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# EXTENSION TO THE SCHEME OF ROHRSCHNEIDER

## II. SUBSTANCE POLARITY FACTORS OF HOMOLOGOUS ESTERS*

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SUMMARY

The values of substance polarity factors for several series of homologous compounds have been reported. These factors have previously only been considered in the introductory work of Rohrschneider, where with thirty compounds selected to cover a wide range of functional classes it was not apparent if the values had any real significance. The calculations here include the mathematical corrections of Leary and f Souter and the values of the various terms in relation to the various structures are discussed.

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INTRODUCTION

The Rohrschneider scheme[2] proposes that the retention index differences $\Delta I$ for a compound A due to polar interactions may be determined by elimination of non-polar interactions by focussing attention on the retention differences observed on a polar and a non-polar (squalane) stationary phase according to eqn. 1:

$$\Delta I^{A} = I_{P}^{A} - I_{Sq}^{A} \qquad (1)$$

where $\Delta I^{A}$ is the increased retention or index difference due to the polar interacting forces, and $I_{P}^{A}$ and $I_{Sq}^{A}$ are the retention indices of substance A on a polar and a non-polar (squalane) column, respectively.

The index difference $\Delta I$ defined in this way was expressed as the sum of a number of product terms, containing factors characteristic of both the solvent and the solute. The factors characteristic of the solvent or the stationary phase polarity factors are readily obtained and have found some acceptance as a means of comparing stationary phases[3], the temperature dependence of the values being ignored.

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The solute or substance polarity factors are more difficult to obtain and must be calculated from retention data of the solute and the stationary phase polarity constants at the arbitrarily specified temperatures[2,4] by solution of eqn. 2, preferably by the method of least squares

$$\Delta I^{A} = ax + by + cz + du + es \qquad (2)$$

Without both sets of constants, eqn. 2 cannot be applied to predict retention data of the solute on other stationary phases.

A detailed study of both series of constants has not been reported although stationary phase polarity factors, *i.e.*, $x \ldots s$, are well known as the Rohrschneider constants or more recently as the McReynolds constants[4], which are finding increasing acceptance, as previously mentioned, following the introductory work of the Supelco Organisation[3].

Values of the substance polarity factors, *i.e.*, $a \ldots e$, however, have only been reported in the original work of Rohrschneider[2] and with only thirty compounds selected to cover a wide range of functional classes it is not apparent if the values have any real meaning when a series of close homologues are considered. The values must be significant if the Rohrschneider scheme is suitable for retention prediction. There has in practice been some difficulty in evaluating the constants for a series of compounds due to the severe temperature limitations imposed by the use of squalane as a basis of reference. Recent work[5] has shown that Rohrschneider-type schemes are based on the difference in intermolecular interactions between a substance and each of two stationary phases according to eqn. 3 and squalane with its low temperature limitations may be eliminated and thus studies may be conducted at more realistic temperatures.

$$\Delta I^{A}_{1,2} = I^{A}_{1} - I^{A}_{2} = a(I^{x}_{1} - I^{x}_{2}) + b(I^{y}_{1} - I^{y}_{2}) + c(I^{z}_{1} - I^{z}_{2}) + d(I^{u}_{1} - I^{u}_{2}) + e(I^{s}_{1} - I^{s}_{2}) \qquad (3)$$

where $I^{A}_{1}$ and $I^{A}_{2}$ are the retention indices for compound A determined on the two stationary phases 1 and 2, and $I^{x}_{1}, \ldots I^{s}_{1}$ and $I^{x}_{2}, \ldots, I^{s}_{2}$ are the retention indices of the five standard substances on columns 1 and 2, respectively.

The present work concerns a study of 175 homologous aliphatic esters where the alkyl groups corresponding to the appropriate acids and alcohols, *i.e.*, acid and alcohol chains, are each straight, branched and with unsaturation and which have been chromatographed on fourteen polysiloxane phases. The reference compounds used were those of Rohrschneider and of McReynolds and with dimethyl polysiloxane as the base stationary phase substance polarity factors of the various series have been determined and discussed.

## EXPERIMENTAL

The experimental conditions and retention data used have been previously reported[5,6] and have been evaluated using the procedure of Rohrschneider[2] but including the corrections to the mathematics as previously reported by Leary *et al.*[7] and by Souter[8]. Briefly, the program used permits the choice of any stationary phase as the base phase (equivalent to squalane in the Rohrschneider and McReynolds classification systems). Using the chosen base phase, retention index differences are calculated for all the observations. Column polarity factors $x, \ldots, s$ are then assigned in terms of the column behaviour for benzene, *n*-butanol, 2-pentanone, nitropropane, and pyridine, five of the standard substances introduced by McReynolds[4].

The substance-specific factors, $a, \ldots e$, are calculated using a standard least-squares criterion which minimises the sum of the squared errors, applied to all stationary solvent phases for each substance separately. The values of $a, \ldots, e$ obtained in this way differ slightly from those obtained by employing the method of Rohrschneider, whose method of calculation used a different criterion. The relative merits of these two approaches have been discussed elsewhere[8].

