increase in Θ-temperature due to any kind of segmental interaction.

The symmetry of our results for the unoriented situation $\alpha = {}^1/_3$ is of course a consequence of our very symmetrical segment model. Despite its extraordinary symmetry, we hope that our model at least qualitatively describes a broad class of real macromolecules. In addition to real macromolecules having symmetrical segments, this model seems to be true for atactic polymers, because the random distribution of isomers becomes effectively quite symmetrical.

**Acknowledgment.** In author is indebted to Prof. Dr. R. G. Kirste for valuable discussions and critical reading of the manuscript.

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# Thermodynamics of Sorption in Glassy Poly(vinyltrimethylsilane)

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ABSTRACT: Sorption thermodynamics in poly(vinyltrimethylsilane) (PVTMS) was studied with inverse gas chromatography. For various solutes (aliphatic and aromatic hydrocarbons, alcohols, and $SO_2$) the retention diagrams were found to be linear in the whole temperature range studied, including the glass transition temperature. This is the result of high diffusivity in PVTMS. It enables one to study bulk sorption and thermodynamic polymer–solute interactions in the glassy region. Enthalpy of solution and excess functions of mixing ($\Delta G_m$, $\Delta H_m$, and $\Delta S_m$) in PVTMS were determined. An extrathermodynamic correlation between $\Delta H_m$ and $\Delta S_m$ was found along with an isoequilibrium constant $\beta = 410$ K. Thermodynamics of sorption in PVTMS, as well as other glassy polymers, is characterized by large negative values of $\Delta H_m$ and $\Delta S_m$ and a wide variation of $\Delta H_m$ and $\Delta S_m$ with solute dimensions. These results are in agreement with the predictions of a dual sorption model for glassy polymers. The dimension of a cavity (Langmuir adsorption site) in PVTMS was obtained.

## Introduction

Studies of organic solute sorption in polymers using inverse gas chromatography (IGC) have shown[1-3] that in the vicinity of the glass transition temperature ($T_g$) diffusion limitations in most "polymer–solute" systems prevent establishment of sorption equilibrium in the bulk polymer. According to ref 3, at temperatures $T < T_g$ the method of IGC permits one to study adsorption on the polymer surface, while at temperatures $T \gg T_g$ it measures mainly bulk sorption. The temperature region in the vicinity of $T_g$ corresponds to the nonequilibrium sorption and gas chromatography. Hence, the study of sorption thermodynamics in polymers using IGC is limited to temperatures in excess of $T_g + 50$ °C and sometimes to temperatures as high as 120 °C above $T_g$.[3] Thus the temperature range of the glassy state and the region of the glass transition, both very important from theoretical and practical points of view, are inaccessible for sorption thermodynamics study by the IGC method.

Later, however, the following studies showed that this was not always the case. First it was demonstrated that in some polymers retention proceeds exclusively by a surface adsorption mechanism even at temperatures above $T_g$.[4] Later for the system *n*-butyl alcohol–poly(*N*-isopropylacrylamide) (PNIPAM) it was reported[5] that bulk sorption retention has been found both below and above $T_g$. Bulk sorption retention has been established for IGC of *n*-alkanes on poly(vinyltrimethylsilane) (PVTMS)[6,7] and for some solvents in aromatic polysulfones (PSF).[8]

In the present paper the sorption of different classes of solutes (alkanes, naphthenes, aromatics, alcohols, and $SO_2$) in PVTMS is investigated below and above the glass transition temperature (170 °C) of this polymer, and the excess thermodynamic functions of mixing are determined.

**Table I**
**Column Parameters**[a]

| *N* | loading, mass % | mass of polymer, g | length, m |
|---|---|---|---|
| 1 | 0 | 0 | 2.0 |
| 2 | 4.6 | 0.150 | 1.5 |
| 3 | 7.0 | 0.240 | 1.7 |
| 4 | 11.8 | 0.211 | 1.0 |
| 5 | 19.3 | 0.305 | 1.0 |
| 6 | 21.2 | 0.799 | 2.0 |

[a] PVTMS. Solvent, benzene, Inert support, Chromosorb W AW DMCS 30/60 mesh; 0.3-cm column diameter.

