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## SORPTION OF *n*-ALKANES IN POLY(VINYLTRIMETHYLSILANE) STUDIED BY INVERSE GAS CHROMATOGRAPHY

Yu. P. YAMPOLSKII\*, S. G. DURGARJAN and N. E. KALIUZHNYI

*Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Leninsky Prospect 29, 117912 GSP-1 Moscow V-71 (U.S.S.R.)*

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### SUMMARY

Inverse gas chromatography was used to study the sorption of C<sub>2</sub>-C<sub>10</sub> *n*-alkanes in poly(vinyltrimethylsilane) (PVTMS) in the region 25-250°C. It is shown that above and below the glass transition temperature,  $T_g$ , bulk sorption takes place, so it was possible to study the thermodynamics of polymer-solute interactions in the glassy region. The measured negative values of the partial molar heats of mixing for C<sub>3</sub>-C<sub>7</sub> *n*-alkanes in glassy PVTMS are consistent with the values predicted by the dual sorption model for glassy polymers.

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### INTRODUCTION

The method of inverse gas chromatography (IGC) has found wide application in studies of polymer solution thermodynamics, as well as for the determination of solubility coefficients in polymers, investigations of phase transitions in polymers and their morphology, etc. In the late '60s Guillet and co-workers<sup>1,2</sup> reported that over a wide temperature range the temperature dependencies of the main experimental parameter obtainable by IGC of polymers, namely the specific retention volume,  $V_g$ , differed substantially from those observed in IGC studies of low-molecular-weight liquids. The  $V_g$  values are not a monotonous function of temperature in the region of the glass transition temperature,  $T_g$ . At temperatures  $T \gg T_g$ , the  $V_g$  values are the measure of the equilibrium sorption (the sum of absorption and adsorption); but at  $T \ll T_g$  they characterize only the adsorption processes, because of the small magnitude of the diffusion coefficients in this temperature range. Consequently, the intrinsic time of diffusion of a solute in the bulk polymer is large in comparison with its residence time in the column. Finally, in the intermediate (non-equilibrium) temperature range, the solute manages to permeate partly the bulk polymer, but fails to attain equilibrium sorption or for only part of the polymer layer. According to ref. 3 such behaviour is a general characteristic of glassy polymers, and the temperature dependencies of  $V_g$  (often referred to as retention diagrams) can be estimated on the basis of free volume theory. Accordingly, the thermodynamics of the polymer-solute interactions can be investigated only at temperatures in excess of  $T_g + 50^\circ\text{C}$ , the glassy region being suitable only for study of the surface properties of polymers<sup>4</sup>.

The absence of a characteristic Z-shaped retention diagram has been accounted for by the prevalence of adsorption mechanisms both below and above  $T_g$ <sup>5</sup>.

On the other hand, recent results<sup>6</sup> have shown that not all glassy polymers have low diffusion coefficients, which are essential for the above phenomena. In particular, the higher the glass temperature of the polymer, the greater are the diffusion coefficients at ambient temperature. For certain polymers with high  $T_g$  the diffusion coefficients for gases reach high values. This suggests that for some glassy polymers the diffusion limitations may not interfere with a study of the sorption thermodynamics. Indeed, it was demonstrated<sup>7</sup> that IGC enables one to determine, at 20–40°C, the solubility coefficients of C<sub>2</sub>–C<sub>4</sub> hydrocarbons in poly(vinyltrimethylsilane) (PVTMS), the glass transition temperature of which is equal to 170°C.

In the present paper the sorption of C<sub>2</sub>–C<sub>10</sub> *n*-alkanes in PVTMS is described over a wide temperature range, 20–250°C, covering both the glassy and rubbery states of the polymer.

