

# Separation of Azeotropic Mixtures Using Hyperbranched Polymers or Ionic Liquids

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*In this work the suitability of selected commercially available hyperbranched polymers and ionic liquids as entrainers for the extractive distillation and as extraction solvents for the liquid–liquid extraction is investigated. Based on thermodynamic studies on the influence of hyperbranched polymers and ionic liquids on the vapor–liquid and liquid–liquid equilibrium of the azeotropic ethanol–water and THF–water systems, process simulations are carried out, which allow evaluating the potential of hyperbranched polymers and ionic liquids as selective components for the mentioned applications in terms of feasibility and energetic efficiency. Both hyperbranched polymers and ionic liquids break a variety of azeotropic systems. Since their selectivity, capacity, viscosity, and thermal stability can be customized, they appear superior to many conventional entrainers and extraction solvents. For the ethanol–water separation, the nonvolatile substances hyperbranched polyglycerol and  $[EMIM]^+ [BF_4]^-$  show a remarkable entrainer performance and therefore enable extractive distillation processes, which require less energy than the conventional process using 1,2-ethanediol as an entrainer. Evaluation of a new THF–water separation process indicates the competitiveness of the suggested process and a considerable potential of using hyperbranched polymers as extraction solvents. © 2004 American Institute of Chemical Engineers *AIChE J.* 50: 2439–2454, 2004*  
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## Introduction

Hyperbranched polymers (HyPol) and ionic liquids (IL) represent two comparatively unexplored classes of substances, which appear promising for a variety of applications in the field of chemical engineering.

Because of their unique structures and properties, highly

branched, three-dimensional polymers such as *hyperbranched polymers* (Seiler, 2002a, 2004) or *dendrimers* (Inoue, 2000) are attracting increasing attention. Hyperbranched polymers represent highly branched, polydisperse macromolecules with a treelike topology and a large number of functional groups. During the last ten years, the rapidly growing interdisciplinary interest in the globular, highly uniform, and monodisperse dendrimers promoted the rediscovery of hyperbranched polymers. The tedious and complex multistep synthesis of dendrimers results in expensive products with limited use for large-scale industrial applications. For many applications, which do

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not require structural perfection, hyperbranched polymers can circumvent this major drawback of dendrimers. Therefore, during the last three years, a wide variety of applications, which originally seemed conceivable only for dendrimers, were investigated for the statistically branched hyperbranched polymers (Crooks, 2001; Duan et al., 2001; Haag, 2001; Klee et al., 2001; Magnusson et al., 2000; Pitois et al., 2001; Tao et al., 1998; Voit et al., 2002; Gao and Yan, 2004; Seiler, 2004).

Unlike dendrimers, randomly branched hyperbranched polymers with similar properties can be easily synthesized by one-step reactions and therefore represent economically promising substances also for large-scale industrial applications. Companies such as the Perstorp Group (Perstorp, Sweden) and DSM Fine Chemicals (Geleen, The Netherlands) already produce commercially available hyperbranched polymers on a ton scale (for about 8 EUR/kg).

Most of the applications of hyperbranched polymers are based on the absence of chain entanglements and on a large number of functional groups within a molecule. The functional groups of hyperbranched polymers allow for the tuning of their thermal, rheological, and solution properties and thus provide a powerful tool to design hyperbranched polymers for a variety of applications. However, until now, the use of hyperbranched polymers in the field of chemical engineering has remained almost unconsidered. Because the polarity of hyperbranched macromolecules can be adjusted by their functional end groups, selective solvents (consisting of either pure hyperbranched polymers or fractions of hyperbranched polymers) can be designed. Unlike the conventional linear polymers, hyperbranched polymers not only show a remarkable selectivity and capacity (Seiler et al., 2003a; Seiler, 2004), but, because of a lack of chain entanglements, also a comparatively low solution and melt viscosity (Hult et al., 1999; Kim, 1998; Mourey et al., 1992; Pirrung et al., 2002; Wooley et al., 1994) as well as an enormous thermal stability (Hult et al., 1999; Kim et al., 1990). Therefore, hyperbranched polymers can be used for the optimization of a number of separation and production processes. Seiler and Arlt suggested the use of hyperbranched polymers as entrainers for extractive distillation and as selective solvents for liquid–liquid extraction (Arlt et al., 2001a; Seiler, 2002a; Seiler et al., 2004). Furthermore, the use of hyperbranched polymers as selectivity- and capacity-increasing solvent additives for absorption processes, as stationary phases for analytical and even preparative chromatography, and as carriers for the controlled release of drugs seems promising (Seiler et al., 2002d; Seiler, 2004).

*Ionic liquids* (IL) (or room-temperature ionic liquids) are another promising class of synthetic substances, which consist entirely of ions. Unlike conventional salts, IL show melting points lower than 373 K. Usually IL constitute an organic cation and an inorganic anion. IL possess no measurable vapor pressure and are relatively low viscous and generally thermally stable up to 473 K. They have a liquid range of up to 300 K and represent good solvents for a wide range of organic, inorganic, and polymeric materials (Seddon, 1997). Furthermore, they are much less corrosive than conventional high melting salts (Gordon, 2001). Because of their properties, IL are promising candidates for solvents in several industrial processes (Freemantle, 2000).

In synthetic chemistry, IL have been explored as solvents and catalysts. Many reactions performed in IL showed advan-

tages such as enhanced reaction rates, improved selectivity, or easier recycling of the catalysts (Gordon, 2001; Wasserscheid and Keim, 2000; Welton, 1999). IL also represent promising electrolytes for electrochemical applications such as studied by Bonhôte et al. (1996).

Although IL have been known since 1914, the research activities on this topic increased dramatically with the development of the first (nearly) air- and moisture-stable tetrafluoroborate ( $[\text{BF}_4]^-$ )–IL in 1992 (Wilkes and Zaworotko, 1992) and with the commercial availability of IL in 1999 (Solvent Innovation, 2003). However, IL-containing fluorinated anions such as  $[\text{BF}_4]^-$  and  $[\text{PF}_6]^-$  are expensive and show an insufficient stability to hydrolysis for long-term applications (Hilgers and Wasserscheid, 2002). Because of the hydrolysis, they form small amounts of HF, which is corrosive and toxic. For applications of these IL, industrial requirements such as the environmentally acceptable disposal of halogen compounds in considerable quantities also have to be taken into consideration. For these reasons, the recent development of halogen-free and hydrolysis-stable IL such as  $[\text{BMIM}][\text{octylsulfate}]$  (ECOENG<sup>TM</sup> 418) has been carried out (Solvent Innovation, 2003).

At present, commercially available IL are produced on a small scale with a price between 300 and 1800 EUR/dm<sup>3</sup> (Solvent Innovation, 2003). The medium-term production of halogen-free IL on a ton scale is expected to decrease the price to 25–50 EUR/dm<sup>3</sup> (Hilgers and Wasserscheid, 2002).

A prediction concerning the most suitable IL for certain applications is still not possible. However, the increasing comprehension on how the structure of an IL affects its physical properties will allow exploitation of the advantages of IL compared to volatile organic solvents. IL are truly designer solvents. By variation and combination of ions about 10<sup>18</sup> accessible IL can be formed (binary and ternary mixtures included) (Holbrey and Seddon, 1999). This large number of possible IL can be used to optimize production costs and IL properties such as solubility, melting point, and thermal stability.

This work aims to demonstrate the suitability of hyperbranched polymers (HyPol) and ionic liquids (IL) as entrainers for the extractive distillation and as extraction solvents for liquid–liquid extraction. We are the first group that suggested HyPol and IL as selective compounds for the separation of azeotropic mixtures (Arlt et al., 2001a–d). Ternary vapor–liquid and liquid–liquid equilibria of azeotropic systems containing HyPol and IL are presented. Based on the underlying thermodynamic phenomena, the separation of azeotropic mixtures by extractive distillation and solvent extraction is discussed. Process simulations are carried out to evaluate the feasibility and energy demand of the suggested processes and to compare them with conventional separation processes.

## Experiments and Simulations

### Experimental procedures

*Investigations of Phase Equilibria.* The influence of HyPol or IL on the vapor–liquid equilibria (VLE) of selected azeotropic systems was investigated by headspace gas chromatography (HSGC) (Hachenberg et al., 1996). The experimental approach was described previously (Seiler et al., 2002b). The liquid–liquid equilibria (LLE) of the ternary systems HyPol–

THF–water and IL–THF–water were analyzed by phase-separation experiments as well as by visual cloud-point measurements according to the experimental procedure described by our group (Seiler et al., 2003a).

**Materials.** The hyperbranched polymers used are the hyperbranched polyglycerol PG ( $M_n = 1400$  g/mol,  $M_w/M_n = 1.5$ , 20 OH groups per molecule), synthesized and described by Kautz et al. (2001), the hyperbranched polyesteramide Hybrane S1200 ( $M_n = 1200$  g/mol,  $M_w/M_n \approx 5$ , 8 OH groups per molecule, provided by DSM, The Netherlands), and the esterified hyperbranched polyester Boltorn H3200 ( $M_w = 10500$  g/mol,  $M_w/M_n \approx 1.6$ , about 32 esterified OH groups per molecule, provided by Perstorp, Sweden). The phase behavior and further details of the latter hyperbranched polymers are described in detail elsewhere (Kautz et al., 2001; Seiler et al., 2002a, 2003a,b).

The ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate ( $[\text{EMIM}]^+[\text{BF}_4]^-$ , molar mass = 198 g/mol), 1-butyl-3-methyl-imidazolium tetrafluoroborate ( $[\text{BMIM}]^+[\text{BF}_4]^-$ ), 3-octyl-1-methyl-imidazolium tetrafluoroborate ( $[\text{OMIM}]^+[\text{BF}_4]^-$ ), and 1-butyl-3-methyl-imidazolium chloride ( $[\text{BMIM}]^+[\text{Cl}]^-$ ) were provided by Solvent Innovation GmbH (Cologne, Germany). For further IL properties see Solvent Innovation (2003). The purities of the ionic liquids were specified as  $\geq 98\%$ . These IL were dried several days at 363–383 K under vacuum to separate the IL from volatile by-products and humidity.

The solvents ethanol, tetrahydrofuran (THF), and 1,2-ethanediol (ED; solvent purity > 99.8 mol %) were provided by Merck (Darmstadt, Germany) and used as delivered. Distilled water was degassed and repeatedly filtered using a 0.02- $\mu\text{m}$  Millipore (Milford, MA) filter to remove dust.

### Process simulation

In this work, process simulations were carried out using the Aspen Plus<sup>®</sup> simulator (V.11.1) of Aspen Technology, Inc. (Cambridge, MA).

The nonvolatility of HyPol and IL was taken into account by fitting the parameters of Aspen's extended Antoine equation to imaginary values of negligibly small vapor pressures. The temperature dependency of the specific isobaric heat capacity  $c_p$  of a HyPol or a IL could be described well by fitting the parameters of a polynomial equation (see Eq. 6 below, Table 2) to experimental differential scanning calorimetry (DSC) data, determined for a temperature range from 293 to 443 K.

