Thermodynamics of Poly[methyl(trifluoropropyl)siloxane]-Alkane Systems by Gas-Liquid Chromatography

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ABSTRACT: The specific retention volumes of C_6 to C_{10} *n*-alkanes on poly[methyl(trifluoropropyl)siloxane] (PMTFPS) stationary phase at temperatures within 30-95 °C are reported. Three packed columns with different loadings of the solid support with the polymer have been used. The differences in the results obtained from the three columns have been attributed to the uncertainties in composition of the column packings rather than to the effect of interfacial adsorption. The activity coefficients and interaction parameters of the *n*-alkanes at infinite dilution in PMTFPS have been calculated from the specific retention volumes. The partial molar excess enthalpies ($\Delta\bar{H}_1^{E\infty}$) of the *n*-alkanes have been obtained from the temperature dependences of the activity coefficients. The values of $\Delta\bar{H}_1^{E\infty}$ at 60 °C range from 6 to 10 kJ/mol. The nonpolar component of the solubility parameter of PMTFPS has been estimated as a function of temperature. The results are compared to the respective quantities in the poly(dimethylsiloxane)-alkane systems.

Introduction

Gas chromatography has often been used to study the thermodynamics of interaction of polymers with small molecules in the limit of infinite dilution of the low-molecular-weight component. In spite of some fundamental theoretical difficulties caused by the intrinsically dynamic (i.e., nonequilibrium) nature of the chromatographic process, gas chromatography has actually become one of the standard experimental techniques for polymer solution studies. Activity coefficients, Flory-Huggins interaction parameters, and partial molar excess thermodynamic functions can be calculated from gas chromatographic retention data. In this respect, a considerable effort was spent to investigate the poly(dimethylsiloxane) (PDMS)-alkane systems employing both packed[1-10] and capillary[11,12] columns. In comparison, the thermodynamics of interaction of alkanes (or other solutes) with other siloxane polymers received little attention.[7] This statement applies to both gas chromatographic and static[13] methods of polymer solution studies. Recently, however, the importance of the thermodynamic characterization of siloxane polymers has increased again because these polymers have been used as stationary phases in the rapidly growing field of capillary supercritical fluid chromatography.

In this paper, the results are presented of a gas chromatographic study of the thermodynamics of poly[methyl(trifluoropropyl)siloxane] (PMTFPS)-alkane systems. These particular systems have been chosen because they may be expected to display significant enthalpies of mixing. Specific retention volumes, mass-fraction-based activity coefficients, and partial molar excess enthalpies of C_6 to C_{10} *n*-alkanes at infinite dilution in PMTFPS are reported and compared to the respective characteristics of the alkane-PDMS systems. The nonpolar component of the solubility parameter of PMTFPS has also been estimated from the results.

Experimental Section

Materials. Reagent grade *n*-alkanes, *n*-hexane through *n*-decane (Fluka AG, Buchs, Switzerland), were used as received. The PMTFPS sample was a gas chromatographic stationary phase (Carlo Erba, Milan, Italy) supplied under the commercial name QF-1. It was used without further treatment to prepare the column packings.

Apparatus and Procedures. The experimental setup for chromatographic measurements has been described previously.[9] In the present study, the flow rate of the nitrogen carrier gas did not exceed 12 cm^3 min^{-1}, and the column inlet pressure was not higher than 8 kPa above the atmospheric pressure. The column packings were prepared by a common method,[14] employing acetone as a volatile solvent and 0.40-0.63 mm Inerton AW HMDS (Lachema, Brno, Czechoslovakia) as a solid support. In order to disclose possible effects of interfacial adsorption, three columns (a, b, and c) containing packings of different compositions were used. The packings of the columns a, b, and c contained 5.08%, 9.80%, and 15.3% (by mass) of PMTFPS, respectively. To determine the mass of polymer in the column packing, the polymer has to be removed from a sample of the packing. The mass of polymer is then given by the difference between the masses of the sample before and after this operation. To remove the polymer from the packing, two different methods have generally been employed, namely, the calcination method and the extraction method. With siloxane polymers, however, neither of the two methods gives reliable results. The calcination method often used with hydrocarbon-based polymers is obviously unsuitable for siloxanes because of the formation of solid silicon dioxide that obscures the results of weighing. The results of the extraction method have been shown to suffer from an incomplete extraction of the polymer from the packing, at least with PDMS polymers.[9] Therefore, the percentages of PMTFPS in the three column packings quoted above are the theoretical values calculated from the masses of the polymer and the dried support taken to prepare the packing. The resultant effects on the precision of the results are described in the Results and Discussion.

