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Studies on the selectivity of porous polymers based on polyaromatic esters

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SUMMARY

Four types of porous polymers containing ester groups were synthesized as stationary phases for gas chromatography using the monomers 1,4-di(methacryloyloxymethyl)naphthalene or 9,10-di(methacryloyloxymethyl)anthracene and styrene or divinylbenzene. The influence of the ester groups in the copolymer skeletons on their selectivities was studied. To determine the selectivities of these copolymers, two procedures were applied: the selectivity triangle and the general selectivity.

INTRODUCTION

Porous polymers are known under various tradenames and differ in their chemical and porous structures. The chemical structure of porous polymers depends on the chemical structure of the monomers used, whereas the porous structure is mainly dependent on the copolymerization conditions. The chemical structure is responsible for the chromatographic properties of porous polymers, in particular the selectivity.

Among various schemes for describing the selectivity of stationary phases, that of Rohrschneider[1], modified by McReynolds[2], is the most succesful. Using this scheme, the selectivity of the phase is characterized by five constants represented by the differences in the Kováts retention indices of test substances (benzene, *n*-butanol, 2-pentanone, 1-nitropropane and pyridine) on the phase under study and on a reference column prepared from squalane, at the same temperature.

In order to determine the selectivity of porous polymers, Smith *et al.*[3] adopted the McReynolds method using graphitized thermal carbon black (GTCB), a non-polar sorbent with the same retention mechanism as porous polymers, as a reference phase.

In order to distinquish the contribution of the common retention mechanism (hydrogen-bond donor, acceptor and dipole interaction) in the selectivity of porous polymers, Hepp and Klee[4] introduced the selectivity triangle, developed earlier by Snyder[5] for liquid stationary phases in liquid chromatography. In this method, *n*-butanol (hydrogen-bond donor) is used to measure hydrogen-bond acceptor

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characteristics, 1,4-dioxane (hydrogen-bond acceptor) to measure hydrogen-bond donor characteristics and nitropropane to measure the dipole characteristics of porous polymers. As retention is governed by the total energy of interaction, the extent to which any selectivity is exhibited depends on the amount of polar interaction relative to non-polar interaction. In order to determine the solute–sorbent dispersive interaction, in this method GTCB was also used as a reference phase.

The aim of this work was to study the influence of the ester groups present in the copolymer skeletons, coming from the monomers of different chemical structure, on their selectivities. In addition to earlier copolymers based on 1,4-di(methacryloyloxymethyl)naphthalene (DMN) and divinylbenzene (DVB)[6–8] some new porous copolymers containing ester groups were synthesized. They were formed from constant molar fractions of the following monomers: 1,4-di(methacryloyloxymethyl)-naphthalene and styrene; 9,10-di(methacryloyloxymethyl)anthracene and divinylbenzene; and 9,10-di(methacryloyloxymethyl)anthracene and styrene. Their structures are shown in Fig. 1.

In order to determine the selectivities of these copolymers, two procedures were applied: the selectivity triangle[4,5] and the general selectivity[3].

EXPERIMENTAL

Preparation of copolymers

The preparation of porous copolymers was carried out by suspension copolymerization of the following monomers: 1,4-di(methacryloyloxymethyl)naphthalene with divinylbenzene (DMN–DVB), 1,4-di(methacryloyloxymethyl)naphthalene with styrene (DMN–ST), 9,10-di(methacryloyloxymethyl)anthracene with divinylbenzene (DMA–DVB) and 9,10-di(methacryloyloxymethyl)anthracene with styrene (DMA–ST).

