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STATIONARY PHASE POLARITY CLASSIFICATION AT HIGH TEMPERATURE

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SUMMARY

The Rohrschneider classification system for stationary phase polarity has been extended to high-temperature evaluation at 180°. This is made possible by the use of a new non-polar reference phase, hydrogenated Apiezon M, and a set of high-temperature probes consisting of *n*-butylbenzene, octanol, 2-octanone, 1-nitrohexane and collidine. The system has been tested using six stationary phases and a method of transposing the data obtained at 180° into McReynolds constants for phase classification is given.

INTRODUCTION

Many substances which are potential high-temperature stationary phases in gas–liquid chromatography may not be evaluated at lower temperatures due to their high melting points if they are pure monomeric substances, or if they are vinyl polymers the glass-to-rubber transition temperature (T_g) may be high and the viscosity of the material just above the transition temperature will certainly be so high that the coefficients of mass transfer will be unacceptably large. *p*-Terphenyl (melting point 171°) is an example of the former whilst polystyrene (T_g 110°) and poly(methyl methacrylate) (T_g 120°) are examples of the latter class of substances. The properties of polystyrene as a stationary phase have been reported[1], the material being suitable for use in the temperature range 240°–340°. The behaviour of poly(methyl methacrylate) as a stationary phase has also been reported[2], and whilst the material was not capable of giving column packings which led to columns of high efficiency, with a maximum operating temperature of 280°, this polyester may find some application in the field.

A new method of stationary phase classification is not necessary. With the large amount of data now available on phase classification by Rohrschneiders' method[3] and by the modifications proposed by McReynolds[4], it would be of value to have a method of classifying phase polarity at high temperature which could then be related to Rohrschneider or McReynolds constants as published by commercial suppliers of stationary phases. The main problem, however, has been that squalane, the non-polar reference phase, cannot be used with column temperature in excess of 130°. Now, with the development of a new non-polar reference phase which gives probe indices comparable to squalane but has a maximum operating temperature of 200°, the problem has been eliminated. This non-polar reference phase for high-temperature work is hydrogenated Apiezon M (Apiezon MH, ApMH)[5]. Assessments of stationary phases using a set of aromatic compounds have been made at a temperature of 180° for polystyrene and polybenzyl hydrocarbon phases[1], for the range of Apiezon greases[5] and for several polyesters[2]. These probes were *n*-butylbenzene, benzyl alcohol, acetophenone, nitrobenzene and aniline used with the intention of obtaining information relevant to that obtained using the McReynolds probes benzene, 1-butanol, 2-pentanone, nitropropane and pyridine. Apart from the functional group, there is little similarity in the two sets of probes and even this disappears in the case of pyridine and aniline. Whereas pyridine can yield useful information on interactions due to the fact that it has proton acceptor but no proton donor properties, in aniline the amine hydrogen atoms are available for hydrogen bonding to an oxygen lone pair. *n*-Butylbenzene will serve very well as a dispersion probe, however the proton donor/acceptor properties of benzyl alcohol will hardly compare with butanol. Dipole orientation properties of acetophenone and nitrobenzene will bear little resemblance to 2-pentanone and nitropropane, in all three cases conjugation will have profound and differing degrees of effect and of course dispersion forces due to the aromatic ring are present in each case.

n-Butylbenzene (b.p. 180°) is a useful dispersion probe for a column temperature corresponding to its boiling point. Rohrschneiders' intial system employed benzene with a working temperature of 80° for this purpose and the comparison is direct. For the selection of the other four probes it is necessary to follow McReynolds example of substituting 1-butanol for ethanol, 2-pentanone for methyl ethyl ketone, and nitropropane for nitromethane when switching to a working temperature of 120°. Availability of the materials was also a consideration, accordingly the other four probes selected were octanol, 2-octanone, 1-nitrohexane and collidine (trimethylpyridine).

For the determination of column polarities at 180°, it is necessary to chromatograph each of the five probes together with the appropriate *n*-paraffins on the column to be evaluated and on an ApMH reference column at the same temperature. On the reference phase, the lowest retention index is around 940 so the *n*-paraffins required are from *n*-nonane upwards. The retention index dispersions, ΔI, for each solute are obtained from

$$\Delta I = I_p - I_{\mathrm{ApMH}} \tag{1}$$

where I_p is the retention index of the solute on the phase to be evaluated.

