Mass Fraction Activity Coefficients at Infinite Dilution Measurements for Organic Solutes in the Dendritic Polymer PAMAM-C_{12} Using Inverse Gas Chromatography

Urszula Domańska* and Zuzanna Żołek-Tryznowska

Department of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3,
00-664 Warsaw, Poland

The mass fraction activity coefficients at infinite dilution, Ω_{13}^{∞}, for 20 different solutes: alkanes (C_6-C_9), alkenes (C_6, C_7), alkynes (C_6, C_7), cycloalkanes (C_6, C_7), aromatic hydrocarbons (benzene, toluene, thiophene), alcohols (C_1-C_3), ethers (diethyl ether, dipropyl ether, tetrahydrofuran), and propanone were measured in the commercially available dendritic polymer PAMAM-C_{12} generation number 3, by inverse gas chromatography (IGC), at the temperatures from (298.15 to 318.15) K. The partial mass excess enthalpies of mixing at infinite dilution $\Delta H_1^{E,\infty}$ were calculated from the experimental Ω_{13}^{∞} values over the temperature range. The selectivity for different separation problems was calculated from Ω_{13}^{∞} and compared to the literature values for the other polymers.

Introduction

Dendrimers (Ds) are a class of macromolecules which besides their high cost have become important compounds in interdisciplinary fields such as chemical engineering,[1,2] biotechnology,[3−7] catalysis,[8] luminophores, and holography.[9,10] These applications benefit from the molecular interactions offered by dendritic polymers with polar solvents and are characterized in a recently published review.[7] Ds are characterized by a highly branched structure of great regularity and a compact shape, with a large number of polar end groups, symmetry in structure, and space between the branches for including the guest molecules.[7,11] The cost is connected with multistep synthesis. Because of their unique properties such as wide liquid range, stability at high temperatures, and their globular structure, Ds were considered as new polymers for chemical and biochemical technologies. Physical and chemical properties of Ds are not only influenced by the large number of the functional groups but also by the polarity of the groups. For Ds to be effectively used in different fields, the knowledge of the density, viscosity, phase equilibria, and thermodynamic properties is fundamental. Probably because of the cost of Ds, only few thermodynamic and physicochemical data were published.[1,2,12,13]

Recently we studied the phase equilibria[14,15] and mass-fraction activity coefficients at infinite dilution, Ω_{13}^{∞}, for different hyperbranched polymers with different separation problems.[16−18] The hyperbranched polymers reveal also a highly branched structure with a large number of functional polar groups, but showing irregularity in the structure. They are possessed in one-step synthesis. Thus, the main differences between Ds and hyperbranched polymers are regularity of structure and possible different penetration of solvent and cost. The functional groups, the structure, viscosity, and density of hyperbranched polymers or Ds have influence on thermodynamic properties and the possible use of Ds as solvents in the specific extraction problem. The hyperbranched polymers are known from a previous work[16−18] (and literature cited in this work) to be more active in the separation of the water + tetrahydrofuran (THF) mixture, water + ether mixtures, the water + ethanol mixture, or alcohol + ether mixtures (i.e., methanol + THF).[18] The purpose of this work is to present the difference between the dendritic and the hyperbranched polymer on the interaction with solvents. The characteristic investigated here includes also the effect of the important difference in polar end groups between hyperbranched polymer Boltorn W-3000, Boltorn U-3000, Boltorn H-2004, and PAMAM-C_{12}. The first time the $-NH$ and $-NH_2$ end groups known from strong interaction with alcohols (negative excess molar enthalpies and volumes) are included in dendritic polymer. The important interaction with alcohols may show interesting extraction possibilities, beside the cost and high viscosity.

