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Separation of an Alcohol and a Tetrahydrofuran, Methyl *tert*-Butyl Ether, or Ethyl *tert*-Butyl Ether by Solvent Extraction with a Hyperbranched Polymer at $T = 298.15$ K

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Liquid−liquid phase equilibria (LLE) of six ternary mixtures, {methanol (1) + tetrahydrofuran (THF) (2) + hyperbranched polymer (HBP) Boltorn U3000 (B-U3000) (3)}, {ethanol (1) + THF (2) + B-U3000 (3)}, {methanol (1) + methyl *tert*-butyl ether (MTBE) (2) + B-U3000 (3)}, {ethanol (1) + MTBE (2) + B-U3000 (3)}, {methanol (1) + ethyl *tert*-butyl ether (ETBE) (2) + B-U3000 (3)}, or {ethanol (1) + ETBE (2) + B-U3000 (3)}, have been measured at $T = 298.15$ K. The results are discussed in terms of the selectivity of alcohol (methanol or ethanol) and THF or ether (ETBE or MTBE) separation. Sloping of the tie-lines toward the B-U3000 vertex is observed for all mixtures. The results indicate an acceptable selectivity for the separation of methanol and THF and/or ether with the tested HBP utilizing solvent extraction. The nonrandom two-liquid (NRTL) model was successfully used to correlate the experimental tie-lines, with the maximum mean square deviation in mass fraction being 0.008.

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1. Introduction

Because of heightened environmental awareness of the impact of volatile organic solvents, there has been much interest to investigate the use of new potential solvents such as ionic liquids (ILs) or hyperbranched polymers (HBPs) as possible entrainers. Volatile organic solvents which are frequently used as entrainers to break azeotropes in binary mixtures have the potential for solvent loss to the atmosphere, and therefore alternative solvents which have a fairly low vapor pressure are sought.

A large number of industrial processes are needed to separate azeotropic systems, for example, those containing an alcohol and tetrahydrofuran (THF) or an alcohol and tertiary ether. Often distillation processes are used, but they have a high energy consumption to create a fluid phase system. On the contrary, liquid−liquid separation based on the immiscibility between two liquid phases is beneficial in separation processes because of the reduced energy consumption. Extractive distillation is often used to remove certain compounds from azeotropic systems.[1] The addition of a new solvent (entrainer) can be used to change the interaction between the components of the original mixture and thus alter their relative volatilities. In this way the azeotropic mixture can be separated. The selectivity of the entrainer, calculated from different physicochemical measurements (liquid−liquid equilibria, LLE, or activity coefficients at infinite dilution, γ^{∞}) is an important parameter in characterizing the solvent.

From many years, as a result of the reduction of lead content in gasoline, tertiary ethers and alcohols have coexisted as additives for gasoline. The most widely used antiknock additive for gasoline is methyl *tert*-butyl ether (MTBE), but shortly it could be replaced by ethyl *tert*-butyl ether (ETBE) because of its possible cheap synthesis from renewable sources, its lower solubility in water, and its much safer storage in the underground tanks. The azeotropic and close boiling point mixture of ETBE and ethanol, as an unreacted substance from the synthesis of ETBE, is difficult to separate using conventional distillation. This separation is usually undertaken industrially with water.

New entrainers for the separation of the ethanol and ETBE,[2−4] as well as for ethanol and *tert*-amyl ethyl ether (TAEE)[5−7] were investigated previously using ILs.

ILs and HBPs have interesting properties, which allow them to be possible substitutes for classic organic solvents, with the advantage of less damage to the environment. HBPs are highly branched, polydisperse macromolecules with a large number of functional groups. Properties of HBPs, which include a remarkable selectivity and capacity, low melting point, and high solubility, show great promise for use in separation processes.[8] Therefore, processes such as extractive distillation, liquid−liquid extraction, absorption, and emulsion liquid membranes represent promising fields of applications. 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.[9]

A comparative investigation of the separation potential of two different solvents, that is, ammonium IL, namely, hexyl(2-hydroxyethyl)dimethylammonium tetrafluoroborate and HBP Boltorn U3000 (B-U3000), has been conducted in our previous study in an attempt to elucidate the nature of the interactions in ternary systems. LLE were measured experimentally at $T = 298.15$ K for the systems: (C_6BF_4 + ethanol + hexane) and (B-U3000 + ethanol + hexane).[10]

The aims of the present work is to study the influence of the HBP B-U3000 on the six ternary LLE mixtures: {methanol (1)

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+ THF (2) + B-U3000 (3)}, {ethanol (1) + THF (2) + B-U3000 (3)}, {methanol (1) + MTBE (2) + B-U3000 (3)}, {ethanol (1) + MTBE (2) + B-U3000 (3)}, {methanol (1) + ETBE (2) + B-U3000 (3)}, or {ethanol (1) + ETBE (2) + B-U3000 (3)} at $T = 298.15$ K.

