by scanning very slowly (1 s/point) and by using 1024-point spectra. The free spectral range was chosen to optimize resolution and peak height. All the precautions noted above were taken. Thus the existence of the depolarized Rayleigh dip in the *n*-alkanes has been demonstrated. A full study of the depolarized Rayleigh spectra in a wider range of *n*-alkanes is presently being carried out. Also a discussion of the significance of the value of *R* and the correlation between the value of *R* and molecular structure is presented in a forthcoming paper.[12]

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Gas-Chromatographic Investigation of the Thermodynamic Interactions of Poly(dimethylsiloxane) or Poly(diethylsiloxane) with Some Solvents between 60 and 180 °C

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ABSTRACT: Gas–liquid chromatography has been used for the thermodynamic study of the interactions between poly(dimethyl- or (diethylsiloxane) and various aliphatic or aromatic hydrocarbons within the temperature range 60–180 °C. The experimental results related to PDMS are in good agreement with literature data obtained either by dynamic or static methods and restricted to the lower temperatures. The thermodynamic interaction parameters were discussed in terms of Flory and Prigogine–Patterson theories.

In the last 10 years, the study of the thermodynamics of interactions between polymers and solvents by "inverse gas chromatography" has received increased attention.[1] This dynamic method is now being applied to a growing number of complex systems even when the liquid–vapor equilibrium is not reached instantaneously (glassy or crystalline polymers as opposed to liquid polymers) and even when specific interactions may occur between polymers and solvents (as opposed to nonpolar systems).

Because of the conjugated effects of its low glass transition temperature and of its enhanced chain flexibility poly(dimethylsiloxane) (PDMS) behaves as a nearly ideal system with respect to inverse gas-chromatography experiments, and thus it has been investigated by several authors.[2–4] Most of these studies are related to the systems PDMS–hydrocarbons (linear or branched alkanes or aromatic hydrocarbons) within a narrow range of temperature (20–60 °C).

In the present work we have focused our interest on three points: the study of interactions between PDMS and aliphatic or aromatic hydrocarbons over a wide range of temperature up to 180 °C (the experimental variations of the activity coefficient of the probe at infinite dilution (Ω^∞) and of the Flory χ parameter with temperature were discussed according to Flory and to Prigogine–Patterson theories); the study of the influence of the chain structure using both linear samples and model PDMS networks; the comparison between PDMS and its next higher homologue poly(diethylsiloxane) (PDES), since the thermodynamics of PDMS solutions cannot be accurately described according to classical theories.

Experimental Section

Apparatus. The gas chromatograph used was a dual column apparatus (INTERSMAT IGC 15) fitted with a thermal conductivity detector; the column oven temperature was controlled to within ±0.05 °C. The flow rate of helium used as carrier gas (10–30 mL/min) was measured at the column outlet by a soap-bubble flowmeter; inlet pressure (850–1400 Torrs) was monitored to within 1 Torr with a mercury manometer. The outlet pressure was the atmospheric pressure.

Probe Molecules and Stationary Phases. The probe solutes were the best reagent grade and were used in most cases without further purification; chloroform was eluted over activated alumina and dioxane was distilled over the disodium–benzophenone complex.

The PDMS samples used as the stationary phase were obtained from the Rhône-Poulenc Co.; two samples were involved: PDMS $\overline{M}_n = 3 \times 10^4$, $\overline{M}_w/\overline{M}_n = 3$, Si-OH end groups; PDMS $M_n = 1.7 \times 10^4$, $\overline{M}_w/\overline{M}_n = 1.2$, Si-H end groups. They were heated for 24 h at 100 °C under vacuum (0.1 Torr) to remove any low-boiling component.

The PDMS network was prepared by polycondensation of PDMS bearing silane end groups ($\overline{M}_n = 3770$) and tetraallyloxyethane.[5] This sample may be considered as a model network; the fluctuations in the length of the elastic linear chains between two consecutive nodules were low and the functionality of the cross-linking points was constant and equal to 4.

The PDES sample (Dow Corning Co.) was a generous gift of Dr. Manley (Pulp and Paper Research Institute of Canada, Montréal), $\overline{M}_n = 1.12 \times 10^5$, $\overline{M}_w/\overline{M}_n = 2.5$. Its molar specific volume was measured by dilatometry between 25 and 85 °C. The experimental values fit the following relation obtained by second-order regression analysis

$$\frac{1}{v_{sp}}\,(\text{cm}^3\ \text{g}^{-1}) = 1.0046 - 6.2556 \times 10^{-4}t + 1.1648 \times 10^{-6}t^2 \quad (1)$$

Table I
Description of Columns

Code	Column length, cm	Wt of Chromosorb W, g	Wt of stationary phase, g: Calcd	Wt of stationary phase, g: Extracted	Column loading[a]	Polymer characteristics: $\overline{M}_n$	Polymer characteristics: $\overline{M}_n/\overline{M}_n$
PDMS 1	152	1.544	0.300		16.27	30 000	3
PDMS 2	200	2.232	0.590	0.592	20.91	30 000	3
PDMS 3	160	1.834	0.373	0.375	16.90	17 100	1.2
PDMS network	28	0	0.419		100	3 770[b]	
PDES	150	1.368	0.157	0.153	10.30	112 000	2.5

[a] 100 × polymer weight/total weight. [b] $\overline{M}_n$ of the linear segment between two consecutive cross-linking points.