Using the Rohrschneider concept of dividing the dispersion into a linear summation of probe and phase properties:

$$\Delta I = \mathrm{a}x + \mathrm{b}y + \mathrm{c}z + \mathrm{d}u + \mathrm{e}s \tag{2}$$

where a, b, c, d and e are probe constants for *n*-butylbenzene, octanol, 2-octanone, 1-nitrohexane and collidine, respectively, and x, y, z, u and s represent contributions to stationary phase polarity, it is possible to evaluate the latter by defining each of the probe constants as unity for that particular probe and zero for the other four. Thus for *n*-butylbenzene $\Delta I = x$, for octanol $\Delta I = y$, etc.

An evaluation of this system of stationary phase polarity determination and a comparison of the results obtained with corresponding values obtained on the phases using the McReynolds probes at 120° is the subject of this work.

EXPERIMENTAL

All gas chromatographic data were obtained using a Pye Series 104 gas chromatograph with flame ionization detector. All columns were 2 m × 6 mm O.D. copper tubing packed with a 20% (w/w) loading of stationary phase on Universal Support, a special silanized Celite of very low surface activity. Columns were conditioned at 180° with a carrier gas flow of 10 ml/min of nitrogen for 24 h. All measurements were made with a carrier gas flow-rate of 20 ml/min. Column evaluation using the McReynolds probes was carried out at 120° and using the high-temperature equivalents at 180°.

Stationary phases

ApMH was prepared as described[5], Apiezon L, Silicone SE-30, Silicone QF-1 and Carbowax 20M were used as supplied by Phase Separations. Two polyesters, poly(ethanediol adipate) (PEGA) and poly(ethanediol succinate) (EGS) were prepared by mixing exactly equimolar proportions of pure diol and dibasic acid and heating at 140° for 12 h.

Dead-times were determined by injection of methane. Retention indices of the solutes were obtained by chromatographing with the two appropriate *n*-paraffins and using the Kováts formula[6]. All retention times were measured by stop-watch. Sample sizes were 1 µl or less.

TABLE I

RETENTION INDICES, TEMPERATURE COEFFICIENTS AND SPECIFIC RETENTION VOLUMES (V_g) ON THE REFERENCE PHASE APIEZON MH

Solute	*I*					
	100°	*110°*	*120°*	*130°*	*10 $\Delta I/T$*	V_g
Benzene	668	671	674	677	3	7.71
1-Butanol	599	599	599	599	0	4.53
2-Pentanone	631	631	631	631	0	5.82
1-Nitropropane	663	665	667	669	2	7.68
Pyridine	740	740	740	740	0	12.32
Solute	*I*					
	160°	*170°*	*180°*	*190°*	*10 $\Delta I/T$*	V_g
Butylbenzene	1076	1080	1085	1089	4.5	15.77
Octanol	955	954	954	955	0	8.09
2-Octanone	940	941	942	944	1.3	7.73
1-Nitrohexane	985	986	988	990	1.7	9.89
Collidine	1005	1008	1012	1015	3.3	11.10

TABLE II

RETENTION INDICES AND SPECIFIC RETENTION VOLUMES OF THE TWO SETS OF PROBES ON SIX STATIONARY PHASES

Solute	*Temp. (°C)*	*Stationary phase*											
		Apiezon L		*SE-30*		*QF-1*		*Carbowax 20M*		*PEGA*		*EGS*	
		I	V_g	*I*	V_g	*I*	V_g	*I*	V_g	*I*	V_g	*I*	V_g
Benzene	120	687	8.69	663	4.93	769	3.58	931	7.62	1022	4.88	1050	3.34
1-Butanol		627	5.79	643	437	787	4.00	1073	16.64	1183	11.10	1191	8.14
2-Pentanone		651	6.86	666	5.06	937	8.59	949	8.82	1086	9.45	1103	4.44
1-Nitropropane		700	9.37	717	6.84	1066	16.24	1170	27.59	1294	19.62	1343	15.62
Pyridine		770	15.18	757	8.81	984	11.10	1162	27.27	1409	32.78	1427	52.77
Butylbenzene	180	1101	17.18	1072	7.96	1174	4.40	1330	9.90	1452	5.42	1457	3.19
Octanol		1008	10.73	987	5.53	1136	3.80	1344	10.61	1505	6.35	1495	3.56
2-Octanone		958	8.47	977	5.31	1268	6.19	1272	7.91	1438	5.03	1453	3.13
1-Nitrohexane		1020	11.42	1034	6.67	1419	12.46	1477	18.34	1675	12.10	1713	8.32
Collidine		1033	12.22	1018	6.25	1178	4.35	1391	13.53	1897	17.06	—*	—

* Severe tailing made peak maximum impossible to determine accurately.