The column temperature was controlled to ±0.02 °C by means of a water thermostat. Glass columns 2.5 m long × 3 mm i.d. were used. The specific retention volumes were measured within a temperature range of 30-95 °C in about 5 °C steps. Four to five measurements were performed at each temperature. The scattering of the individual retention volumes did not exceed ±0.5% of the mean value. After each run was completed replicate measurements at 30 °C were done to check the significance of the bleeding of PMTFPS from the column. In all the three columns, the bleeding proved to be negligible. Samples (70-100 μL) of a gaseous mixture of the alkane vapors with methane were injected. To obtain the true dead retention time, the methane retention time was corrected for the solubility of methane in PMTFPS employing the solubility data reported by Shah et al.[15] The experimental retention times of methane ranged from 75 to 92 s while the respective true dead retention times

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were only slightly (by less than 1 s) lower. The retention times of the *n*-alkane solutes ranged from 3–53 min.

Data Reduction. The infinite-dilution mass-fraction-based activity coefficients[16] at zero total pressure were calculated from the equation[17]

$$\Omega_1^\infty = [273.15R/(V_g{}^\circ P_1{}^0 M_1)] \exp[(V_{1L}{}^0 - B_{11})P_1{}^0/(RT)] \times \exp[(2B_{13} - \bar{V}_{1L}{}^\infty)P_o J_3{}^4/(RT)] \quad (1)$$

where R is the gas constant, T the thermodynamic temperature of the column, $V_g{}^\circ$ the specific retention volume of the solute, $P_1{}^0$ the vapor pressure of the solute, M_1 the molar mass of the solute, $V_{1L}{}^0$ the molar volume of the pure liquid solute, $\bar{V}_{1L}{}^\infty$ the partial molar volume of the solute at infinite dilution in the polymer, B_{11} the second virial coefficient of the solute, B_{13} the solute–carrier gas second cross-virial coefficient, and P_o the column outlet pressure. The approximation $\bar{V}_{1L}{}^\infty \approx V_{1L}{}^0$ was adopted throughout the calculation. The symbol $J_3{}^4$ is given by[18]

$$J_3{}^4 = (3/4)[(P_i/P_o)^4 - 1]/[(P_i/P_o)^3 - 1] \quad (2)$$

where P_i is the column inlet pressure. The vapor pressures of the alkane solutes were calculated from the Antoine equation using the constants tabulated by Reid et al.[19] The saturated-liquid molar volumes of the solutes were obtained from the Rackett equation modified by Spencer and Adler.[20] The second virial coefficients of the solutes were calculated from the Hayden-O'Connell correlation.[21] The *n*-alkane–nitrogen second cross-virial coefficients were obtained from the Tsonopoulos correlation[22] fitted to the respective experimental B_{13} data.[23]

From the temperature dependence of the activity coefficients, the infinite-dilution partial molar excess enthalpy of the solute, $\Delta\bar{H}_1{}^{E\infty}$, and the infinite-dilution partial molar excess isobaric heat capacity of the solute, $\Delta\bar{C}_{P1}{}^{E\infty}$, may be estimated by differentiation as described before.[9]

If the solute is infinitely diluted in the polymer and the molar mass of the polymer is very high, the Flory–Huggins interaction parameter is related to the activity coefficient by

$$\chi = \ln \Omega_1^\infty - \ln (v_1/v_2) - 1 \quad (3)$$

where v_1 and v_2 are the specific volumes of the solute and the polymer, respectively. The specific volumes of the *n*-alkanes were calculated from the molar volumes (see above) and the molar masses. The specific volume of PMTFPS (cm^3 g^{-1}) was approximated by

$$v_2 = 0.774 \exp[0.001(t - 25)] \quad (4)$$

where t is the temperature (°C). The factor 0.774 is the specific volume of PMTFPS at 25 °C.[15] The factor 0.001 is an estimate of the thermal expansion coefficient for PMTFPS. This value is based upon the temperature variation of the partial specific volume of PMTFPS in solution.[24]

