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THE NEAREST NEIGHBOUR TECHNIQUE AS A MEANS OF INDICATING STATIONARY PHASE SELECTIVITY

J. K. HAKEN*, M. S. WAINWRIGHT and N. DO PHUONG

Departments of Polymer Science and Industrial Chemistry, The University of New South Wales, P.O. Box 1, Kensington 2033 (Australia)

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SUMMARY

A nearest neighbour technique has been developed to indicate the selectivity of stationary phases towards various homologous series of different functional classes. The technique also readily allows the effect of phase substitution to be considered.

INTRODUCTION

Leary *et al.*¹ proposed a scheme which they have described as a "nearest neighbour technique" for reducing the necessity for a large number of stationary phases. Using the ΔI values for the McReynolds test solutes² determined on 226 stationary phases a classification to determine groups and similarities of phases was established. A series of twelve generally acceptable phases was selected covering the range of polarities as shown by their nearest neighbour distances from squalane while the distances of the other phases from the nearest appropriate preferred phases were calculated. The authors suggested a similarity of performance of XE-60 and OV-225 mathematically from McReynolds data and discussed literature data³ for a series of glycol ethers and their acetyl derivatives where retention index variations of less than 5% and generally less than 2% were observed with the two phases.

The nearest neighbour technique was chosen by Leary *et al.*¹ for its ability to point out true similarity in high dimensional data. In this technique, the data are represented as n-dimensional pattern vectors. Patterns that exist close together in the n-dimensional space are considered to be similar, with the degree of similarity determined by the Euclidian distance between patterns. When comparing phases, the distance is an effective guide as to whether one particular phase can be replaced by another.

The distance (D) between phases A and B is calculated by

$$D = \left[\sum_{i=1}^m (\Delta I_{Ai} - \Delta I_{Bi})^2 \right]^{\frac{1}{2}}$$

* To whom correspondence should be addressed.

TABLE I
 NEAREST NEIGHBOUR DISTANCES FOR POLYSILOXANE STATIONARY PHASES AND HOMOLOGOUS CARBONYL COMPOUNDS
 The ranking of the phases for the various groups of compounds is indicated in parentheses.

Stationary phase	General polarity ^a	Robinschneider probes	Saturated esters ⁷	Unsaturated esters ⁸	Pivalate esters ⁹	Simple ketones ¹⁰	Diketones ¹⁰	Pyruvate esters ¹⁰	Glycol ethers ³	Glycol ether acetates ³
SE-30	219	0	0	0	0	0	0	0	0	0
F-61	353	(1)	--	--	--	--	--	--	11	6
DC-230	395	19 (2)	2 (2)	3 (2)	4 (2)	15 (2)	15 (2)	11 (2)	--	--
OV-7	449	39 (3)	6 (4)	8 (3/4)	14 (3/4)	31 (3)	34 (3)	23 (3)	--	--
F-400	744	52 (4)	10 (6)	13 (5/6)	32 (5)	64 (5)	56 (5)	42 (5)	--	--
DC-530	781	61 (5)	5 (3)	8 (3/4)	14 (3/4)	80 (6/7)	79 (6/7)	57 (6/7)	--	--
DC-710/OV-17	908	62 (6)	9 (5)	13 (5/6)	23 (5)	47 (4)	54 (4)	36 (4)	36	40
F-500	965	78 (7)	14 (7/8)	18 (7)	46 (8)	80 (6/7)	79 (6/7)	57 (6/7)	--	--
OV-25	1206	91 (8)	14 (7/8)	19 (8)	--	--	--	--	47	46
85% Phenyl	1301	-- (9)	--	--	--	--	--	--	59	51
100% Phenyl	1452	121 (10)	18 (10)	25 (10)	41 (7)	96 (10)	101 (10)	70 (10)	--	--
QF-1/OV-210	1483	138 (11)	26 (3)	30 (13)	76 (13)	139 (13)	146 (13)	101 (13)	55	73
XE-60	1823	149 (12)	21 (11)	28 (11)	57 (11)	125 (14)	144 (12)	96 (11)	88	84
OV-225	1855	155 (13)	22 (12)	29 (12)	58 (12)	128 (12)	142 (11)	97 (12)	80	77
SILAR-5CP	2432	208 (14)	29 (14)	39 (14/15)	79 (14)	171 (14)	201 (14)	134 (14)	--	--
XF-1150	2438	229 (15)	30 (15)	39 (14/15)	87 (15)	191 (15)	221 (15)	148 (15)	128	123
No. of compounds	--	5	99	75	9	6	8	6	21	20

where i represents the compound run on both phases. The result of this calculation is that for each liquid phase, the most similar liquid phase has the smallest value of D , and the least similar, the largest.

The calculations of Leary *et al.*¹ were performed using both the ten ΔI values provided by McReynolds, and those five dimensions used in McReynolds' summation. Very similar results for both five and ten dimensions were obtained indicating that most of the significant polarity information is contained in the first five dimensions. The first five standard compounds were considered to be sufficient for the characterization of most liquid phases, and the tabulated results of Leary *et al.*¹ were calculated using the first five dimensions. This assumption would appear to be reasonable as recent works have suggested that three predominant types of solute-solvent interactions occur⁴, that only four functional probes⁵ are necessary to characterise liquid phases while Lowry *et al.*⁶ have considered sets of two and three of the McReynolds probes.

