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POROUS POLYAROMATIC BEADS

III*. A METHOD FOR CLASSIFYING THE SELECTIVITY OF POROUS POLYAROMATIC BEADS

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SUMMARY

The selectivities of seventeen porous polyaromatic and chemically modified polyaromatic beads have been determined by the method of McReynolds. The McReynolds' constants on some phases have negative values but when the method is altered by replacing the non-polar reference liquid phase, squalane, by a non-polar solid adsorbent, graphitized thermal carbon black, all the modified McReynolds' constants are positive. The effect of chemical modification on the selectivity of porous polyaromatic beads is discussed.

INTRODUCTION

Over the last ten years porous polymers prepared from a variety of alkenes have become commercially available for use in gas chromatography (GC)^{1,2}. These polymers which range from the relatively non-polar polyaromatic beads made from divinylbenzene and styrene or ethylvinylbenzene to more polar materials based on such monomers as acrylic esters, acrylamide, acrylonitrile, and N-vinylpyrrolidone have found numerous applications in chemical analysis^{1–4}. To extend the range of uses of these materials and to improve their chromatographic behaviour some of these polymers have been altered either by surface coating^{5–9} or by chemical modification^{10–13}.

The physical properties and chemical compositions of many of the porous polymers have been measured^{1–3,12,13} and in some instances these properties have been related to the chromatographic behaviour of these polymers^{4,14,15}. Further, retention data, the linear relationships between the logarithms of retention data of compounds in homologous series with their carbon number or molecular weight, and the thermodynamic parameters of adsorption of selected compounds on porous

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polymers have led to conclusions about the nature of the interaction between adsorbate and polymer¹⁶⁻²⁰.

Despite these extensive studies on porous polymers, and unlike the related work on liquid phases in gas-liquid chromatography, there have been few attempts to classify porous polymers or indeed other solid adsorbents used in GC. In this paper we use a selection of closely related chemically modified polyaromatic beads^{10,13} to develop a method for quantifying the selectivities of polymers used as solid phases in GC.

EXPERIMENTAL

Porous polyaromatic beads

Three of the polymers used in this study were commercial materials, Porapak Q and T (Waters Assoc., Milford, Mass., U.S.A.) and Chromosorb 102 (Johns-Manville, Denver, Colo., U.S.A.), and the preparations of the others have been described (see refs. 10 and 13).

Gas chromatography

All GC results were determined isothermally on Pye Series 104 chromatographs equipped with dual flame ionization or thermal conductivity detectors attached to a Goertz RE 511 recorder.

All the columns were made of Pyrex glass and they ranged in length from 0.42 to 1.5 m and in I.D. from 2 to 4 mm.

TABLE I

SYMBOLS USED TO REPRESENT POLYMERS IN THIS STUDY

<i>Symbol</i>	<i>Composition (mole %) or description of column</i>
SD	Styrene-DVB-EVB (55:40:5)
SD-Br	4-Bromostyrene-DVB-EVB (40:55:5)
SD-Ph	4-Vinylbiphenyl-DVB-EVB (42:53:5)
SD-OMe	4-Methoxystyrene-DVB-EVB (48:47:5)
SD-CO ₂ Me	4-Carbomethoxystyrene-DVB-EVB (25:67:8)
SD-NO ₂	4-Nitrostyrene-DVB-EVB (45:50:5)
SD-Br/Br	SD-Br brominated with bromine in tetrachloromethane
ED	EVB-DVB (50:50)
ED/Br(Tl)	ED brominated with bromine and thallium(III) acetate in tetrachloromethane
ED/Ac	ED acylated with acetyl chloride
ED/NO ₂	ED nitrated with fuming nitric acid
PQ	Porapak Q
PT	Porapak T
C-102	Chromosorb 102
C-102/Br	C-102 brominated with bromine in tetrachloromethane
C-102/Br(Tl)	C-102 brominated with bromine and thallium(III) acetate in tetrachloromethane
C-102/Br (H ₂ O)	C-102 brominated with bromine in water

TABLE II

KOVATS' RETENTION INDICES, I_K , FOR THE McREYNOLDS' TEST SUBSTANCES ON SOME POROUS POLYMERS

Flow-rate, 50 ml/min (nitrogen); temperature, 140° except where indicated otherwise.

