

CHROM. 12,212

GAS CHROMATOGRAPHY OF ESTERS

XII*. LINEAR EXTRATHERMODYNAMIC RELATIONSHIPS

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(Received July 16th, 1979)

SUMMARY

A series of five simple and inter-related extrathermodynamic relationships developed by Fellous and co-workers with several series of ethers and suggested to be applicable to homologous series of any functional class have been examined with an extensive series of alkyl esters. The low-polarity esters with alkyl substituents which are not equivalent as are those of the ethers, present a more realistic series to determine general application.

INTRODUCTION

Fellous and co-workers¹⁻⁴ reported a series of five simple and inter-related extrathermodynamic relationships (eqns. 1-5) developed with several homologous series of alkyl and allyl ethers and suggested them to be generally applicable to homologous series with any functional groups.

The first correlation is the familiar linear relationship between the logarithm of relative retention times of two homologous series of one functional class on a common stationary phase. Methyl and ethyl ethers were studied on six stationary phases and eqn. 1 was established:

$$\log t'_{R(\text{ROEt})} = a \log t'_{R(\text{ROMe})} + b \quad (1)$$

where R = 2 to 8, with straight- and branched-chain homologs.

Values of the correlation constant of a were found to be very close to 1, which indicates the analogous intervention of the substituent group R in both series under the same physico-chemical condition, *i.e.* with identical stationary phase.

The intercept, b , characterises the difference of the retention data of two homologous series with regard to the same stationary phase. To obtain the best possible separation of the homologues, it is desirable to select the stationary phase that provides the highest value of b .

* For Part XI, see J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 135 (1977) 67.

In an attempt to provide a simple polarity scale for stationary phases, the following linear relationship was established, relating the logarithms of relative retention times of one series on two different stationary phases:

$$\log t'_{R(\varphi_1)} = a \log t'_{R(\varphi_2)} + b \quad (2)$$

where φ_1 and φ_2 represent any two stationary phases and a and b are regression coefficients.

The calculation was applied with ROEt and Apiezon L was used as φ_2 . The value a of the slope was found to be inversely proportional to the polarity of the column. This characteristic may be used as criterion for a classification of stationary phases based on polarity.

The applicability of the Taft equations⁵ for gas chromatography under isothermal condition was also considered by Fellous *et al.*¹⁻⁴. The effects of the polarity, steric hindrance and hyperconjugation of the substituent on the retention data were investigated according to the suggested Taft type extrathermodynamic linear relationships.

As the retention values of the ROEt compounds were plotted against the Taft polar constant, σ^* , the graphs obtained for each stationary phases were characterised by four series of points, according to the number of hydrogen atoms bonding to the α -C atom of the oxygen. These graphs have indicated the Taft relationship:

$$\log t'_R = \sigma^* \rho^* + h(n - 3) \quad (3)$$

where:

σ^* = the polar constant of the substituent, developed by Taft⁵;

ρ^* = a constant, representing the sensitivity of the stationary phase to the polar effect;

n = the number of hydrogen atoms on the carbon bonding with the oxygen atom;

h = the hyperconjugation constant;

ρ^* and h are determined by regression analysis to give the best fit to the data.

When the bulk of the substituent has a strong effect on retention data, the steric constant is suggested to be included to give the modified relation:

$$\log t'_R = \sigma^* \rho^* + \sigma E_s + h(n - 3) \quad (4)$$

where E_s = Taft steric parameter; and σ = a constant adjusted to give the best fit of the data and simultaneously determined with ρ^* and h .

It was found that inclusion of a constant allowing for the steric effects slightly improved the quality of the correlations, especially for polar phases.

The slope ρ^* obtained through eqns. 3 and 4 for the six selected stationary phases varied in the same way as the relative polarity a , as previously defined by eqn. 2. Hence, a linear relationship between ρ^* and a was established:

$$\rho^* \varphi_1 = \lambda a + \beta \quad (5)$$

where $\rho^*\varphi_1$ is determined by eqn. 3 or 4 for stationary phase φ_1 ; a is determined by eqn. 2; and λ and β are correlation constants.

From this relationship, it was possible to use $\rho^*\varphi_1$ instead of a , to approach a classification of the polarity of the stationary phases with regard to the solute used.

Eqn. 1 considering the behaviour of a series of ethyl and methyl ethers was generalised to consider any mono- or polyfunctional families of compounds:

$$\log t'_{R(RZ)\varphi_1} = a_2 \log t'_{R(RZ)\varphi_2} + b_2 \quad (1a)$$

Eqn. 1 was also developed as shown by the general equation (1b):

$$\log t'_{R(RZ)\varphi_2} = a_1 \log t'_{R(RZ)\varphi_1} + b_1 \quad (1b)$$

where a_1 indicates the relative polarity of the stationary phase φ_1 .

Eqns. 1 and 2 can be combined to form a single equation:

$$\log t'_{R(RZ)\varphi_2} = a \log t'_{R(RZ')\varphi_1} + b \quad (1c)$$

These correlations implied that the experimental retention data of various authors could be used to establish linear relationships between the retention time of two groups of substances RZ and RZ'.

The Taft-type relationship (eqn. 3) was also suggested to be generally applicable to any functional group series.

Examinations of the relationships has largely considered the ethers where the influence of a carbon atom is equivalent on either side of the central oxygen atom and even so some divergence occurred with the polar phases.

These relationships have now been examined with the homologous acetates ($RZ' = RCH_3COO$) as reference homologs and 16 series of esters consisting of straight- and branched-chain isomers with saturated and unsaturated homologs of 14 stationary phases of varying polar character.

EXPERIMENTAL

Relative retention volumes, V'_R , using *n*-nonane as standard and retention indices of 14 series of homologous esters and 10 series of unsaturated esters each examined on 14 stationary phases of varying polar character at 150° were taken from the work of Ashes and Haken^{6,7} together with data of alkyl pivalates⁸ and alkyl pyruvates⁹ each on 13 stationary phases determined at the same temperature.

The retention data were converted into the correlation equations of Fellous *et al.*¹⁻⁴ using line regression analysis with two variables and multiple variables. A Digital Equipment PDP 11/40 mini-computer was used with an off-line programme BASIC language. The analyses evaluated the regression coefficients that would give the best correlation for the various populations of data points.

RESULTS AND DISCUSSION

The relationship shown in eqn. 1 relating two different homologous series on the same stationary phase was examined with the ester data, with the acetate group being used as the reference homolog ($RZ' = RCH_3COO$). The results were extremely satisfactory: values of the correlation coefficients from the linear regression analysis were excellent (>0.99), indicating the quality of the correlation established. The results are summarised in Table I.

