Thermodynamics of Sorption in the Binary Liquid Crystalline System Composed of the Poly(propyleneimine) Dendrimer and *p-n*-Pentyloxy-*p′*-cyanobyphenyl by Inverse Gas Chromatography

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A binary system composed of the liquid crystalline poly(propyleneimine) dendrimer and nematic *p-n*-pentyloxy-*p′*-cyanobyphenyl has been studied by thermomicroscopy, scanning calorimetry, and inverse gas chromatography. In this system, there is the columnar phase being stable within broad ranges of temperature and component ratio. Dependences of the retention volumes of various solutes, namely, hydrocarbons, alcohols, and amines, on composition of the sorbents are revealed to exhibit the maximum. Thermodynamic functions of sorption of *n*-alkanes and *n*-alcohols on the binary sorbents composed of the said liquid crystals have been calculated specifically. Thermodynamic solute−sorbent compatibility characterized by the activity coefficients of the solutes is dependent on the sorbent composition; namely, it is controlled by counterbalancing of the enthalpy or entropy factors. The nonadditive mode of the solute−sorbent interaction is explained by arising of the microdomain nematic structure enclosed in the columnar structure of the dendrimer.

Introduction

There are a few classes of organic chemical substances characterized by distinct geometrical molecular anisotropy, such as polymers and liquid crystals, whose individual properties are favorably combined and, therefore, attract attention to systems based thereupon.[1] Dendrimers belong to a specific class of high-molecular substances whose acyclic molecules are well-ordered and spatially hyperbranched.[2] Dendrite molecules that have the remarkable 3D geometry tend to self-organize into supramolecular assemblies, in particular, ones with the liquid crystalline ordering.[3]

Individual dendrimers and the systems based thereupon may be used as containers for immobilization of chemical species and as the classical core−shell structures for the creation of functional layers of the diverse chemical nature. Therefore, promising areas of application of the said systems are catalysis, delivering of a target component, formation of nanosized assemblies for optoelectronics, and so on.[4] Because application fields of dendrimers are mostly connected to the use of composites and solutions, investigation of the internal structure and conformation mobility of the hyperbranched macromolecules as well as accessibility of macromolecules' chemical groups for various interactions seems of major importance. When composite materials based on mixtures of dendrimers with liquid crystals are designed as well as in the case of linear liquid crystalline polymers, both dispersing of mesogenes into the dendritic matrix and insertion of dendrimers in the ordered liquid crystalline structure is possible.[5] In some cases, the microdomain structure is observed.[6] Actuality of studies on the relationship between the molecular structure and intermolecular interactions of the components in mixtures of dendrimers with low-molecular liquid crystals is determined by a need to optimize composition and decide on potential application of the said composites.

The innverse gas chromatography (IGC) technique is widely applied to study physicochemical properties of individual substances and mixtures by analysis of quantities characterizing chromatographic retention.[7] In this kind of gas chromatography, the systems under investigation are used as stationary phases. Volatile substances whose interactions with the stationary phase strongly depend on the molecular structure are used as probe solutes. For the first time, low-molecular liquid crystals were used as stationary phases by Kelker.[8] Thermodynamic studies on dissolution of organic substances in the liquid crystalline and isotropic state of calamite mesogenes at infinite dilution were conducted in the works.[9,10] Also, the IGC technique was successfully applied to conventional polymers.[11] The data on liquid crystalline polymers used as stationary phases are acquired by the workers.[12,13] However thermodynamic data on the amorphous and mesomorphous phases of comb-like[14] and hyperbranched[15,16] polymers are rather scares.

The workers[17] substantiated empirically the mechanism of geometrical recognition of dissolved substances by naturally aligned alkyl chains of hyperbranched polymers. The further study[18] shows that the addition of rod-like fragments of low-molecular liquid crystals into the lateral alkyl chains of comb-like polymers does not entail increasing in sorption selectivity. This fact proves that the free interalkyl space in the modified macromolecular sorbents is less accessible for small molecules because of a tighter packing of the hydrocarbon chains. Nowadays, the modifying effect of low-molecular substances on dendrimer properties is practically unstudied. When calamite mesogenes are used as an additive, one expects a high orientation correlation thereof with segments of the dendrimer molecules, domain-like localization of the mesogenes, and resultant formation of the supramolecular structures with nontrivial physicochemical properties.[19]

This work aims at the investigation of sorption properties of the binary systems composed of the mesomorphous dendrimer and calamite nematic liquid crystal as well as revealing

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dependences of thermodynamic characteristics of dissolution of volatile organic substances on the phase state, temperature, and composition of the said binary systems. The work continues a series of chromatographic investigations on the mesomorphous, sorption, and analytical properties of the liquid crystalline poly(propyleneimine) dendrimers.[16,20]

Background

IGC allows us to find a number of thermodynamic sorption parameters on the basis of measurement of the retention time, t_R, and calculation of specific retention volumes, V_g^T, of solutes

$$V_g^T = (t_R - t_M)F_{p,T}j_3^2 \frac{273}{T}/W_L$$

where t_R and t_M stand for retention times of a solute and unretained component (methane); $F_{p,T}$ stands for the volume flow rate of the gas carrier measured at the column outlet at temperature, T, and pressure, p; j_3^2 is the James−Martine coefficient; and W_L stands for the mass of the liquid stationary phase in the column.