The VLE for the extractive distillation processes investigated, were modeled by the common nonrandom two liquids (NRTL) model (Renon and Prausnitz, 1968); that is, because of simplicity, the ionic liquid  $[\text{BMIM}]^+[\text{BF}_4]^-$  was treated like a nondissociating component. The assumption of an ideal vapor phase was made. Therefore, the investigated VLE could be described by the liquid concentrations, the activity coefficients, and the vapor pressures of the pure substances. The phase behavior of the ternary system THF–water–hyperbranched polyester was modeled using the POLYNRTL (Polymer Non-Random Two-Liquid) model (Chen, 1993). Both the NRTL and the POLYNRTL parameters were fitted to several experimental equilibrium data sets, so that the  $x$ -,  $T$ -, and  $P$ -ranges of interest were reflected well. After the determination of the process operating conditions (see below), further energetic process optimizations such as heat integration were investi-

**Table 1. Separation Task for Extractive Distillation: Fixed Parameters and Process Variables to Be Optimized**

Fixed Parameters			Process Variables
Main column			<b>Main column</b>
Operating pressure, Pa	$1.013 \times 10^5$		Reflux ratio
Theoretical stages	28		Entrainer flow rate
Feed			Entrainer input stage
Flow rate, kmol/h	200		Feed stage
$x_{\text{ethanol}}$	0.7		Entrainer purity
$x_{\text{water}}$	0.3		
Condition	Boiling liquid		
$T_{\text{entrainer}}$ , K	348.15		<b>Entrainer regeneration unit(s)</b>
Distillate			Entrainer purity
Flow rate, kmol/h	140		Operating pressure
$x_{\text{ethanol}}$	0.998		Operating temperature
$x_{\text{entrainer}}$	<0.0001		Reflux ratio
			Flow rate of dry air
			Heat duties

gated. The operability of the distillation columns in terms of feasible gas and liquid loads was checked.

**Extractive Distillation.** To evaluate the potential of using HyPol and IL as new nonvolatile entrainers for the separation of the azeotropic ethanol–water mixture by extractive distillation, a process consisting of a main column and an entrainer regeneration unit was designed, energetically optimized, and compared with a conventional extractive distillation process using 1,2-ethanediol as an entrainer. While the entrainer regeneration of the HyPol and the IL process was carried out by combining a flash drum with an air-operated, atmospheric stripping column (see Figure 7), the 1,2-ethanediol regeneration was simulated using a distillation column operated at 10 kPa.

The separation task reads as follows: a preconcentrated saturated liquid feed (200 kmol/h), consisting of 70 mol % ethanol and 30 mol % water, is to be separated by extractive distillation in such a way that the ethanol purity of the distillate (140 kmol/h) amounts to 99.8 mol % and a minimum of energy is used. For the determination of the minimum energy demand of the respective extractive distillation process, the following variables had to be optimized: (1) entrainer flow rate, (2) reflux ratio, (3) entrainer feed stage, (4) ethanol/water feed stage, (5) temperature and pressure of the entrainer regeneration unit(s), and (6) air flow and air temperature of the stripping column.

Table 1 summarizes the separation task and gives an overview of the fixed separation parameters and the process variables to be optimized. Product cooling and energy loads for air compression and air drying have not been considered (that is, dry air is used as stripping medium).

**Solvent Extraction.** The potential of using the hyperbranched polyester Boltorn H3200 as extracting agent for the separation of the azeotropic THF–water system was investigated by designing a process, which combines a solvent extraction unit with distillation steps (see Figure). A 50 wt % THF/50 wt %  $\text{H}_2\text{O}$  mixture of 1000 kg/h is to be separated. The purity requirements were set to  $x_{\text{THF}} = 0.999$  for the THF product and  $x_{\text{water}} = 0.999$  for the water product. The minimum usage of hot and cold utilities was ensured by optimizing the following process parameters (remarks refer to Figure 9;  $w$ : weight fraction,  $x$ : mol fraction):

- Recycle flow rates: The THF (product)-containing recycle

flow rates have to be minimized. Because the distillate of the two columns is characterized by an azeotrope-like THF–water mixture, the amount of water in the respective column feed has to be minimized, that is, the amount of bottom product (water) from the *water column* should be as large as possible.

- Mixing point of the liquid–liquid extraction unit: For a minimization of the recycle flow rates the location of the overall mixing point of the liquid–liquid extraction unit (see Figure 5) has to be optimized. The location of the mixing point and the corresponding tie line determine the compositions, viscosity, and settling time of the coexisting liquid phases.

- Reflux ratio and number of theoretical separation stages in the columns.

- Location of the feed-stage of the columns.

- Operating conditions ( $T$ ,  $P$ ) of the distillation columns and the flash drum. The choice of the operating conditions of the distillation columns and the flash drum should take into account the thermal stability of the (hyperbranched) extraction solvent Boltorn H3200, which degrades at  $T > 520$  K. Furthermore, the condensation of the THF product should be feasible at ambient temperature.

- The viscosity of the bottom product of the flash (polymer recycle) should be reduced by choosing an appropriate stream temperature and residual THF fraction.

## Results and Discussion

### *Influence of hyperbranched polymers and ionic liquids on the phase behavior of azeotropic systems*

**Vapor–Liquid Equilibria.** Figures 1 and 2 illustrate the influence of selected HyPol and IL on the VLE of the azeotropic systems ethanol–water and tetrahydrofuran (THF)–water. The hyperbranched polyglycerol PG and the hyperbranched polyesteramide Hybrane S1200 selectively interact with water (Figure 1). The formation of hydrogen bonds between polymer and water molecules leads to a decrease in the water activity and thus to a relative volatility of ethanol (Figure 1A) or THF (Figure 1B), which increases with PG or Hybrane S1200 concentration. For the latter hyperbranched polymers, at a polymer weight fraction around  $w_{\text{polymer}} \approx 0.3$  the azeotropic system behavior is broken, indicating the potential of using HyPol as entrainers in the field of extractive distillation. Unlike the latter polymers, the addition of 70 wt % of the hyperbranched polyester Boltorn H3200 results in a decrease of the relative THF volatility and a corresponding shift of the azeotropic point to smaller THF concentrations (see Figure 1B). Further details concerning the phase behavior of hyperbranched polymer solutions can be found elsewhere (Seiler, 2004).

In accordance with the HyPol samples PG and Hybrane S1200, because of selective interactions, also the IL  $[\text{EMIM}]^+[\text{BF}_4]^-$ ,  $[\text{BMIM}]^+[\text{Cl}]^-$ ,  $[\text{BMIM}]^+[\text{BF}_4]^-$ ,  $[\text{OMIM}]^+[\text{BF}_4]^-$ , substantially decrease the water activity and break the azeotropic behavior of the ethanol–water and the THF–water systems (see Figure 2). As recently shown, imidazolium-based IL, which are composed of small anions and small cations, exhibit the best entrainer performance with respect to the investigated aqueous azeotropic mixtures (Jork et al., 2003a). The influence of the conventional entrainer 1,2-ethanediol (ED) on the ethanol–water VLE is compared in detail with those of selected HyPol (such as PG) and

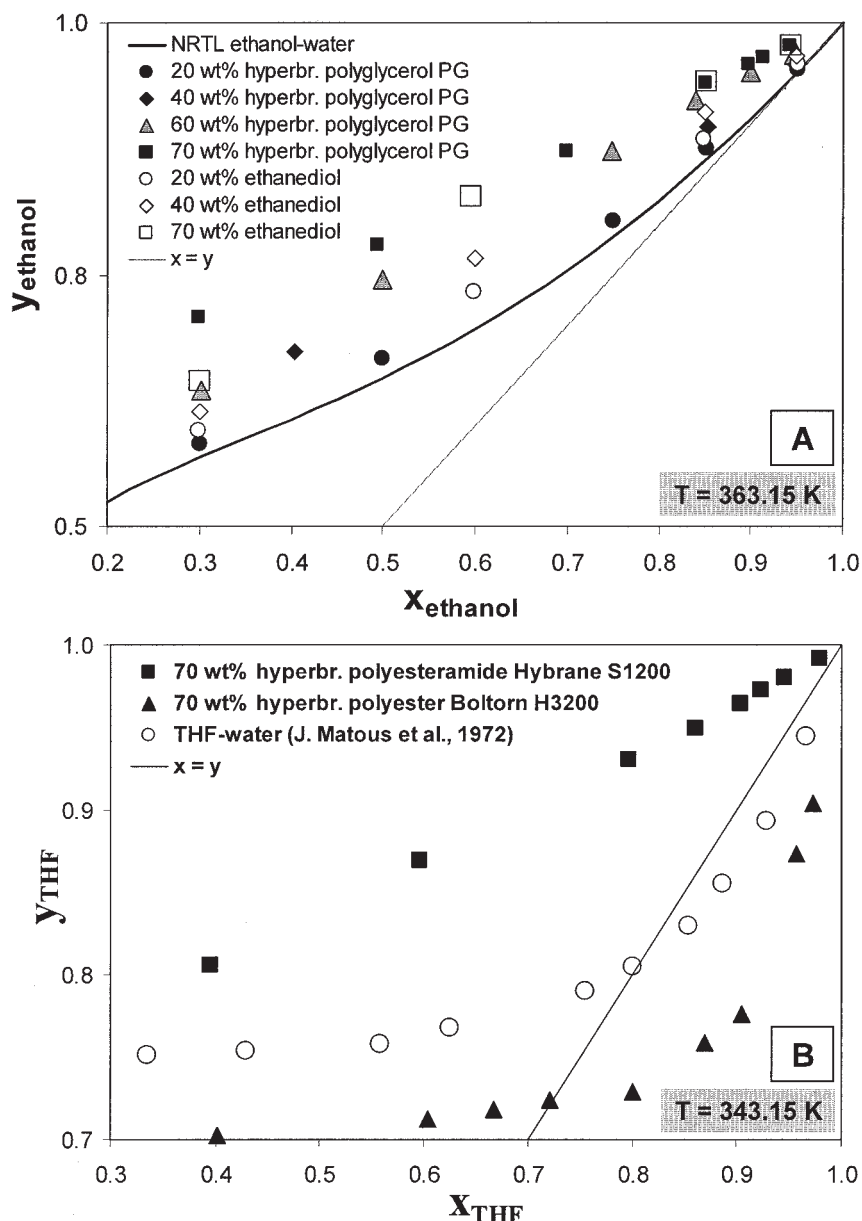
IL (such as  $[\text{EMIM}]^+[\text{BF}_4]^-$ ) elsewhere (Seiler et al., 2002b,c, 2003a; Jork et al., 2003b).