For this study the mass fraction activity coefficient, Ω_{13}^{∞}, for the 20 different solutes: alkanes (C_6-C_9), alkenes (C_6, C_7), alkynes (C_6, C_7), cycloalkanes (C_6, C_7), aromatic hydrocarbons (benzene, toluene, thiophene), alcohols (C_1-C_3), ethers (diethyl ether, dipropyl ether, THF), and propanone were measured in the commercially available dendritic polymer PAMAM-C_{12} generation number 3. The partial mass excess enthalpy at infinite dilution ($\Delta H_1^{E,\infty}$) was calculated from the temperature dependence of Ω_{13}^{∞}. Since the Ds have a negligible vapor pressure, inverse gas chromatography (IGC) was a suitable method for measuring Ω_{13}^{∞}.[19]

Experimental Section

Materials. The dendritic-polymer, PAMAM-C_{12} generation number 3 (CAS 204401-84-3, Aldrich, methanol mass fraction 0.20) is a polyamidoamine dendritic polymer including 24 amine groups and 8 [*N*-(2-hydroxydodecyl)] groups. PAMAM-C_{12} generation number 3 is a dendrimer of 75 % amino groups and 25 % [*N*-(2-hydroxydodecyl)] surface groups. It is very viscous (about $1.0 \cdot 10^5$ mPa at $T = 298$ K) and slightly yellow wax at room temperature with a very high density. Unfortunately, the density was not possible to measure.

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* Author to whom correspondence should be addressed. E-mail: ula@ch.pw.edu.pl.

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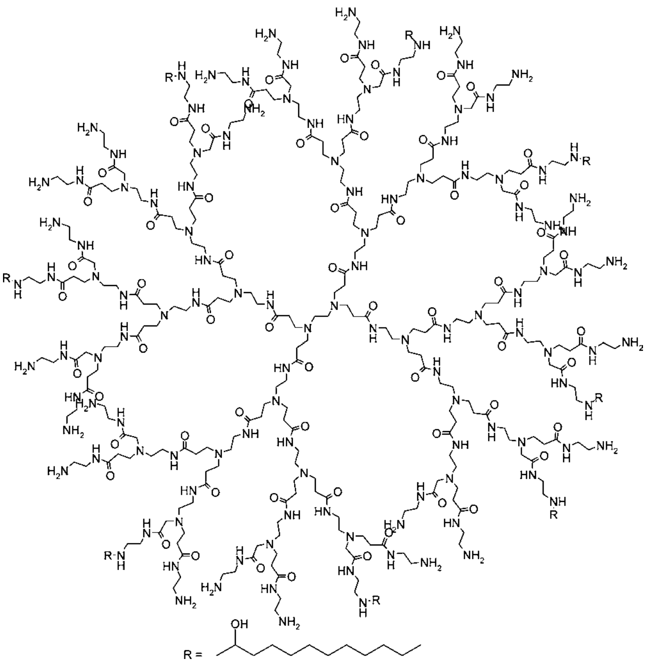

Figure 1. Schematic image of PAMAM-C_{12}.

Table 1. Investigated Dendrimer PAMAM-C_{12}: Molecular Mass (M), Glass Transition Temperature (T_g), and Heat Capacity Change at T_g ($\Delta C_{p(g)}$)

structure	M / g·mol^{-1}	T_g / K	$\Delta C_{p(g)}$ / kJ·mol^{-1}·K^{-1}
$C_{494}H_{992}N_{122}O_{76}$	9857.93	266.0	7.763

The PAMAM-C_{12} was purified by subjecting the liquid to a very low pressure of about $5 \cdot 10^{-3}$ Pa at the temperature T = 330 K for approximately 8 h. This procedure removed any volatile chemicals and water from the polymer. The structure of the polymer is shown in Figure 1.

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 dendritic polymer, that is, glass transition temperature (T_g) and heat capacity change at T_g ($\Delta C_{p(g)}$), were measured with a differential scanning microcalorimetry technique (DSC). 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 mole fraction purity indium sample. The uncertainty of the calorimetric measurements was estimated to be ± 3 %. Results are shown in Table 1 and in Figure 2.

