Liquid−Liquid Phase Equilibria of Binary Systems Containing Hyperbranched Polymer B-U3000: Experimental Study and Modeling in Terms of Lattice Cluster Theory

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The phase behavior of binary mixtures containing hyperbranched polyester Boltorn U-3000 and organic solvents such as hydrocarbon, ether, and linear aliphatic 1-alcohol was studied in the temperature range from about 250 K up to the boiling point of the solvent. The polymer is completely soluble in hydrocarbons (hexane, heptane, benzene, toluene) and ethers (methyl-*tert*-butyl ether, MTBE, or ethyl-*tert*-butyl ether, ETBE) but only partially miscible with alcohols. Liquid−liquid phase equilibria (LLE) diagrams have been determined for binary systems containing the polymer and methanol, ethanol, 1-propanol, or 1-butanol. The solubility of the polymer in alcohols increases with an increase of the chain length of the solvent. Corresponding LLE phase diagrams in 1-propanol and 1-butanol, including spinodal as well as binodal liquid−liquid coexistence curves, were calculated in terms of the statistical mechanics based on the lattice-cluster theory, based only on the upper critical solution temperature and the polymer chain architecture. The results show a semi-qualitative agreement of predicted and experimental equilibrium compositions and temperatures.

Introduction

Since the beginning of 2000s, dendritic polymers (including monodisperse dendrimers as well as polydisperse hyperbranched polymers) became the focus of research in both academic and industrial context and new applications in the field of chemical engineering.[1−6]

Hyperbranched polymers (HPs) are highly branched, globular, three-dimensional macromolecules with a large number of functional end groups increasing exponentially with a generation of the polymer. Because of new properties, HPs are recognized as chemicals with interdisciplinary research exploring a remarkable variety of potential applications. The properties of HPs like remarkable selectivity and capacity, low viscosity and high solubility give the possibility to use them in the separation processes.[2,4,6] Therefore, processes such as extractive distillation, liquid−liquid extraction, absorption, and emulsion in liquid membranes represent promising field of applications. An area of application was widely discussed in the review given by Seiler in recently published paper.[6] It is possible to “tailor” desired properties of HP for the specific industrial tasks and technology by modification of the functional groups or structural variations. The low-viscous branched polymers as polyethers and hyperbranched polyester Boltorn U3000 (B-U3000) have been used for gas separation with supercritical CO_2.[7] It has been shown that branched polymers are promising candidates for gas absorbents with a high capacity for CO_2 and with large selectivities.[7] Polyester materials are being recognized as the most promising family of dendritic materials, much more due to unique factors such as high functional group density with a wide range of substituents, biocompatibility, biodegradability, nontoxicity, and high solubility (sometimes even in water), as well as storage stability.

Polymer solutions often exhibit liquid−liquid phase equilibria (LLE), which occurs at low polymer concentration and depends on temperature, pressure, molecular mass, and the molecular mass distribution of the polymer in the solution. Polymer solution can reveal the upper or lower critical solution temperature (UCST or LCST) in the mixtures with water, alcohol, ketone, or aliphatic hydrocarbons.[8−11] However, there is still a lack of accurate phase equilibria and thermodynamic experimental data for HPs. Because of the polar functional groups and of the intrinsically strong orientation-dependent nature of interaction forces in the (HP + water, or organic solvent) binary mixtures, UCST occurs at the experimentally observed solubility curve or reveals complete miscibility.[2,4] Significant structure, molecular mass, and composition effects are expected to occur in HP systems. The experimental investigation of the phase behavior of HP systems is a crucial requirement for a successful introduction of new application to highly competitive markets.

