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Influence of Ionic Liquids on the Phase Behavior of Aqueous Azeotropic Systems

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The use of ionic liquids (ILs) in chemistry and electrochemistry has been studied for some decades. Only recently, researchers have focused on the suitability of ILs as selective solvents in the field of separation technology. ILs represent suitable entrainers and extraction solvents for the separation of azeotropic mixtures by means of extractive distillation and solvent extraction. In this work, ternary vapor−liquid and liquid−liquid equilibria of the azeotropic mixtures ethanol + water and THF + water containing different kinds of commercially available ILs are presented. The four ionic liquids used are derived from butyl-methylimidazolium tetrafluoroborate [BMIM]$^+$ [BF$_4$]$^-$ by systematic variation of the cation or the anion. The influence of the IL structure on the relative volatility of the low boiling component in extractive distillation and on the selectivity in solvent extraction processes is discussed in this work.

1. Introduction

Room-temperature ionic liquids, sometimes referred to as molten salts or ionic liquids (ILs), are substances consisting entirely of ions, and like a typical salt, they exhibit a negligibly low vapor pressure. In contrast to conventional salts, ILs are defined as having a melting point lower than 373.15 K.[1] This arbitrary limit of the IL's melting point is defined as such in reponse to the dramatically increasing number of possible applications in technical processes below this temperature. Most ILs are in a liquid state at temperatures below 340 K, though in exceptional cases it extends below 180 K.[2] Although knowledge of ILs has existed since 1914,[3] the research activities on this topic increased drastically with the development of the first air-stable and *nearly* moisture-stable IL in 1992[4] and with the commercial availability of ILs in 1999.[5] However, these IL-containing fluorinated anions such as [BF$_4$]$^-$ and [PF$_6$]$^-$ are expensive and not satisfactorily hydrolysis stable in long-term applications.[6] The danger of hydrolysis lies in the formation of small amounts of HF, a substance that is corrosive and toxic. For industrial application of these ILs, the environmentally acceptable disposal of great quantities of halogen compounds has to be taken into consideration as well. For these reasons, halogen-free and hydrolysis-stable ILs like butyl-methylimidazolium [BMIM]$^+$[octylsulfate]$^-$ (ECOENG 418) have been recently developed.[5,7] Because of their lack of vapor pressure, the emission of IL in technical applications will be considerably lower than for volatile organic solvents. Therefore, ILs are labeled as "green solvents". However, only a few investigations concerning the toxicological hazards have been carried out. Until now, only a few LD50 values, which indicate a minor toxicity, have been published (e.g., about 1400 mg/kg for rats for 3-hexyloxymethyl-1-methylimidazolium tetrafluoroborate[8] and about 2200 mg/kg for mice for ECOENG 500).[9] For this reason, some imidazolium salts appear to be innocuous for humans, but ILs show antimicrobial activities,[10] and a risk assessment for the ecosystems should be done before using IL on an industrial scale. A strategy for the development of sustainable, "green" ILs has been presented recently.[11]

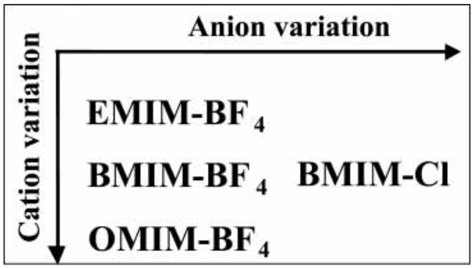

Figure 1. Systematics of the IL variation.

Unlike conventional high melting salts, typical ILs have relatively low viscosities and are much less corrosive.[12] They are thermally stable up to 473 K, have a liquid range of about 300 K, and are good solvents for a wide range of organic, inorganic, and polymeric materials.[13]

Presently, ILs are produced on a small scale, and the price of commercially available ILs is in the magnitude of 300 euro to 2600 euro per dm^3.[5] The medium-term production of halogen-free ILs on a ton scale will decrease the price to 25 euro to 50 euro per dm^3.[6]

Because of their properties, ILs are serious candidates for solvents in several industrial processes.[14,15] In synthetic chemistry, ILs have been explored as solvents and catalysts. Many reactions performed in ILs showed advantages with regard to enhanced reaction rates, improved selectivity, or easier reuse of the catalysts.[1,12,16,17] The use of ILs also has compelling potential in electrochemical applications such as electrolytes in batteries and photoelectrochemical devices.[18,19] The use of ILs as solvents or entrainers in separation technology is promising.[20] The application as an entrainer in extractive distillation is protected by pending patents of our group.[21] However, thermodynamic data are rare, and presently only a few investigations on