2. Experimental Section

2.1. Materials. The details of the chemicals (in parentheses are the Chemical Abstract Registry Nos., the supplier, and the purities by mass) used in the investigation were as follows: methanol (67-56-1, Aldrich, 0.998 mass fraction) and ethanol (64-17-5, Acros Organics, 0.998 mass fraction). Solvents were fractionally distilled over different drying reagents to a mass fraction purity of ≥ 0.998 mass fraction. Solvents were also stored over freshly activated molecular sieves of type 4 Å (Union Carbide). The refractive indexes for the solvents, $n_D(298.15)$, were 1.32655 and 1.37226 for methanol and ethanol, respectively.

The HBP used was B-U3000 (462113-23-1, Perstorp, Sweden, 0.98 mass fraction). B-U3000 is fatty acid modified dendritic polyester. It has a highly branched polymer backbone, and there are on average 14 unsaturated fatty ester groups in the molecule. B-U3000 is formed in an esterification reaction of hyperbranched polyester Boltorn H30 with sunflower oil, that consists of C_{16} and/or C_{18} fatty acids.[11] It is a highly viscous, slightly yellow liquid at room temperature. The refractive index of B-U3000, $n_D(298.15)$, is 1.48034. The physicochemical properties of the investigated IL and HBP were presented earlier.[10] The polymer was degassed and purified before use, typically for 48 h under low pressure at the temperature $T = 323$ K.

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

All of the 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 Mercury 400 MHz spectrometer. The composition was detected for two solvents (not for the polymer) by weighing with the internal standard, dichloromethane (CH_2Cl_2). A description of spectra in ternary system is presented in Figure 1S of Supporting Information. The uncertainty of the mass fraction did not exceed $\pm 5 \cdot 10^{-3}$.

Table 1. Tie-Line Compositions for the Ternary Mixture {Methanol (1) + THF (2) + B-U3000 (3)} in Mass Fraction w_i, Together with Values of the Solute Distribution Ratio (β) and Selectivity (S) at $T = 298.15$ K

polymer-rich layer			methanol-rich layer					
$w_{\mathrm{MeOH}}^{\mathrm{I}}$	$w_{\mathrm{THF}}^{\mathrm{I}}$	$w_{\mathrm{B\text{-}U3000}}^{\mathrm{I}}$	$w_{\mathrm{MeOH}}^{\mathrm{II}}$	$w_{\mathrm{THF}}^{\mathrm{II}}$	$w_{\mathrm{B\text{-}U3000}}^{\mathrm{II}}$	β_{MeOH}	β_{THF}	$S_{\mathrm{THF/MeOH}}$
0.061	0.000	0.939	1.000	0.000	0.000	0.06		
0.111	0.018	0.871	0.941	0.041	0.018	0.12	0.45	3.75
0.112	0.056	0.832	0.895	0.093	0.012	0.13	0.60	4.61
0.125	0.078	0.797	0.808	0.169	0.024	0.15	0.46	3.07
0.162	0.150	0.688	0.706	0.264	0.030	0.23	0.57	2.48
0.208	0.229	0.564	0.543	0.345	0.112	0.38	0.66	1.74
0.295	0.337	0.367	0.424	0.379	0.197	0.70	0.89	1.27

Table 2. Tie-Line Compositions for the Ternary Mixture {Ethanol (1) + THF (2) + B-U3000 (3)} in Mass Fraction w_i, Together with Values of the Solute Distribution Ratio (β) and Selectivity (S) at $T = 298.15$ K

polymer-rich layer			ethanol-rich layer					
w_{EtOH}	w_{THF}	$w_{\mathrm{B\text{-}U3000}}$	w_{EtOH}	w_{THF}	$w_{\mathrm{B\text{-}U3000}}$	β_{EtOH}	β_{THF}	$S_{\mathrm{THF/EtOH}}$
0.169	0.000	0.831	0.980	0.000	0.020	0.17		
0.182	0.018	0.801	0.913	0.042	0.045	0.20	0.42	2.10
0.244	0.060	0.697	0.817	0.079	0.104	0.30	0.76	2.53
0.290	0.100	0.610	0.654	0.145	0.201	0.44	0.69	1.57
0.415	0.143	0.442	0.590	0.168	0.242	0.70	0.85	1.21