## EXPERIMENTAL

A LCM-8MD chromatograph with catharometer and helium as carrier gas was used. The chromatograph was also equipped with a precision manometer for measuring the pressure gradient in the column in order to correct for compressibilities. The characteristics of the columns used are presented in Table I. PVTMS, with a molecular weight of about  $5 \cdot 10^5$ , obtained by anionic polymerization and poly(vinyl chloride) (PVC) for comparison purposes were deposited on the surface of the solid support Chromosorb W in a rotary evaporator using benzene as a solvent in the case of PVTMS and dichloromethane in the case of PVC. The precise weight content of the polymer phase was determined by back extraction of the sample in a Soxhlet apparatus. The injection of the gas samples was accomplished by use of a special valve. The samples of hydrocarbons, which are liquids under ambient conditions, were introduced as vapours by a microsyringe. The syringe was purged several times with air to achieve infinite dilution conditions (until the retention time becomes independent of the peak height).

The net retention volumes,  $V_N$ , were determined relative to the retention volume of a non-sorbed component (air). The solutes were used as received; they contained no impurities according to the chromatographic analysis.

TABLE I  
CHROMATOGRAPHIC COLUMNS

Solid support Chromosorb W.

No.	Polymer	Weight of polymer (g)	Content of polymer (%)	Length (cm)	Diameter (cm)
1	—	0	0	200	0.3
2	PVTMS	0.2400	7.0	170	0.3
3	PVTMS	0.2108	11.8	100	0.3
4	PVTMS	0.3050	19.3	100	0.3
5	PVTMS	0.7986	21.2	200	0.3
6	PVC	0.3243	15.0	100	0.3

The specific retention volumes,  $V_g$ , were calculated using the equation<sup>8</sup>

$$V_g = \frac{t_R F_C}{w_1} \cdot \frac{T_0}{T_r} \cdot J_3^2 \quad (1)$$

where  $t_R = t_S - t_{N_2}$  is the net retention time,  $F_C$  is the carrier gas flow-rate,  $w_1$  is the mass of polymer in the column,  $T_r$  is the ambient temperature (295°K),  $T_0 = 273°K$  and  $J_3^2$  is a correction for the pressure gradient in the column, tabulated in ref. 9.

At infinite dilution of the solute, the relationship between the activity coefficients,  $(a_1/w_1)^\infty$ , and the bulk retention volume can be expressed by the equation<sup>10</sup>

$$\ln (a_1/w_1)^\infty = \ln (273.2R/V_g p_1^0 M_1) - (p_1^0/RT) (B_{11} - V_1) \quad (2)$$

where  $p_1^0$  and  $V_1$  are the vapour pressure and molar volume of the solute at temperature  $T$ ,  $M_1$  is its molecular weight and  $B_{11}$  is the second virial coefficient. The temperature dependence of  $p_1^0$  was given previously<sup>11</sup>. The values of  $V_1$  and  $B_{11}$  at different temperatures were calculated using the methods described in refs. 12 and 13.

## RESULTS AND DISCUSSION

Investigations of polymer solution thermodynamics using IGC are based on the fulfilment of several conditions:

- (1) the sorption equilibrium is achieved sufficiently rapidly
- (2) the solute concentration range usually must conform to the infinite dilution region, *i.e.*, the primary region of the sorption isotherm
- (3) the adsorption on the gas-polymer and gas-solid support interfaces may be neglected.

These conditions are often believed to be attained in the rubbery, but not in the glassy, region<sup>4</sup>. We studied the effects of the polymer content in the column, of the carrier gas flow-rate and of the sample size on the retention volumes.

A plot of  $V_g$  for *n*-heptane *versus* the carrier gas flow-rate is shown in Fig. 1. It is seen that as the temperature is lowered it is more difficult to establish sorption equilibrium, however there are ranges of  $F$  values at which  $V_g$  is independent of  $F$  as indicated by the arrows in Fig. 1. Similar dependencies, obtained for other alkanes, show that the range of equilibrium values of  $V_g$  increases with decreasing molecular weight of the solute, other conditions being equal.

To determine the rôle of adsorption on the solid support surface the retention times on the column containing pure supports were measured. They were found to be close to the dead time of the column, suggesting that adsorption on the gas-solid support interface could be neglected.