Polymer	Benzene	Butan-1-ol	Pentan-2-one	1-Nitropropane	Pyridine
SD	634	645	683	704	735
SD-Br	615	673	692	695	747
SD-Ph	647	684	704	735	809
SD-OMe	631	650	687	707	723
SD-CO ₂ Me	623	646	675	697	718
SD-NO ₂	658	708	758	790	797
SD-Br/Br	615	644	689	701	727
ED	612	600	646	659	665
ED*	632	622	666	687	706
ED/Br(TI)	614	628	671	679	734
ED/Ac	637	696	698	732	756
ED/NO ₂	644	770	799	797	856
ED/NO ₂ *	669	766	817	833	886
PQ	617	607	651	654	660
PT	657	723	736	788	781
C-102	622	608	653	671	686
C-102/Br	623	618	667	682	699
C-102/Br (TI)	615	616	674	681	690
C-102/Br (H ₂ O)	630	635	688 ^f	708	736

* Temperature, 193°.

RESULTS AND DISCUSSION

Gvozdoch *et al.*¹⁸ and Kiselev and Yashin²¹ have classified Chromosorb 102, and Porapak Q and P as weakly specific adsorbents and Porapak T, Chromosorb 104 and polyacrylonitrile, which contain polar functional groups, as strongly specific phases. However, porous polymers have not been characterized more systematically.

Of the many methods for describing the selectivity of phases²² that of Rohrschneider^{23,24} which has been modified by McReynolds²⁵ is the most successful. Using this method the selectivity of a phase is characterized by five constants, which are derived from the difference in the Kovats' retention indices of five test substances (benzene, butan-1-ol, pentan-2-one, 1-nitropropane and pyridine) on the phase under study and on a reference column prepared from squalane, at the same temperature.

Following the method of McReynolds, the retention indices of the five test substances were calculated from their adjusted retention times on a selection of closely related porous polymers (Tables I and II) at 140° (and for two phases at 193°) using the equation

$$I_x = 100 \left[\frac{\log V_g^x - \log V_g^n}{\log V_g^{n+1} - \log V_g^n} + n \right]$$

where V_g^x is the specific retention volume of substance x and V_g^n and V_g^{n+1} are the specific retention volumes of alkanes $\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_3$ and $\text{CH}_3(\text{CH}_2)_{n-1}\text{CH}_3$

respectively, such that $V_g^{n+1} \geq V_g^x \geq V_g^n$. The variations of the retention indices with temperature are comparable with those values reported by Kalashnikova *et al.*²⁶ for other solid phases.

The McReynolds' constants for the porous polymers at 140° were calculated from the retention indices of the test substances and their Kováts' retention indices on squalane (Table III). The constants show clearly the changes in selectivity of the polymers with chemical derivatization. However, the method is not entirely satisfactory since the negative values found for benzene and pyridine imply that the porous polymers are less polar than squalane towards these compounds. Similarly Engewald *et al.*²⁷ found that retention indices for cycloalkanes, cycloalkenes, and cycloalkadienes on squalane are higher than on graphitized thermal carbon black (GTCB). A further drawback to the use of squalane as the reference is its volatility which prevents its use as a liquid phase above *ca.* 140°.

Since the above characterization relates a solid porous polymer and an adsorption process to a standard non-polar liquid phase and an absorption process, we considered some alternative non-polar solid phases as standards to replace squalane. The substitution of squalane by other reference phases has been suggested previously²⁸.

