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Mass-Fraction Activity Coefficients at Infinite Dilution Measurements for Organic Solutes and Water in the Hyperbranched Polymer Boltorn W3000 Using Inverse Gas Chromatography

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Thermodynamic properties of hyperbranched polymer, Boltorn BW3000, were investigated by inverse chromatography with 42 different solvents: alkanes (C_5-C_{10}), cycloalkanes (C_5-C_8), alkenes (C_5-C_8), alkynes (C_5-C_8), aromatic hydrocarbons (benzene, toluene, ethylbenzene, *o*-, *m*-, *p*-xylene, thiophene), alcohols (C_1-C_5) and water, ethers (diethyl-, di-*n*-propyl-, di-*n*-butylether, methyl-*tert*-butylether, MTBE, tetrahydrofuran, THF), and ketones (propanone, 2-pentanone, 3-pentanone, 2-hexanone, 3-hexanone, cyclopentanone) at the temperatures ranging from (308.15 to 348.15) K. The density and thermophysical properties of polymer were described. The specific retention volume (V_g), the mass-fraction activity coefficient at infinite dilution (Ω_{13}^{∞}), the Flory−Huggins parameter (χ_{13}^{∞}), the molar enthalpy of solute's absorption in the polymer ($\Delta_s H$), the partial molar excess enthalpy at infinite dilution ($\Delta H_1^{E,\infty}$), the partial molar Gibbs excess energy at infinite dilution ($\Delta G_1^{E,\infty}$), and the solubility parameter of the polymer (δ_3) were calculated.

Introduction

The hyperbranched polymers (HBPs) have attracted considerable engineering attention as new entrainers in the different separation processes, membrane processes, and gas separation applications.[1−7] These applications benefit from the molecular interactions offered by hyperbranched polymers with polar solvents and are characterized in a large numbers of reviews.[1,8,9] HPBs are highly branched, polydisperse macromolecules with a three-dimensional topology and a large number of different functional end groups. Due to their unique properties such as wide liquid range, stability at high temperatures, low viscosity in relation to the molecular mass conventional polymers, and their globular structure, HBPs were considered as good replacements for conventional volatile often flammable and toxic organic solvents in chemical industry. HBPs have been used in industrial processes as gas absorbents with a high capacity for CO_2 and with large selectivities.[5] Polyester materials have been recognized as the most promising family of HBPs, much due to unique properties such as high functional group density with a wide range of substituents, biocompatibility, biodegradability, nontoxicity, high solubility (sometimes even in water), as well as storage stability.[10,11] HBPs also have a wide array of applications in the field of chemical engineering, as recently was shown by Seiler.[6] HBP like Boltorn was found to be capable of breaking the THF and water azeotrope[6] but was not suitable for the separation of the hexane and ethanol azeotropic mixture.[11] Physical and chemical properties of HBP are influenced not only by the number of the functional groups but also by the polarity of the groups. For HBP to be effectively used as entrainers in liquid−liquid extraction, or in other fields, the knowledge of the density, solubility parameter, and activity coefficient at infinite dilution is fundamental.

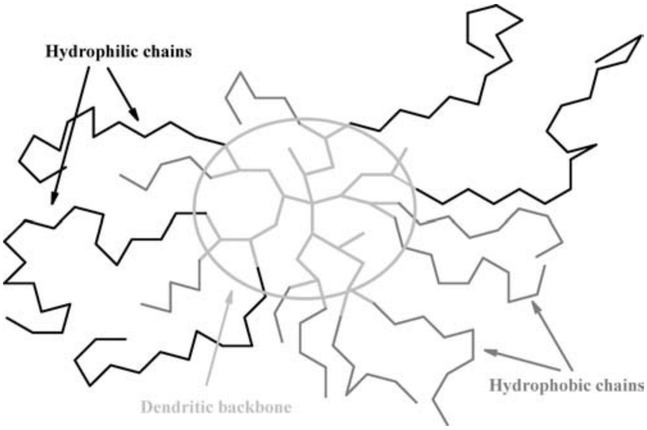

Figure 1. Schematic image of B-W3000.

In separation processes, both properties of solvent (polymer) are important, namely, selectivity and capacity,[12] and can be directly calculated from the mass-fraction activity coefficient at infinite dilution (Ω_{13}^{∞}) for different separation problems. The structure of polymer has high influence on the values of Ω_{13}^{∞}. The important measure of this property is given by the mass-fraction activity coefficient at infinite dilution, which describes the nonideality for chosen species in a mixture. Since the HBPs have a negligible vapor pressure, the inverse gas chromatography (IGC) is a suitable method for measuring Ω_{13}^{∞}.[13]

The hyperbranched polymer, Boltorn W3000 (B-W3000), is an amphiphilic dendritic polymer (see Figure 1). It contains long unsaturated fatty acid chains. It is a viscous liquid or a wax at room temperature. Our experimental density data of B-W3000 at $T = 308.15$ K are presented in Table 1. There is a large number of studies of weight-fraction activity coefficients at infinite dilution for HBP.[14−19] It allows expanding our knowledge about the nature of the HBP and influence of polar functional groups and the structure on thermodynamical proper-

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Table 1. Investigated Polymer B-W3000: Molecular Mass (M), Fusion Temperature (T_{fus}), Enthalpy of Fusion ($\Delta_{\text{fus}}H$), Glass Transition Temperature (T_g), Heat Capacity Change at T_g ($\Delta C_{p(g)}$), and Density (d) at $T = 308.15$ K

M	T_{fus}	$\Delta_{\text{fus}}H$	T_g	$\Delta C_{p(g)}$	d
$\text{g}\cdot\text{mol}^{-1}$	K	$\text{kJ}\cdot\text{mol}^{-1}$	K	$\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\text{g}\cdot\text{cm}^{-3}$
9000[a]	301.2 ± 0.2[b]	339.70 ± 5[c]	205.2 ± 0.2[b]	2.76 ± 0.04[c]	1.0408

[a] Provided by Perstorp, Sweden. [b] The uncertainty of the temperature measurements was ± 0.2 K. [c] The uncertainty of the calorimetric measurements was estimated to be ± 1.5 %.

