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RETENTION OF SULPHUR AND SULPHUR ORGANICS IN REVERSED-PHASE LIQUID CHROMATOGRAPHY

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SUMMARY

In reversed-phase systems with purely or mainly methanolic eluents, sulphur homocycles S_n exhibit clearly higher retention than *n*-alkanes or cycloalkanes that have the same skeleton atom number ($n_C + n_S$). If normalized to equal surface area values, the retention difference is even higher. It has to be concluded that alkanes interact more strongly with the methanol eluent than the (proton-free) sulphur rings. This is reflected by a more negative sorption enthalpy and a more positive sorption entropy of sulphur rings. With more water in the eluent, the retentions of alkanes and sulphur rings approach each other, because alkane–eluent interactions are suppressed by solvophobic forces.

The retention behaviour of polysulphanes H_2S_n is very similar to that of sulphur rings. Thia substitution in alkanes, yielding thiols, thioethers, or multisulphides, invariably lowers retention, to a degree that depends on the number of non-vicinal substitution sites and their relative locations in the molecule. In an eluent of pure methanol the retention loss caused by thiol formation is *ca.* 200 index units; the thioether function is somewhat more effective. The retention decrease is attributed to the formation of local polar centres, which are surrounded by "solvation patches".

Among aromatic systems, thia substitution causes some retention increase rather than decrease.

In aliphatic polysulphides, both retention loss due to the formation of local polar centres and retention increase due to the presence of undisturbed sulphur atoms, can be observed. The former effect is predominant in short-chain polysulphides, the latter in solutes with long sulphur chains.

INTRODUCTION

The separation and the general analysis of complex mixtures of sulphur and thia compounds has long been regarded as very difficult, if not impossible. Even in 1977 Meyer, one of the greatest authorities in this field, stated that the identification of sulphur compounds in mixtures is an art[1]. On the other hand, the thorough analysis of sulphur-containing samples has become a necessity in, only to mention an example, environmental chemistry.

In principle, high-performance liquid chromatography on bonded, reversed

phases (RPLC) has the power to yield the desired separations. The only problem was that virtually nothing was known about the retention behavior of sulphur and its compounds. We have made systematic studies of the RPLC of a wide variety of sulphur solutes, and this paper presents the main characteristics.

EXPERIMENTAL

The apparatus was assembled as required from commercial parts, mainly from Knauer, Kratos, Rheodyne, Varian and Waters. Several experiments were performed at ambient temperature, but in most cases the columns were thermostatted. Steel columns were kept in water jackets, radially compressed columns (Waters) in air ovens.

Whereas most chemicals were bought from Aldrich, some had to be synthesized according to methods described in the literature. Solvents were analytical or Chrom AR grade from Merck or Baker. Water was obtained from a Millipore battery.

Retention times were measured with Autolab 1 (Spectra Physics) or CDS 111 (Varian) integrators.

The columns used for particular separations are described in the Results section.

DATA TREATMENT AND QUOTATION

Averaging, decimals, error quotation

All measurements were repeated at least twice, mostly up to five times. Averaging was done on the raw time data, taken from the integrator printout. These data include the column dead-time and the extra-column dead-time. The latter needs to be determined only once, since it is constant for a given apparatus.

The data from the integrator give times to a hundredth of a minute. From the computed mean raw retention times, three decimal places were used for further calculations. When errors are given, they are in terms of a variation coefficient which is the $n - 1$ standard deviation, divided by the mean and multiplied by 100.

Column dead-volume determination

An indicator solute, eluted with the dead-volume V_m, would be characterized by $K = 0$ for the distribution between stationary and mobile phases. Since it is not known, *a priori*, whether a solute fulfills that condition (it seems impossible to find one), an indirect determination of V_m has been proposed[2-4]. It makes use of the linear dependence of the ln k' of a true homologous series on the number, n, of homologue units, most frequently methylene groups:

$$\ln k' = a + bn \tag{1}$$

However, this holds only for a limited range of solute molecular size[4,5]. Using the chromatographic definition of the capacity factor

$$k' = \frac{V_{ms} - V_m}{V_m} = \frac{t_{ms} - t_m}{t_m} \tag{2}$$

where subscript ms indicates gross values, and subscript m dead-values, the dead-volume or dead-time is found by iteration, until the linearity of eqn. 1 is achieved. In practice, this procedure is quite limited, since it takes at least five extremely accurate retention values per series. In most cases, we have determined t_m by collecting linearization t_m data for as many eluent compositions as possible and then finding the best-fitting curve for $t_m = f$(methanol percentage), which generally is a parabolic function.