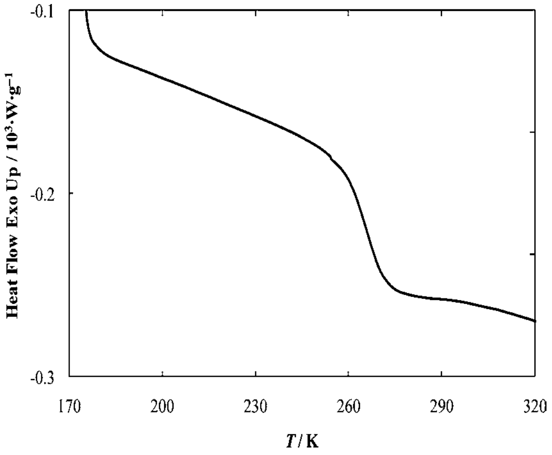

Figure 2. DSC of PAMAM-C_{12}.

Table 2. Column Specification and Chromatograph Condition

	column 1	column 2
mass fraction loading	0.20	11
mass coated/g	0.8264	0.2345
column length/m	4	
column i.d./mm	4	
column temperature/K	298.15 to 318.15	
injector temperature/K	423.15	
detector temperature/K	423.15	
carrier gas	helium	
flow/mL·min^{-1}	20 to 50	

Inverse Gas Chromatography. 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. Chromosorb W/AW-DMCS 120−140 mesh was used as the solid support and was supplied by Sigma (cat. no. C8639-1006). Coating the solid support material with the polymer was performed by dispersing a certain portion of Chromosorb in a solution of the polymer in methanol 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 of ± 0.0001 g. The solvent column packing is described in Table 2. Different mass percentages of the polymer were used. For each temperature the measurements were repeated by using two different columns with different mass percent packing. Care was taken to ensure that the methanol had completely evaporated from the polymer-coated solid before making up the column. Before the experiment each column was conditioned by blowing carrier gas at a high flow rate (about 3.5 cm^3·s^{-1}) at the high temperature (T = 340 K) through about 8 h.

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 carrier gas. The pressure drop was measured by gas chromatograph with an uncertainty of ± 0.1 kPa. The atmospheric pressure was measured using a digital barometer with an uncertainty of ± 0.1 kPa.

The carrier gas was helium. The flow rate of carrier gas was determined using a calibrated soap bubble flow meter 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. Solute injections ranged 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 three temperatures (in steps of 10 K) in the range from T = 298.15 K to T = 318.15 K. The temperature of the column was maintained constant to within ± 0.02 K. At a given temperature, each experiment was repeated twice to check the reproducibility. Retention times were generally reproducible within (0.001 to 0.01) min. 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 uncertainties in Ω_{13}^{∞} was expected as 0.3 to 2.3 for the lowest and highest values in temperature range (298.15 to 318.15) K, 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.[20]

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:[19]

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

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.

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

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

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

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

$$\Delta H_1^{E,\infty} = R \frac{\partial \ln \Omega_{13}^\infty}{\partial (1/T)} \qquad (4)$$

Results and Discussion

Table 3 lists the average Ω_{13}^∞ values for a 0.20 mass fraction loading of polymer on the column packing in the temperature range from $T = 298.15$ K to $T = 318.15$ K, determined from eq 3. For the lower loading of the column (see Table 1S in the Supporting Information, SI), the results were much higher. Oppositely, for the higher than 0.20 mass fraction loading of polymer on the column, inconsistent retention times were obtained, which had to be a result of possible residual adsorption of solutes onto the column packing. It is well-known that polymer loading has an influence on the retention volume. The mass percent of loading leads to the variability in the retention time measurements and has influence on the final thermodynamic result.[21] The first data on polymers suggested 0.10 mass fraction of loading to be sure of the full coverage of the support.[21] It was, however, the work with poly(styrene), a totally different structured polymer, and the maximum loading tested was chosen.[21] In this work, the first column was prepared as the literature suggestion as 0.11 mass fraction. However, in our all previous experimental work with hyperbranched polymers B-W-3000, B-U3000, and B-H3000, the column packing on a level of mass fraction of 0.17 to 0.25 has given constant mass fraction activity coefficients at infinity.[16−18] To compare new data of PAMAM-C_{12} with that previously determined for hyperbranched polymers, we decided to choose from many others a 0.20 mass fraction of loading for the later thermodynamic description and a 0.11 mass fraction to present in the SI. In most of the published works in this field only one column loading is presented; thus, it is not easy to find out the proper retention times as a function of loading.[22,23]