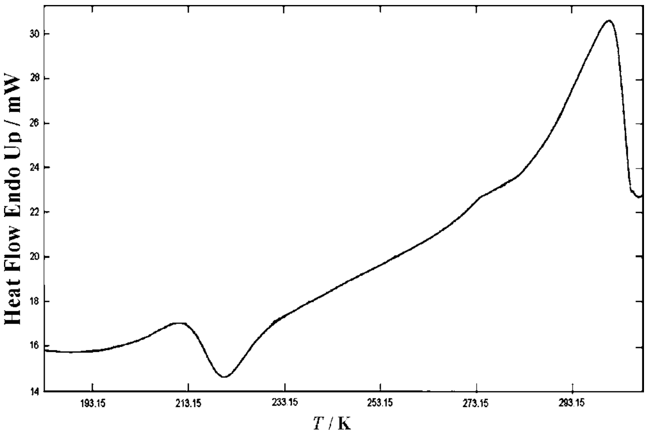

Figure 2. DSC thermogram of Boltorn W3000.

Table 2. Column Specification and Chromatograph Condition

	column 1	column 2
loading/mass %	20	25
mass coated/g	0.6437	0.8068
column length/m	1	
column i.d./mm	4	
column temperature/K	308.15 to 348.15	
injector temperature/K	423.15	
detector temperature/K	423.15	
carrier gas	helium	
flow/$\text{mL}\cdot\text{min}^{-1}$	100 to 150	

ties of HBP and designing a suitable solvent for a specific extraction problem. It was shown earlier in many investigations that the selectivities of hyperbranched polymers[3−6] in separating organic liquids are often higher than those for commonly used solvents, such as *N*-methyl-2-pyrrolidinone (NMP) or (NMP + water).[20] However, the examination has to always be done of the selectivity together with capacity for a variety of solutes in entrainers to provide a picture of interactions and costs.

For this study, the mass-fraction activity coefficient at infinite dilution, Ω_{13}^{∞}, for the 42 different solutes, alkanes (C_5-C_{10}), cycloalkanes (C_5-C_8), alkenes (C_5-C_8), alkynes (C_5-C_8), aromatic hydrocarbons (benzene, toluene, ethylbenzene, *o*-, *m*-, *p*-xylene, thiophene), alcohols (C_1-C_5), water, ethers (tetrahydrofuran (THF), methyl-*tert*-butylether (MTBE), diethyl-, di-*n*-propyl-, di-*n*-butyl ether), and ketones (propanone, 2-pentanone, 3-pentanone, 2-hexanone, 3-hexanone, cyclopentanone), was studied in the hyperbranched polymer Boltorn W3000 at the temperatures from (308.15 to 348.15) K using inverse gas chromatography (IGC). The specific retention volume (V_g), the Flory−Huggins parameter (χ_{13}^{∞}), molar enthalpy of solute's absorption in the polymer ($\Delta_s H$), partial molar excess enthalpy at infinite dilution ($\Delta H_1^{E,\infty}$), the partial molar Gibbs excess energy at infinite dilution ($\Delta G_1^{E,\infty}$), and the solubility parameter (δ_3) were calculated.

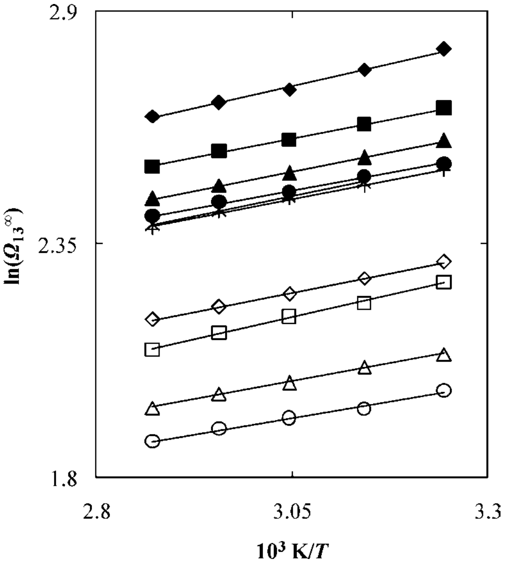

Figure 3. Plot of ln Ω_{13}^{∞} versus $1/T$ for the solutes: ◆, pentane; ■, hexane; ▲, heptane; ●, octane; +, nonane; ×, decane; ◇, cyclopentane; □, cyclohexane; ○, cycloheptane; △, cyclooctane.

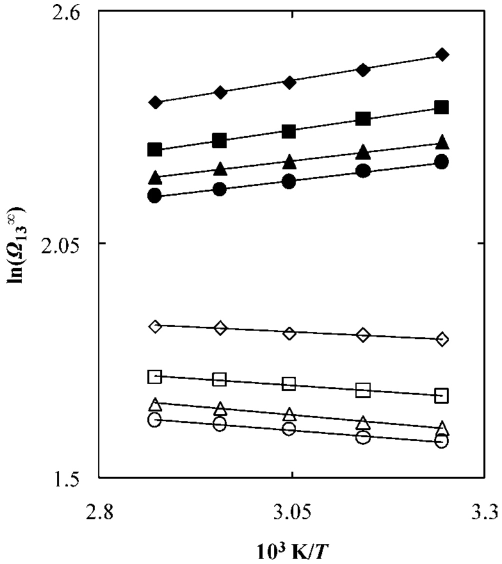

Figure 4. Plot of ln Ω_{13}^{∞} versus $1/T$ for the solutes: ◆, 1-pentene; ■, 1-hexene; ▲, 1-heptene; ●, 1-octene; ◇, 1-pentyne; □, 1-hexyne; ○, 1-heptyne; △, 1-octyne.

Experimental Section

Materials. The hyperbranched polymer, Boltorn W3000 (B-W3000) (Perstorp, Sweden, 0.98 mass fraction), is a fatty acid modified dendritic polyester. It is highly viscous and a slightly yellow liquid or wax at room temperature. The density, d(308.15 K), is 1.0408 $\text{g}\cdot\text{cm}^{-3}$. The B-W3000 was further purified by subjecting the liquid to a very low pressure of about $5\cdot10^{-3}$ Pa at temperature $T = 330$ K for approximately 48 h. This procedure removed any volatile chemicals and water from the polymer.

The solutes, purchased from Aldrich and Fluka, were used without further purification because the IGC technique separated any impurities on the column.