The phase volume ratio ø

The determination of ln ø (see later) is easy, only if sufficiently precise data are available on the retention of homologous series at as many eluent compositions as possible. For a hypothetical solute with $K = 1$, in the general ln k' equation

$$\ln k' = \frac{-\Delta H^*}{RT} + \frac{\Delta S^*}{R} + \ln ø + n\left(\frac{-\Delta\Delta H}{RT} + \frac{\Delta\Delta S}{R}\right) \tag{3}$$

all enthalpy and entropy terms add up to zero, since $\Delta G_{m\to s}$ vanishes:

$$\frac{-\Delta H_{m\to s}}{RT} + \frac{\Delta S_{m\to s}}{R} = 0 \tag{4}$$

and

$$\ln k' = \ln ø \tag{5}$$

We can solve eqn. 3 for a hypothetical homologue number, $\tilde{n}$,

$$\tilde{n} = \frac{-\Delta H^* + \Delta S^* T}{-\Delta\Delta H + \Delta\Delta S T} = \frac{\Delta G^*}{\Delta\Delta G} \tag{6}$$

Inserted into the general retention equation, $\tilde{n}$ yields the phase ratio ø according to eqn. 5. The value of $\tilde{n}$ for a narrow range of eluent compositions can be found as the intersection point of the retention equation for one homologous series at two slightly different eluent compositions. For common ODS phases and methanol–water eluents, the phase ratio has values of *ca.* 0.2 for 100% methanol and *ca.* 0.02 for methanol–water (50:50). The eluent composition dependence is non-linear in general, but can be reasonably well approximated by a linear function in many cases[6].

The retention index system

Alkane retention in RPLC systems is reasonably well understood. For describing the influence on retention of substitution, *e.g.* the replacement of one or more methylene groups by sulphur atoms, it is most informative to compare the retention of the substitution product with that of the original hydrocarbon. A way to express this "relative" retention is the use of a retention index I_K, which is completely analogous to the well-known Kováts index in gas chromatography[7]. The reference solutes are *n*-alkanes. Their retention in RPLC depends, within certain limits, on the solute molecular chain lengths of the solute molecules:

$$\ln k'(\text{alk}) = a(\text{alk}) + b(\text{alk}) n_C \tag{7}$$

where alk refers to an *n*-alkane, and n_C is the number of carbon atoms.

The retention index of *n*-alkanes is $100n_C$ by definition. If we have determined the ln k' of a substitution product A, we can treat it formally as a hypothetical *n*-alkane. By substituting ln k'(A) into eqn. 7, we find the theoretical carbon number of this alkane, generally a non-integer. Multiplication by 100 yields the retention index of A, I_K(A). The calculation is simple:

$$I_K(A) = \frac{100}{b(alk)} [\ln k'(A) - a(alk)] \tag{8}$$

Sometimes it is useful to compare retention index changes. ΔI_K is the difference between the retention of a thia-compound with a skeleton atom number of $n_C + n_S$, and that of the corresponding *n*-alkane:

$$\Delta I_K = I_K(A) - 100 (n_C + n_S) \tag{9}$$

It will be shown that most of the thia substitutions are characterized by certain ΔI_K values, so that the retention of the product can easily be predicted.

Thermodynamic data

The enthalpy or heat of sorption, $\Delta H_{m \to s}$, can be determined from the temperature dependence of retention, ln k'. The ln k' values are linear functions of the inverse of the absolute temperature:

$$\ln k' = \alpha + \beta \frac{1}{T} \tag{10}$$

It can be shown that

$$\alpha = \frac{\Delta S_{m \to s}}{R} + \ln \varnothing \tag{11}$$

$$\beta = - \frac{\Delta H_{m \to s}}{R} \tag{12}$$

The sorption entropy can be determined only if the phase volume ratio is known. The same holds, of course, for the free energy of sorption, $\Delta G_{m \to s}$.

THEORETICAL BACKGROUND

Thermodynamic formalism

The capacity ratio, k', is used to express retention. It links the thermodynamic distribution coefficient, K, to a physical column parameter, the phase volume ratio, $\varnothing$:

$$k' = K\varnothing \tag{13}$$

where

$$\varnothing = V_{stationary}/V_{mobile} \tag{14}$$

The distribution coefficient is defined for the partition of a solute between two homogeneous fluid systems. Despite the fact that in RP systems it is true neither that the stationary phase is a really homogeneous liquid nor that the sorbed state represents a real fluid solution, it appears justifiable to transfer the distribution coefficient concept to ODS or OS phases used with eluents of high organic solvent content. The main reasons are the active participation of considerable amounts of the eluent in stationary phase formation and the fact that k' values, and consequently K, are virtually constant over a surprisingly wide range of solute sample size, which is quite untypical for adsorption systems. Furthermore, the surface energy of ODS phases is low (20–40 erg cm^{-2})[10], and the thermodynamic sorption data are of the order of magnitude expected for partition.