Mixtures of the monomers containing 0.5 mole fractions of each monomer with α,α′-azobisisobutyronitrile as an initiator in the presence of a mixture of toluene and *n*-decanol (20:80, v/v) were suspended in an aqueous solution of poly(vinyl alcohol) and polymerized at 80°C for 16 h. The copolymers in the form of beads were washed

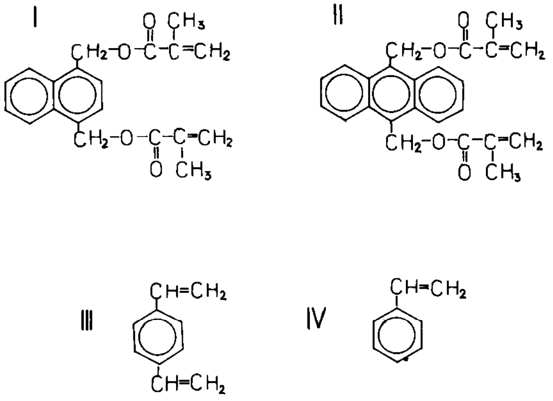


Fig. 1. Structure of the monomers used: I = 1,4-di(methacryloyloxymethyl)naphthalene; II = 9,10-di(methacryloyloxymethyl)anthracene; III = 1,4-divinylbenzene; IV = styrene.

with distilled water, filtered off, dried and extracted in a Soxhlet apparatus with boiling acetone, benzene and methanol. Then the polymer beads were separated on sieves.

For DMN–DVB and DMN–ST copolymers, the volume ratio of diluents to monomers was 1.8:1 but with DMA–DVB and DMA–ST copolymers, the volume ratio of diluents to monomers was increased to 2.8:1 because of their weak solubility in the diluent mixture.

The properties of the synthesized copolymers are summarized in Table I.

Column preparation

The columns were packed with porous polymers in the form of spherical beads. The shape of the beads was confirmed by microscopic examination. The diameter of the sorbent beads was always 0.15–0.20 mm.

Before use, all the columns were conditioned in a stream of hydrogen. The columns (DMN–DVB, DMN–ST and DMA–DVB) were conditioned with temperature programming from 60 to 250°C at 4°C/min and then overnight isothermally at the final temperature. The column packed with DMA–ST copolymer was heated from 60 to 230°C in the same way. Subsequently, the columns were filled and conditioned until the retention times for *n*-alkanes were constant.

Chromatographic measurements

Chromatographic measurements were carried out on a GCHF-18.3 gas chromatograph (Chromatron, Berlin, G.D.R.) equipped with a thermal conductivity detector, using stainless-steel columns (100 cm × 4 mm I.D.), sieve fraction of the copolymers beads 0.15–0.20 mm and hydrogen as carrier gas at a flow-rate of 50 ml/min.

