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## PHYSICO-CHEMICAL AND CHROMATOGRAPHIC PROPERTIES OF PYRAZOLE-CONTAINING POLYMER SORBENTS

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### SUMMARY

Logarithms of the specific retention volumes of some pyrazole-containing polymer sorbents with different alkane sorbates (from pentane to dodecane) and Rohrschneider series sorbates have been investigated. The sorption mechanism has been examined by correlating the retention, swelling and calorimetric data.

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### INTRODUCTION

In previous work the gas chromatographic properties of pyrazole-containing polymer sorbents (analytical possibilities, influence of temperature, polarities) were studied<sup>1</sup>. The polymers concerned are of the amorphous type and their physical state is dependent on temperature: glassy, highly elastic or high-viscosity liquid. Each of these states is characterized by different mobilities. For chromatography the glassy and the highly elastic states are of particular interest. The transition state is also of interest, because during this transition changes in the sorption mechanism can take place.

The investigation of pyrazole-containing sorbents showed that they have some properties that differ from those of other sorbents. We therefore considered it of interest to attempt to elucidate the peculiarities of the sorption mechanism with pyrazole-containing sorbents and to study the dependence of HETP on temperature for temperature ranges covering the different physical states of the sorbents.

### EXPERIMENTAL

Pyrazole-containing sorbents based on copolymers of N-vinyl-3(5)-methylpyrazole with divinyl substances such as divinylbenzene and ethylene glycol dimethacrylate, obtained in the presence of *n*-nonanol-polysorbazole and -polysorbatazole polymers were studied. The sorbent index corresponds to the amount of the cross-linking agent used in the synthesis. The sorbents investigated differ in their specific surface area, which was determined by the heat of desorption of nitrogen.

Gas chromatographic analyses were carried out in stainless-steel columns (1 m × 3 mm I.D.) at 50–270°C with helium as the carrier gas at a flow-rate of 30 ml/min and with a katharometer detector.

## RESULTS AND DISCUSSION

The dependence of the logarithms of the specific retention volumes for C<sub>5</sub>–C<sub>12</sub> alkane, methyl ethyl ketone, ethanol, nitromethane, benzene and pyridine sorbates on the reciprocal of temperature was investigated for pyrazole-containing polymer sorbents synthesized with the use of different amounts of cross-linking agents (Figs. 1–6).

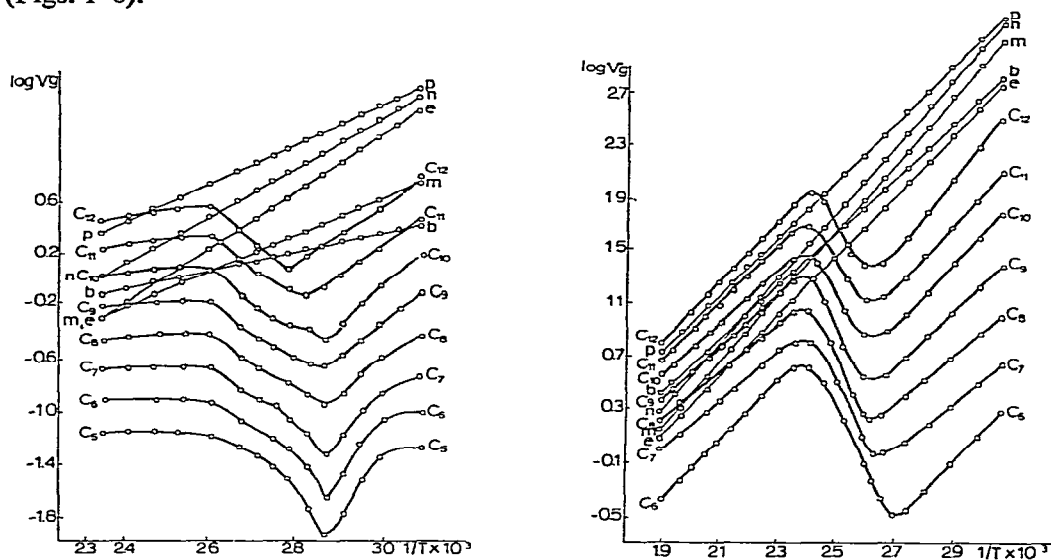


Fig. 1. Dependence of  $\log V_g$  on  $1/T$  for polysorbazole-8. C<sub>5</sub>–C<sub>12</sub> = *n*-Alkanes, b = benzene, m = methyl ethyl ketone, e = ethanol, n = nitromethane and p = pyridine.