Table II
Values of Specific Retention Volume V^0_g (cm^3/g) and of Thermodynamic Parameters for PDMS—Hydrocarbon Systems[a]

t, °C	n-Hexane V^0_g	n-Hexane Ω^∞	n-Hexane χ^*	n-Hexane χ_H	n-Heptane V^0_g	n-Heptane Ω^∞	n-Heptane χ^*	n-Heptane χ_H	Cyclohexane V^0_g	Cyclohexane Ω^∞	Cyclohexane χ^*	Cyclohexane χ_H
40	120.8	6.01	0.48	0.06								
55	70.7				167.9				121			
60	59.9	6.02	0.48	−0.12	138.1	5.99	0.50	0.04	101.2	5.28	0.49	−0.22
80	32.4	6.09	0.50	−0.29	68.5	6.02	0.50	−0.12	52.9	5.37	0.50	−0.21
100	18.9	6.22	0.52	−0.45	37.0	6.11	0.52	−0.24	30.3	5.43	0.51	−0.19
120	11.7	6.40	0.55	−0.62	21.6	6.21	0.53	−0.31	18.7	5.47	0.53	−0.17
140	7.7	6.62	0.58	−0.79	13.5	6.31	0.55	−0.36	12.2	5.51	0.54	−0.15
160					8.9	6.42	0.57	−0.41	8.4	5.55	0.55	−0.12
180					6.2	6.54	0.59	−0.46	6.1	5.62	0.56	−0.10

t, °C	Benzene V^0	Benzene Ω^∞	Benzene χ^*	Benzene χ_H	Toluene V^0_g	Toluene Ω^∞	Toluene χ^*	Toluene χ_H	Ethylbenzene V^0_g	Ethylbenzene Ω^∞	Ethylbenzene χ^*	Ethylbenzene χ_H
40	191.4	6.32	0.79	0.31								
55	109.2				259.9							
60	91.6	6.23	0.78	0.30	212.8	6.33	0.76	0.42	446.1	6.53	0.78	0.28
80	48.8	6.12	0.76	0.28	104.1	6.23	0.75	0.37	201.1	6.43	0.77	0.25
100	28.3	6.02	0.74	0.26	56.2	6.11	0.73	0.31	100.6	6.35	0.76	0.22
120	17.7	5.94	0.73	0.23	32.7	6.02	0.71	0.23	54.9	6.27	0.74	0.20
140	11.6	5.87	0.72	0.20	20.3	5.97	0.70	0.14	32.3	6.21	0.73	0.16
160	8.1	5.84	0.71	0.16	13.3	5.94	0.70	0.04	20.2	6.16	0.73	0.13
180	5.8	5.80	0.71	0.11	10.9	5.94	0.70	−0.02	13.3	6.14	0.72	0.08

[a] Standard deviation of the various thermodynamic parameters: $\Omega^\infty \pm 0.05$, $\chi^* \pm 0.01$, $\chi_H \pm 0.2$.

The thermal expansion coefficient α may be expressed as

$$\alpha = \frac{1}{v_{sp}}\left(\frac{\partial v_{sp}}{\partial T}\right)_P = 6.227 \times 10^{-4} - 1.931 \times 10^{-6}t \qquad (2)$$

with t in degrees Celsius. At 25 °C $\alpha = 0.575 \times 10^{-3}$ deg^{-1}.

Column Preparation. Chromosorb W (60–80 mesh, AW-DMCS) was mixed with a polymer solution in hexane, then the solvent was eliminated under vacuum in a rotavapor, and finally the coated support was dried at 60 °C to remove the last traces of solvent. The support loading, calculated directly from the known weights of polymer and support, was checked by Soxhlet extraction with hexane. The fair agreement observed between both methods (Table I) shows that our silanized chromosorb sample is free from soluble organic material.

The cross-linked PDMS was powdered and fractionated on a 60–80 mesh sieve.

The characteristic parameters of the various columns (stainless-steel tubing, 2.17 mm i.d.) are given in Table I.

