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GAS CHROMATOGRAPHY OF HOMOLOGOUS ESTERS*

X. DATA PREDICTION PROPERTIES OF A ROHRSCHEIDER-TYPE SCHEME

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SUMMARY

The data-predicting properties of a Rohrschneider-type scheme are reported for a series of 179 homologous esters on fourteen polysiloxane stationary phases: This consideration has previously been restricted to the introductory work of Rohrschneider, where thirty compounds selected to cover a wide range of functional classes were used. Other reports of prediction with various solute probes have been reported and these are briefly discussed.

INTRODUCTION

While the theoretical basis of the scheme proposed by Rohrschneider² comprising the additivity of various particular interactions has been shown to be an oversimplification³⁻⁵, it is apparent that the scheme is the most satisfactory yet proposed for stationary phase classification and with the McReynolds modifications the solvent values would appear to be finding increasing acceptance and appearing in the annual catalogues of Supelco since 1970 and in the 1976 catalogue of Applied Science Labs. The solute or substance polarity factors have recently been described for saturated esters⁶ and certain trends relevant to structure are apparent.

The use of the Rohrschneider scheme for retention prediction has been restricted, although varying numbers and types of solute probes have been reported. In the present work the solute probes of Rohrschneider/McReynolds have been considered for retention prediction of a series of 179 saturated and unsaturated esters on fourteen polysiloxane stationary phases of varying polar character. Squalane, the base stationary phase of Rohrschneider² and McReynolds⁷, has been replaced with di-

* For part IX, see ref. 1.

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methylpolysiloxane, a material of considerably greater utility. The effect of varying the number of the solute probes is also considered in this work.

Weiner *et al.* have proposed a scheme⁸⁻¹¹, based on factor analyses, which utilises eigen vectors to select physical and chemically significant parameters which best fit the problem to be analysed. In this manner eqn. 1 was established, *i.e.*

$$I_{(i,\alpha)} = \sum_{j=1}^n C_{(j,\alpha)} P_{(j-i)} \quad (1)$$

where $I_{(i,\alpha)}$ represents the retention index of solute i on stationary phase α ; j corresponds to the n test factors; $C_{(j,\alpha)}$ represents the multiplicative constants associated with solvent α ; and $P_{(j,i)}$ represents the n test parameters evaluated for solvent, i .

This equation is essentially the same as that devised by Rohrschneider², the major difference being that Weiner *et al.* statistically determine their parameters, many of which are interrelated. Weiner *et al.* have produced entirely different parameters which fit reasonably closely related sets of retention data. Rohrschneider adopted the more practical approach and assigned the retention behaviour of five classes of compounds as the parameters in his scheme and to date this has proved to be the more accurate method, *i.e.*, Rohrschneider's error is 4.1 index units², while for a set of the results of Weiner and Howery¹⁰ the average error was 8.4 units for a similar number of parameters but a different data set.

In Rohrschneider's earlier work¹², three parameters were used to predict data, with an average error of 12.6 index units; the later inclusion of two additional parameters² reduced the error to 4.1 index units. It has been suggested previously^{3,4} that the number n of these parameters can be readily varied, according to eqn. 2:

$$\Delta I = \sum_{i=1}^n ax \quad (2)$$

A principal component analysis¹³ of McReynolds' data⁷ showed that to reproduce the data within about 30 index units three units have to be introduced. The work described the attributes of the components used, and while advantages of the scheme are claimed, they are not readily apparent, as the precision indicated is unsatisfactory.

The Rohrschneider approach for characterising stationary phases and the extension of the solubility parameter theory of Hildebrand and Scott¹⁴ and Hildebrand *et al.*¹⁵ have recently been reviewed by Hartkorf¹⁶ with the conclusion that three predominant types of solute-solvent interactions exist, these being concerned with dispersion, dipole interaction, and hydrogen bonding.

Hartkorf *et al.*¹⁷ then demonstrated the use of four functional probes to characterise liquid phases and demonstrated the conclusion with a four-term form of the Rohrschneider equation, which allowed prediction of ΔI values with the accuracy of the five-term equation, *i.e.*, 6 index units.

Further consideration of the significance of various groups of probes is obviously necessary as 3^{13,16}, 4¹⁷, 5², 6⁷, 7, 8, or 10¹⁰ materials have been variously suggested with differing claims of precision.

EXPERIMENTAL

The experimental conditions and retention data have been previously reported^{18,19} 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 reported¹⁸.

RESULTS AND DISCUSSION

The data were processed according to eqn. 2 and the average column errors are shown in Table I for 179 esters and standard substances with SE-30 as the base stationary phase. Here the number of standard substances or parameters is varied between two and six, *i.e.*, $n = 2, \dots, 6$, the parameters being represented by: $x =$ benzene, $y =$ butanol, $z =$ 2-pentanone, $u =$ nitropropane, $s =$ pyridene, $H =$ 2-methyl-2-pentanol, $T =$ *tert.*-butyl acetate and $B =$ butyl acetate. Corrections to the mathematics reported by Rohrschneider² as suggested by Leary *et al.*²⁰ and by Souter²¹ were employed.

In this manner all the possible combinations of the usual standard substance parameters (*xyzus*) were evaluated for five or less parameters in order to observe the effects on the prediction properties of these standard substances defined by Rohrschneider and later modified by McReynolds.

