

CHROM. 12,076

## POLYFUNCTIONAL POLYMER SORBENTS

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### SUMMARY

The gas chromatographic properties of polyfunctional polymer sorbents, particularly those based on triethylene glycol methacrylate and butyl methacrylate and N-vinyl-3(5)-methylpyrazole and ethylene glycol dimethacrylate copolymers, have been studied. The thermodynamic characteristics of sorption on these polymer sorbents have been investigated. The correlation between changes in the sorption energy and entropy has been determined. It has been shown that in the system sorbate-polymer sorbent, the mechanism of interaction depends on the chemical nature, physical state and structural characteristics of the sorbent and the chemical nature and molecular size of the sorbate.

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### INTRODUCTION

Further developments in gas chromatography are dependent mainly on the increased utilization of specific polyfunctional porous polymer sorbents together with functional groups of different chemical natures. Such studies are reported in this paper.

### EXPERIMENTAL

#### *Sorbents*

Porous sorbents based on copolymers of butyl methacrylate (BMA) and triethylene glycol dimethacrylate (TGM) in the presence of the inert diluent *n*-heptane (Polysorbacrylate) and sorbents based on copolymers N-vinyl-3(5)-methylpyrazole (N-VMP) and ethylene glycol dimethacrylate<sup>1</sup> (EG-DMA) (Polysorbazole) as polyfunctional polymer sorbents with an abnormally high specificity of intermolecular interactions have been investigated.

The availability of the ether and ester active groups in one instance<sup>2</sup> and groups of the ester and pyrazole in the other<sup>1</sup> causes high specificity and polyfunctionality. Studies of the structural characteristics have shown that all of these sorbents are microporous, but differ in their specific molecular surface areas and pore volumes (Table I), depending on the different conditions used for their synthesis.

For example, of the sorbents based on BMA and TGM, the polyfunctional sorbents obtained by the copolymerization of 25% TGM and 75% BMA in the

TABLE I

## COMPOSITION AND STRUCTURAL CHARACTERISTICS OF POLYSORBACRYLATES AND POLYSORBAZOLES

Sorbent	Components			Pore volume (cm <sup>3</sup> /g)	Surface area (m <sup>2</sup> /g)
	Monovinyl monomer (%)	Cross-linking agent (%)	Diluent (%)		
Polysorbacrylate-1	BMA (75)	TGM-3 (25)	<i>n</i> -Heptane (80)	1.02	4.1
Polysorbacrylate-2	BMA (60)	TGM-3 (40)	<i>n</i> -Heptane (70)	1.44	0.9
Polysorbazole-1	N-VMP (80)	EG-DMA (20)	Isooctane (55)	0.92	3.2
Polysorbazole-2	N-VMP (40)	EG-DMA (60)	Polar solvent (100)	0.68	110

presence of 80% *n*-heptane have the most homogeneous pore size distribution. The specific surface area is 4 m<sup>2</sup>/g. Increasing the of cross-linking agent content from 25% to 40% causes a sharp increase in the pore volume and a decrease in the specific surface area.

It is possible to obtain polymer sorbents based on N-VMP and EG-DMA with different structural characteristics by changing the ratio of the monomers being copolymerized. Sorbents with a low specific surface area (less than 4 m<sup>2</sup>/g) and a very large pore size (up to 30,000 Å) were obtained by suspension copolymerization using 20–60% of the non-polar diluent isooctane. Pyrazole-containing polymer sorbents with a large specific surface area (100–300 m<sup>2</sup>/g) were obtained by polymerization in the presence of a polar diluent. The amount of the cross-linking agent was 50–80% of the total mixture of the monomers.

According to Kiselev, the investigated polymer sorbents, when classified by the local electron density of oxygen atoms in the ether groups and nitrogen atoms, are specific sorbents of the third type. We used Rohrschneider's method to estimate the specificity<sup>1</sup>. The retention indices of the polar molecules on the polymer sorbents investigated and the polarities of the sorbents are presented in Table II.

