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CORRELATION BETWEEN REVERSED-PHASE RETENTION AND SOLUTE MOLECULAR SURFACE TYPE AND AREA

I. THEORETICAL OUTLINES AND RETENTION OF VARIOUS HYDRO-CARBON CLASSES

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SUMMARY

A method to calculate $\ln k'$ values in an octadecylsilica (ODS)-methanol chromatographic system from solute molecular area data is described. After a short review of other retention descriptors, the basis of the surface area to retention relationship is given. Calculations of the surface areas of homologous series and other solute classes are presented, as well as the respective retention data. For various types of hydrocarbonaceous solute surfaces, quality factors are derived which convert surface area increments into $\ln k'$ increments. From the retention and surface area of the series benzene to *p*-quaterphenyl, a value of 0.16 for the phase ratio was calculated.

INTRODUCTION

A great variety of descriptors has been used to predict retention in reversed-phase chromatographic systems. The most comprehensive approach seems to be the one by Horváth *et al.*¹ who deduced retention from molecular properties. This multi-parameter model does not treat processes at the stationary phase in detail. Martire and Boehm² placed heavy emphasis on stationary phase mechanisms using a rather formal lattice model.

Entirely formal descriptors are the connectivity index, χ , and the correlation factor, F_i^{3-7} . Another class of parameters was thought to describe solute behaviour in homogeneous solutions, mainly the solubility or partition between two real liquids. The most prominent of these are the extended solubility parameter, $\delta^{8,9}$, the Hansch parameter, π^{10-12} , Rekker's fragmental constant, f^{13-15} , and the Taft π^* ¹⁶. Other approaches correlate retention with solute solubility in the eluent^{5,17-19}. Yet another class of descriptors are semi-empirical parameters based on simplified solute molecular data as well as experimental retention data. Here we find the ratio of the length to breadth, L/B^4 , the shape parameter, $\eta^{4,20}$, the interaction index, $I_x^{21,22}$, and the more intuitive "compactness of solutes"^{23,24}. The number, p , of eluent molecules

displaced from the stationary phase upon solute sorption²⁵ seems to imply an adsorption mechanism. For homologues a linear relationship between the carbon atom number or solute molecular weight and retention has frequently been cited.

The most direct approach appears to be the correlation between $\ln k'$ and the solute molecular surface area (SA) for several reasons^{3,5,26-28}. First, within homologous series and comparable groups, experiments have shown that the correlation holds perfectly. Secondly, the surface area can be directly related to molecular interactions and thermodynamic parameters. Thirdly, following Pearlman's calculation procedures, SA values are readily available^{29,30}.

In a reversed-phase liquid chromatographic (RPLC) system, a solute can be in one of two possible states, either dissolved in the mobile phase or somehow sorbed in or at the stationary phase. The free energy of solution consists of four terms^{1,31,32}:

$$\Delta G_{\text{solution}} = \underset{\text{I}}{\Delta G_{\text{cavity}}} + \underset{\text{II}}{\Delta G_{\text{inter}}^{\text{mob}}} + \underset{\text{III}}{\Delta G_{\text{cohesion}}} + \underset{\text{IV}}{RT \ln (RT/p\bar{V})} \quad (1)$$

where p is the pressure on the system and \bar{V} is the molar volume of solvent. The first term gives the free energy necessary to create a cavity within the eluent suitable to accommodate the solute molecule. Depending on the structure of the eluent, ΔG_{cavity} comprises various energy and entropy contributions. For low polarity solutes in strongly polar, appreciably structured solvents like water or methanol-water, the entropy term is the deciding factor^{33,34}. The eluent molecules forming the cavity are in a state of higher density and higher degree of order compared to the bulk eluent (Fig. 1). When the solute molecule is transferred from a potential-free state into the cavity it interacts with the surroundings, producing $\Delta G_{\text{inter}}^{\text{mob}}$. The third term is necessary to bring the solute from its natural state to a (hypothetical) gaseous state, where there is practically no intermolecular potential. For liquids this is the free energy of vaporization, for solids that of sublimation, both at solution temperature. The last term describes the change of free volume of the eluent, basically a statistical entropy effect.

