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COMPARISON OF THE POLARITY OF POROUS POLYMER-BEAD STATIONARY PHASES WITH THAT OF SOME LIQUID PHASES

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SUMMARY

The polarities of Porapak and Chromosorb "Century Series" porous polymer-bead stationary phases (PPBs), obtained by measuring the ΔI values for McReynolds' polarity probes with respect to the standard non-polar liquid phase squalane, were compared with those of many stationary phases widely used in gas-liquid chromatography (GLC). The different elution orders of the polarity probes benzene, butanol, 2-pentanone, pyridine and 1-nitropropane on PPB and GLC columns, and the average polarity calculated from sum of the ΔI values for the probes, are reported.

INTRODUCTION

The average "polarity" of Porapak and Chromosorb "Century Series" porous polymer bead (PPB) stationary phases has been evaluated on the basis of the retention indices, I , of Rohrschneider's¹ and some of McReynolds's² polarity probes, by using as reference the less polar of the available PPBs (Chromosorb 106)³ or the standard liquid phases squalane and $C_{87}H_{164}$ (Apolane)^{4,5}. It was calculated as the sum of the ΔI_{200} values, *i.e.*, the differences between the I values at 200°C of each polarity probe on the various PPBs and on the reference standard Chromosorb 106, squalane or Apolane column.

Different values of the average polarity are available: Σ_R^5 is the sum of ΔI for ethanol (ETA), methyl ethyl ketone (MEK), nitromethane (NM), benzene (BE) and pyridine (Py), *i.e.*, the Rohrschneider probes, while Σ_{MR}^5 is the sum of ΔI for butanol (BUA), methyl propyl ketone (MPK), 1-nitropropane (1NP), BE and Py, *i.e.*, some of the McReynolds probes.

These parameters do not permit a comparison of all the available PPBs, because nitromethane and 1-nitropropane were found to react with some polymers (Porapak S, Chromosorb 103), yielding very broad or multiple peaks. The Σ^4 values (as above but excluding the ΔI values for nitro compounds) have therefore been used in order to compare the behaviour of the Porapak and Chromosorb PPBs⁴.

Of course, the Σ^4 and Σ^5 values permit the behaviour of the PPBs to be compared with that of many available liquid phases on an average basis, because the

different chemical compositions of the polymers are expected to interact in different ways with the various probes. The sums of the ΔI values partially compensate for this behaviour and an overall polarity scale is therefore obtained. In some instances, the possibility of such a comparison will be very useful when choosing a polymeric (GLC) column in order to obtain the same separation of a gas-liquid chromatographic (GLC) column, mainly when the use of very sensitive detectors at high temperatures requires a low bleeding rate from the stationary phase. The ΔI_{200} values for some polarity probes were therefore measured on many PPB and GLC stationary phases, and compared graphically in order to permit an easy choice between the nearly equivalent columns.

EXPERIMENTAL

The analyses were carried out with a Varian 3760 gas chromatograph at 200°C and with an helium flow-rate of 20 cm³/min. A thermal conductivity detector was used and the results were monitored with a Varian Vista 402 data system. Stainless-steel columns (3 m × 2.4 mm I.D.) packed with Porapak (N, P, Q, R, S and T types) and Chromosorb "Century Series" (101, 102, 103, 104, 105, 106, 107 and 108 types) PPBs (80–100 mesh) or with different stationary phases, prepared with 15% (w/w) of the liquid on Chromosorb G HMDS (80–100 mesh), were used. The reference columns were packed with Chromosorb 106 (80–100 mesh) or with 15% (w/w) squalane and Apolane on Chromosorb G HMDS (80–100 mesh).

All the columns were preconditioned at 200°C or at their maximum usable temperature. In order to use squalane as the standard non-polar liquid phase in Rohrschneider's and McReynolds' classification, the f_{20}^s values were obtained by extrapolation of Arrhenius plots of the logarithm of the adjusted retention values as a function of the reciprocal of the column absolute temperature. The same procedure was followed for other liquid phases with temperature limits lower than 200°C. Moreover, the linear relationship between the I values of the polarity probes on squalane and the I values on Apolane⁴ permitted the Δf_{20}^s values to be calculated within 2–3 index units, which is good enough for classification purposes. Furthermore, the use of different batches of PPBs or of liquid phases obtained from different suppliers yielded retention values that differ by the same order of magnitude (up to 5 index units).

