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STUDIES OF CHROMATOGRAPHIC PACKINGS CONSISTING OF POROUS POLYMERS

III*. INFLUENCE OF SILANIZATION OF POLICHROM A ON THE SEPARATION OF SHORT-CHAIN FREE FATTY ACIDS BY GAS CHROMATOGRAPHY

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SUMMARY

A previously described cross-linked porous styrene polymer has been used for the separation of aqueous solutions of short-chain free fatty acids (SFFA) at low concentrations by gas chromatography. The unmodified polymer Polichrom A can separate C_2–C_7 SFFA in samples containing up to 1 μq of each component with considerable tailing, but the peaks tend to disappear at the 10 ng level. Silanization of Polichrom A with dimethyldichlorosilane (DMCS) allows the separation of SFFA at the 10 ng level without tailing. Secondary silanization with hexamethyldisilazane (HMDS) worsens the chromatographic separation. McReynolds constants, the number of theoretical plates and the resolutions obtained with unsilanized and silanized samples of Polichrom A and Chromosorb 101 are compared.

INTRODUCTION

Porous polymer packings are especially useful in the chromatographic analysis of aqueous solutions of strongly polar substances. One of the important but also difficult analytical problems is the analysis of short-chain free fatty acids (SSFA) in aqueous solutions. In this work, we attempted to use polymer packings whose synthesis and properties were described in previous paper[1,2] to analyse SFFA in aqueous solutions. The polymer called ST-DMN in the previous work is now commercially available as Polichrom A, and the latter name will be used here and in subsequent papers.

According to Ottenstein and Bartley[3] and Cochrane[4], Chromosorb 101 is the best polymer packing for this type of analysis. Therefore, the applicability of Polichrom A in SFFA analysis was compared with that of Chromosorb 101.

It was found that with Polichrom A the separations of SFFA exhibited considerable tailing, especially at low concentrations. To obtain effective separations, we

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* For Parts I and II, see refs. 1 and 2.

attempted to modify the polymer surface with the silanizing agents dimethyldichlorosilane and hexamethyldisilazane. Polichrom A modified by dimethyldichlorosilane appeared to be the most effective in SFFA separations at low concentrations. In this paper, the comparison of silanized and unsilanized samples of Polichrom A and Chromosorb 101 is described.

EXPERIMENTAL

Polichrom A

Samples of Polichrom A (0.15–0.2 mm fraction) whose synthesis was described previously[2] were used.

Washing with hydrochloric acid

A suspension of 20 g of Polichrom A in a mixture of 12 M hydrochloric acid and methanol (70:30, v/v) was prepared. Methanol was added to the acid in order to improve the wettability of Polichrom A. After 25 min, the liquid was decanted off and 150 ml of the same 12 M hydrochloric acid–methanol mixture was added. After 24 h the suspension was filtered off under reduced pressure and washed with 30% aqueous methanol solution until Cl^- ions were no longer detected. The chloride-free polymer was washed with anhydrous methanol (5 × 50 ml) and then left in methanol for 1 h. The polymer was then dried at 120°C for 2 h in a laboratory oven under reduced pressure.

Silanization

A 20-g amount of hot Polichrom A was poured to 120 ml of 5% (v/v) dimethyldichlorosilane (DMCS) solution in anhydrous toluene. After 1 h, 100 ml of toluene were added to the mixture and then the liquid was decanted off. Decantation was repeated and then the polymer was filtered off under reduced pressure. The polymer was washed with methanol (6 × 50 ml) and, after filtration, placed in a vacuum dryer at 120–125°C for 24 h.

Half of the silanized sample was subjected to secondary silanization with 5% (v/v) hexamethyldisilazane (HMDS) in anhydrous toluene. The procedure was analogous to that with DMCS.