General Procedure of the Gas-Chromatography Experiments. Solutes were injected through a silicone rubber septum using 10-μL Hamilton syringes. The conditions of infinite dilution of the solute were simulated by introducing vapor–air mixtures leading to a measurable signal. The peaks were always symmetrical, and the elution times at their maximum were independent of sample size over the range 0.001–0.1 μL. Most of the measurements were carried out every ten degrees within the temperature range 60–180 °C.

Results and Discussion

Specific Retention Volumes. The retention time is converted to a specific retention volume (measured at 273.2 K) at infinite dilution through the classical relation of Littlewood et al. (see for instance ref 3 and 85 in ref 1).

The V^0_g values for PDMS are calculated as an average of three or more independent runs, two different loadings, and two or three different flow rates. The experimental accuracy is about ±1%, in good agreement with literature data.[2,3,6] The data are collected in Tables II and III. Measurements on PDES were performed at a single-column loading and their confidence interval is estimated to be about ±2%.

The systems PDMS ($\overline{M}_v = 5 \times 10^5$)–hexane, –heptane, –benzene, and –toluene at 40 and 55 °C have already been studied independently by two research groups[6] and they may thus be considered as reference systems to check the reliability of our own measurements. Our experimental results for PDMS 1, 2 ($\overline{M}_n = 3 \times 10^4$) fall systematically in the range previously defined ($V^0_g = \pm 3.5\%$), moreover they are in excellent agreement with the values of Lichtenthaler et al. ($\overline{M}_v = 6 \times 10^5$).[3b] For PDMS 3 ($\overline{M}_n = 1.7 \times 10^4$), however, our V^0_g values are quite close or even greater than the admitted upper limit. At 60 °C, the comparison between our experimental data PDMS ($\overline{M}_n$ = 3 and 1.7×10^4) and literature data ($\overline{M}_n = 3.7 \times 10^3$)[7] shows that V^0_g is a slightly decreasing function of molecular weight (Table IV). This dependence, restricted to the low molecular weight range ($\overline{M}_n < 2 \times 10^4$), may be tentatively correlated with end-group effects.

For the tetrafunctional PDMS network, V^0_g values are strongly dependent on the flow rate of the gas in the range of 10–30 mL/min. Moreover the equivalent height of the theoretical plate H and the slopes of Van Deemter curves are

Table III
Values of Specific Retention Volume V^0_g (cm^3/g) and of Thermodynamic Parameters for PDES–Hydrocarbon Systems[a]

t,	*n*-Hexane				*n*-Heptane				Benzene				Toluene			
°C	V^0_g	Ω^∞	χ^*	χ_H	V^0_g	Ω^∞	χ^*	χ_H	V^0_g	Ω^∞	χ^*	χ_H	V^0_g	Ω^∞	χ^*	χ_H
60	5—/2	6.18	0.55	−0.08	138.5	5.97	0.53	0.19	90.7	6.29	0.82	0.65	230.6	5.84	0.72	0.32
70	42.4	6.21	0.55	−0.23	96.8	5.95	0.53	0.02	66.2	6.16	0.80	0.56	159.2	5.79	0.71	0.25
80	31.5	6.27	0.56	−0.38	69.1	5.97	0.53	−0.15	49.2	6.07	0.79	0.46	112.5	5.76	0.71	0.17
90	23.7	6.36	0.57	−0.53	50.2	6.02	0.54	−0.34	37.2	6.0	0.78	0.35	81.2	5.75	0.70	0.08
100	18.2	6.47	0.59	−0.69	37.1	6.10	0.55	−0.52	28.6	5.96	0.77	0.22	59.8	5.75	0.70	−0.02
110	14.1	6.61	0.61	−0.84	27.9	6.20	0.57	−0.71	22.3	5.94	0.77	0.09	44.9	5.76	0.70	−0.21
120	11.1	6.77	0.64	−1.00	21.3	6.32	0.59	−0.85	17.7	5.94	0.77	−0.05	34.1	5.78	0.71	−0.22
130	8.84	6.94	0.66	−1.14	16.6	6.40	0.60	−1.01	14.1	5.96	0.77	−0.20	26.4	5.82	0.71	−0.33

[a] Standard deviation of the various thermodynamic parameters: Ω^∞ ±0.1, χ^* ±0.02, χ_H ±0.4.

Table IV
Retention Volumes of Various Solutes in PDMS of Different Molecular Weights and in a PDMS Network

	V^0_g, cm^3/g, at 60 °C			
Solute	PDMS $\overline{M}_n$ = 30000	PDMS $\overline{M}_n$ = 17100	PDMS $\overline{M}_v$ = 3700[a]	PDMS network $\overline{M}_n$ = 3770[b]
n-Hexane	59.9	61.0	60.91	59.1
n-Heptane	138.1	140.4	144.30	131.6
Cyclohexane	101.2		106.14	
Benzene	91.6	95.3	105.46	95.6
Dioxane	124.7	127.8		

[a] Data from ref 7. [b] $\overline{M}_n$ of the linear segment between two consecutive cross-linking points.