Assuming that all noncombinatorial contributions to the excess Gibbs energy are accounted for by the regular solution theory, the interaction parameter is related to the solubility parameters of the two components by[25]

$$\chi = V_{1L}{}^0(\delta_1 - \delta_2)^2/(RT) \quad (5)$$

Rearranging eq 5, one obtains

$$\delta_1{}^2/(RT) - \chi/V_{1L}{}^0 = 2\delta_1\delta_2/(RT) - \delta_2{}^2/(RT) \quad (6)$$

According to eq 6, a plot of the left-hand side of the equation versus the solubility parameter of the solute, δ_1, should yield a straight line with a slope of $2\delta_2/(RT)$ and an intercept of $-\delta_2{}^2/(RT)$, so that the polymer solubility parameter, δ_2, may be evaluated. In order to obtain the δ_2 values at several different temperatures (see Results and Discussion), the solubility parameters of the solutes at the respective temperatures are required. The solubility parameter of a solute is defined by

$$\delta_1 = (\Delta U_{c1}/V_{1L}{}^0)^{1/2} \quad (7)$$

The cohesive energy of the solute, ΔU_{c1}, is given by

$$\Delta U_{c1} = \Delta H_{v1} - RT + P_1{}^0[V_{1L}{}^0 - B_{11} + T(dB_{11}/dT)] \quad (8)$$

where ΔH_{v1} is the enthalpy of vaporization of the solute. For the C_6 to C_{10} *n*-alkanes at temperatures within 30–95 °C, ΔH_{v1} may be calculated with sufficient accuracy by using the Antoine equation, the second virial coefficient of the solute, and the saturated-liquid molar volume of the solute.

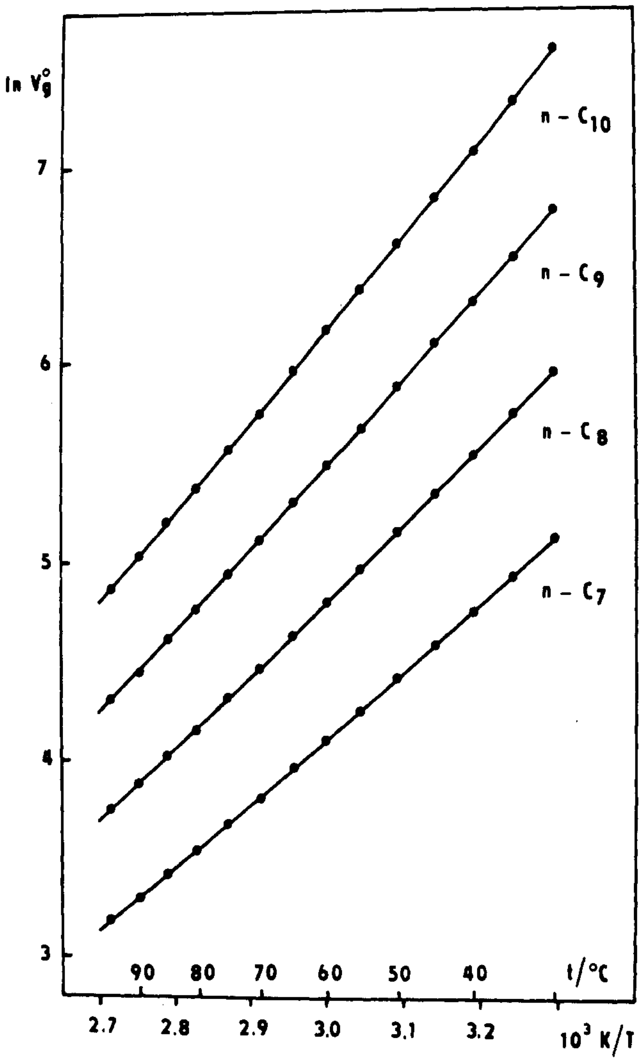

Figure 1. Temperature dependences of the specific retention volumes for the PMTFPS–alkane systems (column a).