Chromatographic measurements

The gas chromatographic measurements were carried out on a Chromatron GCHF-18.3 gas chromatograph (Chromatron, Berlin, G.D.R.) equipped with a flame-ionization detector. Helium at a flow-rate of 30 ml/min was used as the carrier gas and the flow-rate of hydrogen was 27 ml/min. The injector temperature was 250°C. Measurements were carried out on the columns made of Sovirel glass (1.5 m × 2.5 mm I.D.) at 170°C. The samples were injected by means of a 1-μl syringe (SGE, North Melbourne, Australia). Injections were made of 10, 1, 0.1 aqueous solutions of acetic, propionic, isobutyric, butyric and valeric acids and 0.01% aqueous solutions of acetic, propionic, isobutyric, butyric, valeric, isovaleric, capronic and enanthic acids.

Measurements of retention indices for McReynolds substances (benzene, butanol-1, pentanone-2, 1-nitropropane, pyridine) were made on the stainless-steel col-
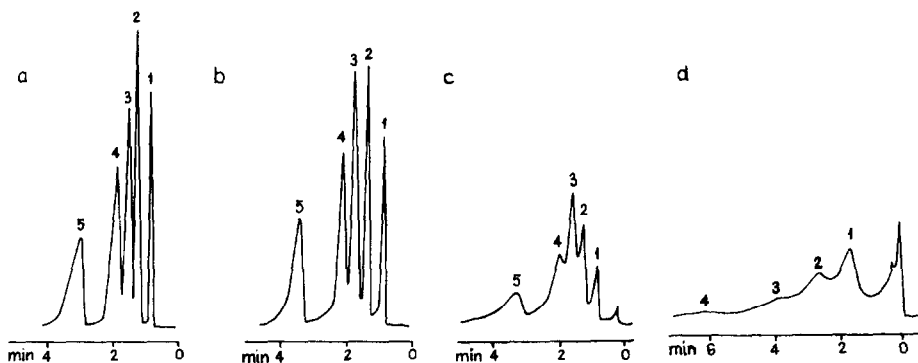
Fig. 1. Comparison of chromatograms of aqueous solutions of free fatty acids on Polichrom A. Samples of 0.1 μl were injected, containing (a) 10 μg of each acid (sensitivity $6.3 \cdot 10^{-8}$ A full-scale (AFS), (b) 1 μg of each acid (sensitivity $6.3 \cdot 10^{-9}$ a.f.s.), (c) 100 ng of each acid (sensitivity $6.3 \cdot 10^{-10}$ a.f.s.) and (d) 10 ng of each acid (sensitivity $6.3 \cdot 10^{-11}$ a.f.s.). Glass column, 1.5 m $\times$ 2.5 mm I.D.); column temperature, 170°C; flow-rate of helium carrier gas, 30 ml/min; flow-rate of hydrogen, 27 ml/min; injector temperature, 250°C; flame-ionization detector. Peaks: 1 = acetic acid; 2 = propionic acid; 3 = isobutyric acid; 4 = n-butyric acid; 5 = n-valeric acid [in (a), (b) and (c)]. In (d) the following mixture was chromatographed: acetic acid, propionic acid, isobutyric acid, n-butyric acid, isovaleric acid, n-valeric acid, capronic acid, enanthic acid.

umns (1 m $\times$ 4 mm I.D.) at 140°C (ref. 5) using a thermal conductivity detector. For individual substances such as benzene, butanol-1, pentanone-2, 1-nitropropane and pyridine, trace amounts were injected by dipping the syringe needle (at the zero position of the piston) into the sample for 1 sec. Chromatographic characteristics were calculated using the equations published previously[2].

Measurements of the specific surface areas of polymers

Measurements of the specific surface areas of modified and unmodified Polichrom A were carried out by the method of nitrogen adsorption at low temperatures using a Sorptomatic 1806 instrument (Carlo Erba, Milan, Italy). The specific surface area was calculated by the BET method, assuming that the area of a single nitrogen molecule is 16.2 Å[2].