The partial molar enthalpies, ΔH_s, and entropies, ΔS_s, characterizing dissolution of a probe solute were calculated from the equations

$$\Delta H_S = -R\frac{\partial \ln V_g^T}{\partial (1/T)}$$

$$\Delta S_s = \Delta S_1^\infty - (\Delta H_1^\infty - \Delta H_s)/T$$

The weight fraction activity coefficient at infinite dilution ($a_1/w_1)^\infty$ was then calculated from the following relationship[21]

$$\ln(a_1/w_1)^\infty = \ln\frac{273.2R}{V_g^T p_1^0 M_1} - \frac{p_1^0}{RT}(B_{11} - V_1)$$

where a_1 and w_1 stand for activity and weight fraction; p_1^0 stands for pressure of saturated vapor at T; B_{11} and V_1 stand for the second virial coefficient and the molar volume; and M_1 stands for molecular mass. (All symbols refer to a probe solute.)

The weight fraction activity coefficient is connected to the partial molar free energy of mixing, ΔG_1^∞, by the ratio

$$\Delta G_1^\infty = RT \ln(a_1/w_1)^\infty = \Delta H_1^\infty - T\Delta S_1^\infty$$

The partial molar enthalpy, ΔH_1^∞, and entropy, ΔS_1^∞, of mixing of a solute were assumed to be temperature-independent and were found from the $\ln(a_1/w_1)^\infty - (1/T)$ relationship.

Dissolution of a solute in a liquid sorbent can be represented as a sequence of two stages: first, condensation of solute vapor that results in a liquid-phase solute; second, dissolution of a liquid-phase solute in a liquid sorbent that results in the infinitely diluted solution.

The vaporization enthalpies for pure solutes, ΔH_v, were found from the ΔH_1^∞ and ΔH_s values
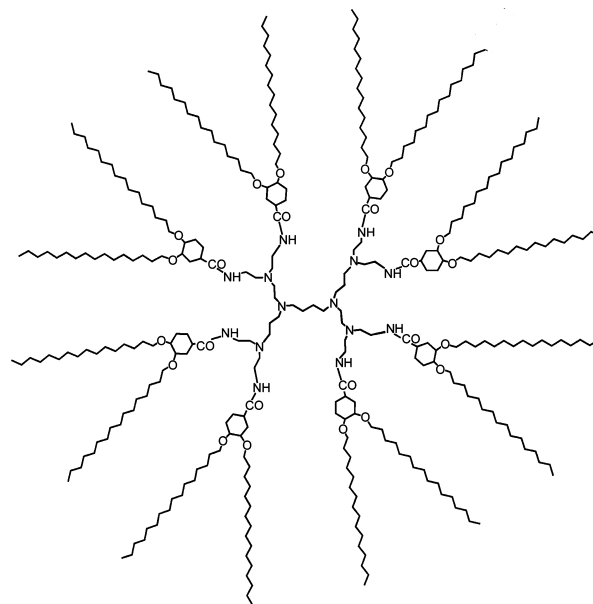
$$\Delta H_v = \Delta H_1^\infty - \Delta H_s$$

Figure 1. Molecular structure of the dendrimer G2.

IGC may be used provided that the whole bulk of a stationary phase participates in the distribution of a volatile solute and, as a result, the local sorbent−solute equilibrium is established. Our experiments[16,20] have shown that diffusion restrictions of the IGC method do not impede the study of the equilibrium sorption on the dendrimers because of the large internal space and gas permeability of the dendrite structure. The measurements have been conducted under equilibrium conditions within the Henry law region, as proven by independence of the retention times on the injected volume, symmetry of the chromatographic peaks, and linearity of the $\ln V_g^T - (1/T)$ plots.

Experimental Section

Materials. Sorption of *n*-alkanes (C_7−C_9) and *n*-alcohols (C_5−C_8) on the mixtures of the poly(propyleneimine) dendrimer and *p*-*n*-pentyloxy-*p*′-cyanobyphenyl (5OCB) has been studied by ICG. The 3,4-di(hexadecyloxybenzoyl)-poly(propyleneimine) dendrimer (G2) was synthesized in the University of Bayreuth (Germany) and kindly presented for thermodynamic studies. The detailed procedure for preparation of the 3,4-di(alkoxyben-zoyl)poly(propyleneimine) dendrimers is given elsewhere.[22] Structural identification thereof was conducted by element analysis, thermogravimetry, IR, H^1 NMR, and mass and electron spectroscopy techniques. The purity of the dendrimer determined by size exclusion chromatography was found to be 98%. The molecular structure of the dendrimer G2 is given in Figure 1. The liquid crystalline 5OCB shown below has been obtained from BDH, Ltd. (Advanced Materials Division, Poole, U.K.).
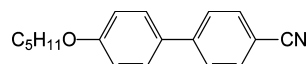
All probe solvents (Aldrich, St. Louis, MO) are 99% pure or better.

Apparatus and Procedure

Differential Scanning Calorimetry (DSC) and Microscopy. Calorimetric measurements have been performed on a DSC 204 F1 apparatus (Netzsch GmbH, Germany). All scans were run at a heating rate of 10 °C min^{-1}. Phase-transition temperatures

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determined by DSC are accurate within ±0.1 °C. The accuracy of phase-transition enthalpies is ±0.1 J/g. Phase-transition temperatures have been also determined by polarized light microscopy using a microscope of the Leitz LaborLux 12 Pol model equipped with a programmable heating stage Mettler FP-82. The measurements have been performed cyclically at a heating/cooling rate of 2 K/min.