When the solute leaves the mobile phase for the stationary phase, $\Delta G_{\text{solution}}$ reappears with the opposite sign. In addition, we have the free energy of interaction with the stationary phase, $\Delta G_{\text{inter}}^{\text{stat}}$.

Using the ΔG terms, we find for the sorption free energy

$$\Delta G_{\text{sorption}} = \Delta G_{\text{inter}}^{\text{stat}} - \Delta G_{\text{inter}}^{\text{mob}} - \Delta G_{\text{cavity}} - \Delta G_{\text{cohesion}} - RT \ln(RT/p\bar{V}) \quad (2)$$

and for the logarithmic capacity factor:

$$\ln k' = \underset{\text{I}}{\frac{-\Delta G_{\text{inter}}^{\text{stat}}}{RT}} + \underset{\text{II}}{\frac{\Delta G_{\text{inter}}^{\text{mob}}}{RT}} + \underset{\text{III}}{\frac{\Delta G_{\text{cavity}}}{RT}} + \underset{\text{IV}}{\frac{\Delta G_{\text{cohesion}}}{RT}} + \underset{\text{V}}{\ln \frac{RT}{p\bar{V}}} + \underset{\text{VI}}{\ln \varphi} \quad (3)$$

Term VI contains the phase volume ratio, $\varphi = V_{\text{stat}}/V_{\text{mob}}$, which is poorly defined in RPLC. According to several investigations³⁵⁻³⁸ it depends on the eluent composition and has its highest value for strongly aqueous eluents. Term V has been men-

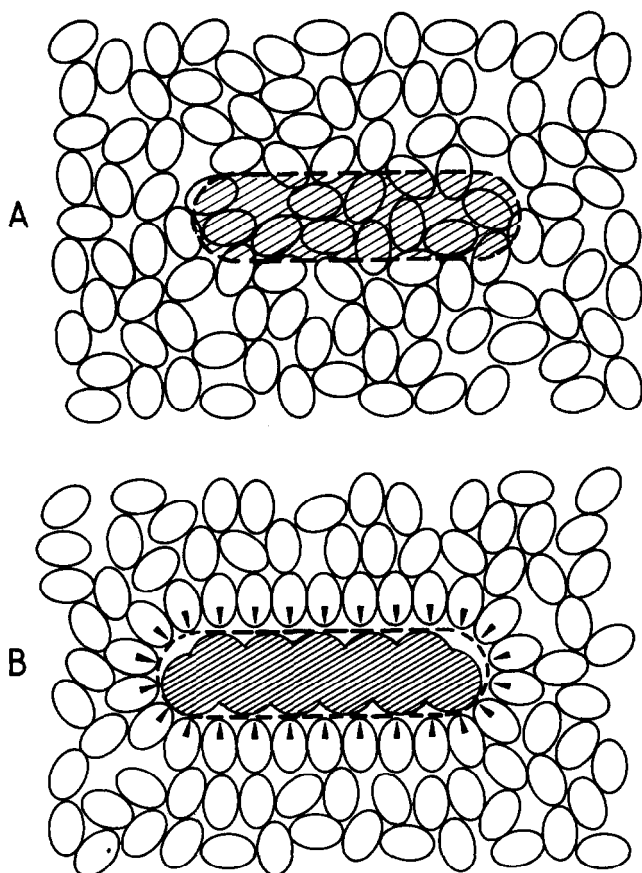


Fig. 1. Model of the change in order of a polar eluent upon intrusion of a non-polar solute (*n*-undecane). (A) Undisturbed liquid eluent. The shaded area indicates the location where the cavity will be formed. (B) $C_{11}H_{24}$ residing in the cavity with an highly ordered eluent shell.

tioned. Term IV is the free energy required to separate the solute molecules in the pure state. It reflects the well known fact that, of a group of chemically similar solutes (non-ionized), the one with the lowest boiling point or melting point has the highest solubility and the smallest retention.

In Term III, ΔG_{cavity} can be expressed as the product of the solute molecular surface area (SA) and eluent surface tension, γ_m . For small solutes, γ_m needs a minor correction for cavity curvature^{1,39}.