Table 3. Tie-Line Compositions for the Ternary Mixture {Methanol (1) + MTBE (2) + B-U3000 (3)} in Mass Fraction w_i, Together with Values of the Solute Distribution Ratio (β) and Selectivity (S) at $T = 298.15$ K

polymer-rich layer			methanol-rich layer					
$w_{\mathrm{MeOH}}^{\mathrm{I}}$	$w_{\mathrm{MTBE}}^{\mathrm{I}}$	$w_{\mathrm{B\text{-}U3000}}^{\mathrm{I}}$	$w_{\mathrm{MeOH}}^{\mathrm{II}}$	$w_{\mathrm{MTBE}}^{\mathrm{II}}$	$w_{\mathrm{B\text{-}U3000}}^{\mathrm{II}}$	β_{MeOH}	β_{MTBE}	$S_{\mathrm{MTBE/MeOH}}$
0.061	0.000	0.939	1.000	0.000	0.000			
0.116	0.040	0.844	0.913	0.075	0.011	0.13	0.54	4.15
0.131	0.081	0.788	0.822	0.169	0.009	0.16	0.48	3.00
0.137	0.125	0.738	0.722	0.252	0.025	0.19	0.49	2.58
0.152	0.145	0.703	0.693	0.281	0.026	0.22	0.52	2.36
0.185	0.206	0.609	0.604	0.367	0.028	0.31	0.56	1.81
0.187	0.223	0.590	0.556	0.409	0.035	0.34	0.55	1.62
0.210	0.262	0.527	0.516	0.433	0.051	0.41	0.61	1.49

Table 4. Tie-Line Compositions for the Ternary Mixture {Ethanol (1) + MTBE (2) + B-U3000 (3)} in Mass Fraction w_i, Together with Values of the Solute Distribution Ratio (β) and Selectivity (S) at $T = 298.15$ K

polymer-rich layer			ethanol-rich layer					
$w_{\mathrm{EtOH}}^{\mathrm{I}}$	$w_{\mathrm{MTBE}}^{\mathrm{I}}$	$w_{\mathrm{B\text{-}U3000}}^{\mathrm{I}}$	$w_{\mathrm{EtOH}}^{\mathrm{II}}$	$w_{\mathrm{MTBE}}^{\mathrm{II}}$	$w_{\mathrm{B\text{-}U3000}}^{\mathrm{II}}$	β_{EtOH}	β_{MTBE}	$S_{\mathrm{MTBE/EtOH}}$
0.169	0.000	0.831	0.980	0.000	0.020	0.17		
0.243	0.033	0.724	0.869	0.064	0.068	0.28	0.51	1.82
0.300	0.085	0.616	0.746	0.148	0.107	0.40	0.57	1.42
0.353	0.138	0.509	0.634	0.185	0.181	0.56	0.74	1.32
0.387	0.180	0.433	0.558	0.213	0.229	0.69	0.84	1.22

Table 5. Tie-Line Compositions for the Ternary Mixture {Methanol (1) + ETBE (2) + B-U3000 (3)} in Mass Fraction w_i, Together with Values of the Solute Distribution Ratio (β) and Selectivity (S) at $T = 298.15$ K

polymer-rich layer			methanol-rich layer					
$w_{\mathrm{MeOH}}^{\mathrm{I}}$	$w_{\mathrm{ETBE}}^{\mathrm{I}}$	$w_{\mathrm{B\text{-}U3000}}^{\mathrm{I}}$	$w_{\mathrm{MeOH}}^{\mathrm{II}}$	$w_{\mathrm{ETBE}}^{\mathrm{II}}$	$w_{\mathrm{B\text{-}U3000}}^{\mathrm{II}}$	β_{MeOH}	β_{ETBE}	$S_{\mathrm{ETBE/MeOH}}$
0.061	0.000	0.939	1.000	0.000	0.000			
0.078	0.037	0.885	0.902	0.083	0.015	0.09	0.44	4.89
0.092	0.069	0.840	0.878	0.116	0.005	0.10	0.59	5.90
0.094	0.082	0.824	0.744	0.243	0.013	0.13	0.34	2.61
0.126	0.125	0.749	0.700	0.268	0.033	0.18	0.47	2.61
0.154	0.191	0.655	0.639	0.334	0.027	0.24	0.57	2.37

3. Results and Discussion

The measured compositions of the experimental tie-line ends of the ternary systems of {methanol (1) + THF (2) + B-U3000 (3)}, {ethanol (1) + THF (2) + B-U3000 (3)}, {methanol (1) + MTBE (2) + B-U3000 (3)}, {ethanol (1) + MTBE (2) + B-U3000 (3)}, {methanol (1) + ETBE (2) + B-U3000 (3)}, or {ethanol (1) + ETBE (2) + B-U3000 (3)} at the temperature $T = 298.15$ K are reported in Tables 1 to 6 and in Figures 1 to 6.