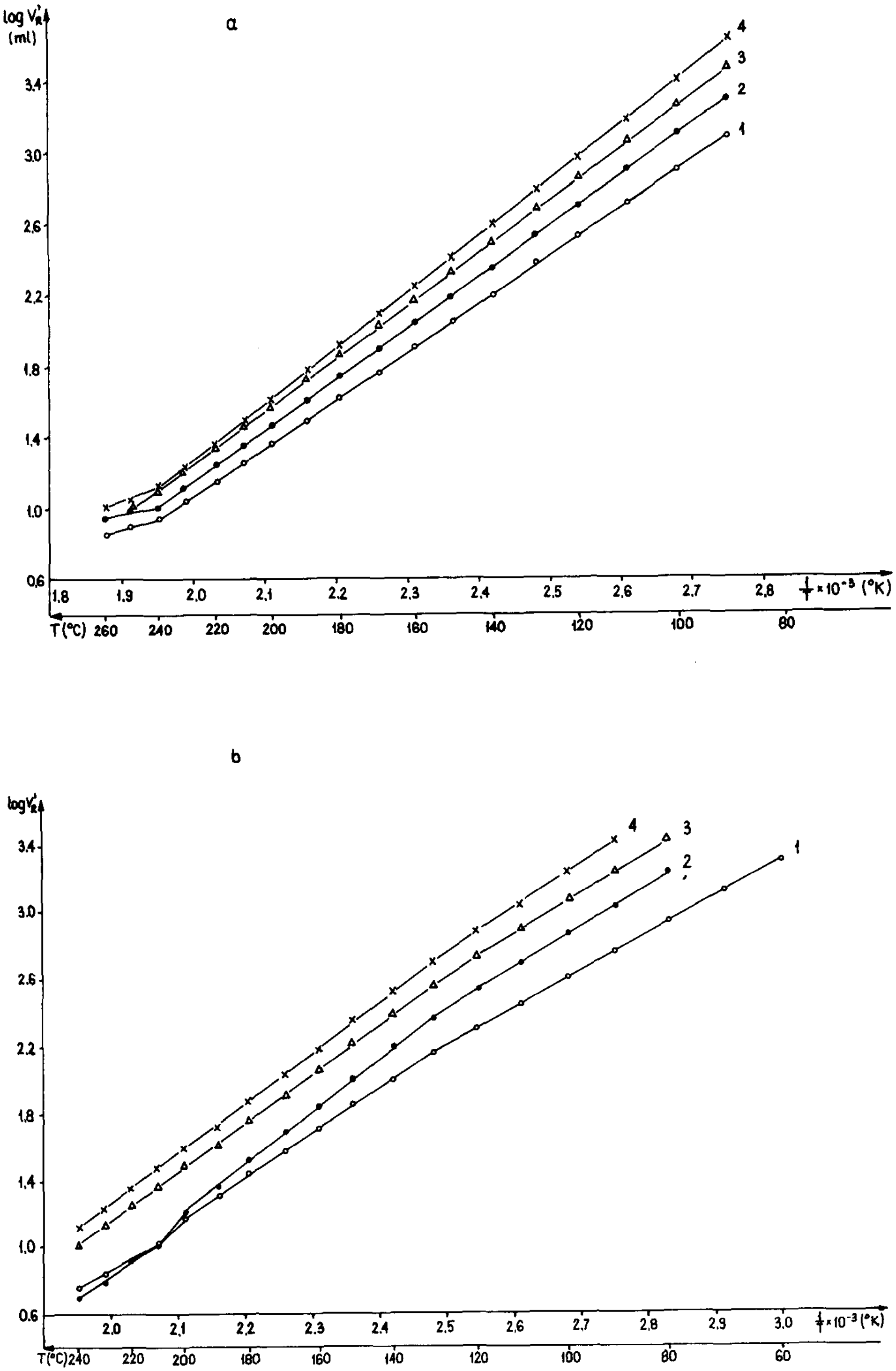
The measurements of retention indices for McReynolds substances (benzene, *n*-butanol, 2-pentanone, nitropropane and pyridine) were carried out at 140°C[3] and those of the selectivity parameters (*n*-butanol, nitropropane and 1,4-dioxane) at 200°C[4]. For all the porous copolymers, the relationships between log V_R and carbon number of *n*-alkanes (C_5–C_{12}) were linear at 140 and 200°C; hence the retention indices could be applied for selectivity measurements. The retention time of the peak of air was considered to be the dead time[9].

TABLE I

PROPERTIES OF COPOLYMERS USED

The specific surface areas were measured on a Sorptomatic 1800 apparatus (Carlo Erba, Milan, Italy) using a standard nitrogen adsorption method; the initial decomposition temperature was determined from the course of the thermogravimetric curve. The thermogravimetric measurements were carried out on a MOM (Budapest, Hungary) derivatograph at a heating rate of 5°C/min in the range 20–500°C in air.