For the simulation of the separation of ethanol–water by extractive distillation using the hyperbranched polyglycerol PG or the ionic liquid  $[\text{EMIM}]^+[\text{BF}_4]^-$  as new nonvolatile entrainers, an extensive thermodynamic basis was created by fitting the NRTL parameters of the entrainer–ethanol and the entrainer–water systems to a variety of experimental binary and ternary VLE data sets (PG data sets at: 343.15, 363.15, 371.15, 373.15, and 393.15 K;  $[\text{EMIM}]^+[\text{BF}_4]^-$  data sets at: 343.15, 363.15, 373.15, 378.15, 383.15, and 403.15 K). The authors are aware of the fact that the  $g^E$  model chosen does not account for ions. However, the results can be considered as a good mathematical approximation. To enable a comparison between the suggested nonvolatile entrainers and the conventional entrainer ED, NRTL parameters were also determined for the VLE ED–water and ED–ethanol according to the procedure described elsewhere (Seiler et al., 2002c). Furthermore, the NRTL parameters for the ethanol–water system were determined by fitting them to four selected binary VLE data sets from the literature (343.15 and 363.15 K: Pemberton and Mash, 1978; 423.15 K: Barr-David and Dodge, 1959;  $10^5$  Pa: Rieder and Thompson, 1949). This procedure allowed for an accurate description of the underlying phase behavior over the temperature and concentration range of interest. Figures 3 and 4 show selected regression results for the systems entrainer–ethanol–water, entrainer–water, and entrainer–ethanol (entrainer of Figure 3: PG; entrainer of Figure 4:  $[\text{EMIM}]^+[\text{BF}_4]^-$ ). For the accuracy of the Aspen Plus® simulation it is of prime importance that the binary entrainer–water VLE, that is, the partial pressure curve of water (see Figures 3C and 4B), can also be described well by the  $g^E$  model chosen because it dominates the entrainer regeneration and the conditions in the lower stripping section of the main column. As seen in Figures 3 and 4, a good agreement between the experimental and the NRTL results is achieved (NRTL parameters, see Table 2). In particular, the ternary VLE for the relevant entrainer concentration range of the main column ( $30 \text{ wt } \% < w_{\text{PG}} < 70 \text{ wt } \%$ ;  $30 \text{ mol } \% < x_{\text{EMIM BF}_4} < 65 \text{ mol } \%$ ; see Figures 3A and 3B and 4A) and the binary entrainer–water VLE at  $10^4 \text{ Pa} \leq P_{\text{regeneration unit}} \leq 10^5 \text{ Pa}$  (see Figures 3C and 4B) can be described well.

The solution viscosities of the  $[\text{EMIM}]^+[\text{BF}_4]^-$ –ethanol–water mixture and the PG–ethanol–water mixture are slightly higher than those for conventional entrainer–ethanol–water mixtures. However, the solution viscosities are still far below the acceptable distillation limit of  $100 \text{ mPa s}^{-1}$ , a barrier above which the number of required transfer units drastically increases and the manageability of the separation becomes increasingly difficult (Böcker and Ronge, 2003). At 343 K (that is, more than 50 K below the bottom temperature and more than 15 K below the temperature at the entrainer feed stage of the main column), the dynamic viscosity of a binary PG–water solution amounts to 70 mPa s at 70 wt % PG (Seiler et al., 2004). The solution viscosity of the  $[\text{EMIM}]^+[\text{BF}_4]^-$ –water solution is even smaller (Jork et al., 2003b).

**Liquid–Liquid Equilibria.** Figures 5 and 6 show the phase behavior of the ternary systems THF–water–Boltorn H3200 at 321.15 K and THF–water– $[\text{EMIM}]^+[\text{BF}_4]^-$  at 337.15 K.



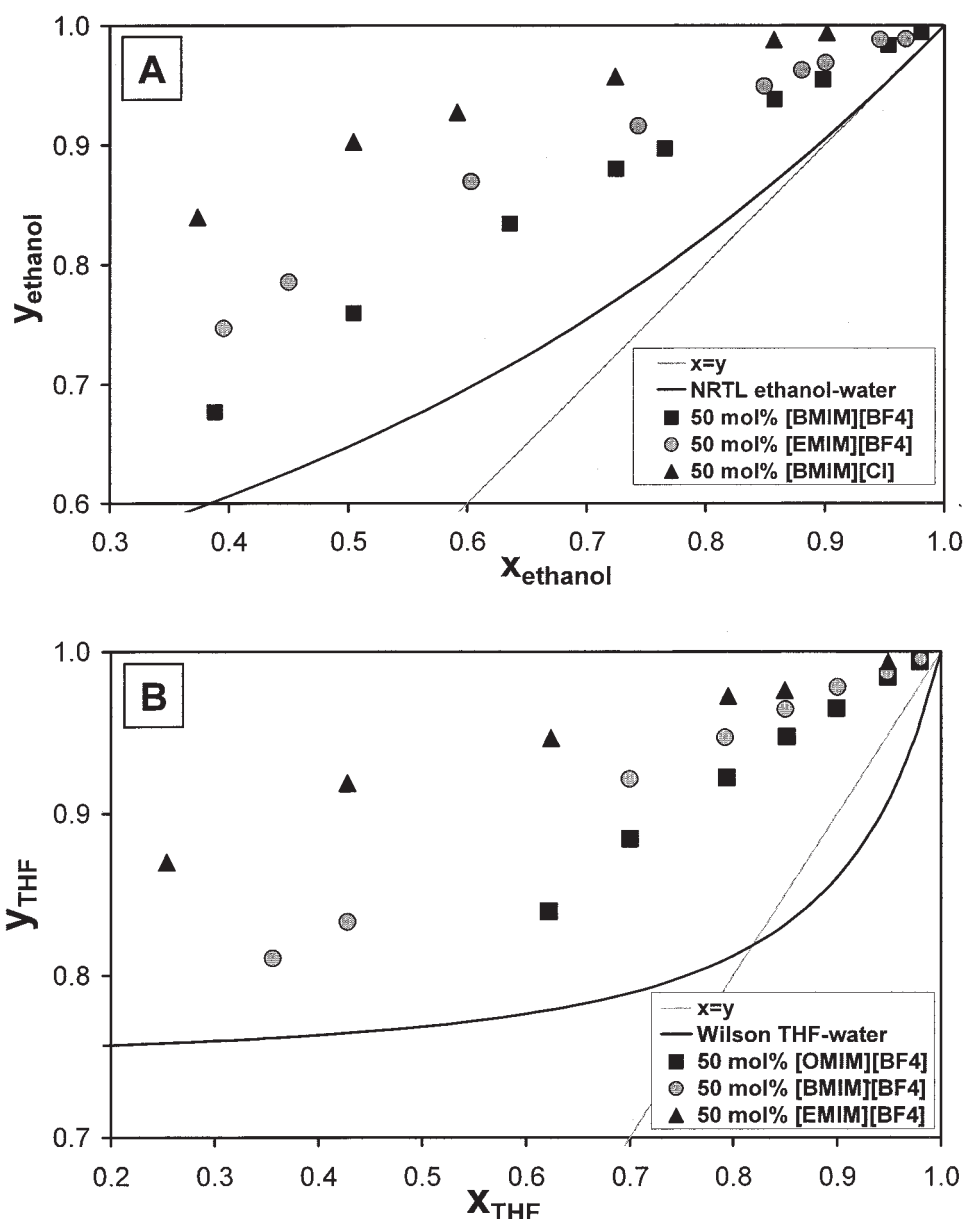


**Figure 1. Influence of hyperbranched polymers on the VLE of azeotropic systems (Seiler et al., 2002b, 2003c).**

(A) Ethanol–water–hyperbranched polyglycerol PG at 363.15 K; (B) THF–water–hyperbranched polyesteramide Hybrane S1200 and THF–water–hyperbranched polyester Boltorn H3200 at 343.15 K.

Because of the esterified hydroxyl groups of the hyperbranched polyester, a broad area of immiscibility originates from the binary system Boltorn H3200–water (Figure 5). As indicated by the run of the LLE tie lines, a remarkably distinct solutropic effect can be observed. Focusing on the LLE, the compositions of the polymer-rich phase confirm the breaking of the THF–water azeotrope ( $w_{\text{THF, azeotrope}} = 0.942$  at  $10^5$  Pa), indicating a possible application of Boltorn H3200 as extraction solvent for the THF–water separation (Seiler et al., 2003a). From the fitting of the polymer–NRTL model (Chen, 1993) to binary VLE and ternary LLE data, parameters were obtained (see Table 3), which reflect both the width of the liquid–liquid miscibility gap and the solutropic phase phenomenon (see Figure 5).

Moreover, the liquid–liquid miscibility gap of the binary THF–[EMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>−</sup> system at 337.15 K (Figure 6) can be used for a THF–water separation by solvent extraction. The addition of up to 15 mol % [EMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>−</sup> to a preconcentrated binary THF–water solution (such as 75 mol % THF, 25 mol % water) causes a phase split. Although the upper phase contains about 92 mol % of THF, 8 mol % of water, and only traces of IL, the lower phase consists of about 30 mol % [EMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>−</sup>, 40 mol % water, and 30 mol % THF. Figure 6 indicates the potential of ionic liquids as extraction solvents, particularly when taking into account that the IL used has not been optimized for this separation problem. The optimization of the IL's selectivity by the change of its structure allows for the tailoring of the size of the LL-miscibility gap, and thus to



**Figure 2.** Influence of selected ionic liquids ([EMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup>, [BMIM]<sup>+</sup>[Cl]<sup>-</sup>, [BMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup>, [OMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup>) on the VLE of azeotropic systems (Jork et al., 2003a; Seiler et al., 2002c).

(A) Ethanol-water-IL at 363.15 K. (B) THF-water-IL at 337.15 K.

meet industrial requirements for applications in the field of solvent extraction.

### Extractive distillation

The potential of the suggested nonvolatile entrainers PG and [EMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> for the ethanol-water separation was evaluated by Aspen Plus<sup>®</sup> process simulations. The investigated process is depicted in Figure 7. Based on the separation task defined above, the ethanol-water feed is separated by an extractive distillation main column and entrainer regeneration units. For the regeneration of a nonvolatile entrainer a variety of unit operations are feasible (Seiler et al., 2003a). In this context, from an energetic perspective, one of the most prom-

ising regeneration options is the combination of a flash drum and an atmospheric stripping column. The flash drum, operated at  $P_{\text{flash}} = 10^4$  Pa and an optimized temperature  $T_{\text{flash}}$  (see Table 3), allows for a preconcentration of the nonvolatile entrainer. The remaining water fractions are separated from the entrainer using an adiabatic stripping column at  $P = 1.013 \times 10^5$  Pa without reboiler and condenser. Dry air ( $P = 1.013 \times 10^5$  Pa,  $T = 293.15$  K) is used as the stripping medium. Subsequently, the regenerated entrainer ( $x_{\text{entrainer}}$ ,  $T_{\text{entrainer}}$ ; see Table 3) is recycled to the main column (Figure 7). In Figure 8 and Table 3 this process is compared with a conventional extractive distillation process using ED as entrainer. The main column is operated at  $1.013 \times 10^5$  Pa and the ED regeneration