Table 6. Tie-Line Compositions for the Ternary Mixture {Ethanol (1) + ETBE (2) + B-U3000 (3)} in Mass Fraction w_i, Together with Values of the Solute Distribution Ratio (β) and Selectivity (S) at T = 298.15 K

polymer-rich layer			ethanol-rich layer					
w_{EtOH}	w_{ETBE}	$w_{B\text{-}U3000}$	w_{EtOH}	w_{ETBE}	$w_{B\text{-}U3000}$	β_{EtOH}	β_{ETBE}	$S_{ETBE/EtOH}$
0.169	0.000	0.831	0.980	0.000	0.020			
0.234	0.068	0.698	0.915	0.069	0.016	0.26	0.99	3.81
0.241	0.092	0.667	0.776	0.161	0.063	0.31	0.57	1.84
0.263	0.099	0.638	0.735	0.172	0.093	0.36	0.57	1.58
0.330	0.138	0.531	0.637	0.208	0.156	0.52	0.67	1.29
0.376	0.189	0.435	0.489	0.225	0.286	0.77	0.84	1.09

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

$$\beta_i = \frac{w_i^{I}}{w_i^{II}} \tag{1}$$

$$S_{2,1} = \frac{\beta_2}{\beta_1} = \frac{w_1^{I} w_2^{II}}{w_1^{II} w_2^{I}} \tag{2}$$

where w is the mass fraction; superscripts I and II refer to the polymer-rich phase and alcohol-rich phase, respectively. Subscripts 1 and 2 refer to alcohol (methanol, ethanol) and THF or ether, respectively.

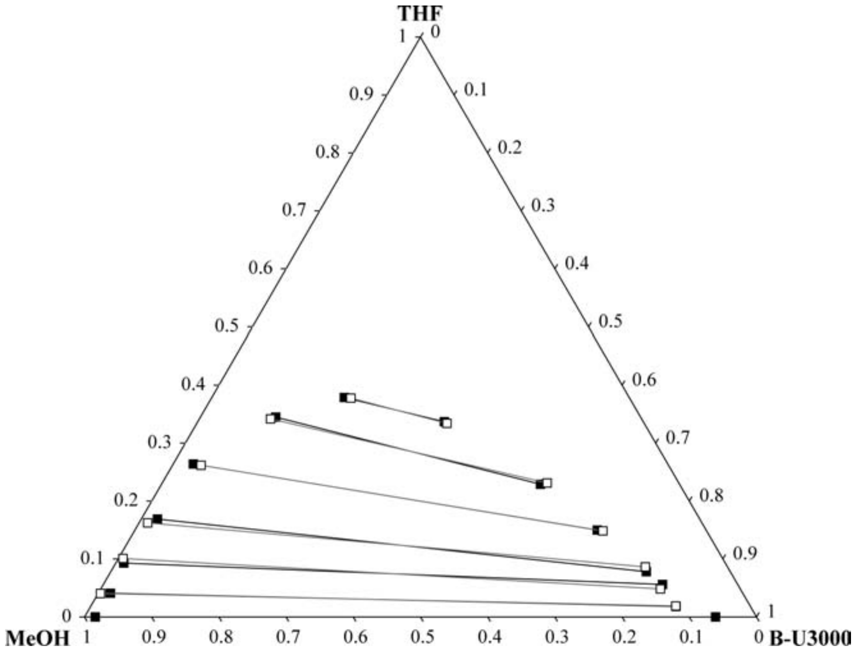

Figure 1. Tie-lines for the {methanol (1) + THF (2) + B-U3000 (3)} ternary system at T = 298.15 K and ambient pressure (in mole fraction): ■, experimental tie-lines (solid line); □, NRTL correlation (α = 0.2) (solid line).

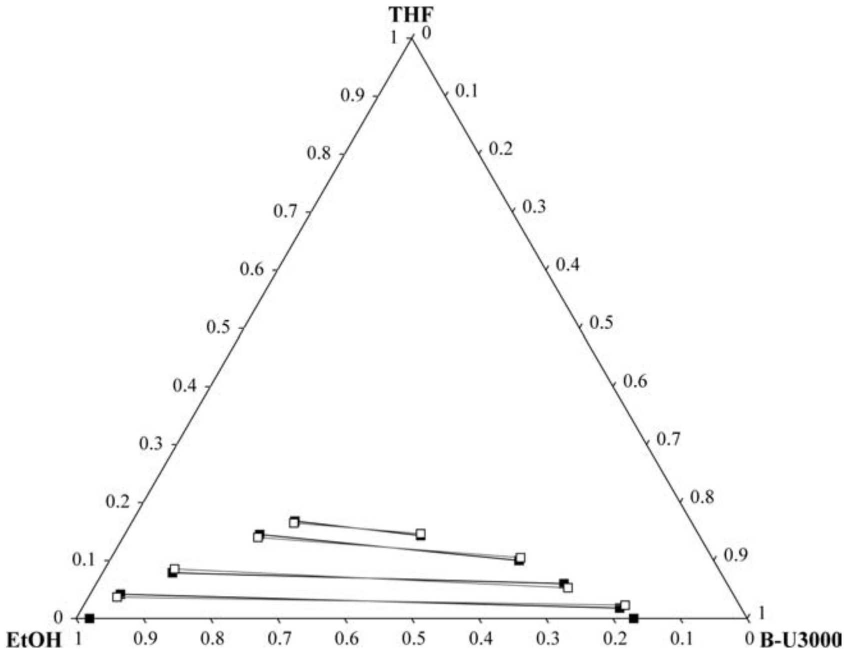

Figure 2. Tie-lines for the {ethanol (1) + THF (2) + B-U3000 (3)} ternary system (in mass fraction) at T = 298.15 K and ambient pressure: ■, experimental tie-lines (solid line); □, NRTL correlation (α = 0.4) (solid line).