Sorbent	*Mole fraction of monomers*				*Volume ratio of diluents to monomers*	*Specific surface area, area, S (m²/g)*	*Initial decomposition temperature, T (°C)*
	DMN	*ST*	*DMA*	*DVB*			
DMN–DVB	0.5			0.5	1.8	265.0	300
DMN–ST	0.5	0.5			1.8	144.0	280
DMA–DVB			0.5	0.5	2.8	263.0	265
DMA–ST		0.5	0.5		2.8	72.5	250


a
log V_R' (ml)
3,4
3,0
2,6
2,2
1,8
1,4
1,0
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1,9
2,0
2,1
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2,3
2,4
2,5
2,6
2,7
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$\frac{1}{T}\times10^{-3}$ (°K)
T(°C) 260
240
220
200
180
160
140
120
100
80
4
3
2
1
b
log V_R'
3,4
3,0
2,6
2,2
1,8
1,4
1,0
0,6
2,0
2,1
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2,3
2,4
2,5
2,6
2,7
2,8
2,9
3,0
$\frac{1}{T}\times10^{-3}$ (°K)
T(°C) 240
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140
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100
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60
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1

Fig. 2.

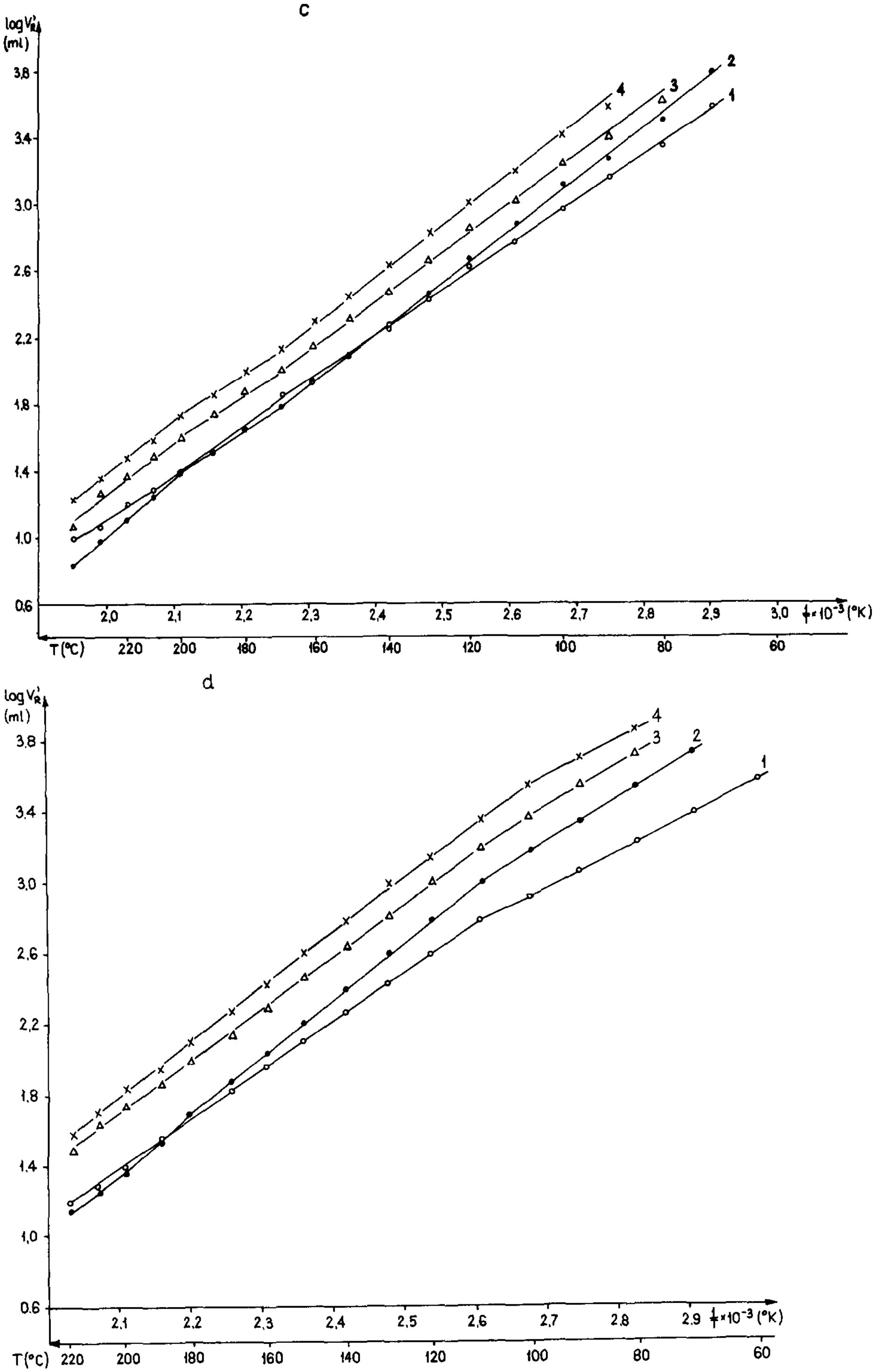

Fig. 2. Specific retention volume as a function of reciprocal of absolute temperature for the copolymers (a) DMN–DVB, (b) DMN–ST, (c) DMA–DVB and (d) DMA–ST. Curves: 1 = Acetone; 2 = hexane; 3 = chloroform; 4 = benzene.

The samples were injected by means of a 1-μl syringe (SGE, North Melbourne, Australia). Each probe was injected separately, dipping the needle (at the zero position of the piston) into the sample for 1 s[3]. At least three injections were made for each substance and averaged. The mixture of polar test solutes (acetonitrile, 2-propanol, triethylamine, 1,2-dichloroethane and octane)[10] was also injected at 200°C in an amount of 0.2 μl.

To determine the phase transition curves of the copolymers, the retention volumes of acetone, *n*-hexane, benzene and chloroform were studied in the range 60–240°C at 10°C intervals. Only for DMA–ST copolymer was the range shortened to 220°C.

Selectivity calculations

The selectivity parameters (x_i) were calculated and plotted on the face of the selectivity triangle by using the equation[4]

