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Liquid−Liquid Equilibrium in Systems with an Ionic Liquid: Experimental Data for an Example of the Biphasic Acid Scavenging Utilizing Ionic Liquids Process

Katya Sahandzhieva, Deyan Naydenov, Álvaro Pérez-Salado Kamps, Hans-Jörg Bart, and Gerd Maurer*

Department of Mechanical and Process Engineering, University of Kaiserslautern, D-67653 Kaiserslautern, Germany

Experimental results (and a correlation) are presented for the liquid−liquid equilibrium of an example for the **B**iphasic **A**cid **S**cavenging utilizing **I**onic **L**iquids (BASIL) process: for the binary system (butylacetate + 1-methyl imidazolium chloride) and for the partitioning of 1-butanol and 1-methyl imidazole to the coexisting liquid phases at temperatures from (363 to 373) K.

Introduction

Biphasic **A**cid **S**cavenging utilizing **I**onic **L**iquids (BASIL) processes[1,2] are among the most important examples for applications of ionic liquids in chemical technology. In a BASIL process, an organic base is used to catalyze a chemical reaction and, at the same time, to scavenge an acid that is an undesired side product of that reaction. The BASIL processes replace former processes where the acid was scavenged by an inorganic base (e.g., sodium hydroxide) or an organic base (e.g., triethylamine) that—when neutralizing an inorganic acid (e.g., hydrogen chloride)—results in the formation of solids which might cause the handling of suspensions. A properly selected organic base might accelerate the reaction kinetics by several orders of magnitude. A large number of examples for such processes have been described in the literature. One further and particular advantage of such a process is related to the large liquid−liquid miscibility gap that the product might reveal with the ionic liquid (that is formed by neutralizing the acid with an appropriate organic base). That large miscibility gap enables an economic separation of the product from the reaction mixture. Basic derivatives of imidazole, pyridine, and pyrrolidone have proven to be interesting organic bases for the BASIL processes. Despite the already important and still increasing importance of the BASIL processes in industrial chemistry, the amount of experimental data on the encountered liquid−liquid equilibrium for the reaction process itself as well as for the process that is required to recover the organic base is still scarce.

In the present work, the liquid−liquid equilibrium that is observed when 1-butanol and acetylchloride react to butylacetate and hydrochloric acid

$$CH_2OH-CH_2-CH_2-CH_3 + CH_3-COCl \rightleftharpoons CH_3-COO(C_4H_9) + HCl \qquad (1)$$

that is scavenged by the organic base 1-methyl imidazole (1-MIM) by a reaction that results in the ionic liquid 1-methyl imidazolium chloride (HMIMCl)

$$C_4H_6N_2 + HCl \rightleftharpoons H(C_4H_6N_2)Cl \qquad (II)$$

was studied. The experimental work covers (1) the measurement of the liquid−liquid equilibrium of the phase-forming binary system (butylacetate + HMIMCl) at temperatures between about 356 K (i.e., close to the temperature of the solid−liquid−liquid phase equilibrium) and about 380 K and (2) the determination of the distribution of small amounts of 1-butanol and 1-MIM to those liquid phases at temperatures between about (364 and 373) K. The experimental results were correlated applying the UNIQUAC model to describe the excess Gibbs energy of a liquid phase.

Experimental Section

Materials. All chemicals were from commercial suppliers: 1-butanol (CAS No. 71-36-3, fraction ≥ 0.999 GC) from Fluka, butylacetate (CAS-No. 123-86-4, ACS reagent, fraction ≥ 0.995) from Sigma-Aldrich, and HMIMCl (CAS No. 35487-17-3, fraction ≥ 0.95) and 1-MIM (CAS No. 616-47-7, fraction = 0.99 GC) both from BASF SE. All chemicals were used as supplied.

Apparatus and Method. Figure 1 shows a scheme of the phase behavior of the binary system (butylacetate + HMIMCl).