From Table I, it is evident that the data prediction properties were affected by the number of standard substances, n , included in eqn. 2, and to a lesser degree by the nature of the standard substances. The errors of the prediction scheme were calculated in the form of the average RMS error, which gave an estimate of the average error for a set of parameters. Of the five classes of compounds chosen by Rohrschneider, the members of which were later modified by McReynolds, this combination of parameters resulted in an average RMS error of 6.72 index units; however, the inclusion of a sixth parameter, H , as also recommended by McReynolds, resulted in only a minor improvement with an average error of 6.32 index units. An additional two substances T and B were successively introduced in an attempt to improve branched-chain ester and n -ester predictions, respectively. The T factor proved to be of less value than H , while the inclusion of a normal ester, B , improved the prediction properties by 1 unit to 5.76 index units. On this basis, there is apparently little justification in increasing the number of parameters introduced by Rohrschneider, as the average prediction properties were not sufficiently improved.

Predictably, the effect of reducing the number of standard substances was to increase the average column error. With four standard substances the average error for all combinations of Rohrschneider/McReynolds' five-standard substances was 10.12 index units, with combinations of three-standard substances the error was 15.57 index units, and with two-standard substances the error was 22.7 index units. In Rohrschneider's earlier scheme¹², the mean error employing three factors, *xyz*, was 12.6 index units, which is in reasonable agreement with the value of 14.95 index units determined here for *xyz*, considering that Rohrschneider evaluated a range of compound classes, many of which were closely related to the standard substances and also

TABLE I

EFFECT OF THE NUMBER OF STANDARD SUBSTANCE PARAMETERS ON THE DATA PREDICTION PROPERTIES OF A ROHRSCHEIDER TYPE SCHEME

Number of parameters	Combination of parameters	Average RMS error	Number of parameters	Combination of parameters	Average RMS error
6	<i>xyzusH</i>	6.32	3	<i>xyz</i>	14.95
	<i>xyzusT</i>	6.40		<i>xyu</i>	16.34
	<i>xyzusB</i>	5.76		<i>xys</i>	17.85
	Av. 6.16			<i>xzu</i>	17.81
5	<i>xyzus</i>	6.72		<i>xzs</i>	14.13
	<i>xyzuH</i>	9.73		<i>xus</i>	11.72
	<i>xyzsH</i>	9.37		<i>yzu</i>	14.87
	<i>xyusH</i>	9.28		<i>zus</i>	16.89
	<i>xzusH</i>	10.72		Av. 15.57	
	<i>yzusH</i>	7.36	2	<i>xy</i>	42.06
	Av. 8.86			<i>xz</i>	23.46
5	<i>xyzuT</i>	10.24		<i>xu</i>	18.80
	<i>xyzsT</i>	9.46		<i>xs</i>	19.14
	<i>xyusT</i>	10.07		<i>yz</i>	24.13
	<i>xzusT</i>	10.37		<i>yu</i>	17.75
	<i>yzusT</i>	7.61		<i>ys</i>	22.87
	Av. 8.86		<i>zu</i>	19.76	
5	<i>xyzuB</i>	7.93		<i>zs</i>	18.78
	<i>xyzsB</i>	6.00		<i>us</i>	17.90
	<i>xyusB</i>	6.12		Av. 22.47	
	<i>xzusB</i>	6.08	2	<i>xB</i>	10.02
	<i>yzusB</i>	6.91		<i>yB</i>	10.57
Av. 6.63		<i>zB</i>		12.47	
4	<i>xyzu</i>	10.39		<i>uB</i>	11.74
	<i>xyzs</i>	10.94		<i>sB</i>	10.25
	<i>xyus</i>	10.40		Av. 10.61	
	<i>xzus</i>	10.92			
	<i>yzus</i>	7.93			
	Av. 10.12				

considered a much smaller data set. The average errors determined when employing less than five standard substances as parameters in the system were quite remarkable, *i.e.*, two factors gave an overall average error of 22.7 units, while with four parameters the minimum average error was obtained with *xyzu*, where the error was 6.72 units, but reached as high as 10.72 units depending on the combination of the four parameters employed. The ease of employing a system containing less than five standard substances or parameters is obvious, and while the average error in many cases may be acceptable, the chance of predicting values that differ markedly from the experimental values is greatly increased.

While the nature of the standard substance did not have as much effect on the errors as the number of standard substances, or parameters, included in the system,

some effect on the errors was apparent. When factors H and then T were included with the standard substances, and one of the usual factors x to s successively eliminated in order to obtain combinations of five factors, the average column error increased approximately 3 index units above the errors obtained when the usual $xyzus$ terms were used in the system. This would support Rohrschneider's original selection of types of standard substances, even for a set of esters that have little resemblance to the structures represented by these standard substances, with perhaps the exception of the ketone parameter "z". Only when an n -alkyl ester, B , was included with various combinations of four of the usual parameters were the errors reduced below the error obtained with $xyzus$, although the results show only a minor improvement. For the usual five parameters in various combinations of between two and four parameters, the errors were very similar for a given number of parameters. Combinations of parameters existed that exhibited significantly lower errors than the average for a set number of parameters, *i.e.*, zuy s and xus , while another exhibited errors that were higher than the average, *i.e.*, xy , although there is insufficient evidence to relate this behaviour to any specific types of parameters.

With the use of two parameters the selection is of major importance as it is evident from Table I that while a combination of any two of the standard solutes provides an average error of 22.47 index units, the use of one of these factors and that of an n -alkyl ester shows an average error of 10.61 index units.

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