The success of the relationship indicates that the contribution of the alkyl substituent (R) to the value of $\log t'_R$ is the same for both series on a common phase. Variation of the slope with different series is easily observed by plotting them against various phases. Most slopes had the highest values with diphenylpolysiloxane,

TABLE I

VALUES OF SLOPE (*a*) AND INTERCEPT (*b*) DETERMINED FOR EQN. 1 LINKING TWO HOMOLOGOUS SERIES ON A COMMON STATIONARY PHASE

	<i>Stationary phase</i>					
	<i>SE-30</i>	<i>OV-7</i>	<i>DC-710</i>	<i>OV-25</i>	<i>100% Phenyl</i>	<i>DC-230</i>
<i>Slopes</i>						
Formate	1.07368	1.04578	1.05759	1.06379	1.05432	1.02723
Propionate	0.96357	0.964652	0.968863	0.994751	0.998143	0.98277
Butyrate	0.952345	0.926006	0.94184	0.962803	0.980851	0.937734
Pentanoate	0.931919	0.900129	0.912873	0.954015	0.966811	0.917249
Hexanoate	0.912753	0.896993	0.902658	0.943164	0.96483	0.88834
Isobutyrate	0.959476	0.921427	0.930368	0.97937	0.985052	0.931196
Isopentanoate	0.925292	0.900102	0.916755	0.959200	0.960128	0.913518
Isohexanoate	0.90775	0.889434	0.903808	0.926964	0.957791	0.899152
2-Methylpentanoate	0.895773	0.872274	0.89219	0.926705	0.936052	0.889787
2-Ethylbutyrate	0.89723	0.869797	0.894644	0.940117	0.931467	0.897153
2-Propenoate	0.969879	0.966268	0.985297	1.0223	1.04627	0.951517
2-Methyl-2-propenoate	0.943398	0.932336	0.946803	0.985259	1.00453	0.946393
2-Butenoate	0.946064	0.923511	0.947053	1.01051	1.00758	0.945347
3-Butenoate	0.941585	0.927921	0.934492	0.970942	0.986754	0.944852
3-Methyl-2-butenoate	0.925957	0.928622	0.934089	0.975686	0.983311	0.920263
<i>Intercepts</i>						
Formate	0.189147	0.196471	0.213126	0.228789	0.205286	0.18765
Propionate	0.208157	0.220596	0.215499	0.199358	0.176304	0.209426
Butyrate	0.403225	0.424952	0.420693	0.393446	0.359719	0.427449
Pentanoate	0.623948	0.648291	0.648407	0.608015	0.569639	0.652569
Hexanoate	0.835083	0.894333	0.875753	0.821444	0.775947	0.863712
Isobutyrate	0.314868	0.308638	0.302108	0.262224	0.227071	0.319707
Isopentanoate	0.521039	0.531802	0.523012	0.4738	0.436902	0.543784
Isohexanoate	0.761619	0.791221	0.787562	0.72344	0.690453	0.79371
2-Methylpentanoate	0.694541	0.708867	0.708134	0.655122	0.654271	0.716271
2-Ethylbutyrate	0.686319	0.701393	0.695614	0.637242	0.636952	0.702069
2-Propenoate	0.190959	0.206644	0.203966	0.201415	0.209356	0.204675
2-Methyl-2-propenoate	0.376902	0.391302	0.390306	0.372618	0.377664	0.394196
2-Butenoate	0.511259	0.567449	0.595797	0.58127	0.608506	0.560284
3-Butenoate	0.370659	0.406654	0.423471	0.406362	0.414875	0.399475
3-Methyl-2-butenoate	0.677335	0.746108	0.779778	0.769743	0.760597	0.738453

which is probably to be expected due to interaction of the donor ester groups with the strongest donor phase, and the lowest values with low polarity phases and highly polar or strong acceptor phases.

The slopes of plots relating two homologous series of esters on a single phase decrease as the number of carbon atoms in the acid chain is increased¹⁰; similarly for the same number of carbon atoms in the alcohol chain the slopes decrease as the alcohol chain length increases with the phases considered.

In comparing *n*-alkyl and branched-chain esters, the branching reduces the slope which also decreases the closer the position of the branching is to the functional group and as the length of the branched chain is increased.

The slopes are influenced by unsaturation, the closer the double bond to the carbonyl group the greater the value of the slope; branching again also reduces the

DC-530	XE-60	XF-1150	OV-225	SILAR 5CP	F-400	F-500	QF-1
1.01148	1.06824	1.0399	1.03859	1.04096	1.02409	1.01862	0.998997
1.08995	0.968655	0.963762	0.985324	0.964676	0.986152	0.994723	0.975226
0.947223	0.953052	0.934654	0.94941	0.925108	0.956447	0.972329	0.94476
0.923365	0.928337	0.914902	0.924611	0.907174	0.942902	0.941653	0.924868
0.916012	0.90254	0.896775	0.913517	0.887914	0.933513	0.941917	0.901745
0.95735	0.948158	0.944895	0.955217	0.942546	0.957826	0.973723	0.939943
0.931349	0.926563	0.913271	0.924861	0.902856	0.950748	0.959544	0.917739
0.911642	0.900474	0.902256	0.910536	0.888444	0.941136	0.936771	0.895198
0.905707	0.855653	0.895808	0.902025	0.882608	0.913945	0.931778	0.897816
0.902284	0.899475	0.892312	0.906204	0.884398	0.923646	0.933576	0.896577
0.932957	0.97867	0.96848	0.994241	0.962159	1.00342	1.37336	0.942775
0.94207	0.946698	0.944449	0.954438	0.934948	0.971621	0.981407	0.951768
0.951117	0.947361	0.943495	0.960137	0.93669	0.975815	0.977966	0.99634
0.947945	0.925424	0.92451	0.937084	0.916987	0.973161	0.968431	0.940279
0.927527	0.90688	0.916575	0.93315	0.909628	0.971744	0.964282	0.908237
0.138174	0.146062	0.0969421	0.146398	0.13493	0.19282	0.186069	0.14414
0.244133	0.172051	0.160585	0.175441	0.18013	0.188287	0.18706	0.142004
0.380238	0.348497	0.326775	0.357476	0.359403	0.381142	0.380946	0.340943
0.592927	0.543067	0.505696	0.567246	0.555395	0.603263	0.601342	0.535056
0.801905	0.75132	0.688763	0.76195	0.751773	0.810629	0.809709	0.705557
0.278749	0.239875	0.195202	0.229562	0.206513	0.286067	0.273511	0.249221
0.480477	0.430537	0.386816	0.443905	0.424721	0.503813	0.491829	0.431606
0.722948	0.67622	0.612713	0.69141	0.64854	0.741196	0.745974	0.639476
0.657093	0.609394	0.512351	0.60165	0.548949	0.676054	0.660583	0.553989
0.675531	0.587646	0.501974	0.585096	0.534342	0.653987	0.644663	0.530249
0.273209	0.174626	0.205254	0.19426	0.210212	0.176799	0.1729339	0.153395
0.322582	0.320814	0.314515	0.349575	0.341503	0.353024	0.350086	0.272129
0.566151	0.528991	0.551354	0.573029	0.593358	0.536314	0.547608	0.448855
0.49798	0.383454	0.483732	0.41112	0.432253	0.36209	0.368175	0.313183
0.67443	0.654379	0.643733	0.705581	0.706427	0.680678	0.691552	0.545314