RESULTS AND DISCUSSION

Table I gives the retention data for both sets of probes on the reference phase ApMH together with the temperature coefficients of the retention indices. The spread of retention indices within a set is seen to be numerically similar with butanol and pyridine being respectively the lowest and highest of the low temperature set and octanone and butylbenzene of the high-temperature probes. Table II gives the retention indices and specific retention volumes for the McReynolds solutes as determined at 120° and for the set of high-temperature probes at 180°. On inspection of this table it is obvious that the same kind of data on retention characteristics and stationary phase selectivity is to be had from the retention indices of both sets of probes. Thus, of the two silicone phases studied, QF-1 displays ketone selectivity in both sets due to the presence of trifluoropropyl groups in the phase. Carbowax 20M displays selective retention for butanol and octanol when compared with the silicones and Apiezon, whilst the two polyesters are the most polar phases and also demonstrate selectivity for alcohols. Table III lists the retention index dispersions for the two sets of probes and the six phases. These dispersions are derived from eqn. 1 using McReynolds data[4] on squalane for the low temperature probes and the retention indices at 180° given in Table I for the high-temperature set. The data in Table III, therefore, consists of the McReynolds constants (x, y, z, u and s) and the high-temperature constants (x_h, y_h, z_h, u_h and s_h) of the six stationary phases studied.

Several important deductions can be drawn from the data in Table III. If the assumption is made that the retention dispersion represents the degree of interaction between the probe and the stationary phase, this interaction being zero for a paraffin or saturated hydrocarbon phase, then it may be seen that these degrees of interaction are of similar magnitudes for the same functionality in both sets of probes. This is an important concept if information obtained at 180° with the high-temperature probes is to be interpreted in terms of McReynolds constants for the phase. In Table III there are two departures from this relationship, butanol and octanol behave differently on Carbowax 20M. This predominantly electron donor phase displays selective retention

TABLE III

RETENTION INDEX DISPERSIONS FOR THE PHASES STUDIED

Solute	ΔI					
	Apiezon L	*SE-30*	*QF-1*	*Carbowax 20M*	*PEGA*	*EGS*
$\Delta I = I_p - I_{squalane}$ *(120°)*						
Benzene	34	10	116	278	369	397
1-Butanol	37	53	197	483	583	601
2-Pentanone	24	39	310	322	459	476
1-Nitropropane	48	65	414	518	642	691
Pyridine	71	58	285	463	710	728
$\Delta I = I_p - I_{ApMH}$ *(180°)*						
Butylbenzene	16	—13	89	245	367	372
Octanol	54	33	182	390	551	540
2-Octanone	18	37	328	332	498	518
1-Nitrohexane	32	46	431	489	687	725
Collidine	21	6	166	379	885	—

for alcohols as shown by the butanol dispersion. The degree of interaction of octanol with the phase is much lower than would be expected and, as strong interactions are involved, the difference must be explainable in terms of the differences in dipole moments of the two alcohols. The second anomaly again involves strong interactions and selective retention, the anomalous probe again being octanol which displays a stronger interaction with PEGA than with EGS. The octanol probe is much more hydrocarbon-like than butanol and, on the more polar EGS will be subjected to a larger energy squeeze-out with the collapse of the solvent hole and the formation of bonds between solvent molecules. The partial molal enthalpy of this process $\Delta(h_{ss})$ will be very large and the solute will be excluded from the phase. Also to be considered is the fact that for butanol and the strongly proton accepting EGS, high degrees of orientation between solute and stationary phase are to be expected with the consequent entropy contribution.

