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Ternary Liquid−Liquid Equilibria for Six Systems Containing Ethylacetate + Ethanol or Acetic Acid + an Imidazolium-Based Ionic Liquid with a Hydrogen Sulfate Anion at 313.2 K

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Liquid−liquid-phase equilibria studies of systems containing acidic ionic liquid (IL) + ethylacetate + ethanol or acetic acid are reported, and the influence of the alkyl chain length on the cation on the liquid−liquid equilibra (LLE) was measured. The ILs used are 1-methylimidazolium hydrogen sulfate ([HMIM][HSO_4]), 1-ethyl-3-methylimidazolium hydrogen sulfate ([EMIM][HSO_4]), and 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO_4]). The experimental data was obtained at (313.2 ± 0.5) K and correlated with the UNIQUAC model to obtain the binary interaction parameters. All studied systems were of type I, with ethylacetate + IL as immiscible pairs.

Introduction

Room-temperature ionic liquids (IL) are a class of new green solvents. Due to their unique properties, they can be an alternative to conventional organic solvents for different industrial applications.[1,2] The majority of literature about ILs is concerned with their synthesis and applications in electrochemistry and as solvents or catalysts for chemical reactions.[1−4] Another potential application of the ionic liquids is as solvents for extraction processes. Due to their low volatility, they can be easily recycled through removing volatile solutes by simple distillation. Examples for their potential use for extractive separation processes can be found elsewhere.[5−11]

By combining reaction and liquid−liquid separation, also known in the literature as reactive extraction or extractive reaction, improved conversion can be achieved, when some of the products are removed from the system and back reaction is prevented. There is some data about the use of ILs, particularly acidic IL with, e.g., hydrogen sulfate or hydrogen phosphate anions, which act simultaneously as catalyst and as solvent for biphasic esterifications.[12−14] In some cases, the conversions of the esterification reactions could be improved, combined with an easy separation of products and recycling of the ionic liquid catalyst. Unfortunately, such studies are mainly focused on the chemical activity, and additional data on phase behavior of the systems and its influence on the reaction equilibrium are usually not provided.

Though the use of ILs as solvents and catalysts for (reactive) extraction processes is promising, the development of an industrial process or the choice of an appropriate IL is prevented by the lack of information on the liquid−liquid-phase equilibrium for the corresponding compounds. There are some systematic investigations on binary and ternary systems containing, e.g., mixtures of IL and alcohols or water;[15−18] nevertheless, the data available on the liquid−liquid-phase behavior of ILs are still scarce. It should also be mentioned that the studies already published are conducted with relatively few “common” ionic liquids, compared to the possible combinations of anions and cations. Binary and ternary LLE data, e.g., for hydrogen sulfate containing ILs, are rare in the literature. The liquid−liquid-phase behavior of systems containing ILs and esters is only marginally studied, too.

As a representative esterification reaction, the reaction of ethanol with acetic acid was chosen. Due to their availability and Brønsted acidity, the ionic liquids 1-methylimidazolium hydrogen sulfate ([HMIM][HSO_4]), 1-ethyl-3-methylimidazolium hydrogen sulfate ([EMIM][HSO_4]), and 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO_4]) seemed most suitable for a systematic study from a chemical point of view, although they are highly viscous liquids, which is not favored in an extraction process. However, these ILs are commercially available, which is not always granted with other ILs reported for esterifications in the literature.[12−14]

All the above ILs are totally miscible with water and partly miscible with the ester (ethylacetate) at 313 K. Initially, tests showed that after reaction completion two phases are present: an organic phase, containing mainly ester, and an ionic phase with most of the water. Therefore, these ILs are in principle suited for separating the products of the esterification reaction from each other. It is to evaluate how the reactants (alcohol, acetic acid) are distributed between the two phases and whether the IL can be used for processing the reaction mixture. The model system, ethanol + acetic acid ↔ ethylacetate + water in an IL, is a five-component system which is difficult to graphically present in any diagram. In addition, because acidic ILs are used, which catalyze the reaction, measurements can only be performed when both phase and reaction equilibria are reached. For this reason, measurements on ternary nonreactive systems are more appropriate and the information gained from them should be used to estimate the phase equilibrium for the quinary system.

The experimental liquid−liquid equilibria (LLE) of ternary systems containing ethylacetate + ethanol + an acidic IL or ethylacetate + acetic acid + an acidic IL at (313.2 ± 0.5) K are presented here, and the influence of the alkyl chain length of the cation on the phase behavior is discussed. Additionally, the experimental LLE data are used to obtain the binary interaction parameters of excess Gibbs energy models like

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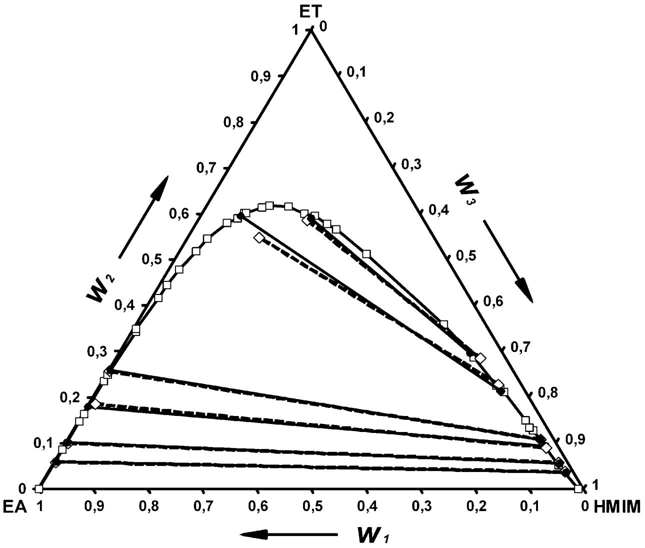

Figure 1. Liquid−liquid equilibria for the system ethylacetate (1) + ethanol (2) + [HMIM][HSO$_4$] (3) at 313 K: □, solid line, experimental binodal curve; ●, solid lines, experimental tie lines; ◇, dashed lines, tie lines calculated from UNIQUAC.