value of the slope. The presence of a second carbonyl group, as, for example, in pyruvate compounds, lowers the value of the slopes enormously in comparison to the propionates with the same number of carbon atoms.

The value of the slope depends on the stationary phase, on the functional class and on the structure of the homologs. When two homologs are related by the relationship $y = ax + b$, the slope a is always positive since the insertion of a methylene group always increases the retention. If $a=1$ then the contribution of the alkyl group to two homologs is exactly the same. If $a > 1$, then R in homolog Y has a higher affinity to the stationary phase considered.

In the case where a reference series is used, the difference in slopes of two homologs related to that reference can be compared with zero for the same meaning. For example, if we have two homologs Y_1 and Y_2 related with reference homolog x , then the following relationships are formed:

$$Y_1 = a_1 x + b_1 \text{ and } Y_2 = a_2 x + b_2$$

which reduces to:

$$Y_1 - Y_2 = (a_1 - a_2) x - (b_1 - b_2)$$

If $(a_1 - a_2) = 0$, then the contribution of two homologs Y_1 and Y_2 to R is equal. If $(a_1 - a_2) > 0$, then Y_1 will have a higher retention time increment as both R's increase together. If $(a_1 - a_2) < 0$, Y_2 will be retained longer for each methylene increment in R.

Values of the intercept for eqn. 1 are shown in Table I. Fig. 1 shows plots of the variation of the intercept with a range of stationary phases for various series of homologous esters. In contrast to the slopes, the intercepts are well separated and show an increase with increasing chain length in the homologs. Chain branching results in further increases in the intercept. The effect of isomerism is illustrated with esters containing 5 or 6 carbon atoms in the acid chain, the intercepts decreasing as the branched chain becomes closer to the carbonyl group. A comparison of pyruvate and propenoate esters which have the same number of carbon atoms shows that the intercepts for the pyruvates are very much greater than there for the propenoates.

With the acetate esters used as reference homologs, there is a tendency for the intercepts to decrease as the phase polarity is increased for all of the saturated series which have greater acid carbon chain values than the acetates, while the opposite behaviour occurs with the formates and the keto esters (*i.e.*, pyruvates).

The value of the intercept in the relationship characterises the retention increments of one series to another for a common stationary phase. The possibility of separation of two series can be estimated from a study of the b values with retention relative to n -nonane a corresponding b value of at least 0.4 would achieve a satisfactory separation of two homologs considered. For instance, the relation between acetates and 2-methyl-2-propenoates on OV-7 gave an intercept of 0.39, which indicates that reasonable separations of the lower members of the series are possible on OV-7. For the best separation of each homolog values of the slope must also be considered, *i.e.* $a > 1$ and $b > 0.4$. With two homologs related to a

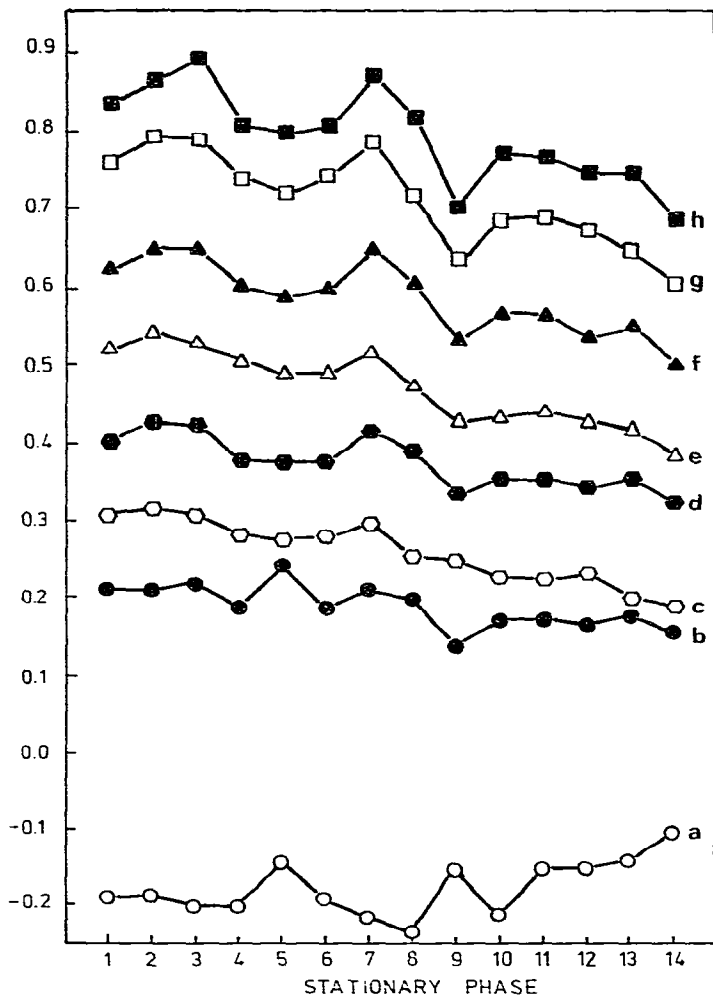


Fig. 1. Plots showing intercept variation of various homologous ester series with varying stationary phase polarity. The stationary phases are (1) SE-30; (2) DC-230; (3) OV-7; (4) F-400; (5) DC-530; (6) F-500; (7) DC-710; (8) OV-25; (9) QF-1; (10) 100% Phenyl; (11) OV-225; (12) XE-60; (13) SILAR 5CP; (14) XF-1150. The plots show homologous (a) formates; (b) propionates; (c) isobutyrate; (d) butyrates; (e) isopentanoates; (f) pentanoates; (g) isohexanoates; (h) hexanoates.

reference homolog separation of the two is good when $a_1 - a_2 > 0$ and $b_1 - b_2 > 0.4$.