Gas Chromatography. The dissolution process has been studied on a gas chromatograph "Chrom-5" (Laboratory Instruments Works, Czech Republic) with a flame-ionization detector operating in the isothermal mode. Temperature has been kept within ±0.1 K. The mixtures containing 5 (I), 10 (II), 15 (III), 20 (IV), and 25 (V) mass % of 5OCB have been studied. These mixtures have been deposited onto a solid support, namely, Chromaton N-AW, 0.125 to 0.160 mm (Chemapol, Czech Republic), from solutions in tetrahydrofuran by evaporation at room temperature with mass control. The deposited quantities have been equal to ones before evaporation. In all cases, the 10% mass loading of the liquid stationary phase has been used. Glass microcolumns (0.4 m × 1 mm) have been packed in vacuum. The liquid film thickness is estimated to be ca. 0.20 μm. Every column has been heated to a temperature of 20 K higher than the nematic—isotropic transition point. Heating of the columns has been followed by cooling to the room temperature; then, temperature has been raised gradually and controlled within ±0.2 K. The gas carrier is helium with the flow rate of 25 mL/min. A Hamilton 1 μL microsyringe (Switzerland) has been used for injection. Dead time has been measured using methane as a reference. Five measurements have been made in every experimental run. Deviations from the average value fall within ±0.5%.

Results and Discussion

The present work deals with sorption properties of the binary stationary phases based on the mesomorphous poly(propylene-imine) dendrimer of the second generation (G2) and *p-n*-pentyloxy-*p*′-cyanobyphenyl (5OCB). Liquid crystals derived from alkoxy-substituted cyanobyphenyls are well studied by various physicochemical methods as well as by IGC.[23] Theses substances are used as fragments in design of new dendrite mesogenes and are recommended as components of mixtures with thermotropic poly(propyleneimine) dendrimers for application in electrooptical devices.[6] The 5OCB mesogene has been selected for the reason of the overlapping liquid-crystalline temperature ranges of the components.

Figure 2 shows a portion of the phase diagram of the system under investigation at 5OCB concentrations of not more than 40 mass % being the eutectic point. The whole diagram is given elsewhere.[24] The diagram exhibits a small decrease in the melting point and significant one in the clearing point of the binary mixtures relative to the individual dendrimer occur upon 5OCB addition to the dendritic structure. As a result, the temperature range of the columnar phase gets narrowed. This phase characterized by a complex supramolecular structure constructed from the globular and rod-like molecules is stable within a broad range of temperature (18 K at the eutectic point) and concentration (>50% of 5OCB).

Table 1 shows the phase-transition temperatures of the samples under investigation acquired by thermomicroscopy and DSC. The values acquired by two techniques practically coincide. Figure 3 shows the DSC data. The highest endothermic effect of 55.9 J/g is observed when the individual dendrimer is melted into the columnar phase. The addition of 5OCB to the dendritic structure results in decreasing of the enthalpy of the
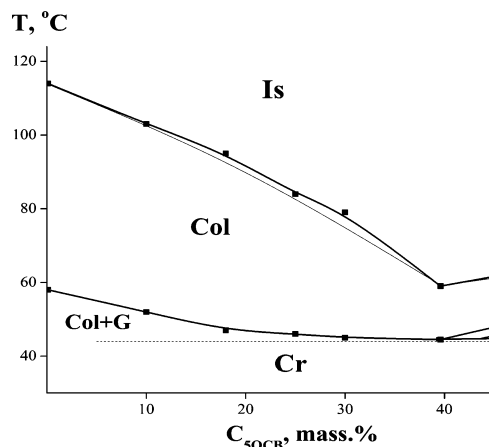

Figure 2. Portion of the phase diagram of the binary G2-5OCB system. Abbreviations correspond to ones for Table 1.

TABLE 1: Phase-Transition Temperatures (°C) for the Individual Liquid Crystals and the Binary Mixtures I—V by Microscopy and DSC[a]

sorbent	microscopy	DSC
G2	Cr 58.5 Col 114.0 Is	Cr 58.2 Col 113.9 Is
5OCB	Cr 53.0 N 68.0 Is	Cr 53.0 N 67.8 Is
2 + 5% 5OCB (I)	Cr 56.5 Col 108.5 Is	Cr 56.1 Col 108.2 Is
G2 + 10% 5OCB (II)	Cr 55.0 Col 102.0 Is	Cr 54.9 Col 102.0 Is
G2 + 15% 5OCB (III)	Cr 52.5 Col 95.5 Is	Cr 52.3 Col 95.1 Is
G2 + 20% 5OCB (IV)	Cr 50.0 Col 90.5 Is	Cr 49.9.0 Col 90.3 Is
G2 + 25% 5OCB (V)	Cr 48.0 Col 86.5 Is	Cr 47.8 Col 86.1 Is

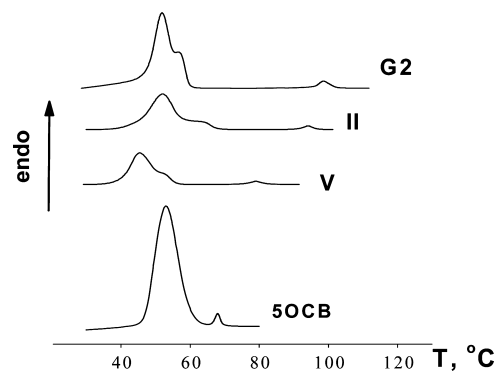[a] Abbreviations: Cr, crystalline phase; Col, hexagonal columnar mesophase, I, isotropic phase.

