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Evaluation of the polarity of packed and capillary columns by different classification methods

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ABSTRACT

The behaviour of packed gas chromatographic columns filled with 30 different stationary phases was compared by using various polarity indicators: the difference in apparent carbon number of linear alkanes and alcohols with the same retention time, ΔC, the sum of the first five McReynolds constants, Σ^5_{MR}, Snyder's selectivity parameters, the Kováts coefficient, K_c, and the retention polarity, *RP*. The correlation between these different systems for polarity evaluation is discussed. The polarity of some wide- and narrow-bore capillary columns, filled with non-polar, polar and modified carbon layer phases, was also evaluated as a function of temperature, in the range 60–120°C for Σ^5_{MR} and selectivity parameters and in the range 60–190°C for ΔC.

INTRODUCTION

In previous papers [1,2], a method for the classification of the polarity order of gas chromatographic columns, based on the difference in apparent carbon number of linear alkanes and alcohols with the same retention time, ΔC, was introduced and compared with other polarity indicators, such as the McReynolds constants [3] and Snyder's selectivity parameters [4–6].

Twenty-three liquid stationary phases, six Porapak types and polar and non-polar wide-bore bonded-phase capillary column were tested, and the effect of the series connection of different capillary columns on the overall polarity was investigated.

In order to evaluate the correspondence between the polarity values obtained by ΔC measurement with those given by other methods for the classification of polarity, experiments were carried out by using packed columns filled with the liquid phases tested previously [2] and with other columns. The polarity values obtained with the ΔC, the McReynolds constants [3,7], Snyder's triangle [4–6], the Kováts coefficient, K_c [8,9], and the retention polarity, *RP* [10], values were compared.

EXPERIMENTAL

The characterization of the packed columns was carried out by injecting samples of *n*-alkanes (C_4–C_{12}) and *n*-alkanols (C_2–C_8), of the first five McReynolds probes (benzene, *n*-butanol, 2-pentanone, nitropropane and pyridine) and, for the determination of Snyder's constants, dioxane. The columns were prepared with a concentration of 20% of liquid phase on Chromosorb W (80–100 mesh) in order to permit a comparison with previously published values [2,7] and to reduce the interfacial and adsorption effects on the solid support. Phase loadings of 10% were also tested, with no significant influence on the results.

In Table I, the liquid phases used in the experiments are denoted "e" and those for which V_g values at 120°C previously published by

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McReynolds [7] were used in order to evaluate the applicability of the classification method to literature data are denoted "m".

Some of the columns whose ΔC values were previously calculated by using literature data [2] were tested experimentally and the results agreed fairly well. The best fitting between experimental and literature data was obtained by using liquid phases of definite chemical composition (*e.g.*, esters), whereas columns prepared with silicone polymers or with hydrocarbon mixtures (*e.g.*, Apiezon) showed an appreciable fluctuation of ΔC and the other polarity indicators (up to $\pm 2\%$), owing to the different distributions of molecular masses in the various commercially available products.

Varian (Palo Alto, CA, USA) Model 3700 and 1220 gas chromatographs equipped with thermal conductivity detectors were used. The analyses were performed at 100, 120 and 140°C on columns of various diameters, lengths and tubing material. Helium was used as the carrier gas at a flow-rate of 30 $\text{cm}^3\ \text{min}^{-1}$.

The capillary columns used were narrow-bore Supelcowax-10 and SPB-1 bonded phases (30 m × 0.32 mm I.D.), film thickness 0.25 μm, and a Carbopack B carbon layer open-tubular (CLOT) column, modified with polyethylene glycol liquid phase (Supelco, Bellefonte, PA, USA), a narrow-bore DB-1 (30 m × 0.32 mm I.D.), 0.25 μm film thickness (J & W Scientific, Folsom, CA, USA), and wide-bore Supelcowax-10 and SPB-1 (60 m × 0.75 mm I.D.) (Supelco).

The wide-bore glass columns were installed in a Varian Model 3700 and the fused-silica narrow-bore columns in a Varian Model 3600 gas chromatograph. Both instruments were equipped with flame ionization detectors; nitrogen and helium were used as the carrier gases. The same standard substances as used for characterization of the packed columns, obviously in less concentrated solutions, were injected in splitless (wide-bore columns) and split (narrow-bore columns) modes. The carbon number range of *n*-alkanes and *n*-alkanols was increased to C_{22} and C_{13}, respectively.

