Ternary Liquid−Liquid Equilibria for Systems Containing Alcohol or Acetic Acid + Ester + 1-Ethyl-3-methylimidazolium Hydrogen Sulfate at 313.2 K Using Headspace Gas Chromatography

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The ternary liquid−liquid equilibria for four systems containing an alcohol (1-propanol or 1-butanol) or acetic acid + ester + the ionic liquid 1-ethyl-3-methylimidazolium hydrogen sulfate [EMIM][HSO_4] were studied at (313.2 ± 0.5) K. In this paper, we investigated the effect of the alkyl chain on the alcohol and ester on the phase equilibria for these systems containing reactants and products of esterification reactions. The measurements were done by headspace gas chromatography. All studied systems are of type I, with ester and [EMIM][HSO_4] as the only immiscible pair. The increase of the alkyl chain length on alcohol and ester leads to bigger immiscibility regions and better solubility of the alcohol in the ester phase. The distribution of the acetic acid between the two phases is almost independent of the esters for the measured systems and is dependent mainly on the ionic liquid. The obtained information on the influence of the alkyl chain on the equilibrium can be used to roughly estimate the behavior of unknown systems as illustrated on several examples.

Introduction

Ionic liquids (IL) are relatively new organic compounds which have attracted the attention of scientists during the last years due to their specific properties. Besides their application in chemistry as solvents and catalysts,[1−3] they may be used in many different fields. Examples are with extraction[4] or other separation processes[5] and also in analytical chemistry.[6] To develop processes using ionic liquids, information on their physical properties and phase equilibria of the corresponding systems is essential. The data for (ternary) liquid−liquid phase equilibria (LLE) with ionic liquids is relatively scarce and limited to few a "commonly used" liquids. Since there is a very high number of possible combinations of cations and anions (estimated at about 10^{18}), they cannot all be measured. This is why not only data on the phase equilibrium but also the knowledge of general trends, e.g., how the equilibrium changes with the alkyl chain length on the cation, are important. This is decisive in respect to process design in an early stage. Though there are systematic studies,[7−10] few of the known ionic liquids have been extensively investigated.

We have previously investigated[11] the influence of the alkyl chain length on the cation for systems containing reactants/products of the esterification reaction of ethanol with acetic acid and three immidazolium-based ionic liquids (ILs) with a hydrogen sulfate anion: 1-methylimidazolium hydrogen sulfate, 1-ethyl-3-methylimidazolium hydrogen sulfate, and 1-butyl-3-methylimidazolium hydrogen sulfate. Such ILs are often reported for esterification reactions since they exhibit Brønsted acidity and can be used as both catalysts and solvents.[12] As a continuation of this study, here the phase behavior of ternary systems containing products/reactants of two further esterification reactions (esterification of 1-propanol and 1-butanol with acetic acid to propylacetate and butylacatate) and the IL 1-ethyl-3-methylimidazolium hydrogen sulfate ([EMIM] [HSO_4]) at 313.2 K is investigated. The results of this study in combination with a previous one[11] should reveal more general trends for the LLE of esterification systems with ILs.

Due to the nonvolatility of IL, the ternary LLE are often measured using methods referred to as "property methods", where a physical property along the binodal curve is determined[13] and used to calculate the tie lines. These methods require that the measured property changes sufficiently along the binodal curve, which limits their application. A more sophisticated analytical alternative is headspace gas chromatography, which is applied here.

Experimental Section

Materials. The chemicals used were acetic acid (HAc; ≥ 99.8 %), 1-butylacetate (BA; ≥ 99.5 %), 1-butanol (BU; ≥ 99.5 %), 1-propylacetate (PA; Kosher, ≥ 98 %), and 1-propanol (PR; ≥ 99.8 %). They were used as received. The ionic liquid [EMIM] [HSO_4] (≥ 95 %) was supplied by BASF and purified as described elsewhere.[11] Its purity was estimated to be ≥ 0.98 mass fraction (^{1}H NMR). The mass fraction of water in the ionic liquid was determined by Karl Fischer titration and was ≤ 0.05 %.

