Separation of Hexane/Ethanol Mixtures. LLE of Ternary Systems (Ionic Liquid or Hyperbranched Polymer + Ethanol + Hexane) at T = 298.15 K†

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Liquid−liquid phase equilibria (LLE) of hexyl(2-hydroxyethyl)dimethylammonium tetrafluoroborate (C_6BF_4) or hyperbranched polymer (a fatty-acid-modified dendritic polymer, Boltorn U3000) B-U3000 + ethanol + hexane, at T = 298.15 K have been measured. The results are discussed in terms of the selectivity of ethanol and hexane separation. Sloping of the tie lines toward the ethanol vertex is observed for both mixtures (C_6BF_4 or B-U3000 + ethanol + hexane). The results indicate high selectivity for separation of ethanol and hexane with the ammonium ionic liquid in solvent extraction. The nonrandom two-liquid NRTL model was successfully used to correlate the experimental tie lines. The maximum mean square deviation in mole fraction was 0.01.

Introduction

A great number of industrial processes need to separate azeotropic systems, for example, those containing alcohols and saturated hydrocarbons. Extractive distillation is often used to remove certain compounds from azeotropic systems.[1] The addition of a new solvent (entrainer) can be used to interact with the components of the original mixture, altering their relative volatilities. In this way, the azeotropic mixture can be separated. The separation potential and feasibility of entrainers for commercial applicability are dependent on physical properties such as the boiling point, vapor pressure, thermal stability, ease of recovery, toxicity, and corrosive nature of the substance. However, the selectivity of the entrainer, calculated from different physicochemical measurements (liquid−liquid equilibria (LLE) or activity coefficients at infinite dilution, γ^∞) is an important peculiarity in characterizing the solvent.

For many years, as a result of the reduction of lead in gasoline, ternary ethers and alcohols have coexisted as additives for gasoline. Different azeotropic mixtures of alcohols and alkanes are present in various industrial processes. As an alternative to extractive distillation and other industrially used separation methods that require a large amount of energy, volatile compounds, or high pressure, the LLE presents an environmentally friendly extraction process. A liquid−liquid separation process is based on the immiscibility of the two liquid phases that exhibit preferential affinity or selectivity toward one or more components in the feed. This kind of process reduces the energy consumption, and it avoids the release of possible loose solvent to the atmosphere.

Ionic liquids have interesting properties that allow them to substitute classic organic solvents with less damage to the environment. The separation of aliphatic hydrocarbons from alcohols is challenging because they mostly form azeotropic mixtures. The imidazolium ILs, 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMIM][PF_6]), 1-butyl-3-methylimidazolium methyl sulfate ([BMIM][CH_3SO_4]), and 1,3-dimethylimidazolium methyl sulfate ([MMIM][CH_3SO_4]) were found to be suitable for use in petrochemical extraction to break the heptane and ethanol azeotropic mixture, and the selectivity of removing heptane from the azeotropic mixture has been observed to be very high.[2−4] The imidazolium ILs have been found to be very attractive entrainers in separating different industrially important mixtures: thiophene from aliphatic hydrocarbons C_6−C_{16}[5] or aromatic hydrocarbons from aliphatic hydrocarbons.[6] Recently, we have presented the suitability of the ammonium ILs for the separation of aromatic/aliphatic hydrocarbons.[7,8] LLE data have been presented for four ternary systems of an alkane, aromatic compound, and ethyl(2-hydroxyethyl)dimethylammonium bis{(trifluomethyl)sulfonyl}imide (C_2NTf_2) at T = 298.15 K: {hexane + benzene + C_2NTf_2}, {hexane + *p*-xylene + C_2NTf_2}, and {hexane or octane + *m*-xylene + C_2NTf_2}.[7] The distribution ratio of separation was observed on the same level as that for imidazolium IL with the same $[NTf_2]^-$ anion as that of 1-ethyl-3-methylimidazolim bis{(trifluomethyl)sulfonyl}imide ([EMIM][NTf_2]).[9] We obtained promising results in the LLE measurements for the separation of *p*-xylene and hexane azeotropic mixture with hexyl(2-hydroxyethyl)dimethylammonium tetrafluoroborate (C_6BF_4).[8]