While the behaviour of the GLC columns did not change substantially after the first conditioning, some of the PPBs showed a slow change in performance for a long time after the first conditioning. This behaviour was investigated previously⁶ and the change in retention of some PPB columns was found to be too large to be neglected in the classification. As an example, Fig. 1 shows the chromatogram of some of the polarity probes and of linear alkanes on a freshly prepared and thermally aged Chromosorb 108 column after 3 and after 23 days at 200°C under a carrier gas flow-rate of 20 cm³/min.

When the change in the retention times and of the elution order of the polarity probes were too large to be neglected (greater than 5 index units over an ageing time of about 20 days), the I values on the new and aged column were taken into account.

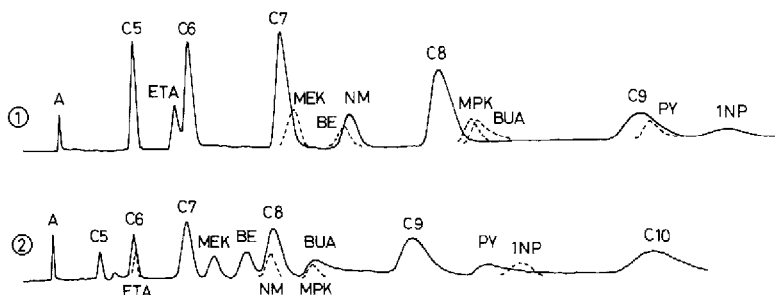


Fig. 1. Effect of the ageing of a Chromosorb 108 column (at 200°C for 23 days under a helium flow-rate of 20 cm³/min) on the retention times of linear alkanes and polarity probes. (1) New column; (2) aged column. For the analysed compounds see text.