Polysorbacrylate-1, a copolymer of 25% TGM with 75% BMA, was obtained in the presence of 80% *n*-heptane. Polysorbazole-1, a copolymer of 20% EG-DMA with 80% N-VMP, was obtained in the presence of 55% isooctane. Polysorbazole-2, a copolymer of 40% N-VMP and 60% EG-DMA, was obtained in the presence of 100% polar diluent.

TABLE II

## RETENTION INDICES OF ROHRSCHEIDER TEST SUBSTANCES ON POLYSORBACRYLATE-1 AND POLYSORBAZOLE-1 AND -2

Compound	Sorbent					
	Squalane	Porapak T	Chromosorb 104	Polysorbacrylate-1	Polysorbazole	
					-1	-2
Ethanol	384	570	690	700	1140	550
Methyl ethyl ketone	531	700	680	775	1150	645
Benzene	649	755	835	980	1120	653
Nitromethane	457	715	935	880	1243	635
Pyridine	695	845	1025	988	1335	863
Polarity	0	869	1449	1607	3272	630

## RESULTS AND DISCUSSION

The results in Table II demonstrate that polyfunctional polymer sorbents with low specific surface areas surpass the most polar polymer sorbents (Porapak T and Chromosorb 104) with the same specific properties. Polysorbazole-2, with the highest specific surface area, is a sorbent of medium polarity, being slightly less polar than Porapak T.

In Fig. 1, it can be seen that the polyfunctional polymer sorbents display an abnormally high selectivity towards the compounds classified as Type D sorbates according to Kiselev's classification (aldehydes, alcohols, acids, primary amines, nitriles and nitro compounds).

Because of the high specificity of the intermolecular interactions, polyfunctional polymer sorbents with ether functional groups permit the separation of compounds with similar molecular weights (Table III) and approximately the same boiling points (Fig. 2).

When investigating the properties of these polymer sorbents, it was found that they are selective towards aromatic compounds (Table IV).

Pyrazole-containing polymer sorbents with low specific surface areas and abnormally high specificity possess the further advantageous property that they change the chromatographic polarity ( $\Sigma I$ ) by 23% when the column temperature is increased from 70° to 150°; the polarity with Polysorb increases by only 8.5% with the same temperature increase (Fig. 3). This difference in polarity increase is related to the fact that the pyrazole-containing polymer sorbent with a low specific surface area (up to 4 m<sup>2</sup>/g) changes its physical state from glass-like to elastic. This has been demonstrated by measuring the heat capacity with a scanning micro-calorimeter.

The properties of polyfunctional sorbents with pyrazole and ether functional groups, having a low specific surface area, permit the sorbent selectivity to be controlled simply by changing the temperature. This also means changing the elution sequence of polar and non-polar compounds.

The pyrazole-containing polymer sorbents based on N-VMP and EG-DMA with high specific surface areas (100–300 m<sup>2</sup>/g) are sorbents of medium polarity, and are better than Porapak with respect to the efficiency of chromatographic separations. For example, the HETP of the investigated sorbent was 1 mm using ethanol and 1.7 mm using *n*-pentane, compared with 3.2 and 2.3 mm, respectively, for Porapak Q under the same conditions. Because of their properties, these sorbents can be used successfully for the trace analysis of air and water contaminants.

*Mechanism of sorption on polymer sorbents*

At present, there is no unified opinion concerning the mechanism of sorption on the polymers. Some workers believe that the main factor determining the retention on polymer sorbents is adsorption on to the large polymer surface<sup>2-5</sup>, but others suggest that the decisive factor is the dissolution of the sorbates in the polymer matrix<sup>6,7</sup>. However, the majority believe that the separation on porous polymers is the result of a combination of simultaneous adsorption and absorption processes<sup>8</sup>.

