

# Thermodynamic Properties of Hyperbranched Polymer, Boltorn U3000, Using Inverse Gas Chromatography

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Mass-fraction activity coefficients at infinite dilution ( $\Omega_{13}^\infty$ ) of alkanes (C<sub>5</sub>–C<sub>10</sub>), cycloalkanes (C<sub>5</sub>–C<sub>8</sub>), alkenes (C<sub>5</sub>–C<sub>8</sub>), alkynes (C<sub>5</sub>–C<sub>8</sub>), aromatic hydrocarbons (benzene, toluene, ethylbenzene, *o*-, *m*-, *p*-xylene, thiophene), alcohols (C<sub>1</sub>–C<sub>5</sub>), 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) in the hyperbranched polymer, Boltorn U3000 (B-U3000), have been determined by inverse gas chromatography (IGC) using the polymer as the stationary phase. The measurements were carried out at different temperatures between 308.15 and 348.15 K. The density and thermophysical properties of polymer were described. The specific retention volume ( $V_g$ ), the Flory–Huggins interaction parameter ( $\chi_{13}^\infty$ ), the molar enthalpy of sorption (the partial molar enthalpies of solute dissolution) ( $\Delta_s H$ ), the partial molar excess enthalpy at infinite dilution of the solute and polymer ( $\Delta H_1^{E,\infty}$ ), the partial molar Gibbs excess energy at infinite dilution ( $\Delta G_1^{E,\infty}$ ), and the solubility parameter ( $\delta_3$ ) were calculated.

## Introduction

Replacing volatile organic compounds by less polluting substances as ionic liquids or hyperbranched polymers (HBPs) is an aspect of major interest in the field of “green chemistry”. Hyperbranched polymers have attracted considerable scientific attention as possible new materials in the separation processes, in membrane processes, and in gas separation applications including CO<sub>2</sub> absorption from flue gas.<sup>1–8</sup> All mentioned applications are the result of the molecular interactions offered by specific end groups of hyperbranched polymers, which were characterized in the past years in a large number of reviews.<sup>1,9,10</sup> HBPs are highly branched, polydisperse macromolecules with a three-dimensional topology. A large number of possible combinations of functional end groups and the molecular weight of polymer may tailor the polymer properties for a specific purpose.<sup>1</sup> Due to their unique properties such as wide liquid range, stability at high temperatures, low viscosity in relation to molecular weight compared to conventional polymers, and their globular structure, which hampers chain entanglement and negligible vapor pressure, HBPs were considered as good replacements for conventional volatile and often flammable and toxic organic solvents in the chemical industry. HBPs have been used in scientific investigations as a possible entrainer in industrial processes for more than a decade, and their applications continue to expand. For instance, it has been shown that branched polymers are promising candidates for gas absorbents with a high capacity for CO<sub>2</sub> and with large selectivities.<sup>5</sup> Hyperbranched polymer Boltorn H2004 was tested as an entrainer for the tetrahydrofuran (THF)/water azeotrope separation or desulfurization of the diesel oils.<sup>8</sup> Polyester materials have been recognized as the most promising family of HBPs, mostly due to unique properties, biocompatibility, biodegradability, nontoxicity, high solubility (sometimes even in water), as well as storage stability.<sup>11,12</sup> Water-soluble HBP was syn-

thesized for drug delivery applications.<sup>12–15</sup> The polymers could be used in various applications in nanobiotechnology and nanomedicine. HBPs also have a wide array of applications in the field of chemical engineering, as recently was shown by Seiler.<sup>6</sup> However, HBP like Boltorn B-U3000 was found not suitable for the separation of *n*-hexane and ethanol azeotropic mixtures.<sup>16</sup> HBPs reveal a remarkable thermal stability<sup>17–19</sup> and show a lower viscosity in comparison to linear analogues.<sup>1,20</sup> Many of the HBPs are liquid at room temperature.<sup>1–6,21</sup> Physical and chemical properties of HBPs are not only influenced by the number of the functional groups but also by the polarity of the group. For HBPs to be effectively used as solvents in liquid–liquid extraction, or other fields, the knowledge of the density, solubility parameter, and activity coefficient at infinite dilution is fundamental.

In separation processes, both properties of solvent are important, namely, selectivity and capacity,<sup>22</sup> and can be directly calculated from the mass-fraction activity coefficient at infinite dilution ( $\Omega_{13}^\infty$ ) for different separation problems. The structure of the polymer has a large influence on the values of  $\Omega_{13}^\infty$ . For HBP to be used effectively as solvents, it is essential to know how they interact with different solutes. 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. The primary appeal of HBPs is based on their unique physical properties, including the ability to solvate a wide range of materials. The mass-fraction activity coefficient at infinite dilution is especially important because it describes the extreme case in which only solute–solvent interactions contribute to nonideality. Since the HBPs have a negligible vapor pressure, inverse gas chromatography (IGC) is a suitable method for measuring  $\Omega_{13}^\infty$ , where “1” is the solvent, the low-molecular-weight component of the mixture of higher volatility, and “3” is a polymer, the high-molecular-weight component of negligible volatility. The hyperbranched polymer, Boltorn U3000 (B-U3000), is a fatty acid modified dendritic polyester. It has a highly branched polymer backbone and in average 14

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**TABLE 1: Investigated Polymer B-U3000: Thermophysical Properties, Molecular Mass ( $M$ ), Polydispersity ( $M_w/M_n$ ), Glass Transition Temperature ( $T_{tr(g)}$ ) and Heat Capacity Change at  $T_{tr(g)}$  ( $\Delta C_{p(g)}$ ), Density ( $d$ ) at  $T = 298.15$  K and Dynamic Viscosity ( $\eta$ ) at  $T = 298.15$  K**

property	B-U3000
$M/(\text{g} \cdot \text{mol}^{-1})$	6500 <sup>a</sup>
$M_w/M_n$	1.5 <sup>a</sup>
$T_{tr(g)}/\text{K}$	$234 \pm 0.1^b$
$\Delta C_{p(g)}/(\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	$1.81 \pm 0.003^b$
$d^{298.15}/(\text{g} \cdot \text{cm}^{-3})$	$0.9840 \pm 0.0001$
	0.9888 <sup>c</sup>
$\eta^{298.15}/(\text{mPa} \cdot \text{s})$	1016

<sup>a</sup> Provided by Perstorp (Sweden). <sup>b</sup> Ref 16. <sup>c</sup> Ref 5.

unsaturated fatty ester groups in the molecule. B-U3000 is formed in an estrification reaction of hyperbranched polyester Boltorn H30 with sunflower oil that consists of  $C_{16}$  and/or  $C_{18}$  fatty acids.<sup>5</sup> For HBP to be effectively used as solvents in liquid–liquid extraction, or other fields, the knowledge of the viscosity and density is fundamental. Our experimental density data of B-U3000 as a function of temperature in a wide range of temperatures from 290 to 360 K were presented earlier.<sup>21</sup> The full set of basic information concerning investigated B-U3000, including glass transition temperature and heat capacity at the glass transition temperature, is presented in Table 1.

It was shown earlier in many investigations that the selectivities of hyperbranched polymers<sup>3–6</sup> in separating organic liquids are often higher than those for commonly used solvents, such as *N*-methyl-2-pyrrolidinone (NMP) or (NMP + water).<sup>23</sup> 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.