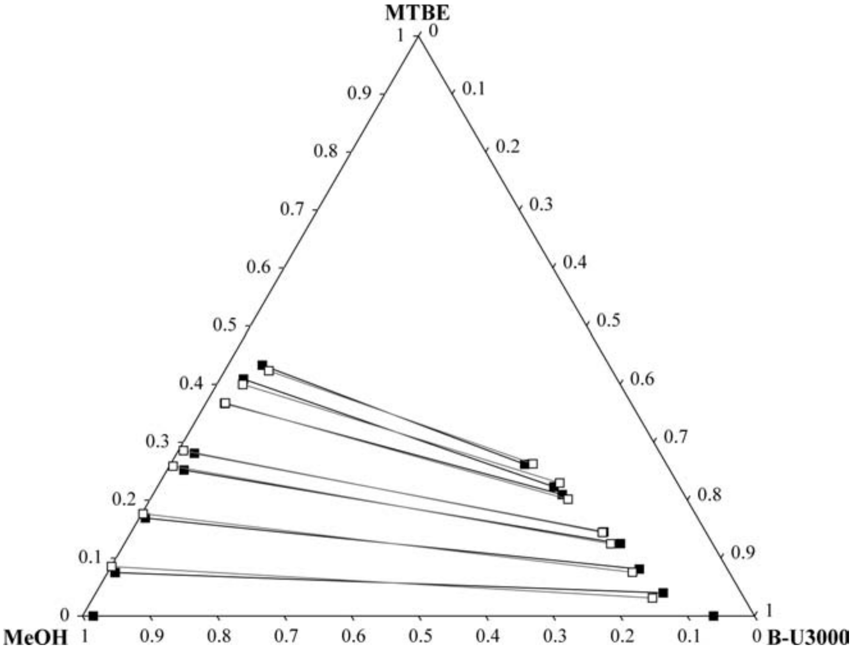

Figure 3. Tie-lines for the {methanol (1) + MTBE (2) + B-U3000 (3)} ternary system (in mass fraction) at $T = 298.15$ K and ambient pressure: ■, experimental tie-lines (solid line); ☐, NRTL correlation ($\alpha = 0.1$) (solid line).

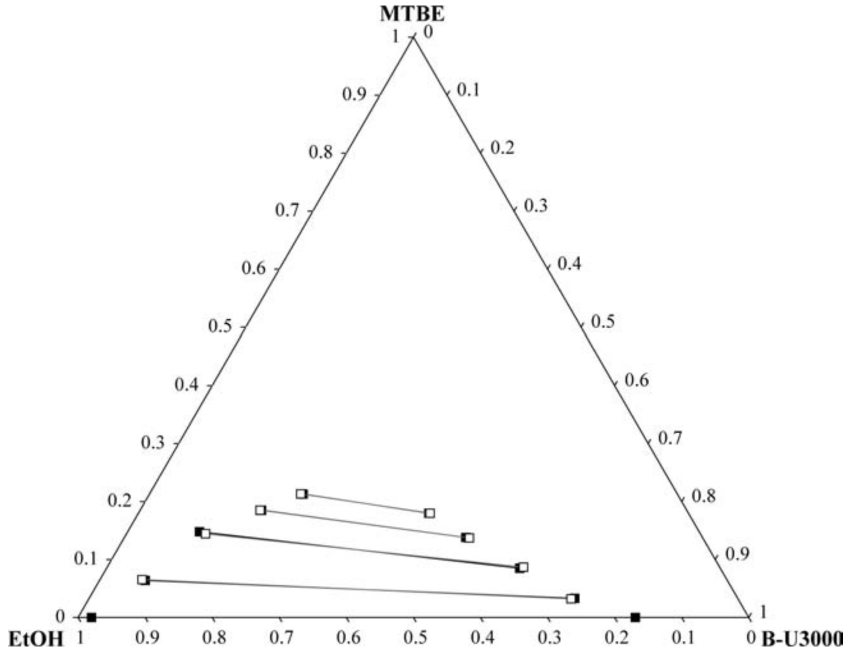

Figure 4. Tie-lines for the {ethanol (1) + MTBE (2) + B-U3000 (3)} ternary system (in mass fraction) at $T = 298.15$ K and ambient pressure: ■, experimental tie-lines (solid line); ☐, NRTL correlation ($\alpha = 0.1$) (solid line).