Figure 3. DSC heating curves for G2, 5OCB, and the mixtures II and V.

phase transition from the solid to mesomorphous state, namely, 41.2 and 31.4 J/g for the mixtures II and V, respectively. By far, weaker endothermic effects of 1.0 J/g for the individual dendrimer and 0.4 and 0.3 J/g for the mixtures II and V, respectively, correspond to the transition from the liquid crystalline to isotropic state.

The data above are summarized as follows. The binary liquid crystalline system is found to be highly stable despite the drastic difference in the molecular shape of the components. This fact may be rationalized by the microsegregation phenomenon.[2,25] In particular, the 5OCB molecules penetrate into the free interalkyl space of the dendritic macromolecules without perceptible steric hindrances. Then, a separate microphase being inherent in the pristine 5OCB liquid crystal seems to be formed. Such a kind of a structure was previously proposed by the workers[6] for the mixtures of the liquid crystalline poly(propy-leneimine) dendrimer with nematic alkoxy-cyanobiphenyls. Thermodynamic stabilization of the columnar dendrimer-5OCB
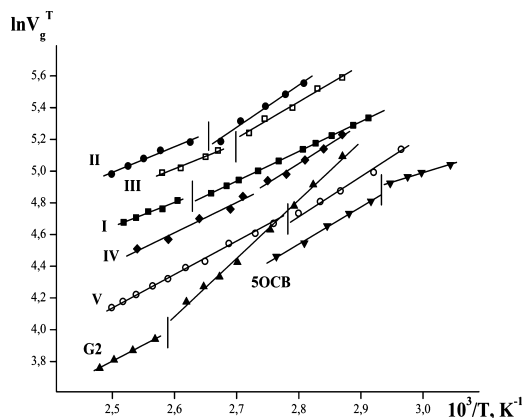
Figure 4. Retention diagram of *n*-heptane on the sorbents G2, 5OCB, and I−V. The vertical lines show the clearing points determined by thermomicroscopy.
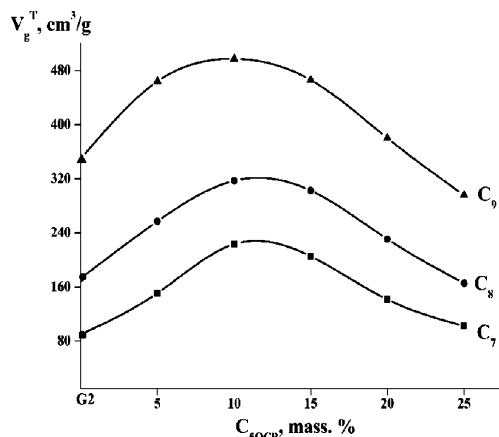

Figure 5. Retention volume of *n*-alkanes (C_7-C_9) versus concentration of the 5OCB component in the binary sorbents I−V at 364 K.
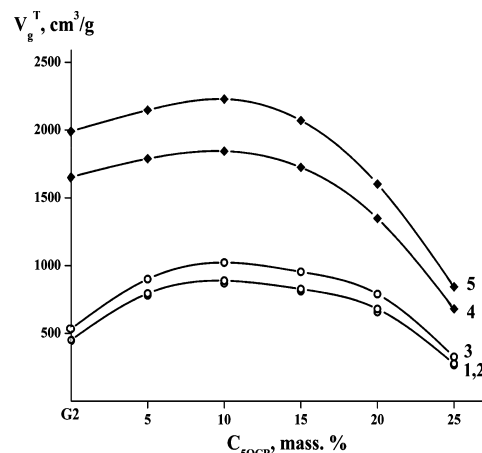

Figure 6. Retention volume of *p*-xylene (1), *m*-xylene (2), *o*-xylene (3), 3,5-lutidin (4), and 3,4-lutidin (5) versus concentration of the 5OCB component in the binary sorbents I−V at 364 K.
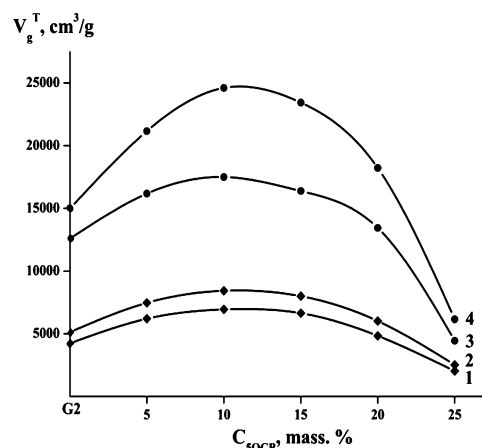

Figure 7. Retention volume of *p*-toluidine (1), *m*-toluidine (2), β-methylnaphthalene (3), and α-methylnaphthalene (4) versus concentration of the 5OCB component in the binary sorbents I−V at 364 K.

structure seems to be favored by an unusually large internal space of the dendrimer molecule terminated with the linear alkyl substituents.