The various polarity indicators were calculated from experimental V_g and t'_R values as follows. The difference in apparent carbon number between linear alkanes and alkanols with the same retention, ΔC, was determined both graphically, by measuring the horizontal distance between the two straight lines having the equation

$$\ln V_g = a + bZ \tag{1}$$

obtained by plotting $\ln V_g$ as a function of the number of carbon atoms, Z, for *n*-alkanes and *n*-alkanols, and mathematically, with the equation

$$\Delta C = (a_{\text{OH}} - a_{\text{P}})/[(b_{\text{OH}} + b_{\text{P}})/2] = \Delta a/b^0 \tag{2}$$

where the subscripts OH and P refer to the coefficients of eqn. 1 for alkanols and alkanes, respectively, and b^0 is the average slope value [2]. The adjusted retention times, t'_R, can be used instead of V_g, mainly when the polarity of capillary columns is measured.

The overall McReynolds polarity, Σ^5_{MR}, was obtained as the sum of the McReynolds' constants, ΔI, of the first five polarity probes listed above, *i.e.*, the difference between the retention index values of the probes on each liquid phase and those on squalane.

Snyder's selectivity parameters, x_b for *n*-butanol, x_n for nitropropane and x_d for dioxane, were calculated with the equation

$$x_i = \frac{\Delta I_i}{\Delta I_b + \Delta I_n + \Delta I_d} \tag{3}$$

and give a measure of the relative importance of hydrogen bonding (*n*-butanol having an active hydrogen atom, dioxane two electron-donor oxygen atoms) and of dipole interactions (nitropropane showing a large dipole moment of 3.7 D) [4–6].

For solute–solvent pairs whose polar interaction depends only on hydrogen bonding (*e.g.*, alkanols with polyethylene glycols), the relative importance of the active hydrogen *vs.* donor oxygen atom was evaluated by normalization of the values of the selectivity parameters x_b for *n*-butanol and x_d for dioxane:

$$y_b = \frac{x_b}{x_b + x_d} = \frac{\Delta I_{\text{butanol}}}{\Delta I_{\text{butanol}} + \Delta I_{\text{dioxane}}} \tag{4}$$

The Kováts coefficient, K_c, was calculated as

$$K_c = -100a_P/b_P \tag{5}$$

where a_P and b_P are the two coefficients of the straight line representing eqn. 1 for the *n*-alkanes [8,9].

The retention polarity, *RP*, was calculated with the equation

$$RP = 20 \sum_{i=1}^{5} (\Delta I/I_{sq})_i \tag{6}$$

where ΔI is the McReynolds constant and I_{sq} the retention index of the probe *i* on squalane, being the summation calculated with the values for the first five McReynolds probes [10].

RESULTS AND DISCUSSION

Table I gives the values obtained with the above-described methods. Some of the ΔC, Σ^5_{MR} and selectivity parameters have been published previously [2] and are reported here to permit a direct comparison with the other polarity parameters. For some of the ester-type liquid phases, the new experimental values are reported instead of those calculated from literature data. The differences in ΔC values are about ±1% (change in the second decimal figure). Some of the liquid phases tested are nowadays of reduced interest, as they are often replaced with silicone polymers modified with a suitable number of polar groups.

