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CHARACTERIZATION OF SOME STYRENE–DIVINYLBENZENE SORBENTS FOR REVERSED-PHASE CHROMATOGRAPHY

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SUMMARY

The preparation and characterization of laboratory made polymeric columns of Chromosorb 101 and Porapak Q are described, with reference to a PRP-1 column packed under the same conditions. Column parameters such as permeability, efficiency and peak asymmetry factor were calculated. The swelling propensity of the materials was measured and the dependence of peak shape on the type of organic solvent used was investigated. The efficiencies of Chromosorb 101 and Porapak Q columns were satisfactory but the spherical material PRP-1 gave better results. Porapak Q exhibited very good physical properties such as high rigidity and permeability. The swelling of polymers in acetonitrile is higher than in methanol, so a better column performance is obtained when acetonitrile is employed as the eluent.

INTRODUCTION

In the current practice of high-performance liquid chromatography (HPLC), alkyl-bonded silica-based stationary phases dominate the field of separations. However, there are serious drawbacks to their use owing to hydrolysis of the siloxane bond at low pH and dissolution of the silica at high pH. In the last decade, macroporous polystyrene–divinylbenzene resins gained popularity and many papers have been devoted to their characterization[1–9] or to their application[10–18] as useful phases in HPLC.

In previous work[3], the preparation and characterization of polymeric columns was described. The polymer employed was Chromosorb 101, which has good chromatographic properties but is less efficient than a similar commercial column packing, PRP-1. The relatively low pressure used during the packing procedure was probably responsible, but irregular particle shapes could have a significant effect.

In this work, laboratory-made polymeric columns of Chromosorb 101 and Porapak Q were prepared and characterized, comparison being made with a PRP-1 column packed under the same conditions.

The extent to which efficiency depends on the packing procedure is discussed. The swelling propensity of the materials was measured and the dependence of peak symmetry on the type of organic solvent used was also investigated.

EXPERIMENTAL

The apparatus and chemicals employed have been described previously[3]. PRP-1 packing of 10 μm particle diameter was supplied by Hamilton (Bonaduz, Switzerland), Chromosorb 101 (CH 101) and Porapak Q (PQ) were obtained from Supelchem (Milan, Italy) as 80–100-mesh particles. The grinding and handling procedures used to obtain sized polymer fractions have been reported previously[3]. The particle size distribution curve was obtained by Coulter counter analysis; $d_{10\%}$, $d_{50\%}$ and $d_{90\%}$, characterizing the collected polymer fractions, were determined to be 11, 14 and 21 μm, respectively for Chromosorb 101 and 12, 17 and 22 μm, respectively, for Porapak Q. The modal particle diameters were 11 and 14 μm, respectively. A wet filling technique was employed for packing the column. The packing material, slightly wetted with methanol, was dispersed in a solution of 50% glycerine and 2.5% sodium chloride in water. A 20-ml volume of the packing solvent was used to disperse about 2 g of polymer.

A stainless-steel column (15 cm × 4.6 mm I.D.) having two 2-μm fritted end fittings was filled with methanol and connected to the reservoir. Methanol was pumped from a Haskel pneumatic amplifier pump system. A total of about 100 ml of methanol was pumped, after which the pump was turned off and allowed to depressurize completely. After the pressure had been released, the column was disconnected and the fritted end fitting placed at the top.

RESULTS AND DISCUSSION

Chromosorb 101 and Porapak Q polymers are well known packing materials designed for gas chromatography. Chromosorb 101 is a porous styrene–divinylbenzene copolymer having a surface area of 11 m^2 g^{-1} and an average pore diameter of 0.3–0.4 μm[19]. Porapak Q is a porous ethylvinylbenzene–divinylbenzene polymer having a surface area of 557 m^2 g^{-1} and an average pore diameter of 0.0075 μm[19]. PRP-1 is a porous copolymer of styrene–divinylbenzene designed for HPLC, having a surface area of 415 m^2 g^{-1} and an average pore diameter of 0.075 μm[2].