$$x_i = \frac{\Delta I_i}{\Delta I_b + \Delta I_n + \Delta I_d}$$

where ΔI_b, ΔI_n and ΔI_d are the McReynolds constants for *n*-butanol, nitropropane and 1,4-dioxane, respectively. The McReynolds' constants (ΔI_i) were calculated by subtracting the average retention indices of the probe solute on GTCB from those on each of the porous copolymers. The values of the retention indices of *n*-butanol, nitropropane and 1,4-dioxane on GTCB were taken from the paper by Hepp and Klee[4].

The general selectivity ($\Sigma I = x + y + z$) was calculated using the reported retention data of GTCB for benzene (x), *n*-butanol (y) and 2-pentanone (z)[11].

RESULTS AND DISCUSSION

It is generally accepted that below the glass transition temperature (T_g), retention on porous polymers is mainly governed by adsorption, whereas at temperatures higher than T_g the contribution due to bulk absorption may be significant, especially with good solvents for copolymer[12,13].

In Fig. 2 the phase transition curves are presented. For the highly cross-linked copolymers (DMN–DVB and DMA–DVB) the plots depart only slightly from linearity, but for DMN–ST and DMA–ST copolymers significant deviations from linearity in log V'_R *versus* $1/T$ plots occur[14]. It should be noted that only for DMN–DVB copolymer were the selectivity measurements carried out below the glass transition temperature. For the others, dissolution can disturb the adsorptive mechanism for some solutes.

In Table II, modified McReynolds constants and the general selectivities (ΣI) for the porous copolymers containing ester groups are presented. Independently of the chemical structure of the monomers used in the copolymerization, the retention indices for McReynolds substances have similiar values. The general selectivity indices ΣI, defined as a measure of the polarity of the polymers, indicate that all the studied polyaromatic porous copolymers containing ester groups possess a polar character. Comparing ΣI, it can be seen that polymers obtained by copolymerization of two cross-linking agents (DMN–DVB and DMA–DVB) are slightly more polar than the other two.