TABLE I

VALUES OF ΔC AND OF OTHER POLARITY INDICATORS

No.	Liquid phase	ΔC	Σ^5_{MR}	x_b	x_n	x_d	K_c	*RP*	y_b	Source[a]
1	Squalane	1.48	0				157	0.00		e
2	Apiezon L	1.90	143	0.260	0.376	0.365	214	4.38	0.416	e
3	SE-52	2.43	334	0.304	0.413	0.283	212	10.42	0.518	e
4	SE-30	2.48	217	0.329	0.398	0.273	200	6.78	0.547	e
5	OV-101	2.51	229	0.335	0.394	0.270	202	7.18	0.554	e
6	DC-200	2.52	227	0.337	0.390	0.272	201	7.10	0.553	e
7	DC-550	2.90	660	0.279	0.420	0.300	238	19.26	0.482	e
8	Di-2-ethylhexyl sebacate	3.40	653	0.369	0.396	0.235	197	20.38	0.611	e
9	Dioctyl sebacate	3.42	651	0.370	0.396	0.233	201	20.38	0.614	e
10	Diisodecyl phthalate	3.43	767	0.332	0.418	0.249	247	23.92	0.571	e
11	Didecyl phthalate	3.45	1150	0.326	0.415	0.260	248	36.14	0.556	e
12	Dioctyl phthalate	3.50	835	0.331	0.420	0.249	246	25.92	0.571	e
13	Di-2-ethylhexyl adipate	3.59	709	0.364	0.396	0.239	204	22.20	0.604	e
14	QF-1	3.67	1500	0.239	0.474	0.287	230	46.54	0.454	e
15	Castorwax	4.16	1023	0.384	0.332	0.284	261	31.92	0.575	e
16	Hallcomid M-18	4.46	845	0.450	0.372	0.178	198	26.62	0.717	e
17	Pluronic L-81	4.90	1183	0.385	0.355	0.260	273	36.98	0.597	m
18	Tricresyl phosphate	5.00	1420	0.338	0.394	0.268	335	44.28	0.558	e
19	Neopentyl glycol adipate	5.62	1849	0.342	0.368	0.290	348	57.57	0.541	e
20	Pluronic P 85	5.75	1561	0.367	0.365	0.268	323	48.74	0.578	m
21	Pluronic P 65	5.90	1581	0.366	0.365	0.268	332	49.36	0.577	m
22	Neopentyl glycol succinate	6.14	2115	0.328	0.378	0.294	382	65.82	0.527	e
23	Pluronic F-68	6.55	1949	0.353	0.371	0.276	374	60.76	0.561	m
24	Carbowax 20M	6.93	2308	0.348	0.371	0.281	395	71.90	0.553	e
25	Pluronic F-88	6.97	1931	0.354	0.371	0.276	352	60.20	0.562	m
26	Carbowax 6000	7.28	2320	0.347	0.371	0.281	423	72.26	0.553	e
27	Ethylene glycol adipate	7.37	2689	0.326	0.367	0.306	492	83.66	0.516	e
28	Diethylene glycol adipate	7.69	2760	0.330	0.365	0.305	516	85.92	0.520	e
29	Carbowax 1000	7.85	2587	0.352	0.363	0.286	445	80.60	0.552	e
30	Diethylene glycol succinate	9.89	3430	0.323	0.367	0.310	649	106.64	0.510	e

[a] e = experimental data; m = taken from ref. 7.

Notwithstanding this, as many of these phases were available in our laboratory, we tested them because they have a reproducible chemical composition and the polarity indicators are not influenced by the molecular mass distribution, number of specific groups bonded to the polydimethylsiloxane backbone, chain branching, etc. It is therefore possible to compare the experimental data with previously published values.

Fig. 1 shows that the values of ΔC establish a polarity order corresponding fairly well with that obtained with the Σ^5_{MR} method, mainly when stationary phases whose interaction is due to hydrogen bonding are considered.

The greatest deviation is shown by solvents whose interaction depend on dipole moment, such as the fluorinated silicone QF-1. For this liquid phase, both the ΔI for nitropropane (462) and Snyder's x_n (0.474) are very high, as shown by the position near the right-hand side of the polarity triangle in Fig. 2. It was previously observed [6,11,12] that the use of 1-nitropropane as one of the probes may overestimate the contribution of the polarizability term, owing to its large dipole moment. This is confirmed by the excessive change in position on the selectivity triangle of some silicon liquid phases, indicated with numbers 3, 4, 5, 6 and 7 in Table I and in Figs. 2 and 3, which show similar behaviour in practice.

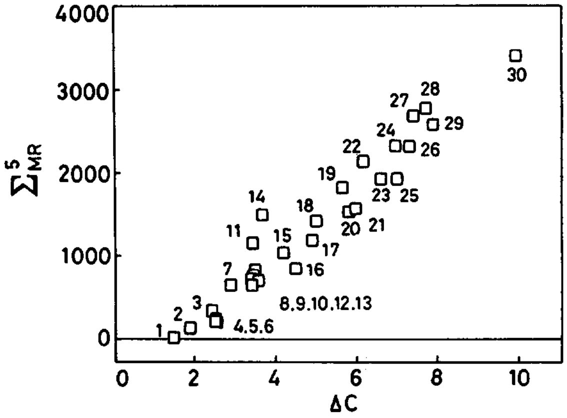

Fig. 1. Trend of the Σ^5_{MR} values for liquid phases with respect to their ΔC values at 120°C. Numbers refer to the list in Table I.