Hyperbranched polymers, HBPs are highly branched, polydisperse macromolecules with a large number of functional groups. Properties of hyperbranched polymers such as remarkable selectivity and capacity, low melting point, and high solubility allow their use in separation processes.[10] Therefore, processes such as extractive distillation, liquid−liquid extraction, absorption, and emulsion liquid membranes represent promising fields of application. HBPs like Boltorn were found to be capable of breaking the THF and water azeotrope. These results show that the HBPs can be used in the field of process engineering as selective solvents for solvent extraction.[11]

A comparative investigation of the separation potential of two different solvents, that is ammonium ionic liquid, namely, hexyl(2-hydroxyethyl)dimethylammonium tetrafluoroborate, and hyperbranched polymer, B-U3000, has been conducted in this study in an attempt to elucidate the nature of the interactions in ternary systems. LLE were measured experimentally at T = 298.15 K. The experimental technique is based on direct analysis

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Table 1. Physicochemical Properties of Pure C_6BF_4 and B-U3000

property	C_6BF_4	B-U3000
$M/\mathrm{g \cdot mol^{-1}}$	261.11	6500[a]
M_w/M_n		1.5[a]
$T_{tr(g)}/\mathrm{K}$	172 ± 0.1[b]	234 ± 0.1[c]
$\Delta C_{p(g)}/\mathrm{kJ \cdot mol^{-1} \cdot K^{-1}}$	0.115 ± 0.003[b]	1.81 ± 0.003[c]
$d/\mathrm{g \cdot cm^{-3}}$ ($T = 298.15$ K)	1.1236 ± 0.0001	0.9840 ± 0.0001; 0.9888[d]
w_{H_2O}	$170 \cdot 10^{-6}$	$200 \cdot 10^{-6}$
appearance ($T = 298.15$ K)	liquid	liquid

[a] Provided by Perstorp (Sweden). [b] Ref 14. [c] Measured by DSC. [d] Ref 13.

of phases at equilibrium using ^{1}H NMR (C_6BF_4+ ethanol + hexane) and refractive index (B-U3000 + ethanol + hexane), which allow quantitative analysis of three compounds. From the tie-line data for ternary systems, the selectivity values, S, were determined to establish the feasibility of the use of these two entrainers for the separation of alcohol and alkane binary mixtures.

Experimental Section

Materials. The origins of the chemicals (in parentheses: CAS registry number, manufacturer reported, and mass percent purity) were as follows: Ethanol (64-17-5, Acros-Organics, 0.998 mass fraction) and hexane (110-54-3, Merck, 0.99 mass fraction) were obtained. Solvents were fractionally distilled over different drying reagents to the mass fraction purity of ≥ 0.998 mass fraction. Solvents were stored over freshly activated molecular sieves of type 4Å (Union Carbide). The refractive index for the solvents was $n_D(298.15) = 1.358\ 74$ and 1.372 26 for ethanol and hexane, respectively. The refractive index for B-U3000 was $n_D(298.15) = 1.480\ 34$.

Hexyl(2-hydroxyethyl)dimethylammonium tetrafluoroborate was synthesized using *N*,*N*-dimethylethanolamine (108-01-0, Sigma-Aldrich) and hexyl bromide (111-25-1, Sigma-Aldrich). The bromide salt was characterized using Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), mass spectroscopy, elemental analysis, differential scanning microscopy (DSC), simultaneous thermogravimetry/differential thermal analysis (TG/DTA), and water content.[12] The synthesis of hexyl(2-hydroxyethyl)dimethylammonium tetrafluoroborate has been performed via a metathesis reaction (1 mol of bromide salt reacts with 1 mol of sodium tetrafluoroborate ($NaBF_4$) in water), as was previously described.[8] Water content in C_6BF_4 after the purification and dried procedure was in mass fraction $170 \cdot 10^{-6}$. The elemental analysis of hexyl(2-hydroxyethyl)dimethylammonium bromide (C_6Br) showed 0.3135 mass fraction of Br, whereas the calculated value was 0.3143 mass fraction.[12]

The hyperbranched polymer, Boltorn U3000 (B-U3000) (462113-23-1, Perstorp, Sweden, 0.98 mass fraction) is a fatty-acid-modified dendritic polyester. It has a highly branched polymer backbone and an average of 14 unsaturated fatty ester groups in the molecule. B-U3000 is formed in the esterification reaction of hyperbranched polyester Boltorn H30 with sunflower oil, which consists of C_{16} fatty acids, C_{18} fatty acids, or both.[13] It has low viscosity and is a slightly yellow liquid at room temperature. The refractive index for B-U3000 was $n_D(298.15) = 1.480\ 34$. The physicochemical properties of the investigated IL and hyperbranched polymer are presented in Table 1. Both entrainers were degassed and purified before use for 48 h under low pressure at temperature $T = 323$ K.