## Experimental Section

The technique has been described previously.[6,7] The characteristics of the basic columns are given in Table I. To cover a wider temperature range for different solutes we varied the length of the columns and therefore the weight of the polymer phase, maintaining a constant concentration of polymer on the carrier. The number of columns actually used was greater than that shown in Table I.

PVTMS, with a molecular weight of about $5 \times 10^5$, was obtained by anionic polymerization, initiated by *sec*-butyllithium at a temperature of about 70 °C.

The data[9,10] for the vapor pressures of solutes $p_1°$ at different temperatures were used when determining coefficients at infinite dilution. The second virial coefficients $B_{11}$ and the molar volume of a solute[12] $V_1$ at various temperatures were used for calculating the corrections for gas-phase nonideality.

While studying different types of solutes we had some problems with the choice of the source of $B_{11}$ values. For some solutes there are direct values. But for others only $B_{11}$ values obtained with correlations or the group contribution approach are available. Since a comparison of various solutes at different temperatures was the main goal of this study, we needed the same accuracy of correction for all the $(a_1/w_1)^\infty$ values. Therefore, a single source of $B_{11}$ values, namely the Berthelot equation,[11] was used. We

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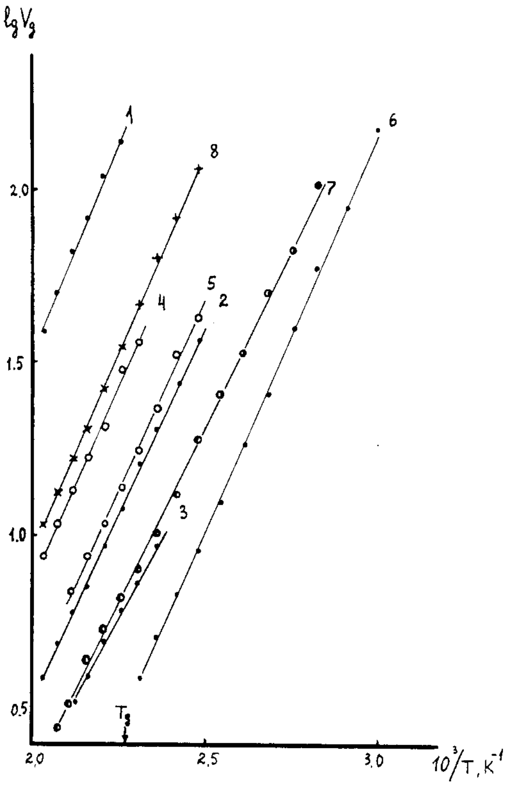

**Figure 1.** Retention diagrams for PVTMS: (1) bicyclohexyl; (2) toluene; (3) cyclohexane; (4) *n*-hexan-1-ol; (5) *n*-pentan-1-ol; (6) *n*-hexane; (7) *n*-heptane ((◐) col 3, (◑) col 6); (8) *n*-decane ((+) col 2, (×) col 6).

checked the errors introduced by the arbitrary choice of $B_{11}$ values at different temperatures and found that the contribution of this factor was not more than 1–2% to $(a_1/w_1)^\infty$ or not more than ±0.1 kcal/mol in $\Delta H_m$.

## Results and Discussion

**Retention Mechanism.** Unlike chromatography on low molecular liquid phases, a Z-shaped retention diagram in the vicinity of the glass transition temperature is typical of IGC on most polymers. Other results are obtained in the IGC study of various solutes on PVTMS. Figure 1 shows a retention diagram of different hydrocarbons (solvents) and alcohols (nonsolvents) in the temperature range in the vicinity of the $T_g$ of PVTMS. The choice of the solutes was based on the differences of retention diagrams that had been obtained previously for solvents and nonsolvents of certain polymers.[3,5] It is seen that the retention diagrams are essentially linear for all solutes studied.

