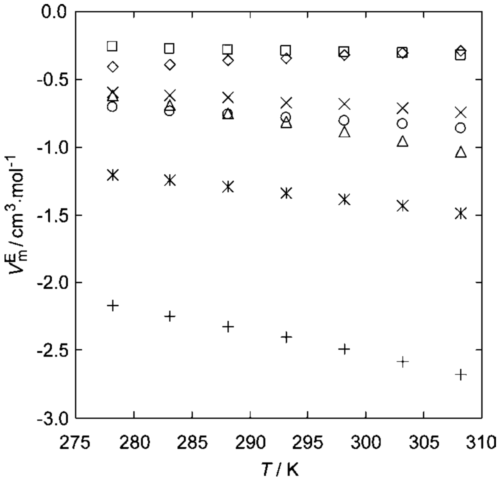

Figure 3. Excess molar volume V_m^E of equimolar binary mixtures of [EMIM][EtSO$_4$] (1) + solvents (2) as a function of the temperature T at atmospheric pressure: □, propylene carbonate; ◇, water; ×, ethanol; ○, methanol; △, dichloromethane; ∗, acetonitrile; +, acetone.

between the mixture components and a high degree of occupation of IL interstitials with solvent molecules.[22]

To show the complexity of the interpretation of the V_m^E data, the results for the IL mixtures with water and acetone are exemplarily compared. The mixtures with acetone show the largest deviation from ideal mixing behavior. In contrast, the excess molar volume for water mixtures is quite large, although one could expect effective occupation of interstitials formed by the IL due to the small molecular size of water. For the mixtures with water, interstitials may not be easily accessed because of the strong internal hydrogen bonds between the protic water molecules. For water mixtures with other ILs such as [b3mpy][BF$_4$][29] or [C$_4$mim][BF$_4$],[32,33] even positive excess molar volumes were found and attributed to additional weakening of the strong electrostatic attractions between the ion pairs. For the aprotic solvent acetone, internal bonding should be distinctly weaker, possibly allowing the effective occupation of interstitials by single solvent molecules.

The temperature dependence of V_m^E is exemplarily discussed for the binary mixtures with equimolar composition. Figure 3 shows that the excess molar volume decreases with increasing temperature for all solvents except water, which corresponds with literature data for IL−solvent mixtures with the same IL[24−28] as well as for mixtures with different ILs.[22,23,26−28] For higher temperatures, increased thermal motion of molecules may allow a more effective occupation of interstitials. For this, also enlargement of interstitials indicated by the decreasing density of the mixture could be of importance. For mixtures with water, the increasing excess molar volumes with increasing temperature may result from the temperature dependence of the strength of hydrogen bonds, see, for example, ref 24.

Conclusions

The excess molar volumes determined from density measurements for binary mixtures of the IL [EMIM][EtSO$_4$] with various solvents solely showed negative values indicating denser molecular packing than in the pure liquids. For all mixtures, the minimum of the excess molar volume lies in the solvent-rich region. The position of the minimum and the absolute value of the excess molar volume are possibly affected by steric effects and the strength of the interactions of the solvent molecules among each other and with the IL. The strongest deviation from ideal mixing behavior was found for the aprotic solvent acetone which seems to occupy interstitials of the IL more easily than all other solvents. Only a weak mixing effect was observed for water despite its smallest molecule size among all solvents studied. Here, strong internal hydrogen bonds of the solvent molecules seem to prevent dense molecular packing. Except for water, the excess molar volume becomes more negative with increasing temperature.

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