Results and Discussion

Specific Retention Volumes. Figure 1 shows the plot of ln $V_g{}^\circ$ against $1000/T$ obtained with the column a. The appearance of the respective plots with the other two columns is similar. The plots are nonlinear because of the nonzero temperature derivative of the enthalpy of sorption.[9] The experimental $V_g{}^\circ$ data were smoothed by using the relation

$$\ln V_g{}^\circ = d \ln T + e/T + f \quad (9)$$

For all the *n*-alkane solutes and the three columns employed, the resulting values of the constants d, e, and f are compiled in Table I. With all the three columns, the maximum differences between the experimental and calculated values of ln $V_g{}^\circ$ are on the order of 10^{-3} (the units of $V_g{}^\circ$ are cm^3 g^{-1}). With either of the three regression coefficients, d, e, and f, the ratio of the coefficient to its standard deviation is always greater than 14. This value may be compared to the respective quantiles of the Student probability distribution.[26] The comparison (t-test) shows that, in all cases, the actual value of the coefficient d is different from zero with a probability higher

Table I
Coefficients of the Equation $\ln V_g^\circ = d \ln T + e/T + f$

solute	column	d	e	f
n-hexane	a			
	b	6.444	4980	-48.9
	c	5.463	4680	-42.5
n-heptane	a	5.959	5320	-46.5
	b	7.617	5830	-57.6
	c	6.657	5540	-51.3
n-octane	a	6.580	5990	-51.4
	b	8.439	6560	-63.9
	c	7.446	6260	-57.3
n-nonane	a	7.532	6770	-58.6
	b	9.194	7270	-69.7
	c	8.298	7000	-63.8
n-decane	a	8.375	7510	-65.0
	b			
	c			

than 99.9%. The inclusion of the term $d \ln T$ into eq 9 is therefore justified.

Although the data fits obtained with a given column are very good, different values were obtained for V_g° of a given alkane from the three columns, the differences reaching up to 14%. The relative difference between the corresponding V_g° values from any two columns is independent of the solute and only slightly dependent on temperature. Moreover, the retention of any alkane on any one of the three columns does not depend on the injected amount of the alkane. The sorption isotherms are therefore linear for all the n-alkane solutes. Although neither of these observations is conclusive, they all suggest that the differences in the V_g° values are caused by errors in the calculated compositions of the column packings rather than by an effect of interfacial adsorption[27-29] of the solutes. The uncertainty in the composition of the column packing is known[30,31] to be a major source of experimental error in the determination of V_g°. This kind of error affects directly the values of $\ln V_g^\circ$ and $\ln \Omega_1^\infty$. However, the uncertainties caused by this effect are greatly reduced in the resultant values of the solubility parameter of PMTFPS, and the partial molar excess enthalpies of the solutes are not affected at all. With the C_6 to C_8 n-alkanes, the specific retention volumes on PMTFPS are about 1.5–4 times lower than the corresponding V_g° values on PDMS.[9]

Activity Coefficients and Interaction Parameters. A plot of $\ln \Omega_1^\infty$ against $1000/T$ obtained with the column a is shown in Figure 2. The temperature dependence of the activity coefficients may be expressed by an equation analogous to eq 9. The resultant constants of the equation are listed in Table II. The maximum differences between the experimental and calculated values of $\ln \Omega_1^\infty$ are on the order of 10^{-2}; i.e., they are an order of magnitude higher than the respective parameters for the specific retention volumes (see above). The t-test also reveals a lower statistical significance of the coefficients given in Table II as compared to the values listed in Table I.

The PMTFPS–alkane interaction parameters (eq 3) range from 0.7 to 1.9. These values reflect the fact that n-alkanes are poor solvents for PMTFPS. In fact, the interaction parameters exceed the limiting value ($\chi = 0.5$)[32] for complete miscibility of the polymer and the solvent. In comparison, the PDMS–alkane interaction parameters calculated from our previous results[9] range from 0.3 to 0.5. In both the PMTFPS–alkane and the PDMS–alkane systems, the interaction parameters decrease with increasing temperature.