TABLE I

EFFECT OF PACKING PRESSURE ON COLUMN EFFICIENCY (PLATES PER METRE) AT A FLOW-RATE OF 0.5 ml min^{-1}

Packing	Packing pressure (atm)		
	375	460	620
CH 101	6200	9100	6800
PQ	6500	7300	6800
PRP-1	12 500	14 200	13 600

The effect of packing pressure on column efficiency was evaluated by preparing different columns at various back-pressures, namely 375, 460 and 620 atm. The results showed that the best efficiencies were obtained when the intermediate pressure of 460 atm was used. The efficiencies of columns prepared at higher back-pressures did not increase, and at lower values the efficiencies decreased significantly, as reported in Table I. Therefore, the data discussed in this paper refer to columns prepared under such conditions.

In order to evaluate the column performance, the chromatographic parameters permeability ($B°$), efficiency and asymmetry factor (A_s) were determined. Permeability was calculated as $B° = \bar{u}\eta Lf/\Delta p$, where $\bar{u}$ is the linear flow-rate, η the viscosity, L the column length, f the total pore fraction of the column and Δp the pressure drop. Viscosities were taken from the literature[20].

The column permeabilities in methanol, acetonitrile and tetrahydrofuran (THF) are reported in Table II. The permeabilities were constant over the pressure range used, 15–240 atm, independent of solvent sequences, and were reproducible after several experiments. The $B°$ values were smaller than those predicted by the Kozeny–Carman equation[20], especially for Chromosorb 101, and they did not remain constant from one solvent to another. The most likely reason is that swelling of polymeric materials takes place. In fact, the permeability in THF, in which the swelling would be expected to be at a maximum, was the lowest. Porapak Q seems to be less sensitive to swelling and shrinking than Chromosorb 101 or PRP-1, as shown by the swelling propensity (SP factors) reported in Table II. Such factors were calculated according to Nevejans and Verzele[4] as

$$SP = \frac{p(\text{THF}) - p(\text{H}_2\text{O})}{p(\text{H}_2\text{O})}$$

where p is the pressure relative to the viscosity, $p = P/\eta$. It was established that a non-swelling material will have an SP value of zero. The swelling propensity could depend on the degree of cross-linking of the packing material[4], so the three supports were investigated by infrared Fourier-transform spectroscopy in the hope of obtaining some indications.

Spectra were measured with a Bruker IFS88 spectrometer equipped with a DTGS detector. The spectral resolution was 2 cm^{-1}. The samples were prepared as caesium iodide pellets.

TABLE II

PERMEABILITIES ($B° \times 10^{10}$) AND SWELLING PROPENSITY FACTORS (SP)

Packing	Permeability			SP
	Methanol	Acetonitrile	THF	
CH 101	0.7	0.4	0.3	1.4
PQ	5.7	5.8	5.6	0.4
PRP-1	2.4	2.0	1.4	0.7

The spectra showed in Fig. 1 contain the bands normally expected for styrene–divinylbenzene copolymers. In particular, the PRP-1 and Porapak Q spectra are very similar and they are similar to those reported by Sturman *et al.*[8] for PRP-1 and PLRP-S. A band at 760 cm^{-1}, corresponding to monosubstituted phenyl rings, appears in the Chromosorb 101 spectra whereas in the PRP-1 and Porapak Q spectra only *meta* disubstitution (710 and 796^{-1} bands) can be observed. These results indicate that PRP-1 and Porapal Q are more strongly cross-linked than Chromosorb 101. The lower degree of cross-linking of this material could justify its poorer physical properties.