From thermodynamics we find that

$$\ln k' = \frac{-\Delta G_{m\rightarrow s}}{RT} + \ln \varnothing = \frac{-\Delta H_{m\rightarrow s}}{RT} + \frac{\Delta S_{m\rightarrow s}}{R} + \ln \varnothing \qquad (15)$$

For members of a homologous series, both sorption enthalpy, $\Delta H_{m\rightarrow s}$, and sorption entropy, $\Delta S_{m\rightarrow s}$, are linear functions of the number of structural units or skeleton atoms on which the series is based:

$$\Delta H_{m\rightarrow s} = \Delta H^* + \Delta\Delta Hn \qquad (16)$$

$$\Delta S_{m\rightarrow s} = \Delta S^* + \Delta\Delta Sn \qquad (17)$$

$\Delta\Delta H$ and $\Delta\Delta S$ represent the constant contributions of undisturbed methylene groups in alkyl chains or sulphur atoms in polysulphide chains to the respective thermodynamic quantity. They cause the generally observed linearity of ln k' of homologous series with chain length, for example.

In a group of homologous series, R′ (CH$_2$)$_n$R″, where R′ and R″ may be methyl or may carry functional groups, these homologue increments are generally similar, though not necessarily equal, whereas in otherwise homologous series, R′Z$_n$R″, they can be completely different. They depend strongly on the eluent composition.

For a given type of homology, ΔH^* and ΔS^* depend mainly on the functional nature of the terminal groups R′ and R″. Usually, they exhibit some dependence on the eluent composition, but in some cases they are virtually constant (*e.g.* in *n*-alcohols).

Interactions in the mobile phase

Although mainly or purely methanolic eluents were used in the present investigation, the systems can still be clearly classified as reversed-phase systems. Since Horvath's classical work[8], the solvophobicity concept is indispensable in RPLC. As far as the mobile phase is concerned, this concept can be used in water-lean systems equally well, the only difference being that here the solute–solvent interactions will be more important than the solvent–solvent interactions.

The transfer of a solute molecule from outside into the eluent first demands the formation of a cavity within the liquid to accomodate the solute. Cavity formation consumes energy to compensate for the work done against the surface tension

of the eluent. Consequently, $\Delta H_{\text{solution}}^{\text{cavity,mobile}}$ is positive. Upon transfer of the solute into the cavity, it will exert an interaction with the surrounding eluent. Thus, $\Delta H_{\text{solution}}^{\text{inter,mobile}}$ appears negative. When the solute leaves the eluent and the cavity collapses, the respective heats will reappear with the opposite signs:

$$\Delta H_{\text{sorption}}^{\text{mobile}} = -\Delta H_{\text{solution}}^{\text{cavity,mobile}} + \Delta H_{\text{solution}}^{\text{inter,mobile}} \tag{18}$$

The intrusion of a solute molecule into the mobile phase is accompanied by a rearrangement of the eluent molecules around the cavity, causing a decrease of the eluent entropy. When the solute leaves the solution, the entropy lost in ordering the eluent reappears.

$$\Delta S_{\text{sorption}}^{\text{cavity,mobile}} = -\Delta S_{\text{solution}}^{\text{cavity,mobile}} \tag{19}$$

The strongly negative $\Delta S_{\text{solution}}^{\text{cavity,mobile}}$ is the reason for the low water solubility of typical hydrophobic solutes such as alkanes, and represents a decisive driving force towards retention in RPLC with predominantly aqueous eluents[8,9].

The sorption complex

The results presented later show very clearly that the overall sorption entropy is negative, which means that it does not support retention. It is more negative the larger the solute molecules are and the higher the eluent water content is. (This refers to an eluent still rich in methanol, *i.e.* a range of 70–100% methanol.)

The negative value of the sorption entropy, $\Delta S_{\text{m}\rightarrow\text{s}}$, and its dependence on the eluent composition are somewhat surprising from the solvophobicity point of view. Since $\Delta S_{\text{m}\rightarrow\text{s}}$ is the sum of the (positive) entropy change from collapsing cavities and the entropy change arising from the sorbed solute state, the latter must be even more negative. We have estimated that *ca.* 5 cal°K^{-1} mol^{-1} in 100% methanol and *ca.* 20 cal°K^{-1} mol^{-1} in 80% methanol are used in the formation of the sorbed state of hexane on an ODS phase.