Fig. 2 shows that the  $V_g$  values are independent of the mass of polymer as well as its concentration in the column, so it follows that  $V_g$  characterizes the bulk sorption in PVTMS. To determine whether infinite dilution conditions are established for sorption, the effect of the sample size on the retention time was studied. Upon increasing the sample size, the  $t_R$  values decreased by 5–15%, in agreement with the usual form of the sorption isotherm for glassy polymers<sup>14</sup>. This effect is more man-

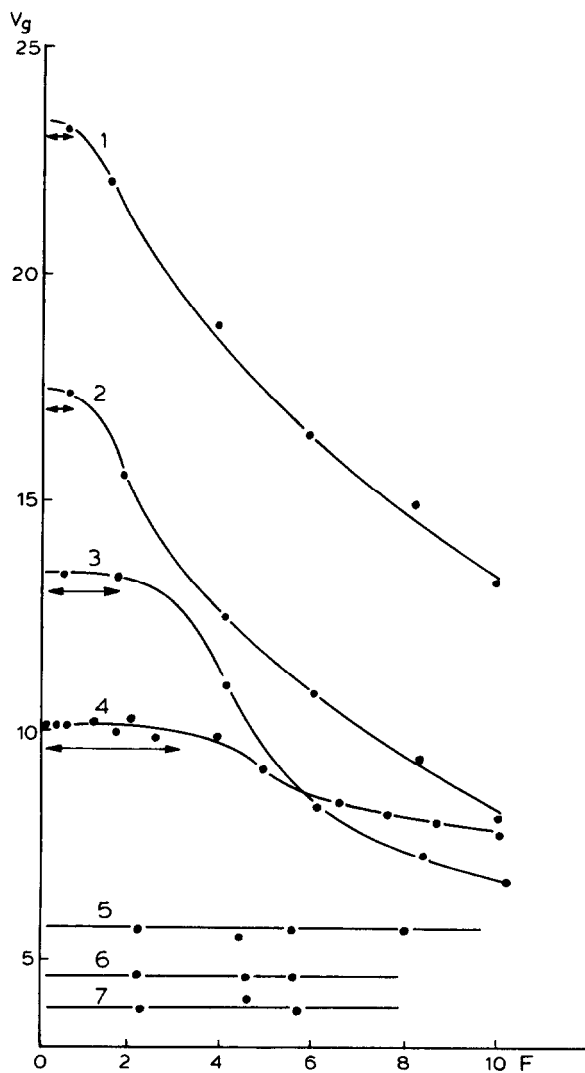


Fig. 1. Effect of the flow-rate,  $F$  (ml/min), on the specific retention volume,  $V_g$  (ml/g), of *n*-heptane at 120 (1), 130 (2), 140 (3), 150 (4), 170 (5), 180 (6) and 190°C (7).

ifest for high-molecular-weight solutes and at lower temperatures. Nevertheless, reduction of sample size allows access to the infinite dilution region.

As the glassy state of a polymer is not in thermodynamic equilibrium, we studied the effect on the  $V_g$  values of heating the polymer phase above the glass transition temperature and subsequent cooling. The  $V_g$  values observed below  $T_g$  did not change upon heating at 1–3°K/min for 0.5–8 h. Column temperatures as high as 250°C did not lead to irreversible changes in retention properties.