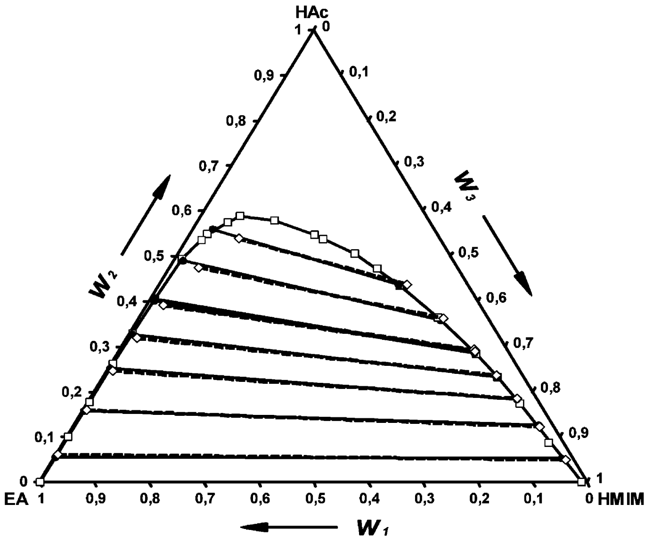

Figure 2. Liquid−liquid equilibria for the system ethylacetate (1) + acetic acid (2) + [HMIM][HSO$_4$] (3) at 313 K: □, solid line, experimental binodal curve; ●, solid lines, experimental tie lines; ◇, dashed lines, tie lines calculated from UNIQUAC.

UNIQUAC. The results of experiments and simulations are presented.

Experimental Section

Materials. The chemicals used were as follows: ethanol (≥ 99.8 %), acetic acid (≥ 99.8 %), ethyl acetate (≥ 99.5 %). These chemicals were used without further purification. The ionic liquid [HMIM][HSO$_4$] was produced by direct reaction of an aqueous solution of 1-methylimidazole (≥ 99 %) with an aqueous solution of H_2SO_4 p.a., and its purity is estimated to be ≥ 98 %. The ionic liquids [EMIM][HSO$_4$] and [BMIM]-[HSO$_4$] were from BASF with a purity of ≥ 95 %. For further purification, the ionic liquids were washed repeatedly with a mixture of ethylacetate and ethanol. Then they were left for several hours in a refrigerator at approximately 258.2 K to crystallize. The solid was ground into small pieces and then treated with a mixture of ethylacetate + ethanol (mass fraction of ethanol < 5 %). A second viscous liquid phase is formed, containing mainly IL. However, we believe that the ratio of impurities to ionic liquid contents in this liquid phase was higher than in the solid phase, because after filtration we obtained a less-colored solid product. To improve the yield, the solvents were removed from the "extract" followed by crystallization. This time-consuming procedure was repeated several times. The above-mentioned technique could not be performed with pure ethanol or with a mixture with higher ethanol content because all the solids dissolved in the liquid. Purification through recrystallization from solution was also impossible because the IL used did not crystallize in the presence of more than (5 to 10) % of other compounds even at approximately 258.2 K (mp 298 K and 301 K, respectively, as stated by the producer). The solid products were further purified by crystal aging.

The ionic liquids were dried under a vacuum at about 343 K. Their mass fractions were estimated by ^{1}H NMR to be ≥ 98.5 % and ≥ 97 %, respectively. The mass fraction of water was determined by Karl Fischer titration and was always ≤ 0.1 %. During the experiments, the ILs were repeatedly used after removing the solvents in a rotary evaporator under reduced pressure.

Apparatus and Procedure. The composition determination of mixtures containing ILs, e.g., by GC, is laborious because of their negligible vapor pressure. For example, Meindersma et al. used a GC with a precolumn to separate IL from volatile compounds.[11] Other, nonconventional techniques are often applied to determine liquid−liquid-phase equilibria. Arce et. al[19] used ^{1}H NMR to determine phase equilibria for systems with IL, a method which is unfortunately not always easily accessible. However, for ternary liquid−liquid equilibria, there are such methods that allow the determination of the compositions of coexisting phases if some easily achieved physical properties along the binodal curve are known.[20−24] Such properties can be, for example, refractive index, density, viscosity, or surface tension. For the studied systems, refractive indices were nearly impossible to measure due to high evaporation losses at 313 K, so density measurements were chosen.

The method(s) used are mainly those described by Letcher et al.[22−24] and are explained for the system [EMIM][HSO$_4$] + ethanol + ethylacetate. All other diagrams are obtained in the same manner. The binodal curve was determined by a "cloud point" titration. The homogeneous mixtures of two compounds (ethylacetate + ethanol or IL + ethanol) were prepared gravimetrically in small flasks and crimped to limit losses due to evaporation. Thereafter, the third compound (IL or ethylacetate) was added dropwise with a syringe, initially at relatively large portions at a temperature close to, but below, 313 K and near the binodal curve at only several drops per addition, until the second phase appeared, which gives one point on the binodal curve. The cloud point was observed visually. As the cloud point was approached, the samples were left for at least (20 to 30) min in the water bath at 313.2 K to ensure that equilibrium was reached (e.g., no change in homogeneity). At lower ethanol concentrations, relatively large droplets of the second phase were observed, and both phases could be easily separated. Approaching the critical point, the mixtures were cloudy and then an addition of several drops of ethanol was necessary to obtain homogeneous mixtures. The amount of the added compounds was determined by weighing using a Sartorius R300S balance (precision of 0.1 mg). Then the density of each sample, practically lying on the binodal curve, was measured. To obtain the entire two-phase region, several samples with different initial ratios of ethanol to ethylacetate (or ethanol to IL) were prepared as described above.