There are a large number of studies of mass-fraction activity coefficients at infinite dilution for HBP and polymers.<sup>24–30</sup> It allows expanding our knowledge about the nature of the polymers and the influence of polar functional groups and the structure on thermodynamical properties of polymers and designing suitable solvent for a specific extraction problem. Recently, we presented the mass-fraction activity coefficients at infinite dilution for hyperbranched polymer Boltorn W3000 (B-W3000).<sup>24</sup> This is the hyperbranched polymer, known as an amphiphilic dendritic polymer. It contains long unsaturated fatty acid chains.<sup>24</sup> The highest values of the mass-fraction activity coefficients at infinite dilution for this polymer were observed for water and for aliphatic hydrocarbons from *n*-pentane to *n*-nonane.<sup>24</sup> The measurements of activity coefficients at infinite dilution of different solvents in bisphenyl-a-polycarbonate polymer (CD material, baby bottles, plastic shields) or in seven hyperbranched polymers [i.e., poly(styrene-*co*-maleic anhydride) or  $C_{22}$  esterified poly(styrene-*co*-maleic anhydride)], using IGC, were presented earlier.<sup>25,26</sup> The values of the mass-fraction activity coefficients of different solutes for these polymers  $\Omega_{13}^\infty$  were (at very high temperatures  $>360$  K) at the same range as for B-W3000. For the simple polymer as isotactic poly(1-butene),<sup>27</sup> for the sucrose monoesters,<sup>28</sup> or for the columnar and isotropic phases of poly(propyleneimine) dendrimers (generation 1–3, G1–G3)<sup>29</sup> and Hybrane 1200,<sup>30</sup> the values of  $\Omega_{13}^\infty$  were very small.

In this work, we extend our measurements of mass-fraction activity coefficient,  $\Omega_{13}^\infty$ , for the 42 different solvents, alkanes, cycloalkanes, alkenes, alkynes, aromatic hydrocarbons, alcohols, water, ethers, and ketones, in polymers to the hyperbranched

polymer Boltorn U3000 (B-U3000) at the temperatures from 308.15 to 348.15 K. Since HBPs have a negligible vapor pressure, the most suitable method for measuring activity coefficients of volatile solutes in HBP is inverse gas chromatography (IGC) using the HBP as the stationary phase. The specific retention volume ( $V_g$ ), the Flory–Huggins interaction parameter ( $\chi_{13}^\infty$ ), the molar enthalpy of sorption (the partial molar enthalpies of solute dissolution) ( $\Delta_s H$ ), the partial molar excess enthalpy at infinite dilution of the solute and polymer ( $\Delta H_1^{E,\infty}$ ), the partial molar Gibbs excess energy at infinite dilution ( $\Delta G_1^{E,\infty}$ ), and the solubility parameter ( $\delta_3$ ) were calculated.

### Theoretical Basis

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<sup>31</sup>

$$V_g = \frac{273V_N}{W_s T} = \frac{273J_2^3 U_0 \left(1 - \frac{p_w}{p_o}\right) (t_r - t_g)}{T_F W_s} \quad (1)$$

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  $p_o$  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 for the influence of the pressure drop along the column given by

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

where  $P_i$  and  $P_o$  are the inlet and the outlet pressure of the GC column, respectively.

The mass-fraction activity coefficient at infinite dilution,  $\Omega_{13}^\infty$ , is

$$\Omega_{13}^\infty = \frac{RW_s T}{V_N P_1^* M_1} \exp\left(-\frac{P_1^*(B_{11} - V_1)}{RT}\right) \quad (3)$$

where  $R$  is the universal gas constant;  $M_1$  is the solute molecular weight;  $P_1^*$  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 (“3”) + solute (“1”) system at low pressures, one can assume that the vapor pressure is considered to contain the pure solute “1”, which can be regarded as an ideal gas (neglecting the vapor pressure of the polymer). The polymer only influences the solute activity coefficient in the liquid phase. Using the activity coefficients, the Flory–Huggins,  $\chi_{13}^\infty$ , interaction parameter values can be calculated at infinite concentrations from the relationship as follows<sup>31</sup>

$$\chi_{13}^\infty = \ln\left(\frac{273.15Rv_3}{V_g P_1^* V_1}\right) - 1 - \frac{P_1^*(B_{11} - V_1)}{RT} \quad (4)$$

where  $v_3$  is the specific volume of the stationary phase at inlet pressure and temperature and  $v_3 = 1/d$  ( $\text{g cm}^{-3}$ ) of polymer.

The molar enthalpy of sorption (the partial molar enthalpies of solute dissolution),  $\Delta_s H$ , was calculated from the equation

**TABLE 2: Linear Regression of the Experimental Mass-Fraction Activity Coefficient at Infinite Dilution,  $\Omega_{13}^\infty$ , Temperature Ranges, Coefficients  $a$  and  $b$ ,<sup>a</sup> Correlation Coefficients  $R^2$ , Extrapolated Value of  $\Omega_{13}^\infty(298.15\text{ K})$ , and the Partial Molar Excess Enthalpy at Infinite Dilution,  $\Delta H_1^{E,\infty}$  at  $T = 298.15\text{ K}$** 