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Table 1. Pseudobinary VLE Data for THF + Water with Different Imidazolium-Based ILs at 337.15 K

I[a]		I/II		II[b]		III[c]		III/IV		IV[d]	
x_{THF}	y_{THF}	x_{THF}	y_{THF}	x_{THF}	y_{THF}	x_{THF}	y_{THF}	x_{THF}	y_{THF}	x_{THF}	y_{THF}
Ia		Ic		IIb		IIIa		IIIc		IVb	
0.428	0.827	0.254	0.870	0.356	0.795	0.428	0.769	0.622	0.840	0.127	0.905
0.623	0.855	0.428	0.919	0.428	0.826	0.622	0.819	0.700	0.885	0.254	0.939
0.792	0.894	0.624	0.947	0.622	0.879	0.700	0.839	0.794	0.922	0.501	0.971
0.849	0.913	0.795	0.973	0.700	0.900	0.794	0.872	0.852	0.948	0.622	0.983
0.949	0.961	0.850	0.976	0.792	0.925	0.852	0.896	0.899	0.965	0.699	0.988
		0.949	0.994	0.851	0.947	0.899	0.922	0.949	0.984	0.792	0.993
				0.900	0.963	0.949	0.956	0.979	0.994	0.950	0.997
				0.948	0.980	0.979	0.982				
				0.980	0.992						
Ib		IIa		IIc		IIIb		IVa		IVc	
0.255	0.827	0.356	0.788	0.356	0.811	0.428	0.757	0.501	0.878	0.127	0.950
0.429	0.887	0.428	0.801	0.428	0.833	0.622	0.837	0.622	0.908	0.255	0.975
0.623	0.902	0.622	0.833	0.700	0.922	0.700	0.869	0.699	0.926	0.358	0.985
0.793	0.944	0.700	0.850	0.792	0.947	0.794	0.906	0.792	0.948	0.428	0.988
0.849	0.956	0.792	0.878	0.851	0.965	0.852	0.932	0.949	0.994	0.500	0.991
0.949	0.985	0.851	0.901	0.900	0.978	0.899	0.953			0.623	0.993
		0.900	0.924	0.948	0.987	0.949	0.976			0.699	0.995
		0.948	0.955	0.980	0.995	0.979	0.991			0.793	0.996
		0.980	0.982								

[a] I = THF + water + [EMIM][BF$_4$], Ia = $x_{[EMIM][BF4]}$ = 0.1, Ib = $x_{[EMIM][BF4]}$ = 0.3, Ic = $x_{[EMIM][BF4]}$ = 0.5. [b] II = THF + water + [BMIM][BF$_4$], IIa = $x_{[BMIM][BF4]}$ = 0.1, IIb = $x_{[BMIM][BF4]}$ = 0.3, IIc = $x_{[BMIM][BF4]}$ = 0.5. [c] III = THF + water + [OMIM][BF$_4$], IIIa = $x_{[OMIM][BF4]}$ = 0.1, IIIb = $x_{[OMIM][BF4]}$ = 0.3, IIIc = $x_{[OMIM][BF4]}$ = 0.5. [d] IV = THF + water + [BMIM][Cl], IVa = $x_{[BMIM][Cl]}$ = 0.1, IVb = $x_{[BMIM][Cl]}$ = 0.3, IVc = $x_{[BMIM][Cl]}$ = 0.5.

Table 2. Pseudobinary VLE Data for Ethanol + Water with Different Imidazolium-Based ILs at 363.15 K