Table 3. Experimental Mass Fraction Activity Coefficient at Infinite Dilution, Ω_{13}^∞, at Different Temperatures and the Partial Mass Excess Enthalpy at Infinite Dilution, $\Delta H_1^{E,\infty}$, for the Column with a 0.20 Mass Fraction Loading (Mass of Polymer 0.8264 g)

	Ω_{13}^∞			$\Delta H_1^{E,\infty}$
	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K	kJ·mol^{-1}
hexane	59.4	47.8	40.5	15.19
heptane	40.3	41.5	37.0	3.32
octane	36.8	39.4	35.6	1.18
nonane	37.9	38.7	36.4	1.64
cyclohexane	59.0	37.1	28.2	29.23
cycloheptane	28.2	26.0	22.5	8.92
hex-1-ene	48.1	37.2	32.4	15.60
hept-1-ene	32.7	33.5	30.4	2.93
hex-1-yne	20.0	19.1	17.8	4.48
hept-1-yne	16.8	18.3	17.3	−1.13
benzene	10.5	10.8	10.1	1.65
toluene	11.2	11.1	10.6	2.28
ethylbenzene	-	-	11.9	-
o-xylene	-	-	10.8	-
m-xylene	-	-	11.9	-
p-xylene	-	-	11.6	-
thiophene	7.6	7.4	6.9	3.67
methanol	6.9	6.8	6.5	2.12
ethanol	7.4	7.3	6.9	2.67
1-propanol		6.3	5.9	5.97
THF	10.1	9.7	8.8	5.16
diethyl ether	30.0	26.7	23.1	10.32
dipropyl ether	29.7	28.2	25.5	5.94
propanone	17.2	16.1	14.0	8.13

It was also not possible to obtain the repeatable results for water at different loadings of the column. After the measurements of hyperbranched polymers[16−18] it was a new experience for us giving evidence that a different interaction exists on the surface between two phases.

Figures 3 and 4 show the temperature dependence of Ω_{13}^∞ for alkanes and alcohols as a function of carbon chain length of

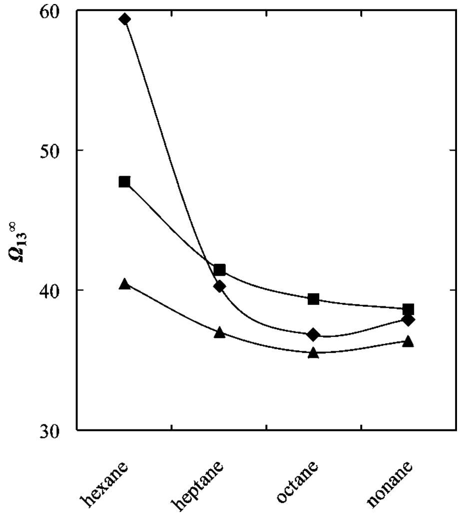

Figure 3. Plot of Ω_{13}^∞ versus the type of hydrocarbon for the temperatures: ♦, 298.15 K; ■, 308.15 K; ▲, 318.15 K.

