

CHROM. 10,927

## STUDY OF SOME POLYMERIC SORBENTS BY ADSORPTIVE AND CALORIMETRIC METHODS

K. I. SAKODYNSKY, V. E. OSTROVSKY and L. D. GLASUNOVA

*Karpov Institute of Physical Chemistry, Ul. Obuka 10, 107120 Moscow B-120 (U.S.S.R.)*

(First received November 3rd, 1977; revised manuscript received February 3rd, 1978)

---

### SUMMARY

The porous structure, specific surface area and surface heterogeneity of two polymeric sorbents, polydivinylbenzene (PDBV) and the co-polymer of divinylbenzene (15%) with 2,5-methylvinylpyridine (Polysorb N), have been studied. A mechanism for the adsorption of linear aliphatic hydrocarbons on these sorbents is discussed.

---

### INTRODUCTION

Polymeric sorbents are extensively used in gas chromatography, but little is known about their adsorptive properties. In this work, in order to study the porous structure and to estimate the specific surface area of sorbents, the pore distribution over the effective radii was measured using both mercury porosimetry and the desorption isotherm of preliminarily-adsorbed (at  $-196^{\circ}$ ) nitrogen (nitrogen porosimetry). Nitrogen and krypton adsorption (at  $-196^{\circ}$ ) and butane adsorption (at  $25^{\circ}$ ) were calculated by the BET procedure. Data on the adsorption equilibria and heats of adsorption of propane, propylene, *n*-butane and *n*-pentane, at  $25^{\circ}$  and 1-500 Torr, were used to examine the surface heterogeneity.

### EXPERIMENTAL

Nitrogen porosimetry was performed with a Sorptomatic instrument (Carlo Erba, Milan, Italy) and mercury porosimetry with a Porosimeter (Carlo Erba). The heats of adsorption were measured in a Foska microcalorimeter<sup>1-4</sup> to an accuracy of  $\pm 1.5\%$ . The adsorption equilibria were studied in a statical type vacuum device, with the ampoule containing the adsorbent located in the calorimeter. The maximum error in the determination of the adsorbed gas was 5%.

### RESULTS AND DISCUSSION

Fig. 1 demonstrates the results of measuring the pore distribution over the effective radii in PDVB and Polysorb N. The pore distribution curve for Polysorb

N has a maximum in the region 130–140 Å (curve 1) whereas for PDVB the curves (2 and 3) have no maxima, *i.e.* PDVB does not contain pores of the prevailing size. The pore distribution in PDVB obtained at 25° by mercury porosimetry differs from that obtained at –196° by nitrogen porosimetry. At room temperature, besides fine pores detected in PDVB at –196°, there are pores with radii greater than 140 Å. This may be due both to the fact that the polymer is thermoreactive, which results in contraction of the matrix on cooling, and to the formation of new pores during expansion of the matrix, which was observed during measurements of the porosity up to 1000 atm. In order to pin-point the reason for this discrepancy, the results of measurements of the surface area at different temperatures should be considered. The concept of the surface area of polymeric sorbents differs from that of crystalline solids. In the former case the surface area is the sum of one-dimensional sections of cross-linked polymeric filaments.

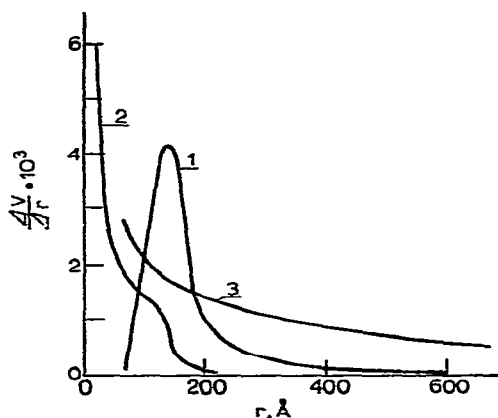


Fig. 1. Pore distribution over the effective radii. 1, Polysorb N (25°); 2, PDVB (–196°); 3, PDVB (25°).