To permit a comparison of results using different stationary phases, the differences between the calculated and the observed values were used to calculate both the root mean square error and the average absolute error for each substance, for each column, and for the complete data set.

## RESULTS AND DISCUSSION

The procedure used to determine the substance polarity constants employs the method of least squares, thus the reliability of the constants determined is increased as the number of stationary phases is increased. Preliminary work using a portion of Rohrschneider's original data set[2] was carried out to ascertain the number of phases required to obtain acceptable constants. In this manner the number of phases considered was varied between eight and the maximum number, twenty-three. When eight stationary phases were used, the average column RMS error in predicting a small section of Rohrschneider's data was 3.0 units, which steadily increased to 4.0 units using twenty-three phases. The numerical values of the substance polarity factors varied considerably as the number of stationary phases in this set was increased, however, these values were observed to reach some type of equilibrium when fifteen or more phases were used, although the actual values were quite sensitive to minor changes in the number and type of stationary phase.

As retention data determined on fourteen stationary phases were available[5,6], the entire set was used to calculate the substance polarity factors for the esters series. These values, as shown in Table I, are based on SE-30, the least polar stationary phase used, and hence the stationary phase polarity factors $x, \ldots s$, shown in Table II more closely resemble the original values as defined by Rohrschneider[2] and later modified by McReynolds[4]. Dimethyl polysiloxanes such as SE-30 have considerable stability and have achieved significant acceptance[9], making them ideal base phases. However, any of the other fourteen phases could have been selected[5,6]. In Table III substance polarity factors are shown for five representative esters, based on each of the fourteen phases. It is apparent, as previously found with change of base calculations, that no trend with polarity or type of stationary phase is evident, although for certain esters and substance polarity factors a range of values is obtained. Again this variation is in part due to the accuracy of the data which is related to the reproducibility of certain stationary phases with time, *i.e.*, XF-1150 (ref. 1).

The values of the substance polarity factors in Table I show quite definite trends when considered in terms of the alkyl ester series. The $a$ and $c$ factors tend to

TABLE I

SUBSTANCE POLARITY FACTORS FOR HOMOLOGOUS ESTERS

| *Compound* | *Substance polarity factors* | | | | |
|---|---|---|---|---|---|
| | *a* | *b* | *c* | *d* | *e* |
| Benzene | 100.00 | 0.0 | 0.0 | 0.0 | 0.0 |