Linear retention diagrams can be observed for columns with very thin films of polymer phase (about 20 Å)[1] and for polymers in which, due to low diffusivity, retention proceeds exclusively by surface adsorption both below and above $T_g$ (e.g., poly(acrylonitrile) (PAN)).[4] To exclude this possibility as a cause of the linear nature of the retention diagrams, one must demonstrate that the retention volumes $V_N$ are directly proportional to the polymer mass or that the specific retention volume $V_g$ does not depend on the polymer-phase concentration or film thickness and has been measured under conditions where $V_g$ is independent of the carrier gas flow rate $F$. Figure 2 shows that this is the case for different solutes in the range well below the glass transition temperature of PVTMS. The retention diagrams, as seen in Figure 1, do not change when the concentration of the polymer phase increases considerably. Control of the independence of the $V_g$ value of the loading and of the mass of the polymer phase always preceded the determination of the thermodynamic parameters.

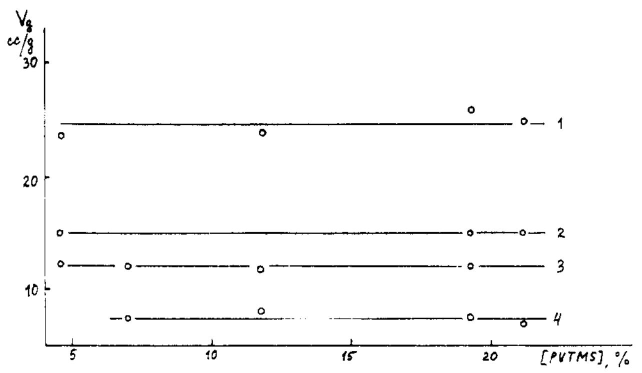

**Figure 2.** Specific retention volumes at different loading: (1) *n*-pentane, 80 °C; (2) *n*-butane, 70 °C; (3) propane, 40 °C; (4) ethane, 25 °C.

To determine the role of adsorption on the solid carrier surface, the retention volumes were measured on column 1, containing pure carrier. They were found to be close to the dead volume of the column, suggesting that adsorption on the gas–solid carrier interface could be neglected.

The values $V_g$ at carrier gas flow rates that are lower than 2–2.5 cm$^3$/min were shown to be independent of $F$. Hence, all the data, used in the calculations of the present work, are based on the values of $V_g$ measured in this range of $F$, i.e., in the equilibrium region.

Finally it is to be noted that only the values of $V_g$ measured in the infinite dilution region (corresponding to the initial parts of sorption isotherms) are considered here. The values of $V_g$ were determined by injection of a sample so minute that $V_g$ did not depend on the sample volume.

An estimate of the average thickness of a polymer film can be made by using the surface area of the carrier (1–2 m$^2$/g), the apparent density of the carrier layer (0.3 g/cm$^3$) and the density of the polymer (0.9 g/cm$^3$). The resulted values of film thickness are in the range 250–2500 Å for the loading in Table I. Therefore, the linear retention diagrams, obtained for PVTMS, must be the result of a high diffusivity level in this polymer.

Indeed, diffusion coefficients of various gases in PVTMS have been shown to be relatively high and close to that in polymers having glass transition temperatures lower by 200–300 °C (polyethylene, polyisobutylene, natural rubber, etc.[13]). Thus, the diffusion coefficient of *n*-butane in PVTMS at 22 °C is equal to $7 \times 10^{-11}$ cm$^2$ s$^{-1}$.[14] The diffusion coefficient of *n*-butane in poly(vinylchloride) (PVC), for which Z-shaped retention diagrams have been obtained,[6] is 2–3 orders of magnitude lower ($2 \times 10^{-13}$ cm$^2$ s$^{-1}$) at 30 °C.[15] Diffusion coefficients $D$ of organic molecules in PAN are very difficult to measure, but using the correlation $D - d_{\text{eff}}$,[16] where $d_{\text{eff}}$ is the effective cross-section diameter of the penetrant molecule, one can find that at ambient temperature the diffusion coefficient of *n*-butane in PAN is about $10^{-31}$–$10^{-30}$ cm$^2$ s$^{-1}$. Although such a low value might be considered dubious, nevertheless diffusivities in PAN are lowest among other common polymers, and the difference between $D$ values in PAN and other polymers increases with the dimensions of the diffusing molecules. Consequently, changes in the type of retention diagrams are in line with the diffusivity differences of polymer phases (cf. ref 1).