$x_{ethanol}$	$y_{ethanol}$	$x_{ethanol}$	$y_{ethanol}$	$x_{ethanol}$	$y_{ethanol}$	$x_{ethanol}$	$y_{ethanol}$	$x_{ethanol}$	$y_{ethanol}$
Ia[a]		Ic		IIb		IIIa[c]		IIIc	
0.602	0.743	0.298	0.685	0.388	0.660	0.724	0.839	0.374	0.840
0.754	0.819	0.396	0.747	0.504	0.735	0.759	0.851	0.504	0.903
0.837	0.885	0.450	0.786	0.636	0.813	0.857	0.905	0.592	0.927
0.849	0.895	0.603	0.869	0.725	0.857	0.890	0.924	0.724	0.957
0.913	0.938	0.743	0.916	0.766	0.876	0.954	0.970	0.857	0.988
0.945	0.955	0.849	0.949	0.858	0.922	0.977	0.985	0.902	0.994
		0.881	0.962	0.898	0.943				
		0.901	0.968	0.953	0.969				
		0.946	0.988	0.980	0.991				
		0.968	0.989						
Ib		IIa[b]		IIc		IIIb			
0.299	0.661	0.388	0.635	0.388	0.677	0.380	0.757		
0.402	0.725	0.504	0.696	0.504	0.759	0.504	0.827		
0.601	0.827	0.636	0.764	0.636	0.834	0.620	0.874		
0.746	0.879	0.725	0.810	0.725	0.880	0.732	0.911		
0.850	0.926	0.766	0.837	0.766	0.897	0.857	0.954		
0.901	0.950	0.858	0.893	0.858	0.938	0.876	0.958		
0.945	0.973	0.898	0.918	0.898	0.955	0.954	0.991		
		0.953	0.957	0.953	0.983				
		0.980	0.985	0.980	0.994				

[a] I = ethanol + water + [EMIM][BF$_4$], Ia = $x_{[EMIM][BF4]}$ = 0.1, Ib = $x_{[EMIM][BF4]}$ = 0.3, Ic = $x_{[EMIM][BF4]}$ = 0.5. [b] II = ethanol + water + [BMIM][BF$_4$], IIa = $x_{[BMIM][BF4]}$ = 0.1, IIb = $x_{[BMIM][BF4]}$ = 0.3, IIc = $x_{[BMIM][BF4]}$ = 0.5. [c] III = ethanol + water + [BMIM][Cl], IIIa = $x_{[BMIM][Cl]}$ = 0.1, IIIb = $x_{[BMIM][Cl]}$ = 0.3, IIIc = $x_{[BMIM][Cl]}$ = 0.5.

vapor−liquid equilibria, liquid−liquid equilibria, respectively, solvent extraction processes, and supercritical fluid extraction process have been accomplished.[22−28]

ILs are very complex solvents. They are capable of interacting simultaneously with other molecules via, e.g., dispersive, ionic, π−π, hydrogen bonding, and dipolar forces. In the presence of polar compounds, some ILs act as a polar solvent and in the presence of nonpolar compounds as a nonpolar solvent.[29]

ILs are truly designer solvents. By variation and combination of ions, approximately 10^{18} accessible IL can be formed (binary and ternary mixtures included).[2] This large number of possible IL can be used to optimize production costs and IL properties such as solubility, melting point, and thermal stability. Until now, it was not possible to predict which ILs were the most suitable ones for certain applications. However, with the increasing comprehension on how the structure of an IL affects its physical and solvent properties, one will be able to use the advantages of ILs over volatile organic solvents.

In this work, the influence of systematic cation and anion variation of imidazolium-based ILs with respect to their entrainer efficiency in extractive distillation and as an extracting agent in solvent extraction is investigated. For this purpose, vapor−liquid equilibria (VLE) and liquid−liquid equilibria (LLE) measurements of ternary systems, composed of an aqueous binary azeotropic system and an ionic liquid, were carried out. The two aqueous azeotropic model systems chosen are tetrahydrofuran (THF) + water and ethanol + water. Two of the four different ILs used as entrainers for the THF + water and the ethanol + water systems were derived from butyl-methylimidazolium tet-