Term II describes solute-eluent interactions. These have inevitably a dispersion contribution. In organic molecules they may involve a CH-CH interaction. Finally, there may be additional contributions of polar origin, according to the chemical functionality of the solute. Dispersion forces are proportional to the molecular volume which, in turn, is proportional to the surface area in one- or two-dimensional species. Also the number of CH bonds is proportional to the non-polar part of the solute surface area. On the other hand, it is well known that a paraffinic surface area produces more retention than an aromatic one having the same size. So we have to

assume that the retention contribution from a certain part of the solute molecular surface will be the product of a quantity term—the area—and a quality term describing the strength of the interactions.

It is much more difficult to define $\Delta G_{\text{inter}}^{\text{stat}}$ in term I, since neither the nature of the RPLC stationary phase nor that of the sorbed solute are known with sufficient certainty. However, a few comments can be made. First, the interactions of the solute with the stationary phase must be qualitatively the same as with the eluent. In addition, there may be some influence of residual silanol groups on highly polar solutes. Secondly, the sorption energies are low and the sorption entropies are strongly negative^{40–42}. The entropy becomes more negative with increasing solute size. Since the eluent entropy lost upon cavity formation reappears upon sorption, the entropy component associated with the formation of the sorbed state, $\Delta S_{\text{inter}}^{\text{stat}}$, must be even more negative. Thirdly, there is a very good correlation between k' and solute solubility in the eluent for many compound classes: $\ln k' = u \cdot \ln x_{\text{sat}} + v$, where x_{sat} is the solute mole fraction in saturated solution and u and v are constants, which depend on the separation system and the solute class. Since $\ln x_{\text{sat}}$ refers to the dissolved state in the eluent only, while $\ln k'$ refers to both the dissolved and sorbed states, the linear relationship indicates that the solute behaviour in the sorbed state is not in principle different from that in the dissolved state. So we tentatively assume that the formation of the sorbed solute state is comparable to the formation of an highly ordered solution.

In the following we describe our results on the RPLC retention of various classes of homologues, quasi-homologues and comparable compound classes as a function of the respective surface areas.

EXPERIMENTAL

The chromatographic apparatus was assembled as required from commercial components. In most cases a Varian 8500 pump was used with a Rheodyne injector. The refractive index (RI) and UV detectors were from Knauer, Melz, Philips or Waters. The column was a radially compressed ODS cartridge (RadPAK A) from Waters, kept in an air thermostat. Detector signals were fed into Varian CDS 111 L or Philips PU 4810 integrators and a chart recorder.

The column dead time was determined using the series of *n*-alkanes ranging from *n*-pentane to *n*-decane according to Berendsen *et al.*⁴³. The extra-column dead time was measured from the elution time of benzene after replacing the column with a capillary of precisely known volume.

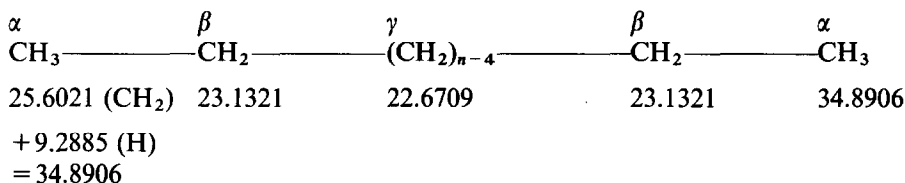
Surface areas were calculated on a Siemens 7880 computer using the Fortran programs COORD and SAREA from Pearlman^{29,30}. Structural data were taken from the literature^{44–46}.

All experiments were performed using pure methanol (Promochem HPLC grade). Most chemicals were obtained from Aldrich. Polysulphides were prepared according to Westlake *et al.*⁴⁷.