These findings suggest that the sorbed solute state is best described as a highly ordered "sorption complex", which consists of C_{18} chains, solute molecules, and a certain number of mobile-phase molecules. This number is, at present almost arbitrarily, thought to be identical with the fraction of the eluent that is immobilized in the stationary phase when solute molecules are absent.

If the entropy lost in the formation of the "sorption complex" is $\Delta S^{\text{complex}}$, the total sorption entropy is

$$\Delta S_{\text{m}\rightarrow\text{s}} = \Delta S_{\text{sorption}}^{\text{complex}} - \Delta S_{\text{solution}}^{\text{cavity,mobile}} \tag{20}$$

It should be kept in mind that this description of the sorption process sees the transition of solute from the mobile to the sorbed state as a partition between a real and a quasi liquid, which causes remarkable changes in the internal state of order of the latter while the volume is not appreciably changed.

The formation of the "sorption complex" is generally accompanied by heat transfer. We will define $\Delta H_{\text{sorption}}^{\text{complex}}$ as the heat exchanged on transfer of solute from outside to a stationary phase, which is constituted such that after addition of the

solute and reorientation of the constituents the sorption complex is formed. During that process, no components are supposed to leave the quasi-fluid for the mobile phase.

Then the total heat of sorption is

$$\Delta H_{m \to s} = \Delta H_{\text{sorption}}^{\text{complex}} - \Delta H_{\text{solution}}^{\text{cavity,mobile}} + \Delta H_{\text{solution}}^{\text{inter,mobile}} \tag{21}$$

For members of a homologous series, each of the terms in eqns. 20 and 21 will be composed of a constant (*) and a homologous increment($\Delta\Delta$).

RESULTS AND DISCUSSION

Alkanes as reference compounds

Alkanes are easily separated in RP systems. With ODS phases, methanol containing up to *ca.* 30% water is usable as eluent. More water causes excessively long retention times and a very low sample load capacity. In such systems, ln k' of the series from pentane to heptadecane is a perfectly linear function of the carbon number, n_C. Both the intercept, a, and the slope, b, in eqn. 1 depend on eluent composition. While b increases linearly with increasing water content of the eluent, the intercept a is an approximately parabolic function of the eluent composition, the highest power of the latter being somewhat below 2. The a values are found to be most negative in neat methanol eluent. The sorption enthalpy and entropy of alkanes are shown in Figs. 1 and 2 for 100% methanol and 80:20 methanol–water eluents on a 5-μm ODS column. With 100% methanol, the sorption enthalpy of pentane is almost zero, and the positive sorption entropy contributes most to C_5 retention. The larger the alkane, the more negative is the sorption enthalpy. Simultaneously, the
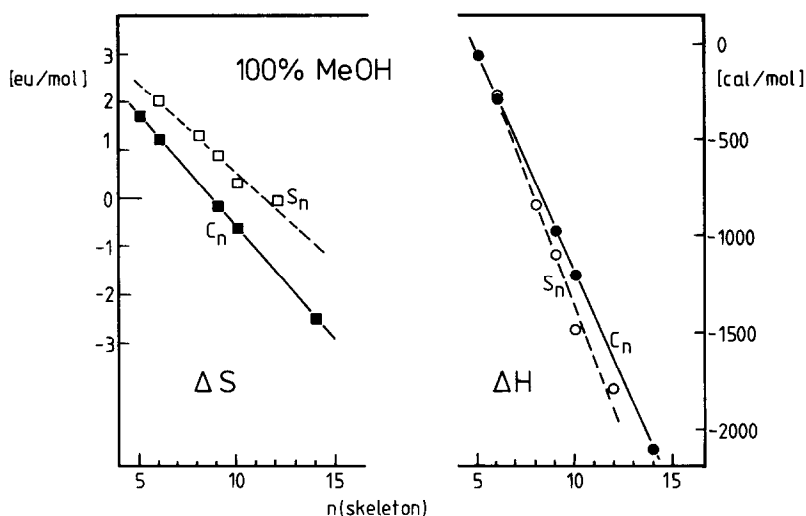

