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From Alcohols to Hyperbranched Polymers: The Influence of Differently Branched Additives on the Vapor−Liquid Equilibria of Selected Azeotropic Systems

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Ternary vapor−liquid equilibria (VLE) of selected aqueous azeotropic systems in the presence of differently branched hydroxyl functional components (additives) have been measured. Three azeotropic mixtures, ethanol + water, 2-propanol + water, and tetrahydrofuran + water, were chosen. The additives used were nonvolatile hyperbranched polymers such as polyesters, polyesteramides, and polyethers as well as low-volatility alcohols (1,2-ethanediol, 1,4-butanediol, 1,6-hexanediol, 1,12-dodecanediol, 1,2,3-propanetriol, 1,2,3,4-butanetetrol, and 2,4-dimethyl-3-pentanol). The experimental results show the influence of differently structured additives, that is, their degree of branching, molecular weight, and number of functionalities, on the VLE of the respective azeotropic system. For the investigated polymer solutions, the extent of inter- and intramolecular hydrogen bond formation has a dominant impact on the solvent activity and therefore determines the partition coefficients and the relative volatilities. Due to their remarkable solution properties, hyperbranched polymers such as hyperbranched polyesteramides or hyperbranched polyglycerols can be used for the separation of azeotropic mixtures by means of extractive distillation.

1. Introduction

Due to their unique structures and properties, highly branched, three-dimensional polymers such as dendrimers[1] or hyperbranched polymers[2] are attracting increasing attention. Hyperbranched polymers represent highly branched, polydisperse macromolecules with a treelike topology and a large number of functional groups. During the past 10 years, the rapidly growing interdisciplinary interest in structurally perfect dendrimers has promoted the rediscovery of hyperbranched polymers.[2,3] 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 not require structural perfection, hyperbranched polymers can circumvent this major drawback of dendrimers. Unlike dendrimers, randomly branched hyperbranched polymers with similar properties can be easily synthesized via one-step reactions and therefore represent economically promising products also for large-scale industrial applications. Companies such as the Perstorp Group (Perstorp, Sweden) and DSM Fine Chemicals (Geleen, Netherlands) already produce commercially available hyperbranched polymers on a large scale (for about 12 euro per kg). Most of the applications of hyperbranched polymers are based on the absence of chain entanglements and the nature and the large number of functional groups within a molecule. The functionalities of hyperbranched polymers allow for the tailoring of their thermal, rheological, and solution properties and thus provide a powerful tool to design hyperbranched polymers for a wide variety of applications.[2,4]

An area of application that, until now, has remained unconsidered in scientific discussions is the field of process engineering. Since the polarity of hyperbranched macromolecules can be adjusted by controlled functionalization of the end groups, selective solvents (consisting of either pure hyperbranched polymers or fractions of hyperbranched additives) can be tailored.[2,4] Unlike the conventional linear polymers, hyperbranched polymers show not only a remarkable selectivity and capacity[4] but in many cases also a comparatively lower solution and melt viscosity[5] as well as an enormous thermal stability.[6] Therefore, hyperbranched polymers can be used for the optimization of a number of separation and production processes. Only recently, the authors suggested the use of hyperbranched polymers as entrainers for extractive distillation[2,4,7,8] and as selective solvents for liquid−liquid extraction.[4,8] Furthermore, the potential of using hyperbranched polymers as selectivity- and capacity-increasing solvent additives for absorption processes and as stationary phases for preparative chromatography was demonstrated.[9,23]

The large body of interdisciplinary research on dendritic polymers, that is, dendrimers and hyperbranched polymers, is a guarantor for emerging applications. However, the understanding of essential fundamentals such as the phase behavior of dendritic polymer solutions is still in its infancy. Particularly experimental data, which allow discussion of the influence of the degree of polymer branching on the vapor−liquid equilibria (VLE) and the liquid−liquid equilibria (LLE) of binary and ternary systems, are extremely scarce. Therefore, this paper aims to provide experimental results which characterize the influence of differently structured components (in this article these components will be termed “additives”) on the VLE of selected aqueous azeotropic systems such as ethanol + water, 2-propanol + water, and THF + water. The additives used represent hydroxyl functional substances (alcohols, hyperbranched polyethers, and hyperbranched poly-