Measurements of nitrogen adsorption and desorption were performed by pumping out the samples under a 10^{-3} mmHg vacuum at 200°C for 2 h.

Thermogravimetric (TG) measurements

These measurements were made by the method described previously[2].

RESULTS AND DISCUSSION

From the chromatograms in Fig. 1, it can be seen that these separations are characterized by relatively large adsorptions of the SSFA on the packing, shown by significant asymmetry of the peaks at high acid concentrations (chromatograms a, b and c) or by disappearance of the peaks (chromatogram d).

Unmodified Polichrom A is useless for quantitative separations of SFFA at low concentrations and washing with hydrochloric acid does not give any improve-
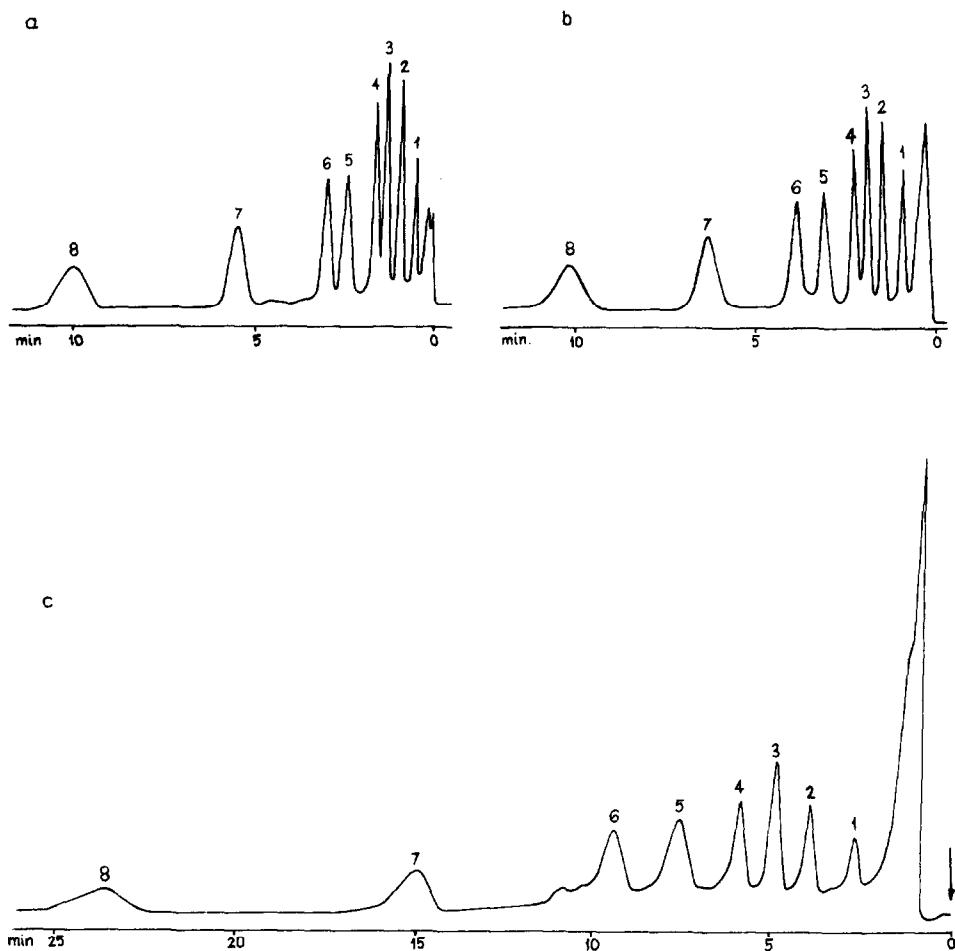
a

b

c

Fig. 2. Comparison of chromatograms of aqueous solutions of free fatty acids on (a) Chromosorb 101, (b) Polichrom DMCS and (c) Polichrom DMCS + HMDS. Samples of 0.1 μl containing 10 ng of each acid were injected. Chromatographic conditions as in Fig. 1. Peaks: 1 = acetic acid; 2 = propionic acid; 3 = isobutyric acid; 4 = *n*-butyric acid; 5 = isovaleric acid; 6 = *n*-valeric acid; 7 = capronic acid; 8 = enanthic acid.