A liquid−liquid miscibility gap exists at temperatures above the liquid−liquid−solid transition where the coexisting solid S is the ionic liquid HMIMCl. As the solubility of butylacetate in HMIMCl is small (mass fraction about 0.01), the temperature at that three-phase equilibrium is only slightly below the melting temperature of HMIMCl. A data sheet[3] provided by the producer reports 75 °C (≈348 K) for the melting temperature. However, our own investigations by differential scanning calorimetry indicate that the melting temperature is around (86 ± 0.5) °C (≈359 K). Investigations by the same technique resulted in (83 ± 1) °C (≈356 K) for the (L_1L_2S) temperature (where S represents solid HMIMCl). The liquid−liquid equilibrium of the binary system (butylacetate + HMIMCl) was determined at temperatures between about (356.4 and 380.6) K, and the liquid−liquid equilibrium of the ternary systems (butylacetate + HMIMCl + (either 1-butanol or 1-MIM)) was investigated at (363 and 373) K.

For the investigations of the liquid−liquid equilibrium of the binary system (butylacetate + HMIMCl), small glass vials (of about 4 mL) were filled so that in equilibrium the volume of

* Corresponding author. Phone: +49 631 205 2410. Fax: +49 631 205 3835. E-mail: gerd.maurer@mv.uni-kl.de.

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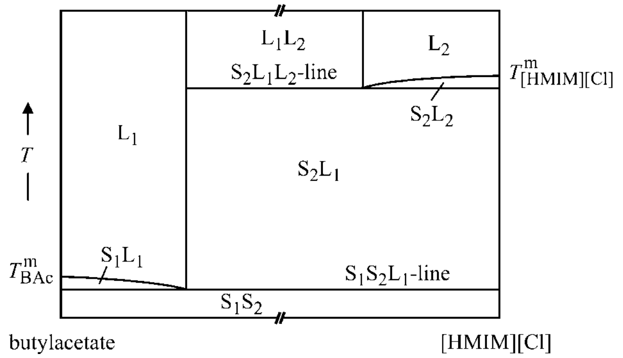

Figure 1. Scheme of the phase equilibrium of the binary system (butylacetate + HMIMCl). (T^m is the melting temperature.)

Table 1. Liquid−Liquid Phase Equilibrium of the Binary System (Butylacetate (1) + HMIMCl (2))

	mass fraction in	
T/K	upper phase $10^4\ w_2^{UP}$	lower phase $100\ w_1^{LP}$
356.4 ± 0.1	1.06 ± 0.10	1.08 ± 0.10
361.2 ± 0.1	1.04 ± 0.12	1.14 ± 0.14
365.9 ± 0.1	1.12 ± 0.10	1.22 ± 0.10
370.8 ± 0.1	1.19 ± 0.10	1.54 ± 0.20
375.6 ± 0.1	1.18 ± 0.10	1.08 ± 0.20
380.6 ± 0.1	1.37 ± 0.25	1.15 ± 0.20

