

CHROM. 16,403

## Note

### Adsorption of polar groups on cross-linked poly(styrene-vinylpyridine) supports

REINALDO RUGGIERO, ROBERT A. M. C. DE GROOTE and MIGUEL G. NEUMANN\*

*Instituto de Física e Química de São Carlos, Universidade de São Paulo, C.P. 369, São Carlos-SP (Brazil)*

(First received June 6th, 1983; revised manuscript received October 31st, 1983)

The use of microporous polymers as gas chromatographic supports is well established. Since early work by Hollis<sup>1</sup>, several commercial products have been developed for specific types of separations covering a wide field of applications. Nevertheless, little work has been done to elucidate the separation mechanism from the point of view of the interactions between the support and the substrates.

Several studies aiming to characterize thermodynamically the behaviour of commercial microporous polymers have been carried out<sup>2-6</sup>, but in general with a lack of knowledge of the chemical structure of the supports. Zado and Fabecic<sup>6</sup> studied the difference in the adsorption of Porapak Q and T using a group contribution approach. Hertl and Neumann<sup>7</sup> studied the adsorption of amines and other compounds on Chromosorb 102, proving the existence of a specific charge-transfer interaction between the terminal vinyl groups and the amino nitrogens. Lindsay Smith *et al.*<sup>8</sup> studied the behaviour of a series of substrates on chemically modified polyaromatic supports, and the interaction effects between various organic compounds and synthesized substituted polystyrene polymers<sup>9</sup>.

From the data in the literature, it can be deduced that styrene-divinylbenzene polymers (Chromosorb 102, Porapak Q, etc.) are not suitable for the analysis of aliphatic amines owing to severe tailing of the elution peaks<sup>10</sup>. On the other hand, vinylpyridine-divinylbenzene polymers have been shown to be good columns for amines<sup>11</sup>. In order to find an explanation for this difference, we studied the adsorption energies of hydrocarbons, amines and alcohols on a series of styrene-divinylbenzene-vinylpyridine polymeric supports with various contents of vinylpyridine, and correlated the results with the chromatographic behaviour.

#### EXPERIMENTAL

Several microporous styrene-divinylbenzene-vinylpyridine copolymers were prepared by emulsion polymerization as described by Woeller and Pollock<sup>12</sup>. The synthesized material was crushed and sieved to 60-100 mesh and packed into 1 m × 1/8 in. O.D. stainless-steel columns. The proportion of vinylpyridine incorporated in the polymer was calculated from the nitrogen content, determined by elemental analysis, and is shown in Table I.

All chemicals were of analytical-reagent grade and were used without further

purification, except for styrene, which was distilled before use in order to separate the polymerized fraction.

Retention times at various temperatures (80–150°C) and constant flow-rates were measured on a C.G. Model 3537 gas chromatograph (Equipamentos Científicos C.G., São Paulo, Brazil) with thermal conductivity detection, using hydrogen as the carrier gas. Minimal amounts (<0.1  $\mu$ l) of substrate were injected directly into the column using a Hamilton microsyringe.

In some experiments, polymer A (with no vinylpyridine) was replaced with a commercial sample of Chromosorb 102.

Adsorption isotherms were determined on a Cahn Model 2000 microbalance.

## RESULTS AND DISCUSSION

Adsorption energies can be calculated from chromatographic data using the relationship

$$\ln V_g^0 = \frac{\Delta H_{\text{ads}}}{RT} + C \quad (1)$$

where  $V_g^0$  is the corrected retention volume at temperature  $T$ ,  $\Delta H_{\text{ads}}$  the adsorption energy,  $R$ , the gas constant and  $C$  an integration constant. Values of  $V_g^0$  are obtained experimentally from retention times, flow-rates and pressures at the inlet and outlet of the chromatographic column:

$$V_g^0 = k f j t'_R \quad (2)$$

where  $t'_R$  are the corrected retention times,  $j = \{1.5 [(P_i/P_0)^2 - 1]/[(P_i/P_0)^3 - 1]\}$  is the James–Martin factor,  $P_i$  and  $P_0$  being the pressures at the inlet and outlet of the column, respectively, and  $k$  is a constant composed of various parameters usually kept constant in a series of experiments (room temperature, atmospheric pressure, mass of absorbent). It can be seen from eqns. 1 and 2 that the adsorption energies can be calculated using corrected retention times instead of retention volumes if the flow-rate and the James–Martin constant (inlet pressure) are kept constant.

For each substrate on each support, the adsorption energies were determined by plotting the logarithm of the experimentally measured retention times ( $\ln t'_R$ ) against  $1/T$ . This procedure could be used because the adjustment of the flow-rate at different temperatures required only very small changes of the inlet pressure ( $\Delta P_i < 0.1 \text{ kg/cm}^2$ )\*. From these graphs the individual  $\Delta H_{\text{ads}}$  values were determined, and are given in Table I.