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Table 1. Polymer Samples Used

sample	molecular weight g/mol	M_w/M_n	number of OH-groups per macromolecule	provider
PG	$M_n = 2000$	1.5	28	H. Kautz, H. Frey[12,8]
Hybrane S1200	$M_n = 1200$	≈5	8	DSM
Boltorn H20	$M_w = 2100$	1.3	16[a]	Perstorp
Boltorn H30	$M_w = 3500$	1.5	32[a]	Perstorp
Boltorn H40	$M_w = 5100$	1.8	64[a]	Perstorp
PEG 400	$M_w = 400$	1.1	2	Polysciences Inc.
PEG 1000	$M_w = 1000$	1.1	2	Polysciences Inc.
PEG 3400	$M_w = 3400$	1.2	2	Polysciences Inc.

[a] See also the investigations of Frey and co-workers (ref 19) and Žagar and Žigon (ref 20).

Table 2. Solvents and Low-Volatility Additives

solvent	provider	purity	CAS no.
ethanol	Fluka	>99.8%	64-17-5
2-propanol	Merck	>99.8%	67-63-0
tetrahydrofuran	Merck	>99.8%	109-99-9
1,2-ethanediol	Merck	>99.8%	107-21-1
1,4-butanediol	Fluka	>99%	110-63-4
1,6-hexanediol	Fluka	>98%	629-11-8
1,12-dodecanediol	Fluka	>98%	5675-51-4
1,2,3-propanetriol	Fluka	>99.5%	56-81-5
1,2,3,4-butanetetrol	Fluka	>99%	149-32-6
2,4-dimethyl-3-pentanol	Fluka	≥98%	600-36-2

esters), which mainly differ in the degree of branching, size, and number of functional groups.

2. Experimental Section

Chemicals. The hyperbranched macromolecular additives used were a hyperbranched polyesteramide, a hyperbranched polyglycerol, and hyperbranched polyesters of different molecular weights. Perstorp Specialty Chemicals AB (Sweden) provided aliphatic hyperbranched polyesters, known as the Boltorn family. The Boltorn samples used (Boltorn H20, Boltorn H30, and Boltorn H40) are hydroxyl functional hyperbranched polyesters, which are produced from polyalcohol cores and hydroxyl acids.[10,20] DSM (The Netherlands) provided the hyperbranched polyesteramide Hybrane S1200.[11] As other differently branched polyglycerol samples used in the past, the hyperbranched polyglycerol PG[12,3,8] was synthesized by H. Kautz and provided by H. Kautz and H. Frey (Johannes-Gutenberg-Universität Mainz, Germany). The latter hyperbranched polyether is synthesized by slow addition of glycidol to a solution containing a partially deprotonated polyol core at 393.15 K as described by Kautz et al.[12] Poly(ethylene glycol) PEG was obtained from Polysciences (USA). The specifications of the macromolecular additives are listed in Table 1.

Apart from these nonvolatile polymers, also low-volatility alcohols were used as additives (1,2-ethanediol, 1,4-butanediol, 1,6-hexanediol, 1,12-dodecanediol, 1,2,3-propanetriol, 1,2,3,4-butanetetrol, and 2,4-dimethyl-3-pentanol). Their specifications are listed in Table 2, together with those of the solvents ethanol, 2-propanol, and tetrahydrofuran (THF). The chemicals were used as delivered without further purification. Distilled water was degassed and repeatedly filtered using a 0.02 μm Millipore filter in order to remove dust.