each liquid phase was at least about 1.5 mL. The vials were closed by screw caps with a Teflon sealing on the inside. The screw cap was mounted to a holder for a syringe. The syringe was used to withdraw samples from the equilibrated, coexisting liquid phases. The complete arrangement (vial + holder + syringe) was placed into a metal block (vial holder) that was kept at a constant temperature via a liquid bath (thermostat: model CF41 by JULABO Labortechnik, Seeheim, Germany). The temperature was monitored by platinum resistance thermometers (Conatex Pt100/B/4, L. Colbus GmbH, St. Wendel, Germany) with an uncertainty of about ± 0.1 K. During equilibration, the vials were shortly removed from the vial holder, vigorously shaken, and placed back into the vial holder. That procedure was repeated several times. After equilibration, at first the top phase and then the bottom phase were nearly completely removed via the syringe. The experimental arrangement allowed us to keep the needle of the syringe at the temperature of the coexisting liquids. To avoid a precipitation of a solid phase during the removal, the syringe was preloaded with about (5 to 8) g of ethanol before the liquid phase (typically about 1.5 g) was sucked into the syringe. The content of the syringe was put into a bigger vial, and its mass was determined by weighing with a precision microbalance. The samples were then prepared for analysis. The butylacetate-rich phase was analyzed by high-pressure liquid chromatography (HPLC) for HMIMCl (when the ternary systems were investigated, also by gas chromatography (GC) for 1-butanol or by chemical titration for 1-MIM). The HMIMCl-rich phase was analyzed by GC for butylacetate (when the ternary systems were investigated, also by GC for 1-butanol or by chemical titration for 1-MIM). The *Internal Standard-Method* was applied for both chromatographic analyses. Hexanol (in most cases) and methyl pyrrolidone (in a few cases) were used as internal standards for GC-analysis. Sodium bromide (added as an aqueous solution with mass fraction 0.001) was used as an internal standard for the HPLC analysis. The eluent for HPLC analysis was a 0.03 mol·dm^{-3} aqueous solution of D,L-tartaric acid. Separation was achieved with an anionic ion exchange column (Shodex IC I-512A from Showa Denko Europe, Munich, Germany) with a precolumn (Shodex IC IA-G from the same company). An electric conductivity detector (CDD-6A) and an integrator (model CR-6A)—both from Shimadzu, Darmstadt, Germany—were used to detect and record the separation. The relative experimental uncertainty of the mass fraction of HMIMCl in a butylacetate-rich liquid phase—as estimated from the scatter in the results of calibration measurements—is ± 3 %. However, multiple analyses of the same sample from LLE experiments indicate that this relative uncertainty can increase to about 10 % at low mass fractions. Commercially available equipment was also used for GC-analysis. The GC-unit (HP 6890 Series from Agilent Technologies, Waldbronn, Germany) was equipped with a capillary column (model SGE, 30 m × 0.25 mm ID-BP1 1,0 from SGE GmbH, Griesheim, Germany) and a flame ionization detector (FID). GC peaks were recorded and evaluated using a commercially available software package (Agilent ChemStation for GC Systems). The results from calibration measurements provide for the relative experimental uncertainty of the mass fraction of butylacetate and 1-butanol in an HMIMCl-rich phase as well as of 1-butanol in a butylacetate-rich phase about ± 1.5 %. However, multiple analyses of the same sample from LLE experiments indicate that the relative uncertainty can increase to more than 20 % at very low mass fractions. The amount of 1-MIM in a butylacetate-rich (HMIMCl-rich) liquid phase was determined by titration with aqueous solutions of HCl (HCl concentration: either (0.1 or 0.01) mol·dm^{-3}). The titration was performed with commercially available equipment (Titroprocessor model 686 with Dosimat model 665 and a Glass Electrode model 6.0204.100 (PE) all from Metrohm, Herisau, Switzerland). From test measurements as well as from the scatter in the results of multiple analyses of the same sample, the relative uncertainty of the mass fraction of 1-MIM in one of the liquid phases is estimated to be ± 6 %. That number only holds as long as it results in an absolute uncertainty in the mass fraction above 0.001, which is the lowest absolute uncertainty of the experimental results for the mass fraction of 1-MIM in one of the coexisting liquid phases. More details of the experimental arrangement and on the analyzing procedures were described by Sahandzhieva.[4]

Experimental Results.

Binary System (Butylacetate + HMIMCl). The experimental results for the liquid−liquid equilibrium of the binary system (butylacetate + HMIMCl) are given in Table 1. The experimental results are average values of at least three single phase equilibrium measurements at each temperature and at least three analyses of each phase. The mutual solubilities are small: the mass fraction of HMIMCl in butylacetate is only about 10^{-4}, and the mass fraction of butylacetate in HMIMCl is about 0.01. The influence of temperature on that liquid−liquid equilibrium is small. Increasing the temperature from about 356 K to about 380 K increases the mass fraction of HMIMCl in butylacetate by about 20 %, whereas the scattering of the experimental results for the mass fraction of butylacetate in HMIMCl is larger than the influence of temperature on that property.