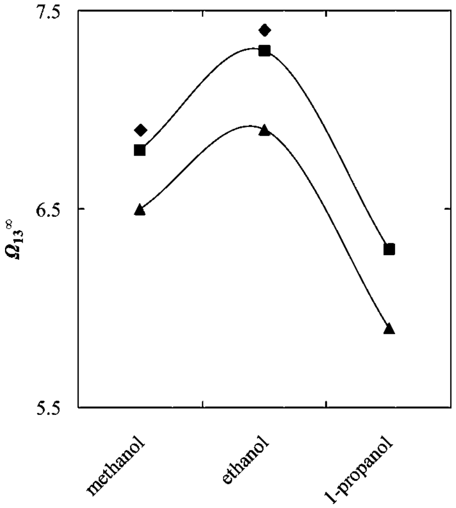

Figure 4. Plot of Ω_{13}^{∞} versus the type of alcohol for the temperatures: ♦, 298.15 K; ■, 308.15 K; ▲, 318.15 K.

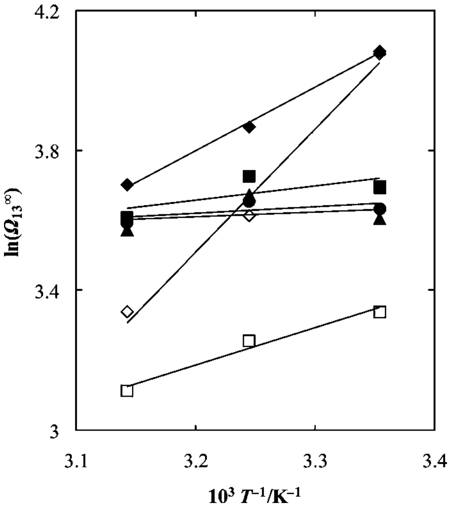

Figure 5. Plot of ln Ω_{13}^{∞} versus 1/T for the solutes: ♦, hexane; ■, heptane; ▲, octane; ●, nonane; ◇, cyclohexane; □, cycloheptane.

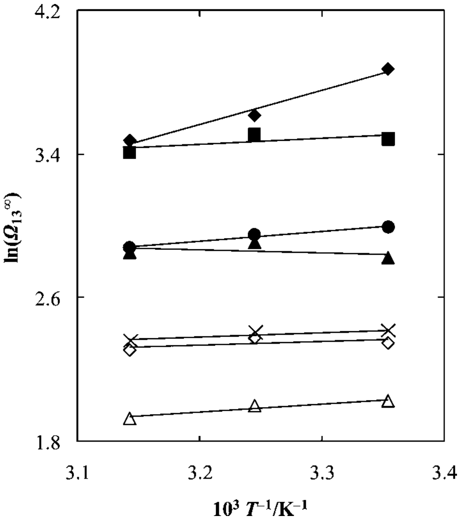

Figure 6. Plot of ln Ω_{13}^{∞} versus 1/T for the solutes: ♦, hex-1-ene; ■, hept-1-ene; ●, hex-1-yne; ▲, hept-1-yne; ◇, benzene; ×, toluene; △, thiophene.

alkanes, or an alcohol, respectively. The values of Ω_{13}^{∞} decrease with an increase of the chain length of alkane. It is a result of the van der Waals polymer−solute interactions in accordance with the alkyl substituents $R = 12$ at the dendrimer periphery (dendrimer surface groups). The characteristic maximum was observed for ethanol in comparison with methanol and 1-propanol. From our results methanol or 1-propanol should be the best solvents for the PAMAM-C_{12}. Methanol can interact with polymer and easy penetrate the large molecule of dendrimer. However, the chemical interactions between solute and dendrimer are significantly influenced by steric factors. Methanol, we expect, has equal access to dendrimer core groups and dendrimer surface groups. Usually, the surface group composition dominates solvent−dendrimer compatibility.[1] Ethanol is expected to penetrate the side part of polymer and show van der Waals interactions with alkane chains. This effect is supposed to continue for longer chain alcohols such as 1-propanol and 1-butanol. For 1-propanol the interaction is higher (lower values of Ω_{13}^{∞}). For 1-butanol the retention time was very long, and the results were not repeatable. Thus, only steric hindrance may help in a qualitative interpretation of the experimental data for ethanol. The strong interaction between amines and alcohols giving the negative deviations from ideality is commonly known; thus, the lower Ω_{13}^{∞} for alcohols may be interpreted as hydrogen bonding between an alcohol and an amine groups of the dendrimer. The values of Ω_{13}^{∞} (see Table 3) definitely show that hydrogen bonds between amine-side groups and alcohols predominate the van der Waals interactions of alkane periphery chains and alkanes. PAMAM-C_{12} does not have unsaturated carbon chains as for example B-W3000[17] and cannot interact with aromatic hydrocarbons; thus, the values of activity coefficients are quite high.