**Enthalpy of Solution.** The temperature dependence of specific retention volumes permits one to calculate the enthalpy of solution

$$\Delta H_S = -R\mathrm{d}(\ln V_g)/\mathrm{d}(1/T)$$

Table II
Enthalpy of Solution (cal/mol) in PVTMS[a]

| solute | $-\Delta H_S$ | $\delta(\Delta H_S)_n^{n+1}$ |
|---|---|---|
| | *n*-Alkanes | |
| $C_2H_6$ | 5400 | -1020 |
| $C_3H_8$ | 6420 ± 150 | -1600 |
| $C_4H_{10}$ | 8020 ± 60 | -1360 |
| $C_5H_{12}$ | 9380 ± 130 | -1330 |
| $C_6H_{14}$ | 10710 ± 130 | +2060 |
| $C_7H_{16}$ | 8650 ± 60 | +650 |
| $C_8H_{18}$ | 8000 ± 120 | -1200 |
| $C_9H_{20}$ | 9290 ± 160 | -1200 |
| $C_{10}H_{22}$ | 10490 ± 40 | |
| | Aromatics | |
| $C_6H_6$ | 9560 ± 80 | |
| $C_6H_5CH_3$ | 9880 ± 40 | -320 |
| | Naphthenes | |
| cyclohexane | 8240 ± 170 | |
| bicyclohexyl | 10990 ± 90 | |
| | Primary Alcohols | |
| $C_3H_7OH$ | 9420 ± 100 | +1350 |
| $C_4H_9OH$ | 8070 ± 100 | -1850 |
| $C_5H_{11}OH$ | 9920 ± 70 | -300 |
| $C_6H_{13}OH$ | 10210 ± 130 | -800 |
| $C_8H_{17}OH$ | 11820 ± 140 | |
| $SO_2$ | 7370 ± 140 | |

[a] The standard error corresponds to the confidence level 0.95.

For solutes having retention diagrams in the region that includes $T_g$, the calculation of $\Delta H_S$ was first completed independently for the temperatures below and above $T_g$. Since the results had coincided within the limits of the standard deviation, the single value $\Delta H_S$ was then determined for the whole temperature range studied. The values of $\Delta H_S$, given in Table II, were found by the least-squares method.

It is interesting to follow the changes of $\Delta H_S$ for regular variations of solute nature, e.g., for a homologous series.

$\Delta H_S$ values for $C_2$–$C_6$ *n*-alkanes decrease monotonously with the number of carbon atoms in the *n*-alkane molecule *n* with an approximately constant increment $\delta\ (\Delta H_S)_n^{n+1} = \Delta H_S^{n+1} - \Delta H_S^n$. For higher alkanes this tendency changes. $\Delta H_S$ values at first become less negative and then continue to decrease. The complex dependence of $\Delta H_S$ and $\delta\ (\Delta H_S)_n^{n+1}$ on *n* is also evident for primary alcohols.

Vapor sorption in polymers is usually considered on the basis of a thermochemical cycle, which involves the processes of condensation and mixing with the polymer. Enthalpies of condensation $\Delta H_c$ steadily decrease for $C_2$–$C_{10}$ *n*-alkanes.[17] Therefore the observed nonmonotonous changes of enthalpy of solution must be related to some peculiarity of the mechanism of mixing.