The general relationship (eqn. 2) was first examined by Fellous *et al.*¹⁻⁴ in the simpler form

$$\log t_{R(\varphi_1)} = a_2 \log t'_{R(\varphi_2)} \quad (2a)$$

with the suggestion that the regression line passed through the origin or $b = 0$. This, however, was found to occur only with non-polar liquid phases. The correlation was generalised according to eqn. 1a and intercepts were determined for the ester data

(Table II). The slope in the relationship expresses the polarity of phase φ_1 relative to phase φ_2 such that the value of slope a will be inversely proportional to the polarity. Table III shows a classification of the phases used according to eqn 2a. As expected a substantial consistency in order is evident with various homologous esters, but examination of alcohols, aldehydes, ketones and ethoxy alcohols¹¹ shows variant results and there is little to suggest that the procedure is of any value as a method of stationary phase classification, particularly as the sequences indicated are different from those obtained by McReynolds and Rohrschneider's procedures. Values of the intercepts increase with the polar character of the phases and with branching the intercepts are reduced.

Correlation between structural parameters is indicated by eqn. 3. In applying the equation to the ester data it is evident that the relative retention of all compounds should be calculated relative to a compound where a CH_3 group is a sub-

TABLE II
VALUE OF SLOPES (a) AND INTERCEPTS (b) DETERMINED FOR EQN. 2 LINKING A SINGLE HOMOLOGOUS SERIES ON TWO STATIONARY PHASES

	<i>Formate</i>	<i>Acetate</i>	<i>Propionate</i>	<i>Butyrate</i>	<i>Pentanoate</i>	<i>Hexanoate</i>	<i>Iso-buturate</i>
<i>Slope</i>							
SE-30	1	1	1	1	1	1	1
OV-7	1.03546	1.06337	1.06477	1.0341	1.02683	1.04522	1.02105
DC-710	1.02872	1.04429	1.05065	1.03287	1.03035	1.033	1.01173
OV-25	0.914481	0.934221	0.966375	0.945301	0.957584	0.965927	0.951798
100% Phenyl	0.87186	0.887869	0.919483	0.913726	0.920486	0.938791	0.910904
DC-230	1.01689	1.06394	1.08605	1.04817	1.04799	1.03656	1.03247
DC-530	0.897274	0.95036	1.07978	0.947608	0.943479	0.956055	0.950061
XE-60	0.88058	0.886953	0.891465	0.887344	0.883016	0.877051	0.876357
XF-1150	0.77801	0.79622	0.797421	0.782562	0.782212	0.783575	0.784613
OV-225	0.86542	0.89651	0.919315	0.896161	0.890809	0.898541	0.892982
SILAR 5CP	0.84091	0.863144	0.865912	0.84035	0.841127	0.84173	0.848777
F-400	0.910776	0.95492	0.977646	0.95915	0.965988	0.976869	0.953241
F-500	0.889085	0.934338	0.965794	0.955117	0.944534	0.964978	0.948706
QF-1	0.78045	0.839506	0.849415	0.832571	0.832681	0.829135	0.821838
<i>Intercepts</i>							
SE-30	0	0	0	0	0	0	0
OV-7	0.145787	0.140094	0.134169	0.137825	0.133619	0.147218	0.116177
DC-710	0.224766	0.230035	0.219882	0.220976	0.216976	0.220839	0.197265
OV-25	0.296186	0.328933	0.326963	0.329318	0.324739	0.32524	0.284071
100% Phenyl	0.392429	0.410505	0.394567	0.393749	0.391979	0.388133	0.344412
DC-230	0.046196	0.040779	0.023744	0.043301	0.0361091	0.034673	0.032552
DC-530	0.143808	0.110251	0.141165	0.104134	0.106655	0.105255	0.085768
XE-60	0.50606	0.455212	0.427373	0.424511	0.414528	0.429764	0.395507
XF-1150	0.729435	0.650658	0.622032	0.619804	0.613101	0.618325	0.563122
OV-225	0.511784	0.47677	0.454727	0.449649	0.452694	0.45279	0.40396
SILAR 5CP	0.703643	0.651292	0.628777	0.623766	0.621708	0.627821	0.553421
F-400	0.210887	0.226005	0.207778	0.210659	0.213577	0.205915	0.20238
F-500	0.312384	0.323254	0.307997	0.310591	0.31654	0.308605	0.28972
QF-1	0.515685	0.51297	0.46537	0.489838	0.48978	0.475649	0.47241

stituent. As the data were available relative to *n*-nonane a corrective term must be included to produce:

$$\log t'_{R(\text{relative to any compound})} = \rho^* \sigma^* + h(n - 3) + \log t'_{R(\text{relative to CH}_3)} \quad (3a)$$

where a general multiple linear regression analysis is applicable. This modified relationship provides an improved correlation, since the correlation coefficient is improved while the behaviour of ρ^* and h is unchanged. With the ester data only compounds where $n = 2$ are available and eqn. 3a is reduced to:

$$\log t'_R = \rho^* \sigma^* - h + b \quad (3b)$$

or

$$\log t'_R = \rho^* \sigma^* - h' \quad (3c)$$

<i>Isopen- tanoate</i>	<i>Isohexa- noate</i>	<i>2-Methyl pentanoate</i>	<i>2-Bu- tyrate</i>	<i>2-Prope- noate</i>	<i>2-Methyl-2- propenoate</i>	<i>2-Bute- noate</i>	<i>3-Bute- noate</i>	<i>3-Methyl-2- butenoate</i>
1	1	1	1	1	1	1	1	1
1.03467	1.04219	1.03575	1.03046	1.050981	1.0509	1.0381	1.04822	1.06659
1.03489	1.03999	1.04021	1.04132	1.06138	1.0484	1.04592	1.03678	1.05387
0.969408	0.954705	0.967092	0.979443	0.985045	0.975797	0.998111	0.963924	0.986013
0.937128	0.928181	0.921778	0.958045	0.958045	0.94602	0.947007	0.930467	0.94319
1.05105	1.05403	1.057	1.06401	1.0444	1.06759	1.06346	1.0682	1.05789
0.956834	0.962911	0.958069	0.916381	0.916381	0.95157	0.957705	0.959585	0.954603
0.887929	0.879772	0.888197	0.895047	0.895047	0.890063	0.887425	0.871398	0.86937
0.787953	0.792811	0.797845	0.794046	0.796386	0.799556	0.796606	0.782178	0.788832
0.899223	0.901714	0.904401	0.907323	0.92211	0.908682	0.910844	0.893973	0.905798
0.846315	0.847963	0.852841	0.853363	0.869314	0.85844	0.857982	0.842791	0.851357
0.981111	0.989902	0.974063	0.983482	0.988409	0.983594	0.985007	0.98698	1.00239
0.970279	0.965029	0.972424	0.973259	0.950320	0.973271	0.96677	0.962294	0.974023
0.83248	0.827767	0.84084	0.83858	0.815836	0.846781	0.884049	0.83829	0.823511
0	0	0	0	0	0	0	0	0
0.118878	0.12216	0.111784	0.115897	0.139769	0.125829	0.166116	0.148211	0.151814
0.194755	0.293465	0.190929	0.186748	0.228106	0.213072	0.279095	0.254263	0.280962
0.284524	0.301456	0.288455	0.274448	0.349694	0.328963	0.403451	0.368642	0.414348
0.351033	0.369997	0.393988	0.3867	0.45593	0.433678	0.538428	0.475059	0.525502
0.033611	0.027662	0.018481	0.084551	0.044247	0.0305036	0.0552408	0.0422567	0.0595968
0.094278	0.095486	0.088804	0.091215	0.131833	0.108655	0.132137	0.179566	0.124015
0.389595	0.416942	0.409502	0.387202	0.44923	0.416298	0.506288	0.481616	0.478573
0.571169	0.596407	0.541585	0.538291	0.683778	0.628492	0.758828	0.715483	0.706029
0.417346	0.439552	0.405083	0.395021	0.493258	0.4627	0.565451	0.527118	0.5377212
0.573123	0.582372	0.532206	0.525479	0.673961	0.62779	0.765901	0.717824	0.723332
0.298465	0.199925	0.206011	0.187896	0.214992	0.201933	0.253279	0.216209	0.221427
0.276896	0.314067	0.286563	0.27882	0.097524	0.300933	0.369779	0.32498	0.343852
0.478567	0.468201	0.430359	0.414533	0.37411	0.441146	0.507944	0.484781	0.453443

TABLE III
CLASSIFICATION OF STATIONARY PHASES BY THE RELATIVE POLARITY METHOD (EQ

Stationary phase	Formate	Acetate	Propionate	Butyrate	Pentanoate	Hexanoate	Isobutyrate	Isopentanoate	Isohexanoate
DC-230	1	1	1	1	1	2	1	1	1
OV-7	3	2	3	2	3	1	2	3	2
DC-710	2	3	4	3	2	3	3	2	3
SE-30	4	4	5	4	4	4	4	4	4
F-400	6	5	6	5	5	5	5	5	5
OV-25	5	8	7	8	6	6	6	7	8
DC-530	7	6	2	7	8	8	7	8	7
F-500	8	7	8	6	7	7	8	6	6
100% Phenyl	10	10	9	9	9	9	9	9	9
OV-225	11	9	10	10	10	10	10	10	10
XE-60	9	11	11	11	11	11	11	11	11
SILAR 5CP	12	12	12	12	12	12	12	12	12
QF-1	13	13	13	13	13	13	13	13	13
XF-1150	14	14	14	14	14	14	14	14	14

TABLE IV
VALUES OF CONSTANT (g^*) REPRESENTING SENSITIVITY OF STATIONARY PHASE POLAR EFFECT AND HYPERCONJUGATION CONSTANT (h')

	Stationary phase					
	SE-30	OV-7	DC-710	OV-25	100% Phenyl	DC-230
<i>g* values</i>						
Formate	-16.3254	-17.043	-17.1719	-15.4566	-14.2907	-16.65
Acetate	-15.5953	-16.4441	-16.2499	-14.7442	-14.071	-16.65
Propionate	-15.0092	-16.0265	-15.8953	-14.6086	-14.1325	-16.42
Butyrate	-14.8947	-15.4672	-15.408	-14.2112	-13.8403	-15.63
Pentanoate	-14.6543	-15.0492	-15.1164	-14.0723	-13.7027	-15.27
Hexanoate	-14.2508	-14.9611	-14.845	-13.8383	-13.6646	-14.97
Isobutyrate	-15.1389	-15.3924	-15.2581	-14.3557	-13.9633	-15.40
Isopentanoate	-14.4562	-15.0368	-14.2965	-14.1257	-13.5488	-15.23
Isohexanoate	-14.2917	-14.8399	-14.9757	-13.7056	-13.5928	-14.98
2-Methylpentanoate	-14.147	-14.602	-14.668	-13.5431	-13.4829	-14.91
2-Ethylbutyrate	-14.1237	-14.2293	-14.6533	-13.929	-13.2689	-14.92
2-Propenoate	-15.0956	-16.002	-15.3042	-14.9849	-14.6427	-16.03
2-Methyl-2-propenoate	-14.8132	-15.4183	-15.5781	-14.4584	-14.1623	-15.76
2-Butenoate	-14.8527	-15.3927	-15.594	-14.5737	-14.2338	-15.83
3-Butenoate	-14.6879	-15.4911	-15.4065	-14.3145	-13.8063	-15.75
3-Methyl-2-pentenoate	-14.5432	-15.3403	-15.3376	-14.33	-13.7623	-15.13
<i>h' values</i>						
Formate	2.57676	2.54051	2.47573	2.13284	1.86047	2.578
Acetate	2.28757	2.25092	2.13004	1.31997	1.64146	2.383
Propionate	1.99297	1.98192	1.87881	1.60216	1.47034	2.145
Butyrate	1.77	1.70876	1.60881	1.36024	1.25275	1.814
Pentanoate	1.51308	1.41921	1.3428	1.12789	1.02351	1.538
Hexanoate	1.24483	1.16104	1.07971	0.883899	0.817723	1.236
Isobutyrate	1.89282	1.80655	1.70674	1.50622	1.40142	1.888
Isopentanoate	1.58786	1.53409	1.4305	1.26866	1.14132	1.640
Isohexanoate	1.2218	1.24637	1.175	0.967605	0.895452	1.354
2-Methylpentanoate	1.36758	1.29768	1.22294	1.01259	0.911328	1.420
2-Ethylbutyrate	1.37363	1.25269	1.23399	1.08194	0.910993	1.437
2-Propenoate	2.01219	1.99299	1.87574	1.64476	1.49311	2.166
2-Methyl-2-propenoate	1.78325	1.72665	1.66183	1.40872	1.27143	1.865
2-Butenoate	1.65481	1.5479	1.45925	1.20946	1.84893	1.708
3-Butenoate	1.77232	1.7222	1.60664	1.35922	1.19108	1.858
3-Methyl-2-pentenoate	1.4436	1.35937	1.2408	1.00652	0.841025	1.438