Calibration Curve. Headspace gas chromatography[14] (HS−GC) is usually applied when there are nonvolatile compounds in the sample to be analyzed that will remain in the inlet system of a conventional gas chromatograph. The principle of this method is that the (liquid or solid) sample is not analyzed, only the vapor in equilibrium with it. The composition of the vapor is strongly influenced by the matrix composition of the sample. For this reason, the calibration curve should best match this matrix and reflect the change of compositions along the binodal curve. Dilution is favorable to gain linearity but introduces some

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Table 1. Settings of the HS Autosampler

	propylacetate systems	butylacetate systems
oven temperature/K	363.2	373.2
loop temperature/K	398.2	
transfer line temperature/K	398.2	
vial equilibration time/min	90	
pressurization time/min	1.5	
loop fill time/min	0.1	
loop equilibration time/min	0.01	
inject time/min	1	

error and reduces the sensitivity, as observed with the acetic acid containing samples. In respect to this, all samples were analyzed without dilution and in the nonlinear range with a calibration curve closely reflecting the binodal curve compositions. To gain higher reliability, the ratio $r = A_1/A_2$ of the peak areas A_i of the two volatile compounds was used for calibration. We found that this parameter changes sufficiently along the binodal curve, and the standard deviation of r for a sample is usually very low (< (2 to 3) %), thus allowing quantitative analysis. The calibration curves were obtained by fitting the mass fractions of the calibration samples at the binodal curve versus the ratio r with polynomials for the organic and ionic phases. Problems with this method may arise if the boiling points of the volatile compounds differ too much. Since the temperature at which the samples are equilibrated in the headspace sampler is determined by the lowest boiling compound, the sensitivity for the higher boiling compound may suffer.

The experimental uncertainty for the binodal curve compositions is estimated to be less than 0.005 mass fraction, and the compositions of the tie lines have an uncertainty about 0.01 mass fraction, which is acceptable for industrial uses. The uncertainty of the tie line compositions was estimated with the standard error of estimate σ_i^{est} for the calibration polynomials calculated by the following equation

$$\sigma_i^{\text{est}} = \sqrt{\frac{\sum_{j=1}^{n} (w_{ij} - w_{ij}')^2}{n}} \tag{1}$$

Here w_{ij} is the experimental mass fraction for the compound i; w_{ij}' is the calculated mass fraction; and n is the number of samples. The standard error of estimate was usually lower than 0.01 mass fraction, and the highest value was 0.012 mass fraction for the IL content in the ionic phase of the system 1-propanol + 1-propylacetate + [EMIM][HSO_4]. In some cases, additional samples were prepared, and their known composition was compared to the results from the headspace analysis.

Apparatus and Procedure. The HS−GC measurements were done with an HP-7694 headspace sampler and an Agilent 6890 gas chromatograph with a DB-5-column (30 m × 250 μm × 0.25 μm) operated at 363.2 K and an FID-detector. Helium was used as a carrier gas at 1.5 $\text{mL}\cdot\text{min}^{-1}$. The inlet heater temperature was 503.2 K, and the inlet pressure was 1.3 bar. Details for the headspace autosampler can be found in Table 1.

The binodal curve was determined at (313.2 ± 0.5) K by the cloud point method.[11] To get higher precision, its position was roughly estimated with chemicals of lower purity, to get good starting points. For all systems, the determination of the binodal curve at high IL content was complicated since the ionic liquid [EMIM][HSO_4] is highly viscous and there is hardly any ester dissolved in it. The samples prepared this way were analyzed by HS−GC to obtain the calibration curves. About 2 mL (± approximately 0.1 mL) of undiluted sample was taken with a syringe and placed in a glass vial of 20 mL. The vials were crimped immediately to minimize the evaporation losses. They were sealed with an aluminum cap with butyl/PTFE-septum (3 mm). Usually two separate samples were taken from each mixture and were equilibrated in the HS autosampler at the desired teperature (see Table 1) for 90 min.