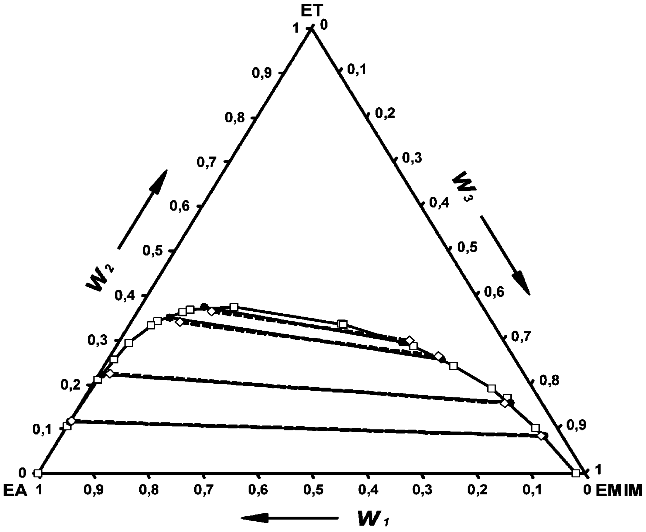

Figure 3. Liquid−liquid equilibria for the system ethylacetate (1) + ethanol (2) + [EMIM][HSO_4] (3) at 313 K: □, solid line, experimental binodal curve; ●, solid lines, experimental tie lines; ◇, dashed lines, tie lines calculated from UNIQUAC.

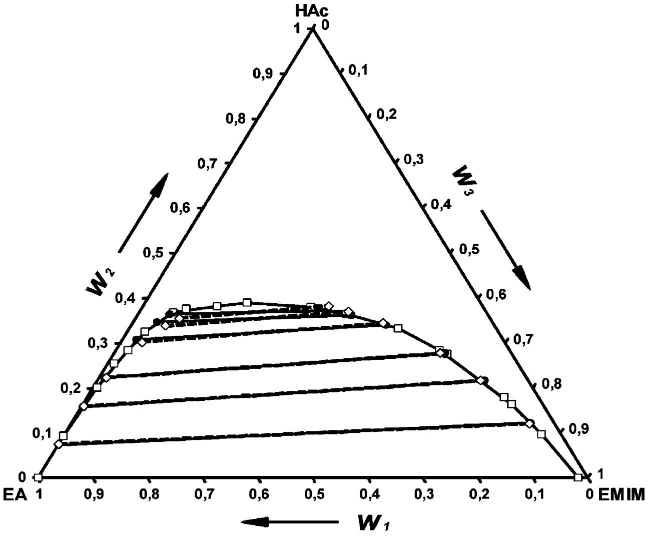

Figure 4. Liquid−liquid equilibria for the system ethylacetate (1) + acetic acid (2) + [EMIM][HSO_4] (3) at 313 K: □, solid line, experimental binodal curve; ●, solid lines, experimental tie lines; ◇, dashed lines, tie lines calculated from UNIQUAC.

Analytical expressions for the relationship between mass fraction w_i and density ρ_i of each component in the organic and ionic phases (along the binodal curve) were obtained by fitting polynomials to the experimental data points (w_i, ρ_i). The plots for the systems containing ethanol had a minimum in density (for the organic phase). For that reason, the experimental data for the organic phase were separated into two data sets: on the left and on the right of the minimum, and each set was fitted separately. The calibration polynomials cannot be used to calculate the concentrations w_i from ρ_i near the density minimum. Here a small change (error) in density causes a high difference (error) in composition, and the calibration becomes difficult and inaccurate. We believe that the impurities play a certain role here, too.

To obtain the tie lines, a series of ternary mixtures in the two-phase region were prepared. The samples were brought to equilibrium by shaking in a constant temperature bath at (313.2 ± 0.1) K for at least 2 h and then left to settle for at least 1 h. Samples of each phase were taken with a syringe, and their density was determined. Using the calibrating polynomials, the mass fractions w_i of the organic and ionic phases were calculated from the density. As a measure of goodness, it was checked whether the compositions of the organic and ionic phases and the overall composition lie on a straight line (within the limits of the experimental accuracy). Tie lines, which did not do so (usually near the density minimum), were excluded. Densities along the binodal curve were measured by means of an Anton Paar DMA 55 density meter (accuracy $\leq 1 \cdot 10^{-4}$ g·cm^{-3}). The density meter was calibrated with distilled water and air at 313.2 K. Samples of about 4 mL were transferred quickly from the sealed vials to the density meter using a syringe with a needle to reduce the loss of volatile components. Densities measured had an estimated uncertainty of ± (0.0001 to 0.0005) g·cm^{-3} (the higher values are for the ionic phases).

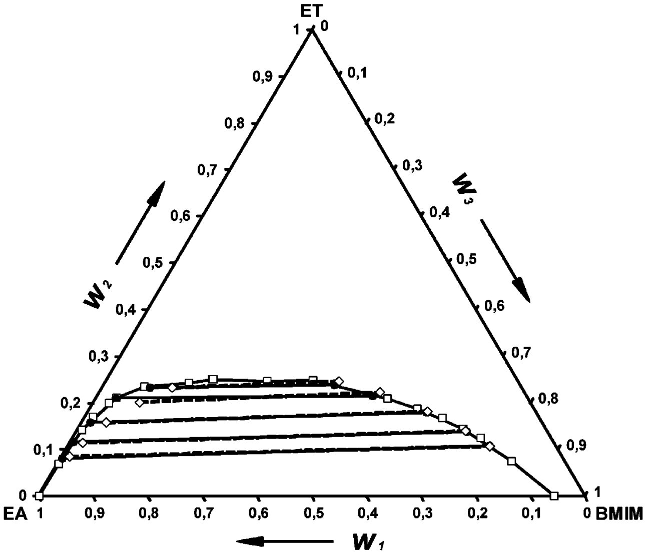

Figure 5. Liquid−liquid equilibria for the system ethylacetate (1) + ethanol (2) + [BMIM][HSO_4] (3) at 313 K: □, solid line, experimental binodal curve; ●, solid lines, experimental tie lines; ◇, dashed lines, tie lines calculated from UNIQUAC.