TABLE I

KOVATS' RETENTION INDICES FOR McREYNOLDS SUBSTANCES RELATIVE TO THE STUDIED POLYMERS AT 140°C

Polymer	Benzene	Butanol-1	Penta-none-2	1-Nitro-propane	Pyridine
Chromosorb 101	706	708	747	797	835
Polichrom A	760	782	793	887	886
Polichrom DMCS	738	763	764	886	885
Polichrom DMCS + HMDS	753	776	788	896	935

TABLE II

PROPERTIES OF THE POROUS POLYMERS

S = Specific surface area; t = initial decomposition temperature; n = number of theoretical plates for n-valeric acid; R_{ij} = resolution for the pair isobutyric acid–n-butyric acids; x, y, z = modified McReynolds constants for benzene, butanol-1 and pentanone-2; I = total selectivity relative to graphitized carbon black. Measurement temperatures: for n and R_{ij}, 170°C; for x, y, z, 140°C.

Polymer	S (m²/g)	t (°C)	n	R_{ij}	x	y	z	I
Chromosorb 101	26	220	835	1.10	132	219	182	533
Polichrom A	91	280	789	1.19	186	293	228	707
Polichrom DMCS	96	280	1081	1.36	164	274	199	637
Polichrom DMCS + HMDS	92	280	609	1.35	179	287	223	689

ment. However, silanization of Polichrom A gives a packing that permits the analysis of SFFA in samples containing 10 ng of each component (Fig. 2b). These separations are comparable to that obtained in Chromosorb 101 (Fig. 2a). The additional silanization of Polichrom A DMCS by HMDS unexpectedly worsens the properties of the packing; the retention times of the acids increase and tailing occurs (Fig. 2c).

From Table I it can be seen that Polichrom A in both the original and modified versions has a higher polarity than Chromosorb 101. However, silanization causes a decrease in the polarity of Polichrom A. The retention indices of benzene, butanol-1 and pentanone-2 on Polichrom DMCS are 20–30 units lower than on Polichrom A, but those of 1-nitropropane and pyridine are almost identical. The retention indices of benzene, butanol-1 and pentanone-2 on Polichrom DMCS + HMDS are almost the same as on Polichrom A, but those of 1-nitropropane and pyridine are higher (in particular, the retention index of pyridine is about 50 units higher on the Polichrom DMCS + HMDS packing).

The Kovát's retention indices for benzene, butanol-1 and pentanone-2 (Table II) indicate that Polichrom DMCS occupies an intermediate position between Polichrom A and Chromosorb 101 and the decrease in polarity is caused by silanization. The x, y, z values decrease by about 20–30 units for the Polichrom DMCS packing but for Polichrom DMCS + HMDS these values decrease insignificantly in comparison with Polichrom A (5 units on average). These data show that double silanization influences the polarity of the polymer insignificantly. Silanization of Polichrom A leads to an increase in resolution. The R_{ij} values for isobutyric and n-butyric acids[6] are higher for Polichrom DMCS and HMDS + DMCS than for Polichrom A, and are significantly higher than that for Chromosorb 101.

The number of theoretical plates (n) calculated for valeric acid is highest with the Polichrom DMCS column and lowest with the Polichrom DMCS + HMDS column. The initial decomposition temperature and specific surface area of Polichrom A and its modified versions do not vary after silanization.

CONCLUSIONS

Silanization of Polichrom A with DMCS leads to a packing that is useful in the separation of SFFA in aqueous solutions at low concentrations (10 ng of each

component). Chromatographic separations of SFFA are comparable to those on Chromosorb 101, but a better resolution of isobutyric and *n*-butyric acids is obtained.

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