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(Liquid + liquid) equilibria of binary systems containing hyperbranched polymer Boltorn® H2004 – Experimental study and modelling in terms of lattice-cluster theory

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ABSTRACT

(Liquid + liquid) phase equilibria (LLE) of binary mixtures containing hyperbranched polymer Boltorn® H2004 and *n*-alkanes (*n*-hexane, *n*-heptane, *n*-octane, and *n*-decane) were studied over the temperature range from about (260 up to 360) K. The polymer is partially miscible with *n*-alkanes and the solubility decreases with an increase of the chain length of the solvent. Corresponding LLE phase diagrams including spinodal and 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 semi-qualitative agreement of predicted and experimental equilibrium compositions and temperatures. Boltorn® H2004 reveals complete miscibility in the liquid phase with alcohols (C_1–C_8), aromatic hydrocarbons (benzene, toluene, and thiophene), and ethers (methyl *tetra*-butyl ether, ethyl *tetra*-butyl ether, and tetrahydrofurane).

1. Introduction

The term hyperbranched polymers (HPs) is used to describe a relatively new class of polymers that are liquid at or near room temperatures. Typically polydisperse hyperbranched polymers are globular, three-dimensional macromolecules with a large number of functional end groups increasing exponentially with a generation of the polymer. The HPs became the focus of research in academic society as new potential solvents of applications in the field of chemical engineering [1–6]. An interesting aspect of HPs is that the physical and chemical properties are dependent on the mass fraction and substituent end groups. HPs have practically negligible vapour pressure and are used as novel solvents with an enhanced degree of tunability. Moreover, these characteristics and other such as toxicity or biodegradability can be tuned by judicious of the combination of polar-end groups constitutive of the HP [6]. The possible application was widely discussed in the review given by Seiler and co-workers [5].

The hyperbranched polymer, Boltorn® H2004 (B-H2004), is a fatty acid modified dendritic polyester. It has a highly branched polymer backbone based on second-generation hydroxy-functional hyperbranched polyester in which 62.5% of the hydroxy-functional end groups have been modified with a 8-carbon-long alkyl acid [3]. The B-H2004 was modified to a greater extent than the previous generation, giving a higher molar mass and a lower amount of remaining hydroxyl groups.

Polymer solutions often exhibit (liquid + liquid) phase equilibria (LLE), which occur at low polymer concentration and depend on temperature, pressure, molecular mass, and the molecular mass distribution of the polymer in the solution. The polymer solution can reveal the upper or lower critical solution temperature (UCST or LCST) in the mixtures with water, alcohol, ketones, or *n*-alkanes [7,8]. The experimental investigation of the phase behaviour of HP systems is a crucial requirement for a successful introduction of new application to highly competitive markets.

This work is a continuation of our previous studies on B-H2004 [9–11], which focused on the LLE of B-H2004. In this study, we investigated the LLE of B-H2004 with *n*-alkanes, alcohols, aromatic hydrocarbons, and ethers. Characteristics investigated here include the effect of the *n*-alkane chain length (from *n*-hexane to *n*-decane). A comparison of the phase behaviour for similar HPs is discussed. In addition to experimental work, all systems are correlated using the Non-Random Two-Liquid (NRTL) equation using two binary interaction parameters [12]. The modelling of the phase behaviour in terms of a lattice-cluster theory (LCT) was also proposed [13–15]. Recently, we have published new results of the measurements of LLE of Boltorn® U3000 with alcohols using the LCT model to predict the LLE phase behaviour [11]. Moreover, the activity coefficients at infinite dilution of various organic solutes in the B-H2004 were recently published [9].

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2. Experimental

2.1. Materials

The hyperbranched polymer, Boltorn H2004 (B-H2004), (Perstorp, Sweden, 0.98 mass fraction) is a fatty acid modified dendritic polyester (see figure 1). The physiochemical properties are listed in table 1. The B-H2004 was purified by subjecting the liquid to a very low pressure of about $5 \cdot 10^{-3}$ Pa at temperature 300 K for approximately 48 h. This procedure removed any volatile chemicals and water from the polymer. The densities and viscosities of B-H2004 were presented earlier [10].

All utilized solvents, *i.e.* *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, methanol, ethanol, 1-propanol, 1-butnol, 1-hexanol, 1-heptanol, 1-octanol, benzene, toluene, thiophene, methyl *tetra*-butyl ether, ethyl *tetra*-butyl ether, and tetrahydrofurane, were obtained from Sigma–Aldrich Chemie GmbH, Steinheim, Germany. Before direct use, they were fractionally distilled over different drying reagents to 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.

2.2. Phase equilibria apparatus and measurements

A dynamic (synthetic) method of the solubility measurements was used in the present work, according to all the procedures described in details previously [9]. (Polymer + 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 $2\ \mathrm{K \cdot h^{-1}}$) 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 $5 \cdot 10^{-4}$. The reproducibility of the LLE measurements was 0.1 K.