Differential Scanning Microcalorimetry. Basic thermal characteristics of the hyperbranched polymer, i.e., temperature of fusion (T_{fus}), enthalpy of fusion ($\Delta_{\text{fus}}H$), glass transition temperature (T_g), and heat capacity change at T_g($\Delta C_{p(g)}$) have been measured with a differential scanning microcalorimetry

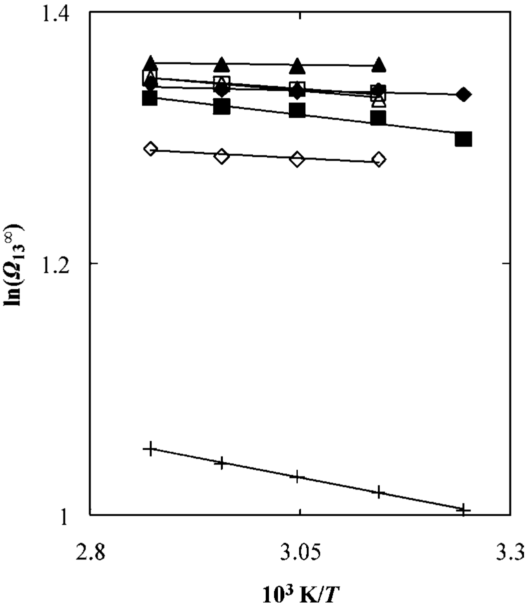

Figure 5. Plot of ln Ω_{13}^{∞} versus 1/*T* for the solutes: ♦, benzene; ■, toluene; ▲, ethylbenzene; ◇, *o*-xylene; □, *m*-xylene; Δ, *p*-xylene; +, thiophene.

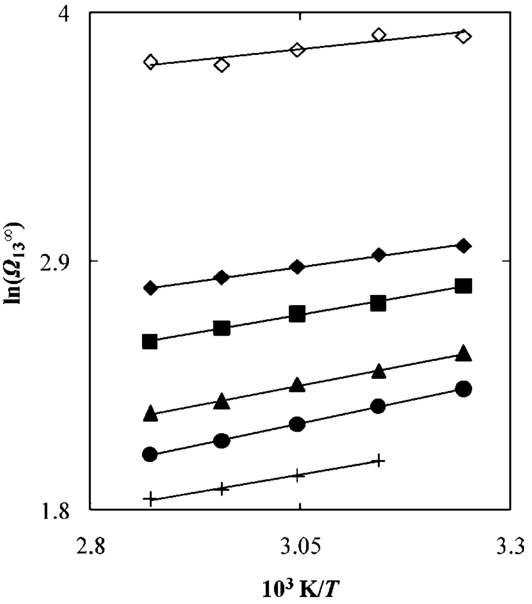

Figure 6. Plot of ln Ω_{13}^{∞} versus 1/*T* for the solutes: ◇, water; ♦, methanol; ■, ethanol; ▲, 1-propanol; ●, 1-butanol; +, 1-pentanol.

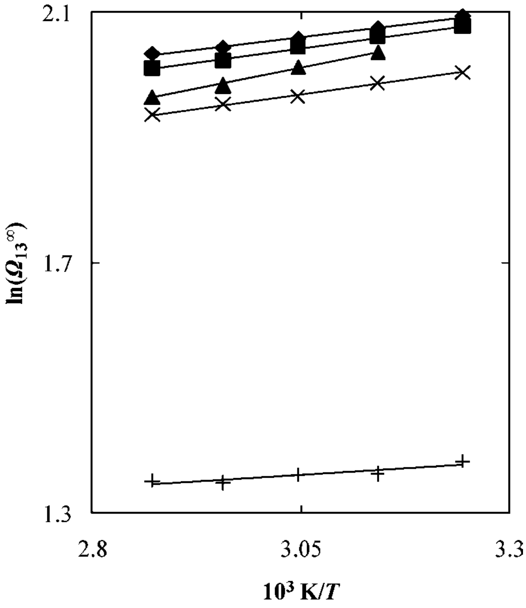

Figure 7. Plot of ln Ω_{13}^{∞} versus 1/*T* for the solutes: ♦, diethylether; ■, di-*n*-propylether; ▲, di-*n*-butylether; ×, MTBE; +, THF.

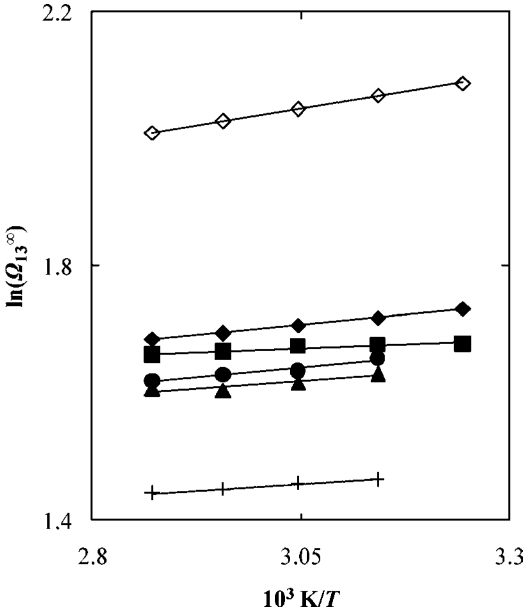

Figure 8. Plot of ln Ω_{13}^{∞} versus 1/*T* for the solutes: ◇, propanone; ♦, 2-pentanone; ■, 3-pentanone; ▲, 2-hexanone; ●, 3-hexanone; +, cyclopentanone.

technique (DSC). No one (solid−solid) phase transitions were observed. The applied scan rate was 5 K·min^{-1}, with power and recorder sensitivities of 16 mJ·s^{-1} and 5 mV, respectively. The apparatus (Perkin-Elmer Pyris 1) was calibrated with a 0.999999 mol fraction purity indium sample. The average value of the melting temperature was 301.2 K (two scans) for B-W3000. The repeatability of that value was (± 0.2 K). The uncertainty of the calorimetric measurements was estimated to be ± 1.5 %. The enthalpy of fusion was (339.7 ± 5) kJ·mol^{-1}, and the T_g was 202.5 K with a $\Delta C_{p(g)}$ of (2.76 ± 0.04) kJ·mol^{-1}·K^{-1}. The thermophysical properties are shown in Table 1 and Figure 2.