Ternary Systems. In an industrial process, 1-butanol reacts with acetylchloride as long as one of both educts is present, and hydrochloric acid is neutralized as long as 1-methyl imidazole is present. As acetylchloride and hydrochloric acid are highly reactive, the feed solution is prepared in such a way that the mole ratio of butanol to acetylchloride as well as the mole ratio of methyl imidazole to acetylchloride are always slightly above one. In such cases, all acetylchloride and all hydrochloric acid are spent in the chemical reactions. Therefore,

Table 2. Liquid−Liquid Phase Equilibrium of the Ternary System (Butylacetate (1) + HMIMCl (2) + 1-Butanol (3))

	mass fraction in			
	upper phase		lower phase	
T/K	$10^4\ w_2^{UP}$	$100\ w_3^{UP}$	$100\ w_1^{LP}$	$100\ w_3^{LP}$
363.7 ± 0.2	1.95 ± 0.40	0.79 ± 0.08	1.06 ± 0.20	0.51 ± 0.08
363.7 ± 0.2	4.06 ± 0.40	1.52 ± 0.15	1.22 ± 0.20	0.87 ± 0.08
363.7 ± 0.2	2.34 ± 0.40	2.36 ± 0.20	1.17 ± 0.20	1.33 ± 0.08
363.7 ± 0.2	3.67 ± 0.40	3.71 ± 0.30	1.31 ± 0.20	1.97 ± 0.10
363.7 ± 0.2	5.21 ± 0.50	5.69 ± 0.30	1.33 ± 0.20	2.79 ± 0.10
363.7 ± 0.2	7.87 ± 0.70	6.59 ± 0.40	1.52 ± 0.20	3.42 ± 0.25
363.7 ± 0.2	12.3 ± 0.8	9.4 ± 0.5	1.58 ± 0.20	5.15 ± 0.30
363.7 ± 0.2	16.6 ± 0.8	10.1 ± 0.5	1.52 ± 0.20	5.36 ± 0.30
363.7 ± 0.2	-	11.4 ± 0.5	1.52 ± 0.20	6.13 ± 0.40
373.9 ± 0.2	1.57 ± 0.30	0.98 ± 0.08	1.15 ± 0.20	0.60 ± 0.10
373.9 ± 0.2	1.68 ± 0.30	0.55 ± 0.40	1.20 ± 0.20	0.43 ± 0.10
373.9 ± 0.2	1.92 ± 0.40	1.58 ± 0.15	1.47 ± 0.20	0.81 ± 0.10
373.9 ± 0.2	1.99 ± 0.40	1.06 ± 0.10	1.33 ± 0.20	0.55 ± 0.10
373.9 ± 0.2	2.11 ± 0.40	1.85 ± 0.15	1.38 ± 0.20	0.88 ± 0.10
373.9 ± 0.2	3.18 ± 0.40	3.38 ± 0.25	1.48 ± 0.20	1.61 ± 0.10
373.9 ± 0.2	4.47 ± 0.50	4.10 ± 0.30	1.33 ± 0.20	2.18 ± 0.10
373.9 ± 0.2	7.01 ± 0.70	5.77 ± 0.30	1.55 ± 0.20	2.96 ± 0.20
373.9 ± 0.2	15.1 ± 0.8	8.92 ± 0.40	-	-
373.9 ± 0.2	26.8 ± 1.0	11.1 ± 0.5	1.68 ± 0.20	6.01 ± 0.30