In order to evaluate the participation of the different groups constituting the substrate molecules, the total adsorption energy was assumed to be formed by the addition of group contributions<sup>13</sup>. As the compounds used were only hydrocarbons, aliphatic amines and alcohols, it was found convenient to divide the total adsorption energies into contributions due to hydrocarbon groups ( $\text{CH}_3$ ,  $\text{CH}_2$  and  $\text{CH}$ ), hydroxy groups ( $\text{OH}$ ), and amino groups ( $\text{NH}_2$ ). Thus, the contribution due to the hydro-

\* This approach corresponds to a maximum error of 0.3 kcal/mole in the group contributions.

TABLE I

ADSORPTION ENERGIES ( $-\Delta H_{\text{ads}}$ , kcal/mole) ON POLYMERIC SUPPORTS

Pyridine contents of polymers: A, 0.0; B, 22.6; C, 39.8; D, 62.7; and E, 99.5%.

Adsorbate	Polymer				
	A	B	C	D	E
<i>n</i> -Heptane	13.8	12.9	16.8	15.4	13.4
<i>n</i> -Octane	16.6	—	15.2	—	—
<i>n</i> -Nonane	—	22.3	—	—	16.1
Isopropylamine	8.5	4.8	4.6	3.6	2.2
Isobutylamine	9.2	6.9	3.3	3.4	1.7
<i>n</i> -Butylamine	10.2	5.3	3.2	—	2.4
Isopropanol	10.1	4.9	4.5	—	2.8
Isobutanol	11.5	6.9	5.1	—	3.0
<i>n</i> -Butanol	12.7	5.8	6.0	—	2.1

carbon groups,  $h_C$ , was calculated for each support by dividing the total adsorption energy by the number of carbon atoms in the hydrocarbons. From this value, the contributions of the amino and hydroxy groups,  $h_N$  and  $h_O$ , respectively, could be calculated from the adsorption energies of the amines and alcohols, respectively, as follows:

$$h_C = \frac{\Delta H_{(\text{ads, hydrocarbon})}}{n_C}$$

$$h_N = \Delta H_{(\text{ads, amine})} - h_C \cdot n_C$$

$$h_O = \Delta H_{(\text{ads, alcohol})} - h_C \cdot n_C$$

The contributions calculated in this way are shown in Table II.

As can be seen from the plot of contributions as a function of the pyridine content of the polymer (Fig. 1), there are well defined trends for  $h_N$  and  $h_O$ . On the other hand, the increase in the pyridine content of the polymer has virtually no effect on the adsorption contribution of the carbon groups, in spite of this contribution being *ca.*  $-2$  kcal/mol in all instances.

TABLE II

GROUP CONTRIBUTIONS TO THE ADSORPTION ENERGIES ON POLYMERIC SUPPORTS ( $-\text{kcal/mole}$ )

Group contribution	Polymer				
	A	B	C	D	E
$h_C$	2.0	2.2	2.2	2.2	1.9
$h_N$	2.0	-2.4	-4.4	-4.2	-4.9
$h_O$	4.1	-2.2	-2.9	—	-4.3

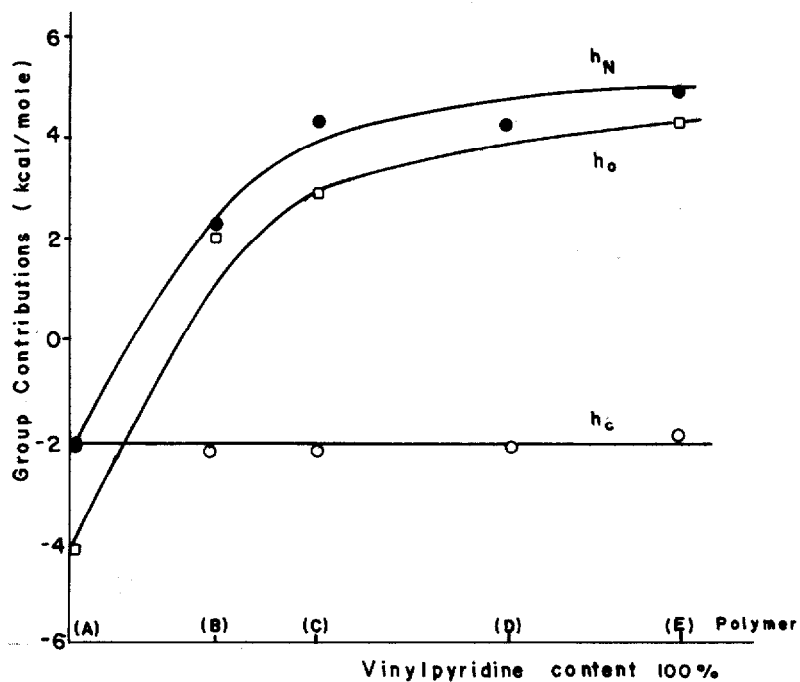


Fig. 1. Hydrocarbon group (○), amine group (●) and alcohol group (□) contributions to the total adsorption energy as a function of the vinylpyridine content of the polymer.