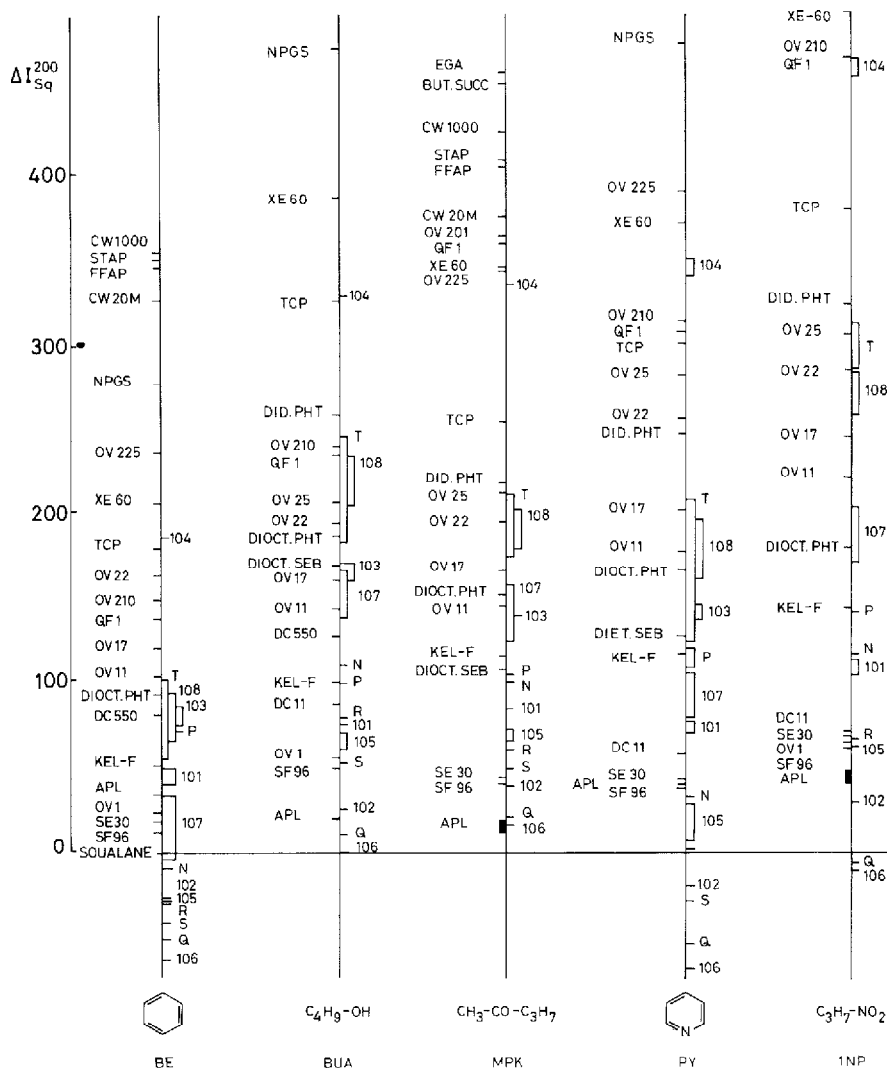


Fig. 2. Values of M_{30}^{200} for some of the McReynolds polarity probes on PPB and GLC stationary phases. For symbols see Table I. N, P, Q, R, S, T are the Porapak types, and 101, 102, 103, 104, 105, 106, 107, 108 are the Chromosorb types.

TABLE I
LIQUID PHASES USED FOR COMPARISON OF THE BEHAVIOUR OF PPB COLUMNS

<i>Liquid phase</i>	<i>Symbol</i>	<i>Temperature limit (°C)</i>
Apiezon L	APL	300
Butanediol succinate	BUT SUCC	225
Carbowax 1000	CW 1000	150
Carbowax 20M	CW 20M	225
Didecyl phthalate	DID PHT	175
Diocetyl phthalate	DIOCT PHT	150
Diocetyl sebacate	DIOCT SEB	125
Ethylene glycol adipate	EGA	225
Diethylene glycol adipate	DEGA	225
Ethylene glycol succinate	EGS	200
Diethylene glycol succinate	DEGS	200
Neopentyl glycol succinate	NPGS	225
FFAP (modified polyglycol)	FFAP	250
KEL-F	KEL F	200
Methyl silicone DC 11	DC 11	300
Methyl-phenyl silicone DC 550	DC 550	250
Fluoro silicone DC QF-1	QF-1	250
Dimethyl silicone OV-1	OV-1	350
Dimethyl silicone OV-101	OV-101	350
Methyl-phenyl silicone OV-11 (35% phenyl)	OV-11	350
Methyl-phenyl silicone OV-17 (50% phenyl)	OV-17	375
Methyl-phenyl silicone OV-22 (65% phenyl)	OV-22	350
Methyl-phenyl silicone OV-25 (75% phenyl)	OV-25	350
Trifluoropropyl silicone OV-210	OV-210	275
Cyanopropyl methyl-phenyl OV-225	OV-225	265
Dicyanoallyl silicone OV-275	OV-275	275
Methyl silicone GE SE-30	SE-30	300
Methyl silicone GE SF-96	SF-96	250
Cyanoethyl silicone GE XE-60	XE-60	250
Squalane	SQUAL	120
STAP (steroid phase)	STAP	200
Tricresyl phosphate	TCP	125
1,2,3-Tris(2-cyanoethoxy)propane	TCEP	180

RESULTS AND DISCUSSION

Fig. 2 shows the A_{200}^{80} values for the McReynolds probes (BE, BUA, MPK, Py and 1NP) measured at 200°C on PPB and GLC columns. The square brackets indicate the ranges of values due to the ageing of the PPB columns, the upper values being that for columns aged at 200°C for 20 days or more under an helium flow-rate, and therefore perfectly conditioned and yielding constant retentions. The symbols used for the GLC phases are listed in Table I, in the order of the commonly accepted McReynolds polarity scale. The temperature limits are also shown.