<i>2-Ethyl- butyrate</i>	<i>2-Propyl- ionate</i>	<i>2-Methyl- propionate</i>	<i>2-Buty- noate</i>	<i>3-Buty- noate</i>	<i>3-Methyl-2- butenoate</i>	<i>Pivalate</i>	<i>Pyruvate</i>
1	3	1	1	1	2	1	1
3	2	2	3	3	1	3	3
2	1	3	2	3	3	2	2
4	4	4	4	4	5	6	4
5	5	5	6	5	4	4	5
6	6	6	5	6	6	not available	not available
8	9	8	8	8	8	8	7
7	8	7	7	7	7	5	8
9	7	9	9	9	9	9	9
10	10	10	10	10	10	10	10
11	11	11	11	11	11	11	11
12	12	12	12	12	12	12	12
13	13	13	13	13	13	13	13
14	14	14	14	14	14	14	14

<i>XE-60</i>	<i>XF-1150</i>	<i>OV-225</i>	<i>SILAR 5CP</i>	<i>F-400</i>	<i>F-500</i>	<i>QF-1</i>
-14.1556	-12.6759	-14.5578	-13.6371	-14.0842	-14.7579	-13.0024
-13.8097	-12.5887	-13.9375	-13.3234	-15.1254	-14.7492	-13.0348
-13.61	-12.165	-14.1232	-13.2076	-14.7439	-14.6184	-12.745
-13.3395	-11.716	-13.5132	-12.6713	-14.3635	-14.3097	-12.3469
-13.1021	-11.5733	-13.0069	-12.46	-14.1823	-14.0197	-12.0911
-12.5853	-11.4218	-12.8452	-12.2024	-14.0164	-13.8887	-11.8642
-13.1617	-11.9781	-12.6095	-12.7718	-14.3402	-14.2444	-12.1453
-12.2433	-11.7308	-13.1951	-12.5042	-14.3774	-13.9704	-12.0626
-12.5503	-11.6025	-12.8469	-12.3693	-14.2235	-13.8274	-11.7309
-12.4598	-11.4173	-12.838	-12.2083	-13.8251	-13.785	-11.8181
-12.3495	-11.4193	-12.8334	-12.0799	-13.8798	-13.7147	-11.6801
-13.5448	-11.942	-14.3247	-13.1354	-14.8503	-14.4863	-12.4199
-13.212	-11.8141	-13.5183	-12.915	-14.5784	-14.3592	-12.5036
-13.1819	-11.9032	-13.5049	-12.8022	-14.6759	-14.4295	-12.2729
-13.03	-11.7498	-13.3705	-12.5992	-14.6084	-14.2153	-12.358
-12.337	-11.7358	-13.2524	-12.4146	-14.4765	-14.1267	-12.0232
1.72697	1.26743	1.77111	1.44498	2.16387	2.01177	1.53023
1.55799	1.8916	1.5532	1.28836	1.97899	1.82622	1.39616
1.36569	0.981132	1.40937	1.11209	1.73876	1.62233	1.21714
1.16054	0.7492	1.15652	0.880973	1.49668	1.39088	0.975619
0.94165	0.581717	0.896851	0.665433	1.25116	1.13647	0.75395
0.679796	0.287981	0.667185	0.444216	1.02172	0.91003	0.56165
1.24571	0.981353	1.29468	1.03703	1.58823	1.48792	1.04035
1.03273	0.72382	1.03567	0.805298	1.3761	1.23556	0.856666
0.741642	0.486114	0.744196	0.570533	1.11951	0.96636	0.611597
1.816935	0.564165	0.881931	0.650631	1.13295	1.03544	0.70827
0.801989	0.577827	0.850834	0.646797	1.16186	1.05297	0.713707
1.35399	0.902803	1.37435	1.074335	1.76262	1.34403	1.17323
1.17226	0.789542	1.16271	0.92719	1.55275	1.42631	1.06295
0.958658	0.566669	0.934705	0.658732	1.38263	1.23951	0.826208
1.09223	0.792733	1.08768	0.80272	1.54743	1.39129	1.0066
0.892323	0.465414	0.778388	0.507167	1.21155	1.05621	0.746546

where ρ^* and h' can be calculated from the line of best fit determined by linear regression analysis. Values of ρ^* and h are shown in Table IV while correlation coefficients indicate that correlations have been successfully established.

The polar factor ρ^* should characterise the sensitivity of the stationary phase to the polar effects. Variation of ρ^* over a range of phases is shown in Figs. 2-4 and it is observed that ρ^* has a tendency to increase with increasing polar character of the phase. With esters ρ^* has a very high value with QF-1 which is to be expected as this phase is well known to have a special affinity to carbonyl compounds¹²; however, the value with DC-710 is greatly reduced and does not follow any systematic pattern with regard to the other phenylpolysiloxanes which contain greater and lesser amounts of phenyl groups.