The changes in nonideality of solute vapors should also have been displayed in the increments of $\Delta H_c$. Therefore, they can not be regarded as a cause of the observed phenomena. It should be noted that studies of solution thermodynamics of *n*-alkanes in low molecular weight liquids (cyclohexane,[18] squalane, benzochinoline[19]), as well as sorption of *n*-alkanes in polymers above their $T_g$[20] indicated a monotonous dependence of $\Delta H_S$ on *n*.

**Excess Functions of Mixing.** With the measured specific retention volumes the activity coefficients at infinite dilution[3] were computed to be

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

where $M_1$ is the molecular mass of a solute and the second term is correction for vapor nonideality. The variation in activity coefficients with temperature for some solute in the temperature range including $T_g$ is shown in Figure 3. Similar data for *n*-alkanes have been presented previously.[6]

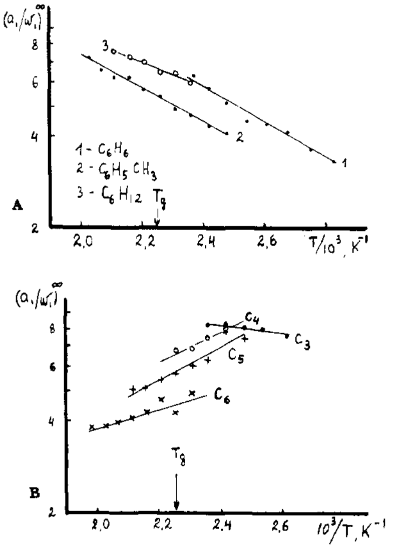

**Figure 3.** Temperature dependence of activity coefficients at infinite dilution: (A) hydrocarbons ((1) benzene, (2) toluene, (3) cyclohexane); (B) primary $C_3$–$C_6$ alcohols.

The only system for which $(a_1/w_1)^\infty$ values have been determined both above and below $T_g$ is the system *n*-butyl alcohol–PNIPAM. Its retention diagram contains a drastic change of slope at the temperature, coinciding with $T_g$ of this polymer (130 °C). The data of the present study show that the transition through $T_g$ is not always accompanied by a change in the partial molar heat of mixing. This result and the conclusions that follow from it will be discussed below.

With the values of $(a_1/w_1)^\infty$, IGC permits one to calculate all of the excess functions of mixing

$$\Delta G_m = RT \ln (a_1/w_1)^\infty$$

$$\Delta H_m = R\mathrm{d}[\ln (a_1/w_1)^\infty]/\mathrm{d}[1/T]$$

$$\Delta S_m = (\Delta H_m - \Delta G_m)/T$$

In spite of the abundance in the literature of data for $(a_1/w_1)^\infty$, $\Delta H_m$ and especially $\Delta S_m$ values have been determined rather rarely. The excess functions of mixing for a glassy polymer seem to be obtained in the present paper for the first time. Values of $\Delta H_m$ and $\Delta S_m$ as well as temperature ranges over which they have been measured are presented in Table III. Values of $\Delta H_m$ measured for PVTMS differ substantially from those observed for most polymers, as can be seen from the values of $\Delta H_m$ cited in literature or estimated by us using the activity coefficients in polysiloxanes,[22] natural rubber,[23] polyolefins, poly(methyl acrylate),[21], polystyrene,[21,24] and other polymers. It should be noted that all of the polymers mentioned have been studied at temperatures above their glass transition temperature. The corresponding $T_g$ values are much lower than $T_g$ of PVTMS.

The unusual behavior of sorption in PVTMS is the exothermic nature of the mixing process for many solutes. Values of $\Delta H_m$ are negative for most good solvents of PVTMS (hydrocarbons) and for some nonsolvents ($SO_2$ and $C_3H_7OH$). The negative values of $\Delta H_m$ can be explained as follows. The process of mixing in PVTMS does not require overcoming cohesion forces, i.e., the work of generating a cavity in polymer. Accordingly, the exothermic mixing can be considered as evidence that during the process of sorption in polymer a molecule of a solute gets into a preexisting cavity, a defect, or a region of de-

