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CLASSIFICATION OF THE "POLARITY" OF POROUS POLYMER BEAD STATIONARY PHASES BY COMPARISON WITH SQUALANE AND APOLANE STANDARD LIQUID PHASES

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SUMMARY

A classification of the "polarity" of porous polymer bead (PPB) stationary phases [Porapak and Chromosorb (Century Series)] with respect to standard polarity reference phases [squalane and $C_{87}H_{167}$ (Apolane)] was carried out by determination of the retention indices of Rohrschneider's and McReynolds' polarity probes (ethanol, butanol, benzene, pyridine, nitromethane, 1-nitropropane, methyl ethyl ketone and methyl propyl ketone). Some PPBs have average polarity values lower than those of squalane and Apolane, whereas the most polar PPBs are comparable to medium polarity liquid stationary phases, *e.g.*, methyl-, trifluoropropyl- and cyanopropylsilicones and some polyesters.

INTRODUCTION

In a previous paper¹, the classification of the "polarity" of Porapak and Chromosorb "Century Series" porous polymer bead (PPB) stationary phases was made on the basis of the retention indices (I) of Rohrschneider's² and some of the McReynolds's³ polarity probes, by using as relative reference of the polarity scale the "less polar" Chromosorb 106, which shows the lowest I values of all the probes and solvent tested. The choice of an "internal reference" polarity scale is accurate enough for comparing the behaviour of commercial PPBs, but does not permit a general comparison of these stationary phases with the wide number of liquid phases available and classified previously²⁻⁴. The main difficulty is that the analysis of liquid samples on long PPB columns requires high temperatures in order to give suitable retention times. The previous classification of PPBs, with retention indices of the probes of up to 1100, required more than 2 h for the elution from some PPB columns.

The standard non-polar liquid phase chosen as a reference for the Rohrschneider's and McReynolds' classification is squalane, but, as it has an upper temperature limit of 100-120°C, it cannot be used in this instance. The calculation of the adjusted retention times of the polarity probes and of *n*-alkanes at 200°C by using Arrhenius plots may permit extrapolated I_{200}^{Sg} values to be obtained, but the resulting accuracy of the $\Delta I_{200}^{Sg}(C)$ (where C indicates the type of PPB tested) may be low,

owing to the large gap between the last experimental and the extrapolated values. A high-temperature liquid phase should therefore be used as the reference. Methyl silicone phases have been proposed⁵, but the distribution of molecular weights that change from batch to batch and from one producer to another does not permit the definition of a standard composition of the reference phase. In addition, severe tailing of some polar probes was observed when an attempt was made to use SE-30 methylsilicone as the reference liquid phase, probably owing to the interaction of the sp^3 -hybridized silicon atoms with weak bases such as methanol or butanol.

The synthetic $C_{87}H_{176}$ hydrocarbon proposed by Riedo *et al.*⁶, 22,24-diethyl-19,29-dioctadecylheptatetracontane (mol.wt. 1222.34), was therefore used, because it can be used as a stationary phase in the temperature range between 30 and 280–300°C, corresponding to the range of application of PPBs.

EXPERIMENTAL

Stainless-steel columns (3 m × 2.4 mm I.D.) packed with Porapak and Chromosorb "Century Series" PPBs (80–100 mesh) were used. The reference columns were filled with 15% (w/w) of squalane and C_{87} on 80–100-mesh Chromosorb G, HMDS. PPBs and C_{87} columns were pre-conditioned at 200°C and the squalane column at 100°C. A Varian 3760 gas chromatograph was used with a constant helium flow-rate of 20 $cm^3 min^{-1}$, monitored before and after each run and corrected when necessary. A high-sensitivity thermal conductivity detector was used and the results were monitored by a Varian CDS-111C data system.

The accuracy of the retention time measurement was ± 0.01 min and the adjusted retention times, t'_R , were calculated with respect to the retention time of air. The analyses on PPB phases were carried out on freshly prepared columns and repeated at regular intervals during an ageing period of up to 25 days, as it was previously shown that the retention times of some compounds on some PPBs change with the column ageing⁷.

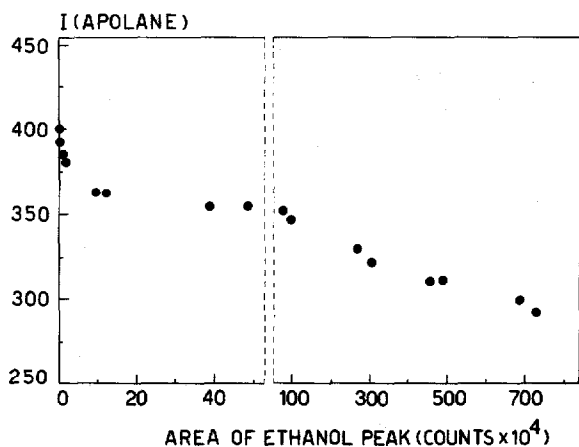


Fig. 1. Effect of the sample volume on retention index (I). Ethanol on Apolane (15%) at 150°C, carrier gas flow-rate 20 $cm^3 min^{-1}$. The largest peak corresponds to about 1 μl and the smallest to $5 \cdot 10^{-4}$ μl of sample.