There are some ways of solving the problem of the ratio of the adsorption and absorption processes on the polymers. One was described by Gearhart and Burke<sup>9</sup>,

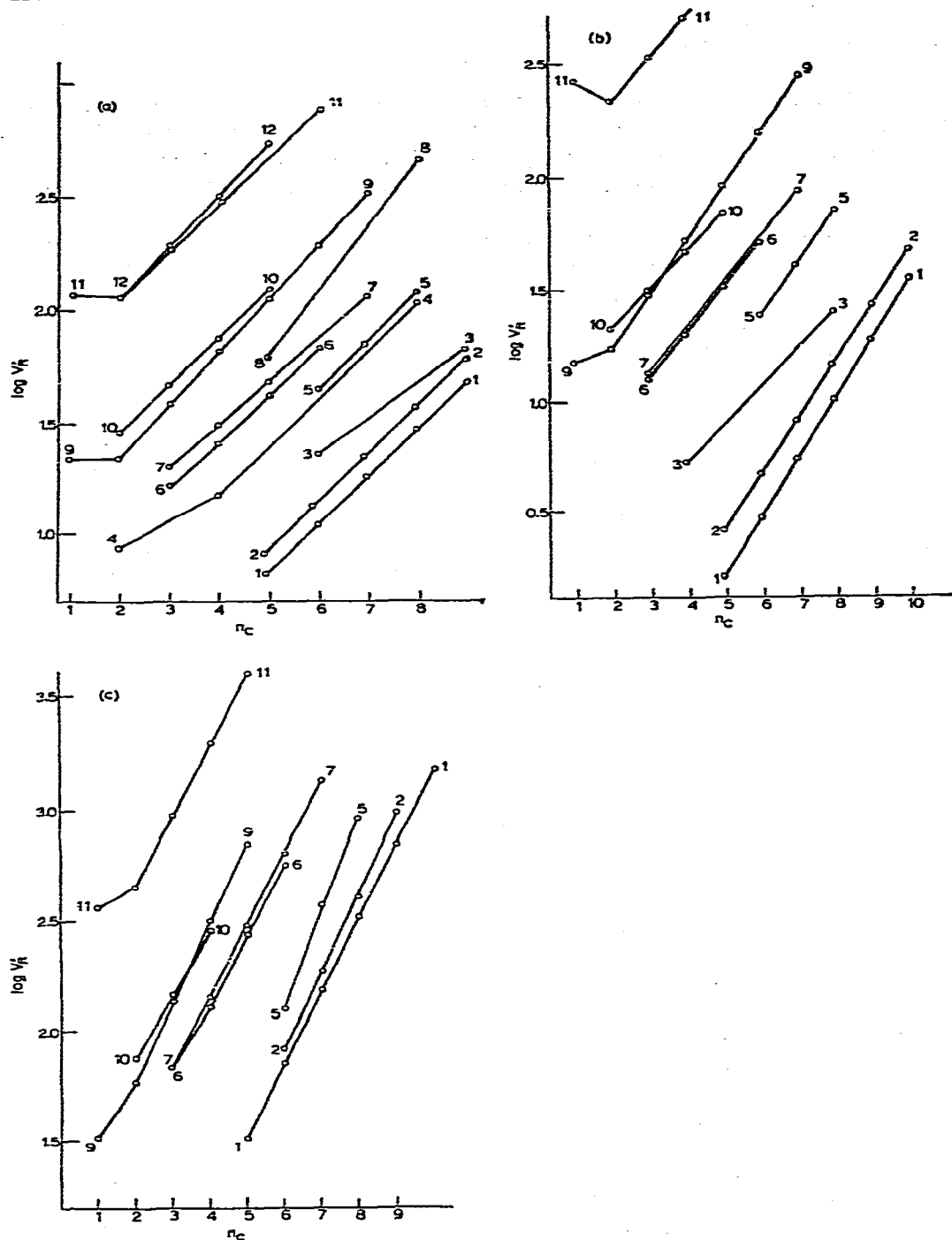


Fig. 1. Dependence of the logarithm of the adjusted retention volume ( $V_R^0$ ) on the number of carbon atoms ( $n_C$ ) for various homologous series at  $150^\circ$  on (a) Polysorbacrylate-1, (b) Polysorbazole-1 and (c) Polysorbazole-2. 1 = *n*-Alkanes; 2 = *n*-alkenes; 3 = *tert.*-amines; 4 = *sec.*-amines; 5 = alkylbenzenes; 6 = acetates; 7 = ketones; 8 = *n*-amines; 9 = alcohols; 10 = nitriles; 11 = acids; 12 = aldehydes.