Experimental Procedure. The experiments were performed using a PerkinElmer Clarus 500 gas chromatograph equipped with a thermal conductivity detector (TCD). The data were collected and processed using TotalChrom Workstation software. Glass columns of length 1 m and internal diameter 4 mm were used. Chromosorb W HP 80/100 mesh was used as the solid support and was supplied by SUPELCO. Coating the solid support material with the polymer was performed by dispersing a certain portion of Chromosorb in a solution of the polymer in MTBE followed by evaporation of the solvent using a rotating evaporator. The masses of the stationary phase and of the solid support were weighed with a precision ± 0.0001 g. The solvent column packing is described in Table 2. High mass percent of the polymer prevents possible residual adsorption of solute onto the column packing, as was discussed in ref 21. For each temperature, the measurements were repeated by using two different columns with different mass percent packing. Care was taken to ensure that the MTBE had completely evaporated from the polymer coated solid before making up the column. Before experiment, each column was conditioned by blowing carrier gas at high flow rate (about 3.5 cm^3·s^{-1}) at the high temperature (T = 340 K) through about 8 h.

Table 3. Specific Retention Volumes, V_g, at Different Temperatures

	V_g				
	$\mathrm{cm^3 \cdot mol^{-1}}$				
solvent	$T = 308.15$ K	$T = 318.15$ K	$T = 328.15$ K	$T = 338.15$ K	$T = 348.15$ K
pentane	38.6	29.4	22.0	17.3	13.4
hexane	115.2	81.8	57.5	42.9	31.7
heptane	331.7	222.0	147.5	104.5	72.9
octane	931.6	583.5	366.6	246.0	164.4
nonane	2537.9	1505.5	889.8	570.6	365.7
decane		3820.6	2148.7	1311.8	799.2
cyclopentane	101.8	75.0	54.4	41.9	31.5
cyclohexane	270.3	191.0	131.4	97.5	71.1
cycloheptane	1133.1	734.7	477.4	329.7	225.9
cyclooctane	3903.9	2413.2	1457.4	953.4	620.2
pent-1-ene	44.2	33.6	25.0	19.7	15.2
hex-1-ene	132.2	93.6	65.7	49.0	35.8
hept-1-ene	375.4	250.4	166.0	117.2	81.9
oct-1-ene	1037.0	652.1	409.9	276.0	183.1
pent-1-yne	125.5	88.7	62.1	46.2	33.8
hex-1-yne	361.2	240.7	158.6	112.5	78.6
hept-1-yne	995.8	628.6	391.9	264.4	176.2
oct-1-yne	2661.2	1595.5	944.0	607.3	386.6
benzene	746.8	495.0	327.1	231.1	159.9
toluene	2058.1	1281.6	802.3	541.3	358.2
ethylbenzene		2837.2	1705.7	1102.8	703.9
o-xylene		4257.7	2512.6	1599.0	1001.4
m-xylene		3281.8	1952.6	1251.8	793.3
p-xylene		3168.2	1878.5	1209.4	767.5
thiophene	1137.8	736.6	474.7	328.5	223.5
methanol	248.8	162.5	106.8	75.0	51.8
ethanol	416.8	268.5	167.8	114.9	77.5
1-propanol	1134.4	690.9	414.4	274.3	176.0
1-butanol	3159.3	1805.1	1045.6	654.7	404.6
1-pentanol		4728.7	2600.1	1552.1	915.4
water	865.1	502.5	315.9	213.0	131.0
THF	463.0	320.9	215.7	157.0	110.3
MTBE	136.7	97.0	68.3	51.0	37.5
diethyl ether	72.1	52.9	38.2	29.3	22.0
di-*n*-propyl ether	403.2	266.4	175.3	124.3	85.8
di-*n*-butyl ether		1665.4	990.7	640.6	405.5
propanone	200.8	140.1	97.0	71.5	51.6
pentan-2-one	1136.8	725.2	459.7	314.0	210.2
pentan-3-one	1162.2	740.0	468.0	319.8	214.0
hexan-2-one		1852.9	1119.7	728.8	463.6
hexan-3-one		1544.0	947.5	617.2	399.1
cyclopentanone		2762.9	1673.3	1094.9	703.8

The outlet pressure P_o was kept at atmospheric pressure. The pressure drop ($P_i - P_o$) was varied between (28 and 42) kPa depending on flow rate of the carrier gas. The pressure drop was measured by a gas chromatograph with an uncertainty of ± 0.1 kPa. The atmospheric pressure was measured using a digital barometer with an uncertainty of ± 0.1 hPa.

The carrier gas was helium. The flow rate of carrier gas was determined using a calibrated soap bubble flowmeter which was placed at the outlet after the detector. The flow rate was set for a series of runs and was allowed to stabilize for at least 15 min before any Ω_{13}^{∞} determinations were made. The flow rates ranging from (0.6 to 1.1) $\mathrm{cm^3 \cdot s^{-1}}$ were corrected for the water vapor pressure. Solute injections ranging from (0.01 to 0.1) μL in the liquid phase were considered to be at infinite dilution on the column (solute was injected as a liquid in temperature of injector of 423 K).

Experiments were carried out at different temperatures (in steps of 10 K) in the range from $T = 308.15$ K to $T = 348.15$ K. The temperature of the column was maintained constant to within ± 0.02 K. At a given temperature, each experiment was repeated 2 times to check the reproducibility. Retention times were generally reproducible within (0.001 to 0.01) min. Absolute values of retention times varied between 1.5 s and 110 min depending on the individual solute. At each temperature, values of the dead time t_G identical to the retention time of a nonretainable component were measured. While our GC was equipped with a TCD detector, air was used as a nonretainable component. The estimated overall error in Ω_{13}^{∞} was less than 5 %, taking into account the possible errors in determining the column loading, the retention times, and solute vapor pressure. The IGC technique was tested for the system hexane in hexadecane at 298.15 K, and the results compared very favorably with the literature values.[22]

Theory. The specific retention volume (V_g) or the net retention volume (V_N) used to describe the elution behavior of solutes was calculated with the following usual relationship[23]

$$V_g = \frac{273 V_N}{W_S T} = \frac{273 J_2^3 U_0 \left(1 - \dfrac{p_w}{p_0}\right)(t_r - t_g)}{T_F W_S} \qquad (1)$$

where W_S is the mass of polymer loaded in the GC column; t_r and t_g are the retention times for the solute and an unretained gas, respectively; and U_0 is the carrier gas flow rate measured at the column outlet at ambient pressure p_0 and temperature T_F. T is the column temperature; p_w is the vapor pressure of water at T_F; and J_2^3 is the James and Martin pressure correction term given by

$$J_2^3 = \frac{2}{3} \frac{(P_i/P_o)^3 - 1}{(P_i/P_o)^2 - 1} \qquad (2)$$

where P_i and P_o are the inlet and the outlet pressures, respectively.