As a next step, temperature dependences of the specific retention volumes of *n*-alkanes, *n*-alcohols, and disubstituted derivatives of benzene, pyridine, and naphthalene have been acquired for the dendrimer, 5OCB, and the mixed stationary phases I−V. Figure 4 shows an example of the retention diagram of *n*-heptane on the sorbents G2, 5OCB, and I−V. A noteworthy feature of the $\ln V_g^T - (1/T)$ plots is an abrupt change of the slope near the phase transition from the columnar to isotropic liquid phase. In all cases, the clearing points found chromatographically are in accordance with the microscopy and DCS data. The V_g^T values being the largest for the sorbent II indicates that the positive deviation of the binary system properties from the additive mode exists. Figures 5−7 show the concentration dependences of V_g^T for the studied solutes. Elution order correlates with boiling points of the solutes. A general trend in the $V_g^T - C_{5OCB}$ plots as well as constancy of the maximum position at 10 mass % 5OCB seem obvious.

Thermodynamics of sorption of *n*-alkanes and *n*-alcohols on the binary sorbents composed of the said liquid crystals has been specifically studied. The thermodynamic characteristics of dissolution for individual dendrimer G2 and the mixtures are summarized in Tables 2 and 3. The given temperatures correspond to a center of the temperature range of phase existence. The comparison of the experiential enthalpies, ΔH_v, of solute evaporation with the enthalpies, ΔH_v^*, calculated by

the Watson relation[26] is indicative of the reliability of the thermodynamic characteristics obtained in the present work. The relative errors for the thermodynamical quantities at 95% confidence are: $V_g^T - 3\%$, $(a_1/w_1)^\infty - 3.1\%$; ΔH_1^∞ and $\Delta H_s - 3.2\%$; ΔS_1^∞ and $\Delta S_s - 3.6\%$; $\Delta H_v - 4\%$.

Figure 8 shows a typical $\ln(a_1/w_1)^\infty - (1/T)$ plot. For all sorbents, the logarithm of the $(a_1/w_1)^\infty$ coefficient depends linearly on inversed temperature within the range of the liquid crystalline and isotropic phases. Also, it suffers a step-like changing at the clearing point. Practically in all systems, the $(a_1/w_1)^\infty$ coefficient is higher than unity (Table 2) and thus indicates that the positive deviation from the ideal mode occurs. In the row of *n*-alkanes, an increase in the molecular length results in an increase in the $(a_1/w_1)^\infty$ coefficient. Such a feature was shown to be connected to the corresponding rising of molecular mobility and a number of possible conformations.[27] The negative deviation from the ideal mode observed in the case of *n*-heptane indicates enhanced thermodynamic compatibility of shorter alkanes with the studied sorbents. In contrast, no dependence of the $(a_1/w_1)^\infty$ coefficient on the carbon number is revealed in the case of *n*-alcohols.

For both individual dendrimer and mixed sorbents, the concentration dependence of the $(a_1/w_1)^\infty$ coefficient exhibits a minimum (Figure 9). In the case of the sorbents I and II, a strong decrease in the $(a_1/w_1)^\infty$ coefficient for *n*-alkanes and *n*-alcohols

TABLE 2: Thermodynamic Parameters for *n*-Alkanes C$_n$H$_{2n+2}$ in the Columnar and Isotropic Phases of the Sorbents G2 and I−V at Infinite Dilution[a]

sorbent	n	$(a_1/w_1)^\infty$	ΔH_s	ΔS_s	ΔH_1^∞	ΔS_1^∞	ΔH_v	ΔH_v*
G2				Col (T = 364 K)				
	7	2.3	−22.6	−69.8	10.8	22.7	33.4	32.2
	8	2.7	−27.9	−85.7	10.4	20.4	38.3	38.1
	9	2.9	−32.1	−97.9	10.5	20.1	42.6	41.4
				I (T = 390 K)				
	7	2.0	−15.8	−45.2	16.5	36.6	32.3	30.3
	8	2.2	−22.3	−62.6	14.5	30.6	36.8	35.1
	9	2.5	−28.6	−79.6	12.2	23.7	40.8	39.5
I				Col (T = 364 K)				
	7	1.6	−15.6	−46.9	17.8	44.8	33.4	32.2
	8	2.2	−20.6	−63.3	17.7	41.8	38.3	36.9
	9	2.6	−28.0	−84.7	14.6	32.3	42.6	41.4
				I (T = 390 K)				
	7	1.1	−12.4	−32.2	19.9	50.7	32.4	30.3
	8	1.5	−17.2	−47.3	19.8	47.6	37.0	35.1
	9	1.8	−21.2	−59.2	19.6	45.6	40.8	39.5
II				Col (T = 364 K)				
	7	1.1	−19.5	−54.5	13.6	36.5	33.1	32.2
	8	1.8	−25.3	−74.5	12.7	29.9	38.0	36.9
	9	2.4	−30.8	−91.7	11.4	24.2	42.2	41.4
				I (T = 390 K)				
	7	0.7	−15.8	−37.2	16.6	45.1	32.3	30.3
	8	1.2	−19.4	−51.5	17.6	43.3	36.9	35.1
	9	1.6	−22.6	−61.9	18.3	42.9	40.9	39.5
III				Col (T = 364 K)				
	7	1.1	−18.6	−54.3	14.5	38.7	33.1	32.2
	8	2.0	−25.7	−76.5	12.4	28.4	38.3	38.1
	9	2.6	−31.6	−95.1	10.1	19.7	42.2	41.4
				I (T = 390 K)				
	7	0.8	−13.2	−34.5	18.2	48.6	31.4	30.3
	8	1.3	−18.1	−50.4	17.9	43.9	36.0	35.1
	9	1.8	−24.1	−66.9	16.7	37.7	40.8	39.5
IV				Col (T = 364 K)				
	7	1.6	−17.8	−53.0	15.3	37.9	33.1	32.2
	8	2.6	−25.3	−77.4	12.5	26.4	37.8	38.1
	9	3.3	−32.3	−98.7	9.8	17.0	42.1	41.4
				I (T = 390 K)				
	7	1.0	−12.6	−35.2	19.6	49.9	32.2	30.3
	8	1.9	−17.4	−53.1	18.7	42.7	36.1	35.1
	9	2.4	−25.7	−77.8	15.2	31.7	40.9	39.5
V				Col (T = 364 K)				
	7	2.4	−17.0	−53.9	16.2	37.0	33.1	32.2
	8	3.5	−25.6	−80.8	12.5	23.8	38.1	38.1
	9	4.0	−33.2	−102.6	9.1	13.6	42.3	41.4
				I (T = 390 K)				
	7	1.7	−10.9	−32.5	21.3	50.1	32.2	30.3
	8	2.5	−17.9	−53.5	19.1	41.4	37.0	35.1
	9	3.1	−27.3	−79.5	13.6	25.6	41.0	39.5