The theoretical plate heights, H, measured at flow-rates from 0.03 to 0.3 cm s^{-1}, were calculated for benzene ($k' \approx 1.0$) in both methanol and acetonitrile. Fig. 2 shows plots of the logarithm of reduced plate height, log h, *versus* the logarithm of reduced liner velocity, log v, in methanol and in acetonitrile, where

$$h = H/d_{\mathrm{p}}$$

$$v = \bar{u}d_{\mathrm{p}}/D_{\mathrm{M}}$$

d_{p} (cm) being the particle diameter and D_{M} (cm^2 s^{-1}) the sample molecule diffusion coefficient calculated with the Wilke–Change equation[21].

Reduced parameter plots have been discussed by Bristow and Knox[22]. Their main advantage is that they make it possible to compare packings having different particle diameters. The shape of the curves in Fig. 2 is similar to those observed for other porous adsorbents[1,2,22]. The PRP-1 column is more efficient, probably owing to the regular spherical shape of the particles. The curve for Chromosorb 101 lies at higher log h values, suggesting that such a column is less uniformly packed. The best efficiencies, obtained in acetonitrile at 0.25 ml min^{-1}, are $N = 25\ 000$ m^{-1} for PRP-1, 11 000 m^{-1} for porapak Q and 18 000 m^{-1} for Chromosorb 101. The improvement in chromatographic properties obtained using acetonitrile can be associated with the increased swelling of the polymers in this solvent.
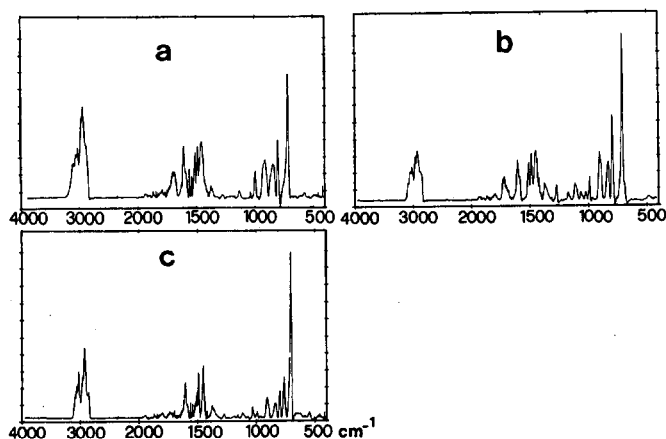

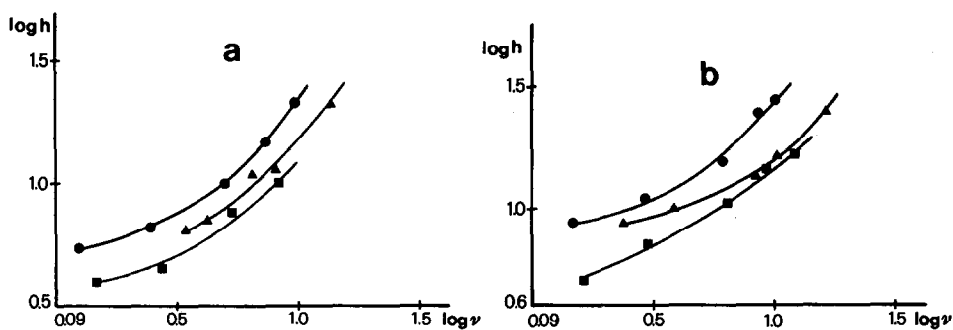Fig. 1. FT-IR spectra of (a) PQ, (b) PRP-1 and (c) CH 101.

Fig. 2. Log (reduced plate height) vs. log (reduced linear velocity) plots for benzene. Mobile phase: (a) 100% acetonitrile; (b) 100% methanol. ●, CH 101; ▲, PQ; ■, PRP-1.