Thus, the investigation of PVTMS by IGC has shown that the criteria for bulk

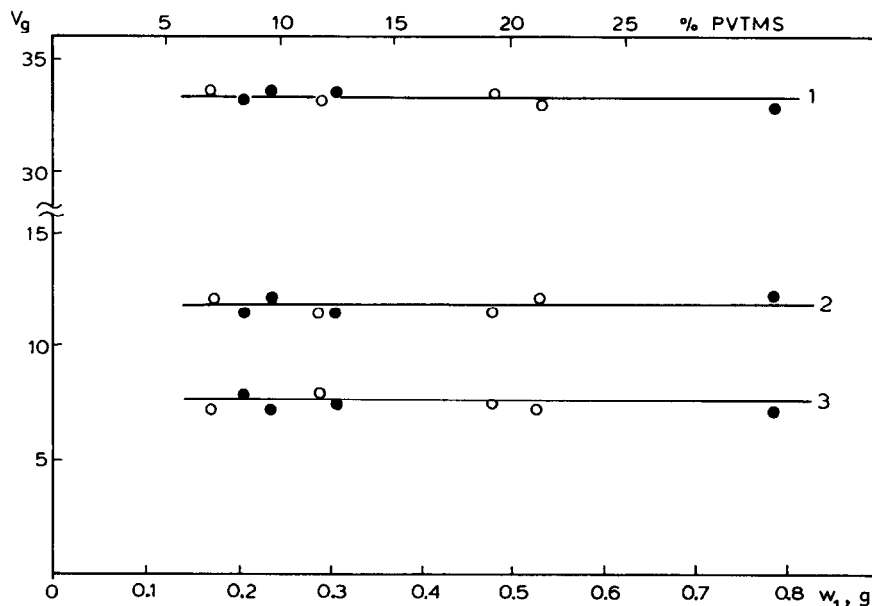


Fig. 2. Effect of the polymer content,  $w_1$  (g) (●), and concentration, wt.-% (O), in the column on the specific retention volume,  $V_g$  (ml/g). Alkanes: 1,  $C_3H_8$  at 25°C; 2,  $C_3H_8$  at 40°C; 3,  $C_2H_6$  at 25°C.

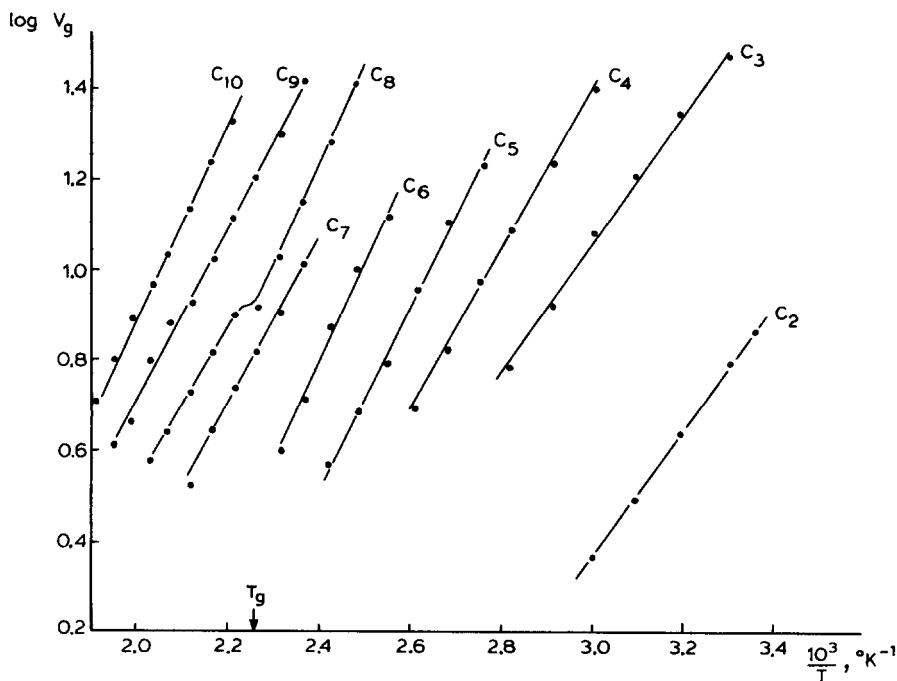


Fig. 3. Retention diagrams for  $C_2$ - $C_{10}$  *n*-alkanes in PVTMS.