[a] Note: Enthalpies and partial molar free energy of mixing are given as kJ mol^{-1}; entropies are given as J mol^{-1} K^{-1}.

TABLE 3: Thermodynamic Parameters for *n*-Alcohols C$_n$H$_{2n+1}$OH in the Columnar and Isotropic Phases of the Sorbents G2 and I−V at Infinite Dilution[a]

sorbent	n	$(a_1/w_1)^\infty$	ΔH_s	ΔS_s	ΔH_1^∞	ΔS_1^∞	ΔH_v	ΔH_v*
G2				Col (T = 364 K)				
	5	3.3	−43.3	−129.5	9.0	14.6	52.3	48.6
	6	3.5	−49.2	−146.0	8.6	13.2	57.8	54.7
	7	3.6	−51.4	−152.4	10.7	18.7	62.1	55.7
	8	3.9	−56.8	−167.8	5.1	2.7	61.9	59.9
				I (T = 390 K)				
	5	2.7	−32.0	−89.4	8.8	14.4	40.8	45.9
	6	2.9	−39.2	−108.4	7.7	10.9	46.9	52.0
	7	3.0	−46.9	−128.2	8.6	13.0	55.5	53.3
	8	3.1	−51.5	−140.2	12.8	23.4	64.3	57.5
I				Col (T = 364 K)				
	5	3.1	−38.1	−115.9	11.3	19.7	49.3	48.6
	6	3.9	−45.7	−136.9	8.1	10.9	53.8	54.7
	7	3.8	−49.3	−146.4	11.3	19.9	60.5	55.7
	8	3.5	−56.0	−164.4	7.9	11.3	63.9	59.9
				I (T = 390 K)				
	5	2.7	−30.1	−85.5	16.6	34.2	46.7	45.9
	6	2.9	−35.0	−98.8	16.4	33.2	51.5	52.0
	7	2.8	−40.2	−111.7	15.2	30.1	55.3	53.3
	8	2.5	−43.9	−120.0	15.1	31.1	58.9	57.5
II				Col (T = 364 K)				
	5	2.8	−36.9	−126.8	12.3	25.4	49.3	48.6
	6	2.8	−43.7	−129.6	10.0	18.0	53.8	54.7
	7	2.6	−51.2	−148.5	9.0	17.0	60.3	55.7
	8	2.7	−53.7	−155.6	10.0	19.3	63.7	59.9
				I (T = 390 K)				
	5	1.9	−18.8	−53.6	27.9	66.2	46.7	45.9
	6	2.2	−34.1	−94.4	17.6	38.5	51.8	52.0
	7	2.1	−45.7	−123.4	11.7	23.8	57.4	53.3
	8	2.2	−50.2	−135.2	8.7	16.0	59.0	57.5
III				Col (T = 364 K)				
	5	3.3	−37.8	−113.7	12.1	23.4	49.9	48.6
	6	3.5	−44.9	−133.8	9.1	14.6	54.0	54.7
	7	3.2	−50.9	−149.7	10.2	18.2	61.1	55.7
	8	3.2	−55.4	−162.0	8.9	14.6	64.3	59.9
				I (T = 390 K)				
	5	2.4	−22.0	−63.6	24.8	56.4	46.8	45.9
	6	2.7	−35.2	−98.4	16.9	35.2	52.1	52.0
	7	2.6	−46.5	−127.1	11.1	20.6	57.6	53.3
	8	2.6	−51.9	−141.1	7.5	11.2	59.4	57.5
IV				Col (T = 364 K)				
	5	3.8	−38.6	−117.0	11.6	20.9	50.2	48.6
	6	4.2	−46.2	−138.9	8.3	10.8	54.5	54.7
	7	3.9	−51.2	−152.0	11.3	19.7	62.5	55.7
	8	3.8	−57.2	−168.3	7.8	10.3	65.0	59.9
				I (T = 390 K)				
	5	2.8	−25.3	−73.6	21.7	46.9	47.0	45.9
	6	3.2	−36.5	−103.3	15.9	31.0	52.4	52.0
	7	3.1	−47.4	−130.9	10.0	16.3	57.4	53.3
	8	3.0	−53.6	−146.7	6.2	6.6	59.8	57.5
V				Col (T = 364 K)				
	5	4.2	−39.4	−120.1	11.1	18.6	50.5	48.6
	6	4.9	−47.6	−144.1	7.0	5.9	54.6	54.7
	7	4.5	−50.4	−150.8	12.5	21.9	62.9	55.7
	8	4.3	−59.2	−174.7	6.9	6.9	66.1	59.9
				I (T = 390 K)				
	5	3.3	−28.7	−83.5	18.6	37.8	47.3	45.9
	6	3.7	−37.5	−107.0	14.9	27.2	52.3	52.0
	7	3.6	−47.9	−133.3	8.6	11.4	56.5	53.3
	8	3.5	−55.4	−137.6	4.7	1.6	60.1	57.5