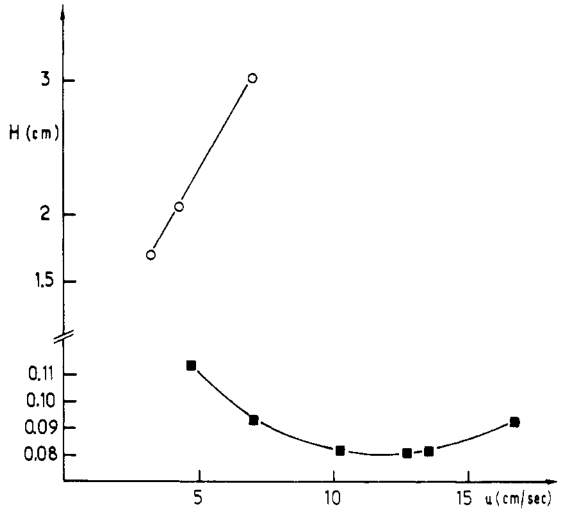

Figure 1. Van Deemter curves for *n*-heptane linear and cross-linked systems at 88 °C: (■) *n*-heptane–PDMS 1; and (○) *n*-heptane–PDMS network.

drastically higher for the network than for the linear precursor (Figure 1). This suggests strong differences between the diffusion processes of the probe molecule in the liquid and the cross-linked PDMS. Reliable V^0_g values for the PDMS network may be nevertheless easily obtained by linear extrapolation to zero flow rate, but this necessary correction lowers the accuracy which is not better than 5%.

The V^0_g values are systematically about 10% lower for the PDMS network than for the linear precursor (Table IV). This small difference is barely significant since the eventual role of the nodules present as chemical heterogeneities (which may reach 4% of the total weight of the polymeric material) may not be neglected. Our measurements, restricted to a single PDMS network, do not allow drawing of any correlation between V^0_g values and polymer structure.

The variation of V^0_g with temperature is most often described by:

$$\partial \ln V^0_g/\partial(1/T) = \Delta H_v/R \tag{3}$$

where ΔH_v is the enthalpy of vaporization of the vapor probe from infinitely dilute solution in the stationary phase. Within the wide range of temperature we have investigated (60–180 °C), ln V^0_g is not a linear function of $1/T$ since the ΔH_v variation with temperature is not negligible. Such a rough approximation would lead to deviations higher than 5% for the upper and lower temperature ranges.

Thermodynamic Interaction Parameters. The activity coefficient at infinite dilution Ω^∞ based on weight fraction may be calculated from the experimental V^0_g values according to Patterson et al.[8]

$$\ln \Omega^\infty = \ln \left(\frac{a_1}{w_1}\right) = \ln \frac{273.2R}{P_1{}^0 V^0_g M_1} - \frac{P_1{}^0}{RT}(B_{11} - V_1) \tag{4}$$

where subscript 1 refers to the volatile component and subscript 2 to the polymer; a_1 is the activity and w_1 the weight fraction; M_1 is the molecular weight; $P_1{}^0$ is the saturation vapor pressure at temperature T; V_1 is the liquid state molar volume; and B_{11} is the gas state second virial coefficient of component 1 at T.

The polymer–solvent interaction parameter at infinite dilution χ^*, as defined in the Flory–Huggins theory based on segment fractions and "hard-core volumes",[9] is correlated with the previous activity coefficient at infinite dilution through:

$$\ln \Omega^\infty = \ln \frac{v_1{}^*}{v_2{}^*} + 1 - \frac{M_1 v_1{}^*}{\overline{M}_2 v_2{}^*} + \chi^* \tag{5}$$

where v^* is the specific hard-core volume (we use respectively χ and χ^* for the interaction parameters defined by Flory and Huggins in their classical lattice theory and in their more recent segment theory).

Because of additivity of enthalpic and entropic contributions, the χ parameter may be written as

$$\chi = \chi_H + \chi_S \tag{6}$$

where $\chi_H = \kappa$ in Flory's nomenclature. χ_H is deduced from the temperature dependence of the activity coefficient at infinite

Table V
Comparison between χ and χ_H Values of Some Solvents at Infinite Dilution in PDMS Deduced from GLC and from Static Measurements