solute	temperature ranges/K	$a$	$b/\text{K}$	$R^2$	$\Omega_{13}^\infty(298.15\text{ K})$	$\Delta H_1^{E,\infty}/\text{kJ mol}^{-1}$
<i>n</i> -alkanes						
<i>n</i> -pentane	308.15–348.15	1.87	138.0	0.922	10.33	1.1
<i>n</i> -hexane	308.15–348.15	1.96	64.9	0.736	8.83	0.5
<i>n</i> -heptane	308.15–348.15	1.78	97.6	0.858	8.21	0.8
<i>n</i> -octane	308.15–348.15	1.79	76.3	0.850	7.30	0.6
<i>n</i> -nonane	308.15–348.15	1.66	104.1	0.822	7.48	0.9
<i>n</i> -decane	318.15–348.15	1.81	50.4	0.665	7.24	0.4
cycloalkanes						
cyclopentane	308.15–348.15	1.63	86.7	0.826	6.80	0.7
cyclohexane	308.15–348.15	1.33	158.2	0.961	6.46	1.3
cycloheptane	308.15–348.15	1.29	126.1	0.889	5.53	1.0
cyclooctane	318.15–348.15	1.32	87.5	0.965	5.00	0.7
alkenes						
1-pentene	308.15–348.15	1.88	79.1	0.854	8.53	0.7
1-hexene	308.15–348.15	1.86	39.9	0.667	7.38	0.3
1-heptene	308.15–348.15	1.91	−3.7	0.012	6.69	0.0
1-octene	318.15–348.15	1.91	−24.4	0.454	6.24	−0.2
alkynes						
1-pentyne	308.15–348.15	2.07	−69.4	0.885	6.29	−0.6
1-hexyne	308.15–348.15	2.07	−119.5	0.967	5.29	−1.0
1-heptyne	308.15–348.15	2.10	−163.8	0.992	4.73	−1.4
1-octyne	318.15–348.15	2.01	−154.0	0.983	4.59	−1.3
aromatic hydrocarbons						
benzene	308.15–348.15	1.27	33.8	0.975	3.98	0.3
toluene	318.15–348.15	1.51	−72.3	0.989	3.55	−0.6
ethylbenzene	318.15–348.15	1.40	−36.8	0.925	3.60	−0.3
<i>o</i> -xylene	318.15–348.15	1.45	−77.1	0.957	3.31	−0.6
<i>m</i> -xylene	318.15–348.15	1.61	−119.4	0.999	3.37	−1.0
<i>p</i> -xylene	318.15–348.15	1.65	−133.9	0.979	3.33	−1.1
thiophene	308.15–348.15	1.06	43.8	0.991	3.33	0.4
alcohols and water						
methanol	308.15–348.15	0.90	845.5	0.998	41.95	7.0
ethanol	308.15–348.15	0.14	973.0	0.996	30.09	8.1
1-propanol	308.15–348.15	−0.06	918.7	0.998	20.50	7.6
1-butanol	308.15–348.15	−0.35	942	0.999	16.52	7.8
1-pentanol	318.15–348.15	−0.02	743.5	0.996	11.87	6.2
water	308.15–348.15	−0.13	1572	0.990	171.54	13.1
ethers						
THF	308.15–348.15	1.46	−65.8	0.867	3.47	−0.5
MTBE	308.15–348.15	1.86	−54.7	0.663	5.34	−0.5
diethyl ether	308.15–348.15	2.02	−59.9	0.761	6.14	−0.5
di- <i>n</i> -propyl ether	308.15–348.15	1.76	−5.2	0.016	5.73	0.0
di- <i>n</i> -butyl ether	318.15–348.15	1.63	12.9	0.180	5.31	0.1
ketones						
propanone	318.15–348.15	1.21	333.1	0.997	10.26	2.8
2-pentanone	308.15–348.15	1.34	132.5	0.994	5.98	1.1
3-pentanone	308.15–348.15	1.48	73.9	0.966	5.65	0.6
2-hexanone	308.15–348.15	1.34	93.5	0.930	5.21	0.8
3-hexanone	308.15–348.15	1.20	138.6	0.934	5.28	1.2
cyclopentanone	308.15–348.15	1.15	141.7	0.984	5.06	1.2

<sup>a</sup> From the equation  $\ln \Omega_{13}^\infty = a + (b/T)$ .

$$\Delta_s H = -R \frac{\partial \ln V_g}{\partial (1/T)} \quad (5)$$

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

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

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

**TABLE 3: Selectivities  $S_{ij}^\infty$  and Capacities  $k_j^\infty$  at Infinite Dilution for B-U3000 for Different Separation Problems at  $T = 298.15\text{ K}$** 

separation mixture	$S_{ij}^\infty$	$k_j^\infty$
<i>n</i> -hexane/thiophene	2.7	0.30
<i>n</i> -hexane/benzene	2.2	0.25
<i>n</i> -hexane/toluene	2.5	0.28
methanol/propanone	4.1	0.10
methanol/MTBE	7.9	0.18
methanol/THF	12.1	0.29
H <sub>2</sub> O/ethanol	5.7	0.04
H <sub>2</sub> O/THF	49.4	0.29

**TABLE 4: Linear Regression of the Experimental Flory–Huggins Interaction Parameter,  $\chi_{13}^\infty$ , Temperature Ranges, Coefficients  $c$  and  $d$ ,<sup>a</sup> Correlation Coefficients  $R^2$ , and Extrapolated Value of  $\chi_{13}^\infty(298.15\text{ K})$** 

solvent	temperature ranges/K	$c$	$10^{-2} \cdot d$	$R^2$	$\chi_{13}^\infty(298.15)$
<i>n</i> -alkanes					
<i>n</i> -pentane	308.15–348.15	0.87	−0.24	0.980	0.14
<i>n</i> -hexane	308.15–348.15	0.47	−0.14	0.958	0.04
<i>n</i> -heptane	308.15–348.15	0.47	−0.16	0.957	0.01
<i>n</i> -octane	308.15–348.15	0.35	−0.13	0.965	−0.02
<i>n</i> -nonane	308.15–348.15	0.38	−0.14	0.929	−0.04
<i>n</i> -decane	318.15–348.15	0.21	−0.09	0.946	−0.05
cycloalkanes					
cyclopentane	308.15–348.15	0.33	−0.14	0.953	−0.10
cyclohexane	308.15–348.15	0.50	−0.20	0.980	−0.11
cycloheptane	308.15–348.15	0.25	−0.16	0.939	−0.22
cyclooctane	318.15–348.15	0.04	−0.11	0.996	−0.29
alkenes					
1-pentene	308.15–348.15	0.58	−0.20	0.980	−0.02
1-hexene	308.15–348.15	0.27	−0.13	0.977	−0.12
1-heptene	308.15–348.15	0.01	−0.06	0.878	−0.18
1-octene	318.15–348.15	−0.13	−0.03	0.777	−0.22
alkynes					
1-pentyne	308.15–348.15	0.02	−0.09	0.978	−0.25
1-hexyne	308.15–348.15	−0.50	0.04	0.893	−0.39
1-heptyne	308.15–348.15	−0.74	0.09	0.994	−0.47
1-octyne	318.15–348.15	0.76	0.08	0.985	−0.51
aromatic hydrocarbons					
benzene	308.15–348.15	−0.21	−0.09	0.987	−0.47
toluene	318.15–348.15	−0.64	0.02	0.772	−0.59
ethylbenzene	318.15–348.15	−0.56	−0.01	0.566	−0.58
<i>o</i> -xylene	318.15–348.15	−0.76	0.04	0.984	−0.65
<i>m</i> -xylene	318.15–348.15	−0.86	0.07	0.950	−0.65
<i>p</i> -xylene	318.15–348.15	−0.91	0.08	0.993	−0.66
thiophene	308.15–348.15	−0.18	−0.09	0.986	−0.46
alcohols and water					
methanol	308.15–348.15	4.32	−0.86	1.000	1.77
ethanol	308.15–348.15	4.31	−0.97	0.998	1.43
1-propanol	308.15–348.15	3.77	−0.91	0.999	1.06
1-butanol	308.15–348.15	3.60	−0.92	1.000	0.85
1-pentanol	318.15–348.15	2.64	−0.71	0.996	0.53
water	308.15–348.15	7.63	−1.42	0.993	3.38
ethers					
THF	308.15–348.15	−0.59	0.00	0.024	−0.60
MTBE	308.15–348.15	−0.23	−0.04	0.681	−0.35
diethyl ether	308.15–348.15	−0.05	−0.06	0.930	−0.24
di- <i>n</i> -propyl ether	308.15–348.15	−0.09	−0.06	0.820	−0.27
di- <i>n</i> -butyl ether	318.15–348.15	−0.12	−0.06	0.959	−0.31
ketones					
propanone	318.15–348.15	1.57	−0.40	0.998	0.37
2-pentanone	308.15–348.15	0.40	−0.18	1.000	−0.15
3-pentanone	308.15–348.15	0.21	−0.14	0.990	−0.19
2-hexanone	308.15–348.15	0.13	−0.14	0.981	−0.28
3-hexanone	308.15–348.15	0.26	−0.18	0.982	−0.26
cyclopentanone	308.15–348.15	0.34	−0.17	0.997	−0.15