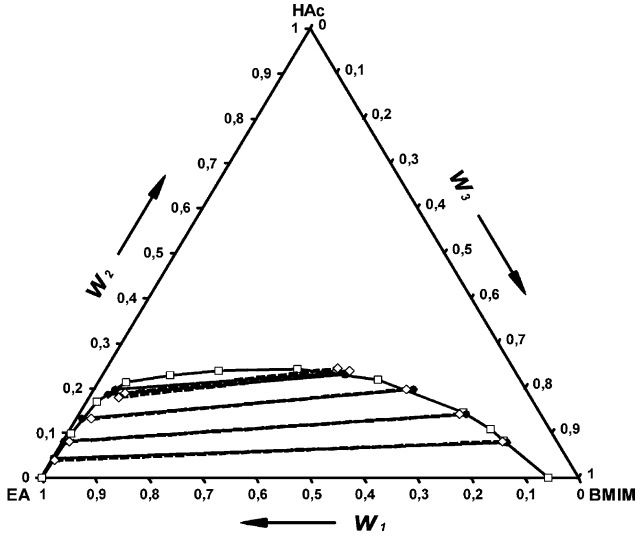

Figure 6. Liquid−liquid equilibria for the system ethylacetate (1) + acetic acid (2) + [BMIM][HSO_4] (3) at 313 K: □, solid line, experimental binodal curve; ●, solid lines, experimental tie lines; ◇, dashed lines, tie lines calculated from UNIQUAC.

In some cases, the results obtained by the above-mentioned technique were not satisfactory; i.e., compositions were not on a straight line. This was typical for the ethanol systems near the density minimum for the organic phase. In particular, for

Table 1. Mass Fractions w_i and Densities ρ along the Binodal Curve for Ethylacetate (1) + Ethanol (2) + [HMIM][HSO$_4$] (3) at 313 K

ester-rich phase			[HMIM][HSO$_4$]-rich phase		
w_1	w_2	ρ/(g·cm^{-3})	w_1	w_2	ρ/(g·cm^{-3})
0.998	0.000	0.87639	0.010	0.000	1.46294
0.913	0.085	0.86580	0.019	0.052	1.40296
0.850	0.148	0.85793	0.029	0.128	1.32482
0.833	0.164	0.85670	0.034	0.133	1.31709
0.762	0.235	0.84892	0.031	0.149	1.29952
0.749	0.248	0.84726	0.041	0.211	1.24011
0.651	0.342	0.83914	0.043	0.219	1.23135
0.646	0.348	0.83753	0.047	0.225	1.22522
0.572	0.416	0.83373	0.059	0.286	1.16334
0.540	0.444	0.83109	0.078	0.358	1.09549
0.502	0.478	0.82940	0.141	0.512	0.96152
0.451	0.519	0.82924	0.170	0.565	0.91877
0.417	0.546	0.83046	0.182	0.577	0.90707
0.363	0.579	0.83410	0.194	0.595	0.89457
0.340	0.589	0.83738	0.221	0.586	0.88552
0.321	0.602	0.83991	0.211	0.600	0.88295
0.317	0.602	0.84016	0.235	0.615	0.86652
0.282	0.614	0.84803			
0.265	0.618	0.85306			

Table 2. Equilibrium Phase Mass Fractions w_i and Densities ρ for Ethylacetate (1) + Ethanol (2) + [HMIM][HSO$_4$] (3) at 313 K

ester-rich phase			[HMIM][HSO$_4$]-rich phase		
w_1	w_2	ρ/(g·cm^{-3})	w_1	w_2	ρ/(g·cm^{-3})
0.741	0.256	0.84627	0.025	0.108	1.34578
0.204	0.590	0.89092	0.060	0.296	1.15479
0.896	0.102	0.86389	0.016	0.056	1.40256
0.331	*0.595*	-	*0.045*	*0.213*	-
0.938	0.060	0.86914	0.014	0.036	1,42326
0.818	0.180	0.85454	0.022	0.094	1.36170

Table 3. Mass Fractions w_i and Densities ρ along the Binodal Curve for Ethylacetate (1) + Acetic Acid (2) + [HMIM][HSO$_4$] (3) at 313 K

ester-rich phase			[HMIM][HSO$_4$]-rich phase		
w_1	w_2	ρ/(g·cm^{-3})	w_1	w_2	ρ/(g·cm^{-3})
0.999	0.000	0.87646	0.010	0.000	1.46294
0.897	0.101	0.89151	0.025	0.071	1.41143
0.819	0.178	0.90294	0.025	0.088	1.40977
0.735	0.261	0.91510	0.037	0.173	1.36451
0.665	0.330	0.92572	0.048	0.232	1.32863
0.586	0.406	0.93855	0.061	0.284	1.29483
0.543	0.446	0.94579	0.090	0.365	1.24029
0.481	0.499	0.95755	0.126	0.435	1.18679
0.420	0.549	0.97214	0.171	0.507	1.12841
0.339	0.589	1.00190	0.224	0.546	1.07974
			0.282	0.579	1.03632