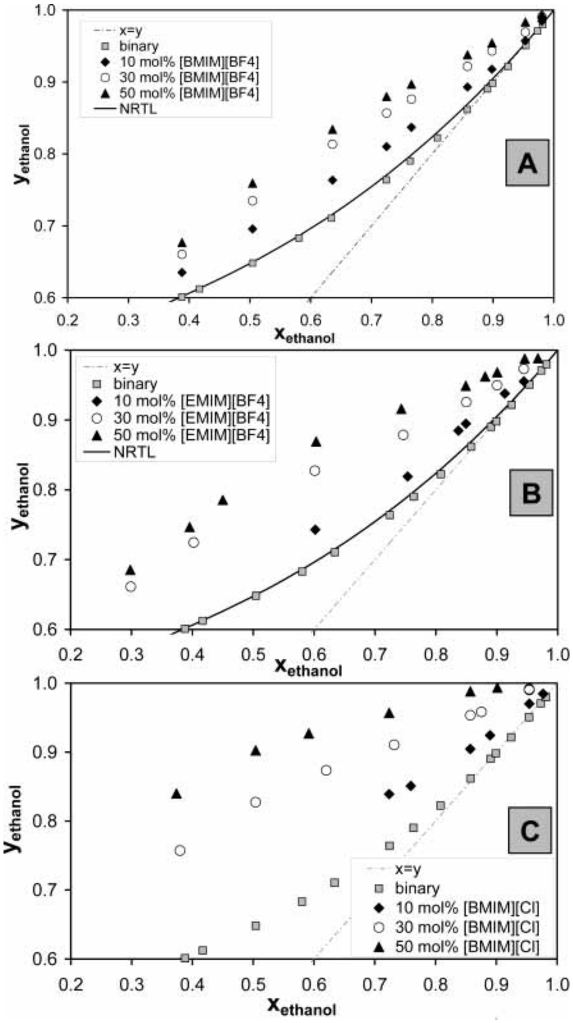

Figure 2. Experimental VLE results of the systems (A) $[BMIM]^+[BF_4]^-$ + ethanol + water, (B) $[EMIM]^+[BF_4]^-$ + ethanol + water, and (C) $[BMIM]^+[Cl]^-$ + ethanol + water at IL concentrations of 10 mol %, 30 mol %, and 50 mol % at $T = 363.15$ K. The ethanol + water VLE taken from Pemberton and Mash.[33]

rafluoroborate ($[BMIM]^+ [BF_4]^-$) by respective shortening or extension of the length of the butyl chain of the cation to an ethyl and an octyl group. The substitution of the tetrafluoroborate ion for a chloride ion leads to the fourth-explored ionic liquid. This systematic IL variation is depicted in Figure 1.

2. Experimental Section

Chemicals. 1-Ethyl-3-methylimidazolium tetrafluoroborate ($[EMIM]^+[BF_4]^-$), 1-butyl-3-methylimidazolium tetrafluoroborate ($[BMIM]^+[BF_4]^-$), 1-methyl-3-octylimidazolium tetrafluoroborate ($[OMIM]^+[BF_4]^-$), and 1-butyl-3-methylimidazolium chloride ($[BMIM]^+[Cl]^-$) were provided by Solvent Innovation (Germany). The purities of the ILs were specified as ≥98%, and the content of chloride in the $[BF_4]^-$ ionic liquids is less than 500 ppm. The ILs were dried several days at 363 K to 383 K under a vacuum to separate the IL from volatile byproducts and humidity. Thus the amount of water in all used ILs is less than 3000 ppm. Ethanol (Lichrosolv, GC purity ≥ 99.9%) was delivered by Merck, and the THF (GC purity ≥ 99.9%) was provided by Riedel de Haen. These chemicals were used without further purification. Distilled water was degassed and repeatedly filtered using a 0.2-μm Millipore filter in order to remove dust.

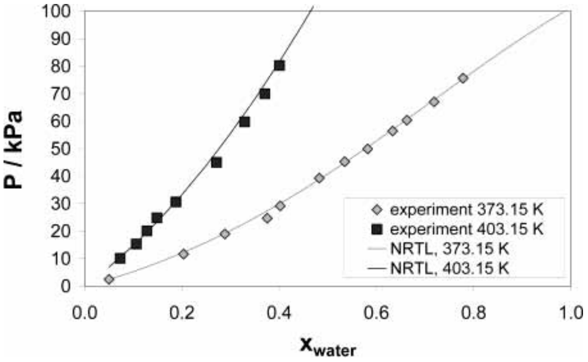

Figure 3. Experimental VLE results of the system $[EMIM]^+[BF_4]^-$ + water at $T = 373.15$ K and 403.15 K.

Apparatus and Procedures. The ternary VLE measurements were carried out using a gas chromatograph (Agilent model 6890) combined with a headspace sampler (Agilent model 7694). The experimental procedure has been previously described by our group.[30] The accuracy of the temperature adjustment is ±0.1 K, and the absolute error in compositions for the systems investigated is smaller than 1.5 mol %.