Polymers	Structure	Polarity class
103 - 106	$\text{-CH-CH}_2\text{-CH-CH}_2\text{-CH-CH}_2\text{-}$	IV
P-101-102	$\text{-CH-CH}_2\text{-CH-}$ $\text{-CH-CH}_2\text{-}$ 	IV
Q	$\text{-CH-CH}_2\text{-CH-}$ Et $\text{-CH-CH}_2\text{-}$ 	IV
S	$\text{-CH-CH}_2\text{-CH-CH}_2\text{-CH-CH}_2\text{-}$ 	IV
N-R	$\text{-CH-CH}_2\text{-CH-CH}_2\text{-CH-CH}_2\text{-}$ 	III
105-107-108	$\text{-CH}_2\text{-CH-CH}_2\text{-CH-CH}_2\text{-CH-}$ 	III
T	$\text{-CH}_2\text{-C-CH}_2\text{-CH}_2\text{-CH}_2\text{-C-CH}_2\text{-}$ 	III
104	$\text{-CH}_2\text{-C-CH}_2\text{-CH-CH}_2\text{-C-CH}_2\text{-CH-}$ 	II

Fig. 3. Chemical structures of the various polymers and their classification according to the Ewell scale⁷. Active hydrogen atoms and electron-donor atoms are shown.

Many of the PPBs have $\Delta I_{260}^{S_0}$ values smaller than the available GLC phases, and than squalane itself, mainly when ring compounds (benzene, pyridine) are used as polarity probes, and are therefore less polar than GLC phases.

On the basis of the solute and solvent classification suggested by Ewell *et al.*⁷, the polarity probes used can be classified as belonging to class II (polar) in the cases of butanol and 1-nitropropane, compounds containing both a donor atom (O or N) and an active hydrogen atom (respectively the hydroxy H and the α -H atom in the nitro compound); to class III (intermediate) in the cases of methyl propyl ketone and pyridine, containing donor atoms but no active hydrogen atoms; to class IV (low polarity) in the case of benzene.

On the other hand, the same classification when applied to the PPBs tested (Fig. 3) shows that these polymers belong to the low or intermediate polarity classes (III or IV), except for Chromosorb 104 which being a nitrile with α -H atoms, has to

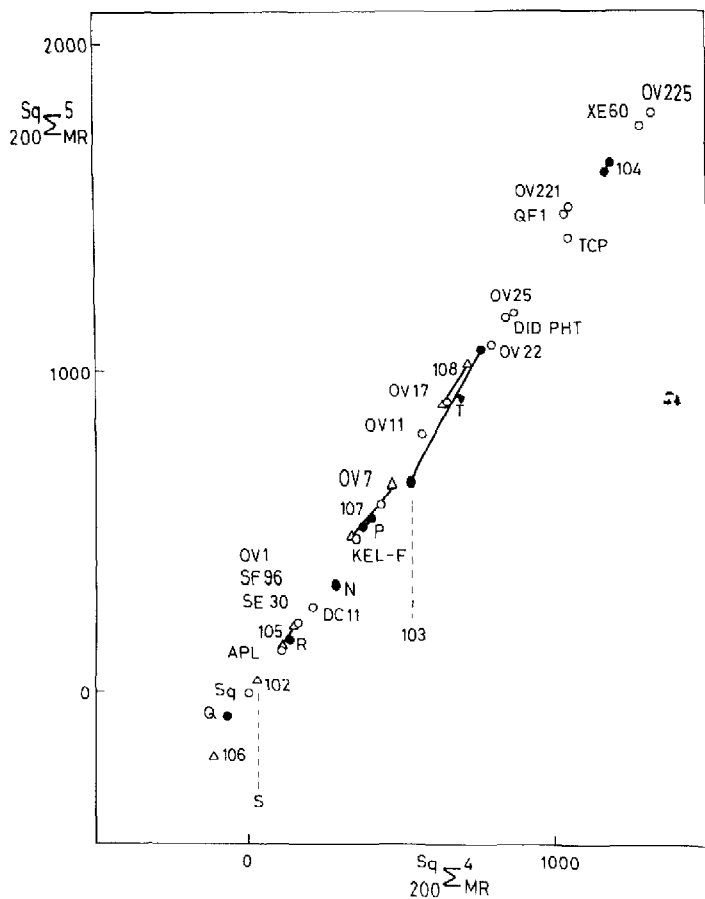


Fig. 4. Average polarity $\frac{S_q \Sigma^5}{200 \Sigma^5 MR}$ of the PPBs and of some liquid stationary phases as a function of the $\frac{S_q \Sigma^4}{200 \Sigma^4 MR}$ values.

be included in class II. The $\Delta I_{200}^{S_q}$ values increase according to the polarity of both the PPB and the probe, the greatest values being found for nitropropane on Chromosorb 104, both the solute and the solvent belonging to the polar (II) class.