Table 4. Equilibrium Phase Mass Fractions w_i and Densities ρ for Ethylacetate (1) + Acetic Acid (2) + [HMIM][HSO$_4$] (3) at 313 K

ester-rich phase			[HMIM][HSO$_4$]-rich phase		
w_1	w_2	ρ/(g·cm^{-3})	w_1	w_2	ρ/(g·cm^{-3})
0.841	0.156	0.89972	0.027	0.125	1.39255
0.586	0.405	0.93836	0.063	0.287	1.29295
0.667	0.328	0.92542	0.048	0.231	1.32848
0.494	0.489	0.95520	0.087	0.359	1.24435
0.403	0.560	0.97667	0.125	0.438	1.18569
0.745	0.251	0.91373	0.038	0.182	1.35827
0.591	0.401	0.93762	0.063	0.286	1.29384
0.943	0.055	0.88474	0.019	0.053	1.42911

Table 5. Mass Fractions w_i and Densities ρ along the Binodal Curve for Ethylacetate (1) + Ethanol (2) + [EMIM][HSO$_4$] (3) at 313 K

ester-rich phase			[EMIM][HSO$_4$]-rich phase		
w_1	w_2	ρ/(g·cm^{-3})	w_1	w_2	ρ/(g·cm^{-3})
1.000	0.000	0.87665	0.017	0.000	1.340
0.893	0.107	0.86289	0.039	0.103	1.24938
0.785	0.211	0.85221	0.075	0.192	1.16494
0.734	0.256	0.84918	0.119	0.243	1.10720
0.687	0.294	0.84850	0.171	0.286	1.05419
0.628	0.332	0.85086	0.277	0.337	0.97867
0.606	0.342	0.85390			
0.537	0.368	0.86703			
0.455	0.375	0.89146			

Table 6. Equilibrium Phase Mass Fractions w_i and Densities ρ for Ethylacetate (1) + Ethanol (2) + [EMIM][HSO$_4$] (3) at 313 K

ester-rich phase			[EMIM][HSO$_4$]-rich phase		
w_1	w_2	ρ/(g·cm^{-3})	w_1	w_2	ρ/(g·cm^{-3})
0.771	0.223	0.85161	0.058	0.159	1.19753
0.883	0.116	0.86161	0.033	0.085	1.26657
0.508	0.375	0.87379	0.187	0.295	1.04157
0.584	0.351	0.85784	0.134	0.257	1.09020

the system [HMIM][HSO$_4$] + ethylacetate + ethanol, this region was unusually large. For several tie lines, an alternative method proposed by Newsham[25] was used. It goes without any property measurements and is based on the graphical application of the lever rule. It must be noted that this method was not always applicable, and the experimental uncertainties were higher than with the density method. The results obtained by this method are marked in italic script.

The uncertainty of the binodal curve compositions is estimated to be ≤ 0.005 mass fractions, and the uncertainty for the tie lines is somewhat above 0.01 mass fractions in the worst case, which is acceptable for industrial applications. The highest errors are expected for the systems containing [BMIM][HSO$_4$] and the lowest for the systems with [EMIM][HSO$_4$]. Our experience indicates that the standard deviations of densities for the ionic phase are, as a rule, higher than that of the organic phase. On the other hand, the slope of the standard plots $\Delta w_i/\Delta\rho_i$ is usually 5 to 10 times smaller for the ionic phase. Generally we believe that the compositions of the ionic phase are more accurate than those of the organic phase.

Results and Discussion

The experimental binodal curves and tie lines for the IL + ethylacetate + ethanol/acetic acid systems are plotted in Figures 1 to 6, and the numerical data are presented in Tables 1 to 12. All data are reported in mass fractions. All investigated ionic liquids are totally miscible with ethanol and acetic acid. The only immiscible pairs are IL + ethylacetate. In all systems studied, there is a negligible amount of the IL present in the organic phase (ester) at low concentrations of the third compound (ethanol or acetic acid). This indicates that in an extraction process there will only be negligible losses of the IL due to the low solubility of IL in the ester.

If the slopes of the tie lines for systems with IL + ethylacetate + ethanol and IL + ethylacetate + acetic acid are compared, one observes that with increasing alkyl chain length on the cation the solubility of both ethanol and acetic acid in the ionic phase noticeably increases. Due to the higher polarity, there is always a little more acetic acid in the ionic phase than ethanol, and vice versa, more ethanol than acetic acid is in the ester phase. A comparison of the diagrams shows that with increasing alkyl chain length on the cation the size of the immiscibility region decreases, and its size is nearly equal for both systems with ethanol and acetic acid. Although the top of the binodal curve for systems containing [HMIM][HSO$_4$] (Figures 1 and 2) lies at about 0.6 mass fraction of ethanol or acetic acid, the systems with [EMIM][HSO$_4$] (Figures 3 and 4) are homogeneous at

Table 7. Mass Fractions w_i and Densities ρ along the Binodal Curve for Ethylacetate (1) + Acetic Acid (2) + [EMIM][HSO_4] (3) at 313 K

ester-rich phase			[EMIM][HSO_4]-rich phase		
w_1	w_2	ρ/(g·cm^{-3})	w_1	w_2	ρ/(g·cm^{-3})
1.000	0.000	0.87665	0.017	0.000	1.34
0.907	0.092	0.89034	0.036	0.096	1.29657
0.791	0.202	0.90833	0.057	0.165	1.26191
0.694	0.284	0.92453	0.129	0.285	1.18684
0.642	0.325	0.93569	0.178	0.333	1.14225
0.571	0.368	0.95597	0.257	0.364	1.09574
0.482	0.383	0.99049	0.314	0.380	1.06409
0.424	0.390	1.01263			

Table 8. Equilibrium Phase Mass Fractions w_i and Densities ρ for Ethylacetate (1) + Acetic Acid (2) + [EMIM][HSO_4] (3) at 313 K

ester-rich phase			[EMIM][HSO_4]-rich phase		
w_1	w_2	ρ/(g·cm^{-3})	w_1	w_2	ρ/(g·cm^{-3})
0.926	0.073	0.88751	0.044	0.122	1.28410
0.838	0.158	0.90070	0.080	0.217	1.23322
0.767	0.223	0.91182	0.120	0.278	1.19174
0.667	0.307	0.93047	0.197	0.340	1.13241
0.610	0.347	0.94386	0.249	0.363	1.09927
0.578	0.364	0.95294	0.287	0.373	1.07879