the reaction mixture is practically free of acetylchloride and hydrochloric acid. It consists predominantly of butylacetate and HMIMCl. These reaction products form a liquid−liquid two-phase system to which small amounts of the remaining compounds of the feed are distributed. Therefore, the experimental investigation of the ternary systems was restricted to the distribution of both single solutes (1-butanol and 1-MIM) to the coexisting liquid phases, and the solute concentrations were always small (i.e., below a mass fraction of 0.1 in the feed for a liquid−liquid phase equilibrium experiment). The feed solutions were prepared in such a way that both coexisting phases had about the same masses. Both ternary systems were investigated at two temperatures (about (364 and 374) K). The experimental results for the mass fractions of the liquid phases at phase equilibrium (at preset temperature and feed composition) are average values of at least three analyses of each phase.

System (Butylacetate + HMIMCl + 1-Butanol). The mass fraction of 1-butanol in the feed was varied between about 0.005 and 0.08. The experimental results for the liquid−liquid equilibrium are given in Table 2 together with their estimated experimental uncertainties. For 364 K, the experimental results are shown in Figure 2 (together with the composition of the feed solution).

As expected, 1-butanol prefers the butylacetate-rich phase over the HMIMCl-rich phase. As shown in Figure 3, the distribution coefficient D_i (which is here defined as the ratio of the mass fraction of a solute i in the upper phase w_i^{UP} (i.e., in the buylacetate-rich phase) to its mass fraction in the lower phase w_i^{LP}) is about two for 1-butanol.

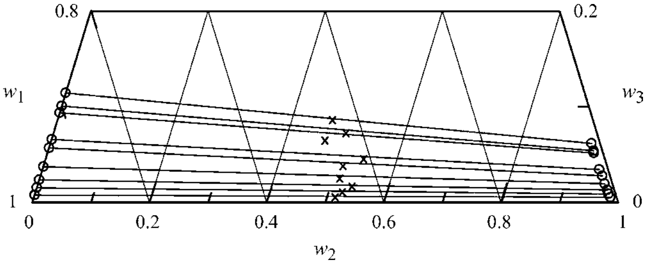

Figure 2. Liquid−liquid phase equilibrium of the ternary system (butylacetate (1) + HMIMCl (2) + 1-butanol (3)) at 364 K (X = feed solution).

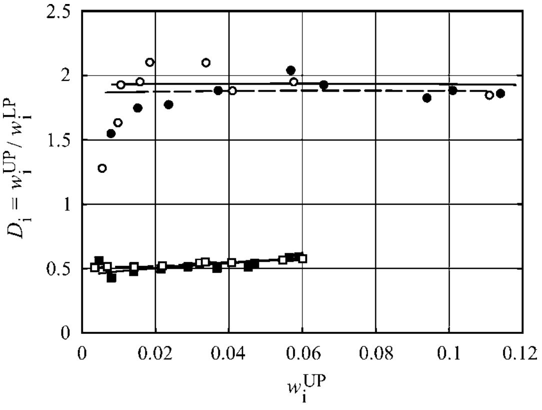

Figure 3. Distribution coefficient D_i (for i = 1-butanol and 1-MIM) in the liquid two-phase systems (butylacetate + HMIMCl). i = 1-butanol: T = 363.7 K (●, experimental; —, correlation); T = 373.9 K (○, experimental; - - -, correlation). i = 1-MIM: T = 363.5 K (■, experimental; —, correlation); T = 373.1 K (□, experimental; - - -, correlation).