Differential Scanning Calorimetry (DSC). The temperature of glass transition was measured by DSC (Perkin-Elmer Pyris 1). Measurements were carried out at a scan rate of $10\ \mathrm{K \cdot min^{-1}}$ with a power sensitivity of $16\ \mathrm{mJ \cdot s^{-1}}$ and with a recorder sensitivity of 5 mV. The DSC was calibrated with a 0.999999 mass fraction purity indium sample. The uncertainty of measured glass-transition temperatures, $T_{tr,(g)}$, was ± 0.5 K, and that of C_p of glass transition was $\pm 3\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. The results are shown in Table 1. DSC of B-U3000 is presented as Figure 1S in the Supporting Information.

Water Content. The water content was analyzed by the Karl Fischer titration technique (method TitroLine KF). Samples of all compounds were dissolved in methanol and titrated with steps of 2.5 μL. The results show a water mass fraction ranging from $170 \cdot 10^{-6}$ to $200 \cdot 10^{-6}$.

Density Measurements. The densities of C_6BF_4 and B-U3000 were measured using an Anton Paar GmbH 4500 vibrating-tube densimeter (Graz, Austria) thermostatted at $T = (298.15 \pm 0.01)$ K. The densimeter's calibration was performed under atmospheric pressure using doubly distilled and degassed water, specially purified benzene (Chemipan, Poland, 0.999) and dried air. The vibrating-tube temperature was measured by an Anton Paar DM 100-30 digital thermometer and was regulated to better than ± 0.01 K using a Unipan 60 thermostat and 202 temperature control system (Unipan, Poland). Two integrated Pt 100 platinum thermometers provided good precision in internal temperature control ($T \pm 0.01$ K). The densimeter included an automatic correction for the viscosity of the sample. The apparatus was precise to within $1 \cdot 10^{-5}\ \mathrm{g \cdot cm^{-3}}$, and the uncertainty of the measurements was estimated to be better than $\pm 5 \cdot 10^{-5}\ \mathrm{g \cdot cm^{-3}}$. The densities are listed in Table 1.

Procedures. We determined the LLE experimental tie lines for the ternary mixtures {C_6BF_4 + ethanol + hexane} by measuring the proton NMR spectroscopy, ^{1}H NMR. Ternary mixtures with compositions lying in the immiscible region were introduced inside jacketed glass cells. The temperature was controlled using a water bath, a Unipan 60 thermostat, and a 202 temperature control system. The temperature was measured with a calibrated Gallenkamp Autotherm II thermometer. The uncertainty of temperature measurements was ± 0.01 K, and that of the mole fraction did not exceed $\pm 5 \cdot 10^{-5}$. The thermometer was calibrated on the basis of ITS-90. All weighing involved in the experimental work was carried out in a Mettler Toledo AB 204-S balance with a precision of $\pm 1 \cdot 10^{-4}$ g.

All mixtures were vigorously stirred for at least 6 h and then allowed to settle for a minimum of 12 h to guarantee that the equilibrium state was completely reached. The indicated times were fixed according to results from preliminary tests. A sample of each layer in equilibrium was withdrawn using glass syringes with coupled stainless steel needles. The samples were then dissolved in deuterated solvent inside NMR tubes, which were properly sealed. The composition of these samples was determined by ^{1}H NMR. ^{1}H NMR spectra in $CDCl_3$ solutions were recorded on a Varian Gemini 2000 spectrometer. A description of spectra in the ternary system is presented in Figure 2S in the Supporting Information. The uncertainty of the mole fraction did not exceed $\pm 1 \cdot 10^{-2}$.