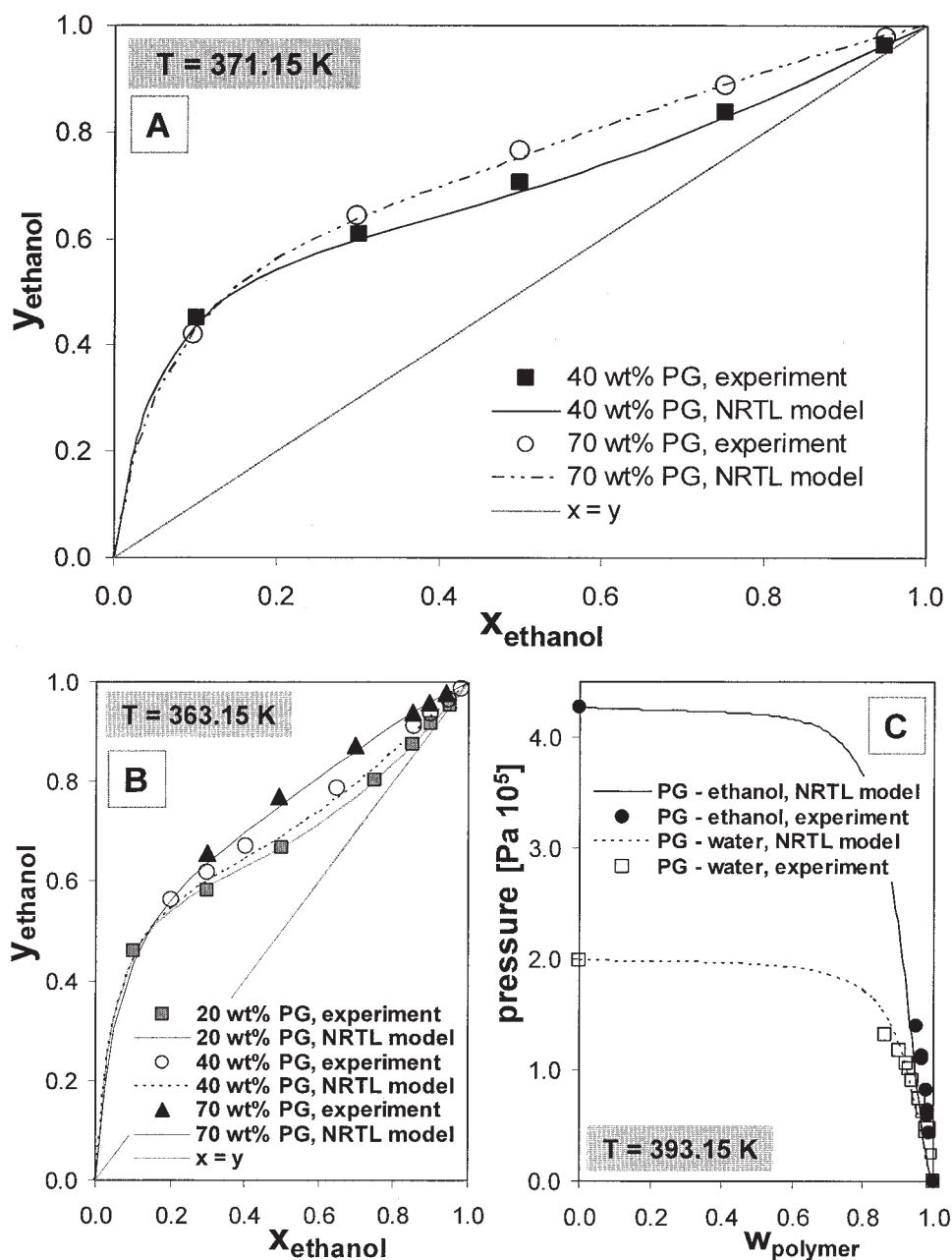


Figure 3. NRTL results for the systems ethanol–water–PG (at 371.15 and 363.15 K), ethanol–PG at 393.15 K, and water–PG at 393.15 K.

at  $10^4 \text{ Pa}$ . Apart from a possible reduction of the required hot and cold process utilities, there is a threefold advantage of using a nonvolatile entrainer:

- (1) The entrainer cannot pollute the distillate.
- (2) No main column separation section and internals are needed for the separation of the entrainer from the high volatile (ethanol) product.
- (3) A variety of entrainer regeneration options is feasible.

Figure 8 and Table 3 show the process simulation results for each entrainer. In comparison to the conventional entrainer ED, the minimum reboiler heat duty of the PG–main column and the  $[\text{EMIM}]^+[\text{BF}_4]^-$ –main column is slightly smaller (see Fig-

ure 8A). This is attributed to a difference in the bottom temperature of the respective main column (given by the binary entrainer–water VLE) and/or a difference of the minimum reflux ratios. Although the entrainer flowrate on a mass basis (*not* on a mol basis; note the different molar masses of the entrainers) and the specific heat capacity are smaller for ED, the important term of the energy balance for the main column  $\dot{n}_{\text{bottoms,mix}} \times c_{P,\text{mix}}^{\text{at } T_{\text{bottoms}}} \times T_{\text{bottoms}}$  is larger for the conventional ED process than for the PG or  $[\text{EMIM}]^+[\text{BF}_4]^-$  process ( $\dot{n}_{\text{bottoms,mix}}$ : mol flow of bottom stream;  $c_{P,\text{mix}}^{\text{at } T_{\text{bottoms}}}$ : isobaric heat capacity of the bottom stream at bottom temperature;  $T_{\text{bottoms}}$ : temperature of the bottom stream). With regard

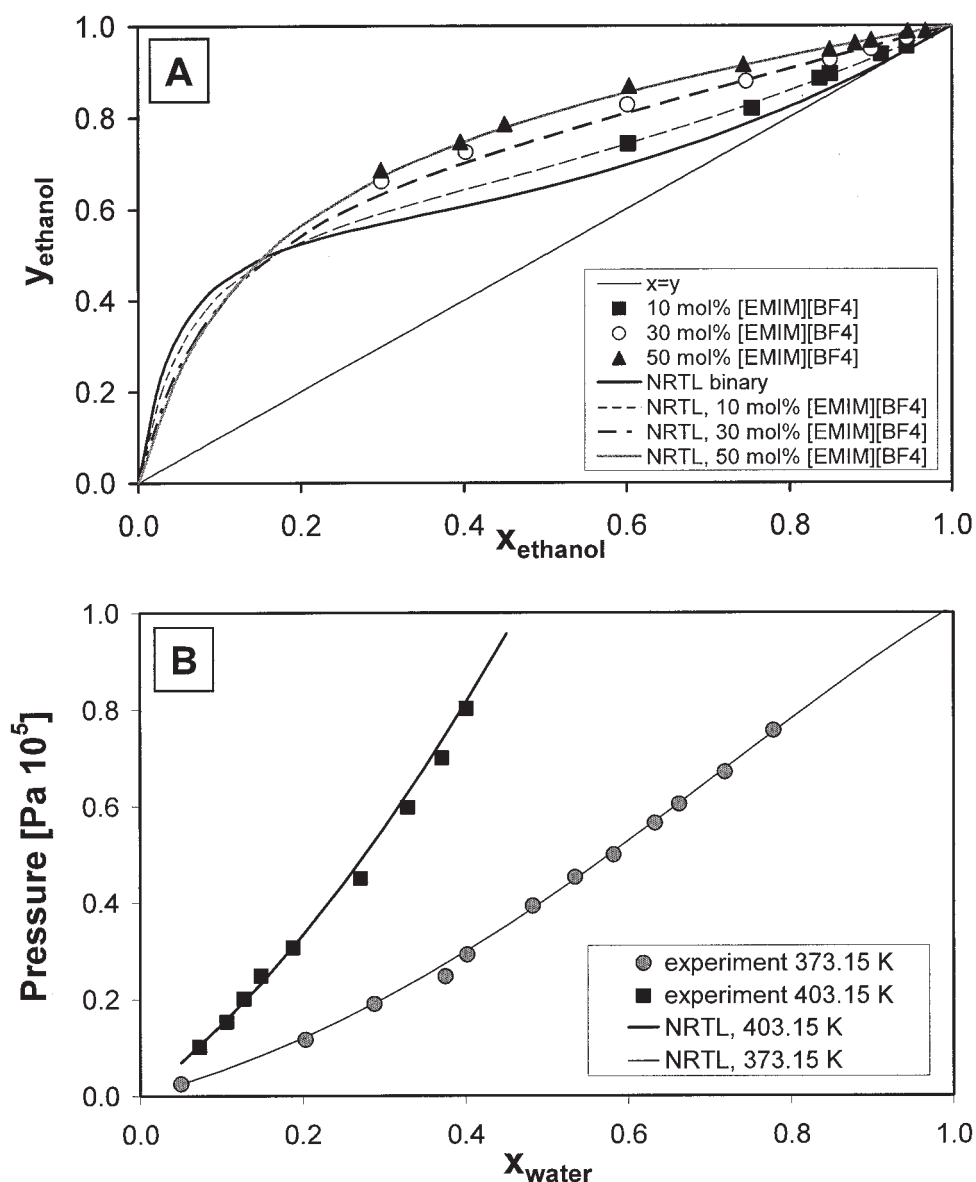


Figure 4. NRTL results for the systems ethanol-water-[EMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> at 363.15 K, and water-[EMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> at 373.15 and 403.15 K.

to the required hot and cold utilities for the entrainer-water separation, the unit combination for the regeneration of the suggested nonvolatile entrainers, consisting of a flash drum and an air-operated atmospheric stripping column, resulted in heat duties that are considerable smaller than the one for ED regeneration by distillation at  $10^4$  Pa (see Figure 8B and Table 3). When composing the overall heat duty curve for the respective entire distillation process as a function of the entrainer flow rate (Figure 8C) it becomes obvious, that (under the defined conditions) the minimum overall heat duty of the ED process amounts to 3959 kW or 2213 kJ/kg ethanol at an optimum ED flow rate of 180 kmol/h or 11,172 kg/h.

Unlike the ED process, the use of the suggested nonvolatile entrainers requires larger entrainer flow rates. There are various coherences that may cause higher investment costs with increasing entrainer flow rates. Thus, the smallest over-

all heat duty of the PG or the [EMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> process would be achieved at great cost when using the highest entrainer flow rate. Therefore, we defined a (subjective) optimum flow rate of PG or [EMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> at that point, for which an increase in entrainer flow rate does not lead to a further change in the gradient of the overall heat duty curve (see Figure 8C). Based on this definition, an optimum PG flow rate of 7.25 kmol/h or 14,500 kg/h corresponds to an overall heat duty of 3747 kW. An increase of the PG flow rate to 30,000 kg/h would reduce the overall heat duty of 15% to 3165 kW or 1769 kJ/kg ethanol. The optimum flow rate of [EMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>-</sup> amounts to 100 kmol/h or 19,800 kg/h and corresponds to a remarkable overall heat duty of 3171 kW or 1772 kJ/kg ethanol.