In present paper we report experimental and theoretical investigation of LLE of binary systems containing hyperbranched polyester B-U3000 and organic solvents: both aliphatic and aromatic hydrocarbons, ethers, and linear aliphatic alcohols. To our best knowledge it is the first paper concerning with phase equilibria in binary systems of B-U3000. Recently, we have published new results of the measurements of physicochemical properties of two HPs: B-U3000 and Boltorn H-2004.[12−16] The atmospheric pressure densities and viscosities of binary mixtures composed of HP and alcohol or ether were reported by us for these two polymers.[12,13] Moreover, the activity coefficients at infinite dilution of various organic solutes in the HPs (B-U3000 and Boltorn H-2004) were recently published.[14,15] Additionally, the separation problem of the hexane/ethanol mixtures was tested with B-U3000 at $T = 298.15$ K with minor results.[16]

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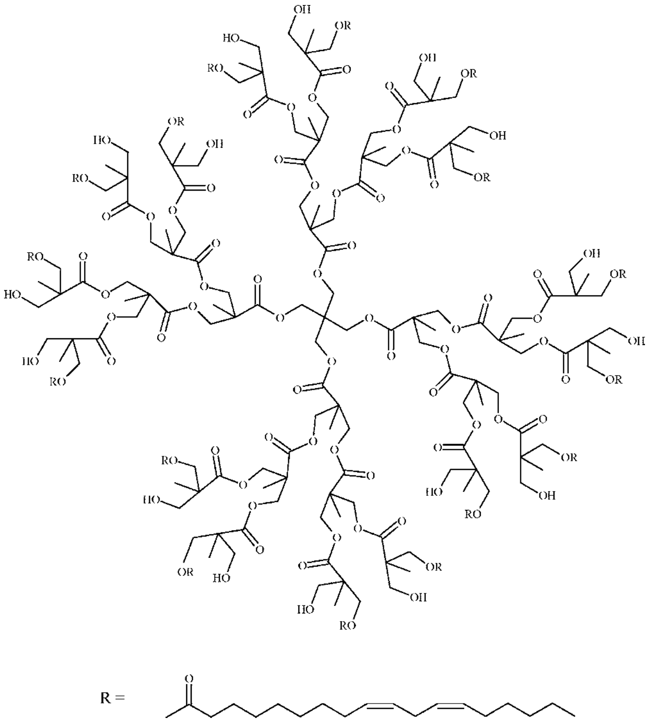

Figure 1. Boltorn U3000 HP chemical structure.

Table 1. Experimental LLE Data for Binary Systems {B-U3000 (B) + an Alcohol (A)}: Equilibrium Mass Fraction (w_B) and Equilibrium Temperature (*T*)

methanol		ethanol		1-propanol		1-butanol	
w_B	T/K	w_B	T/K	w_B	T/K	w_B	T/K
0.8364	342.1	0.6090	345.0	0.1144	316.9	0.0396	283.4
0.8622	335.1	0.6476	339.1	0.1297	315.9	0.0438	283.8
0.9022	317.4	0.6958	330.9	0.1407	315.6	0.0512	284.3
0.9238	300.7	0.7356	323.2	0.1588	314.0	0.0564	284.7
0.9480	271.6	0.7606	316.3	0.1781	313.2	0.0640	285.6
		0.7802	312.0	0.2090	311.7	0.0748	286.0
		0.7973	306.7	0.2449	310.0	0.0868	286.2
		0.8099	302.3	0.2621	309.3	0.0951	286.4
		0.8247	296.9	0.2763	308.3	0.1040	286.5
		0.8357	291.5	0.2911	307.6	0.1196	286.3
		0.8560	285.0	0.3043	307.1	0.1397	285.9
		0.8692	276.5	0.3305	306.1	0.1577	285.6
		0.8824	271.4	0.3634	304.8	0.1774	285.1
		0.8994	258.9	0.3883	303.8	0.1944	284.4
		0.9239	251.9	0.4174	302.4	0.2172	283.5
		0.9323	243.5	0.4532	300.8	0.2402	282.6
				0.4748	299.8	0.2688	281.3
				0.4976	298.6	0.3024	279.9
				0.5218	297.2	0.3321	278.7
				0.5489	295.4	0.3607	277.6
				0.5763	293.3	0.3886	276.4
				0.6173	289.6	0.3959	275.8
				0.6412	286.6	0.4312	274.5
				0.7122	277.2		

In the first part of the present paper, the experimental thermodynamic study on the solubility behavior is described, followed by the second part focusing on the modeling of the phase behavior in terms of a lattice cluster theory (LCT). Unfortunately, the new thermodynamic model, developed for HB mixtures, the perturbed-chain polar statistical association fluid theory (PCP-SAFT)[17] has not given a good representation of the miscibility gaps obtained in this work.