The binodal curve for the ternary system {B-U3000 + ethanol + hexane} was determined through the use of the cloud-point titration technique at the temperature $T = 298.15$ K. The experimental tie-line compositions were determined from the calibrating curves of refractive index, $n_D(298.15\ \mathrm{K})$, of two phases (polymer-rich phase and polymer-lean phase). The refractive index was measured with a Carl Zeiss Jena refractive meter with a precision $n_D = \pm 0.00001$. The uncertainty in the

Table 2. Tie-Line Compositions for the Ternary Mixtures {C_6BF_4(1) + Ethanol (2) + Hexane (3)} at 298.15 K, x_1^I, x_2^I, x_1^{II}, and x_2^{II} Together with Values of the Solute Distribution Ratio (β) and Selectivity (S)

alkane-rich layer		ionic-liquid-rich layer			
x_1^I	x_2^I	x_1^{II}	x_2^{II}	β	S
0.00	0.00	0.99	0.00		
0.00	0.01	0.83	0.16	16.0	1584
0.00	0.02	0.60	0.39	19.5	1911
0.00	0.04	0.45	0.54	13.5	1296
0.00	0.05	0.31	0.65	13.0	308.8
0.00	0.07	0.29	0.66	9.4	175.4
0.01	0.11	0.25	0.69	6.3	92.0
0.01	0.17	0.20	0.72	4.2	43.4
0.03	0.27	0.17	0.73	2.7	18.9

Table 3. Tie-Line Compositions for the Ternary Mixtures {B-U3000 (1) + Ethanol (2) + Hexane (3)} at 298.15 K, w_1^I, w_2^I, w_1^{II}, and w_2^{II} Together with Values of the Solute Distribution Ratio (β) and Selectivity (S)

ethanol-rich layer		polymer- rich layer			
w_1^I	w_2^I	w_1^{II}	w_2^{II}	β	S
0.02	0.70	0.74	0.22	0.12	0.38
0.05	0.64	0.68	0.25	0.24	0.64
0.05	0.65	0.71	0.24	0.19	0.52
0.08	0.62	0.63	0.26	0.34	0.80
0.14	0.57	0.54	0.31	0.49	0.89

measurements in mass fraction was ± 0.01. The calibration curves are shown in Figure 3S in the Supporting Information.

Results and Discussion

The measured compositions of the experimental tie-line ends of the ternary systems of {C_6BF_4 or B-U3000 (1) + ethanol (2) + hexane (3)} at temperature T = 298.15 K are reported in Tables 2 and 3 and in Figures 1 and 2 and Figure 4S in the Supporting Information.

The feasibility of using the IL as a solvent to perform the separation of ethanol and hexane was evaluated by classic parameters such as the solute distribution ratio (β) and the selectivity (S) calculated from the experimental data. These parameters are defined by the following expressions

$$\beta = \frac{x_2^{II}}{x_2^I} \tag{1}$$

$$S = \frac{x_2^{II} \cdot x_3^I}{x_2^I \cdot x_3^{II}} \tag{2}$$

where x is the mole fraction, superscripts I and II refer to the hydrocarbon-rich phase and ionic-liquid-rich phase, respectively, and subscripts 2 and 3 refer to ethanol (solute) and hexane (inert in our mixtures), respectively.

For the ternary mixtures {B-U3000 (1) + ethanol (2) + hexane (3)}, the hexane is the solute and the same parameters are defined as follows

$$\beta = \frac{w_3^{II}}{w_3^I} \tag{3}$$

$$S = \frac{w_3^{II} \cdot w_2^I}{w_3^I \cdot w_2^{II}} \tag{4}$$

where w is the weight fraction, superscripts I and II refer to the alcohol-rich phase and polymer-rich phase, respectively, and subscripts 2 and 3 refer to ethanol and hexane, respectively. The values of β and S are shown in Tables 2 and 3 together with the experimental equilibrium data. The selectivities for C_6BF_4 for the first three tie lines are > 1000 (Table 2), which is quite promising; however, the [HMIM][PF_6] ionic liquid has revealed some higher values.[2] In the middle area of the measured tie lines, the selectivities were from 50 to 300 for the {C_6BF_4 + ethanol + hexane} system, which is less interesting.

The separation of ethanol and aliphatic hydrocarbon was, to our knowledge, never tested with the ammonium IL. The first results were shown by the use of imidazolium ILs for ethanol/heptane mixtures.[2–4] In our previous work, we developed two ternary systems with ammonium ILs: {butyl(2-hydroxyethyl)dimethylammonium tetrafluoroborate (C_4BF_4) or C_6BF_4 + hexane + *p*-xylene} at T = 298.15 K.[8]

The slopes of the tie-lines for the {C_6BF_4 + ethanol + hexane} system are similar. Figure 1 shows that the area of the two-phase region is quite high. The relative solubility of ethanol in hexane or in C_6BF_4 is evident from the tie lines. The slope of the tie lines for {C_6BF_4 + ethanol + hexane} shows that