The expression of a one-dimensional surface area in square metres is conditional, and results from the assignment of a certain surface area to each molecule adsorbed on the polymer. In our calculation of surface area using the BET procedure, we assumed that the area occupied by a nitrogen<sup>5</sup> molecule is 16.2 Å<sup>2</sup>, by a krypton<sup>6</sup> molecule 19.6 Å<sup>2</sup> and by a butane<sup>\*</sup> molecule 27 Å<sup>2</sup>. Table I shows that the specific surface area of Polysorb N determined at –196° by nitrogen and krypton adsorption methods is approximately 0.65 of that determined at 25°. The results obtained by calculating the surface area from the porosity data are in good agreement with those based on butane adsorption at 25° and calculated using the BET procedure. The data show that the polymer is thermoreactive in the temperature region from –196 to

\* Different values of the surface area for the butane molecule appear in the literature. Therefore, we first determined surface areas occupied on wide-pore silica gel by nitrogen and krypton adsorption methods (double measurements). The following values were obtained: 22, 22 and 24 m<sup>2</sup>/g; the mean value was 22.7 m<sup>2</sup>/g. Then, using the adsorption isotherm of butane on silica gel and the BET equations, we calculated the surface area that ought to be assumed for a butane molecule in order to obtain this mean value. The result, 27 Å<sup>2</sup>, thus obtained was used in our calculations on polymeric sorbent surfaces.

TABLE I

CONDITIONS FOR PRELIMINARY TREATMENT OF SORBENTS AND THE SPECIFIC SURFACE AREA AS DETERMINED BY THE BET METHOD ( $S_{\text{BET}}$ ) AND CALCULATED FROM POROSITY ( $S'$ ) DATA

Sorber	Conditions for preliminary treatment	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )			$S'$ ( $25^\circ$ ) ( $\text{m}^2/\text{g}$ )
		Crypton ( $-196^\circ$ )	Nitrogen ( $-196^\circ$ )	Butane ( $25^\circ$ )	
PDVB	$150^\circ$ , $10^{-3}$ torr, 25 h	—	290**	—	—
Polysorb N	$150^\circ$ in helium flow, 24h, evacuated at $25^\circ$ for 14h	44**	38* 40**	61**	59**

\* Before experiments in calorimeter.

\*\* After experiments in calorimeter.