While the interest in the nearest neighbour technique to date has been restricted to the selection of groups and the determination of the similarity of stationary phases it is apparent that the procedure might be of value in determining the selectivity of stationary phases towards a particular functional group. The present work considers the retention behaviour of a variety of types of carbonyl compounds on a range of stationary phases of varying polar character. By determining the nearest neighbour distances on a series of phases for particular homologous compounds, the distances or differences from dimethyl polysiloxane as the low polarity base were obtained and simple comparison allows selectivity to be observed more readily than from a consideration of McReynolds constants where frequently an increase in one of the values is accompanied by increases in the other terms. In these circumstances it is difficult to determine if specific selectivity exists or the separation is due to the generally increased phase polarity.

EXPERIMENTAL

The calculations were conducted using the Fortran programme described¹ with a Cyber 72 computer or rewritten in Basic with a PDP 1140 computer. The data used in the calculations were extracted from earlier reports from this laboratory and for the saturated esters⁷, unsaturated esters⁸, pivalate esters⁹, ketones¹⁰ and pyruvate esters¹⁰ were obtained under the same conditions and were interchangeable. The data for the glycol esters and their acetate derivatives³ were obtained at the same temperature and would be expected to be similar for comparison. All of the data were obtained on polysiloxane phases and while the same phases or number of phases were not used with all of the series, a significant number of common phases were present.

RESULTS AND DISCUSSION

The nearest neighbour distances, the ranking of the phases for the various groups of compounds and the numbers of each type considered are shown in Table I.

The nearest neighbour distances for the phases from SE-30 are also shown in Table I calculated from the five constants of the McReynolds summation. The sequence of the distances and the general polarity is of course the same as these are

simply different representations of the same data. The distances for the phases from SE-30 were also calculated from the first three constants and while in each case a slightly lower value was obtained the sequence was not altered and it is thus likely as has been suggested⁴⁻⁶ that relatively few data are required to characterise phases.

The distances for phases from SE-30 for the saturated esters would indicate that OV-7 and DC-530 are equivalent although the general polarity of the latter material is very significantly higher. The phenyl and amino groups of the two phases both exhibit some electron donor character and it is evident that the polarisability of the ester group and the acceptor character induced is low and elution on DC-530 is enhanced by simple repulsion. The phase F-400 with weaker acceptor character and of lower general polarity than phenyl methyl polysiloxane show equivalent distances from SE-30. Acceptor-acceptor interaction retards elution while donor-acceptor interaction with the phenyl groups enhances elution. The same phenomena are again exhibited with F-500 and OV-25 which may be considered as higher homologs of F-400 and DC-710. The substantial acceptors show progressively greater differences from SE-30 as the polar character is increased.

The elution behaviour on the phases of the unsaturated esters parallels that of the saturated homologs, the actual differences being quite similar except, as might be expected, with the more polar acceptor phases where the unsaturation of the compounds is more significant and the difference distances are slightly increased.

The pivalate esters having the carbonyl group adjacent to a tertiary butyl group tend to show phase distance differences comparable to the simpler saturated esters, *i.e.* OV-7 and DC-530 remaining equivalent.

For the weak acceptor phase F-400 an increased distance relative to OV-17/DC-710 is apparent as compared with the other saturated and unsaturated esters and it is apparent that the character of F-400 has become more significant and the acceptor-acceptor repulsion of solute and solvent causes increased retention.

The increasing influence of the acceptor effect is apparent with F-400 and the donor diphenyl polysiloxane which, while of significantly greater general polarity, shows earlier elution of the branched chain esters.

The elution of the simple ketones on the phases considered tends to parallel the performance of the ester series although the nearest neighbour distances in all cases are greater and the effective distances of the phenyl bearing donor phases is further reduced. It is, however, evident that DC-530, a phase with aminoethylamino-propyl groups¹¹ shows an enhanced retention distance. This is the reverse of the situation with the three ester series and is due to chemical interaction of the carbonyl group with the primary and secondary amino groups¹².

The behaviour of the diketones parallels that of the simpler compounds and for the phases increasing in general polarity to diphenyl polysiloxane the nearest neighbour distances are essentially identical while with the more polar phases the values are increased. Elution of the ketoesters again parallels that of the simple ketones although the nearest neighbour distances are all considerably increased, particularly with the more polar solvents.