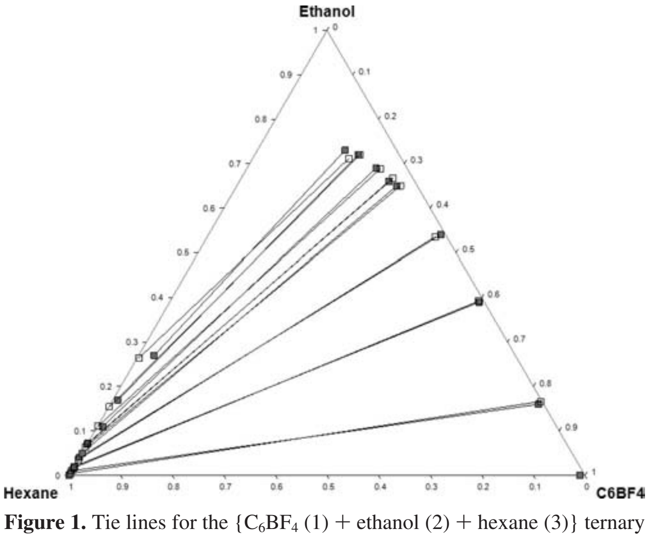

Figure 1. Tie lines for the {C_6BF_4 (1) + ethanol (2) + hexane (3)} ternary system at T = 298.15 K and ambient pressure (in mole fraction): ■, experimental tie lines (solid line); □, NRTL correlation (α = 0.20) (solid line).

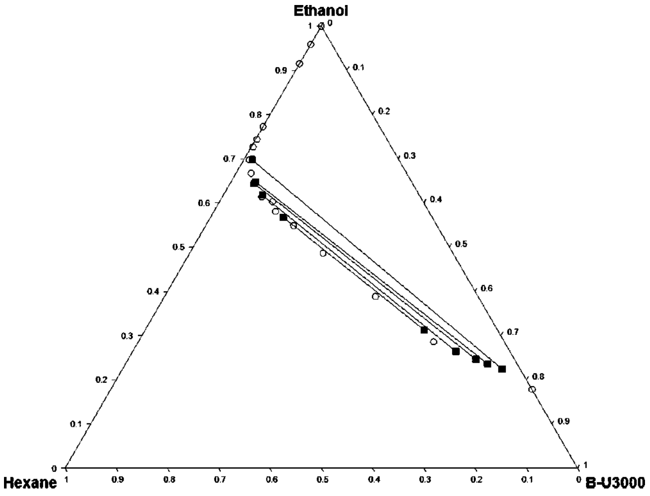

Figure 2. {B-U3000 (1) + ethanol (2) + hexane (3)} ternary system (in mass fraction) at T = 298.15 K and ambient pressure: ○, binodal curve; ■, experimental tie lines (solid line).

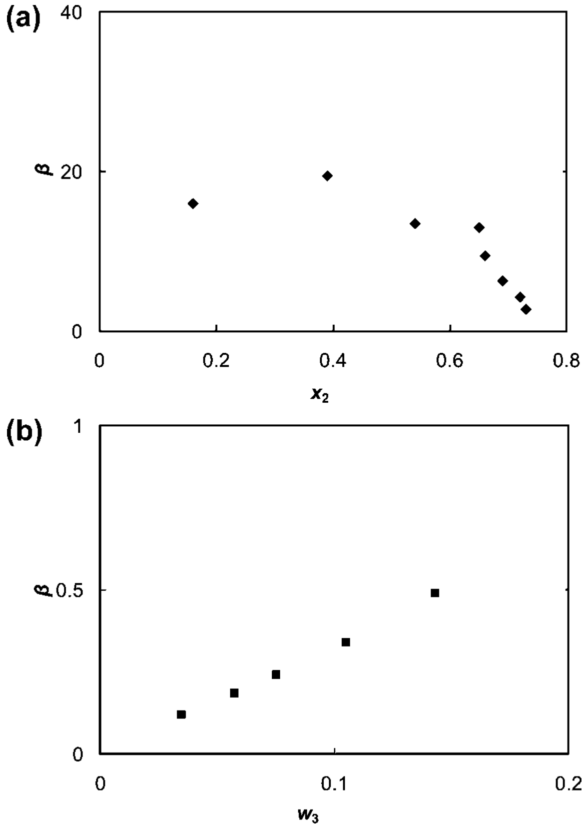

Figure 3. (a) Solute distribution ratio of ethanol, β, for the ternary system $\{C_6BF_4\ (1) + \text{ethanol}\ (2) + \text{hexane}\ (3)\}$ as a function of the mole fraction of ethanol, x_2, in the IL-rich phase at $T = 298.15$ K. (b) Solute distribution ratio of hexane, β, for the ternary system {B-U3000 (1) + ethanol (2) + hexane (3)} as a function of the hexane mass fraction, w_3, in HBP-rich phase at $T = 298.15$ K.