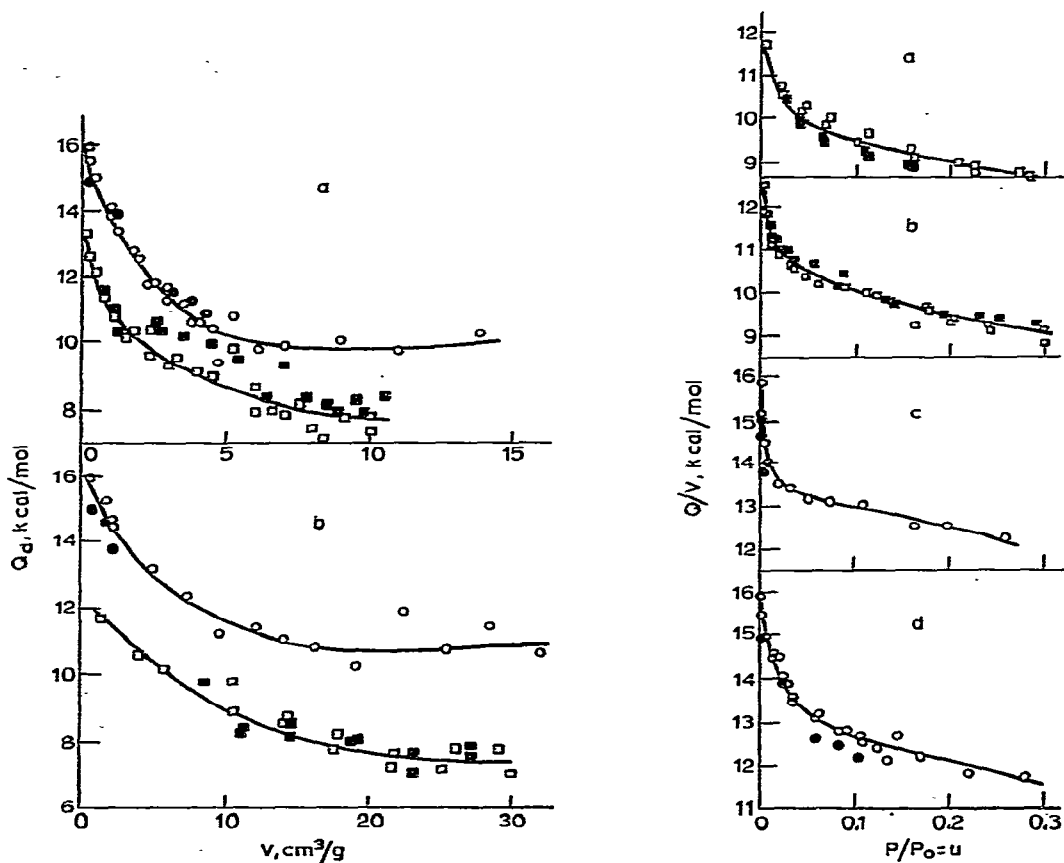


Fig. 2. Differential adsorption heats of *n*-butane and *n*-pentane on Polysorb N (a) and PDVB (b). □, *n*-Butane (adsorption); ■, *n*-butane (desorption); ○, *n*-pentane (adsorption); ●, *n*-pentane (desorption).

Fig. 3. Dependence of integral adsorption heat of *n*-butane and *n*-pentane on relative pressure,  $u$ . (a) *n*-Butane on PDVB; (b) *n*-butane on Polysorb N; (c) *n*-pentane on PDVB; (d) *n*-pentane on Polysorb N.

25°. These results indicate that the nature of the porosity really does change with increasing temperature (see Fig. 1).

Fig. 2 shows the results of measuring differential adsorption heats for *n*-butane and *n*-pentane on PDVB and Polysorb N. Similar dependences were obtained for the adsorption of propane and propylene<sup>7</sup>. It is noteworthy that adsorption is completely reversible in the systems under study, with the time to equilibrium being *ca.* 10 min for both adsorption and desorption. A decrease in differential adsorption heats with increasing adsorption could be explained either by heterogeneity of the sorbent with respect to the adsorption ability or by a polymolecular adsorption model. In the case of polymolecular adsorption, the integral adsorption heat,  $Q$ , is related to the relative pressure,  $u$ , by the equation<sup>8</sup>

$$Q/V = E_1 - (E_1 - E_L)u \quad (1)$$

where  $V$  is the volume of the vapour adsorbed,  $E_1$  is the adsorption heat in the first layer and  $E_L$  is the heat of vapour condensation. Fig. 3 shows that a plot of  $Q/V$  against  $u$  does not give a straight line. This means that the polymolecular adsorption model does not hold. Thus, to explain the dependence of adsorption heats on the amount of the vapour adsorbed, it is necessary to assume that the surface of the sorbents studied is heterogeneous with respect to adsorption ability.

The application of the theory of polymolecular adsorption on heterogeneous surfaces<sup>9,10</sup> makes possible the interpretation of experimental data using hydrocarbon isotherms. Figs. 4 and 5 illustrate adsorption isotherms for *n*-butane on PDVB and *n*-pentane on polysorb N obtained at 25°. The continuous curves were calculated theoretically in accordance with the isotherm equation<sup>10</sup> of polymolecular adsorption on a surface, which is characterized by an exponential distribution of points with respect to the adsorption ability. The equation takes the form:

$$V = \frac{\pi\gamma D}{\sin \pi\gamma} \cdot \frac{u^\gamma}{(1-u)^{\gamma+1}} - \frac{\gamma Du}{(1-u)^2(1-\gamma)} \cdot \left[ 1 - \frac{1-\gamma}{2-\gamma} \left( \frac{u}{1-u} \right) + \frac{1-\gamma}{3-\gamma} \cdot \left( \frac{u}{1-u} \right)^2 - \frac{1-\gamma}{4-\gamma} \cdot \left( \frac{u}{1-u} \right)^3 + \dots \right] \quad (2)$$