Table 9. Mass Fractions w_i and Densities ρ along the Binodal Curve for Ethylacetate (1) + Ethanol (2) + [BMIM][HSO_4] (3) at 313 K

ester-rich phase			[BMIM][HSO_4]-rich phase		
w_1	w_2	ρ/(g·cm^{-3})	w_1	w_2	ρ/(g·cm^{-3})
0.998	0.000	0.87700	0.057	0.000	1.24238
0.927	0.069	0.86779	0.097	0.076	1.17467
0.848	0.143	0.86092	0.151	0.143	1.10987
0.752	0.211	0.86291	0.215	0.187	1.05863
0.688	0.235	0.87131	0.258	0.208	1.03065
0.604	0.242	0.89436	0.372	0.249	0.96708
0.556	0.251	0.90516	0.128	0.124	1.12802
0.555	0.250	0.90641	0.179	0.167	1.08246
0.816	0.169	0.85967			
0.773	0.199	0.86079			
0.675	0.235	0.87490			
0.599	0.242	0.89543			

Table 10. Equilibrium Phase Mass Fractions w_i and Densities ρ for Ethylacetate (1) + Ethanol (2) + [BMIM][HSO_4] (3) at 313 K

ester-rich phase			[BMIM][HSO_4]-rich phase		
w_1	w_2	ρ/(g·cm^{-3})	w_1	w_2	ρ/(g·cm^{-3})
0.915	0.081	0.86660	0.120	0.109	1.14401
0.877	0.116	0.86324	0.147	0.138	1.11498
0.670	0.240	0.87434	0.339	0.238	0.98470
0.826	*0.158*	-	*0.200*	*0.180*	-
0.753	*0.21*	-	*0.281*	*0.214*	-

Table 11. Mass Fractions w_i and Densities ρ along the Binodal Curve for Ethylacetate (1) + Acetic Acid (2) + [BMIM][HSO_4] (3) at 313 K

ester-rich phase			[BMIM][HSO_4]-rich phase		
w_1	w_2	ρ/(g·cm^{-3})	w_1	w_2	ρ/(g·cm^{-3})
0.998	0.000	0.87700	0.057	0.000	1.24238
0.894	0.099	0.89277	0.098	0.083	1.19892
0.811	0.169	0.90748	0.109	0.109	1.18664
0.736	0.212	0.92434	0.142	0.145	1.16514
0.645	0.229	0.95164	0.264	0.218	1.10135
0.550	0.238	0.98270	0.403	0.242	1.03697
0.757	0.203	0.91908			
0.895	0.100	0.89289			
0.647	0.237	0.95175			

Table 12. Equilibrium Phase Mass Fractions w_i and Densities ρ for Ethylacetate (1) + Acetic Acid (2) + [BMIM][HSO_4] (3) at 313 K

ester-rich phase			[BMIM][HSO_4]-rich phase		
w_1	w_2	ρ/(g·cm^{-3})	w_1	w_2	ρ/(g·cm^{-3})
0.955	0.044	0.88307	0.094	0.079	1.20116
0.857	0.133	0.89884	0.209	0.197	1.12719
0.782	0.186	0.91377	0.320	0.230	1.07622
0.917	0.081	0.88881	0.138	0.142	1.16741
0.764	0.196	0.91783	0.346	0.234	1.06426

Table 13. UNIQUAC Structural (Volume and Area) Parameters

	r_i	q_i
HMIM	3.555	2.844
EMIM	4.460	3.568
BMIM	5.418	4.334
ethanol	2.1055	1.972
acetic acid	2.2024	2.072
ethylacetate	3.4786	3.116

$w_{\text{ethanol/acetic acid}} > 0.35$ to 0.4 and the systems with [BMIM][HSO_4] even at compositions above 0.25 mass fractions (Figures 5 and 6). Thus, of all studied ILs, [HMIM][HSO_4] is most suited for extraction processes due to the large immiscibility region and low solubility in the ester. On the other hand, both reactants are more soluble in the organic phase than in the ionic liquid. That means when [HMIM][HSO_4] is used as a reaction medium the ionic liquid will mainly extract water, and only small amounts of reactants and ethylacetate will be present there. For the [EMIM][HSO_4] systems, the reactants are distributed differently between the organic and ionic phases: there is more ethanol in the organic phase and more acetic acid in the ionic phase. This IL will probably not lead to high conversions (in one stage) when used as solvent/catalyst for (biphasic) esterifications, as the educts are separated. On the other hand, it can be used for separating mixtures of ethylacetate + acetic acid or ethylacetate + acetic acid + water (e.g., purifying of raw ethylacetate). For the BMIM systems in Figures 5 and 6, it can be seen that both reactants are slightly more soluble in the ionic phase. However, it must be noted that there is a significant amount of ester present in the IL, up to (30 to 40) %. Also, the two-phase region for these systems is much smaller than for the others, so biphasic reaction or extraction processes are only possible at low ethanol/acetic acid concentrations.

All ILs are, as mentioned in the Introduction, well suited for extracting water from the ester phase. With EMIM, acetic acid can be extracted efficiently. As already reported,[16] the mutual solubility of IL and alcohols decreases with increasing alkyl chain length of the alcohols. Simple preliminary tests showed that the HSO_4^--containing ionic liquids are only partly miscible with 1-butanol. We expect the systems containing higher alcohols and carbon acids (e.g., the reaction 1-butanol + butyric acid ↔ butyl butyrate + water) to be of type II[27] (two immiscible pairs: ester/IL, alcohol/IL) with low IL content in the organic phase and low concentrations of alcohol/acid in the ionic phase. Thus, for these systems, the above ILs, especially [HMIM][HSO_4], are expected to be a well-suited solvent for extracting H_2O from the reaction mixture.