Fig. 2. Dependence of  $\log V_g$  on  $1/T$  for polysorbatozole-20. Compounds as in Fig. 1.

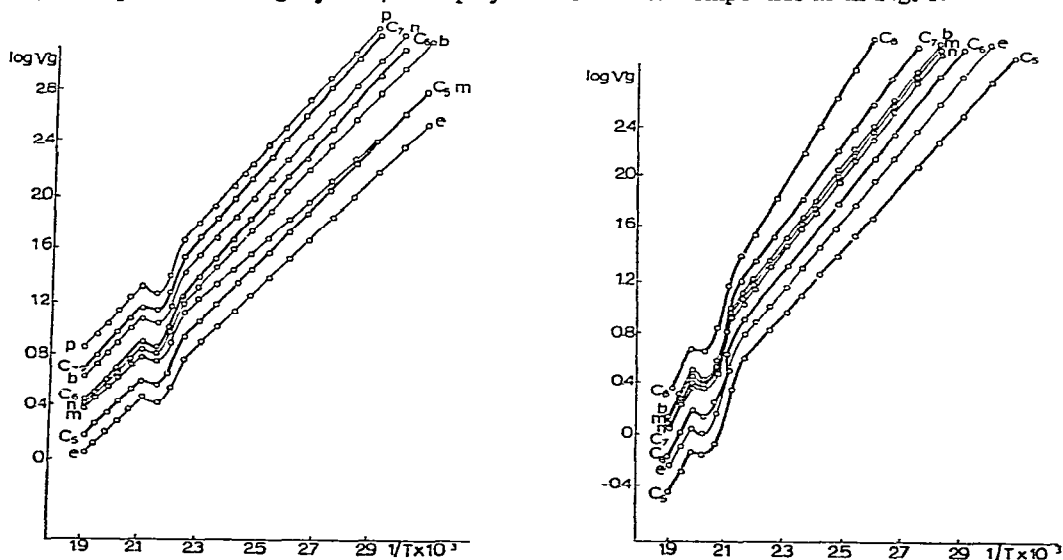


Fig. 3. Dependence of  $\log V_g$  on  $1/T$  for polysorbazole-40. Compounds as in Fig. 1.

Fig. 4. Dependence of  $\log V_g$  on  $1/T$  for polysorbatozole-60. Compounds as in Fig. 1.

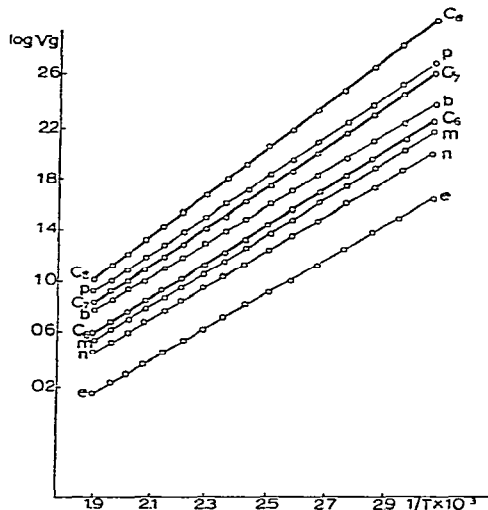


Fig. 5. Dependence of  $\log V_g$  on  $1/T$  for polysorbazole-60. Compounds as in Fig. 1.

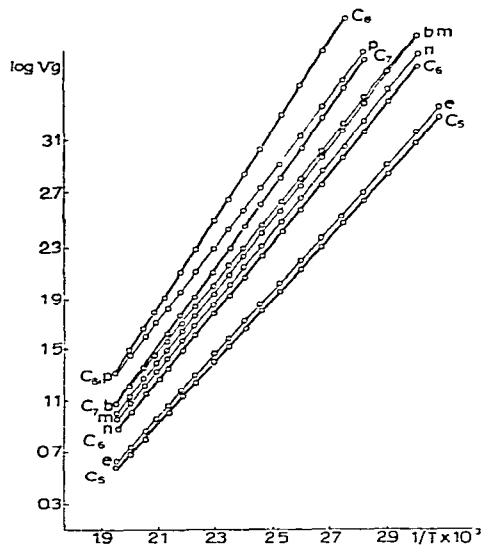


Fig. 6. Dependence of  $\log V_g$  on  $1/T$  for polysorbatozole-80. Compounds as in Fig. 1.