Table 3. Liquid−Liquid Phase Equilibrium of the Ternary System (Butylacetate (1) + HMIMCl (2) + 1-MIM (3))

	mass fraction in			
	upper phase		lower phase	
T/K	$10^4\ w_2^{UP}$	$100\ w_3^{UP}$	$100\ w_1^{LP}$	$100\ w_3^{LP}$
363.5 ± 0.2	0.89 ± 0.20	0.46 ± 0.10	1.49 ± 0.20	0.82 ± 0.10
363.5 ± 0.2	1.03 ± 0.30	0.80 ± 0.10	1.62 ± 0.20	1.88 ± 0.20
363.5 ± 0.2	1.62 ± 0.30	2.15 ± 0.20	1.74 ± 0.20	4.33 ± 0.20
363.5 ± 0.2	1.63 ± 0.40	2.89 ± 0.20	1.87 ± 0.20	5.62 ± 0.40
363.5 ± 0.2	1.86 ± 0.40	3.68 ± 0.30	1.95 ± 0.20	7.33 ± 0.40
363.5 ± 0.2	2.19 ± 0.40	4.70 ± 0.30	1.97 ± 0.20	8.70 ± 0.40
363.5 ± 0.2	2.19 ± 0.40	4.53 ± 0.30	1.94 ± 0.20	8.85 ± 0.40
363.5 ± 0.2	2.44 ± 0.40	5.65 ± 0.30	1.81 ± 0.20	9.64 ± 0.40
363.5 ± 0.2	2.81 ± 0.40	1.41 ± 0.20	1.77 ± 0.20	2.95 ± 0.20
363.5 ± 0.2	3.03 ± 0.40	5.91 ± 0.30	1.84 ± 0.20	9.97 ± 0.40
373.1 ± 0.2	0.90 ± 0.20	0.35 ± 0.10	1.65 ± 0.20	0.69 ± 0.10
373.1 ± 0.2	1.06 ± 0.30	0.69 ± 0.10	1.70 ± 0.20	1.34 ± 0.10
373.1 ± 0.2	1.15 ± 0.40	1.42 ± 0.15	1.75 ± 0.20	2.77 ± 0.10
373.1 ± 0.2	1.76 ± 0.40	3.21 ± 0.10	1.86 ± 0.20	5.91 ± 0.40
373.1 ± 0.2	1.80 ± 0.40	2.19 ± 0.15	1.83 ± 0.20	4.21 ± 0.40
373.1 ± 0.2	2.34 ± 0.40	4.08 ± 0.25	1.92 ± 0.20	7.48 ± 0.40
373.1 ± 0.2	2.50 ± 0.40	5.47 ± 0.30	2.06 ± 0.20	9.65 ± 0.40
373.1 ± 0.2	2.59 ± 0.40	3.36 ± 0.30	1.92 ± 0.20	6.09 ± 0.40
373.1 ± 0.2	3.24 ± 0.40	6.01 ± 0.40	2.12 ± 0.20	10.4 ± 0.4

Figure 3 also shows that—as expected—with decreasing solute concentration the scattering of the experimental results for the distribution coefficient increases. As can be seen from Table 2, 1-butanol increases the solubility of HMIMCl in butylacetate as well as the solubility of butylacetate in HMIMCl. As a rule of thumb, augmenting the mass fraction of 1-butanol by 0.01 increases the mass fraction of HMIMCl in butylacetate by between (1 and 1.5)$\cdot 10^{-4}$ and the mass fraction of butylacetate in HMIMCl by about 0.001.

System (Butylacetate + HMIMCl + 1-MIM). The mass fraction of 1-MIM in the feed was varied between about 0.005 and 0.08. The experimental results for the liquid−liquid equilibrium are given in Table 3 together with their estimated experimental uncertainties. For 364 K, the experimental results are shown in Figure 4 (again together with the composition of the feed solution).

1-MIM prefers the HMIMCl-rich phase over the butylacetate-rich phase. As shown in Figure 3, the distribution coefficient is about 0.5.