TABLE III

## RETENTION INDICES OF COMPOUNDS WITH SIMILAR MOLECULAR WEIGHTS ON POLYSORBACRYLATE

Compound	Molecular weight	Retention index
<i>n</i> -Hexane	86.2	600
Ethyl acetate	88.1	740
<i>tert.</i> -Pentanol	88.1	860
Isopentanol	88.1	990
Valeronitrile	83.1	1060
Butyric acid	88.1	1235
Valeraldehyde	86.1	1350

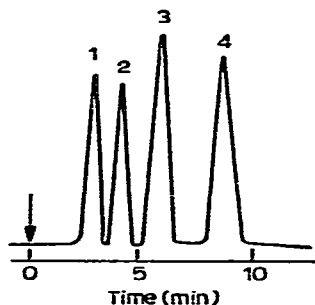


Fig. 2. Chromatogram of compounds with similar boiling points on Polysorbacrylate-1. 1 = Ethanol; 2 = methyl ethyl ketone; 3 = benzene; 4 = nitromethane.

who examined, with the help of the thermodynamic characteristics of the sorption, the retention mechanism of some sorbates on non-polar polymer sorbents. The interdependence between the standard deviation of the partial molar free energy ( $\Delta G$ ) and the entropy of sorption ( $\Delta S$ ) was used by Kiselev for the adsorption characteristics of carbon black<sup>2,10,11</sup>. According to Kiselev's values, the linear correlation between  $\Delta G$  and  $\Delta S$  is typical, at least for non-specific adsorption.

TABLE IV

## RETENTION INDICES OF AROMATIC AND NON-AROMATIC COMPOUNDS ON POLYSORBACRYLATE

Compound	Molecular weight	Boiling point (°C)	Retention index
<i>n</i> -Hexane	86.2	68.7	600
Benzene	78.1	80.2	888
<i>n</i> -Heptane	100.2	98.5	700
Toluene	92.8	110.8	988
<i>n</i> -Octane	106.2	125.8	800
<i>m</i> -Xylene	106.8	139.1	1088
Methyl hexyl ketone	128.2	173.0	983
Acetophenone	120.2	202.3	1393
Hexylamine	101.2	132.0	1042
Aniline	93.1	184.4	1416
Hexanol	102.0	157.0	1195
Phenol	94.1	182.0	1535

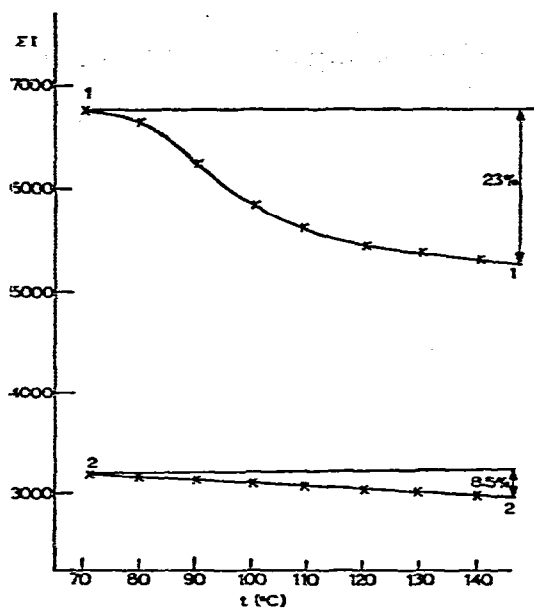


Fig. 3. Dependence of a change in chromatographic polarity ( $EI$ ) on column temperature. 1, Polysorbazole-1; 2, Polysorb-1.

In studying the dependence of  $\Delta G$  on  $\Delta S$  for polymer sorbents, Gerhard and Burke noted a deviation from linearity for some sorbents. They explained this deviation by a different kind of sorption mechanism. They also suggested that this absorption phenomenon leads to a decrease in the specific surface area and to an increase in the absorption capacity, with the changes depending on the form and size of the sorbate molecules. This theory has not been proved experimentally.