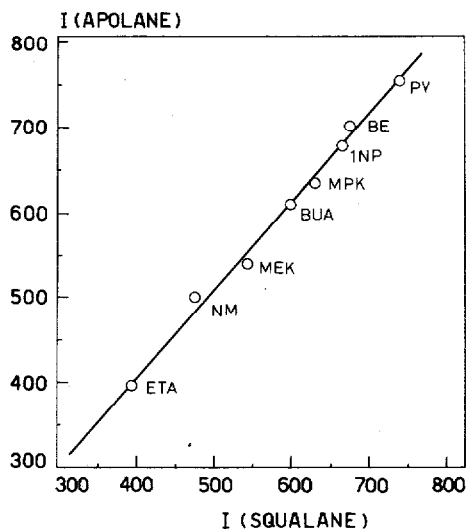


Fig. 2. Retention indices of the polarity probes at different temperatures on Squalane and Apolane (15%) on Chromosorb G HMDS. Values for squalane at 200°C are extrapolated. For symbols, see text.

The Rohrschneider's probes, ethanol (ETA), methyl ethyl ketone (MEK), nitromethane (NM), benzene (BE) and pyridine (PY), and some of the McReynolds' probes, butanol (BUA), methyl propyl ketone (MPK) and 1-nitropropane (INP), were injected together with C_5 – C_{11} *n*-alkanes, in suitable mixtures to avoid peaks interferences. Direct on-column injection was accomplished, with the injector temperature set at the same values as the column. The amount of sample injected influenced the slope of the peaks when non-ideal solute–solvent pairs were considered. Fig. 1 shows the dependence of the retention index of ETA on the volume injected. Therefore, the chromatograms used for the calculation of the retention values were obtained by injecting $0.5 \mu\text{l}$ of air with a microsyringe previously washed with the sample. Only the residual sample vapour was thus injected and, by repeating this procedure several times, series of decreasing and more and more symmetrical peaks were obtained, the smallest corresponding to the injection of about $5 \cdot 10^{-4} \mu\text{l}$ of sample. Extrapolation of the retention times to zero sample volume was also possible with this technique.

RESULTS AND DISCUSSION

The I values of the probes on Apolane, I^{AP} , at 100, 150 and 200°C, and on squalane, I^{SQ} , at 75, 100 and 125°C (experimental) and at 200°C (calculated from t'_R values extrapolated by an Arrhenius plot) are shown in Fig. 2. The values of I at 125°C on squalane agrees with "standard" McReynolds values at 120°C³, as shown in Table I, except for pyridine, probably owing to the asymmetric peak of this compound. An I value of 701 (closer to the McReynolds value) was in fact obtained by injecting an amount of this substance ten times greater than that sampled normally.

Fig. 3 shows a plot of the retention indices of the probes on Apolane *versus* those on squalane; the linearity of the plot was fair (correlation coefficient 0.997,

TABLE I

RETENTION INDICES OF ANALYSED PROBES ON APOLANE AND SQUALANE (15%) AT 100 AND 200°C

Values on squalane at 125°C are also shown and compared with "standard" McReynolds data at 120°C³.

Probe	100°C		200°C		125°C, squalane	120°C, squalane (McReynolds)
	Squalane	Apolane	Squalane*	Apolane		
ETA	396	413	396	397	391	—
MEK	533	541	544	542	534	—
NM	467	500	476	500	463	—
BE	647	670	675	702	652	653
BUA	588	603	600	610	590	590
MPK	624	630	631	636	626	627
Py	707	719	740	757	711	699
INP	647	662	667	678	652	652

* Extrapolated values.

slope 1.034, intercept -3.4°C) and showed that both extrapolated I^{SQ} and experimental I^{AP} should be used as the reference term for the calculation of $\Delta I_{200}^{\text{SQ}}$ values (Tables II and III). Of course, the inherent errors and longer procedure in the extrapolation from low-temperature squalane data suggest that the use of Apolane as the high-temperature reference phase is to be preferred.