<sup>a</sup> From the equation  $\chi_{13}^\infty = c + dT$ .

$$\Delta_{\text{vap}}H^0 = \Delta H_1^{\text{E},\infty} - \Delta_s H$$

The mass-fraction activity coefficient at infinite dilution is connected with the partial molar Gibbs excess energy at infinite dilution,  $\Delta G_1^{\text{E},\infty}$ , by the ratio

$$\Delta G_1^{\text{E},\infty} = RT \ln \Omega_{13}^\infty \quad (8)$$

The solubility parameter of the solute ( $\delta_1$ ) is calculated through the well-known equation

$$\delta_1 = \left( \frac{\Delta H_v - RT}{V_1} \right)^{1/2} \quad (9)$$

The estimated solubility parameter of the polymer ( $\delta_3$ ) is obtained using a combination of the lattice model of solutions and the solubility parameter theory<sup>32,33</sup>

$$\left( \frac{\delta_1^2}{RT} - \frac{\chi_{13}^\infty}{V_1} \right) = \frac{2\delta_3}{RT} \delta_1 - \left( \frac{\delta_3^2}{RT} + \frac{\chi^s}{V_1} \right) \quad (10)$$

where  $\chi^s$  is the entropic factor of the interaction parameter. The

**TABLE 5: Linear Regression of the Partial Molar Excess Gibbs Energy at Infinite Dilution,  $\Delta G_1^{E,\infty}$ , Temperature Ranges, Coefficients  $e$  and  $f$ ,<sup>a</sup> Correlation Coefficients  $R^2$ , and Extrapolated Value of  $\Delta G_1^{E,\infty}(298.15\text{ K})$** 

solvent	temperature ranges/K	$e$	$f$	$R^2$	$\Delta G_1^{E,\infty}(298.15)/\text{kJ mol}^{-1}$
<i>n</i> -alkanes					
<i>n</i> -pentane	308.15–348.15	11.36	−1672.5	0.991	5.8
<i>n</i> -hexane	308.15–348.15	11.23	−1750.8	0.991	5.4
<i>n</i> -heptane	308.15–348.15	10.51	−1588.4	0.990	5.2
<i>n</i> -octane	308.15–348.15	10.39	−1597.6	0.992	5.1
<i>n</i> -nonane	308.15–348.15	9.95	−1487.3	0.985	5.0
<i>n</i> -decane	318.15–348.15	10.45	−1669.7	0.993	4.9
cycloalkanes					
cyclopentane	308.15–348.15	9.60	−1453.6	0.988	4.8
cyclohexane	308.15–348.15	8.60	−1192.1	0.989	4.6
cycloheptane	308.15–348.15	8.07	−1151.2	0.981	4.2
cyclooctane	318.15–348.15	8.02	−1212.4	0.996	4.0
alkenes					
1-pentene	308.15–348.15	10.90	−1676.5	0.993	5.3
1-hexene	308.15–348.15	10.50	−1664.4	0.993	5.0
1-heptene	308.15–348.15	10.41	−1708.8	0.992	4.7
1-octene	318.15–348.15	10.39	−1762.1	0.996	4.5
alkynes					
1-pentyne	308.15–348.15	10.72	−1848.4	0.995	4.6
1-hexyne	308.15–348.15	10.27	−1844.1	0.995	4.1
1-heptyne	308.15–348.15	10.10	−1875.6	0.997	3.9
1-octyne	318.15–348.15	9.84	−1849.1	0.997	3.7
aromatic hydrocarbons					
benzene	308.15–348.15	7.18	−1129.2	0.999	3.4
toluene	318.15–348.15	7.76	−1390.6	0.998	3.1
ethylbenzene	318.15–348.15	7.46	−1292.3	0.998	3.2
<i>o</i> -xylene	318.15–348.15	7.42	−1340.2	0.996	3.0
<i>m</i> -xylene	318.15–348.15	7.94	−1485.6	0.999	3.0
<i>p</i> -xylene	318.15–348.15	8.04	−1523.2	0.996	3.0
thiophene	308.15–348.15	6.12	−942.1	0.999	3.0
alcohols and water					
methanol	308.15–348.15	11.93	−799.1	0.991	9.3
ethanol	308.15–348.15	8.85	−121.7	0.342	8.4
1-propanol	308.15–348.15	7.30	57.4	0.191	7.5
1-butanol	308.15–348.15	5.89	318.3	0.911	7.0
1-pentanol	318.15–348.15	6.08	14.7	0.013	6.1
water	308.15–348.15	12.34	124.0	0.077	12.8
ethers					
THF	308.15–348.15	7.44	−1306.7	0.994	3.1
MTBE	308.15–348.15	9.68	−1659.8	0.989	4.1
diethyl ether	308.15–348.15	10.50	−1800.1	0.993	4.5
di- <i>n</i> -propyl ether	308.15–348.15	9.58	−1575.4	0.989	4.3
di- <i>n</i> -butyl ether	318.15–348.15	9.11	−1498.0	0.994	4.1
ketones					
propanone	318.15–348.15	9.37	−1080.7	0.994	5.8
2-pentanone	308.15–348.15	8.55	−1238.6	0.997	4.4
3-pentanone	308.15–348.15	8.83	−1366.3	0.998	4.3
2-hexanone	308.15–348.15	8.18	−1230.8	0.994	4.1
3-hexanone	308.15–348.15	7.80	−1107.2	0.986	4.1
cyclopentanone	308.15–348.15	7.53	−1056.3	0.995	4.0

<sup>a</sup> From the equation  $\Delta G_1^{E,\infty} = e + fT$ .

plot of the first term of the above equation versus  $\delta_1$  allows us to get the solubility parameter for B-U3000 at different temperatures. The extrapolation to the temperature  $T = 298.15$  K will give the solubility parameter at 298.15 K and could help to predict the solubility of polymer in any organic solvent.

## Experimental Procedures

**Materials.** The hyperbranched polymer, Boltorn U3000 (B-U3000) (Perstorp, Sweden, 98%), is a fatty acid modified dendritic polyester. It is a highly viscous, slightly yellow liquid

at room temperature. The B-U3000 was further purified by subjecting the liquid to a very low pressure of about  $5 \times 10^{-3}$  Pa at temperature  $T = 300$  K for approximately 48 h. This procedure removed any volatile chemicals and water from the polymer. The viscosity and the density for B-U3000 are presented in Table 1.