Table III
Excess Functions of Mixing in PVTMS

| solute | $T$, K | $\Delta H_m$, kcal/mol | $\Delta S_m$, cal/(mol K) |
|---|---|---|---|
| propane | 303–333 | $-2.4 \pm 1.1$ | $-9.8$ |
| butane | 313–383 | $-3.3 \pm 0.3$ | $-12.2$ |
| pentane | 343–423 | $-3.4 \pm 0.4$ | $-12.5$ |
| hexane | 373–433 | $-4.4 \pm 0.5$ | $-14.5$ |
| heptane | 393–483 | $-1.8 \pm 0.2$ | $-8.1$ |
| octane | 403–493 | $-0.4 \pm 0.1$ | $-5.0$ |
| nonane | 403–493 | $+0.7 \pm 0.6$ | $-2.5$ |
| decane | 453–513 | $+0.7 \pm 0.6$ | $-2.5$ |
| benzene | 353–423 | $-2.6 \pm 0.4$ | $-9.8$ |
| toluene | 403–493 | $-2.4 \pm 0.2$ | $-8.8$ |
| cyclohexane | 423–473 | $-1.8 \pm 0.5$ | $-7.5$ |
| propan-1-ol | 383–423 | $-0.6 \pm 0.4$ | $-5.6$ |
| butan-1-ol | 413–443 | $+2.2 \pm 1.1$ | $+1.2$ |
| pentan-1-ol | 403–473 | $+2.2 \pm 0.75$ | $+2.1$ |
| hexan-1-ol | 433–503 | $+1.5 \pm 0.7$ | $+0.3$ |
| octan-1-ol | 413–473 | $+1.2 \pm 0.1$ | $-1.3$ |
| sulfur dioxide | 298–333 | $-1.8 \pm 0.6$ | $-9.5$ |

[a] The standard error corresponds to the confidence level 0.95.

creased density. Since the dual sorption model for a glassy polymer[25,26] is based on the hypothesis of an existence of such "holes" in a glassy polymer and of an adsorption population of sorbed molecules and negative values of $\Delta H_m$ in PVTMS are observed at temperatures below the $T_g$ of this polymer, it would be tempting to explain this result in terms of a dual sorption model. However, as it is seen from Table III, the exothermicity of mixing of many solutes is also found at temperatures well above $T_g$ of PVTMS, i.e., under conditions where the adsorption population must be absent.

Now we have the data for sorption thermodynamics only in three polymers below their glass transition temperatures: PSF[8,32] PVTMS (the results of the present work and of ref 6), and PNIPAM.[5] In all of these polymers the values of $(a_1/w_1)^\infty$ increase with temperature for good solvents; i.e., exothermicity of mixing is observed. If we compare these three polymers with numerous polymers studied above their $T_g$, it will be evident that exothermic mixing is typical of sorption processes in glassy polymers.

In PVTMS the positive $\Delta H_m$ values were obtained only for primary $C_4$–$C_8$ alcohols (while for $n$-$C_3H_7OH$, $\Delta H_m < 0$). In considering these results it should be borne in mind that $H_m$ represents the enthalpy difference of the solute in the pure polymer (at the conditions of infinite dilution) and in the pure liquid phase. Since alcohols are highly associated liquids, the sign of $\Delta H_m$ can characterize the liquid state better than solution in the polymer phase, as has been pointed out by Guillet et al.[5] The endothermicity of the process of rupturing hydrogen bonds appears to be higher than the exothermicity of the process of mixing in PVTMS, so the overall resulting $\Delta H_m$ value is positive.