Figs. 1 and 2 show the dependences of  $\log V_g$  on  $1/T$  for some sorbates using pyrazole-containing polymer sorbents with low specific surface areas (up to  $7 \text{ m}^2/\text{g}$ ). Within the temperature ranges corresponding to the transition from the glassy state to the highly elastic state some distortion of the regularity of the retention takes place. The chromatographic data correlate well with the scanning calorimetric results, shown in Figs. 7 and 8, which illustrate the thermal capacity curves of the polysorbazole-8 and polysorbatozole-20. The temperature transition points established by using gas chromatography are exhibited more clearly.

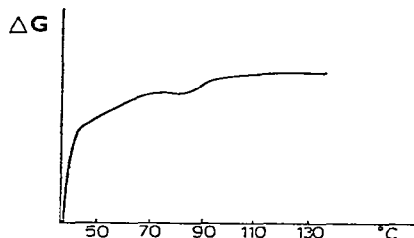
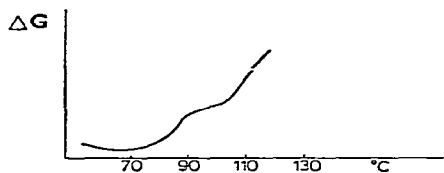


Fig. 7. Change in heat capacity ( $\Delta G$ ) on polysorbazole-8.

Fig. 8. Change in heat capacity ( $\Delta G$ ) on polysorbatozole-20.

The changes in the physical state of the polymer sorbent are detected by using alkanes, the molecules of which are inert towards the polymers because of their very low thermodynamic affinity towards them. Sorbates belonging to the Rohrschneider series cannot detect this transition point (for methyl ethyl ketone, ethanol, nitromethane, benzene and pyridine the dependence of  $\log V_g$  on  $1/T$  is linear).

It appears that when chromatography takes place on the pyrazole-containing polymer sorbents at temperatures lower than the glass transition temperature of the

polymer the alkane molecules do not penetrate into the solid polymer phase and only adsorption at the polymer surface can explain the retention of the alkane molecules. Within the glass transition temperature range intensive penetration of the alkane molecules into the bulk of the polymer sorbent begins. As a result of the incipient diffusion of the alkane molecules into the bulk of the polymer strengthening of the sorbate retention occurs, as the number of vacant sorption sites for the alkane molecules is increased because of the increased flexibility of the polymer sections. At temperatures above the glass transition temperature, when the polymer is already into the highly elastic state and the number of vacant sorption sites is not increased any further, a decrease in the retention volume occurs when the temperature is increased further.

In order to investigate the possibility of penetrating into the polymer sorbent bulk, the swelling process with  $C_5$ – $C_{12}$  alkanes at different temperatures was investigated. The results obtained in the swelling study correlated well with those obtained gas chromatographically, which leads to the conclusion that with pyrazole containing polymer sorbents with a low specific surface area the mechanism of sorption of alkane molecules is determined by the physical state of the polymer sorbent.

Figs. 3 and 4 show the temperature dependences of the specific retention volumes for  $C_5$ – $C_8$  alkanes and Rohrschneider series substances using polysorbazole-40 and polysorbatozole-60, with specific surface areas of 206 and 110  $m^2/g$ , respectively. Within the temperature ranges appropriate to changes in the physical state of the polymer sorbents for all sorbate molecules (polar and non-polar) this dependence is non-linear. Apparently, with these pyrazole-containing polymer sorbents the sorption mechanism for the alkane molecules, benzene and polar molecules would be similar.

Owing to the considerable specific surface areas of the polymer sorbents, the contribution of adsorption of the Rohrschneider series molecules to the total sorption process is increased. This fact was also shown by the results of the swelling investigation on the above-mentioned sorbents using ethanol, methyl ethyl ketone, benzene, pyridine and nitromethane.

When the column temperature is increased above the glass transition temperature of the polymer sorbent, for all of the sorbate molecules investigated a change in the sorption mechanism occurs as a result of the increase in the absorption interaction contribution.

The study of the temperature dependence of  $\log V_g$  for the same sorbate molecules using polysorbazole-60 and polysorbatozole-80, with specific surface areas of 396 and 305  $m^2/g$ , respectively, showed that for all sorbate molecules the dependences are linear. Hence for these pyrazole-containing polymer sorbents the changes in physical state occur at higher temperatures, and one can assume that in all temperature ranges the sorption mechanisms would be similar for the indicated sorbate molecules, *i.e.*, mainly adsorption.