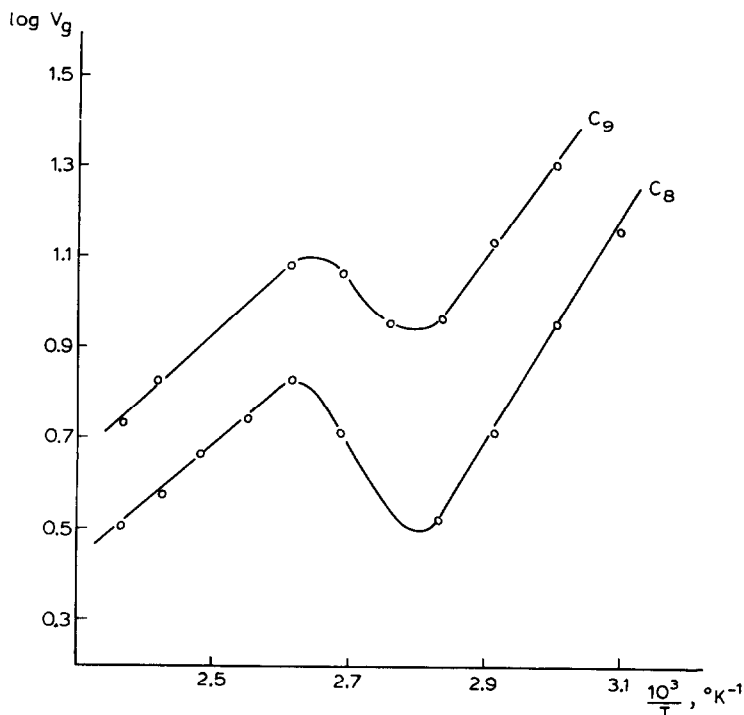


Fig. 4. Retention diagrams for *n*-octane and *n*-nonane in PVC.

sorption of  $C_2$ – $C_{10}$  hydrocarbons below the glass transition temperature are fulfilled, so that IGC enables information to be obtained about the sorption thermodynamics of PVTMS. This conclusion is verified by the form of the retention diagram (Fig. 3) for  $C_6$ – $C_{10}$  hydrocarbons in the temperature range of 130–250°C, which includes the glass transition temperature of PVTMS. The figure shows that these dependencies are entirely different from the retention diagrams observed for most previously studied polymer–solute systems in the glass transition temperature region<sup>4</sup>. Z-shaped regions corresponding to non-equilibrium retention, and appearing at as high as 50–100°C above  $T_g$ , are absent. The curves of  $V_g(T)$  on PVTMS show no inflections or negative temperature coefficients in the vicinity of  $T_g$ . A change in slope and a small “step” is observed only in the  $C_8$  case.

Similar retention diagrams have been observed either for very thin polymer films (polymer phase content 0.02–0.07%<sup>15</sup>), for which the diffusion limitation vanishes, or for polymers, *e.g.*, polyacrylonitrile, having such low diffusivities that retention proceeds by the adsorption mechanism even above  $T_g$ <sup>5</sup>. However, both possibilities of explaining the observed behaviour are inappropriate for the PVTMS columns studied. From the polymer phase content in the column of 19% the average thickness of the polymer film is about 2000 Å, while approximately linear retention diagrams have been observed for polystyrene films of thickness about 20 Å<sup>15</sup>. The possibility of an adsorption mechanism of retention is excluded by the data of Fig. 2.

To ascertain whether the observed retention diagrams are associated with some

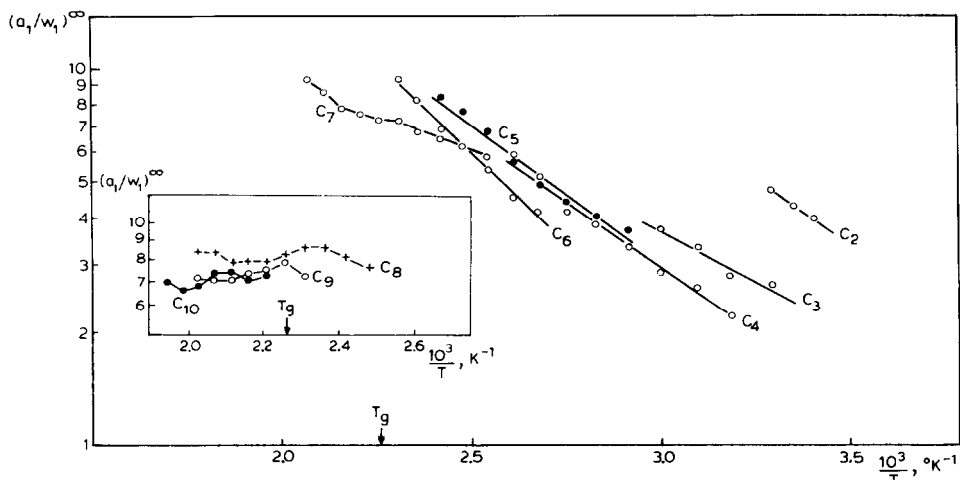


Fig. 5. Temperature dependency of the activity coefficients of  $C_2$ - $C_{10}$  alkanes in PVTMS.

peculiarities of the solid support, the column or the technique, the sorption of  $C_8$  and  $C_9$  hydrocarbons in PVC was studied, for comparison. A Z-shaped retention diagram was obtained (Fig. 4) for a polymer phase content of 15%. In addition, in the non-equilibrium region, the carrier gas flow-rate has a significant influence on the  $V_g$  values.