As can be seen from Table 3, 1-MIM changes the solubility of HMIMCl in butylacetate less than 1-butanol (as a rule of thumb, augmenting the mass fraction of 1-MIM by 0.01 increases the mass fraction of HMIMCl in butylacetate by about

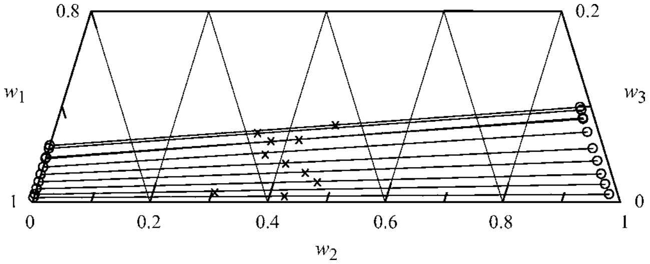

Figure 4. Liquid−liquid phase equilibrium of the ternary system (butylacetate (1) + HMIMCl (2) + 1-MIM (3)) at 364 K (X = feed solution).

Table 4. UNIQUAC Pure Component Size (*r*) and Surface (*q*) Parameters

substance	molecular mass	*r*	*q*
1-butylacetate	116.16	4.83	4.20
HMIMCl	118.56	3.93	2.96
1-butanol	74.12	3.45	3.05
1-MIM	82.1	3.12	2.14

$0.3\cdot10^{-4}$) and shows about the same influence on the solubility of butylacetate in HMIMCl as 1-butanol.

Modeling Section

To enable an application in process design and to allow for interpolations (and also slight extrapolations), the new experimental results were correlated using the UNIQUAC equation of Abrams and Prausnitz[5] for the Gibbs excess energy. For the sake of simplicity, the ionic liquid HMIMCl was treated as a single neutral component. The chemical potential of a component was normalized according to Raoult's law; i.e., the reference state is the pure liquid at equilibrium temperature. As usual, the influence of pressure on the liquid−liquid equilibrium was neglected. Applying UNIQUAC requires the coordination number, which was set to $z = 10$ as usual. The pure component UNIQUAC size (r_i) and surface parameters (q_i) were estimated according to Bondi.[6] They are given in Table 4.

The influence of temperature on all UNIQUAC parameters $U_{i,j}$ for interactions between different molecules i and j was neglected. The parameters for interactions between butylacetate and HMIMCl were fit to the liquid−liquid equilibrium data given in Table 1. The correlation gives a good representation of the experimental data. The remaining parameters for interactions between the phase-forming components and either 1-butanol or 1-MIM were fit to the experimental data shown in Tables 2 and 3. All binary interaction parameters are given in Table 5. Figure 3 shows the correlation results for the distribution coefficients of 1-butanol and 1-MIM. They nicely agree with the experimental results. In most cases, the correlation results for all mass fractions agree with the experimental data within experimental uncertainty.

Table 5. UNIQUAC Parameters $U_{i,j}$ for Interactions between Components *i* and *j*

	$(U_{i,j}/R)/\mathrm{K}^a$			
$i\backslash j$	HMIMCl	butylacetate	1-butanol	1-MIM
HMIMCl	−	31.96	−960.8	−2804
butylacetate	1088	−	−1195	−2527
1−butanol	55.42	362.1	−	−
1-MIM	−146.3	−251.3	−	−

[a] R = universal gas constant.

Conclusions

Phase equilibrium data are required for the basic engineering of many processes in the chemical industries. Such data are of particular interest for new processes, such as, for example, with ionic liquids. *Biphasic Acid Scavenging utilizing Ionic Liquids* (*BASIL*) processes are among the most important examples for such new processes. However, phase equilibrium data for the component systems involved in BASIL processes are scarce, and to the best of our knowledge, no such data are available in the open literature. Therefore, the liquid−liquid equilibrium of a typical BASIL reaction process was studied in experimental work, and the results were correlated with a common model for the Gibbs energy of nonelectrolyte solutions. As in a BASIL process, the organic base that is used to scavenge an acid has to be recovered, and experimental investigations and modeling of liquid−liquid (and liquid−liquid−solid) phase equilibria of such recovery processes are also required. Such investigations will be presented in an upcoming publication.

Acknowledgment

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