Fig. 2 shows an increase in ρ^* with increasing acid chain length of *n*-alkyl

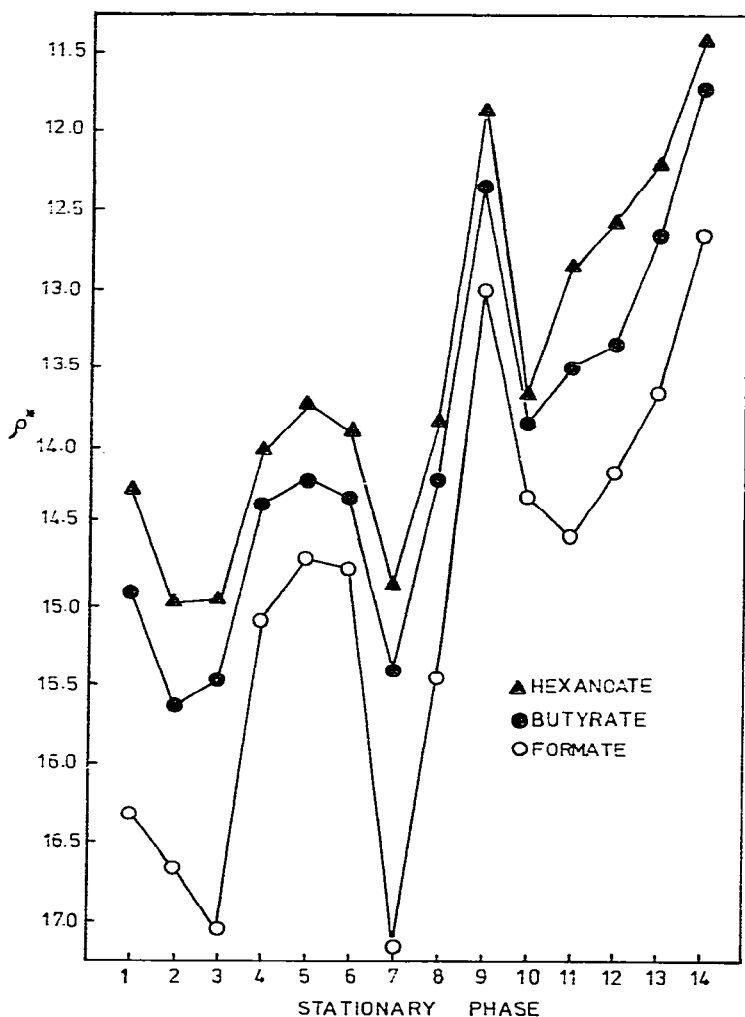


Fig. 2. Plot showing variation of constant representing sensitivity of stationary phase to polar effect of *n*-alkyl esters on stationary phases of increasing polarity according to eqn. 3. The stationary phases used are as in Fig. 1.

esters. Isomerism does not exhibit any marked effect although a slight reduction in ρ^* is evident with branched chain esters on highly polar phases (Fig. 3). The position of unsaturation is of some importance, the value of ρ^* showing a slight reduction as it approaches the functional group. (Fig. 4).

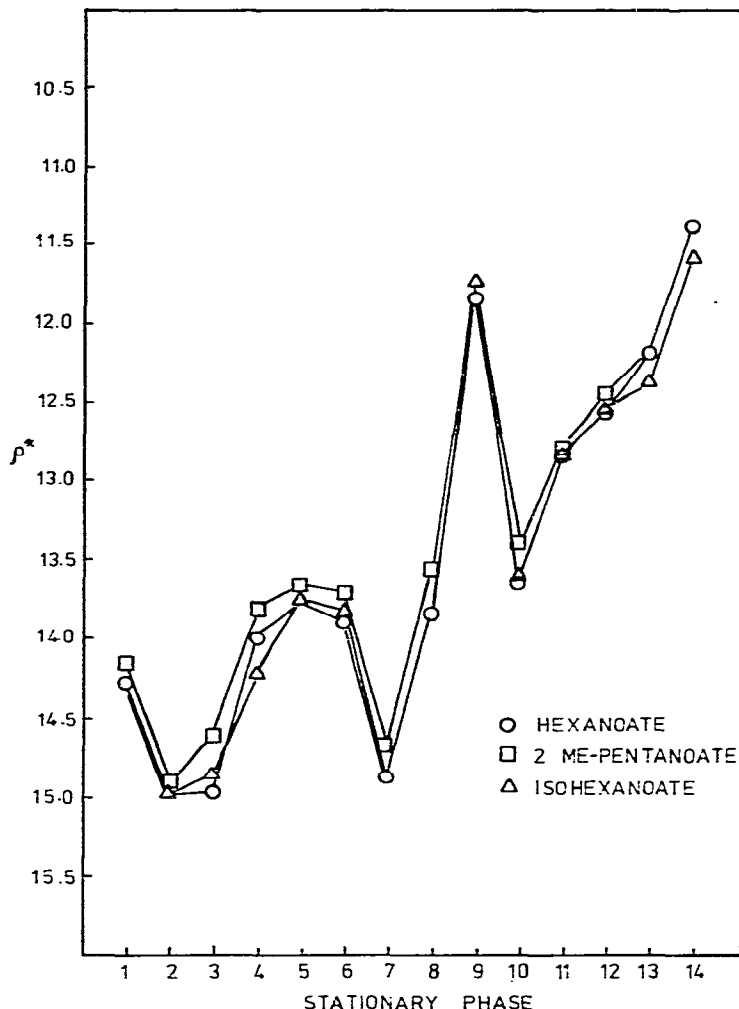


Fig. 3. Plot showing variation of ρ^* of isomeric esters on stationary phases of increasing polarity. The stationary phases used are as in Fig. 1.

The hyperconjugation factor, h , has been determined from the ester data, as with determination of ρ^* only compounds where $n=2$ are available and the relationship is again used in the form shown in eqns. 3b and 3c. From eqn. 3c it is evident that the standard used to determine the relative retention does not effect ρ^* but influences h . As the first member of many homologous series often exhibits anomalous behaviour the use of these compounds as standards produces irregularities in h . There is a tendency for h to decrease with increasing polarity and also with branching. However, study only of compounds where $n=2$ restricts the examination.

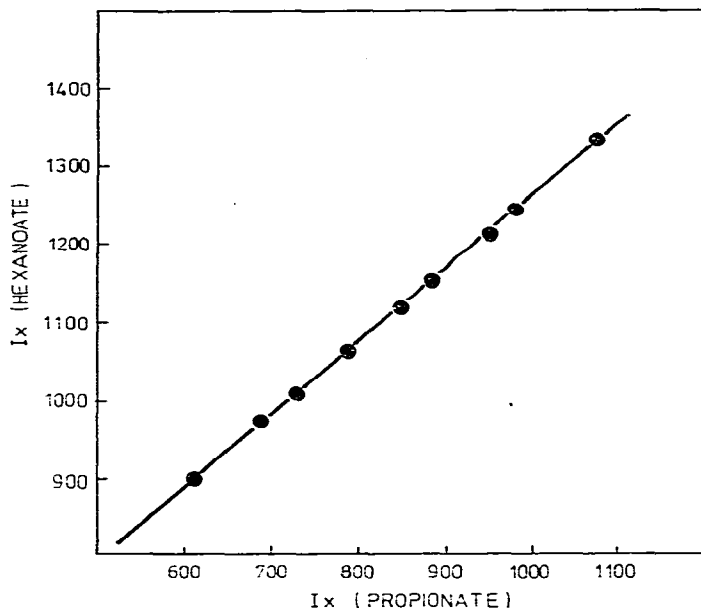


Fig. 4. Plot showing the relationship between the retention of hexanoates and that of propionates on SE-30 (eqn. 1) with retention expressed as retention indices.