Tie Line Correlation

The well-known UNIQUAC model[26] was used to correlate the experimental tie lines. The pure compound volume and surface parameters r_i and q_i were calculated as follows[17]

$$r_i = 0.029281 V_{\text{m}}$$

$$q_i = \frac{(z-2)r_i}{z} + \frac{2(1-l_i)}{z} \qquad (1)$$

Table 14. Fitted Binary Interaction Parameters Δu_{ij} for UNIQUAC and RMSD as Defined by Equation 5

ij	Δu_{ij}/K	Δu_{ji}/K	100*rmsd
Ethylacetate (1) + Ethanol (2) + [HMIM][HSO_4] (3)			
12	292.6695	−71.1243	0.96
13	653.9290	121.5941	
23	363.6379	−71.1633	
Ethylacetate (1) + Acetic Acid (2) + [HMIM][HSO_4] (3)			
12	173.7422	−63.0010	0.7897
13	653.9290	121.5941	
23	486.3055	−234.2659	
Ethylacetate (1) + Ethanol (2) + [EMIM][HSO_4] (3)			
12	328.0143	−164.2832	0.7281
13	876.3176	38.2675	
23	92.5553	−55.6644	
Ethylacetate (1) + Acetic Acid (2) + [EMIM][HSO_4] (3)			
12	396.8879	−163.8889	0.5255
13	876.3176	38.2675	
23	134.0382	−147.7932	
Ethylacetate (1) + Ethanol (2) + [BMIM][HSO_4] (3)			
12	24.1167	23.0650	0.8968
13	552.3468	−38.1940	
23	−107.4003	−6.8460	
Ethylacetate (1) + Acetic Acid (2) + [BMIM][HSO_4] (3)			
12	187.7898	−182.9794	0.9041
13	552.3468	−38.1940	
23	−107.1235	−194.0583	

where $V_m/(\mathrm{cm^3 \cdot mol^{-1}})$ is the molar volume of the pure compounds at 298.15 K; $z = 10$ is the coordination number; and $l_i = 1$ is the bulk factor. A program written in Matlab was used to calculate the binary interaction parameters Δu_{ij}. This program minimizes two objective functions, F_a and F_x[27]

$$F_a = \sum_j \sum_i (a_{ij}^{\mathrm{I}} - a_{ij}^{\mathrm{II}})^2 + P_1 \quad i = 1, 2, 3 \qquad (2)$$

$$F_x = \sum_j \sum_i [(x_{ij}^{\mathrm{I}} - \hat{x}_{ij}^{\mathrm{I}})^2 + (x_{ij}^{\mathrm{II}} - \hat{x}_{ij}^{\mathrm{II}})^2] + P_1 \quad i = 1, 2, 3 \qquad (3)$$

$$P_1 = Q \sum_n p_n^2 \qquad (4)$$

where *i* denotes the compound; *j* is the tie line; *a* denotes the activity in phase I or II; and x and $\hat{x}$ are the experimental and calculated mole fractions, respectively. The second term of the functions F_a and F_x, the so-called penalty term P_1, reduces the size of the interaction parameters, which ensures that no multiple solutions appear.[27]

The minimization starts with the first function, F_a, because no calculation of molar fractions is required, and the minimization converges fast without a good initial approximation of the interaction parameters. The parameters obtained from the first objective function are used as initial guesses for the second function F_x which improves the fits of the experimental compositions. The parameter estimation was started for each system several times with different initial guesses, delivering different sets of UNIQUAC interaction parameters. The parameter set that had the smallest root-mean-square deviation (rmsd) value was finally chosen. The rmsd is defined as

$$\mathrm{rmsd} = \sqrt{\sum_i \sum_j \sum_l (x_{ijl} - \hat{x}_{ijl})^2 / 6K} \qquad (5)$$

where *i* is the compound; *l* is the phase; and *j* is the tie line. *K* is the number of tie lines. The pure compound parameters and the fitted binary interaction parameters are presented in Table 13 and Table 14, respectively. The calculated tie lines are compared to experimental tie lines in Figures 1 to 6.

Conclusions

The liquid−liquid-phase equilibria for ternary systems containing acidic IL with an HSO_4^- anion and educts/products of the esterification reaction ethanol + acetic acid ↔ ethylacetate + water are studied at 313 K. The ILs used are [HMIM][HSO_4], [EMIM][HSO_4], and [BMIM][HSO_4]. All six systems are of type I, with one immiscible pair: IL and ester with low mutual solubility of both compounds. The size of the immiscibility region decreases, for systems with both ethanol and acetic acid, when the alkyl chain length on the cation increases. The distribution of educts between the ionic and organic phases is also very much dependent on the cation. Although acetic acid and ethanol are more soluble in the ester than in [HMIM][HSO_4], they are both more soluble in [BMIM][HSO_4] than in ethylacetate. Acetic acid is always a little more soluble in the ionic phase than ethanol. The ionic liquids [HMIM][HSO_4] and [EMIM][HSO_4] are suitable for (reactive) extraction processes due to the large immiscibility region and can be used for processing the reaction mixture to remove the other compounds from the ester. The experimental data were well correlated with the UNIQUAC model.

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Literature Cited

(1) Wasserscheid, P.; Keim, W. Ionische Flüssigkeiten − neue Lösungen für die Übergangsmetallkatalyse. *Angew. Chem.* **2000**, *112*, 3926−3945.

(2) Wasserscheidt, P. Ionische Flüssigkeiten : Innovative Lösungsmittel für die Zweiphasenkatalyse. *Chem. unserer Zeit* **2003**, *37*, 52−63.

(3) Earle, M. J.; Seddon, K. R. Ionic liquids. Green solvents for the future. *Pure Appl. Chem.* **2000**, *72*, 1391−1398.