Partial Molar Excess Enthalpies. Table III shows the values of $\Delta\bar{H}_1^{E\infty}$ for the n-alkane solutes in PMTFPS at 60 °C. In view of an extreme sensitivity of $\Delta\bar{H}_1^{E\infty}$ to errors in the temperature dependence of the activity coefficients,[9,33] the differences in the $\Delta\bar{H}_1^{E\infty}$ values for a given alkane from the columns a, b, and c are not surprising. The values of $\Delta\bar{H}_1^{E\infty}$ for a given alkane do not change in a monotonous way as the amount of polymer in the column packing is increased from the column a to the column c. This finding supports the view (see above) that the results of this study are not significantly affected by interfacial adsorption of the alkane solutes. The val-

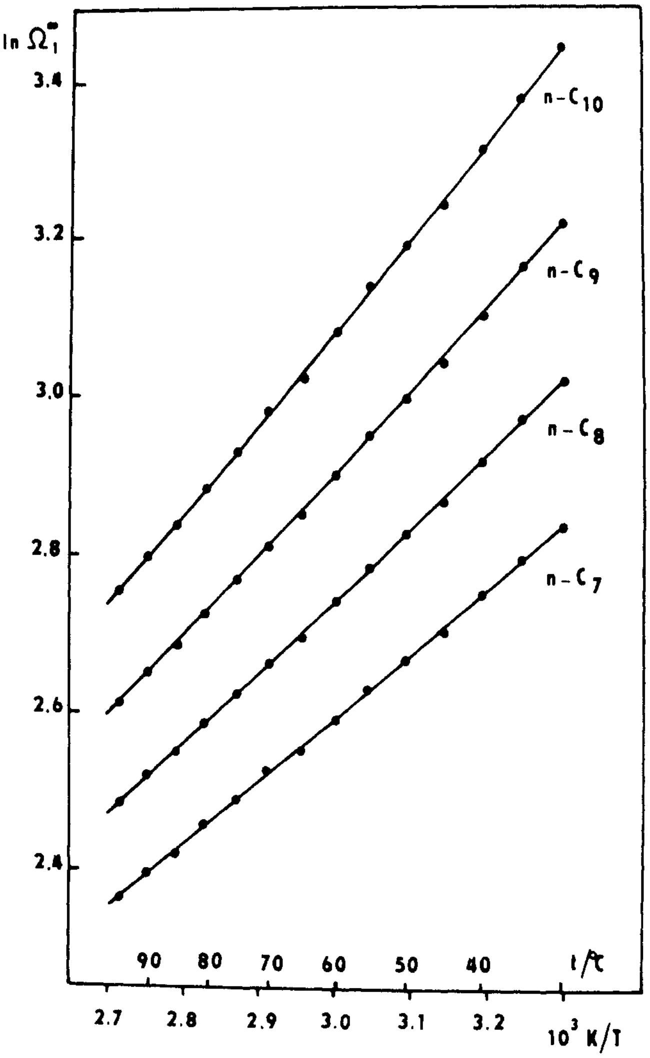

Figure 2. Temperature dependences of the activity coefficients for the PMTFPS–alkane systems (column a).

Table II
Coefficients of the Equation $\ln \Omega_1^\infty = d \ln T + e/T + f$

solute	column	d	e	f
n-hexane	a			
	b	−0.334	638	2.46
	c	0.636	933	−3.94
n-heptane	a	0.848	1090	−5.62
	b	−0.805	589	5.46
	c	0.137	872	−0.733
n-octane	a	1.31	1360	−8.95
	b	−0.546	788	3.51
	c	0.431	1080	−2.93
n-nonane	a	1.93	1680	−13.4
	b	0.270	1180	−2.24
	c	1.18	1450	−8.21
n-decane	a	3.10	2220	−21.6
	b			
	c			

Table III
Infinite-Dilution Partial Molar Excess Enthalpies $\Delta H_1^{E\infty}$ (J mol^{-1}) of *n*-Alkanes in PMTFPS at 60 °C

	column		
solute	a	b	c
n-hexane		6230	6000
n-heptane	6740	7120	6870
n-octane	7640	8060	7820
n-nonane	8620	9060	8820
n-decane	9860		