Apparatus and Procedure. Headspace gas chromatography (HSGC)[13] represents an experimental method which combines a headspace sampler and a gas chromatograph in order to determine the composition of a vapor phase. If the vapor phase is in equilibrium with a liquid or solid phase, VLE or solid−vapor equilibria (SVE) can be measured and related thermodynamic information such as partial pressures, activity coefficients, and interaction parameters can be obtained.[14−16]

In this work, HSGC is used for VLE measurements of ternary mixtures consisting of binary aqueous azeotropic systems and different hydroxyl functional additives. Samples of different liquids (10 mL) were filled into vials (capacity, 20 mL) and sealed with airtight septa. To ensure thermodynamic equilibrium, the vials are mixed at equilibrium temperature for 24 h and then transferred into the headspace oven. Inside the oven of the headspace sampler, the system is mixed by an agitation mode and equilibrated again for another 5 h. A pneumatically driven thermostated headspace sampler (Agilent HP 7694, USA) takes a sample of approximately 0.05 g out of the vial's vapor phase in equilibrium with the liquid phase. A specially designed sample interface delivers the sample to the GC column of the gas chromatograph (Agilent GC 6890, USA). This inert, narrow, heated interface acts as an extension of the headspace transferline inside the GC. An electronic pneumatics control (EPC) monitors pressure and flow. Helium, the carrier gas, transports the sample through a capillary column (Agilent HP Innowax; inner diameter, 0.53 mm; length, 30 m), which separates the sample components. The latter are individually detected by means of a thermal conductivity detector. Evaluation of the individual peak areas is carried out using the software package HP GC ChemStation.

The reproducibility of the experimental results was ensured by means of at least five independent extractions per sample and temperature. The headspace settings (vial pressure, equilibration times, flow rate) were optimized and checked by comparison with high-precision VLE literature data as described in detail previously.[7] The accuracy of the temperature adjustment is ±0.1 K, and the relative error in composition is smaller than 1%.

3. Results and Discussion

The following experimental results show the influence of low-volatility alcohols and polymers on the VLE of different azeotropic mixtures. The influence of different high-boiling alcohols on the ethanol + water VLE at 363.15 K is shown in Table 3. With increasing molecular weight of the additives, the relative volatility $\alpha_{\text{ethanol,water}} = (y_{\text{ethanol}}x_{\text{water}})/(x_{\text{ethanol}}y_{\text{water}})$ and the additive's solubility decrease. This is due to a decreasing degree of hydrogen bonding between the respective additive and water.[7] When comparing the VLE results of systems II and V (Table 3), the influence of the number of the additive's OH-groups on the ethanol + water VLE becomes evident as well. At $x_{\text{ethanol}} \leq 0.9$ and comparable molecular weights of the additives, the 1,2,3-propanetriol mixtures (system V) show a larger molar vapor fraction of ethanol, y_{ethanol}, than the 1,4-butanediol solution (system II). Due to the larger number of hydroxyl groups per additive molecule, the degree of hydrogen bonding between 1,2,3-propanetriol and water is larger than between 1,4-butanediol and water. Therefore, in comparison to the 1,4-butanediol mixtures, the addition of 60 wt % 1,2,3-propanetriol to the ethanol + water system results in a larger relative volatility $\alpha_{\text{ethanol,water}}$ (see Figure 1, Table 3).

Figure 1 and Table 4 show the results of the ethanol + water VLE at 363.15 K in the presence of different macromolecular additives at 363.15 K. For the components added to the azeotropic ethanol + water system, it is obvious that the relative volatility $\alpha_{\text{ethanol,water}}$ increases

Table 3. Influence of Different High-Boiling Additives[a] on the Ethanol + Water VLE at 363.15 K

I		II		III		IV		V		VI		VII	
$x_{ethanol}$	$y_{ethanol}$	$x_{ethanol}$	$y_{ethanol}$	$x_{ethanol}$	$y_{ethanol}$	$x_{ethanol}$	$y_{ethanol}$	$x_{ethanol}$	$y_{ethanol}$	$x_{ethanol}$	$y_{ethanol}$	$x_{ethanol}$	$y_{ethanol}$
Ia		IIa		IIIa		0.500	0.629	Va		0.350	0.609	0.801	0.735
0.300	0.595	0.200	0.475	0.200	0.490	0.800	0.808	0.200	0.576	0.550	0.689	0.900	0.821
0.599	0.734	0.550	0.688	0.400	0.594	0.900	0.900	0.599	0.779	0.800	0.832	0.949	0.871
0.848	0.885	0.800	0.840	0.600	0.695	0.950	0.947	0.802	0.869	0.901	0.911		
0.951	0.959	0.901	0.905	0.800	0.824			0.900	0.926	0.951	0.950		
Ib		0.948	0.939	0.900	0.903			0.949	0.953				
0.101	0.431	IIb		0.950	0.948			Vb					
0.300	0.614	0.339	0.604	IIIb				0.430	0.742				
0.601	0.766	0.850	0.897	0.200	0.442			0.799	0.880				
0.850	0.911	0.901	0.931	0.400	0.577			0.903	0.932				
0.950	0.967	0.947	0.960	0.600	0.687								
Ic				0.800	0.823								
0.100	0.398			0.900	0.907								
0.301	0.645			0.950	0.947								
0.596	0.827			III c									
0.851	0.942			0.899	0.907								
0.943	0.977												