So it follows that in contrast to other polymers, for PVTMS the character of the  $V_g(T)$  curves near  $T_g$  is determined to a much lesser degree by diffusion limitations. From the fact that IGC permits investigation of the sorption thermodynamics over a much wider temperature region in PVTMS than in other polymers, PVC, polystyrene, etc., it can be concluded that the diffusion coefficients of PVTMS are higher than those of other polymers, not only at ambient temperature<sup>6</sup> but also at higher temperatures up to  $T_g$ . It follows that the mechanism of retention in PVTMS, remains the same below and above  $T_g$ .

Let us consider what conclusions can be drawn from the sorption mechanism. Fig. 5 shows the temperature dependency of the activity coefficients  $(a_1/w_1)^\infty$ . The values of  $(a_1/w_1)^\infty$  increase with increasing temperature for all solutes studied at temperatures below  $T_g$ . The monotonous character of the dependencies changes at and above  $T_g$ . The partial molar heat of mixing at infinite dilution,  $\Delta H_m$ , is negative at  $T < T_g$  for all hydrocarbons. In the vicinity of  $T_g$  the values of  $(a_1/w_1)^\infty$  change less regularly with temperature, but the tendency of  $\Delta H_m$  to decrease in magnitude is evident for all solutes. The values of  $\Delta H_m$  for  $C_9$  and  $C_{10}$  alkanes are positive at temperatures above  $T_g$ . It is of interest to compare for an homologous series the variations in activity coefficients or in the excess free energy of mixing:

$$\Delta G = RT \ln (a_1/w_1)^\infty \quad (3)$$

The data of Fig. 5 and Table II show that for the glassy region of PVTMS at constant temperature the values  $(a_1/w_1)^\infty$  and  $\Delta G$  decrease in the series  $C_2H_6$ ,  $C_3H_8$ ,  $C_4H_{10}$ , then remain approximately constant. This means that ethane and propane are some-

TABLE II  
EXCESS THERMODYNAMIC FUNCTIONS OF MIXING FOR GLASSY PVTMS

	<i>n-Alkanes</i>					
	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>
$\Delta G$ (383°K) (cal/mol)	—	1400	1345	1325	1150	1310
$\Delta H_m$ (cal/mol)	-3100*	-2400	-3300	-3400	-4400	-1800
$\Delta S$ (cal/mol · °K)	—	± 1100	± 300	± 400	± 500	± 200
		-9.8	-12.2	-12.5	-14.5	-8.1

\* Approximate value.

what poorer solvents for PVTMS than higher alkanes, and that C<sub>4</sub>–C<sub>7</sub> alkanes are roughly equally good solvents for PVTMS.

Table II also contains other excess functions of mixing, calculated for the glassy state:

$$\Delta H_m = 2.3R \cdot \frac{\partial \log (a_1/w_1)^\infty}{\partial (1/T)} \quad (4)$$