The high values of Ω_{13}^{∞} for alkanes, cycloalkanes, alkenes, alkynes, and ethers signify small interactions between solute and polymer in comparison with alcohols and thiophene. The highest value of Ω_{13}^{∞} is for hexane and cyclohexane ($\Omega_{13}^{\infty} = 59.4$ or $\Omega_{13}^{\infty} = 59.0$ at $T = 298.15$ K) and the lower for 1-propanol ($\Omega_{13}^{\infty} = 6.3$ at $T = 308.15$ K). Generally, the smallest values of Ω_{13}^{∞} indicate the stronger interactions between polymer and solute.

The values of Ω_{13}^{∞} for series of solutes decrease with an increase of temperature, that is, for alkanes, cycloalkanes, 1-alkenes, alkynes, aromatic hydrocarbons, alcohols, ethers, and propanone. It is shown in Figures 5 to 7, where the natural logarithm of the mass fraction activity coefficients in the polymer as a function of the inverse absolute temperature for all investigated solutes is presented. The influence of temperature in the tested range of temperature was not high but the same as was observed for the other polymers.[16−18]

The values of the partial mass excess enthalpy at infinite dilution of the solute and polymer, $\Delta H_1^{E,\infty}$ (see Table 3), are for all solutes positive (with exception of hept-1-yne, -1.13 kJ·mol^{-1}) and in a range between 1.18 kJ·mol^{-1} (octane) and 29.23 kJ·mol^{-1} (cyclohexane). A change is accompanied by a decrease in the $\Delta H_1^{E,\infty}$ values within the homological series of alkanes, cycloalkanes, alken-1-es; this indicates that the entropic factor dominates in the studied systems and is quite high. The lowest values of enthalpies $\Delta H_1^{E,\infty}$ suggest higher interactions of polymer−solute. In a case of octane it is most probably due to high van der Waals interaction between alkane chains, but it is not confirmed by values of the activity coefficient at infinite dilution.

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.[24] From the analysis of selectivity and capacity at tem-

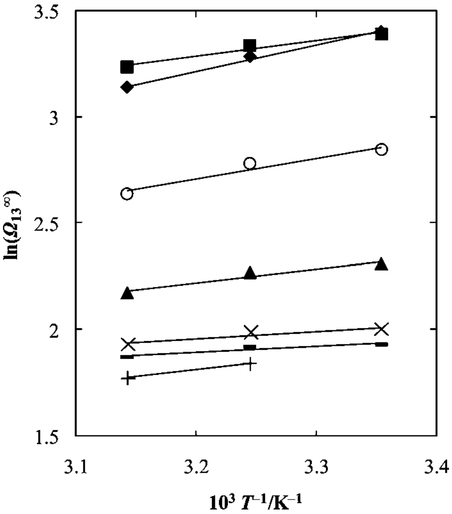

Figure 7. Plot of ln Ω_{13}^{∞} versus $1/T$ for the solutes: ♦, diethyl ether; ■, di-*n*-propyl ether; ○, propanone; ▲, THF; −, methanol; ×, ethanol; +, 1-propanol.