One of the purposes of this work was to determine the correlation between the standard deviation of the partial molar free energy and the entropy of sorption for the investigation of the sorption mechanism on the polymer sorbents. To this end, a comparative study of this dependence on Silochrom C-80 was carried out. Other stationary phases that were investigated were a polar liquid phase with ether functional groups (20% polyethylene glycol adipate coated on Risorb), polyfunctional polymer sorbent with ether functional groups, and Polysorb-1 and Porapak Q. The sorbates chosen for the latter investigation (ethanol, methyl ethyl ketone, benzene, nitromethane, pyridine and  $C_5$ - $C_{10}$  *n*-alkanes characterized the different types of intermolecular interactions.

Fig. 4 shows the correlation between  $\Delta G$  and  $\Delta S$  for the sorbates of interest on the investigated sorbents at different temperatures. It can be seen that a strict correlation between these two parameters is maintained, independent of the sorption mechanism. This study of the dependence of  $\Delta G$  on  $\Delta S$ , therefore, does not solve the problem of the correlation between adsorption and absorption on the pore surface of the polymer sorbents.

Further investigations aimed at determining the peculiarities of the mechanism of sorption on the polymer sorbents were performed. For this purpose, the correlation

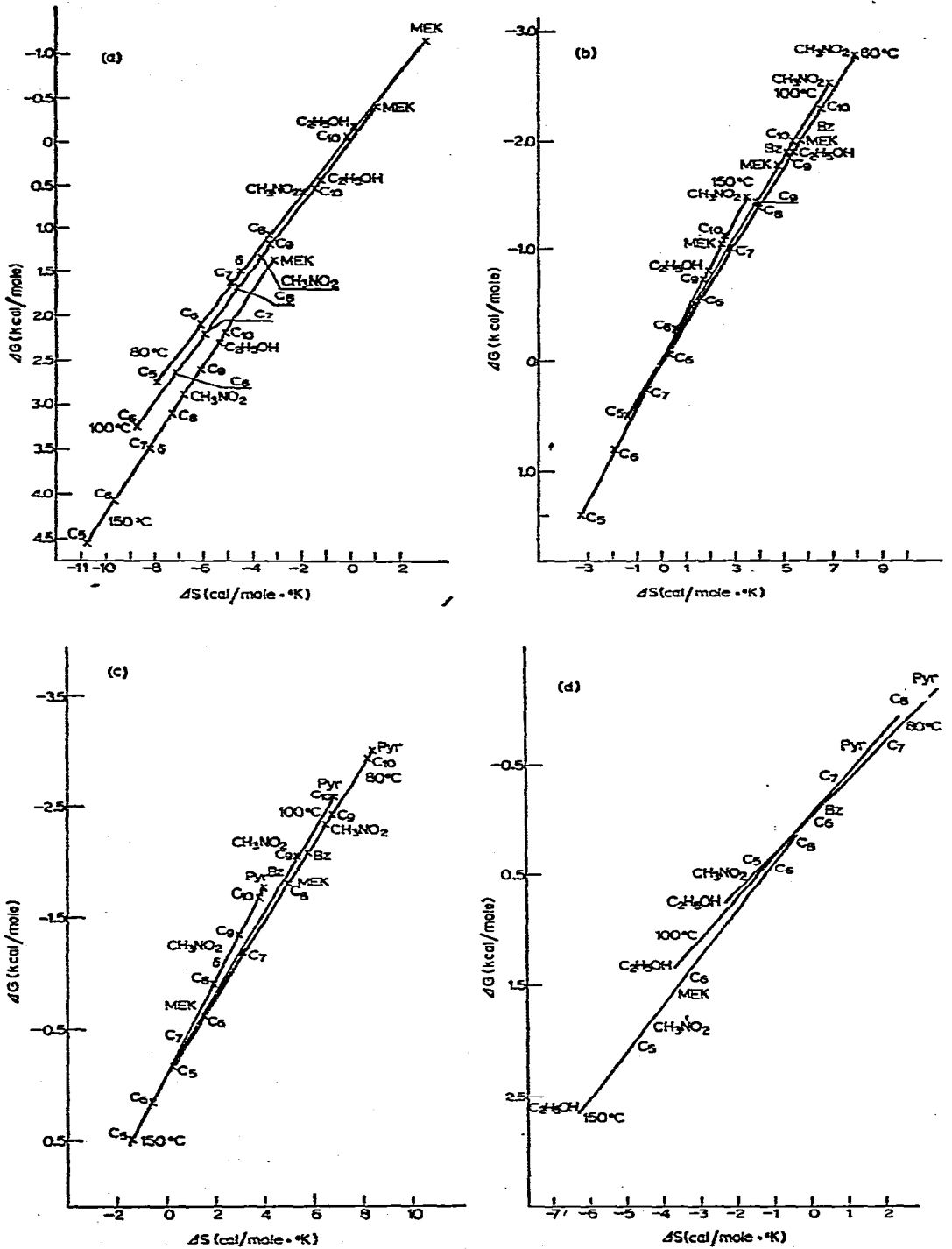


Fig. 4.

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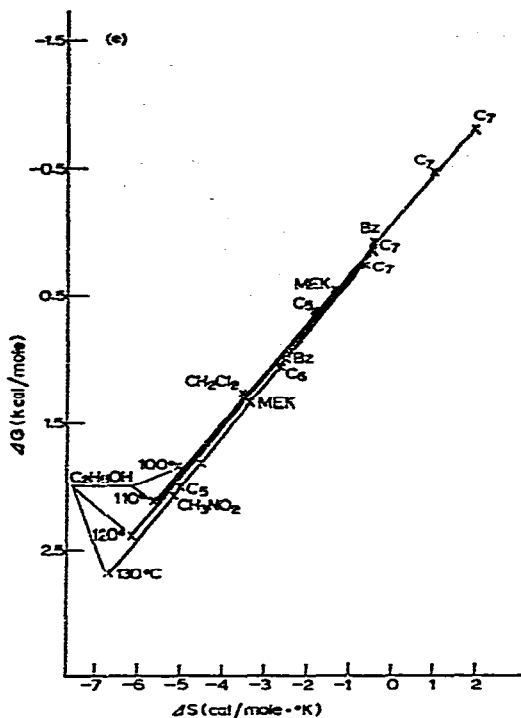


Fig. 4. Dependence of  $\Delta G$  on  $\Delta S$  for ethanol, nitromethane, methyl ethyl ketone (MEK), benzene (Bz,  $\delta$ ), pyridine (Pyr) and  $\text{C}_5$ – $\text{C}_{10}$  *n*-alkanes. (a) Silochrom C-80; (b) PEGA on Risorb BLK; (c) Polysorbacrylate-1; (d) Polysorb-1; (e) Porapak Q.