From the point of view of the choice of the "less polar" reference liquid phase, however, the differences between the I^{AP} and the I^{SQ} , *i.e.*, ΔI^{SQ} (Apolane), are positive. As shown previously⁷, squalane has a higher "polarity" than the corresponding *n*-alkane, whose behaviour can be considered to be similar to that of the hypothetical

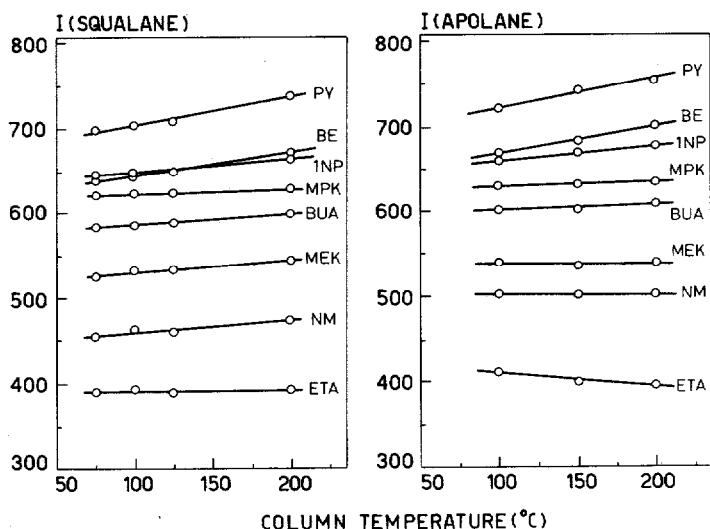


Fig. 3. Retention indices of the polarity probes on Apolane at 200°C versus the extrapolated values for squalane.

TABLE II

 ΔI_{200}^{SO} VALUES OF THE VARIOUS PROBES

Where two values are shown, the upper one refers to the new and the lower one to the aged PPB column (22 days at 200°C under a helium flow).

Stationary phase	ETA	MEK	NM	BE	BUA	MPK	Py	INP
Porapak								
N	94	92	139	-9	108	99	30	117
P	77	96	165	71	98	101	107	142
	93						128	
Q	5	10	4	-52	9	20	-53	-6
R	66	53	84	-28	77	62	1	65
S	49	38	-*	-42	52	49	-27	-*
T	158	161	254	54	182	169	120	284
	223	205	351	102	244	206	205	309
Chromosorb								
101	73	80	144	48	75	83	70	113
			137	41			70	105
102	14	30	45	-27	25	38	-18	30
			153	88	160	145	-*	
103	163	139	-*	81	167	139		136
			337	458				
104	311	327	505	186	329	330	347	467
							6	63
105	42	54	73	-28	61	62	30	63
							56	63
106	-21	6	12	59	-0.6	16	-68	-9
							118	112
107	137	144	216	33	166	156	104	205
							173	171
108	207	191	317	96	234	198	195	284

* Reacts with stationary phase; very broad or multiple peaks.

alkane phase with a ratio of methyl groups to total carbon atoms of zero, where the possible selectivity towards the methyl groups of the solute is minimal; therefore, Apolane, being more "polar" than squalane, is not the "ideal" non-polar reference phase from a theoretical point of view, but nowadays it is the best choice for high-temperature use.

Tables II and III show the values of ΔI_{200}^{SO} and ΔI_{200}^{AP} of the various polarity probes, respectively. Owing to the fact that ΔI_{200}^{SO} (Apolane) values are positive, the "polarity" with respect to squalane is higher than with respect to Apolane. The "average polarity" values (Σ^5) in the Rohrschneider (R) and McReynolds (MR) reference systems are shown in Table IV for squalane and Apolane data. The Σ^4 values, *i.e.*, the sums of the ΔI values, except those for NP and NM, are also shown to permit Chromosorb 103 and Porapak S, which react with these two probes¹, to be compared with the other PPBs.

A comparison of the Σ_{MR}^5 values on squalane with those calculated from McReynolds' data for many liquid phases³ shows that the "average polarities" of many of the tested PPBs range between values typical of non-polar and medium-

TABLE III

 ΔI_{260}^{AP} VALUES OF THE VARIOUS POLARITY PROBES

Where two values are shown, the upper one refers to the new and the lower one to the aged PPB column (22 days at 200°C under a helium flow).