Correlation with polar and steric effects is indicated by eqn. 4. The addition of the steric effect (δE_s) causes slight modifications of the parameters q^* and h . The behaviour of q^* and h with regard to stationary phase polarity is unchanged. Conversely variation of the δE_s is completely unpredictable. If the degree of substituent of the hydrogen atoms at the α -carbon atom is responsible for the steric effect the replacement is suggested of the classic term of the steric factor E_s developed by Taft into

$$E_{s(\text{corrected})} = \delta E_s + h(n - 3)$$

which implies that polarity and steric hindrance alone are the important factors in the chromatographic phenomenon.

The term q^* possesses a much higher value than δ , indicating a dominant effect of polarity. The negative values of δ^* indicate the donating effect of electrons from the alkyl groups. The relationship indicates the existence of a linear extrathermodynamic relationship between retention behaviour and steric and polar effects. The observation is of limited practical value due to the lack of polar and steric data provided by Taft⁵ and by the series of assumptions and approximations that are made in establishing the relationship.

Eqn. 5 indicates a scale of phase polarity with q^* and a_2 . The values calculated with correlation coefficients are shown in Table V where reasonable coefficients are generally obtained except with the pyruvate and pivalate esters. Again it would seem that development is unlikely due to difficulties in obtaining the basic data necessary.

Re-establishment of the relationships using retention index values have been considered and considering the relationship of I_x and t_x application is not unexpected.

TABLE V

VALUE OF CORRELATION COEFFICIENTS (λ AND β) DETERMINED FROM EQN. 5

Compound	λ	β	R
Formate	-16.6719	0.182992	-0.991397
Acetate	-15.1881	-0.428787	-0.994967
Propionate	-15.4973	0.264378	-0.988189
Butyrate	-14.6952	-0.269767	-0.998143
Pentanoate	-14.2616	-0.422783	-0.996998
Hexanoate	-14.0078	-0.355822	-0.997453
Isobutyrate	-14.8925	-0.172884	-0.994348
Isopentanoate	-13.6145	-0.914786	-0.996746
Isohexanoate	-13.6334	-0.668171	-0.995682
2-Methylpentanoate	-13.1745	-0.963573	-0.992624
2-Ethylbutyrate	-13.4918	-0.579732	-0.991603
2-Propenoate	14.8668	-0.257226	-0.287423
2-Methyl-2-propenoate	-14.4522	-0.364341	-0.997272
2-Butenoate	-14.5968	-0.165561	-0.978527
3-Butenoate	-14.1795	-0.620261	-0.99853
3-Methyl-2-butenoate	-13.441	-1.10075	-0.997766
Pyruvate	-12.1862	-2.0823	-0.987103
Pivalate	-12.7469	-1.41936	-0.984217

The following equations:

$$I_{x(RZ)} = a I_{x(RZ')} + b \quad (1d)$$

$$I_{x(\varphi_1)} = a I_{x(\varphi_2)} + b \quad (2b)$$

$$I_x = q^* \sigma^* + h(n-3) + b \quad (3d)$$

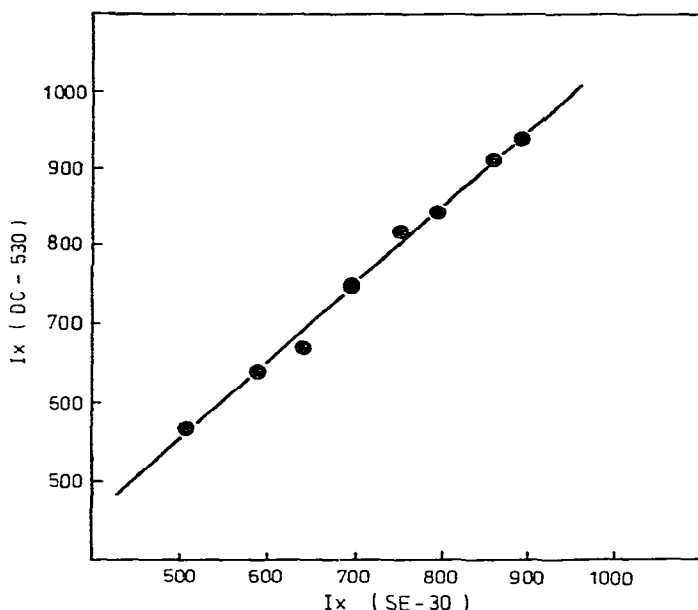


Fig. 5. Plot showing relationship between the retention of homologous acetate esters on DC-530 and SE-30 (eqn. 2).

are shown in Figs. 4 and 5. It is evident in eqn. 3d that if I_x is determined relative to $I_{x(\text{CH}_3\text{Z})}$ the term b will disappear from the equation.

REFERENCES

- 1 R. Fellous, L. Lizzani-Cuvelier, R. Luft and J. P. Rabine, *J. Chromatogr.*, 90 (1974) 149.
- 2 R. Fellous, L. Lizzani-Cuvelier, R. Luft, J. P. Rabine and M. Rouillard, *Bull. Chem. Soc. Fr.*, 2482 (1974).
- 3 R. Fellous, L. Lizzani-Cuvelier, R. Luft and J.-P. Rabine, *J. Chromatogr.*, 110 (1975) 7.
- 4 R. Fellous, L. Lizzani-Cuvelier, R. Luft and J.-P. Rabine, *J. Chromatogr.*, 110 (1975) 13.
- 5 R. W. Taft, in M. S. Newman (Editor), *Steric Effects in Organic Chemistry*, Wiley, New York, 1956, Ch. 13.
- 6 J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 101 (1974) 103.
- 7 J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 111 (1975) 171.
- 8 J. K. Haken, D. K. M. Ho and M. S. Wainwright, *J. Chromatogr.*, 106 (1975) 327.
- 9 J. K. Haken, D. K. M. Ho and C. E. Vaughan, *J. Chromatogr.*, 106 (1975) 317.
- 10 R. W. Germaine and J. K. Haken, *J. Chromatogr.*, 43 (1966) 33.
- 11 J. K. Haken, A. Nguyen and M. S. Wainwright, *J. Chromatogr.*, 179 (1979) 75.
- 12 W. J. A. VandenHeuvel, E. O. A. Haachte and E. C. Horning, *J. Amer. Chem. Soc.*, 83 (1960) 1513.