between the logarithm of the specific retention volume ( $\log V_g$ ) and the reciprocal of temperature ( $1/T$ ) was studied, within the temperature range corresponding to the change in physical state of the polyfunctional polymer sorbents. Fig. 5 demonstrates the dependence of  $\log V_g$  on  $1/T$  for polysorbazoles which differ in their structural properties and chemical compositions.

It can be seen in Fig. 5 that the polymer sorbents investigated with abnormally high specificity exhibit a different kind of dependence of  $\log V_g$  on  $1/T$  than do sorbents with normal specificities. For polar compounds (*e.g.*, ethanol, methyl ethyl ketone, nitromethane and pyridine), the dependence is linear, while for non-polar hydrocarbons in benzene the dependence is not linear within the investigated temperature range. Changes in the physical state of the polymer sorbent are taking place. Probably the different kind of dependence of  $\log V_g$  on  $1/T$  is related to the different type of interaction mechanism in this sorbate–polymer sorbent system than for the molecules with different chemical natures. The non-polar molecules are capable of the adsorption on the surface of the polyfunctional polymer sorbent. Therefore, the deviation of the dependence of  $\log V_g$  on  $1/T$  from linearity can apparently be related to the fact that changes in the structural properties of the polymer occur within the investigated temperature range. For the  $\text{C}_5$ – $\text{C}_8$  *n*-alkanes, *n*-pentane is the most sensitive sorbate to changes in physical state and *n*-octane is the least sensitive. As the