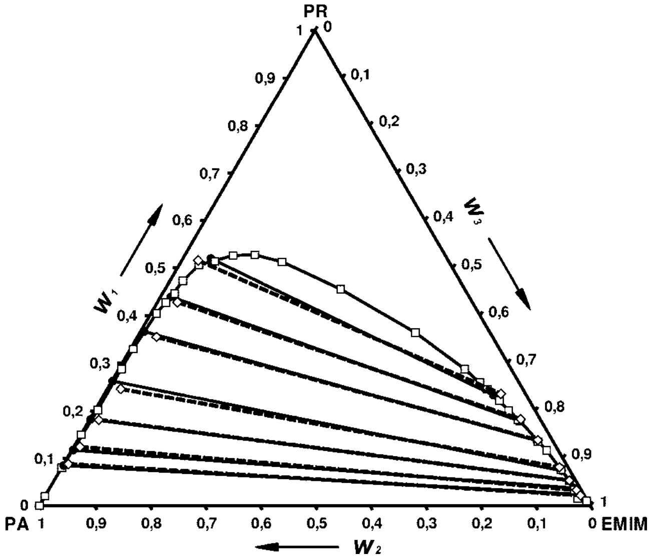

Figure 1. Liquid−liquid equilibria for the system 1-propanol (1) + 1-propylacetate (2) + [EMIM][HSO_4] (3) at 313 K: □, solid line, experimental binodal curve; ●, solid lines, experimental tie lines; ◇, dashed lines, tie lines calculated from UNIQUAC.

High equilibration temperatures of 363.2 K for propylacetate and 373.2 K for butylacetate systems in the headspace sampler were nessesary, since otherwise acetic acid could not be detected in samples below 0.015 mass fraction. However, the equilibration temperature was always chosen to be below the boiling point of the lowest boiling compound. It turned out that there occurs a side reaction at these conditions (alcohol + HSO_4^- ↔ alkylsulfate$^-$ + H_2O), and a prolonged time is needed to reach both phase and reaction equilibrium. In samples with high IL and 1-propanol content (and low ester content), it was found that about 15 % of the initial HSO_4^- reacted to RSO_4^- at 363.2 K. However, since both analytical and calibration samples undergo the same procedure, the effect of this side reaction was neutralized. It was estimated that this reaction is very slow at 313 K, and in the time needed for the preparation of the binodal samples, less than about 0.5 % of the HSO_4^- is converted. Thus, the influence on the liquid−liquid phase equilibrium of the alcohol systems is negligible.

A series of mixtures lying in the two-phase region were prepared to obtain the tie lines as described elsewhere.[11] The ratio r was measured for each sample phase, and the calibration polynomials were then used to calculate its composition.

Results and Discussion

The results of the experiments are presented in Figures 1 to 4 and in Tables 2 to 9. All data are reported in mass fractions. In all studied cases, the ionic liquid [EMIM][HSO_4] and the ester are the immiscible pair. Comparing the diagrams containing acetic acid (Figure 4, published elsewhere,[11] and Figures 2 and 4 from this paper) one can observe that with increasing the alkyl chain length on the ester the size of the two-phase region increases slightly and the top of the binodal curve rises with about (7 to 10) % per carbon atom. In any case, the acetic acid is more soluble in the ionic liquid than in the ester phase. Interestingly, there is hardly any change in the slope of the tie

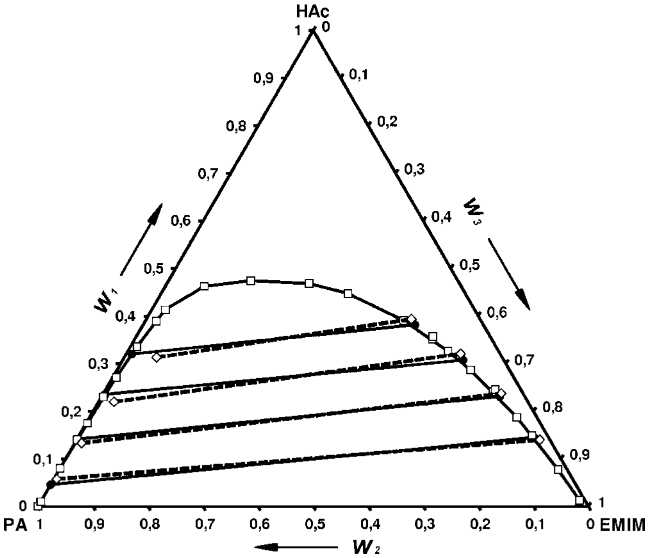

Figure 2. Liquid−liquid equilibria for the system acetic acid (1) + 1-propylacetate (2) + [EMIM][HSO_4] (3) at 313 K: □, solid line, experimental binodal curve; ●, solid lines, experimental tie lines; ◇, dashed lines, tie lines calculated from UNIQUAC.