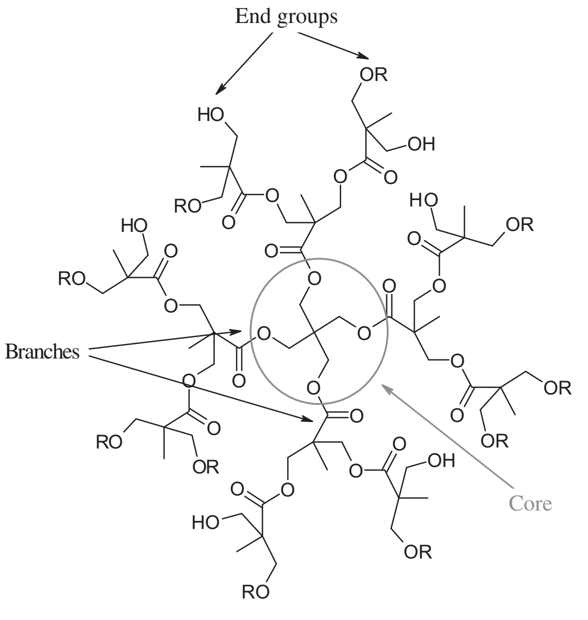

FIGURE 1. Structural formula of the studied hyperbranched polymer Boltorn® H2004 (abbreviated by B-H2004) where R stands for 8-carbon-long alkyl acid.

3. Results and discussion

The direct results of the measurements (mass fraction of hyperbranched polymer, w_1 *vs.* equilibrium temperature, T/K) are presented in table 2.

Polymer B-H2004 is completely miscible with alcohols (methanol, ethanol, 1-propanol, 1-butnol, 1-hexanol, 1-heptanol, and 1-octanol) and aromatic hydrocarbons (benzene, toluene, and thiophene) as well as ethers (methyl *tetra*-butyl ether, MTBE; ethyl *tetra*-butyl ether, ETBE; and tetrahydrofurane, THF) over the temperature range studied, *i.e.* $T > 250$ K. The responsibility for these strong interactions between the polymer and the solvent is made by the polar-end groups of the polymer: hydroxyl group, carbonyl group, esters group, and ether group. However, the binary systems (B-H2004 + *n*-alkanes) exhibit mutual solubility in the liquid phase with Upper Critical Solution Temperature (UCST) behaviour and a wide miscibility gap. The experimental LLE phase diagrams obtained are presented in figures 2 to 5. In these systems, the UCST points were not measured, because the temperatures were higher than the boiling temperatures of the solvent. It was also impossible to determine the experimental data in the low concentration region of polymer using the visual method. The uncertainty of the solubility measurement was $\delta w_i = 5 \cdot 10^{-4}$ and at the mass fraction $w_i = 1 \cdot 10^{-4}$ it was a permanently foggy solution, which means the occurrence of binary phases. In the *n*-alkane-rich region, the solubility was assumed on a level of $w_i = 1 \cdot 10^{-5}$, which leads to the possibility of obtaining the UCST by the correlation with the NRTL equation.

The solubility of B-H2004 in *n*-alkanes decreases with an increase of the chain length of the solvent, which is a typical behaviour for organic, or hyperbranched polymer substances. In addition, an increase of the alkyl chain length of the *n*-alkane causes the decrease of critical temperature (T_c) of the UCST. The trend can be explained as a result of better interstitial accommodation of the shorter carbon chain length of *n*-alkane within the polymer molecule. The nature of the interactions can be related with parallel packing effects due to van der Waals dispersive forces between the *n*-alkane and the RO– group, where R is the rest from the esterification with 8-carbon-long alkyl acid [3].

Table 2
Experimental (liquid + liquid) phase equilibrium data for binary systems {B-H2004 (1) + *n*-alkane (2)}: weight fractions of the polymer (w_1) and temperature (T).

w_1	T/K	w_1	T/K
{B-H2004 (1) + n-hexane (2)}		*{B-H2004 (1) + n-heptane (2)}*	
0.5227	270.1	0.4557	294.3
0.4839	277.5	0.4210	299.1
0.4434	285.2	0.3516	311.8
0.3924	295.0	0.3245	316.5
0.3508	302.2	0.2512	332.0
0.3034	312.0	0.2220	337.8
0.2435	325.4	0.1886	349.8
0.2097	339.1	0.1616	362.8
{B-H2004 (1) + n-octane (2)}		*{B-H2004 (1) + n-decane (2)}*	
0.5025	301.7	0.6706	296.7
0.4500	309.9	0.6196	312.2
0.4065	316.1	0.5589	325.4
0.3368	330.1	0.4905	335.6
0.2891	339.3	0.4371	342.7
0.2437	347.0	0.3745	350.5
0.2048	355.1	0.2980	361.6

TABLE 1
Investigated polymer Boltorn® H2004: measured thermophysical properties, molecular mass (M), glass transition temperature (T_g), and heat capacity change at T_g ($\Delta C_{p(g)}$), density (ρ) at $T = 298.15$ K and dynamic viscosity (η) at $T = 298.15$ K.

Property	$M/(\mathrm{g \cdot mol^{-1}})$	T_g[a]/K	$\Delta C_{p(g)}$[a]/(J mol$^{-1} \cdot$ K^{-1})	ρ (298.15 K)[b]/(g $\cdot$ cm^{-3})	η (298.15 K)[b]/(mPa $\cdot$ s)
Boltorn® H2004	3200	215.0 ± 0.1	1.70 ± 0.003	1.0765	13484

[a] DSC measurements, reference [9].
[b] Reference [10].