The constants  $\gamma$  and  $D$  were determined from the experimental data using the dependence of  $V$  on  $u$ . For small values of  $u$  ( $< 0.02$ ) the second term in eqn. 2 may be neglected. From a plot of  $\log [V(1-u)]$  against  $\log [u/(1-u)]$ , a value for  $\gamma$  can be obtained from the slope of the line and  $D$  can be calculated from the intercept on the ordinate axis. The values of  $V$  at different values of  $u$  were found from eqn. 2, and the theoretical curves then plotted. Figs. 4 and 5 show that the experimental points are described by the theoretical curves within the limits of accuracy imposed by the determination of the volume of adsorbed gas. Thus eqn. 2 describes the experimental data within the range  $0.001 < u < 0.3$ , *i.e.* within a wider range than the BET theory of polymolecular adsorption on homogeneous surfaces ( $0.05 < u < 0.3$ ). This increased range is important, because for  $u < 0.05$  more than half of the monolayer is adsorbed. If  $u > 0.3$ , the theoretical curve deviates from the experimental points. This may be related to the fact that the theory of poly-

molecular adsorption does not take into consideration the adsorbate-adsorbate interactions on the sorbent surface. Heats of adsorption are better described by the theory of polymolecular adsorption than by the common BET theory<sup>11</sup>. All the results indicate that the polymeric sorbents are sufficiently heterogeneous with respect to their adsorption ability.

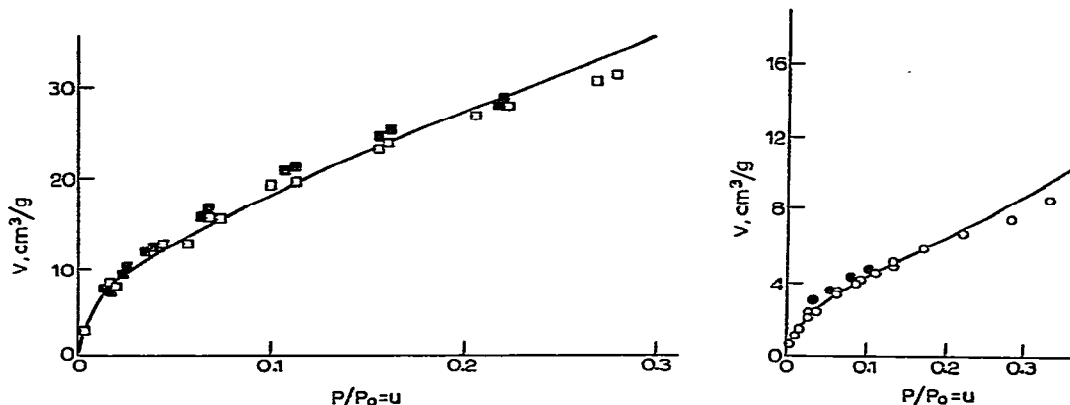


Fig. 4. Adsorption isotherm of *n*-butane on PDVB. The continuous curve is obtained according to the theory of polymolecular adsorption on heterogeneous surfaces; the points are experimental data (□, adsorption; ■, desorption).

Fig. 5. Adsorption isotherm of *n*-pentane on Polysorb N. The continuous curve is obtained according to the theory of polymolecular adsorption on heterogeneous surfaces; the points are experimental data (○, adsorption; ●, desorption).