Compared to the conventional ED process, the maximum saving in overall heat duty amounts to 19% for the PG



Table 2. Simulation Parameters Used\*

NRTL/Polymer NRTL parameters (see Eqs. 1–4)			
component <i>i</i>	ethanol	ethanol	water
component <i>j</i>	water	PG	PG
$a_{ij}$	−2.15	3.96	2.85
$a_{ji}$	4.54	−0.90	−3.17
$b_{ij}$	683.91	1724.63	160.46
$b_{ji}$	−917.85	−1292.40	−832.29
$c_{ij}$	0.3	0.3	0.3
component <i>i</i>	ethanol	ethanol	water
component <i>j</i>	water	[EMIM] <sup>+</sup> [BF <sub>4</sub> ] <sup>−</sup>	[EMIM] <sup>+</sup> [BF <sub>4</sub> ] <sup>−</sup>
$a_{ij}$	−2.15	1.52	0
$a_{ji}$	4.54	2.22	0
$b_{ij}$	683.91	−188.97	−91.22
$b_{ji}$	−917.85	−949.13	−198.41
$c_{ij}$	0.3	0.3	0.3
component <i>i</i>	ethanol	ethanol	water
component <i>j</i>	water	1,2-ethanediol	1,2-ethanediol
$a_{ij}$	−2.15	0.97	−1.54
$a_{ji}$	4.54	−2.22	1.07
$b_{ij}$	683.91	−336.51	155.68
$b_{ji}$	−917.85	900.70	−19.5
$c_{ij}$	0.3	0.3	0.3
component <i>i</i>	tetrahydrofuran	tetrahydrofuran	water
component <i>j</i>	water	Boltorn H3200	Boltorn H3200
$a_{ij}$	1.21	0	0
$a_{ji}$	4.76	0	0
$b_{ij}$	157.78	−10,000.0	1542.08
$b_{ji}$	−733.40	−4105.79	4451.84
$c_{ij}$	0.47	0.2	0.2

All remaining Polymer NRTL parameters are set to their default value in Aspen Plus.

#### Vapor pressure parameters (see Eq. 5)

$P_{oi}^{LV}$ parameters	PG	[EMIM] <sup>+</sup> [BF <sub>4</sub> ] <sup>−</sup>	Boltorn H3200
	<i>T</i> in K, <i>P</i> in 10 <sup>5</sup> Pa	<i>T</i> in K, <i>P</i> in 10 <sup>5</sup> Pa	<i>T</i> in °C, <i>P</i> in 10 <sup>5</sup> Pa
$D_1$	−294.22	6.02	−294.22
$D_2$	66420.46	−5196.34	66420.46
$D_3$	594.07	−88.63	594.07
$D_4$	$−3.71 \times 10^{-3}$	0	$−3.71 \times 10^{-3}$
$D_5$	35.73	0	35.73
$D_6$	$1.08 \times 10^{-7}$	0	$1.08 \times 10^{-7}$
$D_7$	−22.24	0	−22.24

#### Parameters for the specific isobaric heat capacity (see Eq. 6)

$c_p$ parameters	PG	[EMIM] <sup>+</sup> [BF <sub>4</sub> ] <sup>−</sup>	Boltorn H3200
	$c_p$ in J/(kmol K), <i>T</i> in K	$c_p$ in kJ/(kmol K), <i>T</i> in °C	$c_p$ in kJ/(kmol K), <i>T</i> in K
$C_1$	−500.0	287.72	−1000.0
$C_2$	−500.0	−0.27	−10.0
$C_3$	509.46	$+3.7 \times 10^{-3}$	0.94
$C_4$	−3.64	$−1.36 \times 10^{-5}$	$−3.01 \times 10^{-3}$
$C_5$	0.01	$1.5 \times 10^{-8}$	$2.94 \times 10^{-6}$
$C_6$	$−8.47 \times 10^{-6}$	0	0

•NRTL and POLYNRTL parameters using Eqs. 1–4:

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} + e_{ij} \ln T + f_{ij} T \quad (1) \quad \tau_{ij} = \frac{\Delta g_{ij}}{T} \quad \tau_{ii} = 0 \quad (2a,b)$$

$$\alpha_{ij} = c_{ij} \quad (3) \quad G_{ij} = \exp(-\alpha_{ij} \tau_{ij}), \quad G_{ii} = 1 \quad (4a,b)$$

•Vapor pressure  $P_{oi}^{LV}$  according to  $\ln P_{oi}^{LV} = D_1 + \frac{D_2}{T + D_3} + D_4 T + D_5 \ln T + D_6 T^{D_7}$  (5)

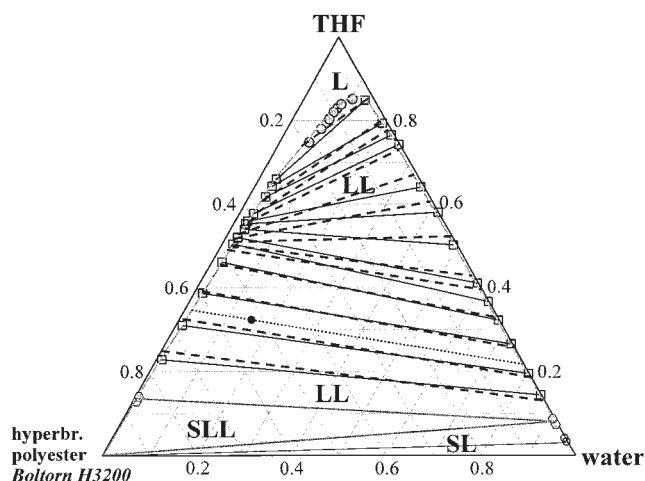
•Specific isobaric heat capacity  $c_p$  according to  $c_p = C_1 + C_2 T + C_3 T^2 + C_4 T^3 + C_5 T^4 + C_6 T^5$  (6)

\*NRTL parameters for the VLE of the ethanol–water–entrainer systems (extractive distillation), POLYNRTL parameters for the phase behavior of the THF–water–Boltorn H3200 system (LL extraction), Antoine parameters, and  $c_p$  parameters of PG, [EMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>−</sup>, and Boltorn H3200.

process (at 30,000 kg/h PG) and to 24% for the [EMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>−</sup> process (at 23,760 kg/h [EMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>−</sup>). The most important results and process parameters are summarized in Table 3. It is worth mentioning that the suggested nonvolatile entrainers represent chemically and structurally nonoptimized compounds. The recently investigated ionic liquid [BMIM]<sup>+</sup>[Cl]<sup>−</sup> (see Figure 2A) indicates that a fur-

ther reduction of the required process heat duties is easily possible, especially when taking advantage of the powerful tool to design a specific HyPol or IL entrainer for a certain separation problem.

The pinch analysis for the respective extractive distillation process showed that heat integration measures are of limited use for a further reduction of the overall heat duties.



**Figure 5.** Ternary phase diagram of the system THF–water–hyperbranched polyester Boltorn H3200 at 321.15 K (Seiler et al., 2003a) and POLYNRTL-calculated tie lines (dashed lines).

Dotted line: tie line corresponding to overall mixing point; black filled circle: overall mixing point; concentrations in weight fractions, polymer:  $M_w = 10,500$  g/mol,  $M_w/M_n = 1.6$ .

Unlike such high purity process feeds, for the separation of fermentation broth, considerable energy reductions are possible using heat integration, as shown by Knapp and Doherty (1990).

#### Liquid–liquid extraction using hyperbranched polymers as extraction solvent

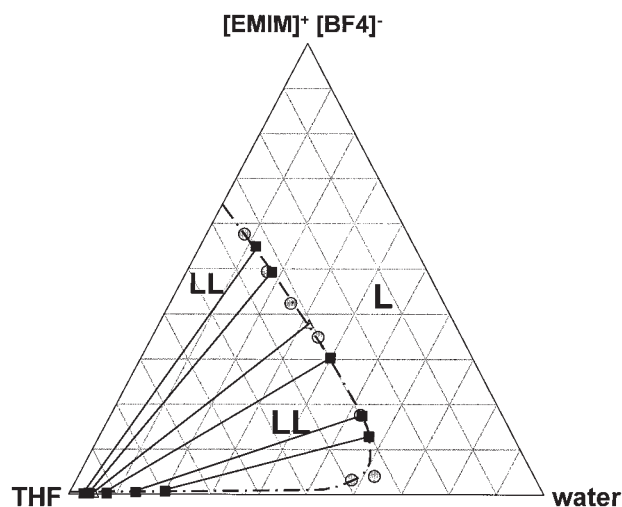
Another azeotropic system of industrial importance represents the mixture of THF and water. THF is produced by dehydrocyclization of 1,4-butanediol in the presence of an acid catalyst. The key step in purification is the breaking of the THF–water azeotrope (Chang and Shih, 1989). Generally, this is achieved by pressure-swing distillation (low/high pressure), extractive distillation, or azeotropic distillation.

Based on the LLE results of Figure 5, different process options for the THF–water separation using HyPol as extraction solvents are conceivable (Seiler et al., 2003a). Energetic optimizations of the latter process options by means of a pinch analysis (see below) and comparison with conventional THF–water separation processes, indicate a noteworthy potential for the separation process illustrated in Figure 9. A 50 wt % THF/50 wt % H<sub>2</sub>O mixture of 1000 kg/h is fed into a mixer–settler. A specific amount of the extraction solvent, the hyperbranched polyester Boltorn H3200, is added to the THF–water mixture so that the (dotted) tie line corresponding to the overall mixing point of Figure 5 is met (overall mixing point:  $w_{\text{THF}} = 32.5$ ,  $w_{\text{Pol}} = 52.5$ ,  $w_{\text{water}} = 0.15$ ). It is worth mentioning that the choice of the overall mixing point and of the continuous phase is of considerable importance for the viscosity of the coexisting phases and their settling time. The larger the THF fraction of the polymer-rich phase, the smaller is the solution viscosity. At 317.15 K, the solution splits into the two liquid phases L1 and L2. Because of the large THF solubility in the polymer-rich phase L1 and its remarkable low density, the polymer-rich phase represents the upper and the water-rich

(polymer-free) phase L2 the lower phase (see also Figure 9). As described elsewhere (Seiler et al., 2003a), the THF–water ratio of the polymer-rich phase L1 is larger than the azeotropic THF–water concentration ( $w_{\text{THF, azeotrope}} = 0.942$  at  $P = 10^5$  Pa). Therefore, when feeding L1 into an atmospheric distillation column (see Figure 9, THF column), the column's feed composition is located at the righthand side of the THF–water minimum boiling azeotrope (see Figure 1B). As shown in Figure 1B, because of the presence of Boltorn H3200, the azeotropic point shifts to smaller THF concentrations. Thus, the composition of the overhead product of the THF column corresponds to the new location of the shifted minimum boiling azeotrope. The bottom product of the THF column contains the remaining THF and all of the polymer. The latter THF–polymer mixture is separated in a flash drum into the THF product ( $x_{\text{THF}} = 0.999$ ) and a concentrated polymer flow (for process parameters see Table 4). Because of remaining THF fractions and a temperature far above the melting temperature of Boltorn H3200 ( $T_{\text{melt, Boltorn H3200}} \approx 333$  K), the concentrated polymer flow still represents a pumpable mixture of acceptable viscosity, which is recycled to the extraction unit. At  $3 \times 10^4$  kPa, the water column (see Figure 9) separates the polymer-free phase L2 within three theoretical stages into water as the bottom product and the THF–water minimum boiling azeotrope as the overhead product. Both distillation columns do not require a rectifying section. The purification of the extract and the raffinate could also be achieved by combining the extraction unit with crystallization steps (Seiler et al., 2004).

**Pinch Analysis.** The process conditions for the separation task described above represent the basis of investigations regarding the possibilities to reduce the energy demand of the designed process (Figure 9). This is done by using the pinch technology presented by Linnhoff (Linnhoff and Lenz, 1987; Linnhoff et al., 1992) and Aspen Pinch<sup>®</sup> (V11.1) from Aspen Technology Inc.