The binary VLE of the nonvolatile $[EMIM]^+[BF_4]^-$ and water were determined using a gravimetric method as described elsewhere.[31] For this experimental setup, the maximum error in pressure is ±2 mbar and the accuracy in temperature is ±0.1 K.

The liquid−liquid equilibrium phase behavior of the ternary system ionic liquid + THF + water was analyzed by phase-separation experiments and by visual cloud-point measurements. Different mixtures of about 45 mL with predefined compositions were prepared. The sealed samples were heated to 64 °C, and then the system pressure was decreased to atmospheric pressure. The samples were mixed at equilibrium temperature by agitation. To ensure thermodynamic equilibrium, the phase-separation process was performed while storing the vials at constant temperature in a thermostat (FD 240, WTB Binder, Germany) for several days. The phase compositions were determined by taking samples of about 20 mL from each phase. The IL concentration of a sample was obtained by evaporating the solvent under vacuum and weighing the difference in mass of the sample flask. The volatile part of the sample (distillate) was condensed and frozen by means of liquid nitrogen. Subsequently, the molten distillate was injected into the GC for determination of the respective composition. Every tie line has been reproduced at least once. The concentration of each component can be determined within an accuracy of ≤2 mol %. The error in temperature for the LLE measurement is ±0.15 K.

3. Results and Discussion

VLE Experiments. All ternary VLEs containing the binary azeotropic system and an ionic liquid are presented in a pseudobinary way in Figures 2, 4, and 5. The specified liquid-phase concentration *x* of the low-boiling component corresponds to the amount of this substance in the volatile part of the liquid phase. The ionic liquid concentration is stated for each curve separately. Because of the nonvolatility of IL, the vapor phase does not contain any ionic liquid. The entrainer suitability of an ionic liquid in extractive distillation increases with a higher relative volatility of the low-boiling component in the presence of a constant concentration of the respective IL. As a result, for a given purity of the distillate, the reflux ratio of the

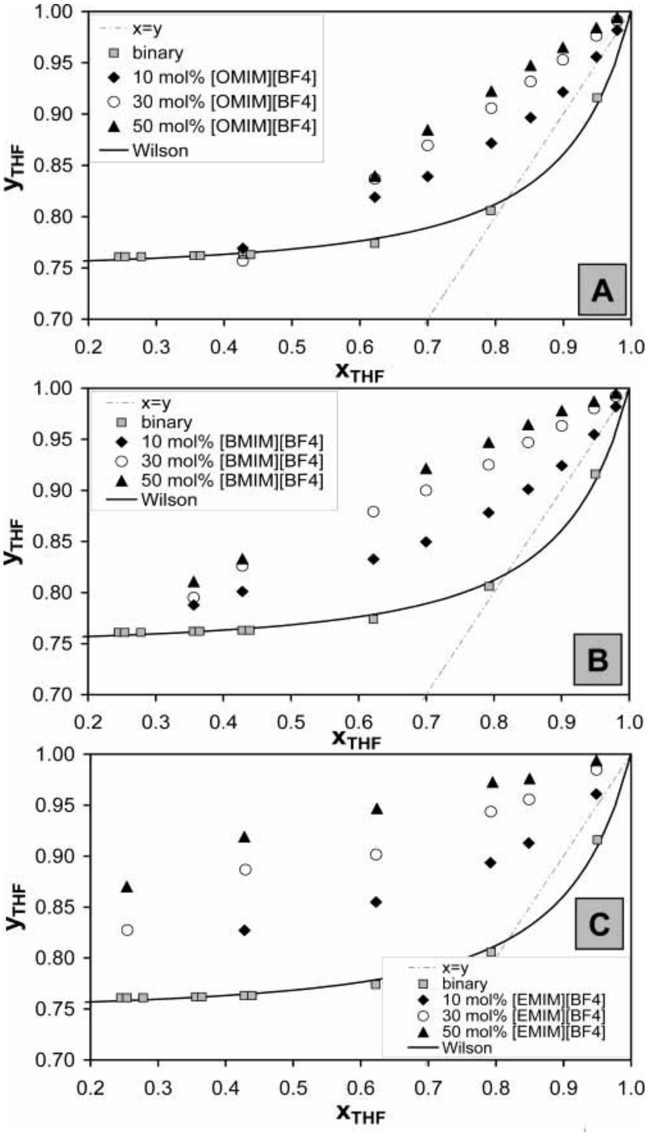

Figure 4. Experimental VLE results of the systems (A) [OMIM]$^+$[BF$_4$]$^-$ + THF + water, (B) [BMIM]$^+$[BF$_4$]$^-$ + THF + water, and (C) [EMIM]$^+$[BF$_4$]$^-$ + THF + water at IL concentrations of 10 mol %, 30 mol %, and 50 mol % at $T = 337.15$ K. The binary THF + water data ($T = 337.15$ K ± 0.5 K) were published by Sada et al.[34]