TABLE II

KOVÁTS RETENTION INDICES FOR THE McREYNOLDS' TEST SUBSTANCES AND GENERAL SELECTIVITIES (ΣI) FOR THE POROUS COPOLYMERS (140°C)

Copolymer	*I*					*x*	*y*	*z*	$\Sigma I = x+y+z$
	Benzene	*n-Butanol*	*2-Pentanone*	*1-Nitropropane*	*Pyridine*				
DMN–DVB	702	745	790	822	831	128	256	225	609
DMN–ST	694	722	749	804	799	120	231	184	537
DMA–DVB	686	751	773	810	857	112	262	208	582
DMA–ST	707	729	757	822	828	133	240	192	565

The retention indices of *n*-butanol (hydrogen-bond donor), 1,4-dioxane (hydrogen-bond acceptor) and nitropropane (dipole) and $\Sigma\Delta I_i$ are given in Table III. It can be seen that for all the copolymers the retention indices for each kind of probe show only small differences. $\Sigma\Delta I_i$, describing the relative polar contributions to retention, are greater than 1000. According to Hepp and Klee[4], phases with $\Sigma\Delta I_i$ values close to or exceeding 1000 exhibit inherent selectivity. On comparing the selectivity parameters (x_i) for the studied copolymers, one can see that they are more selective for molecules with large dipole moments and hydrogen-bond acceptors.

The location of these copolymers on the selectivity triangle is presented in Fig. 3. As all the copolymers are situated further away from the hydrogen-acceptor corner of the triangle, they would be expected to show little affinity towards hydrogen-donor compounds.

The elution order of the test mixture containing 2-propanol (hydrogen-bond donor), triethylamine (hydrogen-bond acceptor), 1,2-dichloroethane (weak dipole), acetonitrile (strong dipole) and octane (which has no polar interactions) is shown in Fig. 4. The retention of these substances on GTCB is due almost solely to dispersive interactions, hence the solutes elute in order of their boiling points and molar volumes (Table IV)[10].

On all the copolymers, acetonitrile (dipole) is retained longer than 2-propanol (hydrogen-bond donor). Additionally, on DMN–ST and DMA–ST copolymers, 1,2-dichloroethane (dipole) is eluted (co-eluted) after octane. This means that the

TABLE III

KOVÁTS RETENTION INDICES FOR *n*-BUTANOL, NITROPROPANE AND 1,4-DIOXANE AND POROUS COPOLYMERS SELECTIVITY PARAMETERS (200°C)

Copolymer	*I*			ΔI_b	ΔI_n	ΔI_d	$\Sigma\Delta I_i$	x_{acc}	x_{dip}	x_{don}
	n-Butanol	*Nitropropane*	*1,4-Dioxane*							
DMN–DVB	779	894	836	293	388	352	1033	0.284	0.375	0.341
DMN–ST	768	897	830	282	391	346	1019	0.277	0.383	0.340
DMA–DVB	777	887	850	291	381	366	1038	0.280	0.367	0.353
DNA–ST	766	902	838	280	396	354	1030	0.272	0.384	0.344

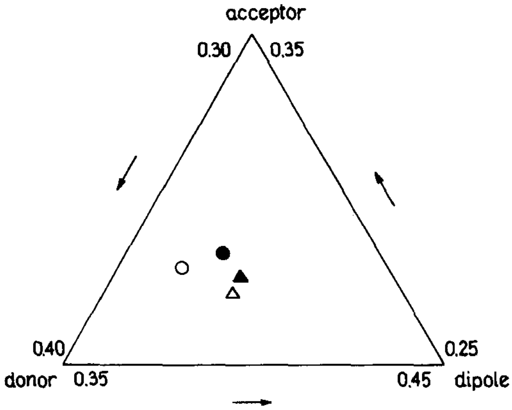

Fig. 3. Selectivity triangle showing relative selectivities of the porous polymers: ● = DMN-DVB; ▲ = DMN-ST; ○ = DMA-DVB; △ = DMA-ST.

selectivities of the copolymers containing ester groups are mainly based on dipole interactions.