The composite curve of the developed process is given in Figure 10A showing the hot and cold process streams. With the assumption of a minimum temperature difference  $\Delta T_{\text{min}} = 10$



**Figure 6.** Ternary phase diagram of the system THF–water–[EMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>−</sup> at 337.15 K (Jork et al., 2003a).

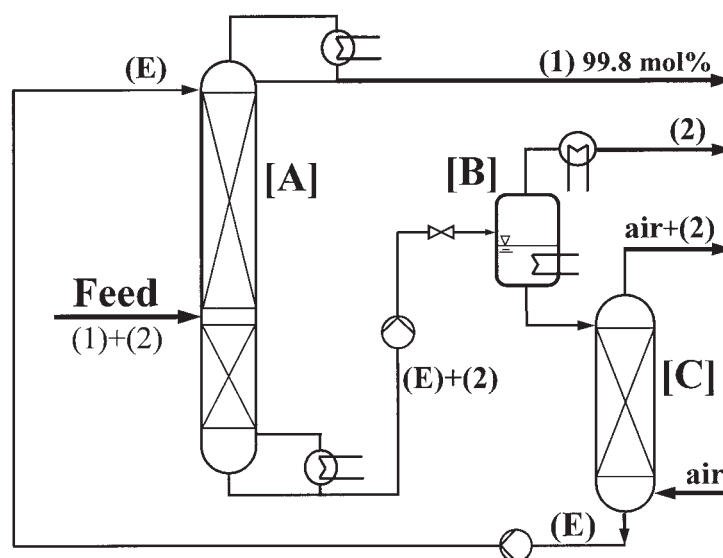
**Table 3. Simulation Results and Process Parameters for the Ethanol–Water Separation by Extractive Distillation Using Three Different Entrainers: 1,2-Ethanediol, Hyperbranched Polyglycerol, and [EMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>−</sup>**

	1,2-Ethanediol		Hyperbranched Polyglycerol		[EMIM] <sup>+</sup> [BF <sub>4</sub> ] <sup>−</sup>	
Entrainer flow rate, kmol/h	180	220	7.25	15	100	120
Entrainer flow rate, kg/h	11,172	13,655	14,500	30,000	19,800	23,760
<b>Main column</b>						
Theoretical stages	28	28	28	28	28	28
Operating pressure [Pa]	$1.013 \times 10^5$	$1.013 \times 10^5$	$1.013 \times 10^5$	$1.013 \times 10^5$	$1.013 \times 10^5$	$1.013 \times 10^5$
Ethanol purity	99.8 mol %	99.8 mol %	99.8 mol %	99.8 mol %	99.8 mol %	99.8 mol %
Reflux ratio	0.70	0.52	0.70	0.07	0.41	0.25
Entrainer stage	3	3	1	1	1	1
Feed stage	22	21	22	22	22	21
Bottom temperature [K]	421.3	427.3	394.8	420.8	412.4	417.8
Reboiler heat duty, kW	3276	3212	3057	3100	2994	2958
<b>Entrainer regeneration</b>						
Entrainer purity	99.9 mol %	99.9 mol %	99.98 wt %	99.98 wt %	99.9 mol %	99.9 mol %
<b>Distillation</b>						
Theoretical stages	12	12	—	—	—	—
Operating pressure, Pa	$10^4$	$10^4$	—	—	—	—
Reflux ratio	0.370	0.541	—	—	—	—
Feed stage	4	4	—	—	—	—
Reboiler heat duty, kW	683	704	—	—	—	—
<b>Flash drum</b>						
Operating pressure, Pa	—	—	$10^4$	$10^4$	$10^4$	$10^4$
Operating temperature, K	—	—	401.2	401.2	383.15	383.15
Heat duty, kW	—	—	690	66	177	5
<b>Stripping column</b>						
Theoretical stages	—	—	8	8	8	8
Operating pressure, Pa	—	—	$1.013 \times 10^5$	$1.013 \times 10^5$	$1.013 \times 10^5$	$1.013 \times 10^5$
Feed stage	—	—	1	1	1	1
Bottom temperature, K	—	—	358.4	358.4	342.1	341.9
Air flow rate, kg/h	—	—	10269	21256	13896	16791
Air temperature, K	—	—	293.15	293.15	293.15	293.15
Heat duty, kW	—	—	0	0	0	0
<b>Overall heat duty, kW</b>	<b>3959</b>	<b>3917</b>	<b>3747</b>	<b>3166</b>	<b>3171</b>	<b>2963</b>

K in the process heat exchangers, the pinch temperature amounts to 335.15 K with a cross-pinch heat transfer of 95.8 kW. To reduce this value and therefore the demand of hot and cold utilities [saturated steam at  $4 \times 10^5$  Pa and cooling water (292.15–297.15 K) with  $\Delta T_{min} = 5$  K is used] the following internal heat exchange is suggested: The polymer recycle

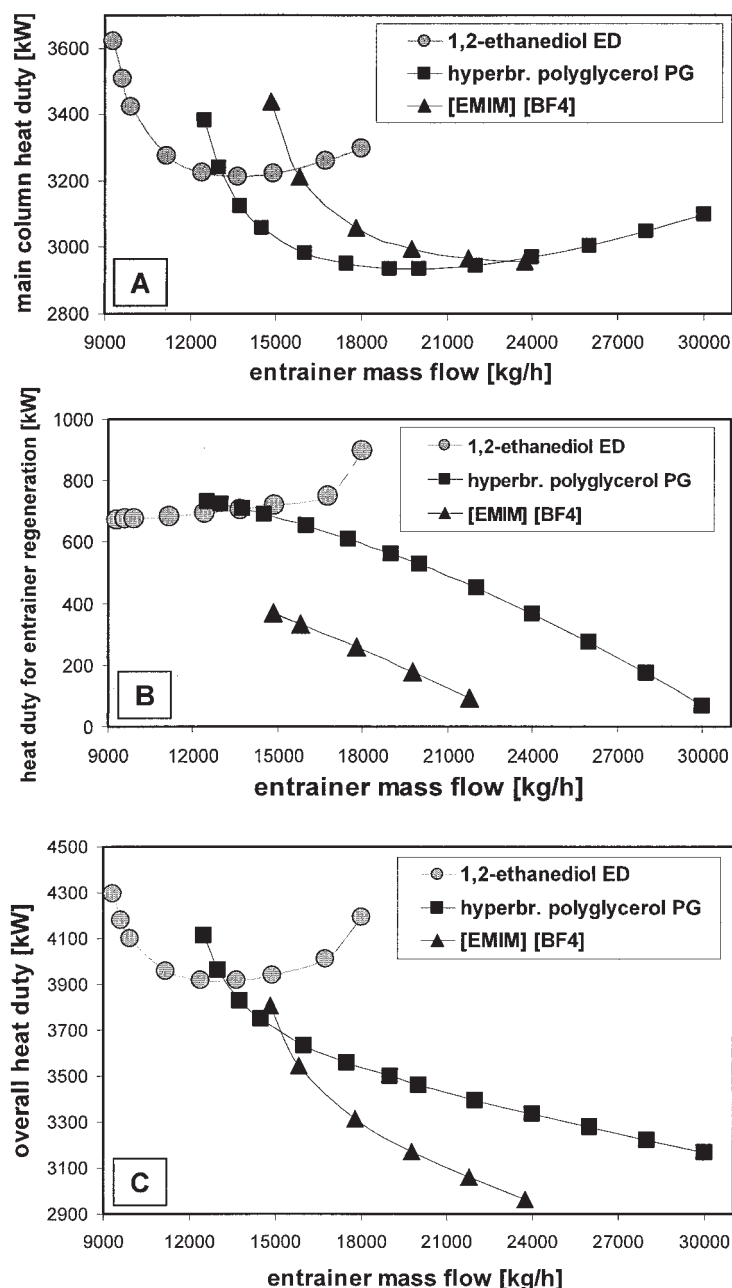
stream from the flash drum is used as hot stream to the reboiler of the water column and to preheat the feed of the THF column (see Figure 9, HX-2 and HX-7).

Since the heat of mixing in the mixer–settler is not taken into account in the simulation and only a small part of the heat in the THF condenser is available at a higher temper-



**Figure 7. Separation scheme for extractive distillation processes using nonvolatile entrainers.**

(1): ethanol, (2): water, (E): nonvolatile entrainer, [A]: main column, [B]: flash drum, [C]: stripping column.



**Figure 8. Simulation results for the ethanol–water separation by extractive distillation using three different entrainers: the hyperbranched polyglycerol PG, the ionic liquid [EMIM]<sup>+</sup>[BF<sub>4</sub>]<sup>−</sup>, and the conventional entrainer 1,2-ethanediol.**

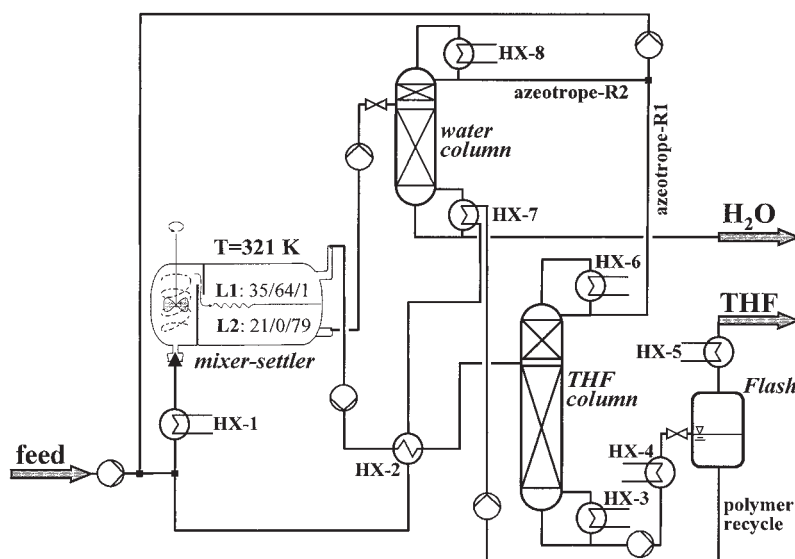
(A) Main column reboiler heat duty vs. entrainer mass flow. (B) heat duty for entrainer regeneration vs. entrainer mass flow. (C) overall process heat duty vs. entrainer mass flow. Lines: aid for the eyes.

ature, these two units were not considered in detail in this study.

The implementation of the mentioned heat integration (see Figure 9) reduces the cross-pinch heat transfer to 28.3 kW, that is, 70.5% of the possible improvements are realized. There are only two consumers of external hot utility remaining. The heat exchanger network for this optimized case, including the pinch temperature, is shown in Figure 10B. The process streams, grouped to hot and cold process streams, are stated with their

temperature change. The connections represent the heat exchangers.