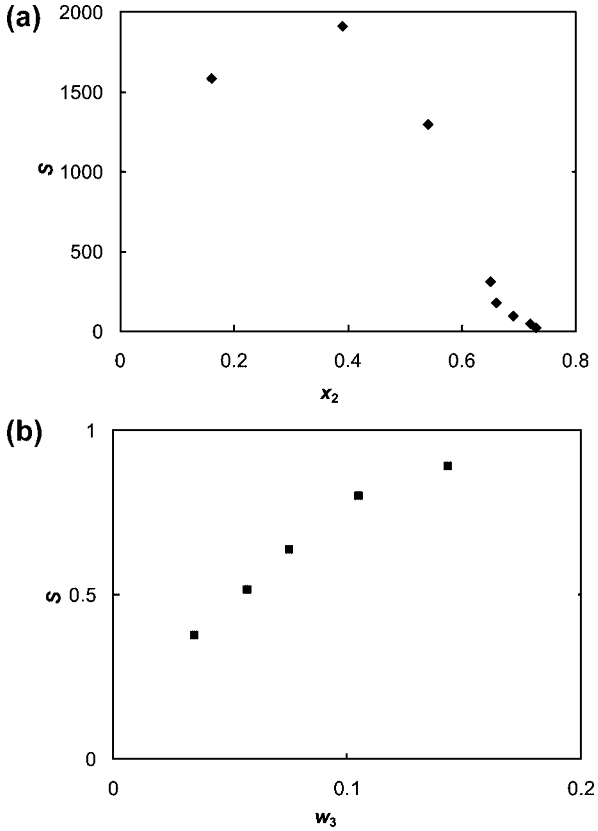

Figure 4. (a) Selectivity, S, for the ternary system $\{C_6BF_4\ (1) + \text{ethanol}\ (2) + \text{hexane}\ (3)\}$ as a function of the mole fraction, x_2, of ethanol in the IL-rich phase at $T = 298.15$ K. (b) Selectivity, S, for the ternary system {B-U3000 (1) + ethanol (2) + hexane (3)} as a function of the hexane mass fraction, w_3, in the HBP-rich phase at $T = 298.15$ K.

Table 4. Values of Parameters for the NRTL Equation for the Ternary Mixtures $\{C_6BF_4$ or B-U3000 (1) + Ethanol (2) + Hexane (3)$\}$

i,j	α_{ij}	$\frac{g_{ij} - g_{jj}}{\text{J}\cdot\text{mol}^{-1}}$	$\frac{g_{ji} - g_{ii}}{\text{J}\cdot\text{mol}^{-1}}$
		C_6BF_4 (0.01)[a]	
1,2	0.20	−7962.49	4052.09
1,3		14 794.28	14311.27
2,3		2580.10	2762.68
		B-U3000 (0.00)[a]	
1,2	0.15	19 992.13	25 259.19
1,3		59 618.61	67 196.68
2,3		11 442.10	−3909.26

[a] rmsd values are given in parentheses.

C_6BF_4 is not soluble in hexane and is soluble in ethanol, which was already presented by us.[14]

The substitution of a hydroxyl group to the ammonium cation, as in the C_6BF_4, increases the interaction with ethanol and probably increases the selectivity of ethanol and hexane separation. The distribution ratio of hexane and ethanol with the C_6BF_4 ionic liquid is the same as was observed for the other ILs used in this process.[2−4] The solute distribution ratio decreases as the mole fraction of ethanol in the IL-rich phase increases in the $\{C_6BF_4 + \text{ethanol} + \text{hexane}\}$ system. It is shown in Figure 3a. The selectivity increases for low values of mole fraction of ethanol (up to $x_2 = 0.4$) and regularly decreases when the mole fraction of ethanol in the IL-rich phases increases. This is a quite usual dependence for IL in many published data. (See Figure 4a.)[2−4]