RESULTS AND DISCUSSION

Surface area calculations

The total surface area (TSA) of *n*-alkanes is comprised of the following contributions (in Å²):



Methane to butane do not contain recurring CH₂ groups. Since the surface areas (SA) of β -methylenes do not deviate greatly from the SA of recurring CH₂, the differences can be lumped together in a residual area (RA). Then:

$$\begin{aligned}
 \text{TSA } (n\text{-alk}) &= 2 \cdot \text{SA}(\text{CH}_3) + (n - 2) \cdot \text{SA}(\text{CH}_2) + \text{RA} \\
 &= 2 \cdot 34.8906 + (n - 2) \cdot 22.6709 + 0.9224
 \end{aligned} \tag{4}$$

In 1-alkenes having *n* carbon atoms we will regard the vinyl group separately, resulting in a vinyl-substituted *n*-alkane having (*n* - 2) carbon atoms. A similar procedure is adopted with 1-alkynes. Generally, we will have SA(CH₃), SA(CH₂), RA and SA (substituent). The respective data are listed in Table I. The surface area data for compounds which cannot be regarded as members of homologous series are given in Table II. Negative residual areas may occur due to increased overlap of a CH₂ group with a neighbouring substituent and/or as a consequence of a shortened bond distance.

Chromatographic results

All results were obtained on octadecylsilica using only pure methanol as eluent. Fig. 2 shows ln *k'* of various classes of solutes as a function of the carbon atom number, *n_C*. For *n*-alkanes (ane), cycloalkanes (cane), *p*-polyphenyls (ϕ_n), dialkyl disulphides (RS₂R), dialkyl nonasulphides (RS₉R) and dialkyl ethers (ROR), *n_C* includes all C atoms. For diphenylalkanes ($\phi R\phi$), phenylalkanes (ϕR), alkenes (ene) and alkynes (yne), *n_C* involves only methyl plus methylene carbon atoms. For meth-

TABLE I
SURFACE AREA INCREMENTS (Å²) FOR SOME HOMOLOGOUS SERIES

Series	SA(CH ₃)	SA(CH ₂)	RA	SA (substituent)
<i>n</i> -Alkanes	34.8906	22.6709	0.9224	—
1-Alkenes	34.8906	22.6709	0.7512	47.8528
1-Alkynes	34.8906	22.6709	0.5826	38.6215
Phenylalkanes	34.8906	22.6709	-0.8079	96.4485
<i>p</i> -Polyphenyls*	—	81.2764	28.6922	—

* Here the recurring unit is -C₆H₄-.

TABLE II
SURFACE AREA INCREMENTS (\AA^2) FOR VARIOUS HYDROCARBONS

Solute	SA Type 1	SA(1)	SA Type 2	SA(2)
Diphenylmethane	Aromatic	191.231	Aliphatic	21.007
Diphenylethane	Aromatic	193.388	Aliphatic	42.907
Diphenylpropane	Aromatic	197.017	Aliphatic	59.650
Diphenylbutane	Aromatic	202.115	Aliphatic	88.110
Toluene	Aromatic	97.328	CH ₃	33.841
<i>p</i> -Xylene	Aromatic	82.489	CH ₃	62.045
1,3,5-Trimethylbenzene	Aromatic	73.130	CH ₃	101.525
1,2,4,5-Tetramethylbenzene	Aromatic	61.974	CH ₃	128.597
Pentamethylbenzene	Aromatic	50.815	CH ₃	155.666
Hexamethylbenzene	Aromatic	39.656	CH ₃	182.735
Cyclopentane	CH ₂	118.36	—	—
Cyclohexane	CH ₂	134.95	—	—
Cycloheptane	CH ₂	142.62	—	—
Cyclooctane	CH ₂	164.84	—	—
Cyclononane	CH ₂	183.09	—	—
Cyclodecane	CH ₂	201.67	—	—
Cyclododecane	CH ₂	238.25	—	—
Methylcyclohexane	C ₆ H ₁₁	125.909	CH ₃	34.426
1,3-Dimethylcyclohexane	C ₆ H ₁₀	113.688	CH ₃	68.852
1,3,5-Trimethylcyclohexane	C ₆ H ₉	101.472	CH ₃	103.282

ylbenzenes (ϕMe_x) and methylcyclohexanes (MCH), n_C involves only methyl groups.