| Butanol | 0.0 | 100.00 | 0.0 | 0.0 | 0.0 |
| 2-Pentanone | 0.0 | 0.0 | 100.00 | 0.0 | 0.0 |
| Nitropropane | 0.0 | 0.0 | 0.0 | 100.00 | 0.0 |
| Pyridine | 0.0 | 0.0 | 0.0 | 0.0 | 100.00 |
| Methyl formate | 47.88 | −40.40 | 68.55 | 20.34 | 2.09 |
| Ethyl formate | 38.99 | −28.67 | 54.76 | 28.25 | −4.34 |
| Propyl formate | 32.95 | −26.07 | 45.92 | 30.81 | −0.71 |
| Butyl formate | 8.98 | −14.40 | 35.84 | 34.45 | 6.46 |
| Pentyl formate | −1.23 | −11.11 | 23.23 | 44.81 | 7.21 |
| Hexyl formate | −13.41 | −9.64 | 19.58 | 48.89 | 11.29 |
| Isopropyl formate | 81.87 | −69.87 | 85.23 | 27.71 | −27.57 |
| Isobutyl formate | 41.31 | −36.38 | 42.28 | 54.08 | −24.00 |
| Isopentyl formate | 9.33 | −21.84 | 33.22 | 49.05 | −4.21 |
| Methyl acetate | 95.49 | −70.83 | 65.87 | 21.93 | −7.44 |
| Ethyl acetate | 58.45 | −60.70 | 52.78 | 19.21 | 14.91 |
| Propyl acetate | 46.47 | −54.28 | 47.29 | 30.59 | 7.62 |
| Butyl acetate | 33.68 | −50.46 | 43.50 | 33.41 | 11.76 |
| Pentyl acetate | 14.22 | −45.48 | 36.68 | 39.10 | 18.00 |
| Hexyl acetate | −4.27 | −39.17 | 33.05 | 39.85 | 24.51 |
| Isopropyl acetate | 56.66 | −74.31 | 58.01 | 25.41 | 7.98 |
| Isobutyl acetate | 19.72 | −46.39 | 57.93 | 27.67 | 10.03 |
| Isopentyl acetate | 7.03 | −37.69 | 38.87 | 36.36 | 14.91 |
| Methyl propionate | 91.35 | −52.88 | 41.62 | 22.17 | −4.95 |
| Ethyl propionate | 76.78 | −60.13 | 52.86 | 23.32 | −5.04 |
| Propyl propionate | 47.56 | −49.08 | 39.49 | 30.55 | 5.85 |
| Butyl propionate | 31.29 | −43.83 | 35.28 | 31.85 | 12.71 |
| Pentyl propionate | 5.10 | −36.47 | 30.31 | 30.15 | 27.90 |
| Hexyl propionate | −13.37 | −30.44 | 25.77 | 33.17 | 33.33 |
| Isopropyl propionate | 51.48 | −59.23 | 52.76 | 30.02 | −4.84 |
| Isobutyl propionate | 33.28 | −51.06 | 44.11 | 42.28 | −3.83 |
| Isopentyl propionate | 17.75 | −44.83 | 44.65 | 31.91 | 11.50 |
| Methyl butyrate | 54.11 | −51.99 | 45.42 | 24.69 | 10.39 |
| Ethyl butyrate | 45.41 | −55.35 | 48.03 | 28.38 | 8.11 |
| Propyl butyrate | 22.00 | −45.49 | 38.20 | 33.26 | 15.13 |
| Butyl butyrate | 4.35 | −40.58 | 35.79 | 33.59 | 22.57 |
| Pentyl butyrate | −12.93 | −36.97 | 34.24 | 32.70 | 31.64 |
| Hexyl butyrate | −29.11 | −31.79 | 29.66 | 34.97 | 37.02 |
| Isopropyl butyrate | 26.95 | −56.45 | 50.24 | 31.79 | 7.49 |
| Isobutyl butyrate | 2.34 | −44.69 | 40.19 | 43.58 | 9.53 |
| Isopentyl butyrate | −12.19 | −40.67 | 38.00 | 38.33 | 22.79 |
| Methyl pentanoate | 45.32 | −51.63 | 48.27 | 28.09 | 7.58 |
| Ethyl pentanoate | 22.64 | −49.57 | 47.00 | 27.47 | 17.62 |
| Propyl pentanoate | 13.32 | −48.45 | 44.91 | 31.92 | 17.76 |
| Butyl pentanoate | −6.37 | −42.44 | 39.57 | 33.23 | 26.78 |
| Pentyl pentanoate | −22.65 | −37.83 | 37.32 | 32.64 | 34.58 |
| Hexyl pentanoate | −47.51 | −28.38 | 30.35 | 32.82 | 46.14 |
| Isopropyl pentanoate | 12.89 | 56.02 | 53.05 | 29.46 | 14.90 |
| Isobutyl pentanoate | −8.08 | −45.03 | 43.39 | 40.35 | 16.07 |