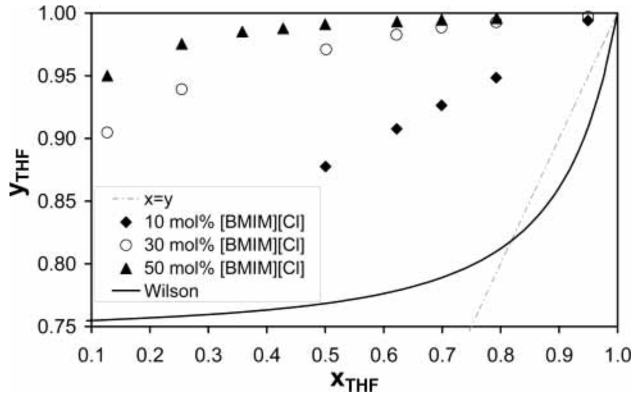

Figure 5. Experimental VLE results of the system [BMIM]$^+$[Cl]$^-$ + THF + water at IL concentrations of 10 mol %, 30 mol %, and 50 mol % at $T = 337.15$ K.

Table 3. Binary VLE for Water+[EMIM][BF$_4$]

$T = 373.15$ K		$T = 403.15$ K	
x_{water}	P/kPa	x_{water}	P/kPa
0.050	2.5	0.073	10.1
0.204	11.6	0.106	15.3
0.288	19.0	0.128	20.1
0.375	24.7	0.149	24.8
0.402	29.2	0.188	30.6
0.483	39.3	0.271	45.0
0.535	45.3	0.329	59.7
0.582	49.9	0.371	70.0
0.633	56.4	0.401	80.2
0.663	60.4		
0.719	67.0		
0.778	75.6		

extractive distillation column can be reduced and the heat demand decreases with an increasing entrainer suitability. The superiority of selected IL to conventional entrainers in terms of energy demand, separation efficiency, and process operability was recently demonstrated by our group.[20] As depicted in Figure 2, all ILs used are suitable to act as an entrainer for separating the azeotropic ethanol + water system by extractive distillation. The addition of the chosen IL to a binary ethanol + water mixture leads to a remarkable increase in the molar vapor fraction of ethanol, and thus the azeotropic system behavior is broken. An increase of the IL concentration leads to a higher ethanol concentration in the vapor phase and, therefore, to a larger relative volatility of the ethanol. This is due to strong selective interactions between these IL and the water molecules. In contrast to the binary ethanol−water mixture, these attractive interactions decrease the water activity and thus result in an increased relative volatility of ethanol. The strong attractive [EMIM]$^+$[BF$_4$]$^-$−water interactions become clearly evident when focusing on the partial-pressure curve of water (Figure 3). Here, the negative system pressure deviation from Raoult's law shows the strong attractive interactions between the water and [EMIM]$^+$ [BF$_4$]$^-$, which gives water activity coefficients that are less than one. The activity coefficient of water in [EMIM]$^+$[BF$_4$]$^-$ at infinite dilution at 373.15 K has a value of 0.45.[32] The shortening of the alkyl group of the cation from a butyl group to an ethyl group according to Figure 2 has only a small but improving influence on the relative volatility of the ethanol (parts a and b of Figure 2). By comparison of the VLE of ethanol + water + [BMIM]$^+$[Cl]$^-$ (Figure 2c) with the VLE of ethanol + water + [BMIM]$^+$[BF$_4$]$^-$ (Figure 2a), it becomes obvious that the exchange of the anion results in a much larger change in the relative volatility of the low-boiling component than the modification of the cation's alkyl chain length. Among the ILs investigated, [BMIM]$^+$[Cl]$^-$ exhibits the most distinct entrainer suitability for the ethanol + water separation.