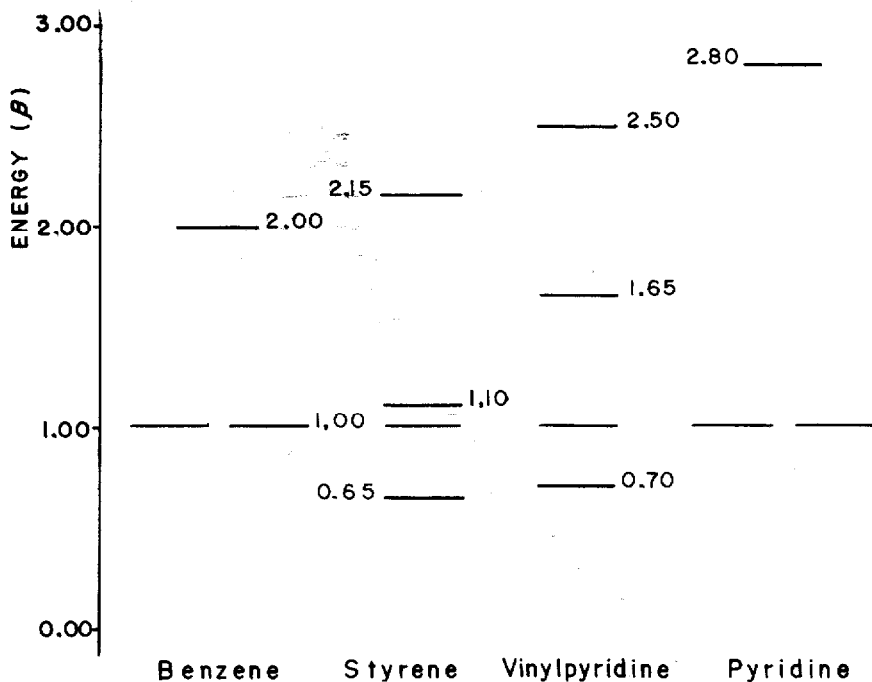


Fig. 2. Unoccupied molecular orbitals for benzene, styrene, vinylpyridine and pyridine calculated by simple Hückel theory.

That contribution, and also  $h_N$  and  $h_O$  on polymer A, correspond to attractive interactions and are in very good agreement with the values that can be calculated from the data of Zado and Fabecic<sup>6</sup> ( $-2.6$  kcal/mole for  $h_C$  and  $-4.3$  kcal/mole for  $h_O$ ) on Porapak Q. This interaction can be ascribed to the formation of a charge-transfer type of complex of those groups with the phenyl and remaining styryl groups on the polymer. It has been shown formerly that the interaction of amines with the non-polymerized styryl groups is largely responsible for the tailing of the amine peaks on Chromosorb 102. Similarly, the bulk of the adsorption process may occur near phenyl rings, but with lower energy, as can be seen from Fig. 2, calculated using a simple Hückel approach<sup>14</sup>. Interactions of the same type have been proposed by Velasco *et al.*<sup>15</sup> for the interaction between aliphatic amines and benzene in solution.

On increasing the pyridine content of the polymers, the contributions due to the polar groups decrease rapidly to  $+4-5$  kcal/mol for the pure divinylbenzene-vinylpyridine polymer. The same effect can be seen from the adsorption isotherms shown in Fig. 3 for methanol and pentane on supports A and E. Whereas the alcohol adsorption, at 80 Torr, decreases by 85% from  $47 \cdot 10^{-4}$  to  $7 \cdot 10^{-4}$  mole/g on passing from styrene-divinylbenzene to divinylbenzene-vinylpyridine, the adsorption of pentane decreases by only 50% from  $10 \cdot 10^{-4}$  to  $5 \cdot 10^{-4}$  mole/g.