A commercial porous polymer was not selected as the reference since such phases contain vinyl and aryl groups and retention data obtained on commercial polymers are known sometimes to vary from one batch of polymer to the next^{2,29-31}. GTCB, a non-polar phase that can be used over a wide temperature range (—196° to 500°) was chosen. The selectivities of the porous polymers using three of the McReynolds' standard substances (benzene, butan-1-ol and pentan-2-one) were determined (Table

TABLE III

McREYNOLDS' CONSTANTS FOR BENZENE (X), BUTAN-1-OL, (Y), PENTAN-2-ONE (Z) 1-NITROPROPANE (U), AND PYRIDINE (S), AND GENERAL SELECTIVITIES (ΣI) OF SOME POROUS POLYMERS

Temperature, 140°. Kováts' retention indices on squalane [20% (w/w) on Gas-Chrom Q at 140° with 50 ml/min nitrogen] were: benzene, 658; butan-1-ol, 590; pentan-2-one, 632; 1-nitropropane, 658; and pyridine, 820 i.u.

Polymer	X	Y	Z	U	S	ΣI
SD	—24	55	51	46	27	155
SD-Br	—43	83	60	37	39	176
SD-Ph	—11	94	72	77	101	333
SD-OMe	—27	60	55	49	15	152
SD-CO ₂ Me	—35	56	43	39	10	113
SD-NO ₂	0	118	126	132	89	465
SD-Br/Br	—43	54	57	43	19	130
ED	—46	10	14	1	—42	—53
ED/Br (TI)	—44	38	39	21	26	80
ED/Ac	—21	106	66	74	48	273
ED/NO ₂	—14	180	167	139	148	620
PQ	—41	17	19	—4	—42	—51
PT	—1	133	104	130	73	439
C-102	—36	18	21	13	—22	—8
C-102/Br	—35	28	35	24	—9	43
C-102/Br (TI)	—43	26	42	23	—18	30
C-102/Br (H ₂ O)	—28	45	56	50	24	147

TABLE IV

MODIFIED McREYNOLDS' CONSTANTS AND GENERAL SELECTIVITY (ΣI) FOR SOME POROUS POLYMERS USING GRAPHITIZED THERMAL CARBON BLACK AS THE REFERENCE

Temperature 140°. Retention index differences were calculated using reported retention data on GTCB³² for benzene (x), butan-1-ol (y), and pentan-2-one (z).

Polymers	x	y	z	ΣI
SD	53	139	102	294
SD-Br	37	137	108	282
SD-Ph	54	138	111	303
SD-OMe	56	147	114	317
SD-CO ₂ Me	49	142	109	300
SD-NO ₂	84	219	192	495
SD-Br/Br	41	155	123	319
ED	38	111	81	230
ED/Br (Tl)	40	139	106	285
ED/Ac	63	207	133	403
ED/NO ₂	70	281	234	585
PQ	43	118	86	247
PT	83	234	171	488
C-102	48	119	88	255
C-102/Br	49	129	102	280
C-102/Br (Tl)	41	127	109	277
C-102/Br (H ₂ O)	56	146	123	325

IV) using retention indices on GTCB reported by Kalashnikova *et al.*³². With GTCB as the reference phase none of the modified McReynolds' constants is negative.

From the data it is possible to classify the porous polymers and to quantify the influence of chemical modification on the selectivity of these phases. Thus the two commercial phases PQ and C-102, prepared from divinylbenzene (DVB) and ethylvinylbenzene (EVB), and DVB and styrene, respectively, have closely similar modified McReynolds' constants with values that lie between those of the corresponding polymers prepared in this study (ED and SD). As expected, derivatization of these polymers changes their selectivities. Bromination [ED/Br(Tl), C-102/Br, C-102/Br(Tl) and C-102/Br(H₂O)] gives a small increase in selectivity, acetylation (ED/Ac) a larger increase and nitration (ED/NO₂) the largest.

It is noteworthy how small is the influence of the substituents in the polymers prepared from a 4-substituted styrene (SD-X polymers); only the nitro-polymer (SD-NO₂) is significantly different, and this is presumably due to the presence of the nitro groups, which are considerably more polar than the groups in the other polymers. As expected PT is more selective than PQ.

The nature of the interactions between the adsorbates and the polymers and how they determine retention times is discussed in a following paper³³. We conclude that GTCB is a more suitable reference for classifying solid phases in chromatography than squalane and that using this modification of McReynolds' system it is possible to obtain a good measure of the selectivity of chemically modified porous polyaromatic beads.

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