A further reduction of the cross-pinch heat transfer is possible but would cause a more complex process scheme with splitting streams and higher investment costs. Moreover, it is noteworthy that the amount of extraction solvent (Boltorn H3200) used can be further reduced by choosing another overall mixing point for the single-stage extraction at larger THF concentrations. In addition, the viscosities of the coexisting



**Figure 9. Separation scheme for the THF–water separation using the hyperbranched polyester Boltorn H3200 as extraction solvent.**

Concentrations in mass percent, THF/polymer/water.

liquid phases can be further optimized, since the THF–water azeotrope is surpassed even at larger system temperatures (such as  $T = 334.15$  K; see Seiler et al., 2003a). This is not considered in this report.

Table 4 summarizes the most important parameters of the optimized separation process and the heat duties of the different separation units and heat exchangers. The process optimization by pinch analysis leads to a required heat demand of 1705 kJ/kg THF product. The comparison of this result with simulation results for conventional THF–water separation processes (azeotropic distillation, pressure-swing distillation) indicates a considerable potential for the use of hyperbranched polymers as extraction solvents and the competitiveness of the suggested process (Seiler et al., 2003d).

## Conclusions and Future Work

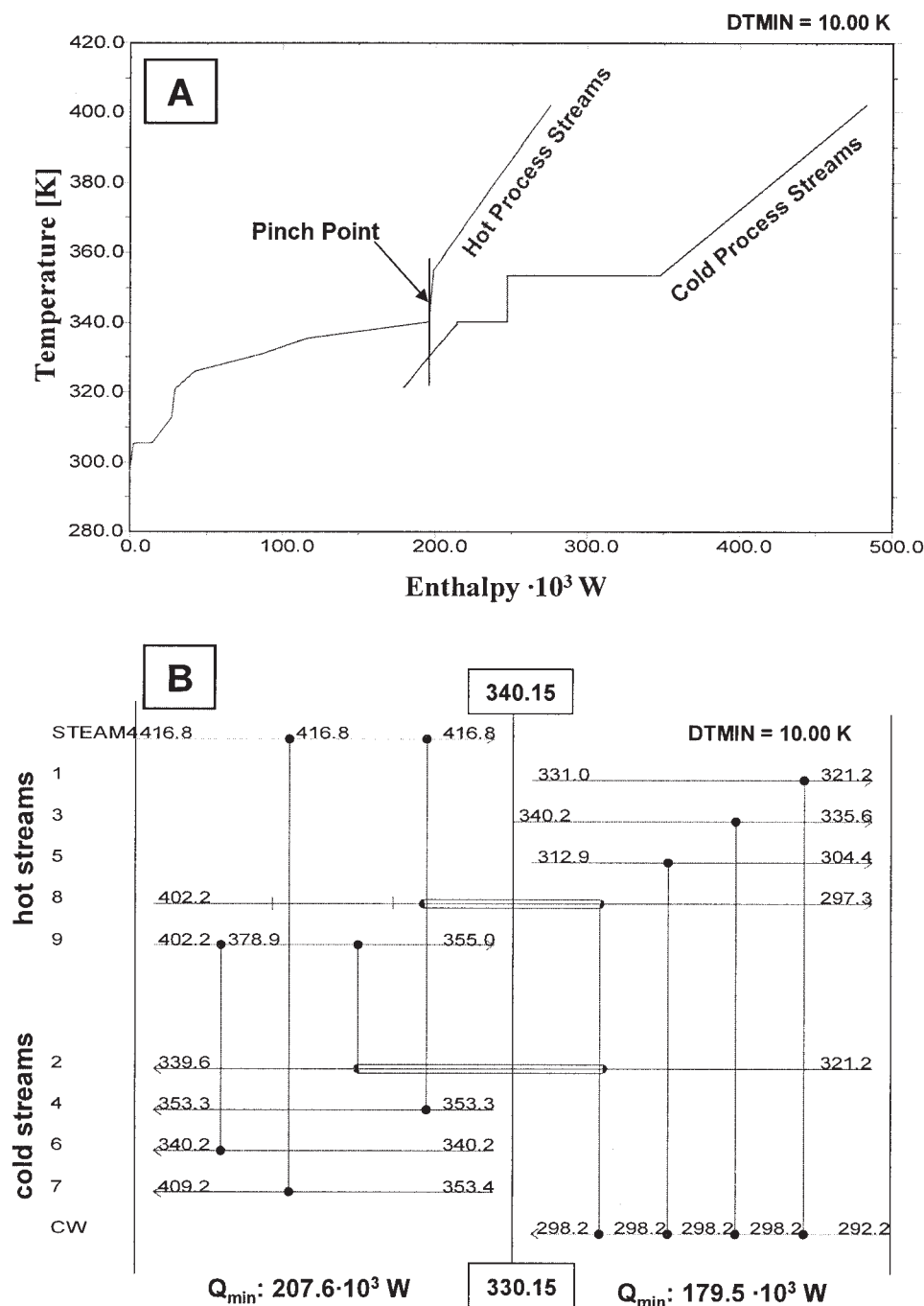
Low-viscosity hyperbranched polymers (HyPol) and ionic liquids (IL) represent promising classes of highly selective components, which can be used for the improvement of a variety of separation processes. Their properties, such as solubility, capacity, selectivity, viscosity, and thermal stability, can be tailored for a specific application. In this work the potential of commercially available HyPol and IL in the field of extractive distillation and solvent extraction is demonstrated. The different HyPol and IL investigated break the azeotropic behavior of a variety of aqueous systems, such as ethanol–water and THF–water. In the case of hyperbranched polyglycerol, the influence on  $\alpha_{\text{ethanol,water}}$  proved to be of the same

**Table 4. Simulation Results and Process Parameters for the THF–Water Separation by Liquid–Liquid Extraction and Distillation (Figure 9) Using the Hyperbranched Polyester Boltorn H3200 as Extraction Solvent**

Stream	Flow Rate (kg/h)		Composition THF/polymer/H <sub>2</sub> O (wt %)				T (K)	
Feed	1000		50/0/50				293.15	
THF product	498.2		99.98/0/0.02				297.33	
H <sub>2</sub> O product	499.9		99.64/0/0.36				340.18	
L1	3004		35/63.78/1.12				321.15	
L2	645.4		21/0/79				321.15	
Azeotrope-R1	504.5		92.72/0/7.28				335.57	
Azeotrope-R2	143.7		92.91/0/7.09				304.4	
Polymer-Recycle	2001.3		4.27/95.73/0				402.15	
Column	P (Pa)		NTU				$\Delta P$ (Pa)	
THF column	$1.013 \times 10^5$		15				0	
H <sub>2</sub> O column	$3 \times 10^4$		3				0	
		P (kPa)	T (K)				Duty (kW)	
Flash drum		21	402.15				0	
Heat Exchanger	HX-1	HX-2*	HX-3	HX-4	HX-5	HX-6	HX-7*	HX-8
Duty, kW	–24.6	34.2	100.5	135.4	–80.4	–79.3	33.3	–23.6

\*NB: the heat exchangers HX-2 and HX-7 are internal heat exchangers of the process.





**Figure 10. Composite curve and heat exchanger network of the suggested THF–water separation process (see Figure 9).**

(A) Composite curve showing the hot and cold process streams. (B) Heat exchanger network for the energetically optimized separation process. Process streams: (1) Feed of mixer–settler, (2) THF–column–feed, (3) THF–column–condenser, (4) THF–column–reboiler, (5) water–column–condenser, (6) water–column–reboiler, (7) THF–flash, (8) THF–product, (9) polymer–recycle.

magnitude, whereas for the ionic liquids  $[\text{BMIM}]^+[\text{CL}]^-$  and  $[\text{EMIM}]^+[\text{BF}_4]^-$  the influence is greater than that of the conventional entrainer 1,2-ethanediol.

The process simulations indicate several advantages when using the suggested nonvolatile entrainers as opposed to conventional entrainers. The most important advantages are: (1) because of their nonvolatility they cannot pollute the distillate; (2) their high selectivities and capacities, in combination with their nonvolatility, allow for a considerable reduction of the

required heat duties, particularly because of a larger variety of feasible entrainer regeneration options; (3) tailor-made properties.

For the ethanol–water system both investigated substances, the hyperbranched polyglycerol PG and the ionic liquid  $[\text{EMIM}]^+[\text{BF}_4]^-$ , represent chemically nonoptimized entrainers. The combined entrainer regeneration (consisting of a flash drum and an atmospheric stripping column) enables an ethanol–water separation process, which, for both suggested non-

volatile entrainers, is energetically superior to the conventional extractive distillation process using 1,2-ethanediol.

Furthermore, the separation of the azeotropic THF–water system by means of solvent extraction, using HyPol or IL as extraction solvent, is studied. The hyperbranched aliphatic polyester Boltorn H3200 and the ionic liquid  $[\text{EMIM}]^+[\text{BF}_4]^-$  exhibit remarkable selectivities and capacities, which allow for the breaking of the THF–water azeotrope by single-stage extraction. The purification of the extract and the raffinate can be achieved by combining the extraction unit with either distillation or crystallization steps. Based on the liquid–liquid equilibrium of the THF–water–Boltorn H3200 system, a new THF–water separation process was designed, optimized, and evaluated in terms of feasibility and energetic efficiency. The amount of the required hot and cold process utilities underline the potential of hyperbranched polymers as extraction solvents and the competitiveness of the suggested process to conventional THF–water separation processes such as azeotropic distillation or pressure-swing distillation.

Future work will focus on the influence of the structure of HyPol and IL on the interactions with different azeotrope-forming polar and nonpolar solvents. The aim is to provide some guidelines on how to choose the most suitable HyPol or IL for the separation of a certain (azeotropic) mixture. Moreover, a set of industrial requirements for HyPol and IL should be defined to characterize their *industrial* suitability as entrainer, extraction solvent, absorption agent, or membrane.