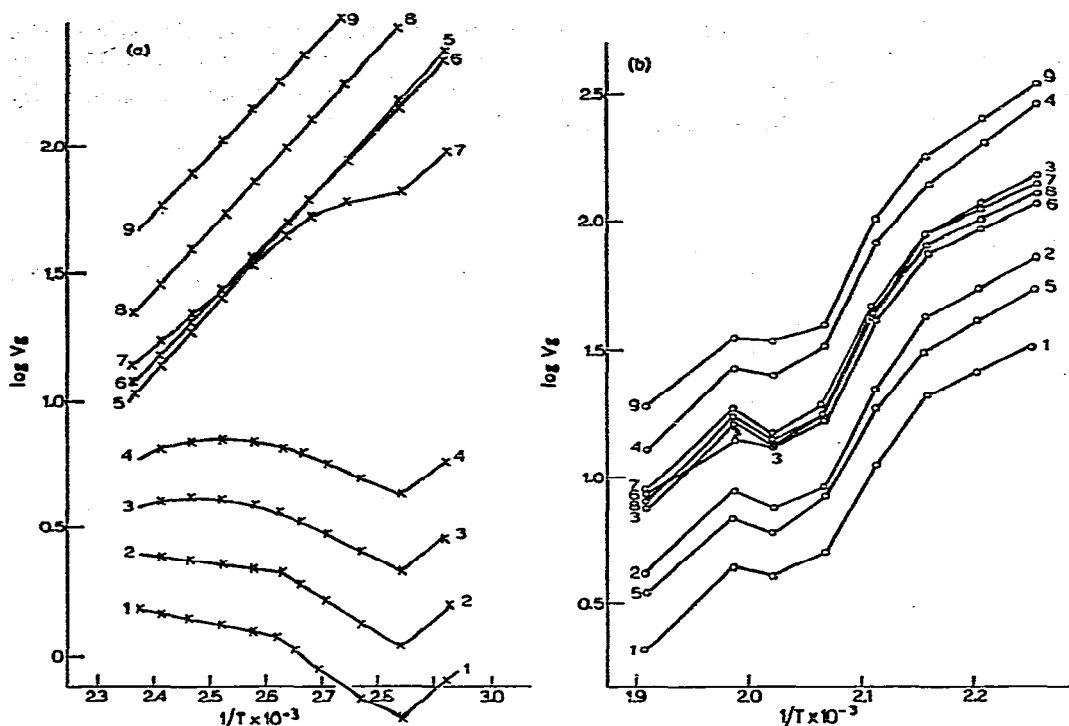


Fig. 5. Dependence of  $\log V_g$  on  $1/T$ . (a) Polysorbazole-1; (b) Polysorbazole-2.

chain length increases, penetration into the narrow pores becomes more difficult. As a result of the lower sensitivity of these molecules to changes in physical state, a change in retention can take place.

The molecules of the polar sorbate have the linear character of the dependence of  $\log V_g$  on  $1/T$ . Apparently these sorbate molecules penetrate into the polymer matrix at any sorbent temperature and change the physical state. The modification of the structural characteristics of the sorbent associated with this process influences the correlation between  $\log V_g$  and  $1/T$  for polar molecules.

The molecule of non-polar benzene is apparently capable of both adsorption on to the surface of the polymer sorbent and penetration into the sorbent matrix, *i.e.*, a combination of adsorption and absorption processes occurs (Fig. 5a). The analogous dependence of  $\log V_g$  on  $1/T$  for sorbate molecules on the polyfunctional polymer sorbent (Polysorbazole-2) is shown in Fig. 5b. On this sorbent, the deviation from the linear dependence of  $\log V_g$  versus  $1/T$ , corresponding to the change in physical state of the polymer in the range 190–230° range, is typical for all molecules, both polar and non-polar. It can be concluded that all molecules are sensitive to a change in the structural characteristics of the sorbent as well as to the interaction of the molecules within the sorbent of interest. The adsorption is also influenced by prior adsorption phenomena on the sorbent surface.

The results obtained permit the conclusion to be drawn that the mechanism of interaction in the system investigated (sorbate-polymer sorbent) has a complicated character that depends on the chemical nature, physical state and structural charac-

teristics of the sorbent, as well as on the chemical nature and molecular size of the sorbate. The distinction between the mechanism of interaction of polar and non-polar molecules with sorbents having a low specific surface area is apparently caused by the high polarities of those sorbents (Table II).

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