Stationary phase	ETA	MEK	NM	BE	BUA	MPK	Py	INP
Porapak								
N	92	93	114	-36	97	94	13	106
	76						91	
P	92	98	141	44	88	96	112	130
Q	4	12	-20	-78	-1	14	-70	-18
R	64	55	60	-54	66	56	-16	53
S	47	39	-*	-68	41	43	-44	-*
	156	163	230	28	172	164	103	272
T	222	207	327	76	233	200	188	297
Chromosorb								
101	71	82	120	22	65	77	60	101
			113	15			53	94
102	12	32	20	-54	14	32	-35	18
	151			61	149		128	
103	161	141	-*	55	156	133	119	-*
							320	447
104	309	329	481	160	319	325	330	456
	41	55			50	56	-11	
105	54	64	49	-54	60	66	13	52
106	-23	8	-36	-85	-11	11	-84	-20
	117	114	144	-31	128	116	56	160
107	135	146	192	6	156	151	87	194
	171	173	144	46	204	172	146	245
108	205	192	293	69	224	193	178	272

* Reacts with stationary phase; very broad or multiple peaks.

polar liquid phases. The Σ_{MR}^5 values of apizons and methyl silicones agree with those for Chromosorb 105 and Porapak R; Porapak T and Chromosorb 104 show values similar to those found for trifluoropropylsilicones (QF-1, OV-210), cyanopropyl phenylsilicones (OV-225), tricresyl phosphate and didecyl phthalate.

Porapak Q and Chromosorb 106 are much less "polar" than squalane itself, and for this reason they were chosen as reference phases for polarity classification restricted to PPBs^{1,8}. The negative Σ_{MR}^5 value on Porapak Q is mainly due to the highly negative values of ΔI for benzene and pyridine, while all ΔI values, except those for ketones, are negative on Chromosorb 106.

CONCLUSIONS

The above results show that the synthetic C₈₇ hydrocarbon Apolane can be used as the reference term to measure the "polarity" of PPB columns at high temperatures with the standard polarity probes. The resulting classification agrees with that obtained through the calculation of retention times and indices on squalane

TABLE IV

VALUES OF THE AVERAGE POLARITIES OF VARIOUS PPBs, DETERMINED FROM THE SUM OF ΔI_{200} VALUES AND THE POLARITY PROBES ON SQUALANE AND APOLANE

Σ_R^5 = Sum of ΔI for ETA, MEK, NM, BE and Py; Σ_R^4 = sum of ΔI for ETA, MEK, BE and Py; Σ_M^5 = sum of the ΔI for BUA, MPK, INP, BE and Py; Σ_{MR}^4 = sum of ΔI for BUA, MPK, BE and Py. When two values are shown, the upper ones refers to new and the lower one to aged columns (22 days at 200°C under a helium flow).

Stationary phase	Squalane				Apolane			
	Σ_R^5	Σ_{MR}^5	Σ_R^4	Σ_{MR}^4	Σ_R^5	Σ_{MR}^5	Σ_R^4	Σ_{MR}^4
Porapak								
N	346	345	207	228	276	274	162	168
P	{ 516	519	351	377	{ 450	449	309	319
	{ 553	540	388	398	{ 487	470	346	340
Q	- 86	- 82	- 90	- 76	-152	-153	-132	-135
R	176	177	92	112	109	105	49	52
S	-	-	18	32	-	-	- 26	- 28
T	{ 747	645	493	525	{ 680	739	450	467
	{ 1086	1066	735	757	{ 1020	994	693	697
Chromosorb								
101	{ 422	396	278	283	{ 355	325	235	224
	{ 401	374	264	269	{ 334	304	221	210
102	44	48	- 1	18	- 25	- 25	- 5	- 43
103	{ -	-	525	532	{ -	-	481	471
			519	523			476	463
104	{ 1666	1640	1161	1182	{ 1599	1571	1118	1124
		1659		1192		1590		1134
105	{ 127	164	74	101	{ 80	93	31	41
	{ 194	208	121	145	{ 126	137	77	85
106	-154	-121	-142	-112	-220	-189	-184	-169
107	{ 465	499	249	327	{ 400	429	256	269
	{ 634	664	418	459	{ 566	594	374	400
108	{ 848	885	580	628	{ 780	813	536	568
	{ 1006	1007	689	723	{ 937	936	644	664

extrapolated from experimental data at lower temperatures. Some PPBs have an average polarity lower than those of squalane and Apolane, while the most "polar" PPBs are comparable to medium-polarity liquid stationary phases (methyl-, trifluoropropyl- and cyanopropylsilicones and some polyesters) and can therefore be used for applications typical of these gas-liquid chromatographic columns.

However, the comparison of PPBs with liquid phases made simply with the average polarity values may be misleading, owing to the different contributions of the various probes to the final Σ values. The ΔI values of probes having different functional groups should be considered in order to select the most suitable phase for a given separation.

Further investigation is necessary for a complete understanding of the interaction mechanism of PPBs in gas chromatography. A better knowledge of the chemical composition and structure of the polymers, information which, in our opinion, could be released by the producers without disclosing preparation know-how, would

probably make this research easier and more useful to the users of these stationary phases.

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