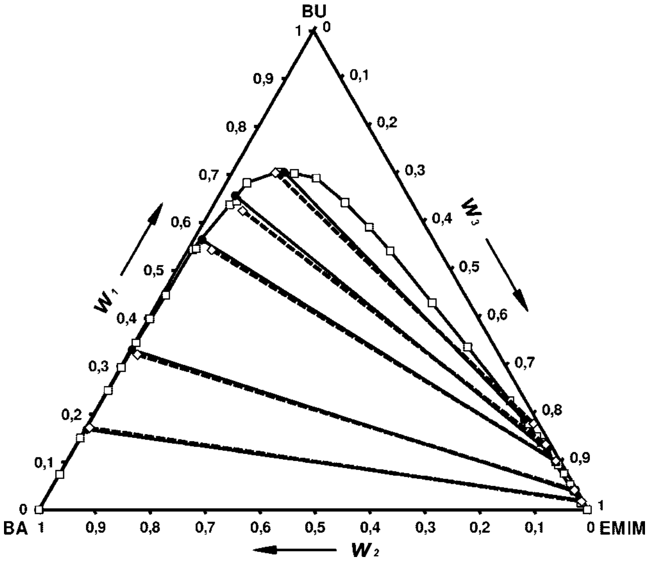

Figure 3. Liquid−liquid equilibria for the system 1-butanol (1) + 1-butylacetate (2) + [EMIM][HSO_4] (3) at 313 K: □, solid line, experimental binodal curve; ●, solid lines, experimental tie lines; ◇, dashed lines, tie lines calculated from UNIQUAC.

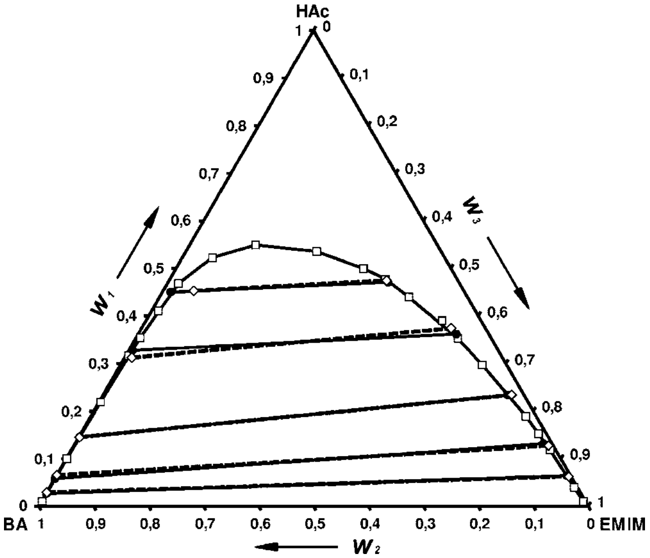

Figure 4. Liquid−liquid equilibria for the system acetic acid (1) + 1-butylacetate (2) + [EMIM][HSO_4] (3) at 313 K: □, solid line, experimental binodal curve; ●, solid lines, experimental tie lines; ◇, dashed lines, tie lines calculated from UNIQUAC.

Table 2. Equilibrium Phase Mass Fractions w_i for 1-Propanol (1) + 1-Propylacetate (2) + [EMIM][HSO_4] (3) at 313 K

ester-rich phase			[EMIM][HSO_4]-rich phase		
w_1	w_2	w_3	w_1	w_2	w_3
0.085	0.914	0.002	0.024	0.012	0.963
0.117	0.881	0.002	0.038	0.013	0.949
0.182	0.816	0.002	0.054	0.011	0.934
0.262	0.736	0.002	0.074	0.016	0.910
0.367	0.627	0.007	0.137	0.029	0.834
0.440	0.541	0.019	0.179	0.039	0.782
0.520	0.429	0.051	0.233	0.059	0.708