$$\Delta S = (\Delta H_m - \Delta G)/T \quad (5)$$

As a rule, for good polymer solvents the values  $\Delta H_m$  are positive and of low magnitude (0.3–0.4 kcal/mol), which is related with the need overcome cohesion forces. The large negative heats of mixing, *i.e.*, exothermic mixing, may be due to placing of the solute molecules in microvoids or “holes” already existing in the polymers<sup>16</sup>, corresponding to the dual sorption model for glassy polymers<sup>14</sup>. So it was interesting to compare the variations in  $\Delta H_m$  for *n*-alkanes. Table II shows that  $\Delta H_m$  is constant within the limits of determination errors for C<sub>2</sub>–C<sub>6</sub> *n*-alkanes. For *n*-heptane the value of  $\Delta H_m$  is lower, but still negative. These results can be considered in terms of the central idea of the dual sorption model<sup>14</sup>, *i.e.*, in glassy polymers a part of the solute is physically dissolved and the other part is sorbed in microvoids or elements of non-equilibrium free volume, “frozen” in the glassy matrix. The ratio of two types of sorption must depend on the molecular dimensions of the solute molecules and the size distribution of the microvoids. If one assumes that there is a limiting size of the solute molecules beyond which adsorption is impossible on the given polymer, then for such molecules sorption can proceed only by the physical dissolution mechanism, so one may expect lower values of the absolute heat of mixing. This is the case for sorption of *n*-alkanes in PVTMS. If the above reasoning is valid, C<sub>7</sub> and C<sub>8</sub> hydrocarbons should have the limiting molecular size, and be adsorbed in the largest available elements of frozen free volume of PVTMS. This is in agreement with the results of a study of PVTMS with the spin-probe method, in which it was found that the elements of free volume in glassy PVTMS can accommodate a probe with a single piperidine ring but not a bicyclic probe<sup>17</sup>.

The values of  $\Delta H_m$  for some hydrocarbons in PVTMS have been measured



using a static technique<sup>16</sup>. Although quantitative agreement between such data and the values obtained by IGC is not always observed, the qualitative result  $\Delta H_m < 0$  in the glassy region was demonstrated by both methods for a series of hydrocarbons and permanent gases in PVTMS (as well as in other polymers<sup>18,19</sup>).

## REFERENCES

- 1 O. Smidsrod and J. E. Guillet, *Macromolecules*, 2 (1969) 272.
- 2 A. Lavoie and J. E. Guillet, *Macromolecules*, 2 (1969) 443.
- 3 J. M. Braun and J. E. Guillet, *Macromolecules*, 9 (1976) 617.
- 4 J. M. Braun and J. E. Guillet, *Advances in Polymer Science*, Vol. 21, Springer, Berlin, New York, 1976, p. 108.
- 5 J. E. Guillet and M. Galin, *J. Polym. Sci., Polym. Lett. Ed.*, 11 (1973) 233.
- 6 Yu. P. Yampolskii, S. G. Durgarjan and N. S. Nametkin, *Vysokomol. Soedin, Ser. A*, 23 (1982) 536.
- 7 N. E. Kaliuzhnyi, Yu. P. Yampolskii, S. G. Durgarjan and N. S. Nametkin, *Dokl. Akad. Nauk SSR*, 265 (1982) 1170.
- 8 S. D. Nogare and R. S. Juvet, *Gas-Liquid Chromatography. Theory and Practice*, Interscience, New York, London, 1962.
- 9 M. S. Vigderhaus, *Calculations in Gas Chromatography*, Chimia, Moscow, 1978.
- 10 J. R. Conder and J. H. Purnell, *Trans. Faraday Soc.*, 64 (1968) 1505.
- 11 M. Gomes-Nieto and G. Thodos, *Ind. Eng. Chem., Fundam.*, 16 (1977) 254.
- 12 R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 1966.
- 13 J. O. Hirschfelder, C. F. Curtis and B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954.
- 14 D. R. Paul, *Ber. Bunsenges, Phys. Chem.*, 83 (1979) 294.
- 15 J. M. Braun and J. E. Guillet, *Macromolecules*, 8 (1975) 882.
- 16 V. V. Volkov, N. S. Nametkin, E. G. Novitskii and S. G. Durgarjan, *Vysokomol. Soedin, Ser. A*, 21 (1979) 927.
- 17 Yu. P. Yampolskii, A. M. Wasserman, A. L. Kovarskii, S. G. Durgarjan and N. S. Nametkin, *Dokl. Akad. Nauk SSSR*, 249 (1979) 150.
- 18 P. Mears, *Trans. Faraday Soc.*, 53 (1957) 101.
- 19 A. S. Michaels, W. R. Vieth and J. A. Barrie, *J. Appl. Phys.*, 34 (1963) 1.