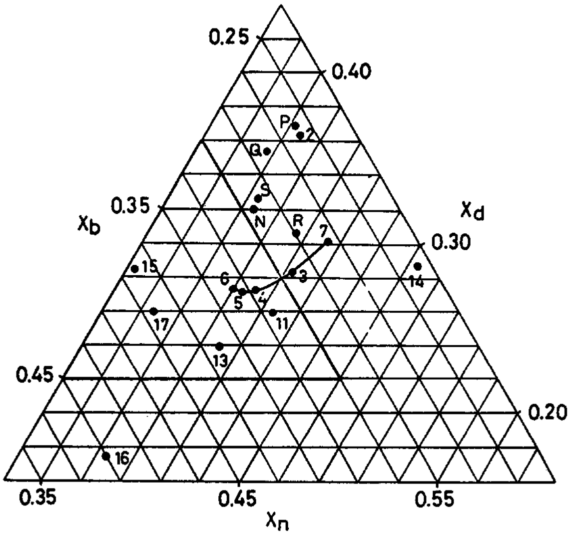

Fig. 2. Selectivity triangle where the values of x_b, x_n and x_d for the various columns at 120°C are shown. Numbers refer to Table I. The positions of Porapak porous polymers are also shown and indicated with identifying letters (from ref. 2). Methyl- and phenylsilicone phases are connected. An enlarged inner portion of the triangle is shown in Fig. 3.

An increasing influence of polarizability is expected on changing from methylsilicones (SE-30, OV-101, DC-200) to methylphenylsilicones (SE-52, DOW-550), but the shift towards in-

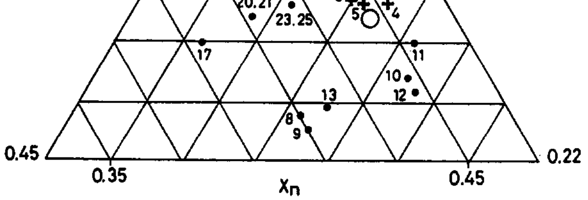

Fig. 3. Enlarged part of the selectivity triangle in Fig. 2. ■ = Carbowax columns; + = methylsilicone columns; ○ = position of capillary DB-1 and SPB-1 columns in the temperature range 60–120°C. The shift of the CLOT and Supelcowax-10 positions in the same range is indicated with arrows (white = Supelcowax-10; black = CLOT).

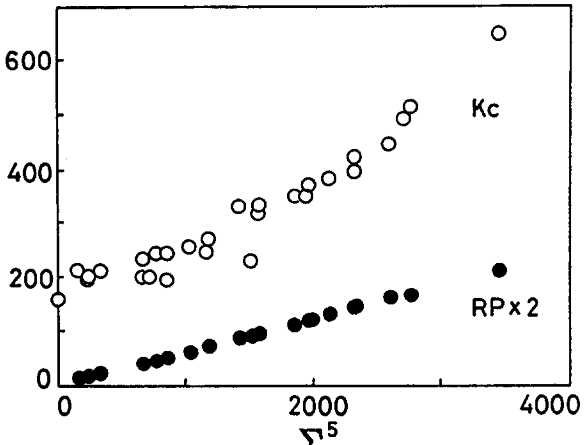

Fig. 4. K_c and RP values at 120°C (the latter multiplied by 2) as a function of Σ^5_{MR} for the liquid phases listed in Table I.

creasing x_n values seems too large, while the position of all these liquid phases is low on all the other polarity scales: ΔC, Σ^5_{MR}, RP and K_c.

The dependence of RP on Σ^5_{MR} is perfectly linear, as these two polarity indicators have the same origin, *i.e.*, the ΔI of the same probes, whereas the plot of K_c as a function of Σ^5_{MR} shows appreciable curvature (Fig. 4). If plotted as a function of ΔC, both RP and K_c show good linearity (Fig. 5).

The values of x_b and x_d are a measure of the interaction of 1-butanol and dioxane with the stationary phase: as the active hydrogen of the OH group interacts with the lone electron pairs of the liquid phase, while the –O– bridges in the dioxane molecules react with active hydrogen atoms of the liquid phase, the values of $\Delta I_{n\text{-butanol}}$ and $\Delta I_{\text{dioxane}}$ are a measure of the relative influence of the two mechanisms. The parameter y_b, calculated with eqn. 4 and reported in Table I, summarizes this effect, and increases with increasing tendency of the liquid phase to behave as an electron donor (Class III following Ewell *et al.*'s classification [13]).