From the IR spectra it could be seen that the relative intensity of the vinyl group band ( $3085 \text{ cm}^{-1}$ ) remained almost constant, independent of the number of pyridine rings in the polymer, indicating that any differences in the behaviour of the

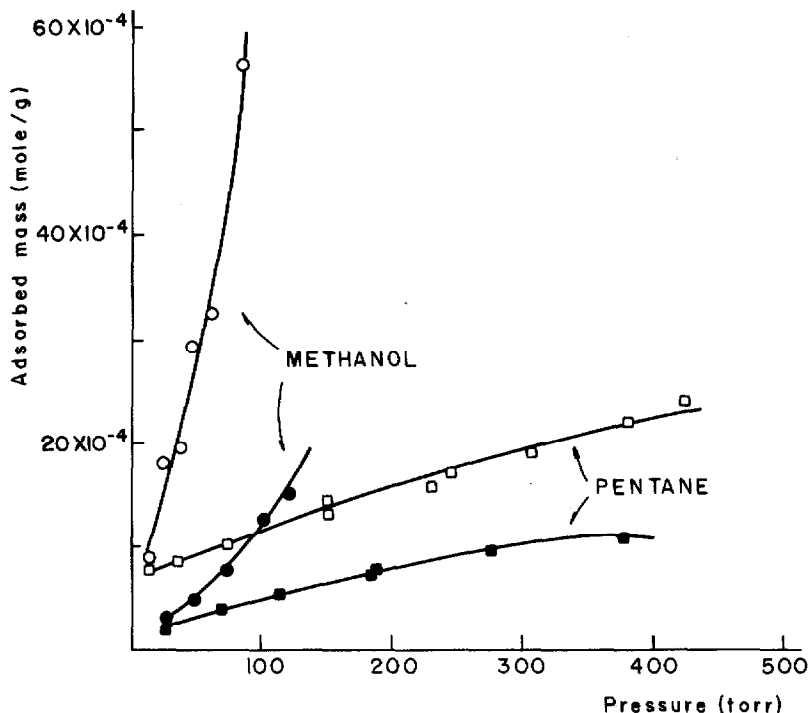


Fig. 3. Adsorption isotherms of methanol and pentane on poly(styrene-divinylbenzene) (O, □) and poly(vinylpyridine-divinylbenzene) (●, ■) at 25°C.

supports are not due to this type of interaction<sup>7</sup>. Further, as can be seen from Fig. 2, the replacement of phenyl rings by pyridine rings does not affect the energies of the LUMO levels of the remaining vinyl entities, making this substitution irrelevant to the formation of charge-transfer interactions with both phenyl-pyridyl or styryl-vinylpyridyl groups. Therefore, we believe that the attractive and repulsive interactions of the polymers with the amine and alcohol groups have different characteristics. The attraction is through the formation of charge-transfer bonds involving the polymer chain  $\pi$ -systems as acceptors of  $n$ -electrons from the nitrogen or oxygen atoms. The repulsion corresponds to a graded increase in the surface negative charge on the polymer due to the increase in pyridine nitrogen lone-pair electrons.

These studies should allow the design of chromatographic columns for specific separations from a knowledge of the group contributions to adsorption energies on specifically synthesized microporous polymers.

#### REFERENCES

- 1 O. L. Hollis, *Anal. Chem.*, 38 (1966) 309.
- 2 K. Sakodinsky, *Chromatographia*, 1 (1968) 483.
- 3 J. D. Burger, *J. Chromatogr. Sci.*, 6 (1968) 177.
- 4 T. N. Gvozdovich, A. V. Kiselev and Y. I. Yashin, *Chromatographia*, 2 (1969) 234.
- 5 T. N. Gvozdovich, A. V. Kiselev and Y. I. Yashin, *Chromatographia*, 6 (1973) 1365.
- 6 F. M. Zado and J. Fabecic, *J. Chromatogr.*, 51 (1970) 37.
- 7 W. Hertl and M. G. Neumann, *J. Chromatogr.*, 60 (1971) 319.
- 8 J. R. Lindsay Smith, A. H. H. Tameesh and D. J. Waddington, *J. Chromatogr.*, 151 (1978) 21.
- 9 J. R. Lindsay Smith, A. H. H. Tameesh and D. J. Waddington, *J. Chromatogr.*, 151 (1978) 27.
- 10 S. B. Dave, *J. Chromatogr. Sci.*, 7 (1969) 389.
- 11 A. Sugii and K. Harada, *J. Chromatogr.*, 178 (1979) 71.
- 12 F. H. Woeller and G. E. Pollock, *J. Chromatogr. Sci.*, 16 (1978) 137.
- 13 A. V. Kiselev, *Discuss. Faraday Soc.*, 40 (1965) 205.
- 14 A. Streitwieser, *Molecular Orbital Theory for Organic Chemists*, Wiley, New York, 1967.
- 15 I. Velasco, S. Otin and C. Gutiérrez-Losa, *J. Chim. Phys.*, 75 (1978) 706.