[a] Note: Enthalpies and partial molar free energy of mixing are given as kJ mol^{-1}; entropies are given as J mol^{-1} K^{-1}.

as compared with the individual dendrimer is observed. On the contrary, for the sorbent V, the $(a_1/w_1)^\infty$ values are higher than those for the dendrimer. Therefore, contrary to expectation, small additions of the 5OCB component poorly interacting with the solutes in bulk seem to promote the incorporation of the solute molecules into the supramolecular solvent.

Therefore, the dual impact of the 5OCB component on the columnar structure is observed. When the 5OCB concentration is <10 mass %, the 5OCB molecules affect the dendrimer's alkyl substituents in such a way that the internal space that is available

for the solute molecules increases, but further 5OCB additions make this space shrink. Such a behavior may be explained as follows. At low 5OCB concentrations, the natural alignment of
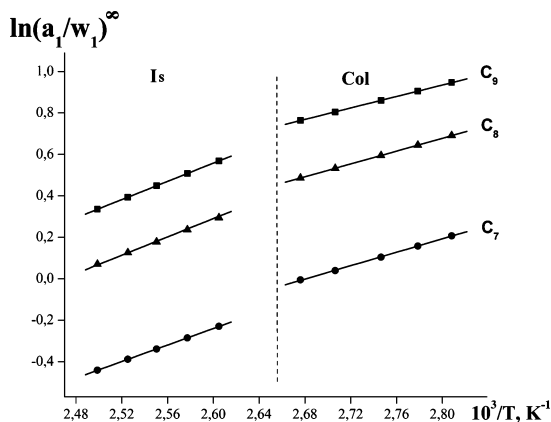
Figure 8. Logarithm of the activity coefficient of *n*-alkanes (C$_7$–C$_9$) versus reciprocal temperature (data for the sorbent II).
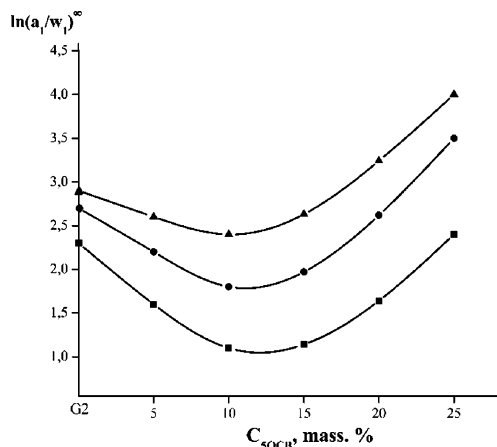

Figure 9. Activity coefficient of *n*-alkanes (C$_7$–C$_9$) versus concentration of the 5OCB component in the binary sorbents I–V at 364 K.

Figure 10. Relationships between the partial molar enthalpies of dissolution of the solutes in the sorbents G2 (●), I–V (○), and molecular polarizability of the solutes. The ΔH_{spG2} and ΔH_{spI-V} symbols indicate contributions of the specific interactions to the enthalpy of dissolution of *n*-alcohols in the individual dendrimer and mixed sorbents, respectively.

the alkyl substituents is disturbed, and the structure of the molecular periphery seems to be "spongy". At high 5OCB concentrations, the 5OCB molecules tend to aggregate, and the microdomain nematic structure[6] enclosed in the columnar one finally arises. As a result, the free interalkyl space of the dendritic macromolecules decreases.