DMA-DVB copolymer, with better hydrogen-donating properties than the others, retains triethylamine (hydrogen-bond acceptor) even longer than *n*-octane, but the peak of triethylamine is not symmetrical.

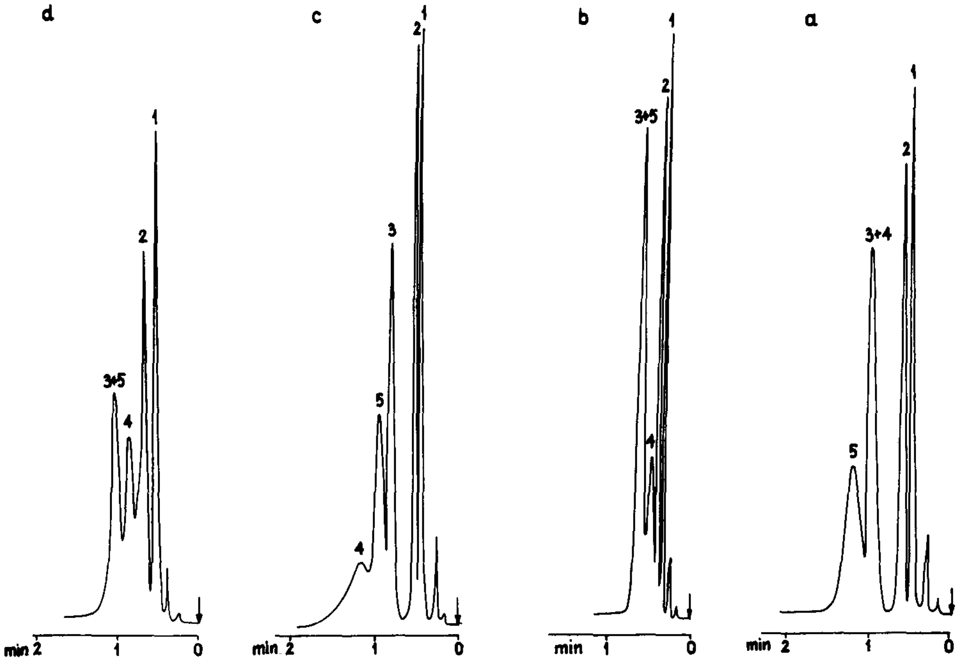

Fig. 4. Chromatograms of the test mixture obtained on copolymers (a) DMN-DVB; (b) DMN-ST, (c) DMA-DVB and (d) DMA-ST. Peaks: 1 = 2-propanol; 2 = acetonitrile; 3 = 1,2-dichloroethane; 4 = triethylamine; 5 = octane.

TABLE IV

PROPERTIES OF TEST MIXTURE PROBES[10]

Solute	*Boiling point (°C)*	*Molar volume (ml/mol)*	*Dipole moment (Debye)*
Acetonitrile	81.6	52.6	3.44
2-Propanol	82.4	76.5	1.66
1,2-Dichloroethane	83.5	79.0	1.86
Triethylamine	89.3	139.1	0.66
Octane	125.7	162.6	0.00

The above results indicate that in spite of the presence of ester groups in the copolymer skeletons, suggesting the same type of interaction between the solute molecules and the sorbents, the polyaromatic copolymers studied show different selectivities. The selectivity of the porous copolymer is a result of the overall chemical structure of the monomers used in the copolymerization.

The important parameters determining the selectivity of the porous polymer towards various compounds are the relative position of the sorbent on the selectivity triangle and the elution order of the test mixture containing a proton donor, proton acceptor, dipole and non-polar probes.

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