Table 4. Selectivities S_{ij}^{∞} and Capacities k_j^{∞} at Infinite Dilution for PAMAM-C_{12} and Three Hyperbranched Polymers for Different Separation Problems at T = 308.15 K

separation mixture	PAMAM-C_{12}		B-W3000[a]		B-U3000[b]		B-H2004[c]	
	S_{ij}^{∞}	k_j^{∞}	S_{ij}^{∞}	k_j^{∞}	S_{ij}^{∞}	k_j^{∞}	S_{ij}^{∞}	k_j^{∞}
hexane + thiophene	7.8	0.13	5.3	0.37	2.6	0.30	5.5	0.20
heptane + thiophene	5.3	0.13	4.9	0.37	2.5	0.30	4.5	0.20
hexane + benzene	5.7	0.10	3.8	0.26	2.2	0.25	3.7	0.17
hexane + toluene	5.3	0.09	3.9	0.27	2.5	0.28	4.3	0.19
methanol + THF	1.6	0.15	4.9	0.25	10.9	0.29	5.1	0.20

[a] Boltorn W3000 from ref 17. [b] Boltorn U3000 from ref 18. [c] Boltorn H2004 from ref 16.

perature T = 308.15 K presented in Table 4 we can conclude that selectivities S_{ij}^{∞} for three chosen separation problems: alkane + thiophene, alkane + aromatic hydrocarbon, and methanol + THF, are not high, and capacities k_j^{∞} are also not optimistic. The selectivities for the investigated polymer PAMAM-C_{12} are compared to the previously hyperbranched polymers[16−18] measured by us for the same separation problems in Table 4 at T = 308.15 K. The value of S_{ij}^{∞} for hexane + thiophene is slightly higher for PAMAM-C_{12} than for B-W3000,[17] B-U3000,[18] and B-H2004[16] but is not making the revolution in this field. The separation of aromatic and aliphatic compounds is an important process in the petrochemical industry and engineering. Unfortunately, as it is presented in Table 4 the dendritic polymer PAMAM-C_{12} is not suitable for the discussed separation problems. The values known from the mole fraction activity coefficients at infinite dilution from the literature for the attractive ionic liquid 1-ethyl-3-methylimidazolium thiocyanate, [EMIM][SCN] (calculated from Ω_{13}^{∞}, S_{ij}^{∞} = 76.4),[25] *N*-methyl-2-pyrrolidinone (NMP) (calculated from Ω_{13}^{∞}, S_{ij}^{∞} = 10.7),[24] and sulfolane (calculated from Ω_{13}^{∞}, S_{ij}^{∞} = 16.9)[26] are very promising for the new technologies or actually used in the industry.

Interesting results were observed for the methanol + THF separation problem with B-U3000[17] and for the water + THF mixture (S_{ij}^{∞} = 12.3) with B-W3000.[17] These values showed the possibility of using polymers as an entrainers for the separation process of the azeotropic mixture of water, or methanol and tetrahydrofuran. Unfortunately, in this work, the retention time for water was dependent on the sample injected into the column, and there was no symmetry of the chromatographic peaks, which means that the measurements have not been at equilibrium for measured dendritic polymer. Thus, it was not possible to compare the results with other hyperbranched polymers for the water + THF separation problem.

Conclusions

Mass fraction activity coefficients at infinite dilution for various solutes in the dendritic polymer PAMAM-C_{12} were measured in the temperature range from T = 298.15 K to T = 318.15 K using the IGC method. It was found that the investigated polymer shows moderate selectivities at infinite dilution in separation processes of the hexane + thiophene separation problem but is better than for aliphatics + aromatics and methanol + THF separation problems.

The values of the Ω_{13}^{∞} indicated that methanol and 1-propanol are the best solvents for the polymer used and alkanes are the worst. This work shows also that the intermolecular interactions between the solute and the polymer strongly depend on both polar fragments of the dendrimer and on the alkane chain lengths. These data are very important to better understand the nature of the polymer.

Supporting Information Available:

Table 1S containing data on the experimental mass fraction activity coefficient at infinite dilution and the partial mass excess enthalpy of mixing. This material is available free of charge via the Internet at http://pubs.acs.org.

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