[a] **I**: ethanol + water + 1,2-ethanediol. Ia: 20 wt % 1,2-ethanediol. Ib: 40 wt % 1,2-ethanediol. Ic: 70 wt % 1,2-ethanediol. **II**: ethanol + water + 1,4-butanediol. IIa: 40 wt % 1,4-butanediol. IIb: 60 wt % 1,4-butanediol. **III**: ethanol + water + 1,6-hexanediol. IIIa: 20 wt % 1,6-hexanediol. IIIb: 40 wt % 1,6-hexanediol. IIIc: 60 wt % 1,6-hexanediol. **IV**: ethanol + water + 1,12-dodecanediol; 20 wt % 1,12-dodecanediol. **V**: ethanol + water + 1,2,3-propanetriol. Va: 40 wt % 1,2,3-propanetriol. Vb: 60 wt % 1,2,3-propanetriol. **VI**: ethanol + water + 1,2,3,4-butanetetrol; 20 wt % 1,2,3,4-butanetetrol. **VII**: ethanol + water + 2,4-dimethyl-3-pentanol; 50 wt % 2,4-dimethyl-3-pentanol.

Table 4. Influence of Different Polymers[a] on the Ethanol + Water VLE at 363.15 K

I		II		III		IV		V		VI	
$x_{ethanol}$	$y_{ethanol}$	$x_{ethanol}$	$y_{ethanol}$	$x_{ethanol}$	$y_{ethanol}$	$x_{ethanol}$	$y_{ethanol}$	$x_{ethanol}$	$y_{ethanol}$	$x_{ethanol}$	$y_{ethanol}$
Ia		0.200	0.529	0.189	0.510	IVa		0.200	0.529	VIa	
0.202	0.535	0.400	0.624	0.400	0.628	0.200	0.523	0.300	0.568	0.200	0.517
0.400	0.628	0.599	0.717	0.600	0.720	0.300	0.571	0.400	0.618	0.300	0.565
0.600	0.719	0.900	0.924	0.800	0.842	0.416	0.618	0.800	0.822	0.400	0.621
0.798	0.835	0.952	0.953	0.900	0.913	0.599	0.705	0.898	0.892	0.600	0.709
0.850	0.872			0.950	0.951	0.802	0.827			0.798	0.825
0.895	0.905					0.902	0.905			0.901	0.905
0.950	0.948					IVb				VIb	
Ib						0.200	0.504			0.800	0.845
0.202	0.531					0.400	0.637			0.900	0.908
0.602	0.748					0.600	0.731			0.951	0.942
0.801	0.860					0.800	0.857				
0.851	0.893					0.951	0.954				
0.900	0.924					IVc					
0.950	0.958					0.401	0.631				
Ic						0.799	0.862				
0.400	0.648					0.901	0.912				
0.699	0.794					0.950	0.959				
0.800	0.862										
0.851	0.897										
0.902	0.929										
0.950	0.959										