Fig. 4 summarizes the results in terms of the average polarity expressed as the $\frac{S_q \Sigma^5}{200 \Sigma^5 MR}$ values plotted as a function of the $\frac{S_q \Sigma^4}{200 \Sigma^4 MR}$ values. The $\Delta I_{200}^{S_q}$ values for nitropropane were not available for Porapak S and Chromosorb 103 columns (see Fig. 2) because these phases react with this probe. Only the X-axis values are therefore shown for these PPBs. The fair linearity confirms that both the Σ^5 and Σ^4 values are suitable for a quantitative evaluation of the average polarity.

The values for some widely used GLC columns are also shown in Fig. 4. The most polar PPB (Chromosorb 104) has an average polarity similar to that of GE XE-60 (cyanoethyl silicone), OV-210 and QF-1 (trifluoropropyl silicones) and tricresyl phosphate (TCP). Fig. 2 shows that the polarity order is more or less similar when the $\Delta I_{200}^{S_q}$ values for the various probes are taken into account, with some changes in the relative ratios of the ΔI values for these liquid phases.

Fig. 5 shows the average polarity range that can be covered by PPB columns

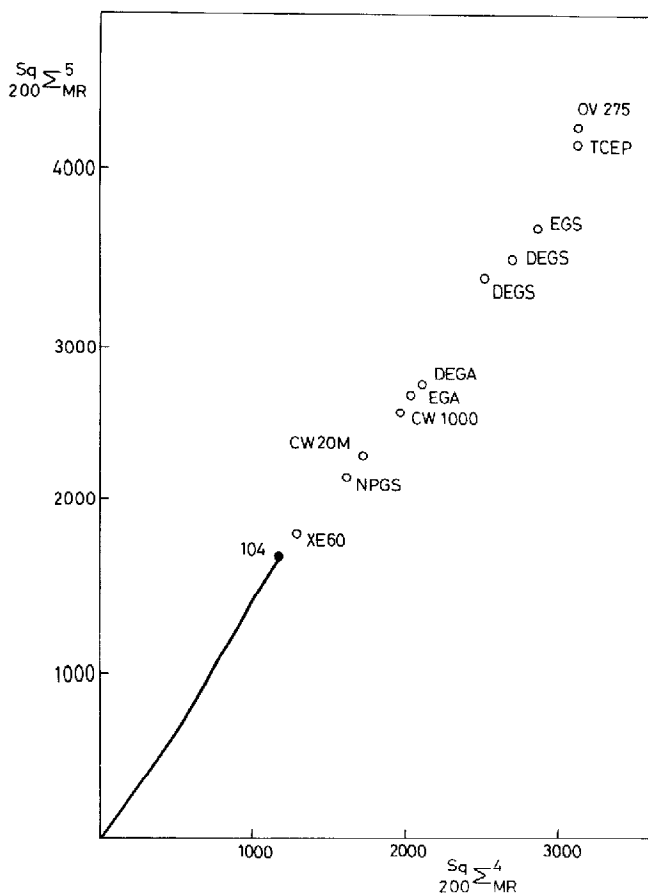


Fig. 5. Reduced scale plot, similar to that shown in Fig. 4, where the polarity range of PPB stationary phases is correlated with that of some polyglycol liquid phases. For points below Chromosorb 104 see Fig. 4.

with respect to some well known and widely used highly polar liquid phases (polyglycols and polyesters). In this instance the polarity order obtained with the different probes (Fig. 2) shows greater fluctuations, *e.g.*, the ratio $\Delta I(CW\ 20M)/\Delta I(104)$ is 1.73 for benzene, 1.63 for butanol, 1.11 for MPK, 1.50 for pyridine and 1.23 for 1 nitropropane, but confirms that the choice of the McReynolds' polarity probes and the determination of their ΔI^{Sq} values permit a suitable classification of both PPB and GLC stationary phases.

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