Experimental Section

Materials. The studied HP B-U3000 ($M_w = 6500\ \text{g}\cdot\text{mol}^{-1}$, $M_w/M_n = 1.5$) was provided by Perstorp Specialty Chemicals AB, Sweden. Before use the polymer was dried under high vacuum at 330 K for 24 h. B-U3000 is fatty modified dendritic polymer produced from pentaerythritol core and bis(hydroxymethyl)propionic acid (*bis*-MPA) and later estrified with long-chain fatty acids (C_{16} and C_{18}; 90 %).[7] The structure of the polymer is presented in Figure 1. The basic thermal characterization of B-U3000 (DSC measurements) was presented by us earlier.[16] The polymer is liquid up to the glass transition temperature, $T_g = 234.1$ K.

All utilized solvents, that is, hexane, heptane, benzene, toluene, *tert*-butyl methyl ether (MTBE), *tert*-butyl ethyl ether (ETBE), methanol, ethanol, 1-propanol, and 1-butanol were obtained from Sigma-Aldrich Chemie GmbH, Steinheim, Germany. Before direct use, they were fractionally distilled over different drying reagents to a mass fraction purity of 0.998. They were also stored over freshly activated molecular sieves of type 4A (Union Carbide) and checked by gas chromatography.

Phase Equilibria Apparatus and Measurements. A dynamic (synthetic) method of the solubility measurements was used in the present work, according to all of the procedures described in detail previously.[18] Mixtures of polymer and solvent were prepared by weighing the pure components within an accuracy of 10^{-4} g to obtain a system of two partially miscible liquid phases of desired mass fraction of the polymer. The sample was heated very slowly (at heating rate less than $2\ \text{K}\cdot\text{h}^{-1}$) with continuous stirring inside a Pyrex glass cell placed in a thermostat. The temperature at which one of the liquid phases disappears was detected visually and was measured with an electronic thermometer P550 (DOSTMANN Electronic GmbH). The thermometer was calibrated on the basis of ITS-90. The accuracy of the temperature measurements was judged to be 0.05 K. Mixtures mass fraction errors did not exceed $5\cdot10^{-4}$. The reproducibility of the LLE measurements was 0.1 K. The direct results of the measurements (mass fraction of HP vs equilibrium temperature) are presented in Table 1.

Theoretical Considerations

To better understand the phase behavior of studied (polymer + alcohol) mixtures, the LLE calculations have been performed in terms of the statistical mechanics LCT proposed by Freed et al.[19−27] The theory is applicable to an arbitrary chain architecture given by complicated branching pattern in which monomers have specified structures. For the homogeneous binary mixture composed of N_A molecules of solvent (A) and of N_B molecules of polymer (B), the LCT is considered as an incompressible lattice composed of N_l sites. Lattice sites can be occupied either by polymer segments or solvent molecules, and each site has z nearest neighbors, that is, z is the coordination number of the lattice.

Since polymer molecules are much larger than solvent molecules, one can assume that solvent molecules have no specified structure and thus occupy one site of the lattice. In turn, polymer's molecules occupy M sites. The number of sites occupied by a HP molecule can be calculated basing on the following input data: the number of branches attached to the polymer core (b), the generation number of polymer (g), and numbers of segment occupied by core (n_0) and an repeatable structural unit of polymer (n). Then

$$M = b(2^g - 1)n + n_0 \qquad (1)$$

From M other structure parameters included in LCT can be calculated:[26]

$$N_1 = M - 1 \tag{2a}$$

$$N_2 = M - 2 + b_3 + 3b_4 \tag{2b}$$

$$N_3 = M - 3 + 2b_3 + 6b_4 \tag{2c}$$

$$N_\perp = b_3 + 4b_4 \tag{2d}$$

$$N_{1,1} = N_1(N_1 - 1)/2 - N_2 \tag{2e}$$

$$N_{1,2} = N_1N_2 - 2N_2 - 2N_3 - 3N_\perp \tag{2f}$$

They correspond to the number of bonds in each polymer molecule (N_1), the number of ways in which three bonds intersect (N_2), the number of ways in which three consecutive bonds can be chosen (N_3), the number of ways in which three bonds meet at a lattice site for polymer chain ($N_\perp$), the number of distinct ways of selecting two nonsequential bonds on the same chain ($N_{1,1}$), and the number of distinct ways of selecting one bond and two sequential bonds on the same chain. Parameters b_3 and b_4 are equal to the numbers of vertices of degree 3 and 4, respectively, and can be derived from polymer chain architecture.