The values of β and S are shown in Tables 1 to 6, together with the experimental equilibrium data. The selectivities for the B-U3000 for the three first tie-lines are > 2.5, what is not very favorable when compared with ILs;[2−4] however, the B-U3000 has revealed some higher values for the azeotrope mixture of methanol−ETBE in the system {methanol (1) + ETBE (2) + B-U3000 (3)}. In the middle area of the measured tie-lines the selectivities ranged from 2.6 to 5.9.

The separation of the azeotropic mixtures, shown in Table 7, were to our knowledge never tested with the HBPs. Some results were shown in literature previously using different Boltorn and Hybrane HBPs[9] or the acetylated polyglycerol[18] in the separation problem concerning THF−water, with much higher selectivity.

The slopes of the tie-lines for all of the systems studied are similar. Figures 1 to 6 show the immiscibility regions for the alcohol−B-U3000 binary systems. The area of the two-phase region is quite high. The relative solubility of an alcohol in B-U3000 is higher than that of B-U3000 in an alcohol, which is evident from the tie-lines. The slope of the tie-lines for all systems shows that polymer is not soluble in an alcohol or in THF or ether.

The graphical presentation of the solute distribution ratio as a function of the THF or ether mass fraction in the polymer-reach phase is shown in Figures 7 and 8, as an example, and in the Figures 2S to 5S in the Supporting Information. The solute distribution ratio, calculated from eq 1, increases regularly with an increase of the THF or ether mass fraction in the polymer-

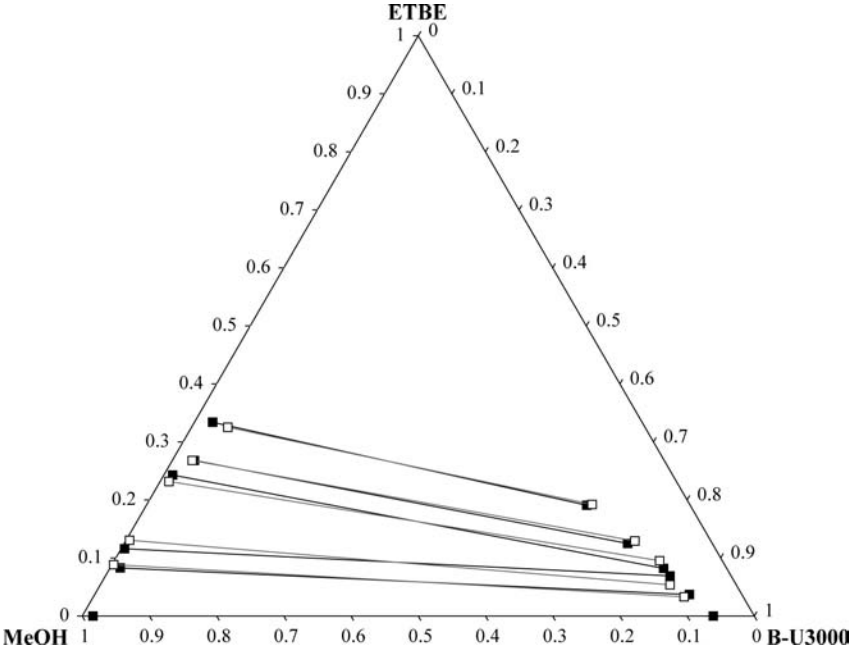

Figure 5. Tie-lines for the {methanol (1) + ETBE (2) + B-U3000 (3)} ternary system (in mass fraction) at T = 298.15 K and ambient pressure: ■, experimental tie-lines (solid line); □, NRTL correlation (α = 0.2) (solid line).