Fig. 1. Sorption enthalpy, ΔH, and entropy, ΔS, values of n-alkanes (C_n) and sulphur homocycles (S_n). Eluent, 100% methanol; column, 20 cm × 4 mm I.D. Nucleosil 5C$_{18}$.
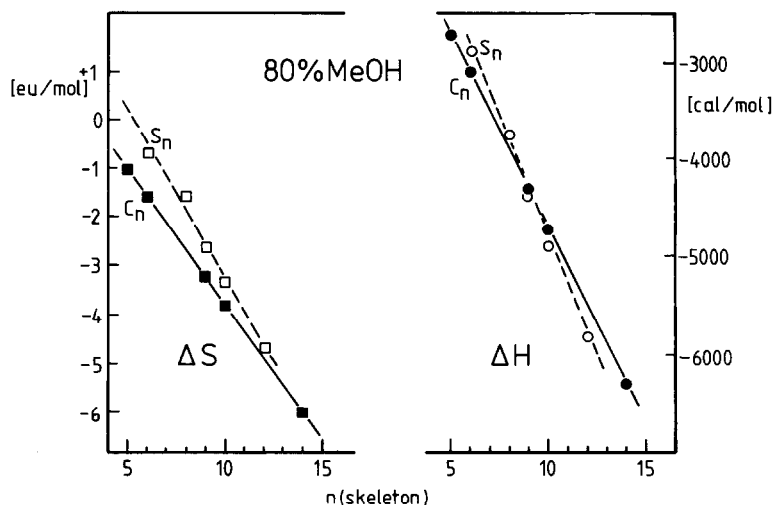
Fig. 2. As Fig. 1, except eluent, 80:20 methanol–water.

sorption entropy also becomes negative, thus acting against sorption. In 80% methanol, sorption entropies and enthalpies of all alkanes are strongly negative.

Branched alkanes always have a lower retention than the non-branched isomers. The degree of branching determines the degree of retention lowering. It has been shown that the retentions of alkanes, expressed in terms of ln k', are linearly related to the molecular surface area of the respective solutes[10].

Sulphur homocycles

We have separated the sulphur homocycles S_6 to S_{26}[11–13]. Cyclopentasulphur probably also exists; we have observed the corresponding peak after thermal decomposition of H_2S_6[14]. The sulphur rings form two homologous series, one of which comprises the members S_5 to S_{10}, the other S_{10} to S_{26}. Fig. 3 shows a chromatogram of S_n up to $n = 12$. The column was a Radial Pak 10-μm C_{18}, 10 cm × 8 mm I.D.;
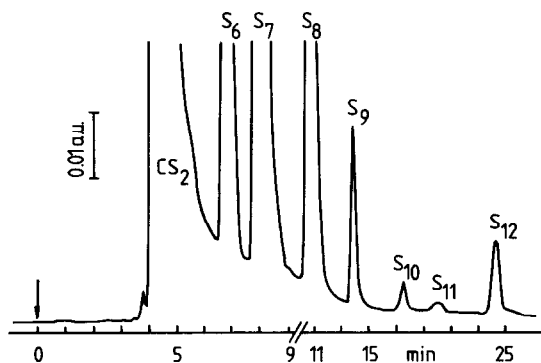
Fig. 3. Chromatogram of sulphur homocycles S_6 to S_{12} (CS_2 extract of the acid decomposition products of $Na_2S_2O_3$). Eluent, methanol–water (98:2); column, RadPAK A, 10 cm × 8 mm I.D. (taken from ref. 16).

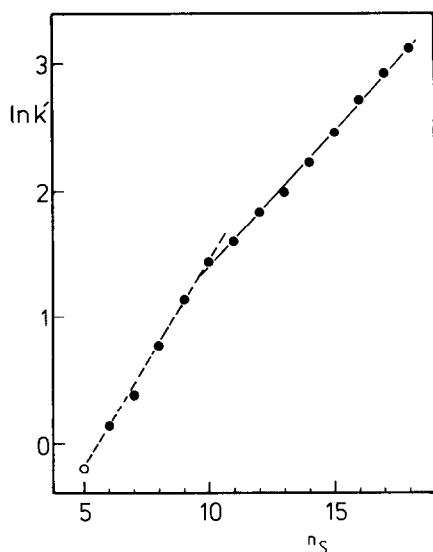Fig. 4. Plot of ln k' *versus* ring size (sulphur atom number n_S) of sulphur homocycles S_6 (S_5?) to S_{18}. Eluent, methanol–cyclohexane (75:25); column, RadPAK A, 10 cm × 8 mm I.D.