A mechanism of hydrocarbon adsorption on polymeric surfaces of this kind has been proposed<sup>12</sup>. Fig. 6 shows that the initial heat of adsorption (at zero filling) of linear aliphatic hydrocarbons on PDVB and Polysorb N is proportional to the

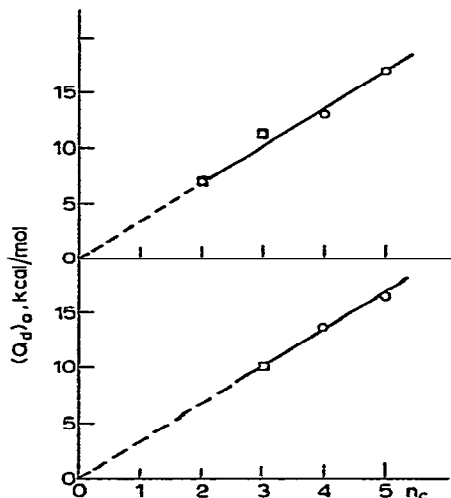


Fig. 6. Dependence of initial heats of hydrocarbon adsorption on the number of carbon atoms,  $n_c$ , in the hydrocarbon molecule. ○, paraffins; □, olefins.

number,  $n_c$ , of carbon atoms in the hydrocarbon molecule. The sorbents under consideration have structures consisting of cyclic groups connected by hydrocarbon bridges. The spatial structure of these bridges is similar to that of the sorbate molecules. The linear relationship shown in Fig. 6 indicates that at low coverages the hydrocarbon molecules are adsorbed on hydrocarbon bridges as if covering them. The heat of adsorption is the sum of the heat effects of twin Van der Waals interactions of sorbent and sorbate carbon atoms.

It should be noted that the initial heats of adsorption of ethane and propane do not differ, within the limits of accuracy, from those of ethylene and propylene, respectively.

#### REFERENCES

- 1 V. E. Ostrovsky, N. V. Kulkova, I. R. Karpovich and M. I. Temkin, *Zh. Fiz. Khim.*, 37 (1963) 2596.
- 2 V. E. Ostrovsky, N. N. Dobrovolsky, I. R. Karpovich and F. Ya. Frolov, *Zh. Fiz. Khim.*, 42 (1968) 550.
- 3 V. E. Ostrovsky, O. S. Veselov and L. D. Glasunova, *Zh. Fiz. Khim.*, 48 (1974) 2375.
- 4 A. N. Abdrakhimova, L. D. Glasunova, V. E. Ostrovsky, L. I. Panina and K. I. Sakodynsky, *Sbornik V Vsesoyuz. Konferenz. po Kalorimetrii*, Izd. MGU, 1971, p. 263.
- 5 W. D. Harkins and G. Jura, *J. Amer. Chem. Soc.*, 66 (1944) 1366.
- 6 R. A. Beebe, J. B. Beckwith and J. M. Honig, *J. Amer. Chem. Soc.*, 67 (1945) 1554.
- 7 L. D. Glasunova, V. E. Ostrovsky, L. I. Panina and K. I. Sakodynsky, *Trudy Khim. i Khim. Tekhnol.*, Vol. 2, Gorky, 1974, p. 99.
- 8 V. E. Ostrovsky, A. N. Abdrakhimova and K. I. Sakodynsky, *Doklady Akad. Nauk SSSR*, 208 (1973) 654.
- 9 M. I. Temkin and V. E. Ostrovsky, *Doklady Akad. Nauk SSSR*, 216 (1974) 1339.
- 10 V. E. Ostrovsky, *Zh. Fiz. Khim.*, 50 (1976) 1221.
- 11 L. D. Glasunova, V. E. Ostrovsky and K. I. Sakodynsky, *Zh. Teor. i Eksp. Khim.*, 12 (1976) 482.
- 12 V. E. Ostrovsky and L. D. Glasunova, *Kinetika i Katalis*, 48(4) (1977) 995.