The composition of the mixture is expressed in terms of volume fractions of solvent and polymer which are defined as:

$$\phi_A = \frac{N_A}{N_l} \qquad \phi_B = \frac{N_BM}{N_l} \tag{3}$$

The Helmoltz free energy of mixing ΔA^M is considered as a sum of two contributions, ΔA^M_{int} and ΔA^M_{ath}, referred as interactions and athermal terms, respectively:

$$\Delta A^M = \Delta A^M_{int} + \Delta A^M_{ath} \tag{4}$$

The former corresponds to both mutual and cross interactions between molecules of polymer and solvent, whereas the latter are related to the athermal limit value of entropy of mixing depending only on polymer structure.

The free energy is given in a double expansion series with $1/z$ and $\beta\varepsilon$ truncated after second-order term, where ε stands for segment−segment interchange energy defined as

$$\varepsilon = \varepsilon_{AA} + \varepsilon_{BB} - 2\varepsilon_{AB} \tag{5}$$

and $\beta = 1/(kT)$, where k is the Boltzmann constant. In equation above, ε_{AA}, ε_{BB}, and ε_{AB} correspond to the interaction energies of solvent−solvent, nonbonded polymer−polymer, and solvent−polymer site contacts, respectively. For the considered mixture the expressions for both contributions, originally developed by Dudowicz et al.,[26] were rearranged and corrected by Zeiner et al.[28] The equations used in this work were presented earlier.[28]

Considering two partially miscible liquid phases and a standard LLE calculation problem, the chemical potentials of both polymer and solvent in each phase must be equal. Thus, to calculate equilibrium compositions, ϕ'_B and ϕ''_B, the following set of equations must be solved:

$$\Delta\mu'_A = \Delta\mu''_A \qquad \Delta\mu'_B = \Delta\mu''_B \tag{6}$$

where $\Delta\mu$ denotes actually the difference between the chemical potential in the mixture and the pure component (the partial free energy of mixing). The expressions for chemical potentials can be derived from the free energy of mixing and Gibbs−Duhem relations:

$$\begin{aligned} \Delta\mu_A &= \frac{\partial \Delta A^M}{\partial N_A} = \frac{\Delta A^M}{N_l} - \phi_B \frac{\partial \Delta A^M/N_l}{\partial N_B} \\ \Delta\mu_B &= \frac{\partial \Delta A^M}{\partial N_B} = \frac{\Delta A^M}{N_l} + (1 - \phi_B) \frac{\partial \Delta A^M/N_l}{\partial N_B} \end{aligned} \tag{7}$$

By solving eq 6, utilizing relations given in eq 7 and expressions for LCT parameters (see ref 28) for different temperatures, it is possible to describe a binodal curve. Moreover, in the calculations of the metastable compositions, the spinodal curve condition as a second derivative of ΔA^M (interaction parameter) with respect to ϕ_B equals zero.

The input data required to calculate LLE in terms of the LCT model are the following: lattice geometry (z), structural data of polymer (b, g, n_0, n), and energetic parameter related to interactions between polymer and solvent (ε). All of them can be set as adjustable parameters which fit experimental data to model calculations. On the other hand, the structural parameters can be chosen based on analysis of polymer structure. In turn, ε could be estimated based on the experimental data, for example, the UCST as a defined quantity. Then LCT becomes a "tool" to LLE phase diagram prediction.