TABLE I *(continued)*

| *Compound* | *Substance polarity factors* | | | | |
|---|---|---|---|---|---|
| | *a* | *b* | *c* | *d* | *e* |
| Isopentyl pentanoate | −4.07 | −47.23 | 40.76 | 41.37 | 14.40 |
| Methyl hexanoate | 14.08 | −34.25 | 30.94 | 32.58 | 20.41 |
| Ethyl hexanoate | −0.11 | −34.66 | 28.57 | 35.37 | 23.31 |
| Propyl hexanoate | −13.02 | −34.96 | 32.60 | 31.70 | 32.12 |
| Butyl hexanoate | −24.83 | −32.30 | 28.97 | 32.79 | 37.60 |
| Pentyl hexanoate | −44.28 | −27.23 | 28.25 | 31.19 | 47.15 |
| Hexyl hexanoate | −61.65 | −20.13 | 23.87 | 31.29 | 54.28 |
| Isopropyl hexanoate | −10.27 | −43.71 | 41.35 | 31.36 | 25.37 |
| Isobutyl hexanoate | −11.68 | −42.95 | 42.92 | 37.94 | 19.17 |
| Isopentyl hexanoate | −25.58 | −39.73 | 40.01 | 35.44 | 30.38 |
| Methyl isobutyrate | 46.65 | −51.70 | 39.20 | 34.49 | 3.30 |
| Ethyl isobutyrate | −18.58 | −30.28 | 21.48 | 44.11 | 25.65 |
| Propyl isobutyrate | 17.54 | −46.51 | 37.52 | 39.63 | 6.75 |
| Butyl isobutyrate | 7.14 | −45.13 | 38.17 | 38.13 | 12.49 |
| Pentyl isobutyrate | −1.95 | −44.78 | 39.66 | 37.62 | 16.65 |
| Hexyl isobutyrate | −22.77 | −35.94 | 34.02 | 39.90 | 22.98 |
| Isopropyl isobutyrate | 21.61 | −54.40 | 46.92 | 36.45 | 0.12 |
| Isobutyl isobutyrate | −3.18 | −42.72 | 36.26 | 50.79 | 0.42 |
| Isopentyl isobutyrate | −14.48 | −38.73 | 33.17 | 44.74 | 13.63 |
| Methyl isopentanoate | 35.59 | −44.95 | 41.47 | 31.41 | 5.65 |
| Ethyl isopentanoate | 24.54 | −49.23 | 42.35 | 32.76 | 8.62 |
| Propyl isopentanoate | 8.10 | −45.91 | 41.48 | 35.12 | 13.92 |
| Butyl isopentanoate | −6.19 | −41.22 | 38.49 | 37.46 | 17.85 |
| Pentyl isopentanoate | −21.99 | −37.76 | 38.14 | 34.43 | 27.74 |
| Hexyl isopentanoate | −37.43 | −32.77 | 35.60 | 35.86 | 32.51 |
| Isopropyl isopentanoate | 20.73 | −56.06 | 41.96 | 37.07 | −0.38 |
| Isobutyl isopentanoate | −5.18 | −45.18 | 43.88 | 46.59 | 3.36 |
| Isopentyl isopentanoate | −14.61 | −42.46 | 41.61 | 42.06 | 13.45 |
| Methyl isohexanoate | 24.23 | −40.20 | 35.64 | 35.22 | 9.93 |
| Ethyl isohexanoate | −7.89 | −36.06 | 32.36 | 36.44 | 22.50 |
| Propyl isohexanoate | −10.66 | −36.51 | 32.03 | 37.52 | 23.26 |
| Butyl isohexanoate | 24.86 | −33.08 | 31.60 | 36.40 | 29.88 |
| Pentyl isohexanoate | −39.91 | −30.39 | 30.64 | 36.29 | 37.29 |
| Hexyl isohexanoate | −54.49 | −25.25 | 27.81 | 36.32 | 43.22 |
| Isopropyl isohexanoate | 7.94 | −53.41 | 49.23 | 34.63 | 10.50 |
| Isobutyl isohexanoate | −34.97 | −33.26 | 31.40 | 45.70 | 22.96 |
| Isopentyl isohexanoate | −41.42 | −33.50 | 33.17 | 41.37 | 30.90 |
| Methyl 2-methylpentanoate | 21.94 | −42.44 | 39.16 | 15.32 | 28.58 |
| Ethyl 2-methylpentanoate | −1.06 | −40.99 | 36.57 | 20.22 | 34.24 |
| Propyl 2-methylpentanoate | −4.73 | −41.34 | 39.28 | 21.58 | 32.36 |
| Butyl 2-methylpentanoate | −23.68 | −36.58 | 36.27 | 19.39 | 44.17 |
| Pentyl 2-methylpentanoate | −36.32 | −33.40 | 35.21 | 20.57 | 47.99 |
| Hexyl 2-methylpentanoate | −52.11 | −27.55 | 33.22 | 20.02 | 54.23 |
| Isopropyl 2-methylpentanoate | 2.84 | −54.93 | 55.01 | 19.49 | 22.86 |
| Isobutyl 2-methylpentanoate | −17.37 | −41.72 | 41.85 | 29.88 | 25.62 |
| Isopentyl 2-methylpentanoate | −40.22 | −39.16 | 43.41 | 25.93 | 40.67 |
| Methyl 2-ethylbutyrate | 16.98 | −33.83 | 33.49 | 12.82 | 31.02 |
| Ethyl 2-ethylbutyrate | −14.21 | −27.70 | 26.99 | 21.02 | 36.97 |
| Propyl 2-ethylbutyrate | −6.76 | −34.63 | 32.65 | 23.57 | 30.74 |
| Butyl 2-ethylbutyrate | −25.48 | −31.14 | 31.37 | 21.87 | 41.19 |