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



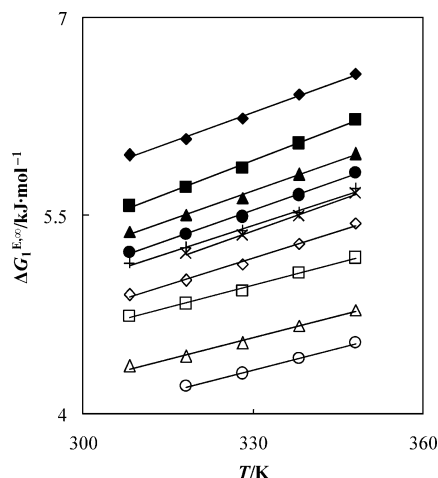
**TABLE 6: Linear Regression of the Calculated Partial Molar Excess Entropy at Infinite Dilution,  $\Delta S_1^{E,\infty}$ , Temperature Ranges, Coefficients  $g$  and  $h$ ,<sup>a</sup> Correlation Coefficients  $R^2$ , and Extrapolated Value of  $\Delta S_1^{E,\infty}$  (298.15 K)**

solvent	temperatures range/K	$g$	$h$	$R^2$	$\Delta S_1^{E,\infty}/J \text{ mol}^{-1} \text{ K}^{-1}$
<i>n</i> -alkenes					
<i>n</i> -pentane	308.15–348.15	−33.15	5427.5	0.991	−14.9
<i>n</i> -hexane	308.15–348.15	−34.70	5681.5	0.991	−15.6
<i>n</i> -heptane	308.15–348.15	−31.48	5154.5	0.990	−14.2
<i>n</i> -octane	308.15–348.15	−31.67	5184.3	0.992	−14.3
<i>n</i> -nonane	308.15–348.15	−29.47	4826.6	0.985	−13.3
<i>n</i> -decane	318.15–348.15	−32.56	5418.5	0.993	−14.4
cycloalkanes					
cyclopentane	308.15–348.15	−28.80	4717.2	0.988	−13.0
cyclohexane	308.15–348.15	−23.63	3868.6	0.989	−10.7
cycloheptane	308.15–348.15	−22.80	3735.8	0.981	−10.3
cyclooctane	318.15–348.15	−23.65	3934.5	0.996	−10.5
alkanes					
1-pentene	308.15–348.15	−33.24	5440.7	0.993	−15.0
1-hexene	308.15–348.15	−33.00	5401.4	0.993	−14.9
1-heptene	308.15–348.15	−33.87	5545.3	0.992	−15.3
1-octene	318.15–348.15	−34.38	5718.3	0.996	−15.2
alkynes					
1-pentyne	308.15–348.15	−36.65	5998.4	0.995	−16.5
1-hexyne	308.15–348.15	−36.57	5984.4	0.995	−16.5
1-heptyne	308.15–348.15	−37.20	6086.6	0.997	−16.8
1-octyne	318.15–348.15	−36.08	6000.7	0.997	−16.0
aromatic hydrocarbons					
benzene	308.15–348.15	−22.40	3664.4	0.999	−10.1
toluene	318.15–348.15	−27.14	4512.6	0.998	−12.0
ethylbenzene	318.15–348.15	−25.22	4193.9	0.998	−11.2
<i>o</i> -xylene	318.15–348.15	−26.15	4349.1	0.996	−11.6
<i>m</i> -xylene	318.15–348.15	−29.00	4821.1	0.999	−12.8
<i>p</i> -xylene	318.15–348.15	−29.72	4943.1	0.996	−13.1
thiophene	308.15–348.15	−18.69	3057.4	0.999	−8.4
alcohols and water					
methanol	308.15–348.15	−15.89	2593.4	0.991	−7.2
ethanol	308.15–348.15	−2.45	394.9	0.342	−1.1
1-propanol	308.15–348.15	1.11	−186.4	0.191	0.5
1-butanol	308.15–348.15	6.29	−1032.9	0.911	2.8
1-pentanol	318.15–348.15	0.32	−47.8	0.013	0.2
water	308.15–348.15	2.36	−402.3	0.077	1.0
ethers					
THF	308.15–348.15	−25.92	4240.6	0.994	−11.7
MTBE	308.15–348.15	−32.89	5386.2	0.989	−14.8
diethyl ether	308.15–348.15	−35.68	5841.6	0.993	−16.1
di- <i>n</i> -propyl ether	308.15–348.15	−31.22	5112.4	0.989	−14.1
di- <i>n</i> -butyl ether	318.15–348.15	−29.22	4861.2	0.994	−12.9
ketones					
propanone	318.15–348.15	−21.43	3507.0	0.994	−9.7
2-pentanone	308.15–348.15	−24.17	4019.3	0.997	−10.7
3-pentanone	308.15–348.15	−26.66	4433.9	0.998	−11.8
2-hexanone	308.15–348.15	−24.01	3994.2	0.994	−10.6
3-hexanone	308.15–348.15	−21.58	3593.0	0.986	−9.5
cyclopentanone	308.15–348.15	−20.60	3428.0	0.995	−9.1

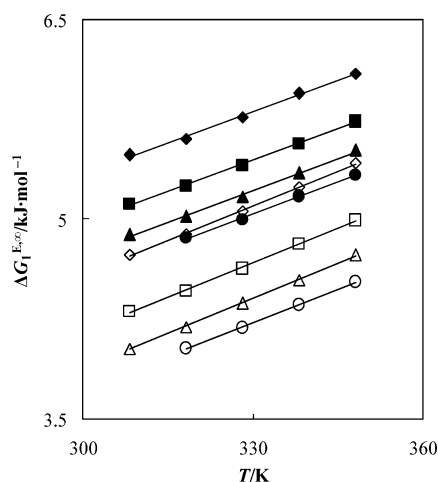
<sup>a</sup> From the equation:  $\Delta G_1^{E,\infty} = \Delta H_1^{E,\infty} - T\Delta S_1^{E,\infty}$  and  $\Delta S_1^{E,\infty} = g + (h/T)$ .

**Apparatus and 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 and 4 mm internal diameter 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 *n*-hexane followed by evaporation of the solvent using a rotating evaporator. The masses of the

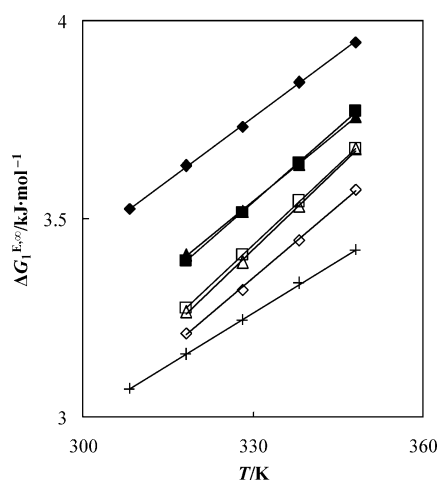
stationary phase and of the solid support were weighed with a precision  $\pm 0.0001$  g. The high mass percent of the polymer prevents possible residual adsorption of solute (especially *n*-alkanes) onto the column packing, as was discussed in previous work.<sup>34</sup> This procedure of maximum mass percent packing columns for the certain solvent was experimentally confirmed in the measurements of activity coefficients at infinite dilution of different solutes in ionic liquids.<sup>35</sup> For each temperature, the measurements were repeated by using two different columns with different mass percent packing (loading 17% and 25%; mass coated 0.5226 g and 0.8589 g).



**Figure 1.** Plot of  $\Delta G_1^{E,\infty}$  versus  $T$  for the  $n$ -alkanes and cycloalkanes: (◆)  $n$ -pentane; (■)  $n$ -hexane; (▲)  $n$ -heptane; (●)  $n$ -octane; (+)  $n$ -nonane; (×)  $n$ -decane; (◇) cyclopentane; (□) cyclohexane; (Δ) cycloheptane; (○) cyclooctane.