Table 4. Experimental Mass-Fraction Activity Coefficient at Infinite Dilution, Ω_{13}^{∞}, at Different Temperatures

	Ω_{13}^{∞}				
solvent	$T = 308.15$ K	$T = 318.15$ K	$T = 328.15$ K	$T = 338.15$ K	$T = 348.15$ K
pentane	16.61	15.83	15.12	14.65	14.18
hexane	14.45	13.90	13.41	13.06	12.60
heptane	13.38	12.87	12.40	12.05	11.69
octane	12.68	12.29	11.86	11.58	11.20
nonane	12.49	12.03	11.68	11.32	10.89
decane		12.14	11.74	11.37	10.98
cyclopentane	10.06	9.68	9.32	9.05	8.78
cyclohexane	9.59	9.13	8.84	8.50	8.17
cycloheptane	8.09	7.85	7.56	7.37	7.13
cyclooctane	7.43	7.11	6.96	6.79	6.59
pent-1-ene	12.17	11.74	11.39	11.13	10.87
Hex-1-ene	10.72	10.45	10.14	9.92	9.70
hept-1-ene	9.88	9.66	9.43	9.30	9.10
oct-1-ene	9.43	9.23	9.00	8.85	8.71
pent-1-yne	6.21	6.27	6.31	6.38	6.41
hex-1-yne	5.44	5.51	5.60	5.65	5.69
hept-1-yne	5.03	5.11	5.21	5.29	5.34
oct-1-yne	4.89	4.93	5.03	5.09	5.13
benzene	3.80	3.81	3.81	3.81	3.83
toluene	3.67	3.73	3.75	3.76	3.79
ethylbenzene		3.89	3.88	3.89	3.90
o-xylene		3.61	3.61	3.62	3.64
m-xylene		3.80	3.81	3.83	3.85
p-xylene		3.78	3.82	3.83	3.85
thiophene	2.73	2.77	2.80	2.83	2.87
methanol	19.48	18.71	17.75	16.93	16.17
ethanol	16.28	15.10	14.40	13.52	12.74
1-propanol	12.10	11.19	10.55	9.78	9.28
1-butanol	10.32	9.55	8.81	8.20	7.72
1-pentanol		7.51	7.03	6.63	6.34
water	49.18	49.65	46.36	43.32	43.84
THF	3.99	3.90	3.90	3.85	3.86
MTBE	7.41	7.29	7.13	7.04	6.92
diethyl ether	8.12	7.96	7.83	7.72	7.65
di-*n*-propyl ether	7.98	7.86	7.71	7.55	7.47
di-*n*-butyl ether		7.67	7.48	7.26	7.13
propanone	8.07	7.91	7.74	7.59	7.46
pentan-2-one	5.65	5.58	5.51	5.44	5.39
pentan-3-one	5.35	5.34	5.33	5.29	5.26
hexan-2-one		5.10	5.03	4.98	4.99
hexan-3-one		5.23	5.13	5.10	5.05
cyclopentanone		4.32	4.30	4.26	4.23

Table 5. Selectivities S_{ij}^{∞} and Capacities k_j^{∞} at Infinite Dilution for B-W3000 for Different Separation Problems at $T = 308.15$ K

separation mixture	S_{ij}^{∞}	k_j^{∞}
hexane/thiophene	5.3	0.37
heptane/thiophene	4.9	0.37
hexane/benzene	3.8	0.26
hexane/toluene	3.9	0.27
methanol/THF	4.9	0.25
H_2O/ethanol	3.0	0.02
H_2O/THF	12.3	0.25

Table 6. Selectivities S_{ij}^{∞} at Infinite Dilution for B-W3000, Several Ionic liquids, NMP, and Sulfolane for the Separation Problem Hexane/Benzene at $T = 308.15$ K

solvent	$S_{n\text{-hexane/benzene}}^{\infty}$ [a]
B-W3000	3.8
$[3C_6C_{14}P][Tf_2N]$[b]	2.5
[EMIM][SCN][c]	76.4
NMP[d]	10.7
sulfolane[e]	16.89

[a] Calculated from $S_{n\text{-hexane/benzene}}^{\infty} = (\Omega_{n\text{-hexane}}^{\infty})/(\Omega_{\text{benzene}}^{\infty}) = (\gamma_{n\text{-hexane}}^{\infty}M_{\text{benzene}})/(\gamma_{\text{benzene}}^{\infty}M_{n\text{-hexane}})$; $\Omega_{13}^{\infty}M_1 = \gamma_{13}^{\infty}M_3$. [b] From ref 28. [c] From ref 29. [d] From ref 20. [e] From ref 30.

The mass-fraction activity coefficient at infinite dilution, Ω_{13}^{∞}, is

$$\Omega_{13}^{\infty} = \frac{RW_{\text{S}}T}{V_{\text{N}}P_1^*M_1}\exp\left(-\frac{P_1^*(B_{11} - V_1^*)}{RT}\right) \qquad (3)$$

where R is the universal gas constant; M_1 is the solute molecular mass; P_1* is the saturated vapor pressure of the solute at temperature T; B_{11} is the second virial coefficient of pure solute; and V_1 is the molar volume of the solute.

The specific retention volume, V_{g}, can be used for the calculation of thermodynamic properties. Considering the binary polymer (here solvent "3") + solvent (here solute "1") system at low pressures, one can assume that the vapor pressure is considered to contain the pure solute "1" as an ideal gas. The polymer only influences the solute activity coefficient in the liquid phase. Using the activity coefficients, the Flory−Huggins, χ_{13}^{∞}, parameter values can be calculated at infinite concentrations from the relationship as follows[23]

$$\chi_{13}^{\infty} = \ln\left(\frac{273.15R\upsilon_3}{V_{\text{g}}P_1^*V_1}\right) - 1 - \frac{P_1^*(B_{11} - V_1)}{RT} \qquad (4)$$

where ν_3 is the specific volume of the stationary phase at inlet pressure and temperature, $\nu_3 = 1/d(\text{g}\cdot\text{cm}^{-3})$ of polymer.