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## Literature Cited

Arlt, W., M. Seiler, G. Sadowski, H. Frey, H. Kautz, and R. Mülhaupt, DE Patent No. 10160518.8 (2001a).  
 Arlt, W., M. Seiler, C. Jork, and T. Schneider, DE Patent No. 10114734 (2001b).  
 Arlt, W., M. Seiler, C. Jork, and T. Schneider, DE Patent No. 10136614 (2001c).  
 Arlt, W., M. Seiler, C. Jork, and T. Schneider, WO Patent No. 02/074718 A2 (2002d).  
 Barr-David, F., and B. F. Dodge, "Vapor–Liquid Equilibrium at High Pressures. The Systems Ethanol–Water and 2-Propanol–Water," *J. Chem. Eng. Data*, **4**, 107 (1959).  
 Böcker, S., and G. Ronge, "Destillation viskoser Systeme," Proc. of VDI/GVC Conference on Thermische Zerlegung von Gas- und Flüssigkeitsgemischen, Weimar, Germany (2003).  
 Bonhôte, P., A. P. Dias, N. Papageorgiou, K. Kalyanasundaram, and M. Grätzel, "Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts," *Inorg. Chem.*, **35**, 1168 (1996).  
 Castells, C. B., D. I. Eikens, and P. W. Carr, "Headspace Gas Chromatography Measurements of Limiting Activity Coefficients of Eleven

Alkanes in Organic Solvents at 25°C," *J. Chem. Eng. Data*, **45**, 369 (2000).  
 Chang, T., and T. T. Shih, "Development of an Azeotropic Distillation Scheme for Purification of Tetrahydrofuran," *Fluid Phase Equilib.*, **52**, 161 (1989).  
 Chen, C.-C., "A Segment-Based Local Composition Model for the Gibbs Energy of Polymer Solutions," *Fluid Phase Equilib.*, **83**, 301 (1993).  
 Crooks, R. M., "Patterning of Hyperbranched Polymer Films," *Chem. Phys. Chem.*, **2**, 644 (2001).  
 Duan, L., Y. Qiu, Q. He, F. Bai, L. Wang, and X. Hong, "A Novel Hyperbranched Conjugated Polymer for Electroluminescence Application," *Synth. Met.*, **124**, 373 (2001).  
 European Federation of Chemical Engineering, *Standard Test Systems for Liquid Extraction*, Institute of Chemical Engineers, Warwickshire, UK (1985).  
 Freemantle, M., "Eyes on Ionic Liquids," *Sci. Technol.*, **78**, 20 (2000).  
 Gao, C., and D. Yan, "Hyperbranched Polymers: from Synthesis to Applications," *Prog. Polym. Sci.*, **29**, 183 (2004).  
 Gordon, C. M., "New Developments in Catalysis Using Ionic Liquids," *Appl. Catal. A, General*, **222**, 101 (2001).  
 Haag, R., "Dendrimers and Hyperbranched Polymers as High-Loading Supports for Organic Synthesis," *Chem. Eur. J.*, **7**, 327 (2001).  
 Hachenberg, H., and K. Beringer, *Die Headspace-Gaschromatographie als Analysen- und Meßmethode*, Vieweg-Verlag, Braunschweig/Wiesbaden, Germany (1996).  
 Hilgers, C., and P. Wasserscheid, *Ionic Liquids in Synthesis*, P. Wasserscheid and T. Welton, eds., Wiley-VCh, Weinheim, Germany (2002).  
 Holbrey, J. D., and K. R. Seddon, *Clean Products and Processes*, Vol. 1, Springer Verlag, New York, p. 223 (1999).  
 Hult, A., M. Johansson, and E. Malmström, "Hyperbranched Polymers," *Adv. Polym. Sci.*, **143**, 1 (1999).  
 Inoue, K., "Functional Dendrimers, Hyperbranched and Star Polymers," *Prog. Polym. Sci.*, **25**, 453 (2000), and references therein.  
 Jork, C., M. Seiler, and W. Arlt, "Influence of Ionic Liquids on the Phase Behavior of Aqueous Azeotropic Systems," *J. Chem. Eng. Data*, **49**(4), 852 (2003a).  
 Jork, C., M. Seiler, and W. Arlt, Unpublished results (2003b).  
 Kautz, H., A. Sunder, and H. Frey, "Control of the Molecular Weight of Hyperbranched Polyglycerols," *Macromol. Symp.*, **163**, 67 (2001).  
 Kim, Y. H., "Hyperbranched Polymers—10 Years After," *J. Polym. Sci. Part A: Polym. Chem.*, **36**, 1685 (1998).  
 Kim, Y. H., and O. W. Webster, "Water Soluble Hyperbranched Polyphenylene: A Unimolecular Micelle?," *J. Am. Chem. Soc.*, **112**, 4592 (1990).  
 Klee, J. E., C. Schneider, D. Holter, A. Burgath, H. Frey, and R. Mülhaupt, "Hyperbranched Polyesters and Their Application in Dental Composites: Monomers for Low Shrinking Composites," *Polym. Adv. Technol.*, **12**, 346 (2001).  
 Knapp J. P., and M. F. Doherty, "Thermal Integration of Homogeneous Azeotropic Distillation Sequences," *AIChE J.*, **36**, 969 (1990).  
 Linnhoff, B., D. W. Townsend, D. Boland, G. F. Hewitt, B. E. A. Thomas, A. R. Guy, and R. H. Marsland, *A User Guide on Process Integration for the Efficient Use of Energy* (1992 Edition), Institution of Chemical Engineers, Rugby, UK (1992).  
 Linnhoff, B., and W. Lenz, "Wärme-Integration und Prozeßoptimierung," *Chem.-Ing.-Tech.*, **59**(11), 851 (1987).  
 Magnusson, H., E. Malmström, and A. Hult, "Structure Buildup in Hyperbranched Polymers from 2,2-Bis(hydroxymethyl)propionic Acid," *Macromolecules*, **33**, 3099 (2000) [and references therein].  
 Matous, J., J. P. Novak, J. Sobr, and J. Pick, "Phase Equilibria in the System Tetrahydrofuran(1)–water(2)," *Collect. Czech. Chem. Commun.*, **37**, 2653 (1972).  
 Mourey, T. H., S. R. Turner, M. Rubinstein, J. M. J. Fréchet, C. J. Hawker, and K. L. Wooley, "The Unusual Behavior of Dendritic Macromolecules: A Study of the Intrinsic Viscosity, Density and Refractive Index Increment of Polyether Dendrimers," *Macromolecules*, **25**, 2401 (1992).  
 Pemberton, R. C., and C. J. Mash, "Thermodynamic Properties of Aqueous Non-Electrolyte Mixtures. II. Vapor Pressures and Excess Gibbs Energies for Water + Ethanol at 303.15 to 363.15 K Determined by an Accurate Static Method," *J. Chem. Thermodyn.*, **10**, 867 (1978).  
 Petri, H. M., and B. A. Wolf, "Concentration-Dependent Thermodynamic Interaction Parameters for Polymer Solutions: Quick and Reliable Determination via Normal Gas Chromatography," *Macromolecules*, **27**, 2714 (1994).

- Pirring, F. O. H., E. M. Loen, and A. Noordam, "Hyperbranched Polymers as a Novel Class of Pigment Dispersants," *Macromol. Symp.*, **187**, 683 (2002).
- Pitois, C., D. Wiesmann, M. Lindgren, and A. Hult, "Functionalized Fluorinated Hyperbranched Polymers for Optical Waveguide Applications," *Adv. Mater.*, **13**, 1483 (2001).
- Renon, H., and J. M. Prausnitz, "Local Compositions in Thermodynamics Excess Functions for Liquid Mixtures," *AIChE J.*, **14**, 135 (1968).
- Rieder, R. M. and A. R. Thompson, "Vapor-Liquid Equilibria Measured by a Gillespie Still. Ethyl Alcohol-Water System," *Ind. Eng. Chem.*, **41**, 2905 (1949).
- Schuld, N., and B. A. Wolf, "Solvent Quality as Reflected in Concentration- and Temperature-Dependent Flory-Huggins Interaction Parameters," *J. Polym. Sci. Part B: Polym. Phys.*, **39**, 651 (2001).
- Seddon, K. R., "Ionic Liquids for Clean Technology," *J. Chem. Technol. Biotechnol.*, **68**, 351 (1997).
- Seiler, M., "Dendritic Polymers—Interdisciplinary Research and Emerging Applications from Unique Structural Properties," *Chem. Eng. Technol.*, **25**(3), 237 (2002a) [and references therein].
- Seiler, M., W. Arlt, H. Kautz, and H. Frey, "Experimental Data and Theoretical Considerations on Vapor-Liquid and Liquid-Liquid Equilibria of Hyperbranched Polyglycerol and PVA Solutions," *Fluid Phase Equilib.*, **201**, 359 (2002b).
- Seiler, M., C. Jork, T. Schneider, and W. Arlt, *Proceedings of the International Conference on Distillation and Absorption*, Baden-Baden, Germany (2002c).
- Seiler, M., W. Arlt, A. Kavarnou, M. Buggert, J. Rolker, M. Y. Falah, and D. Köhler, "Phase Behaviour and New Industrial Applications of Hyperbranched Polymers," *Proc. of Int Polydays Conf.*, Berlin, Germany (2002d).
- Seiler, M., C. Jork, W. Arlt, Y. A. Beste, and H. Schoenmakers, "Ionic Liquids—Promising New Classes of Selective Entrainers for Extractive Distillation," *Proc. of AIChE Annual Meeting*, Indianapolis, IN (2002e).
- Seiler, M., C. Jork, and W. Arlt, Unpublished results (2002f).
- Seiler, M., D. Köhler, and W. Arlt, "Hyperbranched Polymers: New Selective Solvents for Extractive Distillation and Solvent Extraction," *Sep. Purif. Technol.*, **30**(2), 179 (2003a).
- Seiler, M., J. Rolker, and W. Arlt, "Phase Behavior and Thermodynamic Phenomena of Hyperbranched Polymer Solutions," *Macromolecules*, **36**, 2085 (2003b) [and references therein].
- Seiler, M., M. Buggert, A. Kavarnou, and W. Arlt, "From Alcohols to Hyperbranched Polymers: The Influence of Differently Branched Additives on the Vapor-Liquid Equilibria of Azeotropic Systems," *J. Chem. Eng. Data*, **49**, 933 (2003c), Web Release Date May 28 2003.
- Seiler, M., C. Jork, and W. Arlt, "Phasenverhalten von hochselektiven nichtflüchtigen Flüssigkeiten mit designbarem Eigenschaftsprofil und neue Anwendungen in der thermischen Verfahrenstechnik," *Chem.-Ing.-Tech.*, **76**, 735 (2004).
- Seiler, M., J. Rolker, and W. Arlt, Unpublished results (2003d).
- Seiler, M., "Phase Behavior and New Application of Hyperbranched Polymers in the Field of Chemical Engineering," VDI-Fortschritte-Berichte Reihe 3 Nr. 820, ISBN 3-18-382003, VDI-Verlag, Germany (2004).
- Solvent Innovation GmbH, Cologne, Germany (<http://www.solvent-innovation.de>) [Accessed Jan. 2003].
- Sunder, A., J. Heinemann, and H. Frey, "Controlling the Growth of Polymer Trees: Concepts and Perspectives for Hyperbranched Polymers," *Chem. Eur. J.*, **6**, 2499 (2002).
- Tao, X. T., Y. Zhang, T. Wada, H. Sasabe, H. Suzuki, T. Watanabe, and S. Miyata, "Hyperbranched Polymers for Electroluminescence Applications," *Adv. Mater.*, **10**, 226 (1998).
- Voit, B., M. Eigner, K. Estel, C. Wenzel, and J. W. Bartha, "Labile Hyperbranched Polymers Used as Nanopore-Forming Agents in Polymeric Dielectrics," *Macromol. Symp.*, **177**, 147 (2002).
- Wasserscheid, P., and W. Keim, "Ionische Flüssigkeiten-neue 'Lösungen' für die Übergangs-metallkatalyse," *Angew. Chem.*, **112**, 3926 (2000).
- Welton, T., "Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis," *Chem. Rev.*, **99**, 2071 (1999).
- Wilkes, J. S., and M. J. Zaworotko, "Air and Water Stable 1-Ethyl-3-methylimidazolium Based Ionic Liquids," *J. Chem. Soc. Chem. Commun.*, **13**, 965 (1992).
- Wooley, K. L., J. M. J. Fréchet, and C. J. Hawker, "Influence of Shape on the Reactivity and Properties of Dendritic, Hyperbranched, and Linear Polyesters," *Polymer*, **35**, 4489 (1994).

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