The energetic parameter ε was estimated by fitting the experimental UCST to the model calculations. The thermodynamic condition for UCST is that the second and the third derivative of ΔA^M simultaneously equals zero. The following systems of two equations with two unknowns ε and ϕ_B (at UCST) are as follows:

$$\frac{\partial^2 \Delta A^M}{\partial \phi_B^2} = 0 \qquad \frac{\partial^3 \Delta A^M}{\partial \phi_B^3} = 0 \tag{8}$$

Results and Discussion

Phase Equilibria Measurements. B-U3000 is completely miscible with both aliphatic and aromatic hydrocarbons (hexane, heptane, benzene, and toluene) as well as ethers (MTBE and ETBE) in the studied temperature range, that is, above 250 K. However, the binary systems (B-U3000 + alcohol) exhibit liquid phase immiscibility with UCST behavior and a wide miscibility gap. The obtained experimental LLE phase diagrams are presented in Figure 2. In the case of systems with 1-propanol and 1-butanol, UCST points were measured, and the resulting values are (317 and 287) K, respectively. For the systems with methanol and ethanol the UCST were much higher than the boiling point of the solvent, and thus they could not be detected. The second problem was to use the visual method in the alcohol-rich region, which led to the impossibility of obtaining the experimental data at this low concentration region for methanol and ethanol.

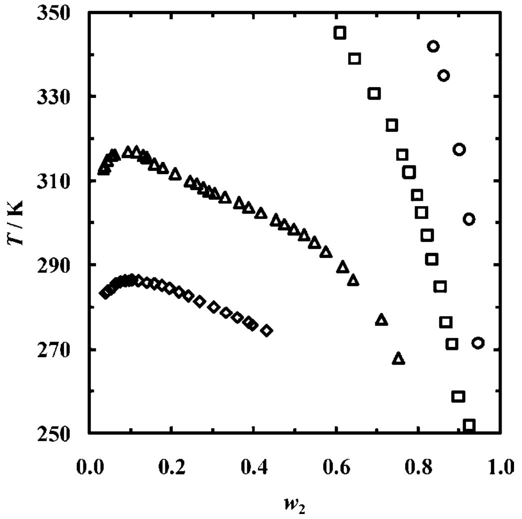

Figure 2. Experimental LLE in binary systems (B-U3000 + alcohol): ○, methanol; □, ethanol; △, 1-propanol; ◇, 1-butanol.

The solubility of B-U3000 in alcohols increases with an increase of the chain length of the solvent which is quite different behavior in comparison with systems containing typical organic substances or ionic liquids. Moreover, an increase of the alkyl chain length of an alcohol causes the decrease in the UCST and shifts the critical composition toward lower polymer concentration. The obtained trend can be explained as a result of higher interactions of polymer molecules with an alcohol molecules as the carbon chain length of an alcohol increases. The nature of the interactions can be related with parallel packing effects due to van der Waals dispersive forces.

LCT Calculations. Two LLE phase diagrams were calculated in terms of the LCT model. First of all, the model parameters were estimated. For the polymer B-U3000, *b* and *g* parameters follow directly from the polymer chain architecture: the polymer of third generation ($g = 3$) with 4 branches ($b = 4$) was assumed. The coordination number of the lattice was assumed to be equal 12, in spite that in the original formulation of LCT a simple cubic with $z = 6$ was considered. Following the paper of Zeiner et al.[28] and Monte Carlo simulations results published by Falsafi and Madden,[29] the assumption was made that each solvent's molecule occupies one site of the lattice. The polymer core and monomer structure was decomposed into functional groups to choose appropriate values of the parameters n_0 and n. The core is composed of five groups (one >C< and four $-CH_2O-$ groups). In turn, the monomer was assumed to be built of three groups: one $C(CH_3)C(O)-$ and two $-CH_2O-$ groups. It results in $n_0 = 5$ and $n = 3$. Thus, following eq 1, the polymer occupies $M = 89$ sites of the lattice. To calculate other geometric properties listed in eqs 2a to 2f, b_3 and b_4 have to be estimated. The core contains no branching points of degree 3 and one branching point of degree 3, while the repeating unit has in its structure just one branching point of degree 3. Therefore $b_3 = 28$ and $b_4 = 1$.

In the case of mixtures with methanol or ethanol the experimental UCST were not obtained experimentally; thus these data were not described by the model. The calculated values of the interaction parameters of LCT are listed in Table 2. Resulting binodal as well as spinodal curves are presented together with respective experimental data for 1-propanol and 1-butanol in Figures 3 and 4.