The influence of the variation of the cation's alkyl chain length on the VLE of the azeotropic system THF + water is similar but more pronounced than for the azeotropic ethanol + water system. Again, the relative volatility of the low-boiling compound increases with the shortening of the alkyl group from an octyl group (Figure 4a) over a butyl group (Figure 4b) to an ethyl group (Figure 4c). Furthermore, [BMIM]$^+$[Cl]$^-$ is superior to the imidazolium salts containing the tetrafluoroborate anion (Figure 5) in terms of selective interactions and on the increasing relative volatility of the THF. It is noteworthy that the IL [EMIM]$^+$[BF$_4$]$^-$ appears suitable to act as an entrainer for long-term application in thermal separation processes. During the last two years, this ionic liquid has been in contact with several different solvents (i.e., acetic acid, water, THF, alcohols, alkanes). It has been continuously recycled by operating a vacuum oven at 110 °C for at least 3 days. Although

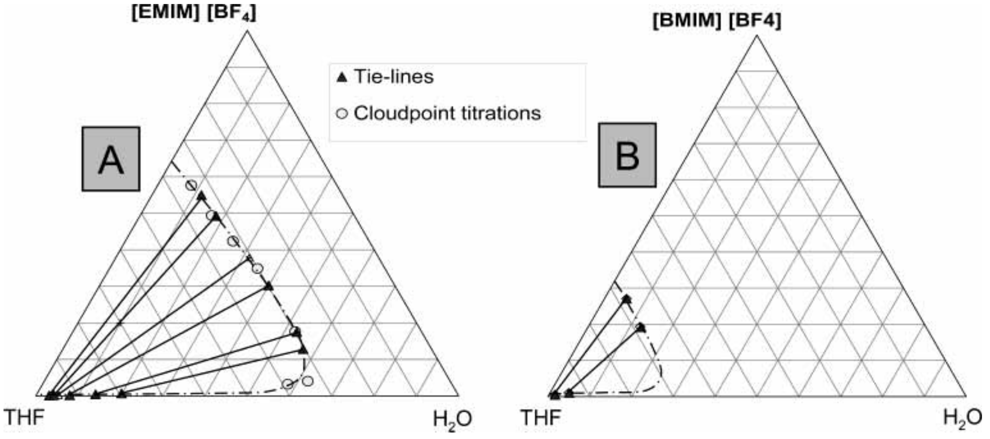

Figure 6. Ternary LLE of the systems (A) THF + water + $[EMIM]^+[BF_4]^-$ and (B) THF + water + $[BMIM]^+[BF_4]^-$ at $T = 337.15$ K.

Table 4. Ternary LLE Data for THF + Water + IL at 337.15 K

I. THF + Water + $[EMIM]^+[BF_4]^-$

tie lines								
upper phase			lower phase			cloud points		
x_{THF}	x_{water}	$x_{\text{[EMIM][BF4]}}$	x_{THF}	x_{water}	$x_{\text{[EMIM][BF4]}}$	x_{THF}	x_{water}	$x_{\text{[EMIM][BF4]}}$
0.919	0.079	0.002	0.298	0.399	0.303	0.301	0.350	0.349
0.794	0.199	0.007	0.304	0.567	0.129	0.322	0.255	0.423
0.945	0.053	0.002	0.306	0.316	0.379	0.337	0.169	0.494
0.856	0.139	0.004	0.296	0.530	0.174	0.344	0.080	0.576
0.967	0.031	0.001	0.334	0.117	0.549	0.299	0.525	0.176
0.956	0.042	0.002	0.328	0.180	0.492	0.337	0.623	0.040
						0.388	0.580	0.032

II. THF + Water + $[BMIM]^+[BF_4]^-$

tie lines					
upper phase			lower phase		
x_{THF}	x_{water}	$x_{\text{[BMIM][BF4]}}$	x_{THF}	x_{water}	$x_{\text{[BMIM][BF4]}}$
0.980	0.015	0.005	0.677	0.053	0.271
0.944	0.046	0.010	0.682	0.126	0.192

the IL's color turned from slightly yellow to black, the ternary VLE THF + water + $[EMIM]^+[BF_4]^-$ did not change at all. Essentially, this is not proof of the chemical stability of the IL investigated in long-term application within aqueous media. Therefore the authors suggest that chemical reactions appearing in this mixture might have very minor impacts on the observed thermodynamic behavior.