Solvent	Static method		Dynamic method (GLC)										
	Patterson[20]		Schreiber[2]		Prausnitz[3b]		DeLigny[4]				This work at 60 °C		
	χ^* 20 °C[d]	χ_H 25 °C[e]	χ^* 25 °C[f]	χ^* 55 °C[f]	χ 25 °C[g]	χ 55 °C[g]	χ^* 20 °C[h,i]	χ^* 60 °C[h,j]	χ_H 20 °C[h,k]	χ_H 60 °C[h,l]	χ^* [m,n]	χ_H [m,o]	X_{12}, cal/cm³ [c,m]
n-Hexane		0.18	0.524	0.539	0.46	0.46	0.501	0.461	0.268	−0.003	0.48	−0.12	2.93
n-Heptane	0.53	0.28	0.556	0.551			0.505	0.464	0.252	0.069	0.50	0.04	3.07
n-Decane		0.80					0.642	0.588	0.514	0.338	0.59		2.97
Cyclohexane	0.60[a]				0.47	0.47					0.49	−0.28	4.15
Benzene	0.87		0.864	0.816	0.79	0.76					0.78	0.30	8.49
	0.84[a]												
	0.90[b]	0.74[b]											
Toluene	0.82	0.66	0.833	0.795	0.75	0.72					0.76	0.42	7.25
Ethylbenzene	0.80	0.64	0.833	0.814	0.77	0.73					0.78	0.26	6.49
Chloroforme											0.69		
p-Dioxane					1.32	1.23					1.24		

[a] Data from ref 13b. [b] Data from ref 21. [c] Calculated by eq 8. [d] χ^*deviation ±0.05, $\overline{M}_v = 5 \times 10^5$. [e] χ_H deviation ±0.02, $\overline{M}_v = 2 \times 10^4$. [f] χ^* deviation ±0.01, $\overline{M}_v = 5 \times 10^5$. [g] χ deviation ±0.015, $\overline{M}_v = 5 \times 10^5$. [h] $\overline{M}_v = 3 \times 10^4$. [i] χ^* deviation ±0.013. [j] χ^* deviation ±0.01. [k] χ_H deviation ±0.1. [l] χ_H deviation ±0.05. [m] $\overline{M}_n = 3 \times 10^4$, $\overline{M}_w/\overline{M}_n = 3$. [n] χ^* deviation ±0.01. [o] χ_H deviation ±0.2.

dilution according to:

$$\chi_H = -\frac{T}{\Omega}\frac{\partial \Omega}{\partial T} = -T\frac{\partial \chi^*}{\partial T} \qquad (7)$$

To eliminate the free-volume contribution which is quite different for the low molecular weight solute and for the polymeric stationary phase, Flory et al.[10] described χ^* at zero pressure and at infinite dilution as the sum of two contributions:

$$\chi^* RT = P_1^* V_1^* \left[3\tilde{T}_1 + \ln\left(\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}_2^{1/3} - 1}\right) + \tilde{v}_1^{-1} - \tilde{v}_2^{-1} \right] + X_{12}\frac{V_1^*}{\tilde{v}_2} \qquad (8)$$

where $\tilde{v}^{1/3} - 1 = (\alpha T/3)(1 + \alpha T)$, $\tilde{T} = T/T^* = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3}$. $\tilde{v}$ and $\tilde{T}$ are reduced quantities and V^*, P^*, and T^* are the reduction parameters. The first term is related to the equation of state contribution arising from differences in the thermal expansion coefficients α of the solute and of the polymer. The second term introduces the contact interaction parameter X_{12} which takes into account interactions between solute segments and the polymeric solvent.

We have also tried to interpret our experimental results according to the Patterson–Prigogine theory through the simplified eq 11

$$RT\chi^* = r_1 A + r_1 B T^2 \left(\frac{1}{r_1} - \frac{1}{r_2}\right)^2 \qquad (9)$$

which is analogous to the Flory eq 8. r is the number of segments in the molecule equal to $(n + 1)/2$, and n is the number of carbon atoms or of repeating units. A and B are two positive parameters independent of temperature; A measures the deviation of the interaction energy per pair of segments in the mixture from the mean of the interaction energy per pair of segments in the pure components. It is correlated to the X_{12} interchange energy parameter through the relation $A = X_{12}v_1^*$ at 0 K. B is nearly independent of the probe nature for nonpolar probes and accounts for the difference between the thermal expansion coefficients of the two components.

To evaluate the various thermodynamic interaction parameters, a number of physical data related to both the solvents and the polymers are required. Vapor pressures and specific volumes of solvents at different temperatures were calculated using critical constants taken from Dreisbach's compilation.[12] Specific volumes of PDMS are literature data[13] and those of PDES were measured by dilatometry (see Experimental Section). The virial coefficients B_{11} of the solvents were computed from the corresponding state equations of McGlashan and Potter[14] for hydrocarbons and from the virial equations of Kreglewski[15] for chloroform and dioxane. The reduction parameters at 25 °C are those given by Patterson et al.,[7] but for our PDMS sample ($\overline{M}_n = 3 \times 10^4$ vs. $\overline{M}_n = 3.7 \times 10^3$ for the Patterson sample) the following values were chosen: $T^* = 5530$ K, $v^* = 0.840$ cm³/g, $p^* = 341$ J/cm³.[13a] They are assumed to be independent of temperature.