The partial molar enthalpy of sorption (the partial molar enthalpies of solute dissolution), $\Delta_{\text{s}}H$, was calculated from the equation

$$\Delta_{\text{s}}H = -R\frac{\partial \ln V_{\text{g}}}{\partial(1/T)} \qquad (5)$$

The partial molar excess enthalpy at infinite dilution of the solute and polymer, $\Delta H_1^{\text{E},\infty}$, is

$$\Delta H_1^{\text{E},\infty} = R\frac{\partial \ln \Omega_{13}^{\infty}}{\partial(1/T)} \qquad (6)$$

The molar enthalpy of vaporization to the ideal-gas state for the pure solutes, $\Delta_{\text{vap}}H^0$, was calculated using the formula

$$\Delta_{\mathrm{vap}}H^{0} = \Delta H_{1}^{\mathrm{E},\infty} - \Delta_{\mathrm{s}}H \tag{7}$$

The mass-fraction activity coefficient at infinite dilution is connected with the partial molar Gibbs excess energy at infinite dilution, $\Delta G_{1}^{\mathrm{E},\infty}$ by the ratio

$$\Delta G_{1}^{\mathrm{E},\infty} = RT \ln \Omega_{13}^{\infty} \tag{8}$$

The solubility parameter of the solute (δ_1) is calculated through the well-known equation

$$\delta_{1} = \left(\frac{\Delta_{\mathrm{vap}}H^{0} - RT}{V_{1}}\right)^{1/2} \tag{9}$$

The estimated solubility parameter of the polymer (δ_3) is obtained using a combination of the lattice model of solutions and the solubility parameter theory[24−26]

$$\left(\frac{\delta_{1}^{2}}{RT} - \frac{\chi_{13}^{\infty}}{V_{1}}\right) = \frac{2\delta_{3}}{RT}\delta_{1} - \left(\frac{\delta_{3}^{2}}{RT} + \frac{\chi^{\mathrm{S}}}{V_{1}}\right) \tag{10}$$

where χ^{S} is the entropic factor of the interaction parameter. The plot of the first term of the above equation versus δ_1 allows us to get the solubility parameter for B-W3000 at different temperatures. The extrapolation to the temperature $T = 298.15$ K has given the solubility parameter at $T = 298.15$ K and would be helpful in the prediction of the solubility of polymer in any organic solvent.

Results and Discussion

Specific retention volumes, V_{g}, were calculated for 42 solutes according to eq 1 at five temperatures and are presented in Table 3. As was expected, the V_{g} values decrease with an increase of temperature as was observed for other polymers, i.e., Hybrane 1200.[18] The values of V_{g} increase for a series of solutes with an increase of the solute alkyl chain length or solute ring in cycloalkanes or the alkyl chain length in alkylbenzenes. The highest value was observed for decane, 3820.6 $\mathrm{cm}^{3}\cdot\mathrm{mol}^{-1}$ at $T = 318.15$ K.

Table 4 lists the average Ω_{13}^{∞} values for the varying amounts of polymer on the column packing in the temperature range from $T = 308.15$ K to $T = 348.15$ K, determined from eq 3. Figures 3 to 8 show the natural logarithm of the mass-fraction activity coefficients in the polymer as a function of the inverse absolute temperature for all investigated solutes. The values of Ω_{13}^{∞} for series of solutes decrease with an increase of temperature, i.e., for alkanes, cycloalkanes, 1-alkenes, 1-alcohols, water ethers, and ketones. The influence of temperature in the tested range of temperature was not high but the same as was observed for the other polymers.[18] For some solutes, for which the interactions with polymer are stronger (1-alkynes, alkylbenzenes, xylenes, THF), an increase of the mass-fraction activity coefficients with an increase of temperature was noted (see Figures 4 and 5).

The values of Ω_{13}^{∞} for a series of solutes decrease with an increase of the solute alkyl chain. It seems to be connected with strengthening of the van der Waals polymer−solute interactions in accordance with the increase in a number of the alkyl substituents at the hyperbranched periphery, i.e., the chains of the fatty acids. The high values of Ω_{13}^{∞} for alkanes, alcohols, and water signify small interactions between solute and polymer. This is the evidence of the interactions of the hydrophobic

Table 7. Flory−Huggins Parameter, χ_{13}^{∞}, at Different Temperatures

	χ_{13}^{∞}				
solvent	$T = 308.15$ K	$T = 318.15$ K	$T = 328.15$ K	$T = 338.15$ K	$T = 348.15$ K
pentane	0.61	0.55	0.53	0.49	0.48
hexane	0.53	0.48	0.48	0.44	0.44
heptane	0.49	0.44	0.44	0.40	0.41
octane	0.47	0.43	0.43	0.40	0.40
nonane	0.47	0.43	0.44	0.40	0.40
decane		0.46	0.46	0.42	0.42
cyclopentane	0.29	0.24	0.24	0.20	0.21
cyclohexane	0.28	0.23	0.23	0.18	0.18
cycloheptane	0.16	0.12	0.12	0.09	0.09
cyclooctane	0.10	0.06	0.07	0.04	0.05
pent-1-ene	0.32	0.27	0.27	0.23	0.23
hex-1-ene	0.25	0.21	0.21	0.18	0.19
hept-1-ene	0.20	0.18	0.19	0.16	0.17
oct-1-ene	0.18	0.16	0.17	0.14	0.16
pent-1-yne	–0.28	–0.28	–0.25	–0.26	–0.23
Hex-1-yne	–0.37	–0.36	–0.31	–0.31	–0.27
hept-1-yne	–0.42	–0.41	–0.36	–0.35	–0.31
oct-1-yne	–0.43	–0.43	–0.37	–0.37	–0.32
benzene	–0.52	–0.52	–0.49	–0.50	–0.46
toluene	–0.57	–0.55	–0.51	–0.52	–0.47
ethylbenzene		–0.51	–0.47	–0.48	–0.44
o-xylene		–0.57	–0.53	–0.54	–0.49
m-xylene		–0.54	–0.50	–0.50	–0.46
p-xylene		–0.54	–0.50	–0.50	–0.46
thiophene	–0.66	–0.65	–0.60	–0.60	–0.55
methanol	1.01	0.97	0.95	0.89	0.88
ethanol	0.83	0.75	0.74	0.66	0.64
1-propanol	0.55	0.47	0.45	0.36	0.34
1-butanol	0.40	0.32	0.27	0.20	0.17
1-pentanol		0.09	0.06	–0.01	–0.01
water	2.18	2.19	2.17	2.10	2.15
THF	–0.47	–0.49	–0.46	–0.48	–0.44
MTBE	–0.03	–0.05	–0.04	–0.07	–0.05
diethyl ether	0.02	–0.01	0.01	–0.02	–0.01
di-*n*-propyl ether	0.06	0.04	0.05	0.02	0.04
di-*n*-butyl ether		0.04	0.05	0.02	0.04
propanone	0.13	0.10	0.11	0.08	0.09
pentan-2-one	–0.21	–0.23	–0.20	–0.23	–0.20
pentan-3-one	–0.26	–0.26	–0.23	–0.25	–0.22
hexan-2-one		–0.31	–0.29	–0.30	–0.27
hexan-3-one		–0.28	–0.27	–0.28	–0.25
cyclopentanone		–0.31	–0.28	–0.30	–0.27