TABLE III

BENZENE PEAK ASYMMETRY FACTORS (A_s)

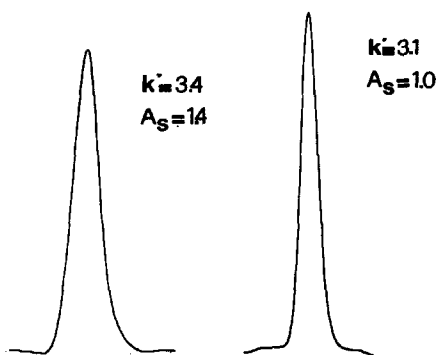| Packing	A_s		Flow-rate (ml min⁻¹)
	Methanol	Acetonitrile	
CH 101	1.3	1.0	0.50
PQ	1.3	1.2	0.50
PRP-1	1.4	1.2	0.50

Fig. 3. Peak shape as a function of the presence or absence of THF on the PRP-1 column. Mobile phase: left trace, methanol–water (60:40); right trace, methanol–water–THF (45:45:10). Solute: phenol. The mobile phases were selected to match k' to avoid any effect on the peak shape.

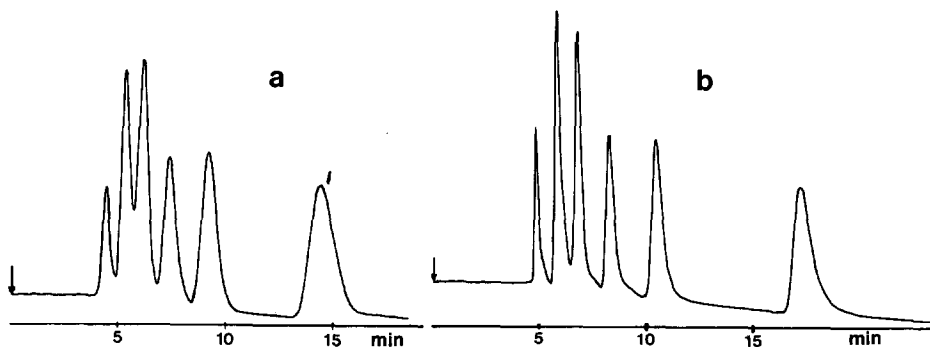Fig. 4. Chromatograms of n-alkylbenzenes on (a) PQ column and (b) PRP-1 column. Mobile phase: acetonitrile–water (85:15). Solutes: benzene and methyl-, ethyl-, propyl-, butyl- and hexylbenzene.

Further, the peak shape depends on the degree of swelling, as shown by the asymmetry factors, measured for benzene at 10% of the peak height in both methanol and acetonitrile, reported in Table III. The A_s values are good and are similar to those observed for other polymeric adsorbents[1]. The peak shape improvement is less pronounced for Porapak Q; probably this material is more rigid. Methanol is a "poorer" solvent than acetonitrile; most likely the degree of polymer swelling in such a solvent is not sufficient to render the entire porous structure accessible to the solvent and solute.

The peak shape does not depend on the water:methanol or water:acetonitrile ratios because the asymmetry factors in such mixtures are similar to these in the pure organic solvents. Sometimes for PRP-1 and Chromosorb 101 an improvement in peak shape is obtained if small amounts of THF are added to water–methanol eluents, as reported as an example in Fig. 3. This behaviour was observed for other styrene–divinylbenzene copolymers and correlated with the swelling of the microporous structure[7,8].

The experimental results showed that all the polymers examined here can be useful packing materials for HPLC columns.

The use of a more reliable packing apparatus than that previously employed[3] made it possible to achieve the best efficiencies. However, particle shape seems to play an important role as the spherical material PRP-1 gave better results. Chromosorb 101 has a lower rigidity than the other polymers examined and its relatively low permeability could translate into either longer analysis times or higher operating pressures, especially using eluents with high water contents. Owing to its higher rigidity and permeability and lower operating pressures, Porapak Q can be useful in the analysis of retained solutes. For example, under the same experimental conditions, the separation of some n-alkylbenzenes on the Porapak Q column (Fig. 4) can be performed in a 15% shorter analysis time than on the PRP-1 column. Acetonitrile and water–acetonitrile mixtures are the best eluents for these stationary phases; however, the addition of small amounts of the "strong" solvent THF to water–methanol mixtures makes it possible to obtain satisfactory column performance.

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