Both eq 4 and 5 involve two approximations. They assume that the carrier gas and its mixtures with the various solvents in the gas phase are ideal. The first assumption for He and for $p_i/p_0 < 1.5$ is well justified, since the correction for the nonideality is about 2×10^{-3}%.[16] The second assumption neglects the solvent–carrier gas interactions in the gas phase measured by expression $(2B_{13} - \overline{V}_1^{\infty})P_1^0 J_3^4/RT$,[17] where B_{13} is the second virial coefficient characterizing the solvent–carrier interaction, J_3^4, is the correction factor for gas compressibility, and $\overline{V}_1^{\infty}$ is the partial molar volume of solute at infinite dilution.

We estimated the importance of this correction factor for He–C_6H_6 mixture at 50 °C. The B_{13} values are very scattered: 12 cm³/mol calculated from the Lennard-Jones potential or from the Beattie–Bridgeman equation of state;[18] 34 calculated by the principle of corresponding states using the Hudson–McCoubrey combining rule; and the −57 experimental value measured by Everett et al.[19] The maximum value of the correction factor (assuming that $B_{13} = -57$ cm³/mol) remains lower than 0.6% over the whole temperature range investigated. Because of the inaccuracy of the B_{13} values and of the relatively weak importance of this correction factor, we have systematically used eq 4 and 5 without any correction.

Study of the System PDMS–Hydrocarbons. In Table II, we have given the V^0_g experimental values and the Ω^{∞}, χ^*, and χ_H values for the interactions of PDMS with aliphatic and aromatic solvents between 60 and 180 °C; in Table V we have compared our calculated χ^* and χ_H values with literature data related to the same systems, obtained either from vapor-sorption equilibria or gas-chromatography measurements.

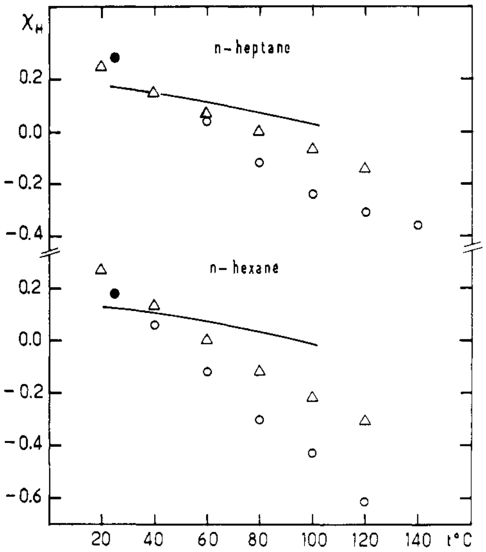

Figure 2. Variations of interaction parameter χ_H versus temperature for alkane–PDMS systems: (△) data of Hammers et al.[4] (GLC method); (○) this work; (●) data of Chahal et al.[20] (static method); and (—) calculated according to Flory theory.

The scattering of the χ^* values deduced from inverse gas-chromatography experiments is high for alkanes but lower for aromatic hydrocarbons (differences of about 15 and 8% respectively exist between the extreme values). This discrepancy has already been pointed out by a coordinated research work at McGill University and at the University of California.[6] The measurement accuracy obviously depends on a number of factors (column preparation, temperature control, operator), and it cannot be significantly improved at this moment in an easy way. On the other hand, the χ^* values deduced from the static determination of the chemical potentials of the solvents and from the dynamic inverse gas-chromatography method may be considered to be in fair agreement taking into account the accuracy of each method.

Comparison of the Experimental Results with Flory Theory. For alkanes, the χ^* values are an increasing function of temperature: χ_H tends to become negative while χ_S drastically increases. This specific feature was already been pointed out by Chahal et al.[20] who suggested that it could not be readily taken into account in terms of differences of free volume of the two components. The dependence of χ_H on temperature may be predicted according to Flory's theory (eq 18 ref 20 $\varphi_2 \rightarrow 1$)

$$\frac{RT\chi_H}{P_1^*V_1^*} = \frac{X_{12}}{P_1^*}\{-\tilde{U}(\tilde{T}_2) + \tilde{T}_2\tilde{C}_p(\tilde{T}_2)\} + [\tilde{U}(\tilde{T}_2) - \tilde{U}(\tilde{T}_1) + (\tilde{T}_1 - \tilde{T}_2)\tilde{C}_p(\tilde{T}_2)] \quad (10)$$

with $\tilde{U} = -\tilde{V}^{-1}$ and $\tilde{C}_p = \alpha T/\tilde{V}\tilde{T}$. The values of the contact interaction parameters X_{12} are directly taken from Morimoto's graphical representation.[21] In Figures 2a and 2b we plotted our experimental results together with Hammers and De Ligny's data (both involving inverse gas chromatography), the single calorimetric value at 25 °C given by Chahal et al.,[20] and the theoretical curve. For temperatures lower than 60 °C, all the experimental values are in fair agreement with the theoretical ones. For higher temperatures, the decrease of χ_H with increasing temperature is much more pronounced than expected from the Flory theory.