It is seen that all dependences are linear in the range of n_C investigated. For the *n*-alkanes, *e.g.*, we can write:

$$\ln k'(\text{ane}) = a(\text{ane}) + b(\text{ane}) \cdot n_C \quad (5)$$

This equation may be used to define a retention index, I_K , which is closely related to the Kováts index^{34,38} known from gas chromatography. The index of an *n*-alkane is $100 \cdot n_C$ by definition. Then, the I_K of any other solute *x* having a retention value of $\ln k'(x)$ is:

$$I_K(x) = \frac{100}{b(\text{ane})} \cdot [\ln k'(x) - a(\text{ane})] \quad (6)$$

Retention changes brought about by chemical changes in the solute molecule may be described by the ΔI_K value. If, *e.g.*, in *n*-heptane one methyl group is replaced by OH, then $\Delta I_K = I_K(\text{C}_6\text{H}_{13}\text{OH}) - 700$, or more generally

$$\Delta I_K = I_K(x) - 100 \cdot n_{\text{Skeleton}} \quad (7)$$

where n_{Skeleton} is the number of atoms other than H.

For each group of compounds having a recurring structural unit (CH₂ in alkanes) we can establish an equation similar to eqn. 5. Such groups may be homologues, quasi-homologues or increasingly substituted molecules. The intercepts, *a*,

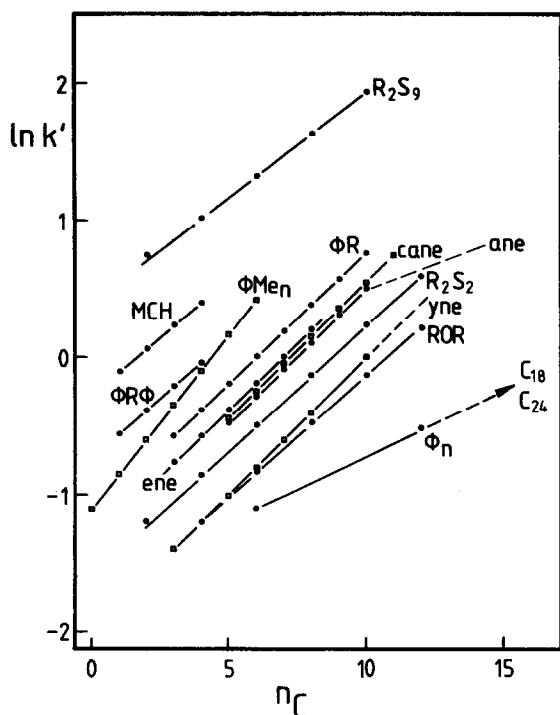


Fig. 2. Dependence of $\ln k'$ on carbon atom number, n_c , comprising (a) all C atoms in ane, cane, ϕ_n , RS_2R , RS_9R , ROR (b) $-\text{CH}_3 + -\text{CH}_2-$ in $\phi R\phi$, ϕR , ene, yne, (c) $-\text{CH}_3$ only in ϕMe_n , MCH. For abbreviations see Fig. 4. System: ODS-methanol; $T = 298 \text{ K}$.

TABLE III

COEFFICIENTS a AND b OF $\ln k'$ AND A AND B OF I_k

For abbreviations see text.

Solutes	n_c type	a	b	A	B
ane	All C	-1.4688	0.1971	0	100
cane	All C	-1.4330	0.1982	18.16	100.56
ene	$\text{CH}_3 + \text{CH}_2$	-1.3469	0.1947	61.85	98.78
yne	$\text{CH}_3 + \text{CH}_2$	-1.9930	0.1996	-265.96	101.27
ϕR	$\text{CH}_3 + \text{CH}_2$	-1.1444	0.1917	164.59	97.26
$\phi R\phi$	CH_2	-0.7320	0.1754	373.82	88.99
ϕMe_x	CH_3	-1.1010	0.2545	186.61	129.12
MCH	CH_3	-0.2704	0.1664	608.02	84.42
ϕ_n	All C	-1.6286	0.0928	-100.56	48.25
RS_2R	All C	-1.5862	0.1830	-59.56	92.85
RS_9R	All C	0.3960	0.1554	946.12	78.84
ROR	All C	-1.8666	0.1740	-201.83	88.28

and slopes, b , for all the groups investigated are given in Table III. From a combination of eqns. 5 and 6 it follows that I_K can be written as $I_K = A + Bn_C$. The coefficients A and B are also listed in Table III. The correlation coefficient, r , for the linear fit of $\ln k'$ data was always better than 0.999 and in most cases greater than 0.99999. While even with r close to 1 some error in the determination of intercepts a and A is possible, the slopes b and B are very reliable. So we conclude that the small deviations of b and B for alkenes, alkynes and phenylalkanes from the alkane values are real, the more so as they are perfectly reproducible. Because there are no surface area changes, we think that the differences originate from small changes in $\Delta G_{\text{inter}}^{\text{mob}}$ and/or $\Delta G_{\text{inter}}^{\text{stat}}$. Aromatic carbon atoms produce distinctly less retention than CH_2 , as seen from an increase of only $B = 48.25$ per C atom in polyphenyls.