LLE Experiments. The THF + water + $[EMIM]^+[BF_4]^-$ system forms a liquid−liquid miscibility gap consisting of an upper THF-rich phase and a lower IL-rich phase. The LLE of the system THF + water + $[EMIM]^+[BF_4]^-$ at a system temperature of 337.15 K is illustrated by the tie lines in Figure 6a. Since the THF-rich phase contains only traces of $[EMIM]^+[BF_4]^-$ and small amounts of water, an extraction of THF from a THF + water mixture using $[EMIM]^+[BF_4]^-$ as an extracting agent is conceivable. However, the large amount (about 30 mol %) of THF in the mentioned IL-rich phase is not sufficient for practical extraction purposes. The comparison of parts a and b of Figure 6 demonstrates that even a small variation in the IL structure has a considerable influence on the size of the miscibility gap. For the ionic liquid $[BMIM]^+[BF_4]^-$, which contains a longer cation's alkyl chain than $[EMIM]^+[BF_4]^-$, the size of the miscibility gap with the THF abates. For a further enlargement of the cation's alkyl chain to an octyl group, the authors did not observe a miscibility gap in the system THF + water + $[OMIM]^+[BF_4]^-$. Therefore, these experimental data indicate the potential of ionic liquids as extracting agents. The optimization of the IL's selectivity by changes of its structure allows for a tailoring of the size of the LL miscibility gap, and thus they are able to meet the requirements concerning applications in the field of solvent extraction.

4. Conclusions

ILs represent a promising class of highly selective, nonvolatile entrainers or entrainer additives for separation processes. The IL's properties can be tailored by varying structure and combination of the ions forming the IL. Properties such as selectivity, viscosity, as well as thermal and chemical stability can be adjusted for a specific application. Because of the nonvolatility of the IL, the entrainer regeneration for extractive distillation and extraction can be carried out by stripping, evaporation, drying, or crystallization.

In this work, the influence of ionic liquids on the phase behavior of the aqueous azeotropic systems THF + water and ethanol + water was investigated. Ternary vapor−liquid and liquid−liquid equilibria of these azeotropic mixtures containing different kinds of commercially available ILs were presented. The four ionic liquids used are derived from butyl-methylimidazolium tetrafluoroborate $[BMIM]^+[BF_4]^-$ by systematic variation of the cation or the anion. The influence of the IL structure on the relative volatility of the low boiling component in extractive distillation and on the selectivity in solvent extraction processes is discussed in this work. The addition of the IL investigated results in a remarkable increase of the relative volatility of the low-boiling component and eliminates the azeotropic system behavior. IL that are composed of small anions and small cations exhibit the best entrainer properties for the investigated polar mixtures. Shortening the length of the alkyl chain of the cation increases the impact of the IL on the VLE slightly. Replacing the tetrafluoroborate anion with a chloride increases the capability of the IL acting as an entrainer in extractive distillation processes more dramatically.

The potential of the IL to be used as extracting agents has also been indicated. Small variations in the IL's structure show a large influence on the LLE behavior. For example, shortening the alkyl chain length of an alkylmethylimidazolium-based IL investigated increases the size of the miscibility gap between THF and IL, while the binary IL + water subsystem remains totally miscible. Therefore, a task-specific tayloring of the IL as an extraction agent appears to be feasible.

List of Symbols

Latin Letters

P/Pa = Pressure
T/K = Temperature
x = Liquid-phase molar fraction
y = Vapor phase molar fraction

Abbreviations

$[\text{EMIM}]^+[\text{BF4}]^-$ = 1-ethyl-3-methylimidazolium tetrafluoroborate
$[\text{BMIM}]^+[\text{BF4}]^-$ = 1-butyl-3-methylimidazolium tetrafluoroborate
$[\text{OMIM}]^+[\text{BF4}]^-$ = 1-methyl-3-octylimidazolium tetrafluoroborate
$[\text{BMIM}]^+[\text{Cl}]^-$ = 1-butyl-3-methylimidazolium chloride
ECOENG 500 = $C_{40}H_{85}NO_{16}S$ or $[\text{CABHEM}][\text{MeSO}_4]$
IL = ionic liquid
LLE = liquid−liquid equilibrium
THF = tetrahydrofuran
VLE = vapor−liquid equilibrium

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