To reveal the effect of the 5OCB component on the specific solute−sorbent interactions, relationships (Figure 10) between the partial molar dissolution enthalpy and polarizability, α, of *n*-alcohols and *n*-alkanes have been compared. The contribution of the specific interactions energy, $\Delta H'_{sp}$, into a general value of the enthalpy of dissolution of *n*-alcohols has been calculated as a difference between the empirically found ΔH_s quantities of the polar solutes and contribution of the energy of nonspecific interactions determined from the ΔH_s–α plots for *n*-alkanes. In the studied systems, the ΔH_S quantities for *n*-alcohols are more negative than ones for *n*-alkanes. This feature results from two kinds of interactions, namely, hydrophilic and hydrophobic, inherent in the alcohol molecules. The data presented indicate that in the columnar and isotropic phases, the ΔH_s enthalpies decrease with the carbon number. This fact is connected to strengthening of the hydrophobic interactions between the aliphatic parts of the solute and dendrimer molecules. Insertion of the 5OCB molecules into the dendritic structure results in a small decrease of the energy of the intermolecular interactions as compared with the individual dendrimer. The ΔH_s values for both *n*-alkanes and *n*-alcohols in the mixed sorbents at various 5OCB concentrations are fairly close and thus indicate a lack of the 5OCB−solute interaction. Consequently, contribu-
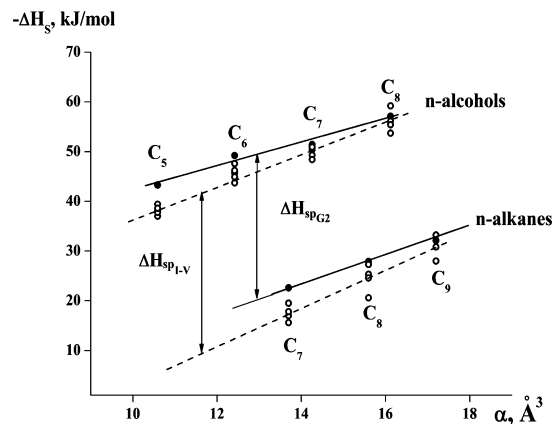
tions of the specific interactions to the enthalpy of dissolution of *n*-alcohols (ΔH_{spG2} and ΔH_{spI-V} in Figure 10) may be estimated as ca. 30 kJ/mol. This value may be attributed to the H bonds that form between fragments of the dendrimer molecule, namely, the ternary amine and the phenyl groups, and the hydroxyl groups of the alcohol molecules.

The ratios between the thermodynamic quantities characterizing the dissolution of *n*-alkanes and, with a few exceptions, *n*-alcohols in both columnar and isotropic phases of both individual dendrimer and mixed sorbents are stated to obey the following nonequalities

$$\Delta H_{S_{G2}} < \Delta H_{S_{I-IV}} \quad \Delta H^{\infty}_{1_{G2}} < \Delta H^{\infty}_{1_{I-IV}}$$
$$\Delta S_{S_{G2}} < \Delta S_{S_{I-IV}} \quad \Delta S^{\infty}_{1_{G2}} < \Delta S^{\infty}_{1_{I-IV}}$$
$$(a_1/w_1)^{\infty}_{G2} > (a_1/w_1)^{\infty}_{I-IV}$$
$$(a_1/w_1)^{\infty}_{G2} < (a_1/w_1)^{\infty}_{V}$$

Comparative analysis on the thermodynamic characteristics of dissolution of *n*-alkanes and *n*-alcohols indicates that sorption on the binary sorbents in comparison with the individual dendrimer is accompanied by weakening of the mesogene−nonmesogene interaction and increasing of solute mobility. The activity coefficient values and consequently deviation from the ideal mode in the studied systems are determined by counterbalancing of the enthalpy and entropy contributions to the Gibbs energy. A decrease in the activity coefficients with the addition of small 5OCB quantities (5−10 mass %) results from the entropy as a key factor. An increase in 5OCB concentration to 25 mass % results in an increase in the $(a_1/w_1)^{\infty}$ coefficient because of the prevalence of the enthalpy factor. On that account, one may infer that the microdomain structure of the columnar−nematic type is characterized by the two mechanisms of thermodynamic compatibility with the solutes.

Conclusions

The present work deals with a system composed of two liquid crystalline components, namely, poly(propyleneimine) dendrimer of the second generation and *p-n*-pentyloxy-*p′*-cyanobyphenyl (5OCB). The system has been studied by thermomicroscopy, scanning calorimetry, and IGC at 5OCB concentration

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to 25 mass %. Attention has been focused on the columnar phase being inherent not only in the individual dendrimer but also the binary system within broad ranges of temperature and component ratio.

Sorption of *n*-alkanes, *n*-alcohols, and some aromatic species used as molecular probes on the columnar and isotropic phases has been studied. Significant geometric differences between the molecules of the dendrimer and 5OCB liquid crystal result in the deviation of the sorption properties of the binary sorbents from the additive mode. In particular, at small 5OCB concentrations in the binary sorbents, the retention volumes are higher than ones for the individual components. The thermodynamic characteristics of dissolution of *n*-alkanes and *n*-alcohols in the individual dendrimer and mixtures have been calculated. In all studied solute−sorbent systems, positive deviations from the ideal mode are observed. In particular, dependences of the activity coefficients on the composition of the binary sorbents exhibit a minimum. Ratios between the thermodynamic characteristics of dissolution in the individual dendrimer and binary sorbents indicate that this deviation is determined by counterbalancing of the enthalpy and entropy contributions into the Gibbs energy. The entropy factor plays a key role at a concentration of 5OCB <10 mass % and promotes a decrease in the activity coefficients of the solutes as compared with the individual dendrimer. A further increase in 5OCB concentration results in an increase in the activity coefficients because the enthalpy factor prevails. In addition, the formation of H bonds between fragments of the dendrimer and the hydroxyl groups of the *n*-alcohols is supposed. Different mechanisms of thermodynamic compatibility of the solutes with the binary system under investigation are explained by the formation of the microdomain structure of the columnar−nematic type.

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