*(Continued on p. 188)*

TABLE I *(continued)*

| *Compound* | *Substance polarity factors* | | | | |
|---|---|---|---|---|---|
| | *a* | *b* | *c* | *d* | *e* |
| Pentyl 2-ethylbutyrate | −40.47 | −26.17 | 28.60 | 22.50 | 47.10 |
| Hexyl 2-ethylbutyrate | −52.34 | −22.66 | 27.69 | 21.63 | 52.39 |
| Isopropyl 2-ethylbutyrate | 21.34 | −53.91 | 54.20 | 22.66 | 7.32 |
| Isobutyl 2-ethylbutyrate | −27.58 | −34.24 | 38.03 | 29.23 | 28.47 |
| Isopentyl 2-ethylbutyrate | −42.32 | −28.36 | 32.22 | 25.77 | 41.40 |
| Methyl 2-propenoate | 69.70 | −42.80 | 64.85 | 6.41 | 2.30 |
| Ethyl 2-propenoate | 64.50 | −44.56 | 54.37 | 19.62 | −2.92 |
| Propyl 2-propenoate | 54.41 | −44.97 | 44.28 | 24.16 | 6.13 |
| Butyl 2-propenoate | 32.46 | −40.08 | 38.51 | 21.14 | 23.24 |
| Pentyl 2-propenoate | 15.24 | −35.66 | 37.71 | 19.45 | 31.90 |
| Hexyl 2-propenoate | −3.82 | −29.14 | 34.00 | 19.51 | 40.12 |
| Isopropyl 2-propenoate | 42.92 | −41.42 | 49.21 | 22.64 | 0.87 |
| Isobutyl 2-propenoate | 32.95 | −46.32 | 48.82 | 25.67 | 11.54 |
| Isopentyl 2-propenoate | 12.52 | −39.41 | 43.73 | 21.12 | 27.70 |
| Methyl 2-methyl-2-propenoate | 70.64 | −44.11 | 38.98 | 13.09 | 11.39 |
| Ethyl 2-methyl-2-propenoate | 56.31 | −45.13 | 39.08 | 17.77 | 12.03 |
| Propyl 2-methyl-2-propenoate | 33.47 | −41.33 | 38.33 | 18.33 | 22.74 |
| Butyl 2-methyl-2-propenoate | 17.19 | −38.10 | 34.94 | 17.37 | 32.60 |
| Pentyl 2-methyl-2-propenoate | 2.01 | −33.99 | 32.99 | 16.66 | 40.32 |
| Hexyl 2-methyl-2-propenoate | −11.62 | −30.03 | 31.03 | 17.48 | 45.29 |
| Isopropyl 2-methyl-2-propenoate | 44.92 | −51.13 | 55.53 | 17.02 | 5.09 |
| Isobutyl 2-methyl-2-propenoate | 21.26 | −43.18 | 40.50 | 26.74 | 16.56 |
| Isopentyl 2-methyl-2-propenoate | −10.80 | −31.43 | 30.27 | 26.39 | 35.42 |
| Methyl 2-butenoate | 31.79 | −41.48 | 39.43 | 8.53 | 48.49 |
| Ethyl 2-butenoate | 40.06 | −49.25 | 42.28 | 20.07 | 32.33 |
| Propyl 2-butenoate | 25.64 | −47.13 | 40.63 | 20.80 | 39.31 |
| Butyl 2-butenoate | 8.73 | −42.73 | 39.31 | 18.10 | 49.27 |
| Pentyl 2-butenoate | −6.72 | −38.38 | 36.48 | 16.97 | 58.05 |
| Hexyl 2-butenoate | −21.28 | −36.38 | 36.27 | 16.97 | 64.65 |
| Isopropyl 2-butenoate | 44.78 | −48.91 | 44.41 | 22.04 | 17.90 |
| Isobutyl 2-butenoate | 3.65 | −49.75 | 48.24 | 23.16 | 43.53 |
| Isopentyl 2-butenoate | −7.26 | −43.05 | 43.34 | 18.52 | 53.73 |
| Methyl 3-butenoate | 56.47 | −27.03 | 39.76 | 13.69 | 14.03 |
| Ethyl 3-butenoate | 54.75 | −34.55 | 45.81 | 12.62 | 12.57 |
| Propyl 3-butenoate | 26.97 | −26.29 | 45.47 | 9.11 | 25.67 |
| Butyl 3-butenoate | 10.13 | −20.77 | 44.91 | 8.19 | 32.00 |
| Pentyl 3-butenoate | −6.22 | −19.38 | 38.78 | 10.51 | 42.65 |
| Hexyl 3-butenoate | −22.80 | −14.37 | 37.17 | 12.13 | 46.83 |
| Isopropyl 3-butenoate | 29.56 | −32.40 | 58.99 | 5.64 | 16.84 |
| Isobutyl 3-butenoate | 11.44 | −27.80 | 49.05 | 18.69 | 18.98 |
| Isopentyl 3-butenoate | −3.51 | −23.35 | 47.00 | 14.56 | 30.94 |
| Methyl 3-methyl-2-butenoate | 44.50 | −34.80 | 30.43 | 9.47 | 38.34 |
| Ethyl 3-methyl-2-butenoate | 20.58 | −35.34 | 29.49 | 2.88 | 57.66 |
| Propyl 3-methyl-2-butenoate | 18.90 | −55.48 | 29.08 | 5.49 | 55.76 |
| Butyl 3-methyl-2-butenoate | 4.62 | −32.94 | 29.00 | 3.85 | 63.55 |
| Pentyl 3-methyl-2-butenoate | −17.11 | −28.60 | 26.65 | 3.35 | 75.03 |
| Hexyl 3-methyl-2-butenoate | −28.69 | −25.22 | 24.18 | 3.87 | 79.93 |
| Isopropyl 3-methyl-2-butenoate | 17.65 | −39.77 | 33.75 | 4.41 | 52.24 |
| Isobutyl 3-methyl-2-butenoate | −0.53 | −33.48 | 29.48 | 9.96 | 56.70 |
| Isopentyl 3-methyl-2-butenoate | −7.31 | −36.35 | 33.55 | 6.34 | 64.50 |