Table 8. Partial Molar Enthalpies of Solute Dissolution, $\Delta_s H$, the Partial Molar Excess Enthalpy at Infinite Dilution of the Solute, $\Delta H_1^{E,\infty}$, the Molar Enthalpy of Vaporization to the Ideal-Gas State of the Solute, $\Delta_{vap}H^0$, the Molar Enthalpy of Vaporization to the Ideal-Gas State of the Solute from the Calorimetric Measurements, $\Delta_{vap}H^{0,lit}$, and the Partial Molar Gibbs Excess Energy at Infinite Dilution, $\Delta G_1^{E,\infty}$, at T = 308.15 K

solvent	$\Delta_s H$ kJ·mol^{-1}	$\Delta H_1^{E,\infty}$ kJ·mol^{-1}	$\Delta_{vap}H^0$ kJ·mol^{-1}	$\Delta_{vap}H^{0,lit\,a}$ kJ·mol^{-1}	$\Delta G_1^{E,\infty}$ kJ·mol^{-1}
pentane	–23.6	3.5	27.2	26.8	7.3
hexane	–28.8	3.0	31.8	31.7	7.0
heptane	–33.8	3.0	36.8	36.7	6.8
octane	–38.7	2.8	41.4	41.5	6.6
nonane	–43.2	3.0	46.2	46.4	6.6
decane	–47.8	3.1	50.9	51.4	6.6
cyclopentane	–26.1	3.0	29.2	28.7	6.0
cyclohexane	–29.8	3.5	33.3	33.0	5.9
cycloheptane	–35.9	2.8	38.7	38.5	5.5
cyclooctane	–41.1	2.6	43.7	43.4	5.2
pent-1-ene	–23.9	2.5	26.4	29.8	6.5
hex-1-ene	–29.1	2.3	31.3	30.6	6.2
hept-1-ene	–33.9	1.8	35.8	35.9	6.0
oct-1-ene	–38.6	1.8	40.4	40.4	5.9
pent-1-yne	–29.2	–0.7	28.5	-	4.9
hex-1-yne	–34.0	–1.1	33.0	-	4.5
hept-1-yne	–38.6	–1.3	37.3	-	4.3
oct-1-yne	–43.1	–1.2	41.9	42.3	4.2
benzene	–34.3	–0.1	34.2	33.9	3.5
toluene	–38.9	–0.7	38.2	38.1	3.5
ethylbenzene	–42.5	0.0	42.5	42.3	3.6
o-xylene	–44.2	–0.3	43.9	43.5	3.4
m-xylene	–43.3	–0.4	43.0	42.7	3.5
p-xylene	–43.2	–0.5	42.8	42.4	3.5
thiophene	–32.0	–1.1	30.9	34.8	2.7
methanol	–34.9	4.2	39.1	37.8	7.7
ethanol	–37.6	5.4	43.0	42.5	7.2
1-propanol	–41.5	5.9	47.4	47.5	6.4
1-butanol	–45.7	6.5	52.3	52.4	6.0
1-pentanol	–50.1	5.2	55.4	55.2	5.3
water	–41.4	3.3	44.6	-	10.3
THF	–28.8	0.7	30.9	32.2	3.6
MTBE	–26.5	1.5	29.5	30.0	5.3
diethyl ether	–34.4	1.3	28.0	27.4	5.5
di-*n*-propyl ether	–43.1	1.5	35.8	35.8	5.5
di-*n*-butyl ether	–30.3	2.3	44.6	36.5	5.4
propanone	–37.6	1.8	32.5	31.3	5.5
pentan-2-one	–37.7	1.1	39.4	38.5	4.5
pentan-3-one	–42.2	0.4	38.8	38.7	4.4
hexan-2-one	–41.0	0.7	42.6	43.2	4.3
hexan-3-one	–41.3	1.0	41.7	42.5	4.4
cyclopentanone	–42.0	0.7	42.4	42.8	3.9

[a] From ref 31.

Table 9. Values of the B-W3000 Solubility Parameter, δ_3, Over the Temperature Range From T = 298.15 K to T = 348.15 K

T/K	slope	δ_3/(MPa)$^{1/2}$
298.15		19.39[a]
308.15	15.01	19.23
318.15	14.42	19.07
328.15	13.87	18.91
338.15	13.39	18.82
348.15	12.88	18.64

[a] Extrapolated from the equation: $\delta_3 = 1531(\mathrm{K}/T) + 14.25$.

substituents of polymer with water and methanol. The highest value of Ω_{13}^{∞} is for water ($\Omega_{13}^{\infty} = 49.18$ at $T = 308.15$ K) and for methanol ($\Omega_{13}^{\infty} = 19.48$ at $T = 308.15$ K). The values of Ω_{13}^{∞} for cycloalkanes and 1-alkynes are lower. Generally, the smallest values of Ω_{13}^{∞} indicate the stronger interactions between polymer and solute. Alkynes, aromatic hydrocarbons, thiophene, and THF reveal small values of Ω_{13}^{∞}. The triple bond in alkynes and six π-delocalized electrons in aromatics can interact more strongly with the polar parts of the polymer. The results also show that ketones interact with polymer more strongly than ethers, alcohols, and water.