Table 3. Mass Fractions w_i along the Binodal Curve for 1-Propanol (1) + 1-Propylacetate (2) + [EMIM][HSO_4] (3) at 313 K

ester-rich phase			[EMIM][HSO_4]-rich phase		
w_1	w_2	w_3	w_1	w_2	w_3
0.000	1.000	0.000	0.010	0.003	0.987
0.020	0.980	0.000	0.015	0.015	0.969
0.080	0.920	0.000	0.033	0.012	0.954
0.150	0.850	0.000	0.053	0.012	0.935
0.202	0.796	0.002	0.076	0.015	0.909
0.289	0.708	0.003	0.117	0.022	0.862
0.330	0.665	0.005	0.135	0.028	0.837
0.405	0.585	0.010	0.179	0.039	0.782
0.427	0.557	0.015	0.181	0.041	0.778
0.447	0.531	0.022	0.200	0.049	0.751
0.473	0.503	0.023	0.221	0.055	0.724
0.507	0.457	0.036	0.245	0.065	0.689
0.513	0.304	0.183	0.259	0.071	0.670
0.514	0.425	0.061	0.288	0.084	0.628
0.527	0.385	0.088	0.364	0.136	0.500
0.528	0.345	0.127	0.456	0.226	0.318

lines with the ester. It seems that the distribution of the acetic acid between the ester and ionic phases varies considerably only with the IL.[11]

For the alcohol + ester + IL systems (Figure 3 published elsewhere[11] and Figures 1 and 3 from this paper), one cannot easily separate the two effects on the LLE since we have here a change in both the alcohol and the ester chain length. The size of the immiscibility region rises dramatically (top rises (15 to 20) %) compared to the acetic acid containing systems (only (7 to 10) %), where only the ester induces the rise. This makes us believe that ester and alcohol contribute equally to that increase of the immiscibility region. Typical for these systems is that the alcohol is always more soluble in the organic phase than in the IL, and the slope of the tie lines increases with the alkyl chain on both alcohol and ester.

Summarizing this experimental information obtained at 313 K, we can conclude that for higher esters, e.g, hexyl-, octyl-, etc. acetate, the immiscibilty regions for the ternary systems become bigger allowing thus biphasic operation at higher alcohol and acid concentrations. A bigger immiscibility region means on the one hand lower solubility of the IL in the ester phase and thus lower loss of the IL in a biphasic process. On the other hand, there will be less ester present in the IL, thus the prospects for achieving higher conversion in a biphasic reactor are better. With increasing the alkyl chain length of the alcohol, alcohols are expected to be more soluble in the ester phase. We suppose that even for higher esters the acetic acid will be more soluble in the ionic liquid [EMIM][HSO_4].

Table 4. Equilibrium Phase Mass Fractions w_i for Acetic Acid (1) + 1-Propylacetate (2) + [EMIM][HSO4] (3) at 313 K

ester-rich phase			[EMIM][HSO$_4$]-rich phase		
w_1	w_2	w_3	w_1	w_2	w_3
0.046	0.954	0.000	0.145	0.026	0.829
0.141	0.857	0.002	0.231	0.046	0.723
0.235	0.760	0.004	0.308	0.074	0.618
0.320	0.669	0.010	0.382	0.124	0.494

Table 5. Mass Fractions w_i along the Binodal Curve for Acetic Acid (1) + 1-Propylacetate (2) + [EMIM][HSO$_4$] (3) at 313 K

ester-rich phase			[EMIM][HSO$_4$]-rich phase		
w_1	w_2	w_3	w_1	w_2	w_3
0.000	1.000	0.000	0.013	0.010	0.977
0.010	0.990	0.000	0.078	0.017	0.906
0.080	0.920	0.000	0.149	0.028	0.822
0.140	0.859	0.001	0.187	0.037	0.776
0.175	0.822	0.002	0.241	0.053	0.705
0.230	0.766	0.004	0.246	0.047	0.707
0.271	0.722	0.007	0.287	0.071	0.642
0.336	0.652	0.012	0.327	0.092	0.581
0.390	0.590	0.020	0.352	0.108	0.541
0.414	0.559	0.028	0.357	0.104	0.538
0.462	0.467	0.071	0.391	0.140	0.469
			0.447	0.213	0.339
			0.468	0.273	0.258
			0.475	0.376	0.149