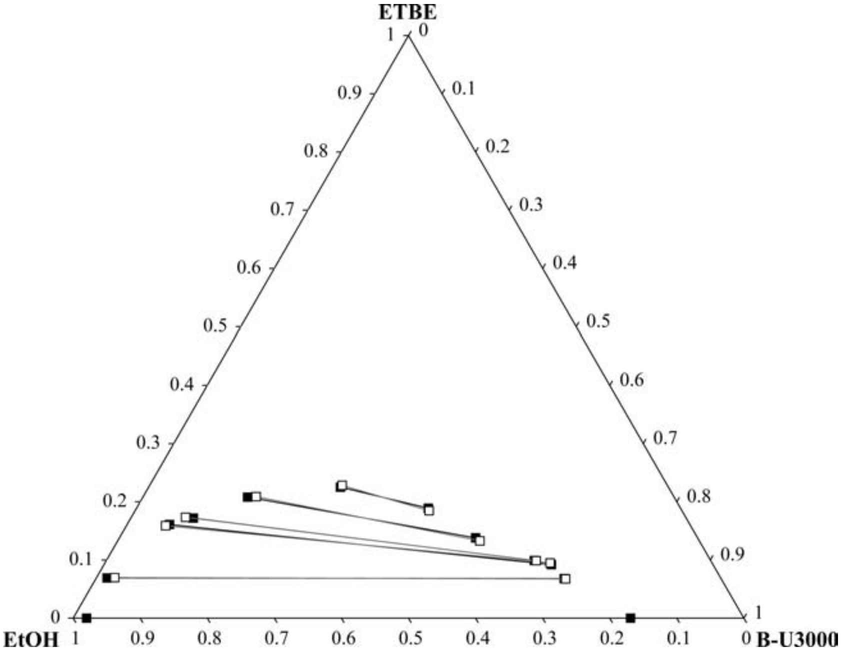

Figure 6. Tie-lines for the {ethanol (1) + ETBE (2) + B-U3000 (3)} ternary system (in mass fraction) at T = 298.15 K and ambient pressure: ■, experimental tie-lines (solid line); □, NRTL correlation (α = 0.3) (solid line).

rich phase, w_2^{I}. Selectivity, S, decreases when the mass fraction of THF or ether in the polymer-rich phase increases. The deviations of these regularities observed in Figures 2 and 2S and 4S of the Supporting Information can be only explained by the summation of the experimental errors of the uncertainties of mass fractions. The use of B-U3000 as an entrainer for alcohol and THF/ether phase separations was expected to have higher efficiency because of the possible interactions with an alcohol and THF/ether in binary systems. It is related to the nature and the number of the functional groups and the polarity of the groups of polymer. In this work the polar fragments of the polymer B-U3000 (ester groups) and the number of carbon atoms of the alkane chains of the acids used in the esterification of the primer polymer are responsible for the lower selectivity rather than for the other polymers' interaction with an alcohol.

Data Correlation. A thermodynamic model such as the nonrandom two-liquid equation, NRTL,[19] is used to correlate

Table 7. Compositions (Mole Fraction) and Boiling Points of the Investigated Binary Azeotropic Systems at Atmospheric Pressure

system	w_1	T_b/K
methanol (1) + THF (2)[a]	0.311	332.3
methanol (1) + THF (2)[b]	0.310	333.9
ethanol (1) + THF (2)[c]	0.063	338.7[d]
methanol (1) + MTBE (2)[e]	0.140	324.3
ethanol (1) + MTBE (2)[e]	0.034	328.1
methanol (1) + ETBE[c]	0.320	330.9
ethanol (1) + ETBE (2)[f]	0.204	338.15[g]

[a] Refs 12, 13. [b] Ref 14. [c] Ref 15. [d] P_{az} = 100.53 kPa. [e] Ref 16. [f] Ref 17. [g] P_{az} = 100.53 kPa.

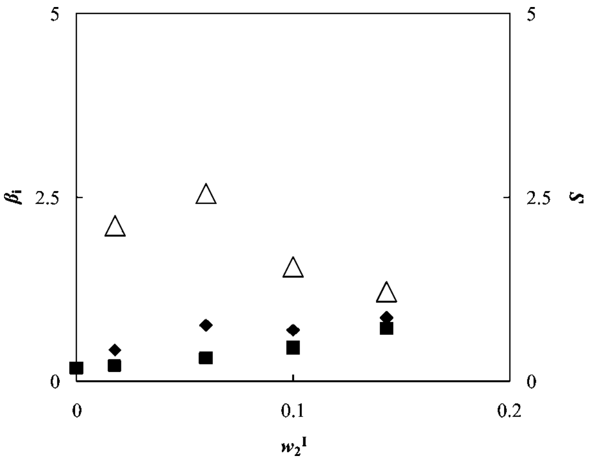

Figure 7. △, selectivity, S; ◆, distribution coefficient β of THF; and ■, ethanol versus mass fraction of THF in the polymer-rich phase I for the LLE ternary system {ethanol (1) + THF (2) + B-U3000 (3)} at $T = 298.15$ K.

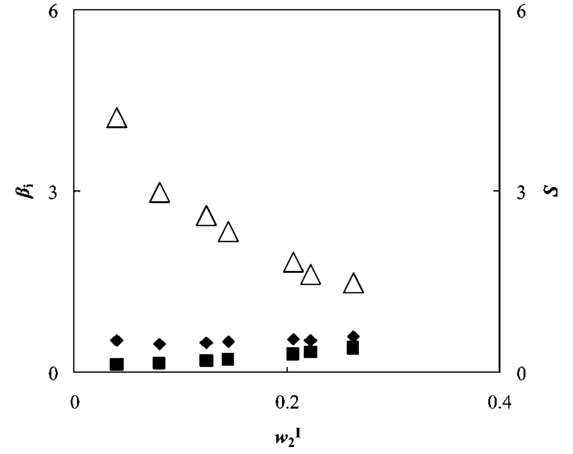

Figure 8. △, selectivity, S; ◆, distribution coefficient β of MTBE; and ■, methanol versus mass fraction of MTBE in the polymer-rich phase I for the LLE ternary system {methanol (1) + MTBE (2) + B-U3000 (3)} at $T = 298.15$ K.