For aromatic hydrocarbons and especially for benzene, the variations of χ_H versus temperature are weaker than for alkanes. Agreement between the dynamic and the static measurements of χ_H is fair only for toluene (χ_H = 0.42 and 0.64, respectively) but bad for benzene (χ_H = 0.3 and 0.87, respectively). Calorimetric measurements are probably more reliable.

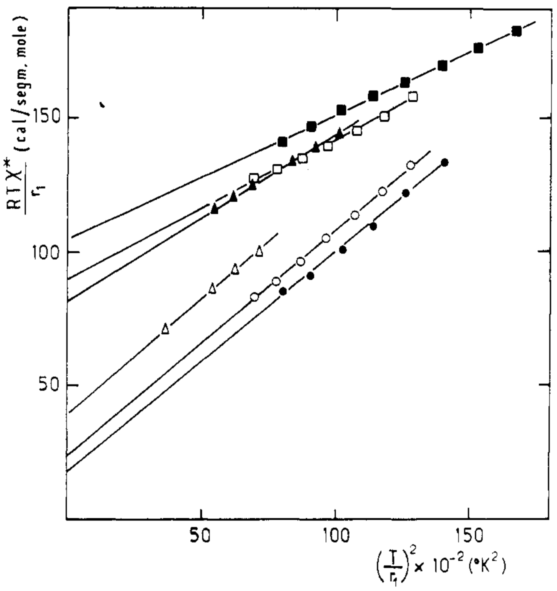

Figure 3. Prigogine–Patterson theory applied to interactions of PDMS with various alkanes and aromatic hydrocarbons: (●) n-hexane, (○) n-heptane, (△) n-decane, (■) benzene, (□) toluene, and (▲) ethylbenzene.

For cyclohexane, χ_H at 60 °C has a negative value of −0.22 and it is a slightly increasing function of temperature. This is in sharp contrast with its theoretical value of 0.27 at 60 °C and its expected variation with temperature according to the Flory theory.

Comparison of the Experimental Results with the Prigogine–Patterson Theory. $RT\chi^*/r_1$ values for the n-alkanes and for the aromatic hydrocarbons are plotted versus $(T/r_1)^2$ in Figure 3, according to eq 9.

The data related to each different alkane seem to fit straight lines of similar slopes, leading to a constant B value of 8×10^{-3} cal/segment mol K^2. The different A values are 18, 23, and 39 cal/segment mol for n-hexane, n-heptane, and n-decane, respectively. Both our A and B values are different from those given by Hammers et al.[4] for the series of alkanes between C$_5$ and C$_{10}$: A = 60 cal/segment mol, B = 5 cal/segment mol K^2. A is an increasing function of the alkane chain length, and the deduced X_{12} parameters of about 1 cal/cm^3 for n-hexane and n-heptane and 1.4 cal/cm^3 for n-decane are compatible with the corresponding values estimated by Morimoto for PDMS at infinite dilution in the same solvents: X_{12} = 1.1, 1.4, and 2.1 cal/cm^3 for n-hexane, n-heptane, and n-decane, respectively.[22] Comparison between n-alkane–PDMS and polyhydrocarbons systems investigated by Hammers et al.[4] may be of interest. The A value of 25 cal/segment mol for the n-hexane–PDMS system does not seem very different from its value of 25, 21, and 17 cal/segment mol for n-hexane–polyisobutylene, -squalane, and -apiezon M systems. On the other hand, the single B value of 8×10^{-3} cal/segment mol K^2 which we determined for n-alkane–PDMS systems is significantly lower than those measured for the polyhydrocarbons: B = 13.5, 10, and 13.5×10^{-3} cal/segment mol K^2 for polyisobutylene, squalane, and apiezon M.