The a and A terms have lower values if the functional group permits an increased solute-eluent interaction. The vinyl group produces about as much retention as 0.6 methylene groups. The acetylene group obviously has a very strong interaction with the eluent methanol and destroys the retention of about 2.7 methylene groups.

Correlation of $\ln k'$ and surface area

To correlate the surface area with retention we multiply the surface area SA_i of a solute structural unit i with a quality factor f_i to get the $\ln k'$ increment λ_i of that unit:

$$\lambda_i = \text{SA}_i \cdot f_i \quad (8)$$

Summation over all λ_i and adding $\ln \varphi$ yields:

$$\ln k' = \Sigma \lambda_i + \ln \varphi \quad (9)$$

From the recurring unit of homologous series we get:

$$b = \text{SA (recurring)} \cdot f \text{ (recurring)} \quad (10)$$

TABLE IV

INCREMENTS OF "CHROMATOGRAPHIC FREE ENERGY" OF SORPTION FROM VARIOUS GROUPS

δG values given at 298 K in J per $6.022 \cdot 10^{23} \text{ \AA}^2$ of accessible group surface area.

Solutes	Recurring group		Other groups	
	Type	$-\delta G$	Type	$-\delta G$
<i>n</i> -Alkanes	CH_2	21.655	CH_3	26.288
1-Alkenes	CH_2	21.308	CH_3	25.867
			$\text{CH}=\text{CH}_2$	15.634
1-Alkynes	CH_2	22.597	CH_3	27.431
			$\text{C}\equiv\text{CH}$	-40.139
Phenylalkanes	CH_2	20.862	CH_3	25.326
			ϕ	13.358
Diphenylalkanes	CH_2	15.674	ϕ	15.149
<i>p</i> -Polyphenyls	ϕ	16.923	ϕ	-
Methylbenzenes	CH_3	27.849	ϕ	13.028

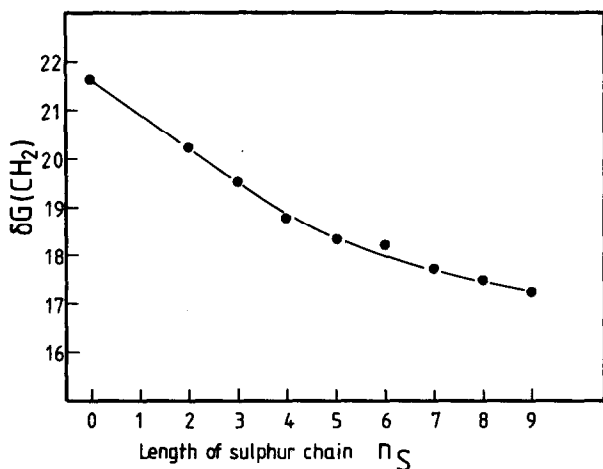


Fig. 3. Dependence of $\delta G(\text{CH}_2)$ in dialkyl polysulphides on the number of sulphur atoms in the polysulphide chain, n_s .

The intercept of $\ln k' = a + b \cdot n$ (rec) is:

$$a = \Sigma \lambda (\text{non-recurring}) + \ln \varphi \quad (11)$$

The regression equation for $\ln k'$ of *p*-polyphenyls is:

$$\ln k' = -1.6286 + 0.5570 \cdot n (\text{ring}); r = 0.999 \quad (12)$$

From b and the TSA regression (Table I) we find:

$$f(\text{C}_6\text{H}_4) = 0.00683 \text{ \AA}^{-2} \quad (13)$$

Since the electron systems of *p*-polyphenyls are conjugated, we assume that the surface area is homogeneous so that we can use the same quality factor for RA, too. With a in eqn. 11 and the TSA regression we get:

$$\ln \varphi = -1.8204 \text{ or } \varphi = 0.162 \quad (14)$$

Having the φ value, we can calculate the respective quality factors for *n*-alkanes. Since experiments have shown that CH_3 groups behave somewhat differently from CH_2 groups in high-performance liquid chromatography (HPLC), even when normalized for equal size, we assume that f_{CH_3} and f_{CH_2} may be different. Since RA originates from the summation of CH_2 groups of slightly different sizes, we assume that $f_{\text{RA}} = f_{\text{CH}_2}$. Then:

$$\ln k' = 2 \cdot \text{SA}(\text{CH}_3) \cdot f_{\text{CH}_3} + (n - 2) \cdot \text{SA}(\text{CH}_2) \cdot f_{\text{CH}_2} + \text{RA} \cdot f_{\text{CH}_2} + \ln \varphi \quad (15)$$

From the $\ln k'$ contribution of the recurring unit, b , we find $f_{\text{CH}_2} = 0.0087 \text{ \AA}^{-2}$.

Multiplication of quality factors by $RT = 2477.69$ yields the "chromatographic free energy" contribution of sorption of the respective type of area for $6.0222 \cdot 10^{23} \text{ \AA}^2$ at 298 K. These δG values are listed in Table IV for some compound classes

we investigated. It is seen that there are some variations of $\delta G(\text{CH}_2)$. The CH_2 groups in alkynes produce a little more retention than those in the alkanes. In phenylalkanes, the CH_2 groups are a little less effective, and in diphenylalkanes the loss is 28%.

These results indicate that the retention contribution of methylene groups in a given RP system does not have a fixed value. Since the cavity energy of structurally identical units of equal size must be constant—external influences being disregarded—we conclude that the differences in δG originate from changes in interaction energy. Electron-withdrawing substituents reduce the electron density in the C–H bond, making it more polar and the respective hydrogen atoms more “acidic”. Symmetrical substitution at both ends of the chain enhances this effect (diphenylalkanes). Another beautiful example of the influence of substituents on δG for methylene groups in alkyl chains was found with the dialkylpolysulphides RS_nR where R varies from methyl to heptyl and n_s ranges from 2 in disulphides to 9 in nonasulphides. The $\delta G(\text{CH}_2)$ for the ODS–methanol system is plotted *versus* n_s in Fig. 3. While the value is $21.655 \text{ J}/\text{\AA}^2 \cdot \text{mol}$ in alkanes, it drops to 20.22 in RS_2R and further to $17.18 \text{ J}/\text{\AA}^2 \cdot \text{mol}$ in RS_9R . Obviously the longer is the sulphur chain, the more electron density is withdrawn from the alkyl chains. The dependence is not linear, indicating that electron withdrawal becomes increasingly more difficult.

The only example for a $\delta G(\text{CH}_2)$ value greater than those in *n*-alkanes was found in the 1-alkynes. It seems that, if the triple bond can slightly increase the electron density in the C–H bond of CH_2 , this decreases the interaction with neighbouring C–H bonds in the eluent.

The most surprising effect connected with the substituent influence on $\delta G(\text{CH}_2)$ is the linear dependence of $\ln k'$ on n_c or, in other words, the fact that $\delta G(\text{CH}_2)$ is constant along the chain. In organic chemistry, common inductive effects are supposed to have only a short range within an alkyl chain. We have tentatively assumed that the propagation of the retention-decreasing effect along the chain is supported “from outside”. Around an *n*-alkane the methanol eluent molecules have on average a certain orientation with respect to the H (alkane), CH_3 , O and hydroxyl proton distances. If a terminal CH_3 is replaced by an electron-attracting group, at least the α -positioned H atoms become activated. As a consequence, the eluent molecules forming the cavity around this portion of the solute will change their orientation in a sense that the methanol oxygen becomes somewhat closer to the activated H and the CH_3 points a little further away. Since the methanol molecules are interconnected via hydrogen bridges, the next such molecule will accommodate the new position. The next H atom down the chain finds itself in a somewhat different electronic environment and may be more subject to induction. At present, however, we have no direct proof for this model.