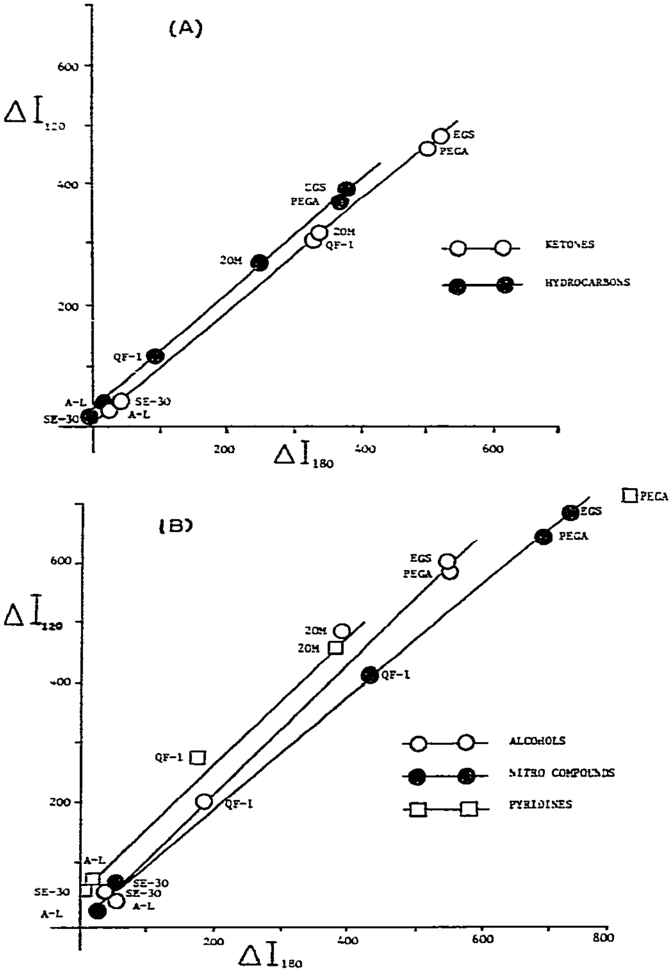

Fig. 1. Retention index dispersions (ΔI) of McReynolds solutes against high-temperature solutes on six stationary phases. (A) Ketones and hydrocarbons. (B) alcohols, nitro compounds and pyridines.

Fig. 1 shows the data from Table III with retention index dispersion of a McReynolds probe plotted against the dispersion of the corresponding high-temperature probe for each stationary phase. Slopes of unity indicate the same degrees of solute–stationary phase interaction for the probe pairs, slopes greater than unity mean a greater degree of interaction for the low temperature probe and vice versa. These slopes, for aromatic hydrocarbons, alcohols, ketones, nitrocompounds and pyridines are 1.00, 1.09, 0.91, 0.95 and 1.25, respectively. Good linear relationships between probe pairs are found for hydrocarbons and ketones, also for alcohols and nitrocompounds with the exception of the phase Carbowax 20M. The relationships between the heterocyclic bases are not good, however, with QF-1 being anomalous and of the polyester phases the one which could be included shows a massive deviation.

In general however, good linear plots are obtained for the six stationary phases examined, allowing the calculation of stationary phase polarity from high-temperature data. The longest relative variations occurred with the non-polar phases Silicone SE-30 and Apiezon L. The high-temperature phase constants were also plotted against Rohrschneider constant data as given by Supina and Rose[7]. The plots are not given here as the agreement between the two sets of data was very poor for the polar phases. The data on the non-polar SE-30 and Apiezon L however, showed much better agreement than was found using the McReynolds probes. It may be that the high-temperature data on non-polar phases transposes well into Rohrschneider constants whilst data on polar phases is expressed with greater clarity by McReynolds constants.

There are definite and clear indications from this preliminary survey of six widely used stationary phases, that phase polarity data obtained with the suggested high-temperature probes can be transposed in to one of the accepted classification systems. What is needed now is a rigorous treatment of results obtainable from many phases for which the constants are known and which have an operating temperature of 180°. Perhaps there will be limitations to transposition of data, a good linear relationship may exist for the silicone group of phases whilst linearity but with a different slope may be exhibited by the polyesters. A large amount of data is now required in order to justify what appears to be a useful approach to the evaluation of stationary phase polarity.

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