Table IV
Solubility Parameters ([J cm^{-3}]$^{1/2}$) of *n*-Alkanes, PMTFPS, and PDMS

	t, °C				
substance	30	45	60	75	90
n-hexane	14.79	14.40	14.01	13.60	13.19
n-heptane	15.11	14.73	14.36	13.99	13.61
n-octane	15.42	15.04	14.67	14.31	13.95
n-nonane	15.67	15.27	14.89	14.53	14.18
n-decane	15.93	15.51	15.12	14.75	14.39
PMTFPS	13.25	12.77	12.33	11.93	11.55
PDMS	14.93	14.56	14.17	13.77	13.35

ues in Table III indicate that the mixing of *n*-alkanes with PMTFPS is much more endothermic than the mixing of *n*-alkanes with PDMS.[9]

The values of $\Delta\bar{C}_{P1}^{E\infty}$ may be estimated to fall within the range from −26 to +7 J mol^{-1} K^{-1}. This corresponds approximately to the range found previously[5,9] in the PDMS–alkane systems.

Solubility Parameters. The solubility parameters of C_6 to C_{10} *n*-alkanes are listed in the first five lines of Table IV. The solubility parameter of PMTFPS may be calculated from the solubility parameters of the solutes and the experimental PMTFPS–alkane interaction parameters. A typical plot according to eq 6 is shown in Figure 3. The δ_2 values for PMTFPS given in Table IV are the mean values obtained from the slopes of plots such as in Figure 3. At each temperature, the scattering of the individual δ_2 values from the columns a, b, and c does not exceed ±1.5% of the mean value. The δ_2 values calculated from the intercepts (cf. eq 6) are somewhat higher than the values given in Table IV. The relative difference between the two sets of δ_2 values drops from 4.8% of the lower value at 30 °C to 3.5% at 90 °C. The cause of the difference becomes apparent when the interaction parameter is split into an enthalpic and entropic component, and eq 5 is assumed to give the enthalpic component only.[25] The intercept-based values of δ_2 exceed the respective slope-based results by the residual-entropy contribution. Therefore, when eq 6 is employed to obtain the polymer solubility parameter, the slope-based result is to be preferred. The temperature dependence of the slope-based δ_2 values for PMTFPS within 30–95 °C may be conveniently expressed by

$$\delta_2 = 14.067 - 0.2834t \qquad (10)$$

where *t* is the temperature (°C). The interaction between an alkane and PMTFPS is solely due to dispersion forces. Equation 10 therefore gives only the nonpolar component of the solubility parameter of PMTFPS. At 25 °C, δ_2 = 13.36 (J cm^{-3})$^{1/2}$. It is interesting to compare this value with the results obtained[13] from the swelling of PMTFPS networks by polar solvents at 25 °C. The respective δ_2 values contain the contributions of polar and/or specific interactions between the polymer and the solvent and average at 18 (J cm^{-3})$^{1/2}$.

The last line in Table IV shows the solubility parameters for PDMS (number-average molar mass of 20 700 g mol^{-1}; weight-average molar mass of 95 300 g mol^{-1}), calculated from the activity coefficients[9] of C_5 to C_8 *n*-alkanes and cyclohexane. The specific volumes of PDMS were obtained from the data of Shih and Flory.[34] The δ_2 values for PDMS in Table IV may be fitted by

$$\delta_2 = 15.735 - 0.02632t \qquad (11)$$

At 25 °C, eq 11 yields a value of 15.08 (J cm^{-3})$^{1/2}$ for the solubility parameter of PDMS. This value is within the range of 14.9–15.6 (J cm^{-3})$^{1/2}$ quoted in the literature.[35]