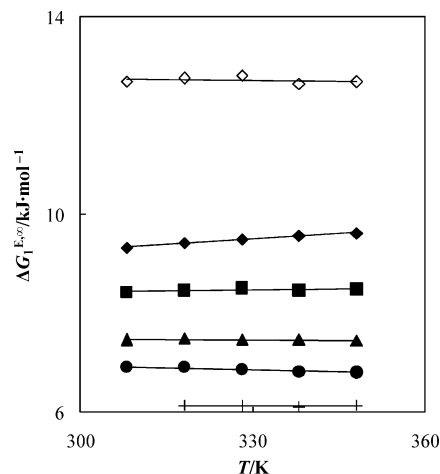


**Figure 2.** Plot of  $\Delta G_1^{E,\infty}$  versus  $T$  for the 1-alkenes and 1-alkynes: (◆) 1-pentene; (■) 1-hexene; (▲) 1-heptene; (●) 1-octene; (◇) 1-pentyne; (□) 1-hexyne; (Δ) 1-heptyne; (○) 1-octyne.

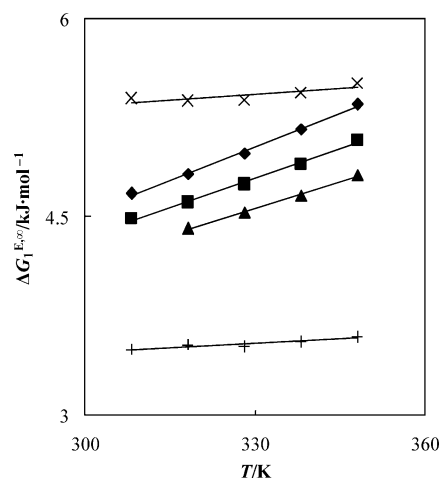


**Figure 3.** Plot of  $\Delta G_1^{E,\infty}$  versus  $T$  for the aromatic hydrocarbons: (◆) benzene; (■) toluene; (▲) ethylbenzene; (+) thiophene; (◇)  $o$ -xylene; (□)  $m$ -xylene; (Δ)  $p$ -xylene.

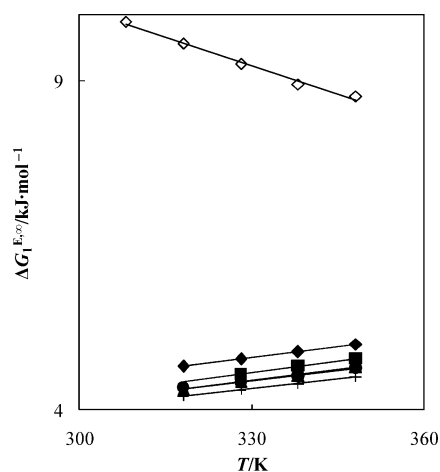
Care was taken to ensure that the  $n$ -hexane had completely evaporated from the polymer-coated solid before making up the column. Before experiment, each column was conditioned by blowing carrier gas at a high flow rate (about  $3.5 \text{ cm}^3 \text{ s}^{-1}$ ) at



**Figure 4.** Plot of  $\Delta G_1^{E,\infty}$  versus  $T$  for the alcohols and water: (◆) methanol; (■) ethanol; (▲) 1-propanol; (●) 1-butanol; (+) 1-pentanol; (◇) water.



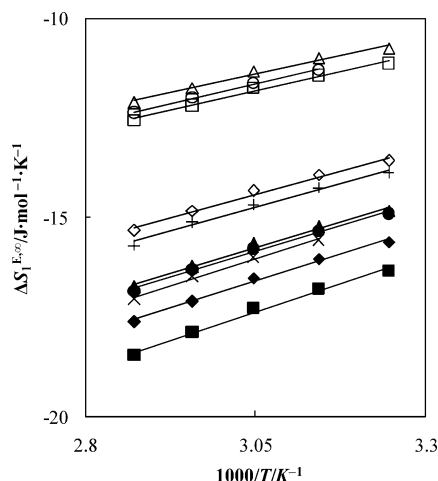
**Figure 5.** Plot of  $\Delta G_1^{E,\infty}$  versus  $T$  for the ethers: (+) THF; (×) MTBE; (◆) diethyl ether; (■) di- $n$ -propyl ether; (▲) di- $n$ -butyl ether.



**Figure 6.** Plot of  $\Delta G_1^{E,\infty}$  versus  $T$  for the ketones: (◇) propanone; (◆) 2-pentanone; (■) 3-pentanone; (▲) 2-hexanone; (●) 3-hexanone; (+) cyclopentanone.

the high temperature (about 373 K) for about 8 h. The retention volumes are presented in Table 1S in the Supporting Information.

The outlet pressure  $P_o$  was kept at atmospheric pressure. The pressure drop ( $P_i - P_o$ ) was varied between (28 and 42) kPa



**Figure 7.** Plot of  $\Delta S_{\ddagger E, \infty}^{\circ}$  versus  $1/T$  for the solutes: (◆) *n*-pentane; (■) *n*-hexane; (▲) *n*-heptane; (●) *n*-octane; (+) *n*-nonane; (×) *n*-decane; (◇) cyclopentane; (□) cyclohexane; (○) cycloheptane; (Δ) cyclooctane.

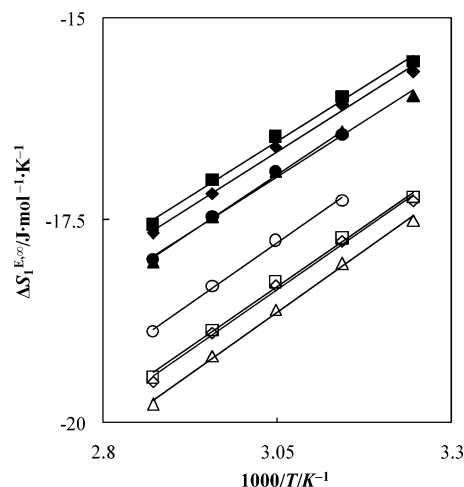
depending on the flow rate of carrier gas. The pressure drop was measured by a gas chromatograph with an uncertainty of  $\pm 0.1$  kPa. The atmospheric pressure was measured using a digital barometer with an uncertainty of  $\pm 0.1$  hPa.

The carrier gas was helium (substance “2”). 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 retention time was determined. The flow rates were corrected for water vapor pressure and ranged from 0.6 to 1.1 cm<sup>3</sup> s<sup>-1</sup>. Solute injections ranging from 0.01 to 0.1  $\mu$ L 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 423.15 K).

Experiments were carried out at different temperatures (in steps of 10 K) between 308.15 and 348.15 K. The temperature of the column was maintained constant to within  $\pm 0.02$  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  $\Omega_{13}^{\infty}$  was less than 3%, 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.<sup>36</sup>

## Results and Discussion

Specific retention volumes,  $V_g$ , were calculated for 42 solutes according to eq 1 at five temperatures. As was expected, the  $V_g$  values decrease with an increase of temperature as was observed for Hybrane 1200<sup>30</sup> or B-W3000<sup>24</sup> and B-H2004.<sup>8</sup> The values of  $V_g$  increase for a series of solutes with an increase of the solute alkyl chain or solute ring in cycloalkanes or the alkyl chain in alkylbenzenes. The highest value was observed for *n*-decane, 6465.5 at  $T = 318.15$  K, which would be higher at  $T = 308.15$  K, and *n*-nonane, 4260.3 cm<sup>3</sup> mol<sup>-1</sup> at  $T = 308.15$



**Figure 8.** Plot of  $\Delta S_{\ddagger E, \infty}^{\circ}$  versus  $1/T$  for the solutes: (◆) 1-pentene; (■) 1-hexene; (▲) 1-heptene; (●) 1-octene; (◇) 1-pentyne; (□) 1-hexyne; (○) 1-heptyne; (Δ) 1-octyne.

