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GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS

XI*. USE OF ESTER SOLUTES IN A ROHRSCHEIDER-TYPE SCHEME FOR DATA PREDICTION

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SUMMARY

The improvements in the retention prediction properties of a Rohrschneider-type scheme with the use of solute probes of similar structure to the compounds is demonstrated. With the use of several series of esters as solute parameters the prediction of a large series of saturated and unsaturated esters was carried out with an average error of 4.7 retention index units compared with 6.7 units using the established probes, a significant improvement of two index units.

INTRODUCTION

The utility of retention prediction of a Rohrschneider-type scheme was briefly considered in the initial report¹ with a restricted number of compounds selected to present a range of different functional classes and recently with a larger group of closely related compounds². In the latter work various groups and combinations of the solvent probes of the types suggested by Rohrschneider¹ and by McReynolds³ were considered and the average errors in predicting retention reported. When any four of the probes of the functional classes suggested by Rohrschneider were considered with 2-methyl-2-pentanol, *i.e.* H as proposed by McReynolds the range of errors with the various combinations were shown to be within the values 7.36-10.72. The difference between the limits being 3.36 index units and the average error of prediction 8.86 index units in comparison with 6.72 index units for the five original probes. The use of *tert.*-butyl acetate designated as T and *n*-butyl acetate, *i.e.* B, instead of H lead to ranges of values of 7.61-10.37 and 6.00-7.93, respectively, with the differences being reduced to 2.76 and 1.93 index units with the average errors of prediction 8.86 and 6.63 index units for the series with T and B.

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The effect of inclusion of an ester is obviously advantageous although the structure is of considerable importance as shown by the influence of the *n*-butyl and *tert.*-butyl esters on the errors when considered in conjunction with any four of the regular solutes. The improved values are not unexpected and if this type of scheme is suggested for retention prediction the inclusion of other solutes more closely related to the substances under study might be expected to reduce further the errors and enhance the reliability of prediction. The present work shows the effect of using several selections of esters as solute probes in a Rohrschneider-type scheme and their use for retention prediction as applied to a series of saturated and unsaturated esters.

EXPERIMENTAL

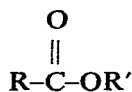
The experimental conditions and retention data have been reported previously⁴ and were obtained using a modified F & M 810/29 Research Chromatograph fitted with improved flow control and with flame ionisation detection at 150°. The stationary phases used were polysiloxane SE-30, OV-7, DC-710, OV-25 polydiphenylsiloxane, DC-230, DC-530, XE-60, XF-1150, Silar 5CP, F-400, F-500 and QF-1, whose composition and polarity have been previously reported⁴.

The data was evaluated using the procedure of Rohrschneider but including corrections to the mathematics as previously reported by Leary *et al.*⁶ and by Souter⁷. For the computations an IBM 360/50-computer with a programme written in Fortran IV was used.

RESULTS AND DISCUSSION

The structures of the compounds that have been used as solute probes bearing little resemblance to those of homologous esters have been replaced with a series of standard parameters selected from the esters concerned which are saturated and unsaturated and with variations in both the acid and alcohol chains R and R' ⁸.

The saturated esters studied may be shown by reference to the structure



where R and R' were (a) both straight chains with R = 0 to 6 and R' = 1 to 6, (b) individually or both branched with R = 4 to 6 and R' = 3 to 5 while the unsaturated esters were both straight-chain and branched-chain with unsaturation in either chain.

The following sets i-v of five esters parameters were arbitrarily selected as being representative of the structures exhibited by the homologous esters used.

(i) *n*-Propyl formate (x); *n*-hexyl acetate (y); isopentyl propionate (z); methyl ethyl-butyrate (u); *trans*-2-hexenyl butyrate (s).

(ii) *n*-Propyl formate (x); *n*-hexyl acetate (y); isopentyl propionate (z); *n*-butyl-2-butenate (u); *trans*-2-hexenyl butyrate (s).

(iii) *n*-Propyl formate (x); *n*-hexyl acetate (y); isopropyl propionate (z); butyl 2-butenate (u); *trans*-2-hexenyl butyrate (s).

(iv) *n*-Propyl formate (x); *n*-hexyl acetate (y); isopropyl propionate (z); methyl 2-ethyl-butyrate (u); butyl 2-propenoate (s).

(v) Methyl acetate (x); *n*-butyl acetate (y); *n*-hexyl hexanoate (z); *cis*-2-hexenyl propionate (u); methyl 2-propenoate (s).

With the esters shown in series i above as solute probes prediction of retention index values was carried out with saturated esters, isomeric acid chain esters, unsaturated acids and on a combination of the three groups. The average errors in prediction in index units are shown in Table I where it is apparent that all four results are similar and prediction with the same group of compounds is enhanced as regards use of the Rohrschneider-McReynolds probes, *i.e.* 6.72 index units. Also shown in Table I are values using the series ii ester probes which again are similar.

TABLE I
RETENTION INDEX PREDICTION USING FIVE ESTERS AS SOLUTE PROBES

<i>Compounds</i>	<i>Number</i>	<i>Average error (index units)</i>
<i>Series i</i>		
Saturated esters	59	4.48
Isomeric acid } Chain esters }	50	5.32
Unsaturated esters	80	4.70
Total series	189	4.94
<i>Series ii</i>		
Saturated esters	59	4.64
Isomeric acid } Chain esters }	50	5.73
Unsaturated esters	80	4.32
Total series	189	4.48

The average RMS error for the four sets of ester parameters are shown in Table II.

It is apparent that all of the average RMS errors are much improved when compared with the value using the Rohrschneider-McReynolds probes and the same data, *i.e.* 6.72 index units. It seems unlikely that the errors can be significantly reduced below this level employing this system of five retention indices, as these substances are directly related to the ester structures considered. In any case the average column error of 4.94 units is comparable with the estimated experimental errors.

TABLE II
COLUMN ERRORS USING FIVE ESTERS AS PARAMETERS

<i>Parameter set</i>	<i>RMS error (index units)</i>
i	4.94
ii	4.48
iii	4.62
iv	5.02
v	4.81
Average	4.77

The program used for substance polarity constants had provision for error reduction by means of calculating values of best fit for the standard substances. By a series of iterations, the error could be further reduced. For example, the average column error for one iteration using x, y, z, u, s was 3.69 index units while it was 3.48 for two iterations, these compared with the 6.72 index units for x, y, z, u, s.

Employing the five esters as standard substances i as before, the average column error for one and two iterations were reduced from 4.94 index units to 3.67 or 3.46 units, respectively. Again it is apparent that the average column errors are well within the experimental error and for this system using iterations to reduce the error there is apparently little advantage in employing esters as standard substances with iteration as the average column errors are very close. It should be remembered that the values obtained from the iteration vary from the original values and are not related to the original definitions nor can they be readily experimentally determined, however using the five standard substances of the Rohrschneider-McReynolds system the average column errors are reduced with one iteration by over 50%, when compared to a system based on the standard five parameters.

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