TABLE I *(continued)*

| *Compound* | *Substance polarity factors* | | | | |
|---|---|---|---|---|---|
| | *a* | *b* | *c* | *d* | *e* |
| *trans*-2-Hexenyl formate | −28.98 | 14.25 | 5.38 | 35.09 | 32.65 |
| *trans*-2-Hexenyl acetate | −5.56 | −28.39 | 26.51 | 14.77 | 56.96 |
| *trans*-2-Hexenyl propionate | −5.49 | −28.87 | 24.16 | 6.97 | 64.36 |
| *trans*-2-Hexenyl butyrate | −19.66 | −25.64 | 21.44 | 7.92 | 69.19 |
| *trans*-2-Hexenyl pentanoate | −34.15 | −23.49 | 21.21 | 5.64 | 78.51 |
| *trans*-2-Hexenyl hexanoate | −52.13 | −18.34 | 15.35 | 8.45 | 84.10 |
| *cis*-2-Hexenyl formate | 14.58 | −4.87 | 16.42 | 40.04 | 7.64 |
| *cis*-2-Hexenyl acetate | 14.35 | −32.31 | 28.09 | 19.96 | 40.39 |
| *cis*-2-Hexenyl propionate | 4.01 | −26.51 | 21.03 | 11.51 | 53.70 |
| *cis*-2-Hexenyl butyrate | 5.52 | −31.22 | 27.52 | 9.19 | 51.91 |
| *cis*-2-Hexenyl pentanoate | −22.79 | −20.76 | 18.60 | 8.39 | 68.00 |
| *cis*-2-Hexenyl hexanoate | −35.24 | −17.83 | 16.07 | 11.23 | 71.03 |
| *trans*-3-Hexenyl formate | 0.37 | −0.84 | 15.94 | 32.31 | 21.12 |
| *trans*-3-Hexenyl acetate | −1.09 | −34.33 | 25.04 | 19.48 | 52.40 |
| *trans*-3-Hexenyl propionate | −6.97 | −29.00 | 25.77 | 10.13 | 58.81 |
| *trans*-3-Hexenyl butyrate | −28.61 | −27.11 | 31.98 | 1.07 | 74.00 |
| *trans*-3-Hexenyl pentanoate | −30.94 | −24.78 | 24.83 | 9.44 | 69.26 |
| *trans*-3-Hexenyl hexanoate | −47.88 | −19.97 | 19.03 | 11.58 | 76.69 |
| *cis*-3-Hexenyl formate | 11.59 | −5.55 | 15.91 | 38.33 | 13.31 |
| *cis*-3-Hexenyl acetate | −0.06 | −30.83 | 29.48 | 21.55 | 45.80 |
| *cis*-3-Hexenyl propionate | 0.59 | −25.71 | 20.92 | 18.00 | 47.69 |
| *cis*-3-Hexenyl butyrate | −13.18 | −22.34 | 18.13 | 17.54 | 53.75 |
| *cis*-3-Hexenyl pentanoate | −29.46 | −18.63 | 16.17 | 16.57 | 63.03 |
| *cis*-3-Hexenyl hexanoate | −45.51 | −18.09 | 16.77 | 15.87 | 71.81 |
| Pent-1-en-3-yl acetate | 14.27 | −35.49 | 33.96 | 30.65 | 19.08 |
| Hex-1-en-3-yl acetate | 5.47 | −33.86 | 35.55 | 28.78 | 23.88 |
| Hept-1-en-3-yl acetate | −0.20 | −30.62 | 32.20 | 32.96 | 21.77 |
| Oct-1-en-3-yl acetate | −7.09 | −26.72 | 23.64 | 36.69 | 23.76 |
| Non-1-en-3-yl acetate | −23.54 | −20.90 | 20.49 | 35.77 | 31.77 |
| Dec-1-en-3-yl acetate | −35.87 | −16.53 | 18.45 | 35.50 | 35.79 |

TABLE II

STATIONARY PHASE POLARITY CONSTANTS WITH SE-30 AS THE BASE PHASE

| *Stationary phase* | *Stationary phase polarity constants* | | | | |
|---|---|---|---|---|---|
| | *x* | *y* | *z* | *u* | *s* |
| SE-30 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| OV-7 | 0.450 | 0.620 | 0.820 | 1.140 | 1.150 |
| DC-710 | 0.930 | 1.160 | 1.190 | 1.740 | 1.720 |
| OV-25 | 1.560 | 1.680 | 1.690 | 2.430 | 2.550 |
| 100% phenyl | 1.860 | 2.250 | 2.430 | 3.000 | 3.670 |
| XE-60 | 1.890 | 3.230 | 3.030 | 4.410 | 3.630 |
| XF-1150 | 3.400 | 5.020 | 4.650 | 6.610 | 5.390 |
| OV-225 | 2.240 | 3.330 | 3.120 | 4.320 | 3.980 |
| Silar 5CP | 3.240 | 4.460 | 4.150 | 5.730 | 5.250 |
| F-400 | 0.460 | 0.710 | 1.270 | 1.690 | 1.300 |
| F-500 | 0.870 | 1.190 | 1.900 | 2.420 | 1.930 |
| QF-1 | 1.280 | 2.170 | 3.430 | 4.330 | 3.310 |
| DC-230 | 0.140 | 0.390 | 0.270 | 0.530 | 0.590 |
| DC-530 | 0.590 | 1.850 | 1.800 | 1.110 | 0.960 |