the eluent was 98% methanol. In Fig. 4 ln k' is plotted *versus* the ring size of sulphur homocycles. The column was the same as in Fig. 3, the eluent was 75:25 methanol–cyclohexane. Owing to the greater solubility of sulphur rings in that solvent, the retention values are lower and, the larger rings can be chromatographed within a
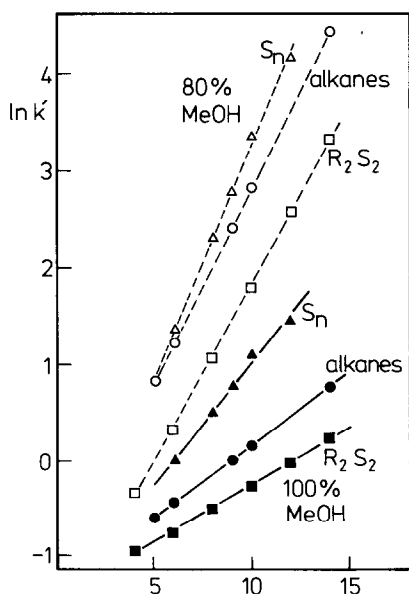
Fig. 5. Plot of ln k' *versus* skeleton atom number for sulphur homocycles, n-alkanes and dialkyl disulphides with 100% methanol and methanol–water (80:20) as eluents. Column, 20 cm × 4 mm I.D. Nucleosil 5C$_{18}$.
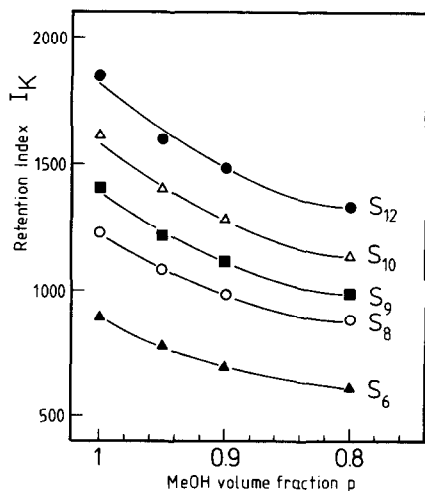
Fig. 6. Retention indices I_K of several sulphur rings as function of the methanol content of the aqueous eluent. Column,·20 cm × 4 mm I.D. Nucleosil 5C$_{18}$.

reasonable time. The reason for the discontinuity of ln k' is that in the smaller rings the molecular surface area per sulphur atom accessible to the eluent is less than in the larger rings. The larger the ring, the more of the surface area is exposed to the eluent. At *ca.* S_{10}, all sulphur atoms become completely accessible to the eluent. At the same time, the accessible area increase per additional sulphur atom is larger for the smaller rings than for the larger rings. Again, at *ca.* S_{10} this increase attains a constant value. Owing to some changes in molecular symmetry and, consequently, polarity as well as exposed surface area, the scatter of individual ln k' data points around the regression lines is somewhat more pronounced than for alkanes, for example. We will refer to a family of solutes such as the sulphur homocycles as a quasi-homologous series.

The retention of sulphur rings in neat methanol is greater than that of *n*-alkanes with the same skeleton atom number, despite the fact that a sulphur ring always has a smaller molecular surface area than the corresponding alkane. This may be seen in Fig. 5, which is a plot of the ln k' values of sulphur homocycles, *n*-alkanes and (for comparison) di-*n*-alkyl disulphides *versus* skeleton atom number. In terms of the retention index, *n*-octane has an $I_K = 800$, cyclooctane $I_n = 809$, and cyclo-octasulphur $I_K = 1243$. If normalized to the molecular size of *n*-octane, then S_8 even has an $I_K = 1364$.

The comparatively high retention of sulphur rings —or rather, the lower retention of alkanes— has its origin partly in a more negative enthalpy of interaction of the alkane solutes with the methanol eluent. This stronger interaction arises from the presence of protons in both solute and solvent. The bare sulphur rings, lacking any such protons, cannot undergo these interactions and thus represent the ideal solvophobic entities in pure methanol.

When more water is added to the eluent, hydrophobic behaviour of solutes is expected to become important. This would mean that the extra interactions between alkyl protons will be more and more suppressed by increasingly stronger eluent-
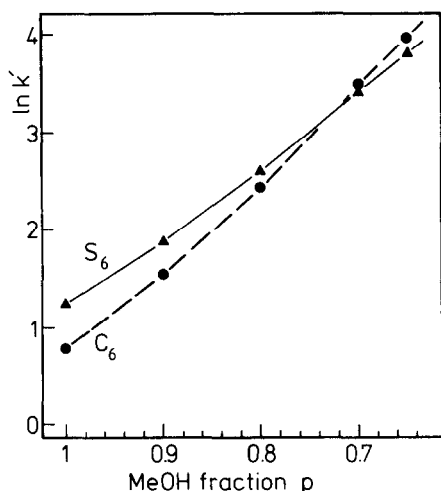
Fig. 7. Plot of ln k' of n-hexane and cyclohexasulphur as a function of the methanol content of the eluent. Column, RadPAK A, 10 cm × 8 mm.

eluent forces. In Fig. 6 it can be seen that with increasing water content of the eluent the retention indices approach the corresponding alkane values. Fig. 7 shows that, with 72% methanol, n-hexane and cyclohexasulphur have identical retentions. At lower methanol content of the eluent S_6 is eluted before hexane.