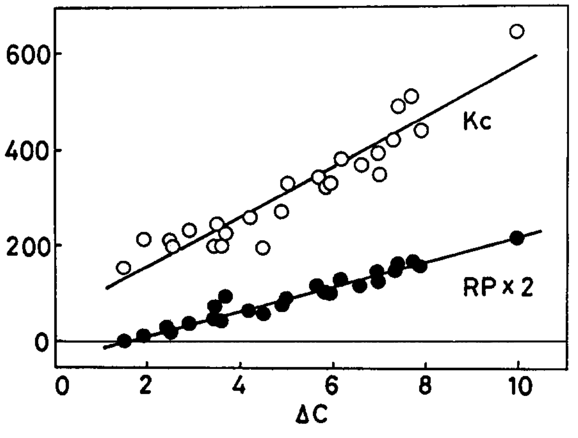

Fig. 5. Linear dependence of K_c and RP on the ΔC values at 120°C for the liquid phases listed in Table I.

Capillary columns

Some of the polarity indicators listed above cannot be applied to capillary columns: K_c cannot be calculated as it depends on a knowledge of V_g values; other indicators (RP, Snyder's selectivity parameters, McReynolds constants) require a knowledge of the ΔI values with respect of squalane, which cannot be used at temperatures above 120°C. Another problem connected with the determination of these values is the choice of the polarity probes: the boiling points of the McReynolds and Snyder probes is low and therefore the retention times at column temperatures above 120°C are so short as to be subject to appreciable errors that impair the accuracy of the calculation of the polarity. The polarity indicators suitable up to 120°C are Σ^5_{MR} and Snyder's selectivity parameters. ΔC can be used up to the maximum allowable temperature of the columns (in this instance 190°C); the ΔC values at 120°C measured on wide-bore columns (SPB-1 and Supelcowax-10; 0.75 mm I.D.) were 2.53 and 7.75, respectively, similar to the values in Table I for methylsilicones (SE-30, OV-101, DC-200) and polyethylene glycol liquid phases (Carbowax 6000 and 1000).

The narrow-bore columns were used to investigate the dependence of ΔC, Σ^5_{MR} and selectivity parameters on the column temperature. ΔC could be measured without problems in the range 60–190°C, as it does not require any reference column, and the n-alkanes and n-alkanols used for the determination of the difference in apparent carbon number can be selected in order to give suitable and well measurable retention times at any temperature.

The determination of Σ^5_{MR}, x_b, x_n and x_d values was only possible in the range 60–120°C, owing to the very short and scattered t'_R values of the polarity probes at higher temperatures.

As no suitable bonded-phase squalane column with the same length, diameter and film thickness as for the columns used is available, the ΔI value may be experimentally measured by comparing the Supelcowax-10 and CLOT data with those obtained on the non-polar methylpolysiloxane column. This procedure, if used to compare highly polar columns, is correct enough as the ΔI values of methylsilicone columns are low with respect to those of, *e.g.*, polyethylene glycols; average values on various SE-30, OV-101 and DC-200 columns are $\Delta I_{\text{benzene}} = 16$, $\Delta I_{\text{butanol}} = 55.7$, $\Delta I_{\text{2-pentanone}} = 44.6$, $\Delta I_{\text{nitropropane}} = 65.7$ and $\Delta I_{\text{pyridine}} = 42.3$.

The ΔI values for McReynolds probes on the two non-polar capillary columns tested were calculated with respect of the average I values obtained in the range 60–120°C on various packed squalane columns (stationary phase concentration between 5 and 20%). An accuracy of about ±10% of the absolute polarity values can therefore be expected but this is of relatively little significance because the aim of the determination was to establish the relative difference between DB-1 and SPB-1 and the effect of temperature.

The Σ^5_{MR} values measured in this way cannot be used for the determination of the absolute polarity of methylsilicone columns, whereas ΔC, being an absolute parameter, permits this determination.

Table II gives the values of ΔC and Σ^5_{MR} on DB-1, SPB-1, CLOT and Supelcowax-10 columns. The difference in Σ^5_{MR} between the two polydimethylsiloxane columns is of the same order of magnitude observed at 120°C on various packed silicone columns: SF-96 = 208, SE-30 = 217, OV-1 = 223, DC-200 = 227, OV-101 = 229.

The change with temperature of the same parameter in the range 60–120°C is about 2% for methylsilicones, 3% for polyethylene glycol and 11% for the CLOT column, which, the carbon substrate being covered with a layer of polyethylene glycol, show an intermediate behaviour between gas–solid and gas–liquid mechanisms, changing in polarity with increasing temperature [14,15].