TABLE III

SUBSTANCE POLARITIES FOR ESTER DATA BASED ON VARIOUS STATIONARY PHASES

| *Compound* | *Base stationary phase* | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *SE-30* | *OV-7* | *DC-710* | *OV-25* | *100% Phenyl* | *DC-230* | *DC-530* | *XE-60* | *XF-1150* | *OV-225* | *Silar 5CP* | *F-400* | *F-500* | *QF-1* | *Average* |
| *a* | | | | | | | | | | | | | | | |
| Butyl acetate | 33.69 | 34.05 | 27.86 | 40.16 | 29.43 | 34.23 | 27.80 | 16.82 | 20.97 | 25.25 | 33.07 | 27.82 | 21.39 | 26.75 | 28.52 |
| Ethyl butyrate | 45.41 | 41.21 | 43.15 | 57.07 | 43.55 | 42.95 | 42.15 | 41.27 | 39.98 | 45.91 | 44.90 | 40.61 | 24.43 | 39.22 | 42.87 |
| Hexyl 2-methylpentanoate | −52.12 | −30.98 | −39.92 | −36.57 | −42.83 | −32.45 | −46.96 | −66.31 | −62.35 | −76.56 | −40.02 | −40.12 | −30.97 | −43.12 | −45.82 |
| Ethyl 2-propenoate | 64.50 | 54.51 | 52.57 | 47.42 | 49.81 | 52.62 | 53.01 | 55.51 | 60.28 | 68.00 | 47.38 | 51.48 | 37.36 | 50.72 | 53.23 |
| *trans*-2-Hexenyl acetate | −5.56 | 6.24 | 10.00 | 29.37 | 6.45 | 22.37 | 3.01 | −20.34 | −7.14 | −8.46 | 2.51 | 15.24 | 8.25 | 5.40 | 4.82 |
| *b* | | | | | | | | | | | | | | | |
| Butyl acetate | −50.45 | −51.62 | −49.00 | −55.05 | −48.98 | −52.91 | −48.97 | −42.82 | −48.26 | −47.38 | −50.31 | −49.02 | −43.77 | −49.69 | −49.16 |
| Ethyl butyrate | −55.35 | −54.13 | −54.94 | −61.86 | −54.53 | −55.01 | −54.37 | −54.03 | −54.30 | −56.88 | −55.22 | −52.18 | −40.12 | −56.54 | −54.25 |
| Hexyl 2-methylpentanoate | −27.56 | −35.60 | −31.75 | −33.95 | −28.87 | −37.73 | −28.69 | −17.98 | −27.26 | −10.28 | −30.62 | −39.15 | −41.83 | −26.24 | −29.82 |
| Ethyl 2-propenoate | −44.57 | −42.31 | −41.49 | −38.93 | −41.65 | −41.44 | −41.98 | −43.08 | −42.41 | −51.08 | −40.23 | −39.41 | −28.97 | −43.20 | −41.48 |
| *trans*-2-Hexenyl acetate | −28.40 | −31.90 | −33.43 | −43.50 | −30.58 | −42.38 | −29.91 | −17.43 | −29.51 | −23.33 | −30.42 | −41.89 | −34.77 | −28.10 | −31.83 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Butyl acetate | 43.50 | 50.25 | 43.87 | 46.74 | 43.27 | 48.95 | 43.91 | 37.80 | 44.13 | 42.56 | 45.20 | 43.91 | 39.67 | 44.92 | 41.83 |
| Ethyl butyrate | 48.03 | 47.27 | 47.91 | 51.68 | 47.71 | 48.85 | 48.56 | 47.74 | 48.31 | 50.20 | 48.91 | 47.32 | 36.56 | 51.15 | 47.87 |
| Hexyl 2-methylpentanoate | 33.22 | 49.06 | 30.49 | 35.25 | 31.30 | 44.24 | 33.19 | 22.10 | 33.40 | 17.36 | 34.58 | 36.87 | 43.28 | 29.09 | 33.82 |
| Ethyl 2-propenoate | 54.37 | 56.71 | 55.29 | 53.87 | 56.36 | 54.87 | 54.52 | 56.56 | 54.89 | 63.02 | 53.75 | 54.27 | 44.87 | 57.38 | 55.05 |
| *trans*-2-Hexenyl acetate | 26.51 | 29.12 | 23.58 | 31.97 | 24.64 | 41.07 | 27.24 | 12.90 | 26.27 | 19.88 | 25.77 | 26.82 | 29.32 | 23.62 | 26.34 |
| *d* | | | | | | | | | | | | | | | |
| Butyl acetate | 33.41 | 29.71 | 31.81 | 31.03 | 34.11 | 30.58 | 31.78 | 34.00 | 28.38 | 31.59 | 31.02 | 31.83 | 30.97 | 31.97 | 31.59 |
| Ethyl butyrate | 28.39 | 27.82 | 27.72 | 26.58 | 29.47 | 27.36 | 27.22 | 27.68 | 26.40 | 27.80 | 27.10 | 25.87 | 25.21 | 27.99 | 28.04 |
| Hexyl 2-methylpentanoate | 20.02 | 16.15 | 23.02 | 20.82 | 27.29 | 18.72 | 21.17 | 25.35 | 13.72 | 19.09 | 20.45 | 28.61 | 23.52 | 20.83 | 21.34 |
| Ethyl 2-propenoate | 19.63 | 15.94 | 16.36 | 16.79 | 11.95 | 16.52 | 16.99 | 15.94 | 20.13 | 17.65 | 17.27 | 14.89 | 14.44 | 16.82 | 16.52 |
| *trans*-2-hexenyl acetate | 14.78 | 16.12 | 18.71 | 15.55 | 21.95 | 13.53 | 16.03 | 21.87 | 12.04 | 16.24 | 17.26 | 19.93 | 17.84 | 16.79 | 17.05 |
| *e* | | | | | | | | | | | | | | | |
| Butyl acetate | 11.77 | 12.92 | 16.40 | 12.58 | 13.15 | 13.66 | 16.42 | 20.52 | 22.88 | 18.12 | 14.90 | 16.39 | 20.40 | 16.72 | 16.20 |
| Ethyl butyrate | 8.11 | 11.21 | 10.34 | 6.04 | 7.90 | 10.34 | 10.59 | 11.01 | 12.75 | 8.18 | 9.887 | 12.57 | 21.68 | 11.51 | 10.87 |
| Hexyl 2-methylpentanoate | 54.23 | 41.20 | 47.73 | 46.91 | 41.90 | 43.93 | 50.05 | 57.38 | 64.73 | 69.87 | 48.13 | 41.78 | 40.22 | 49.05 | 49.79 |
| Ethyl 2-propenoate | −2.93 | 5.34 | 6.33 | 7.92 | 12.54 | 6.35 | 6.37 | 5.25 | −0.74 | −3.82 | 7.82 | 6.02 | 15.88 | 6.83 | 5.80 |
| *trans*-2-Hexenyl acetate | 56.96 | 48.35 | 47.75 | 41.89 | 43.37 | 41.85 | 49.76 | 58.87 | 59.79 | 57.80 | 50.28 | 47.27 | 46.91 | 49.56 | 50.03 |