[a] **I**: ethanol + water + PEG 400. Ia: 20 wt % PEG 400. Ib: 40 wt % PEG 400. Ic: 70 wt % PEG 400. **II**: ethanol + water + PEG 1000; 40 wt % PEG 1000. **III**: ethanol + water + PEG 3400; 40 wt % PEG 3400. **IV**: ethanol + water + Boltorn H20. IVa: 20 wt % Boltorn H20. IVb: 50 wt % Boltorn H20. IVc: 60 wt % Boltorn H20. **V**: ethanol + water + Boltron H30; 20 wt % Boltron H30. **VI**: ethanol + water + Boltorn H40. VIa: 20 wt % Boltorn H40. VIb: 50 wt % Boltorn H40.

with additive concentration, that is, increasing number of hydrogen bonds between the respective polymer and water. This applies particularly to the low-volatility additive PEG 400 and the nonvolatile hyperbranched polymer Boltorn H20 (see Figure 1). In analogy to Table 3, for both kinds of polymers, the poly(ethylene glycols) and the hyperbranched Boltorn polyesters, the molar vapor fraction of ethanol decreases with increasing molecular weight of the macromolecular additive (see Table 4). PEG and 1,2-ethanediol (ED) have two hydroxyl groups that act as hydrogen bond donor sites, while PEG has a much greater number of hydrogen bond accepting oxyethylene units than ethanediol. Kim et al. demonstrated that the presence of PEG molecules in water changes the intermolecular arrangement of the water molecules and thus the hydrogen bond energies. However, PEG does not alter the hydrogen bond basicity of water.[17] Any change in the structure of water by the presence of PEG molecules is caused by a change in the hydrogen bond donor acidity of water.[17] Further details on the interactions of hydroxyl functional polymer + water solutions can be found elsewhere.[7,17−20]

Tables 5 and 6 and Figure 2 focus on the VLE of the azeotropic systems 2-propanol + water and THF + water in the presence of different, commercially available hyperbranched polymers. The influence of hyperbranched polyglycerol (PG) on the 2-propanol + water VLE at 353.15 K is shown in Table 5 and Figure 2A. Moreover, the experimental results of Table 6 and Figure 2B describe the influence of the hyperbranched polyesteramide Hybrane S1200 on the THF + water VLE at 343.15 K. As depicted

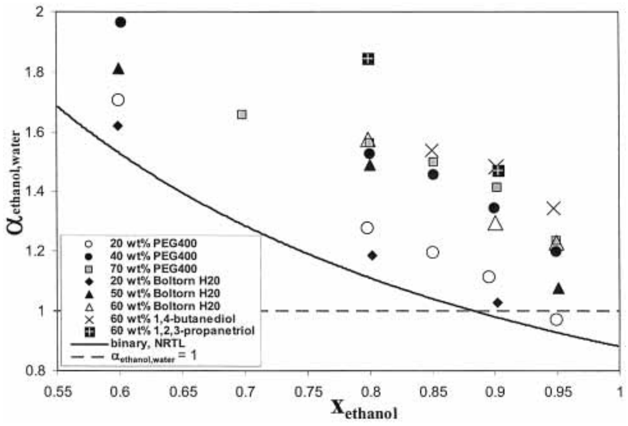

Figure 1. Influence of poly(ethylene glycol), hyperbranched polyester, 1,4-butanediol, and 1,2,3-propanetriol on the relative volatility $\alpha_{ethanol,water}$ at 363.15 K. NRTL results taken from (ref 7).

Table 5. Influence of the Hyperbranched Polyglycerol PG (M_n = 2000 g/mol) on the 2-Propanol + Water VLE at 353.15 K (data taken from ref 8)

I 40 wt % PG		II 60 wt % PG		III 70 wt % PG	
$x_{2-propanol}$	$y_{2-propanol}$	$x_{2-propanol}$	$y_{2-propanol}$	$x_{2-propanol}$	$y_{2-propanol}$
0.202	0.558	0.205	0.626	0.197	0.637
0.508	0.675	0.508	0.767	0.477	0.783
0.659	0.771	0.653	0.839	0.652	0.858
0.744	0.807	0.776	0.885	0.694	0.875
0.852	0.869	0.850	0.924	0.749	0.896
0.951	0.946	0.954	0.972	0.893	0.953
		0.981	0.988	0.958	0.974

Table 6. Influence of the Hyperbranched Polyesteramide Hybrane S1200 (M_n = 1200 g/mol) on the THF + Water VLE at 343.15 K