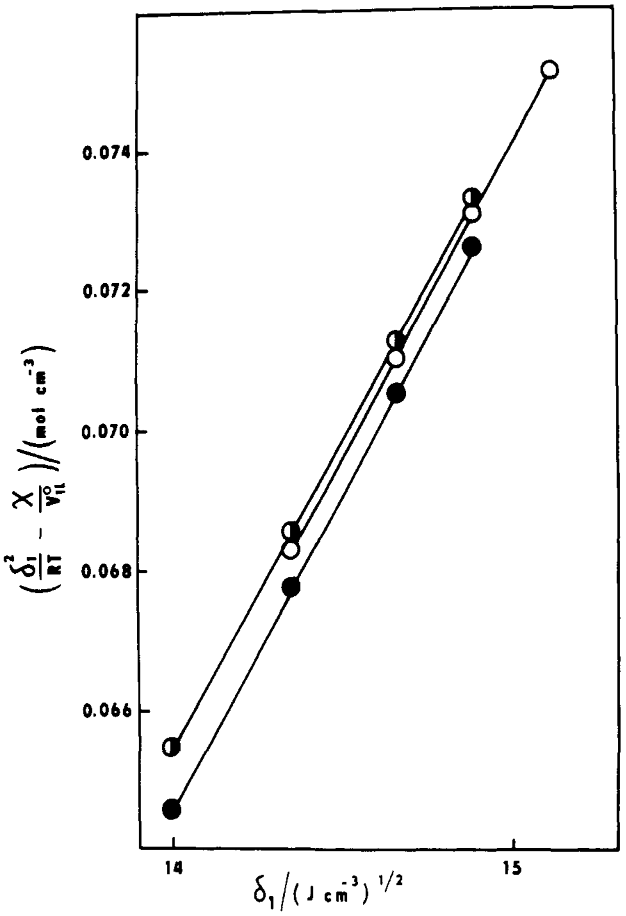

Figure 3. Determination of the solubility parameter of PMTFPS at 60 °C according to eq 6 (○, column a; ◑, column b; ●, column c).

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Registry No. Hexane, 110-54-3; heptane, 142-82-5; octane, 111-65-9; nonane, 111-84-2; decane, 124-18-5.

Fluorescence Energy Transfer Studies of Styrene–Isoprene Diblock Copolymer Solutions[†]

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ABSTRACT: Micelle formation in solutions of chromophore-labeled styrene–isoprene diblock copolymers in selective solvent systems has been investigated using nonradiative energy transfer techniques. Energy transfer donor (carbazolyl or naphthyl) or acceptor (anthryl) chromophores were attached to anionically polymerized block copolymers and used to study micellar solutions as parameters such as concentration, solvent composition, temperature, and molecular weight were varied. Dramatic increases in I_A/I_D, the ratio of acceptor to donor fluorescence intensity, accompanied the formation of micelles. As the solvent quality worsens for the labeled blocks through either a reduction in temperature or the addition of a nonsolvent, micelles are detected first in the more concentrated solutions, consistent with expectations of a phenomenological critical micelle concentration (cmc). The high sensitivity of energy transfer experiments was also demonstrated; multimolecular micelles are observed at very low copolymer concentrations, near 10^{-3} g/L, where turbidimetry is insensitive to micelle formation. With the use of a two-state energy transfer model, it was determined for the block copolymer systems under investigation that at concentrations exceeding the cmc additional copolymer apparently partitions itself between micelles and the homogeneous solution phase. Single photon counting measurements were also performed to observe changes in fluorescence lifetimes of both donors and acceptors upon micellization. Measured lifetimes of anthryl units nearly doubled in micelles due to the time lag caused by the energy transfer process.

Introduction

Heterogeneous structure, such as the existence of multimolecular micelles, occurs in diblock copolymer solutions when the solvent is selective for one of the blocks. A number of studies[2–21] on both diblock and triblock copolymers using techniques such as intrinsic viscosity measurement, light scattering, small-angle X-ray scattering, neutron scattering, and electron microscopy have detailed conditions under which multimolecular aggregates occur. These micelles are formed by aggregation of the precipitated or less soluble blocks into cores surrounded by a shell of the more soluble blocks. For triblock copolymers the solvent must be preferential toward the end blocks.[22]

Temperature has a significant influence on micellar solutions. Typically, at high temperatures the equilibrium between micelles and unassociated chains favor the latter. Upon lowering the temperature, micelles begin to

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[†] Dedicated to Professor Herbert Morawetz on the occasion of his 75th birthday.

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