Another point which is not clearly understood is the high δG for the CH_3 group in alkanes. Since δG is surface area-normalized, it seems that CH_3 has a somewhat lower energy of interaction with the eluent than CH_2 . The $\delta G(\text{CH}_3)$ values in Table IV are calculated from the *n*-alkane value assuming that methyl groups in substituted chains are subject to the same change in δG as methylene groups are.

The δG value for phenyl is most negative in the *p*-polyphenyls. Any increase in electron density in the ring lowers δG . The vinyl group $-\text{CH}=\text{CH}_2$ produces retention, but 27.7 J less than does $-\text{CH}_2-\text{CH}_2-$. This is clearly due to an increased solute–eluent interaction. The acetylene group $-\text{C}\equiv\text{CH}$ obviously has a very strong interaction with the eluent. It greatly overcompensates the cavity energy, leading to

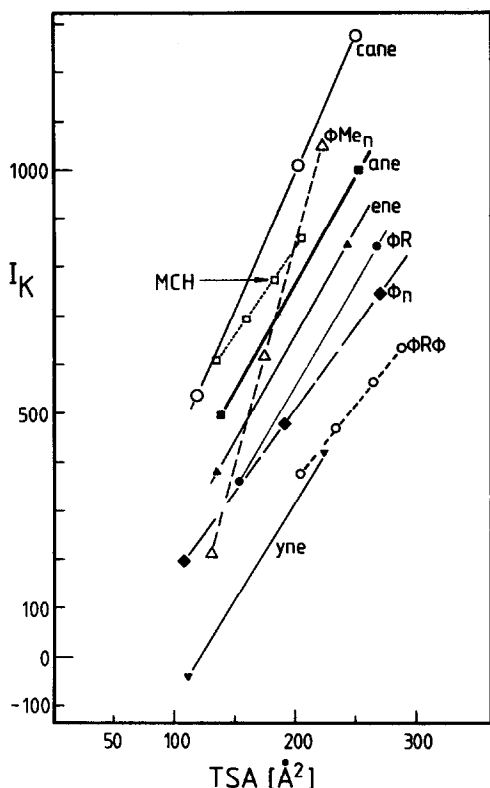


Fig. 4. Retention index, I_K , as a function of the total molecular surface area (TSA) in the system ODS-methanol. Solutes: cycloalkanes (cane) from C_5H_{10} to $C_{12}H_{24}$; n -alkanes (ane) from C_5H_{12} to $C_{10}H_{22}$; 1-alkenes (ene) from C_5H_{10} to $C_{10}H_{20}$; 1-alkynes (yne) from C_5H_8 to $C_{10}H_{18}$; phenylalkanes (ϕR) from ϕ -Et to ϕ -Hept; p -polyphenyls, ϕ_n , from ϕ_1 to ϕ_3 ; diphenylalkanes, $\phi R\phi$, from diphenylmethane to diphenylbutane; methylbenzenes, ϕMe_n , from toluene to mellitene. For the sake of clarity, most data points are omitted.

a strongly positive δG .

The relationship between the retention index, I_K , and the solute molecular total surface area (TSA) is shown in Fig.4. A comparison of alkanes and cycloalkanes yields an interesting result. While in Fig. 2 the $\ln k'$ versus n_c dependence was very similar, the I_K values of species belonging to these solute classes having identical TSA values are clearly different. The I_K value of the cyclic compound is always markedly higher, and the difference from the chain compound grows with increasing TSA. There may be some differences in the eluent surface-tension correction factor for linear and cyclic compounds, but the main reason is believed to be a difference in the sorption entropy. If an alkyl chain forms a sorption complex with ODS chains and some fraction of eluent molecules, the corresponding ΔS_{inter}^{solv} is more negative than with a cyclic alkane having the same size. Consequently, the retention of the chain compound must be lower. An increase in the degree of methylation of cyclohexane has a comparatively small effect on I_K . The reason is that more and more of the highly effective ring surface is occluded by methyl groups. The steepest rise in I_K with increasing TSA is observed with increasing methylation of benzene. This is explained by the fact that the introduction of CH_3 groups not only enlarges the total surface

area but also replaces low retention aromatic surface area by high retention methyl surface area. This does not occur with the isomeric phenylalkanes which, consequently, have a markedly lower I_K for equal TSA.

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