I 40 wt % Hybrane S1200		II 60 wt % Hybrane S1200		III 70 wt % Hybrane S1200	
x_{THF}	y_{THF}	x_{THF}	y_{THF}	x_{THF}	y_{THF}
0.201	0.751	0.096	0.647	0.202	0.714
0.398	0.787	0.204	0.731	0.395	0.806
0.700	0.846	0.396	0.781	0.597	0.870
0.798	0.881	0.601	0.839	0.796	0.930
0.898	0.924	0.700	0.881	0.860	0.950
0.949	0.954	0.800	0.918	0.903	0.965
0.968	0.966	0.900	0.955	0.923	0.973
		0.950	0.975	0.945	0.980
		0.971	0.984	0.979	0.991

in Figure 2, by adding PG or Hybrane S1200 to the binary azeotropic solution, the azeotropic system behavior is eliminated in a remarkable manner, as can be seen for 60 wt % and 70 wt % of the respective hyperbranched polymer.

The extent of the hydrogen bond formation between PG and water or Hybrane S1200 and water as well as the solubility of the respective hyperbranched polymers in the aqueous systems decrease with increasing molecular weight. Furthermore, it seems that the solubility behavior[7] of the different hyperbranched polymers, the number of their functionalities (particularly the functional groups on a molecule's surface), and the polarity of the backbone structure determine the relative volatility of the respective ternary system.

Hence, for an additive concentration of 40 wt % and higher, the decrease in the relative volatility $\alpha_{alcohol,water}$ with increasing molecular weight of the respective additive is much smaller for the hyperbranched polyglycerol PG than for the other additives used. Further details concerning the influence of the degree of polymer branching on the phase behavior of selected systems can be found elsewhere.[18]

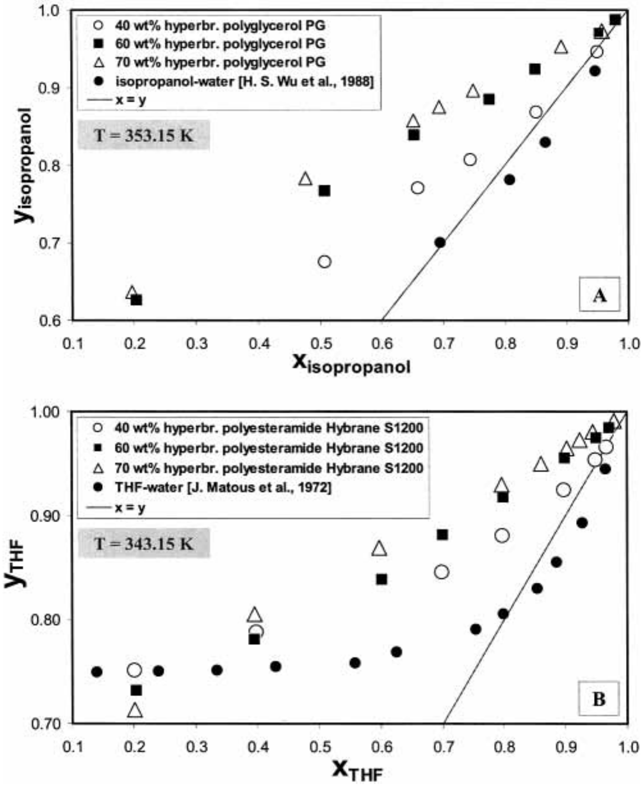

Figure 2. Influence of hyperbranched polymers on vapor−liquid equilibria of aqueous azeotropic systems: (A) 2-propanol + water + hyperbranched polyglycerol PG at 353.15 K (data taken from ref 8); (B) THF + water + hyperbranched polyesteramide Hybrane S1200 at 343.15 K.

Therefore, on the basis of the presented VLE results, it can be concluded that hyperbranched polymers such as the hyperbranched polyesteramide Hybrane S1200 or the hyperbranched polyglycerol PG appear to be promising nonvolatile substances, which can be used as entrainers for the separation of azeotropic mixtures by means of extractive distillation.

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