Substantial negative values of the excess entropy of mixing is another peculiarity of sorption in PVTMS (Table III). Figure 4 shows the correlations between excess functions of mixing $\Delta H_m$ and $\Delta S_m$ in PVTMS. It is evident that the single correlation is fulfilled for the solutes of different nature. Such a correlation for thermodynamic parameters in the series of related compounds is usual in liquid-phase processes and is considered as a display of the compensation effect.[27] Figure 4 shows that this correlation also holds for the polymer–solute equilibrium. The fact that the single correlation $\Delta H_m - \Delta S_m$ holds for different solutes such as hydrocarbons of various classes, alcohols, and $SO_2$ is consistent with the suggestion that interactions of all the solutes with PVTMS are intrinsically similar. The isoequilibrium constant $\beta$ (the slope of the correlation) is equal to 410 ± 24 K. The positive value of $\beta$ means that the deeper the potential well characteristic of the sorption site, the more the conformation transitions and inner rotations in sorbed molecules are rigidly oriented and hindered.

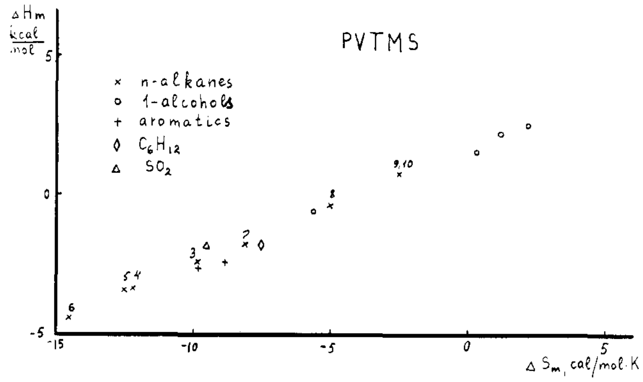

**Figure 4.** Correlation of excess functions of mixing $\Delta H_m$ and $\Delta S_m$ in PVTMS.

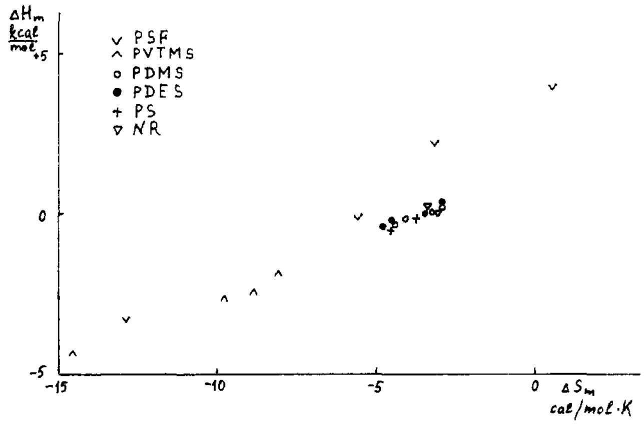

**Figure 5.** Correlation of $\Delta H_m$ and $\Delta S_m$ for $C_6$–$C_7$ aliphatic and aromatic hydrocarbons in PVTMS and PSF.

Using the data on excess functions of mixing for other polymer–solute systems, we plotted similar correlations for polysiloxane,[22] polystyrene,[24] natural rubber[7] (above $T_g$), and glassy PSF.[8] These results as well as some of the data of the present study for PVTMS are compared in Figure 5. In order for the choice of solute not to influence the results of the comparison, we arbitrarily limited ourselves to aliphatic and aromatic $C_6$ and $C_7$ hydrocarbons. The comparison shows not only an exothermicity of the mixing process and high negative $\Delta S_m$ values but also that a much wider range in variations of $\Delta H_m$ and $\Delta S_m$ is specific to glassy polymers (or, perhaps, to polymers, having higher glass transition temperatures). It means that in glassy polymers the same changes in structure (geometry) of a solute lead to much greater changes in $\Delta H_m$ and $\Delta S_m$. On the other hand, a substantially wider spectrum of energy and entropy patterns of the sorption sites seems to exist in PSF and PVTMS. It is of interest to compare this conclusion with the results of the study[28] of polymers using the ESR saturation transfer technique, which has suggested that there is a much wider distribution of rotation frequencies of the paramagnetic probe in glassy polymers than in rubbers. If one assumes that rotation frequencies of a probe are determined by the stiffness of fixation of a probe in the polymer matrix, the results presented in Figures 4 and 5 and the results of ref 28 are manifestations of the same phenomenon.