Table 6. Equilibrium Phase Mass Fractions w_i for 1-Butanol (1) + 1-Butylacetate (2) + [EMIM][HSO$_4$] (3) at 313 K

ester-rich phase			[EMIM][HSO$_4$]-rich phase		
w_1	w_2	w_3	w_1	w_2	w_3
0.168	0.828	0.004	0.021	0.006	0.974
0.334	0.661	0.005	0.037	0.005	0.958
0.564	0.424	0.015	0.101	0.010	0.889
0.656	0.314	0.030	0.125	0.013	0.863
0.704	0.201	0.095	0.189	0.022	0.789

Table 7. Mass Fractions w_i along the Binodal Curve for 1-Butanol (1) + 1-Butylacetate (2) + [EMIM][HSO$_4$] (3) at 313 K

ester-rich phase			[EMIM][HSO$_4$]-rich phase		
w_1	w_2	w_3	w_1	w_2	w_3
0.000	0.999	0.001	0.000	0.002	0.998
0.074	0.925	0.001	0.014	0.006	0.979
0.150	0.850	0.000	0.036	0.005	0.959
0.250	0.750	0.001	0.041	0.006	0.954
0.298	0.701	0.001	0.050	0.007	0.944
0.349	0.649	0.002	0.076	0.006	0.917
0.400	0.599	0.002	0.091	0.008	0.901
0.449	0.544	0.007	0.097	0.009	0.894
0.544	0.448	0.008	0.138	0.015	0.847
0.546	0.441	0.013	0.154	0.017	0.830
0.637	0.334	0.029	0.180	0.020	0.800
0.645	0.317	0.038	0.226	0.028	0.745
0.682	0.280	0.037	0.341	0.047	0.612
0.705	0.212	0.084	0.433	0.066	0.500
			0.540	0.090	0.370
			0.590	0.104	0.306
			0.641	0.122	0.237
			0.691	0.149	0.159
			0.702	0.185	0.114

Table 8. Equilibrium Phase Mass Fractions w_i for Acetic Acid (1) + 1-Butylacetate (2) + [EMIM][HSO$_4$] (3) at 313 K

ester-rich phase			[EMIM][HSO$_4$]-rich phase		
w_1	w_2	w_3	w_1	w_2	w_3
0.026	0.974	0.001	0.064	0.006	0.928
0.058	0.941	0.001	0.132	0.011	0.853
0.145	0.851	0.001	0.234	0.028	0.736
0.328	0.668	0.007	0.362	0.064	0.579
0.450	0.534	0.015	0.471	0.125	0.400

Table 9. Mass Fractions w_i along the Binodal Curve for Acetic Acid (1) + 1-Butylacetate (2) + [EMIM][HSO$_4$] (3) at 313 K

ester-rich phase			[EMIM][HSO$_4$]-rich phase		
w_1	w_2	w_3	w_1	w_2	w_3
0.010	0.989	0.001	0.010	0.004	0.986
0.100	0.899	0.001	0.040	0.006	0.954
0.219	0.778	0.003	0.119	0.011	0.871
0.354	0.638	0.008	0.153	0.015	0.833
0.468	0.512	0.020	0.190	0.019	0.792
0.496	0.438	0.067	0.297	0.044	0.659
0.524	0.421	0.055	0.353	0.061	0.586
			0.391	0.071	0.539
			0.440	0.107	0.453
			0.478	0.131	0.392
			0.500	0.160	0.341
			0.535	0.227	0.238
			0.549	0.331	0.120

Using this experimental information, one could roughly estimate the phase behavior of an unknown system of the same type (alcohol or acid + ester + [RMIM][HSO$_4$]). This could be useful for choosing an IL for an extraction or reactive extraction process and will be illustrated with two examples:

Example 1: As we already know,[11] the two-phase region for systems with alcohol and alcanoic acid with the same carbon atom number (e.g., *ethan*ol and *ethan*oic (acetic) acid) is nearly the same. Further, the alcohol is always more soluble in the organic phase than the acid. Using this information, one could roughly estimate the phase behavior of the system ethanol + 1-butylacetate + [EMIM] [HSO$_4$], which is a reactive system and cannot be directly measured. The two-phase region will be approximately as big as the two-phase region for the system acetic acid + 1-butylacetate + [EMIM] [HSO$_4$] presented in this paper. The alcohol is expected to be somewhat more soluble in the ester phase than acetic acid. This information may be useful if one wishes to use this IL as a catalyst or solvent for, e.g., a transesterification reaction in the early process design.