Table 2. Interaction Parameters of the LCT Model for Binary Systems (B-U3000 + Alcohol) Determined From the UCST of LLE

solvent	UCST/K	ε/k/K
1-propanol	317	38.1156
1-butanol	287	34.4483

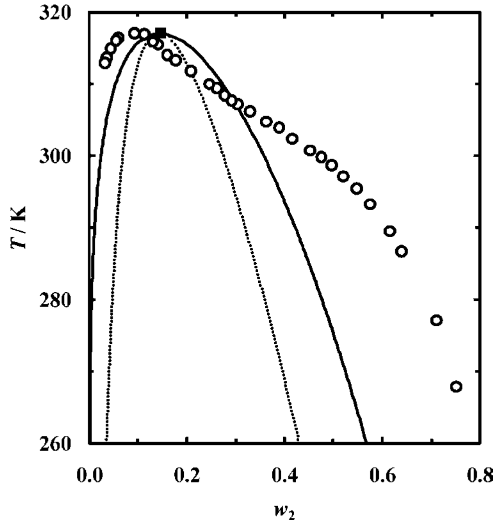

Figure 3. LLE in the binary system (B-U3000 + 1-propanol). Points are designated to experimental data. Solid and dotted lines correspond to binodal and spinodal curves, respectively, calculated in terms of LCT with the interaction parameter $\varepsilon/k = 38.1156$ K.

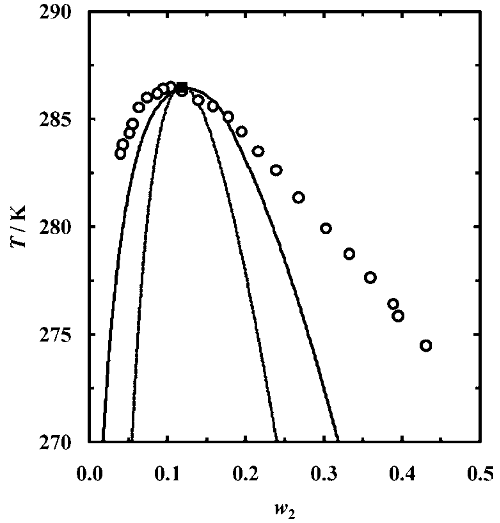

Figure 4. LLE in the binary system (B-U3000 + 1-butanol). Points are designated to experimental data. Solid and dotted lines correspond to binodal and spinodal curves, respectively, calculated in terms of LCT with the interaction parameter $\varepsilon/k = 34.4483$ K.

As one can easily see, the qualitative agreement was obtained between experimental data and calculated results. In the case of each solvent the LCT model predicts higher solubility of B-U3000 in alcohols (the lower immiscibility gap) in comparison with the measured values. The average relative deviation of calculated mass fraction of solubility is about 10 %.

Conclusion

New experimental data sets of (liquid + liquid) phase equilibria in binary systems (hyperbranched polyester B-U3000 + an alcohol) have been reported in the temperature range from 250 K up to the boiling point of an alcohol or UCST. The polymer is completely miscible with aliphatic and aromatic hydrocarbons (hexane, heptane, benzene, toluene) as well as with ethers (MTBE and ETBE).

Semipredictive calculations of liquid–liquid binodal and spinodal curves for studied systems were performed in terms of LCT. Results are in qualitative agreement with experimental data. One might expect that the predicted solubility should be lower because the applied model does not take into account specific interactions contribution into the free energy of mixing. Considering such a contribution, one can obtain the UCST much lower.[30] The LCT applied in the present study assumes only dispersive van der Waals interactions (expressed in terms of the ε parameter) without the hydrogen bonds. The semi-qualitative agreement of experimental data with performed calculations was obtained. The conclusion could be made, however, that essentially steric effects (e.g., parallel packing) predominate significantly over the specific interactions in the systems (HP + an alcohol).

Modeling of the experimental data, even in terms of relatively simple but still molecular consideration-based foundations, allows better understanding and interpreting the molecular nature of the complex systems' phase behavior.

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