From Fig. 1 it is generally evident from all of the plots that the nearest neighbour distances increase with the increasing polar character of the phases. The values of general polarity used in Figs. 1 and 2 have been taken from an earlier work³. These are not completely in agreement with the latest published values¹³ but are more

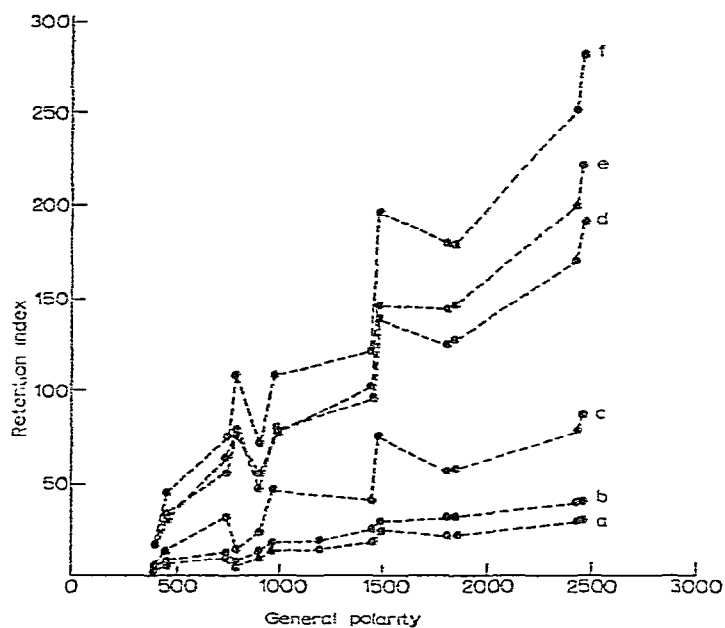


Fig. 1. Plot showing nearest neighbour distances from SE-30 and general polarity for (a) saturated esters, (b) unsaturated esters, (c) pivalate esters, (d) *n*-alkyl ketones, (e) diketones, and (f) pyruvate esters.

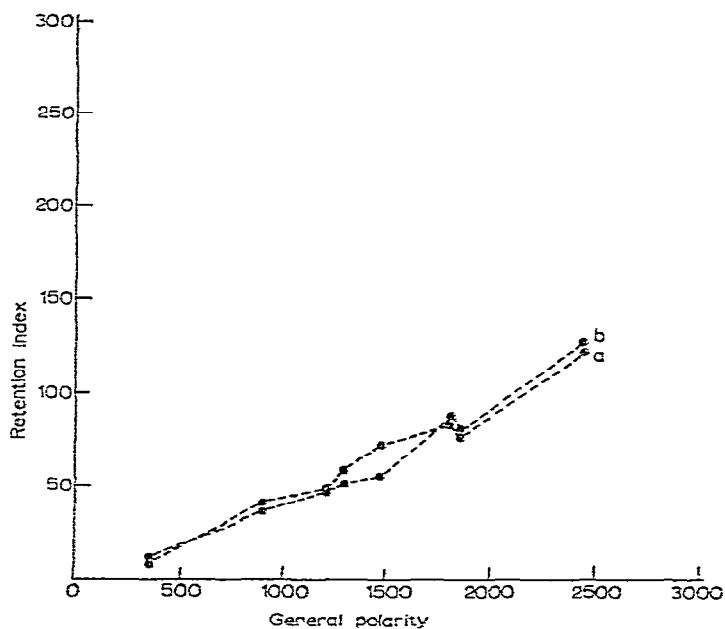


Fig. 2. Plot showing nearest neighbour distances from SE-30 and general polarity for (a) glycol ethers and (b) glycol ether acetyl derivatives.

suitable for comparison as the values of all of the stationary phases considered are included. Details of the polysiloxane stationary phases used, *i.e.*, composition, supplier, polarity, etc., have been previously reported^{3,7}. If a line of best fit were constructed for the plots it becomes apparent that with carbonyl compounds enhanced distances occur with the acceptor phases, even with the weaker members F-400, F-500, as compared with the donor phenyl and amino solvents. Trifluoropropyl methyl polysiloxane (QF-1/OV-210) shows the same effect quite dramatically and from its introduction¹⁴ has been reported to exhibit selectivity towards ketones. Generally the effect would appear to be mildly apparent with esters but much accentuated with the ketone series. The work of VandenHeuvel *et al.*¹⁴ indicated the significant polar character of QF-1 by the determination of separation factors for the $-\text{CH}_2-\text{CH}_2-$ group for a series of homologous long-chain fatty esters. The selective behaviour was apparent as increased retention with oxygen containing functional groups in the order ethers, hydroxy compounds, esters and ketones while the retention of hydroxy and ketosteroids varied greatly with structure. From Fig. 1 the increasing order esters to ketones is apparent while in Fig. 2, which is a similar plot of glycol ethers and their acetyl derivatives, the order ethers to esters occurs. The plots demonstrate the significant polar character of QF-1 quite clearly and more satisfactorily than by a simple consideration of the McReynolds constants or by equating the phases to one of the probes¹⁵.

The similarity of behaviour of XE-60 and OV-225 as discussed by Leary and his co-workers¹ with the glycol ethers and their acetyl derivatives³ is reflected in the similarity of the nearest neighbour distances (Table I) with the two types of homologous series. From this table it is clear that the increased distance observed for the esters with QF-1 does not occur with XE-60 or OV-225. The similarity of XE-60 and OV-225 is further evident by considering the other ester and ketone series examined in this work.

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