The selectivity at infinite dilution $S_{ij}^{\infty} = \Omega_{i3}^{\infty}/\Omega_{j3}^{\infty}$ and the capacity at infinite dilution $k_j^{\infty} = 1/\Omega_{j3}^{\infty}$ can be calculated from the experimental values of Ω_{13}^{∞} for different separation problems.[20] From the analysis of selectivity and capacity at temperature $T = 308.15$ K presented in Table 5, we can conclude that selectivities S_{ij}^{∞} for two separation problems, hexane/thiophene and water/THF, are quite high, and the capacity k_j^{∞} for thiophene is 0.37 and for THF is 0.25. The selectivity for investigated polymer is high for the water/THF mixture ($S_{ij}^{\infty} = 12.3$). This value shows the possibility of using B-W3000 as an entrainer for the separation process of the azeotropic mixture of water and tetrahydrofuran.

The separation of aromatic and aliphatic compounds is an important process in the petrochemical industry and engineering.[20,27−31] Unfortunately, as it is presented in Table 6, the hyperbranched polymer B-W3000 is not suitable for this separation problem. The values recalculated from the mole fraction activity coefficients at infinite dilution from the literature[28−30] for the mass-fraction activity coefficients at infinite dilution for the very attractive ionic liquid 1-ethyl-3-methylimidazolium thiocyanate, [EMIM][SCN],[29] not attractive ionic liquid trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide [$3C_6C_{14}P$][Tf_2N],[28] *N*-methyl-2-pyrrolidinone (NMP),[20] and sulfolane[30] are shown in Table 6.

Table 7 shows the values of the Flory−Huggins interaction coefficient at infinite dilution, defined by eq 4 at the measured temperatures. The parameter χ_{13}^{∞} characterizes the interaction between the vapor phase of the solute and the polymeric stationary phase. In general, values of χ_{13}^{∞} lower than 0.5 at $T = 298.15$ K indicate that these interactions are favorable for solvent dissolution.[26] From Table 7, we can conclude that only pentane, hexane, methanol, ethanol, 1-propanol, and water are not proper solvents for polymer B-W3000. Negative values of χ_{13}^{∞}, as was observed for some 1-alkynes, the aromatic hydrocarbons, thiophene, THF, MTBE, and some ketones, suggest stronger solute−polymer interaction than for other solutes.

The data in Table 8 show that the partial molar enthalpies of solute dissolution are negative for every solute and are the lowest for decane and 1-pentanol. The values are of the same range as for Hybrane 1200 or for poly(propyleneimine)dendrimers G1−G3.[18,19] The values of the partial molar thermodynamic functions of mixing at infinite dilution, partial molar excess enthalpy $\Delta H_1^{E,\infty}$, and the partial molar Gibbs excess energy at infinite dilution, $\Delta G_1^{E,\infty}$, as is listed in Table 8 are for most of the solutes positive and in a range from 0.4 kJ·mol^{-1} to 10.3 kJ·mol^{-1}. A change is accompanied by a decrease in the Ω_{13}^{∞} values within the homological series of alkanes, cycloalkanes, 1-alkenes, and others. This indicates that the entropic factor dominates in the studied systems and is quite high. The lowest values of partial molar excess enthalpies at infinite dilution $\Delta H_1^{E,\infty}$ (for 1-alkynes, alkylbenzenes, xylenes, and thiophene) suggest stronger polymer−solute interaction than for the other solutes.

The molar enthalpies of vaporization to the ideal-gas state for the pure solutes, $\Delta_{vap}H^0$, calculated from the measurements presented in this work are very similar to the molar enthalpy of vaporization to the ideal-gas state, measured traditionally by the calorimetric method or by the vapor pressure, presented in the literature, $\Delta_{vap}H^{0,lit}$.[31] The results of comparison are shown in Table 8.

From the molar enthalpy of vaporization to the ideal-gas state for the pure solutes, $\Delta_{vap}H^0$, the solubility parameters of solutes were determined at higher temperatures than 298.15 K. Assuming that the interaction parameter can be expressed in function of the solubility parameters of the solutes (δ_1), the solubility parameter of the stationary phase (polymer) can be calculated from the linear regression of the left-hand side of eq 10 versus δ_1. The solubility parameter of the investigated polymer, δ_3, was calculated from the slope of the straight line. The solubility parameter of the polymer at temperature T = 298.15 K is 19.39 (MPa)$^{1/2}$ (see Table 9). The values of the solubility parameters of solutes were similar to those generally known from the literature.[26]

The fact that the retention time was independent of the sample injected into the column and of the symmetry of the chromatographic peaks has confirmed that the measurements have been done at equilibrium.

Conclusions

Mass-fraction activity coefficients at infinite dilution for various solutes in the hyperbranched polymer B-W3000 were measured in the temperature range from T = 308.15 K to T = 348.15 K using the IGC method. It was found that the investigated polymer shows high selectivities at infinite dilution in separation processes of water/THF azeotrope and hexane/thiophene separation problem.

The values of Ω_{13}^{∞} and of the Flory–Huggins parameters and other thermodynamic functions indicate that THF, thiophene, and aromatic hydrocarbons are the best solvents for the polymer used, and water is the worst of all the investigated solutes. The solubility parameter decreases linearly with an increase of temperature.

For the first time, the thermodynamic characteristic of dissolution of different organic solvents (here solutes) in hyperbranched polymer B-W3000 was presented. The data obtained indicate an increase in compatibility of homologous series of solvents with the polymer. Thiophene, aromatic hydrocarbons, and THF were revealed to show the higher physicochemical affinity to the polymer than 1-alcohols, water, alkanes, ethers, or ketones. This work shows also that the intermolecular interactions between solute and the polymer strongly depend on both polar fragments of the substances and the alkane chain lengths. These data are very important to better understand the nature of the polymer and are helpful in expanding the thermodynamic models.

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