K, as well as for *o*-xylene, 4568.2 at  $T = 318.15$  K, which also will be higher at  $T = 308.15$  K.

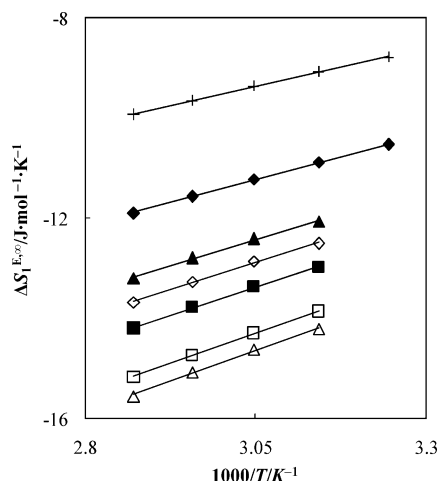
The complete set of data of average  $\Omega_{13}^{\infty}$  values for the varying amounts of polymer on the column packing in the temperature range from 308.15 to 348.15 K, determined from eq 3, is available in the Supporting Information (Table 2S). Figures 1S–6S in the Supporting Information show 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  $\Omega_{13}^{\infty}$  for a series of solutes decrease with temperature, i.e., for *n*-alkanes, cycloalkanes, 1-alkenes, thiophene, 1-alcohols, water, and ketones. The values of  $\Omega_{13}^{\infty}$  have been approximated by the linear regression

$$\ln \Omega_{13}^{\infty} = a + \frac{b}{T} \quad (11)$$

The parameters of the linear regression of the natural logarithm of  $\Omega_{13}^{\infty}$  as a function of the inverse absolute temperature for all investigated series of solutes and  $\Omega_{13}^{\infty}(298.15 \text{ K})$  are listed in Table 2. For some solutes, where the interactions with polymer were stronger (1-alkynes, THF, MTBE), the mass-fraction activity coefficients increase with an increase of temperature (see Figures 2S, 3S, and 5S in the Supporting Information). The influence of temperature in a tested range of temperatures was not high but the same as was observed for other polymers.<sup>8,24,27,28,30</sup> For many solutes, the values are almost constant; i.e., for 1-heptene, 1-octene, benzene, toluene, ethylbenzene, *o*-xylene, di-*n*-propyl ether, and di-*n*-butyl ether, the differences vary from 0.03 to 0.08 and are in the range of error of the experimental work (3%). It means that the specific interaction of these solutes with polymer is independent of temperature.

The values of  $\Omega_{13}^{\infty}$  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 of the solute alkyl chain with the alkyl substituents at the hyperbranched periphery, i.e., C<sub>16</sub> and C<sub>18</sub> chains of the esters. All values of  $\Omega_{13}^{\infty}$  except those for alcohols, water, and ketones are much lower (about 40–70%) than those observed for B-W3000<sup>24</sup> and B-H2004.<sup>8</sup> The high values of  $\Omega_{13}^{\infty}$  for *n*-alkanes signify small interactions between solute and polymer in spite of the long *n*-alkane end groups (C<sub>16</sub> and/or C<sub>18</sub>) from the estrification process. However, the highest value of  $\Omega_{13}^{\infty}$  was for water ( $\Omega_{13}^{\infty} = 141.82$  at  $T = 308.15$



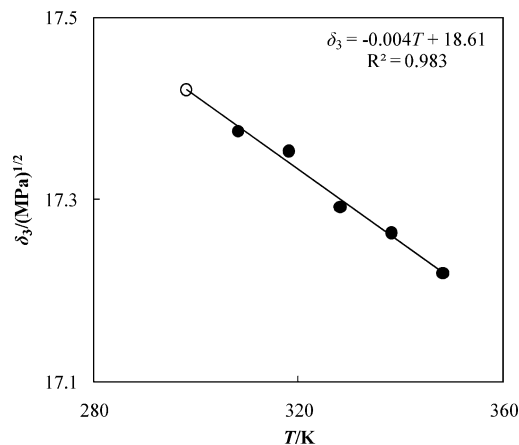


**Figure 9.** Plot of  $\Delta S_1^{E,\infty}$  versus  $1/T$  for the solutes: (◆) benzene; (■) toluene; (▲) ethylbenzene; (◇) *o*-xylene; (□) *m*-xylene; (△) *p*-xylene; (+) thiophene.

K) and the second highest for alcohol (i.e., for methanol  $\Omega_{13}^\infty = 38.05$  at  $T = 308.15$  K). The value of  $\Omega_{13}^\infty$  for water is almost three times higher than that for B-W3000 ( $\Omega_{13}^\infty = 49.18$  at  $T = 308.15$  K)<sup>24</sup> and that for B-H2004 ( $\Omega_{13}^\infty = 58.20$  at  $T = 308.15$  K).<sup>8</sup> This shows that polymer B-U3000 is much more hydrophobic than B-W3000 and B-H2004. Small values of activity coefficients have been found for cycloalkanes as well (see Table 2S, Supporting Information), which are comparable to those of 1-alkynes. 1-Alkenes can interact by a double bond with polar end groups of polymer. This indicates a better solubility of molecules with double bonds in the polymer due to their higher polarizability. Generally, the smallest values of  $\Omega_{13}^\infty$  indicate the stronger interactions between polymer and solute. Values of  $\Omega_{13}^\infty$  for alkynes, aromatic hydrocarbons, thiophene, and THF are distinctly lower in comparison with those of the *n*-alkanes and alkenes. Triple bonds in alkynes and six  $\pi$ -delocalized electrons in aromatics can more strongly interact with the polar parts of polymer than the  $-\text{OH}$  group of alcohols or water. The results also show that ketones interact with a polymer stronger than ethers, alcohols, and water.

A value of the partial molar thermodynamic functions of mixing at infinite dilution and the partial molar excess enthalpy at infinite dilution of the solute and polymer,  $\Delta H_1^{E,\infty}$  (see Table 2), are for most of the solutes positive and in a range between 0 and 13.1 kJ mol<sup>-1</sup> (13.1 kJ mol<sup>-1</sup> is for water). A change is accompanied by a decrease in the  $\Omega_{13}^\infty$  values within the homological series of *n*-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 enthalpies  $\Delta H_1^{E,\infty}$  (for 1-alkynes, alkylbenzenes, xylenes, THF, and diethylether) suggest higher interaction of polymer–solute than for the other solutes.  $\Delta H_1^{E,\infty}$  values are positive and do not change with increasing chain length of alcohols. For 1-octene, alkynes, alkylbenzenes, THF, MTBE, and diethyl ether,  $\Delta H_1^{E,\infty}$  becomes negative. This is most probably due to the high interaction between the solute and polymer.