The change with temperature of the Σ^5_{MR} values for purely gas–liquid chromatographic columns is not justified by a true change in polarity, but depends on the choice of the polarity probes and on the dependence on temperature of their retention values with respect to the reference column and *n*-alkane series. This is confirmed by the constant value of ΔC over a very extended temperature range for polydimethylsiloxane and pure polyethylene glycol columns, whereas the change in the behaviour of

TABLE II

VALUES OF ΔC AND Σ^5_{MR} AT VARIOUS TEMPERATURES ON NARROW-BORE CAPILLARY COLUMNS

Column temperature (°C)	DB-1		SPB-1		CLOT		Supelcowax-10	
	ΔC	Σ^5_{MR}	ΔC	Σ^5_{MR}	ΔC	Σ^5_{MR}	ΔC	Σ^5_{MR}
60	2.596	207	2.690	219	6.002	1595	7.505	2307
70	2.599	207	2.705	205	6.030	1624	7.518	2315
80	2.595	209	2.698	221	6.068	1685	7.520	2354
90	2.596	210	2.693	222	6.095	1707	7.511	2370
100	2.591	211	2.690	223	6.162	1735	7.515	2359
120	2.597	213	2.698	224	6.205	1778	7.531	2373
140			2.690		6.266		7.534	
150			2.704		6.302		7.532	
160			2.698		6.328		7.511	
170			2.715		6.379		7.501	
180			2.693		6.399		7.523	
190			2.711		6.445		7.522	

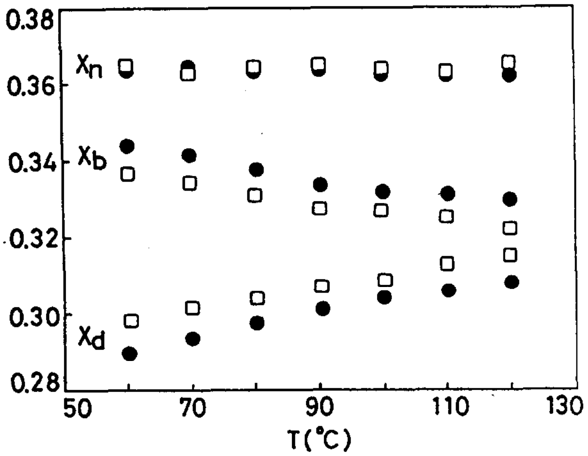

Fig. 6. Change of selectivity parameters of polar capillary columns as a function of temperature. □ = Supelcowax-10; ● = CLOT.

the CLOT column depends linearly on temperature. Three decimal figures are given for ΔC in Table II in order to permit an evaluation of the experimental fluctuations.

The values of Snyder's selectivity parameter of polar columns are shown in Fig. 6 as a function of temperature. Owing to the change in ΔI of *n*-butanol and dioxane on these columns, the x_b and x_d values, showing the influence of hydrogen bonding, change in an inversely proportional way, whereas no appreciable effect on the x_n value is observed, as temperature has no effect on dipole interactions. For the same reason, no hydrogen bonding being possible on non-polar columns, their selectivity parameters remain unchanged within the considered temperature range (60–120°C); for SPB-1 $x_b = 0.334$, $x_n = 0.395$ and $x_d = 0.271$; for DB-1 $x_b = 0.333$, $x_n = 0.398$ and $x_d = 0.269$.

The position of the four narrow-bore columns tested is compared in the selectivity triangle portion of Fig. 3 with that of packed columns, and the change with increasing temperature of the position of CLOT and Supelcowax-10 is indicated with arrows.

CONCLUSIONS

The results show how the various polarity indicators give comparable results in the temperature range where the standard reference phase, squalane, can be used. The polarity order of the tested liquid phases is similar on all the polarity scale tested. Above 120°C, however, where it is impossible to use squalane as the reference phase, some of the polarity systems cannot be used.

Further, owing to the low boiling points of the various polarity probes, the determination of their retention times at high column temperatures is subject to excessive errors.

The difference in the apparent carbon number of *n*-alkanes and *n*-alkanols, ΔC, can be used over a wider temperature range as a suitable range of alkanes and alcohols can be selected at every temperature; no reference column is necessary and an absolute polarity value is obtained. Whereas in previously published papers the dependence of ΔC on temperature could not be exactly determined as packed columns with a restricted temperature range were examined, the use of various capillary columns here permitted it to be confirmed that ΔC can be applied to this type of separation system and that its value remains constant over a wide temperature range when a gas–liquid separation mechanism is involved. On the other hand, when mixed gas–solid, gas–liquid–solid and gas–liquid mechanisms are simultaneously present, as in the carbon black columns modified with a layer of polar liquid phase, the ΔC values change linearly with temperature, indicating the regular variation of the separation mechanism.

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