From Fig. 1 it is evident that the high sulphur retention has both enthalpic and entropic reasons. ΔH and ΔS of sorption are shown as functions of the skeleton atom number with neat methanol as eluent. The respective data with an eluent of 80% methanol are given in Fig. 2. The sorption enthalpy difference between sulfur ring and alkane has decreased for smaller solutes. The sorption entropy difference is smaller, in general, and seems to vanish for larger solutes.

Polysulphanes

A chromatogram of the recently[14] separated polysulphanes H_2S_2 to H_2S_{13} is given in Fig. 8. The peaks form a perfect homologous series. As seen in Fig. 9, a chain HS_nH has a slightly lower retention than a sulphur ring S_n $(n > 8)$. The overall retentions of H_2S_n as well as the homologue increment (b in eqn. 1) are distinctly higher than the respective alkane C_nH_{2n+2} values. For ease of comparison the retention data of an dialkyl-substituted polysulphide series (diethyl polysulphides, Et_2S_2 to Et_2S_{10}) have been included. Although the overall retention of Et_2S_n is much lower than the H_2S_n retention, the homologue increments (slopes) are almost equal and clearly higher than in the corresponding alkanes. This indicates that, in sulphur chains, a sulphur atom contributes more to retention than a methylene group does in alkanes.

Isolated (non-vicinal) thia substitution

Alkane and cycloalkane systems

Thiols. (a) Monothiols. The substitution of CH_2 by S in a CH_3 group yields a thiol RSH. Fig. 10 shows the chromatogram of some alkanethiols on an ODS
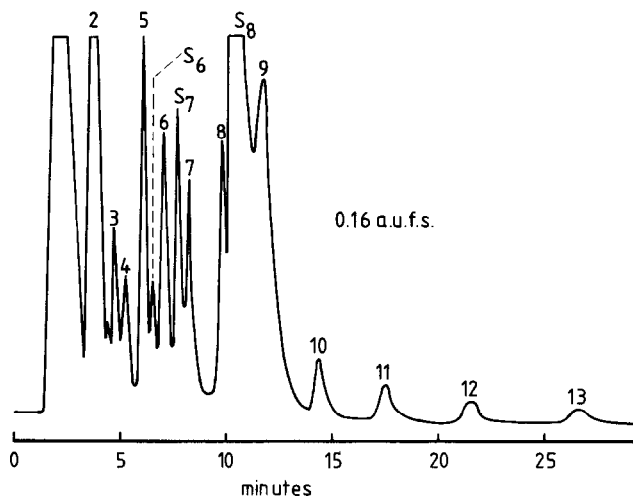
Fig. 8. Chromatogram of polysulphanes H_2S_2 to H_2S_{13} (from the reaction of Na_2S_n + S_2Cl_2 in deaerated ethanol). The numbers with the peaks indicate the sulphur chain length, n_S. Three sulphur rings (S_6, S_7, S_8) are also present. Eluent, 100% methanol; column, RadPAK $5\mu C_{18}$, 10 cm × 8 mm I.D.

column with 70% methanol and, for comparison, that of the corresponding alcohols. In Table I some retention indices I_K and index differences ΔI_K (eqn. 8) are given. It is seen that thiol formation causes an index decrease of 180–210 units, depending on the length of the alkyl group. Retention lowering by alcohol formation is much more pronounced: the index decrease is ca. 510 units. Fig. 11 shows that the methylene group contributions, $\Delta\Delta G$, to the free energy of sorption of alkanes and thiols are
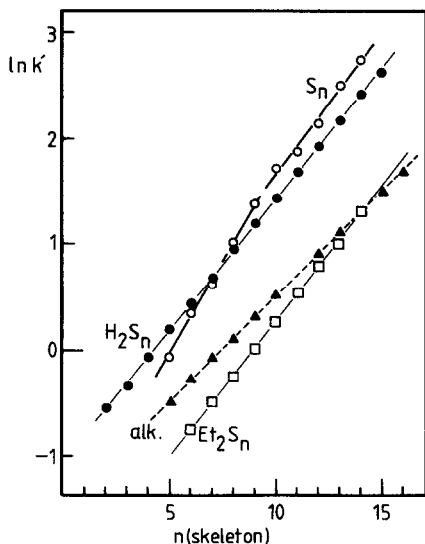