From experimental values of  $\Omega_{13}^\infty$ , 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 for different separation problems.<sup>22</sup> The best results for the obtained separations of different azeotropic mixtures are listed in Table 3. From the analysis of the selectivity and capacity at temperature  $T = 298.15$  K (extrapolated values) presented in Table 3, we can conclude that selectivities  $S_{12}^\infty$  for two separation problems, methanol/THF and



**Figure 10.** Linear regression of the solubility parameter,  $\delta_3$ , of the B-U3000 on temperature  $T$ ; (●) solubility parameter; (○) extrapolated value of  $\delta_3$  to  $T = 298.15$  K.

water/THF, are quite high, and the capacity  $k_2^\infty$  for THF at infinite dilution for B-U3000 is 0.29. The selectivity for the investigated polymer is extremely high for the water/THF mixture. The value of 49.4 shows the possibility of using B-U3000 as an entrainer in the separation process of an azeotropic mixture of water and tetrahydrofuran. These results revealed that polymer B-U3000 is more than three times better than B-W3000<sup>24</sup> and B-H2004<sup>8</sup> in the same separation problem, which is a result of higher hydrophobicity of the polymer. This is a result of the different interaction of polymer and solute (water, methanol, and THF). B-U3000 is a fatty acid modified dendritic polyester, with in average 14 unsaturated fatty ester groups in the molecule of C<sub>16</sub> and/or C<sub>18</sub> fatty acids. B-W3000 contains long unsaturated fatty acid chains,<sup>24</sup> and B-H2004 is hydrophobic and a fatty acid modified dendritic polyester with hydroxyl groups  $-\text{OH}$  and about 62% of ester groups from the estrification with C<sub>8</sub> acid.<sup>8</sup> The B-H2004 is evidently but less hydrophobic than B-U3000 because of the  $-\text{OH}$  groups.<sup>8</sup>

Table 3S in the Supporting Information shows the values of the Flory–Huggins interaction parameter at infinite dilution, defined by eq 4 at the measured range of temperatures. Table 4 presents the parameters of the approximation of the Flory–Huggins interaction parameter at infinite dilution by the linear regression as a function of temperature. The coefficients  $c$  and  $d$ , the correlation coefficients  $R^2$ , and the values of  $\chi_{13}^\infty(298.15$  K) calculated with these coefficients are given in Table 4. The parameter  $\chi_{13}^\infty$  characterizes the interaction between the vapor phase of the solute and the polymeric stationary phase. In general, values of  $\chi_{13}^\infty$  greater than 0.5 at  $T = 298.15$  K represent unfavorable polymer–solvent interactions, while values lower than 0.5 at  $T = 298.15$  K indicate that these interactions are favorable for solvent dissolution.<sup>37</sup> The extrapolated to the temperature  $T = 298.15$  K values of  $\chi_{13}^\infty$  again indicate that only alcohols and water are bad solvents for polymer B-U3000. Negative values of  $\chi_{13}^\infty$ , as was observed for some *n*-alkanes, cycloalkanes, 1-alkenes, 1-alkynes, aromatic hydrocarbons, thiophene, ethers, and ketones, suggest high solute–polymer interaction.

The thermodynamic data, the partial molar Gibbs excess energy at infinite dilution,  $\Delta G_1^{E,\infty}$ , and the partial molar excess entropy at infinite dilution,  $\Delta S_1^{E,\infty}$ , and their linear dependence on temperature (for  $\Delta G_1^{E,\infty}$ ) and inverse temperature (for  $\Delta S_1^{E,\infty}$ ) including the extrapolated to the  $T = 298.15$  K values are presented in Tables 5 and 6, respectively. The graphic presentation is shown in Figures 1–6 for  $\Delta G_1^{E,\infty}$  and in Figures 7–9 for

$\Delta S_1^{E,\infty}$  as examples. The results of  $\Delta S_1^{E,\infty}$  for the other groups of substances are presented in Figures 7S–9S in the Supporting Information. The  $\Delta G_1^{E,\infty}$  decreases with an increase of temperature only for water and propanone. This underlines the hydrophobicity of the B-U3000. All data of  $\Delta S_1^{E,\infty}$  (without 1-butanol) reveal the same dependency on temperature; the  $\Delta S_1^{E,\infty}$  decrease with an increase of temperature.  $\Delta S_1^{E,\infty}$  values reveal positive values only for 1-alcohols and water.

The complete set of the thermodynamic data, including the molar enthalpy of vaporization to the ideal-gas state for the pure solutes,  $\Delta_{\text{vap}}H^0$ , is also available in the Supporting Information (Table 4S). The partial molar enthalpies of solute dissolution,  $\Delta_s H$ , are negative for every solute and the lowest for *n*-decane. The values are of the same range as for Hybrane 1200, or for poly(propyleneimine)dendrimers G1–G3, or for B-H2004.<sup>8,29,30</sup>

From the vaporization enthalpies  $\Delta H_v$ , the solubility parameters of solutes may be 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 ( $\delta_1$ ), the solubility parameter of the stationary phase (polymer) can be calculated from the linear regression of left-hand side of eq 9 versus  $\delta_1$ . The solubility parameter of the investigated polymer,  $\delta_3$ , is calculated from the slope of the straight line (see Figure 10S in the Supporting Information). The solubility parameter of polymer at temperature  $T = 298.15$  K is  $17.43 \text{ (MPa)}^{1/2}$ . Figure 10 gives the plot of a polymer solubility parameter as a function of temperature with parameters expressing linear dependence.

### Concluding Remarks

Mass-fraction activity coefficients at infinite dilution for various solutes in hyperbranched polymer B-U3000 were measured in the temperature range from 308.15 to 348.15 K using the IGC method. It was found that the investigated polymer shows high selectivities at infinite dilution in the separation processes of methanol/THF and of water/THF azeotropes.

The values of the  $\Omega_{13}^\infty$  and of the Flory–Huggins interaction parameters and other thermodynamic functions indicate that the best solvents for the investigated polymer B-U3000 are THF, thiophene, and aromatic hydrocarbons. Water is the worst of all the investigated solvents. The solubility parameter of polymer decreases linearly with an increase of temperature.

For the first time, the thermodynamic characteristic of dissolution of different organic solvents in hyperbranched polymer B-U3000 was presented. The data obtained indicate an increase in compatibility of a homologous series of solvents with the polymer. Thiophene, aromatic hydrocarbons, and THF were revealed to show much higher physicochemical affinity to the polymer than alcohols, water, *n*-alkanes, ethers, or ketones. This work shows the strong influence of the intermolecular interactions between the solute and the polymer solubility, thermodynamic functions, and selectivity in the different separation problems. This is always the result of the molecular mass of the polymer, the nature and the number of the functional groups, and polarity of the groups. In this work, the polar fragments of the polymer (ester groups) and the number of carbon atoms of the alkane chains of the acids used in the estrification of the primer polymer were responsible for the higher hydrophobicity than for other polymers. These data are very important to better understand the nature of the polymer and are needed to expand thermodynamic models.

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**Supporting Information Available:** Specific retention values data, calculated mass-fraction activity coefficients for two column pickings, the mass-fraction activity coefficients at infinite dilution, the Flory–Huggins interaction parameters, the thermodynamic functions in Tables 1S–4S, the plots of activity coefficients vs  $1/T$  (Figures 1S–6S), plot of excess infinite enthalpy vs  $1/T$  (Figures 7S–9S), and the determination of the solubility parameter of polymer. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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