decrease as the number of carbon atoms in the alcohol chain ($R^1$) increase, while the *b*, *d* and *e* factors tend to increase with an increase in $R^1$. Variation from this behaviour does occur, but is centred around the *d* factor, which in many cases exhibits very little change with increases in the acid and alcohol chains, especially with unsaturated ester series. When the substance polarity factors are considered in terms of alcohol ester series, essentially the same trends are apparent although the values exhibit a greater scatter. This would, in part, be due to the loss of linearity of these series on polar stationary phase plots[5].

It is not possible to compare the actual numerical values of the substance polarity constants with other values as the only data reported are those of Rohrschneider[2]. Rohrschneider published data for one ester, *n*-butyl acetate and it is worth comparing the two sets of values, *i.e.*,

| *a* | *b* | *c* | *d* | *e* |
|---|---|---|---|---|
| −3.77 | −13.31 | 57.29 | 13.88 | 19.98 |
| 33.69 | −50.46 | 43.50 | 33.41 | 11.77 |

The top values are those determined by Rohrschneider and show considerable variation with respect to the values determined in this work. When it is considered that the values determined by Rohrschneider were obtained at 100° and with some unstable phases, variations are to be expected; also, it has been shown that stationary phase polarity factors exhibit considerable variation with temperature[9] and hence it is reasonable to expect the substance polarity factors to change, although this has not been examined to date. These two sets of values are of similar magnitudes, the *a* factor being the only exception; however, it is considered that hexyl acetate has an *a* value of −4.28; the values for butyl acetate are more reasonable. As expected, most esters as carboxyl compounds exhibit a large *c* factor, which decreases as both the acid, R, and the alcohol, $R^1$, chain lengths are increased. Of the other factors, the *d* factor is of medium magnitude and relatively constant while *e* increases from negative to positive with R and $R^1$; the reverse is apparent with *a*, while *b* is a large negative factor that becomes more positive with increased R and $R^1$ chain length. By Rohrschneider's original theory a measure of orientation forces was defined as factor *c*, charge transfer forces as *a* donor, and *d* acceptor, and hydrogen bonding as *b* donor, and *e* acceptor. In this manner these trends observed with *a* to *e* should represent a measure of the change in the above forces; that is, as the R and $R^1$ chain lengths increase, the electron donor and orientation forces decrease while the hydrogen bonding acceptor and donor forces increase and the electron acceptor forces remain relatively constant. While it would be expected that the electron acceptor and donor forces of these esters would change due to the altering proximity of weakly donor methyl groups and acceptor carboxyl groups, and that the *c* factor would decrease with increased R and $R^1$ due to a dilution and shielding effects, changes in hydrogen bonding factors are unexpected with these esters. In fact, it is becoming more apparent that these factors are not entirely a measure of forces of interaction, as defined by Rohrschneider, but more a measure of a similarity or dissimilarity in retention behaviour between the substance to be characterised and the standard substances employed in the classification summation[1,10].

The effect of structural changes in the ester molecule is not entirely clear as it would be expected that the effect of isomeric structures, as well as unsaturation, would be to increase the electron donor factor *a* with respect to the normal and saturated esters. While this is observed for certain lower isopropyl esters, this trend is not obvious for the other isomeric structures. With unsaturation the donor factor *a* for small $R^1$ chain lengths was decreased in comparison with the saturated ester and only in certain cases did *a* become greater with increased length of $R^1$. Again this indicates that these factors are not entirely a measure of the forces of interaction as defined by Rohrschneider. When it is considered that dominant stationary phase polarity factors are rare with most stationary phases, and that the base stationary phase of the classification scheme can be altered without affecting the numerical values of the substance polarity factors or the prediction properties of the scheme, the entire theory that Rohrschneider proposed must be queried.

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