The experimental data have been considered separately for each of the three PDMS–aromatic hydrocarbon systems investigated. Calculation leads to A = 105, 90, and 82 cal/segment mol and B = 4.6, 5.2, and 6.2 cal/segment mol K^2 for benzene, toluene, and ethylenebenzene, respectively. The X_{12} values deduced from the A parameter, 5.3, 4.2, and 3.7 cal/cm^3, are in good agreement with the calorimetric values obtained by Morimoto (6.0, 3.8, and 3.9 cal/cm^3) for infinitely diluted

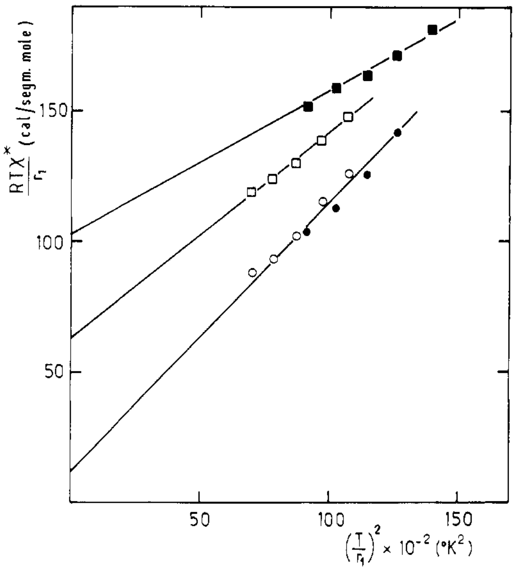

Figure 4. Prigogine–Patterson theory applied to interactions of PDES with: (●) *n*-hexane, (○) *n*-heptane, (■) benzene, and (□) toluene.

solutions of PDMS.[22] Within the homologous series C_6H_5–R, the X_{12} decrease noticed when going from R = H to CH_3 to C_2H_5 suggests that the behavior of the system PDMS–aromatic hydrocarbons mainly depends on the balance between the aromatic and the aliphatic character of the probe. On the other hand, X_{12} parameters are systematically lower than those calculated according to the Flory theory but the difference is less than that for aliphatic hydrocarbons.

Study of the System PDES–Hydrocarbons. Our experimental data and calculated parameters ($V^0{}_g$, Ω^∞, χ^*, and χ_H) related to the interactions of PDES with *n*-hexane, *n*-heptane, benzene, and toluene between 60 and 130 °C are collected in Table III.

There is no fundamental difference between PDMS and PDES. The thermodynamic parameters Ω^∞, χ^*, and χ_H are of the same order of magnitude, as expected from the similar chemical structures of the two polymers. For *n*-hexane and *n*-heptane, the dependence of χ_H on temperature is stronger for PDES than for PDMS, leading quickly to negative χ_H values.

The experimental results may be discussed according to the Prigogine–Patterson theory as was done for PDMS. The $RT\chi^*/r_1$ values of the solutes are plotted versus $(T/r_1)^2$ in Figure 4.

The data related to *n*-hexane and *n*-heptane may be taken into account altogether and lead to $A = 11.5$ cal/segment mol and $B = 10.4 \times 10^{-3}$ cal/segment mol K^2. The A value is decreased by a factor of about 0.5 with respect to PDMS. The deviation of the interaction energy per pair of segments in the system polymer–solute from the mean of the interaction energy per pair of segments in the pure components is lower for PDES than that for PDMS–alkanes systems. Substitution of a methyl by an ethyl group in the polysiloxane tends to decrease the structural and chemical differences between the two components. The B value is significantly higher for PDES than for PDMS and slightly lower than that for polyisobutylene and squalane. This may be correlated with the fact that the thermal expansion value of PDES $\alpha = 0.575 \times 10^{-3}$ deg^{-1} is far lower than that of PDMS ($\alpha = 0.907 \times 10^{-3}$ deg^{-1}) and close to that of polyisobutylene ($\alpha = 0.555 \times 10^{-3}$ deg^{-1}).

Conclusion

The use of gas chromatography to study thermodynamic interactions quantitatively in polymer–solute systems rests upon the assumption that the dynamic measurements actually represent the thermodynamic equilibrium between the vapor and the liquid phases. In the convenient case of polysiloxane–hydrocarbon systems, good agreement is generally observed between gas chromatographic and static vapor pressure measurements for the χ^* interaction parameter. On the other hand, calorimetry probably remains the more accurate method for χ_H determination.

Discussion of the experimental data in terms of Flory and Prigogine–Patterson theories points out two major features:

Experimental values of the different thermodynamic parameters are not completely interpreted by the Flory theory. The χ_H interaction parameter decreases more rapidly than expected with increasing temperature and thus becomes negative in a low-temperature range; this specific behavior is even more pronounced for PDES than for PDMS. A lack of thermodynamic equilibrium would lead to large positive χ_H values and the deviation of the experimental results from the Flory theory seems to be well ascertained.

The Prigogine–Patterson theory allows a more self-consistent interpretation of the experimental results obtained either by the static or the dynamic method (interchange energy X_{12} parameter). The difference between PDMS and polyolefins may be readily explained by the high thermal expansion coefficient of the polysiloxane chain or its high flexibility. These differences significantly decrease for PDES since the substitution of a methyl by an ethyl group on the polysiloxane backbone tends to confer a more paraffinic character to the polymer.

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