A completely different picture was obtained for B-U3000, which was soluble in hexane and revealed the immiscibility with ethanol. The results for the system {B-U3000 + ethanol + hexane} in weight fraction, w_i, are shown in Figure 2, and those in mole fraction are shown in Figure 4S in the Supporting Information. In this system, hexane is a solute, and the interpretation of data is different. The graphical presentation of the solute distribution ratio as a function of the hexane weight fraction in HBP-rich phase is shown in Figure 3b. The solute distribution ratio, calculated from eq 3, increases with an increase in the hexane mass fraction in HBP-rich phase. Selectivity regularly increases when the mass fraction of hexane in the HBP-rich phase increases. (See Figure 4b.) The use of HBPs as an entrainer for ethanol and hexane phase separation cannot be discussed because of the different interactions in binary systems with ethanol and hexane.

Data Correlation. A thermodynamic model such as the nonrandom liquid equation, NRTL,[15] is used to correlate the experimental data for two ternary systems discussed here. The equations and algorithms used in the calculation of the compositions of liquid phases follow the method used by Walas.[16] The objective function $F(P)$, was used to minimize the difference between the experimental and calculated concentrations

$$F(P) = \sum_{i=1}^{n}\sum_{j=1}^{n}\left\langle\left[x_{ij}^{\mathrm{I,exptl}} - x_{ij}^{\mathrm{I,calcd}}(PT)\right]^2 + \left[x_{ji}^{\mathrm{II,exptl}} - x_{ji}^{\mathrm{II,calcd}}(PT)\right]^2\right\rangle \quad (5)$$

where P is the set of parameters in the vector, n is the number of experimental points, $x_{ij}^{\mathrm{I,exptl}}$, $x_{ji}^{\mathrm{I,exptl}}$, $x_{ij}^{\mathrm{I,calcd}}(PT)$, and $x_{ji}^{\mathrm{I,calcd}}(PT)$

are the experimental and calculated mole fractions of one phase for $i = 2$ and $j = 3$, and $x_{ij}^{\mathrm{II,exptl}}$, $x_{ji}^{\mathrm{II,exptl}}$, $x_{ij}^{\mathrm{II,calcd}}(PT)$, and $x_{ji}^{\mathrm{II,calcd}}(PT)$ are the experimental and calculated mole fractions of another phase.

For the NRTL model, the third nonrandomness parameter, α, was set at optimized values of 0.20 and 0.15 (Table 4) for C_6BF_4 and B-U3000, respectively. The starting values of the parameters were not known, and thus the calculations were made by the correlation of the experimental points in the ternary systems. The parameters and root-mean-square deviations (rmsd) calculated in this way are included in Table 4. The rmsd values, which can be taken as a measure of the precision of the correlations, were calculated according the equation

$$\mathrm{rmsd} = \left(\sum_i \sum_l \sum_m [x_{ilm}^{\mathrm{exptl}} - x_{ilm}^{\mathrm{calcd}}]^2/6k\right)^{1/2} \qquad (6)$$

where x is the mole fraction and the subscripts i, l, and m designate the component, phase, and tie line, respectively. As can be seen from Table 4 and Figures 1 and 2, the correlation obtained for the system {C_6BF_4 + ethanol + hexane} was similar to that for the {B-U3000 + ethanol + hexane} system.

Conclusions

Liquid−liquid equilibrium data for two ternary systems {C_6BF_4 or B-U3000 + ethanol + hexane} were determined at $T = 298.15$ K. Selectivity values and the distribution ratios, derived from the tie-line experimental values, indicated that only investigated ammonium ionic liquid can be a suitable solvent for the liquid−liquid extraction of hexane from the azeotropic system with ethanol. The tie-line data have been correlated through the use of the NRTL model with the maximum rmsd equal to 0.01. Hyperbranched polymer, B-U3000, shows immiscibility with ethanol and incapacity (low distribution ratio and selectivity) in the alcohol and alkane separation.

Supporting Information Available:

DSC of B-U3000, ^{1}H NMR spectra of ternary system with C_6BF_4, calibration curve for ternary data with B-U3000, binodal curve and experimental tie lines for the {B-U3000 + ethanol (2) + hexane (3)} ternary system (in mole fraction), and LLE for ternary data with B-U3000. This material is available free of charge via the Internet at http://pubs.acs.org.

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