The curves in Figs. 1–6 show that with increasing amount of cross-linking agent in the pyrazole-containing polymer sorbents the glass transition temperature of the investigated sorbents increases and the transition temperature becomes less significant.

When the amount of the cross-linking agent is 60–80%, which results in sorbents with large specific surface areas, these dependences become linear (Figs. 5

and 6). Evidently, this phenomenon is related to the increasing adsorption contribution to the sorbate-polymer sorbent interaction.

Braun *et al.*<sup>2</sup> expressed a similar opinion concerning the influence of adsorption on the detection of the transition temperature.

For the polymer sorbents investigated the sorption mechanism is very complicated and depends on the thermodynamic affinity of the sorbate molecules towards the polymer sorbent, chemical composition, physical state and porous structure of the polymer sorbent, and the column temperature.

For the pyrazole-containing polymer sorbents the transition from the glassy to the highly elastic state influences not only the dependence of  $\log V_g$  on  $1/T$  but also the dependence of HETP on  $T$  (Figs. 9 and 10). In Fig. 9 this type of dependence is shown for polysorbatozole-40, which has a glass transition temperature of about 180°C. It is at this temperature that some deterioration of the efficiency of sorbates of interest (pentane, hexane and nitromethane) is seen.

This phenomenon is observed more sharply for the dependence of HETP on  $T$  with polysorbatozole-20 when the sorbate is an alkane. In this instance, for alkane molecules at the glass transition temperature the HETP is maximal, but the decrease in the efficiency within the glass transition temperature range is greater for alkane molecules with a large molecular mass (for nonane it is greater than for hexane) and at high temperatures.

At temperatures above the glass transition temperature the interaction of the alkane molecules is mainly absorption, and in this instance when the temperature increases the HETP decreases. This is confirmed by the character of the dependence

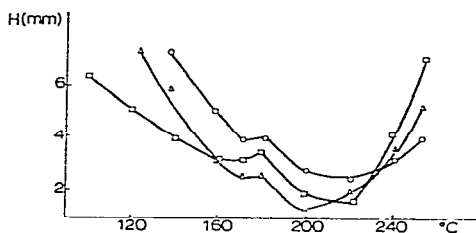


Fig. 9. Dependence of HETP on  $T$  for polysorbatozole-40.  $\Delta$ , Pentane,  $\circ$ , hexane;  $\square$ , nitromethane.

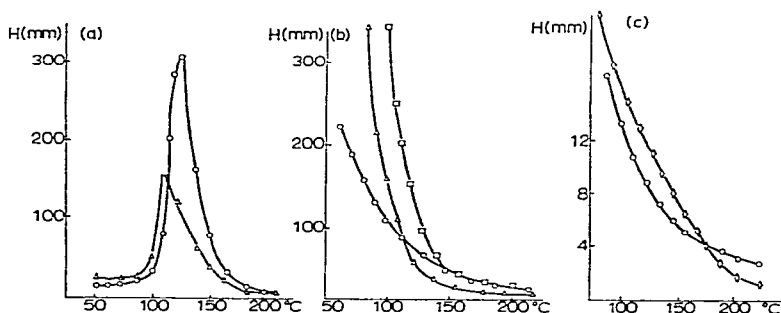


Fig. 10. Dependence of HETP on  $T$  on polysorbatozole-20. (a)  $\Delta$ , Hexane;  $\circ$ , nonane; (b)  $\circ$ , pyridine;  $\square$ , benzene;  $\Delta$ , methyl ethyl ketone; (c)  $\diamond$ , ethanol;  $\circ$ , nitromethane.

of HETP on  $T$  with polysorbazole-20 for polar substances that are capable of absorption interactions. For this type of sorbate molecule, on increasing the temperature monotonous decreases in HETP (Fig. 10) and  $\log V_g$  with  $1/T$  (Fig. 2) occur.

For the alkane molecules, at the glass transition temperature their partition coefficient and diffusion coefficient change, and a new stationary phase is created with physico-chemical characteristics that differ from the initial ones.

#### REFERENCES

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- 2 J.-M. Braun, A. Lavoia and J. Guillet, *Macromolecules*, 8 (1975) 311.