Table 8. Values of Parameters for the NRTL Equation for the Ternary Mixtures {Alcohol (1) + THF or Ether (2) + B-U3000 (3)}

i, j	$g_{ij} - g_{jj}$ J·mol^{-1}	$g_{ji} - g_{ii}$ J·mol^{-1}	α_{ij}	rmsd
	MeOH + THF + B-U3000			
1, 2	3979.97	−3229.96	0.2	0.006
1, 3	13731.89	1728.68		
2, 3	1619.30	1295.10		
	EtOH + THF + B-U3000			
1, 2	−4254.00	6541.97	0.4	0.004
1, 3	8769.89	6400.30		
2, 3	1090.54	−1568.54		
	MeOH + MTBE + B-U3000			
1, 2	−7126.48	13675.00	0.1	0.008
1, 3	26683.04	−4238.35		
2, 3	6812.73	−398.88		
	EtOH + MTBE + B-U3000			
1, 2	−2876.90	23858.62	0.1	0.003
1, 3	10345.23	−2119.17		
2, 3	8684.40	3732.23		
	MeOH + ETBE + B-U3000			
1, 2	−134.62	7430.96	0.2	0.008
1, 3	16553.75	2489.65		
2, 3	1293.69	6463.41		
	EtOH + ETBE + B-U3000			
1, 2	6673.03	−240.15	0.3	0.005
1, 3	9457.44	2600.59		
2, 3	790.94	6609.37		

the experimental data for the six ternary systems discussed here. The equations and algorithms used in the calculation of the compositions of liquid phases follow the method used by Walas.[20] The objective function $F(P)$ was used to minimize the difference between the experimental and the calculated concentrations:

$$F(P) = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle [w_{ij}^{\mathrm{Iexp}} - w_{ij}^{\mathrm{Icalc}}(PT)]^2 + [w_{ji}^{\mathrm{IIexp}} - w_{ji}^{\mathrm{IIcalc}}(PT)]^2 \rangle \tag{3}$$

where P is the set of parameters vector, n is the number of experimental points, w_{ij}^{Iexp} and w_{ji}^{Iexp} and $w_{ij}^{\mathrm{Icalc}}(PT)$ and $w_{ji}^{\mathrm{Icalc}}(PT)$ are the experimental and calculated mass fractions of one phase for $i = 2$ and $j = 3$, and w_{ij}^{IIexp} and w_{ji}^{IIexp} and $w_{ij}^{\mathrm{IIcalc}}(PT)$ and $w_{ji}^{\mathrm{IIcalc}}(PT)$ are the experimental and calculated mass fractions of the other phase.

For the NRTL model, the third nonrandomness parameter, α, was set at optimized values of 0.1, 0.2, or 0.3 (see Table 8). The starting values of the parameters were not known; thus, the calculations were made by the correlation of the experimental points in the ternary systems. The parameters and root-mean-square deviations, rmsd's, calculated in this way are included in Table 8. The rmsd values, which can be taken as a measure of the precision of the correlations, were calculated according to the equation:

$$\mathrm{rmsd} = (\sum_{i} \sum_{l} \sum_{m} [w_{ilm}^{\mathrm{exp}} - w_{ilm}^{\mathrm{calc}}]^2/6k)^{1/2} \tag{4}$$

where w is the mass fraction and the subscripts i, l, and m designate the component, phase, and tie-line, respectively. As can be seen from Table 8 and Figures 1 to 6, the correlations obtained for all systems were acceptable. Because of difficulties in the measurements of the tie-lines in the region close to the plaint point, there were incomplete tie-line points for some systems. This precluded the correlation of binodal curves to the data.

4. Conclusions

Liquid−liquid equilibrium data for six ternary systems {an alcohol + THF or tertiary ether + B-U3000} were determined at $T = 298.15$ K. ^{1}H NMR spectroscopy was used to carry out the analysis of the phases in equilibrium. This technique can quantitatively measure the composition of two components. For the polymer, the mass fraction was determined by difference. The distribution ratios and the selectivity values derived from the tie-lines obtained experimentally indicate that the investigated HBP can be a suitable solvent for the liquid−liquid extraction of THF or tertiary ether from the azeotropic systems with methanol or ethanol with a lower selectivity than those published earlier for ILs. The selectivity is higher than 1 for these systems, whereas when using water as the solvent (the industrially used solvent) it is around 1. The selectivity decreases when the THF or tertiary ether composition increases, which restrains operation to the low THF/ether region. The tie-line data have been correlated with the NRTL model with a maximum rmsd equal to 0.008. The HBP B-U3000 shows immiscibility with methanol and ethanol.

Supporting Information Available:

^{1}H NMR spectra of the {ethanol (1) + THF (2) + B-U3000 (3)} ternary system (in mole fraction). This material is available free of charge via the Internet at http://pubs.acs.org.

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