Example 2: In the case of an extractive separation of a mixture of higher ester CH_3COOR_1 + alcohol R_1OH, using [EMIM-][HSO$_4$] is most probably not suitable. Since the higher alcohols are expected to have a much higher solubility in the ester phase, an extraction process will be ineffective or even impossible. However, the opposite is true if water or other polar solutes (acetic acid) have to be extracted.

Tie-Line Correlation. The experimental results were used to obtain the UNIQAC[15] binary interaction parameters. The pure compound volume and surface parameters r_i and q_i were calculated as follows

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

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

More details on the correlation can be found elsewhere.[11] The root-mean-square deviation rmsd is defined as

$$\mathrm{RMSD} = \sqrt{\sum_i \sum_j \sum_l (x_{ijl} - \hat{x}_{ijl})^2 / 6K} \tag{3}$$

where i is the compound, l the phase, and j the tie line. K is the number of tie lines. The pure compound parameters and the correlated binary interaction parameters are presented in Table 10 and Table 11, respectively. The calculated tie lines are compared to experimental tie lines in Figures 1 to 4.

Conclusions

The liquid−liquid equilibria for four ternary systems were determined at (313.2 ± 0.5) K. The systems under investigation

Table 10. UNIQUAC Structural (Volume and Area) Parameters

	r_i	q_i
[EMIM][HSO_4]	4.46	3.568
1-propanol	2.7799	2.512
1-propylacetate	4.153	3.656
1-butanol	3.4543	3.052
1-butylacetate	4.8274	4.196
acetic acid	2.2024	2.072

Table 11. Binary Interaction Parameters Δu_{ij} for UNIQUAC and RMSD as Defined by Equation 3

ij	Δu_{ij}/K	Δu_{ji}/K	100 rmsd
1-propanol (1) + 1-propylacetate (2) [EMIM][HSO_4] (3)			
12	–228.8	239.7	0.963
13	2002.3	298.0	
23	448.74	155.44	
acetic acid (1) + 1-propylacetate (2) + [EMIM][HSO_4] (3)			
12	35.86	–41.36	1.15
13	–148.69	–177.05	
23	448.74	155.44	
1-butanol (1) + 1-butylacetate (2) + [EMIM][HSO_4] (3)			
12	–353.45	833.82	1.094
13	408.61	–110.26	
23	745.45	133.95	
acetic acid (1) + 1-butylacetate (2) + [EMIM][HSO_4] (3)			
12	–111.73	381.61	0.928
13	197.31	–132.31	
23	745.45	133.95	

are 1-propanol + 1-propylacetate + [EMIM][HSO_4], acetic acid + 1-propylacetate + [EMIM][HSO_4], 1-butanol + 1-butylacetate + [EMIM][HSO_4], and acetic acid + 1-butylacetate + [EMIM][HSO_4]. This paper is a continuation of our systematic study[11] on the phase equilibrium for IL with products and reactants of esterification reactions. The measurements were done by headspace gas chromatography, and the UNIQUAC binary interaction parameters were determined.

All studied systems are of type I, with ester and [EMIM][HSO_4] as the only immiscible pair. The increase of the alkyl chain length on alcohol and ester leads to bigger immiscibility regions and better solubility of the alcohol in the ester phase. Interestingly, the distribution of the acetic acid between the two phases is almost independent of the esters for all the measured systems. The obtained information on the influence of the alkyl chain on the equilibrium can be used to roughly estimate the behavior of systems that have not been measured yet. This information can be useful for the development of reactive extraction processes with HSO_4^- containing ionic liquids.

Acknowledgment

We would like to thank BASF for the ionic liquid [EMIM][HSO_4].

Supporting Information Available:

Calibration curves for the system acetic acid + 1-butylacetate + 1-ethyl-3-methylimidazolium. This material is available free of charge via the Internet at http://pubs.acs.org.

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