Interesting information about the intimate details of the sorption mechanism can be obtained by considering changes in excess functions of mixing of a homologous series. It is seen in Figure 4 that for the primary members of an *n*-alkane homologous series the elongation of a carbon chain by a methylene group leads to a decrease of enthalpy and entropy of mixing, both values being below zero. This trend changes drastically beyond *n*-hexane as $\Delta H_m$ begins to increase, rapidly getting into the positive range usual for polymers at temperatures above the glass transition temperature. These results demonstrate once more that the nonmonotonous change in $\Delta H_m$ along the homologous series was a cause of the mentioned differences in increments of sorption enthalpy.

The following interpretation can be given to the observed phenomena in the region of glassy state. According to the dual sorption model[26] there are two populations of sorbed molecules in the glassy polymer: physically dissolved molecules, which obey the Henry law, and those adsorbed in "holes" or nonequilibrium elements of free volume of polymer. Concentration of the latter population is limited by saturation of all the sites available and can be described by Langmuir isotherms. The fraction of the Langmuir sorption is highest at low vapor pressures of a solute. This takes place in a chromatographic experiment where conditions of infinite dilution are fulfilled. The most exothermic mixing must be observed for the Langmuir part of the sorption.[25]

However, the possibility of adsorption must also depend on whether the dimensions of a solute molecule correspond to those of an element of free volume of the polymer. The paramagnetic probe technique has provided evidence[29] that the dimensions of the free volume element in glassy PVTMS is such that it can accomodate a single piperidine ring probe but not a bicyclic probe. From propane to hexane the dimensions of the solute (probe) molecule gradually approach the average or limiting dimensions of the free volume element, hence the adsorption of the probe is accompanied by a progressive decrease in $\Delta H_m$ and $\Delta S_m$ values.

The molecular dimensions of $C_7$ and higher alkanes hamper their adsorption. Accordingly, physical dissolution becomes the predominant mode of sorption. This is reflected in the excess functions of mixing ($\Delta H_m$ and $\Delta S_m$) that acquire values characteristic of the temperature range above $T_g$.

This interpretation however does not explain why the negative $\Delta H_m$ values are observed in PVTMS even above $T_g$. There is a possible explanations for this.

Probably, for this polymer microvoids or cavities exist at temperatures above $T_g$. It should be noted that many low molecular weight liquids and solutions (water, low alcohols, highly polar compounds, etc.) are characterized by the presence of intraassociate cavities with distinct geometric dimensions, comparable to the dimensions of small molecules.[31,32]

Finally, we stress the fact that the polymers for which it has been possible to study sorption thermodynamics in the glassy state have the highest $T_g$ values (130–190 °C) among polymers investigated so far with the IGC technique. This suggests that large negative $\Delta H_m$ and $\Delta S_m$ values and their wide range of variation, on the one hand, and the high glass transition temperatures in PSF, PVTMS, and PNIPAM, on the other hand, are in some way connected and reflect a certain peculiarity in the structure of these polymers. One can only hope that future studies will make this problem more clear.

**Registry No.** $C_2H_6$, 74-84-0; $C_3H_8$, 74-98-6; $C_4H_{10}$, 106-97-8; $C_5H_{12}$, 109-66-0; $C_6H_{14}$, 110-54-3; $C_7H_{16}$, 142-82-5; $C_8H_{18}$, 111-65-9; $C_9H_{20}$, 111-84-2; $C_{10}H_{22}$, 124-18-5; $C_6H_6$, 71-43-2; $C_6H_5CH_3$, 108-88-3; $C_3H_7OH$, 71-23-8; $C_4H_9OH$, 71-36-3; $C_5H_{11}OH$, 71-41-0; $C_6H_{13}OH$, 111-27-3; $C_8H_{17}OH$, 111-87-5; $SO_2$, 7446-09-5; PVTMS (homopolymer), 25036-32-2; cyclohexane, 110-82-7; bicyclohexyl, 92-51-3.

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