(4) Welton, T. Room-temperature ionic liquids. Solvents for Synthesis and Catalysis. *Chem. Rev.* **1999**, *99*, 2071−2083.

(5) Marsh, K.; Deev, A.; Wu, A. C.-T.; Tran, E.; Klamt, A. Room temperature ionic liquids as replacements for conventional solvents - a review. *Korean J. Chem. Eng.* **2002**, *19*, 357−362.

(6) Uerdingen, M. Entschwefelung von Dieselkraftstoff. *Chem. Unserer Zeit* **2004**, *38*, 212−213.

(7) Selvan, M.; McKinley, M.; Dubois, R.; Atwood, J. Liquid−liquid Equilibria for Toluene + Heptane + 1-Ethyl-3-methylimidazolium Triiodide and Toluene + Heptane + 1-Butyl-3-methylimidazolium Triiodide. *J. Chem. Eng. Data* **2000**, *45*, 841−845.

(8) Fadeev, A. G.; Meagher, M. Opportunities for ionic liquids in recovery of biofuels. *Chem. Commun.* **2001**, *1*, 295−296.

(9) Zhang, S.; Zhang, Q.; Zhang, Z. C. Extractive Desulfurization and Denitrogenation of Fuels Using Ionic Liquids. *Ind. Eng. Chem. Res.* **2004**, *43*, 614−622.

(10) Zhao, H.; Xia, S.; Ma, P. Use of ionic liquids as ‘green’ solvents for extractions. *J. Chem. Technol. Biotechnol.* **2005**, *80*, 1089−1096.

(11) Meindersma, G. W.; Podt, A.; de Haan, A. Ternary liquid−liquid equilibria for mixtures of an aromatic + an aliphatic hydrocarbon + 4-methyl-N-butylpyridinium tetrafluoroborate. *J. Chem. Eng. Data* **2006**, *51*, 1814−1819.

(12) Fraga-Dubreuil, J.; Bourahla, K.; Rahmouni, M.; Bazureau, J. P.; Hamelin, J. Catalysed esterifications in room temperature ionic liquids with acidic counteranion as recyclable reaction media. *Catal. Commun.* **2002**, *3*, 185−190.

(13) Gui, J.; Cong, X.; Liu, D.; Zhang, X.; Hu, Z.; Sun, Z. Novel Brønsted acidic ionic liquid as efficient and reusable catalyst system for esterification *Catal. Commun.* **2004**, *5*, 473−477.

(14) Zhu, H.-P.; Yang, F.; Tang, J.; He, M.-Y. Bronsted acidic ionic liquid 1-methylimidazolium tetrafluoroborate: a green catalyst and recyclable medium for esterification. *Green Chem.* **2003**, *5*, 38−39.

(15) Heintz, A. Recent developments in thermodynamics and thermophysics of non-aqueous mixtures containing ionic liquids. A review. *J. Chem. Thermodyn.* **2005**, *37*, 525−532.

(16) Crosthwaite, J. M.; Aki, S. N. V. K.; Maginn, E. J.; Brennecke, J. F. Liquid phase behaviour of imidazolium-based ionic liquids with alcohols. *J. Phys. Chem. B* **2004**, *108*, 5113−5119.

(17) Domanska, U.; Marciniak, A. Solubility of ionic liquid [emim][PF6] in alcohols *J. Phys. Chem. B* **2004**, *108*, 2376−2382.

(18) Wu, C.-T.; Marsh, K. N.; Deev, A. N.; Boxall, J. A. Liquid−liquid equilibria of room-temperature ionic liquids and butan-1-ol. *J. Chem. Eng. Data* **2003**, *48*, 486−491.

(19) Arce, A.; Rodriguez, O.; Soto, A. tert-Amyl Ethyl Ether Separation from Its Mixtures with Ethanol Using the 1-Butyl-3-methylimidazolium Trifluoromethanesulfonate Ionic Liquid: Liquid−Liquid Equilibrium. *Ind. Eng. Chem. Res.* **2004**, *43*, 8323−8327.

(20) Treybal, R. E. *Liquid Extraction*, 2nd ed.; McGraw-Hill: New York, 1963.

(21) Novák, J. P.; Matouš, J.; Pick, J. *Liquid-Liquid Equilibria*; Elsevier: Amsterdam, 1987.

(22) Letcher, T. M.; Wooton, S.; Shuttleworth, B.; Heyward, C. Phase equilibria for (n-heptane+water+an alcohol) at 298.2 K *J. Chem. Thermodyn.* **1986**, *18*, 1037−1042.,

(23) Letcher, T. M.; Reddy, P. Ternary (liquid+liquid) equilibria for mixtures of 1-hexyl-3-methylimidazolium (tetrafluoroborate or hexafluorophosphate)+benzene+an alcane at T = 298.2 K and p = 0.1MPa *J. Chem. Thermodyn.* **2005**, *37*, 415−421.

(24) Deenadayalu, N.; Ngcongo, K. C.; Letcher, T. M.; Ramjugernath, D. Liquid−Liquid Equilibria for Ternary Mixtures (an Ionic Liquid + Benzene + Heptane of Hexadecane) at 298.2 K and Atmospheric Pressure. *J. Chem. Eng. Data* **2006**, *51*, 988−991.

(25) Newsham, D. M.; Ng, S. B. Liquid−Liquid Equilibria in Mixtures of Water, n-Propanol and n-Butanol. *J. Chem. Eng. Data* **1972**, *17*, 205−207.

(26) Gmehling, J.; Kolbe, B.; *Thermodynamik; 2.überarb. Aufl*; VCH: Weinheim, 1992.

(27) Sørensen, J. M.; Arlt, W. *Liquid−Liquid Equilibrium Data Collection 1,2,3*; DECHEMA: Frankfurt/Main, 1979.

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