Fig. 9. Plot of ln k' versus skeleton atom number of sulphur rings S_n, polysulphanes H_2S_n, n-alkanes alk, and diethyl polysulphides, Et_2S_n. Eluent, 100% methanol; column, RadPAK $5\mu C_{18}$, 10 cm × 8 mm I.D.
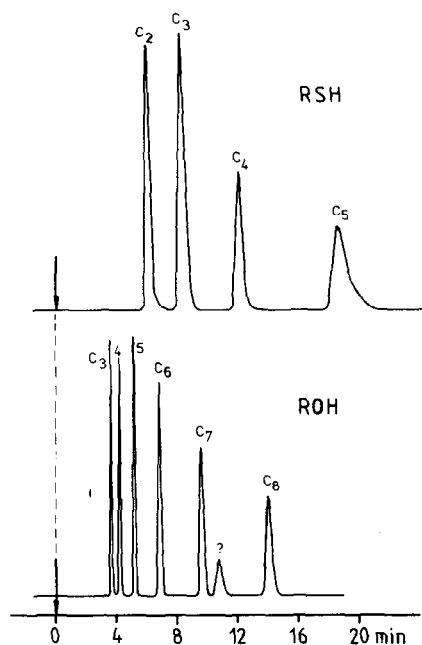
Fig. 10. Chromatograms of alkanethiols and alkanols under identical conditions. Eluent, methanol–water (70:30); column, RadPAK A.

similar with pure methanol as eluent and do not differ much, even in 70:30 methanol–water. They certainly cannot account for the actual retention differences. On the other hand, the very weak hydrogen bridge formation tendency of SH groups cannot be responsible either for the retention loss caused by thiol formation.

(b) Dithiols. For equal skeleton atom numbers the retention of 1,ω-dithiols

TABLE I

RETENTION INDICES, I_K, AND RETENTION DECREASE, ΔI_K, OF SOME THIOLS AND ALCOHOLS

Eluent, methanol–water (70:30); column, 20 cm × 4 mm I.D. Nucleosil 5C_{18}; temperature, 25°C.

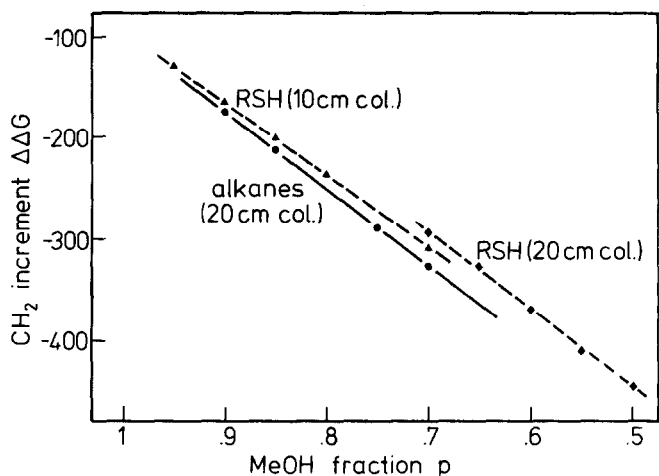| Solute	I_K	ΔI_K
Et-SH	120	−180
Pr-SH	217	−183
Bu-SH	312	−187
Pent-SH	407	−193
Hex-SH	504	−196
Hept-SH	599	−201
Oct-SH	694	−206
Pr-OH	−110	−510
Bu-OH	−13	−513
Pent-OH	85	−515
Hex-OH	181	−519

Fig. 11. Sorption free enthalpy increments for methylene groups in alkanethiols and n-alkanes *versus* methanol content of the eluent. Columns, 10 cm × 4 mm I.D. Nucleosil $5C_{18}$ (10 cm col.) and 20 cm × 4 mm I.D. Nucleosil $5C_{18}$ (20 cm col.).

(1,2-ethanedithiol to 1,9-nonanedithiol) is less than that of monothiols, as can be seen in Fig. 12. It appears that the retention decrease from n-alkanes to thiols is about the same as that from thiols to dithiols. On an ODS column with 95% methanol as eluent the following retention equations are found:

$$\ln k'(\text{alkane}) = -1.3673 + 0.2453 n_C \tag{22}$$
$$\ln k'(\text{thiol}) = -1.6765 + 0.2170 n_{(C+S)} \tag{23}$$
$$\ln k'(\text{dithiol}) = -2.0578 + 0.2043 n_{(C+S)} \tag{24}$$

They indicate that retention lowering is mainly, but not completely, located immediately adjacent to the SH groups. To a lesser degree, the methylene group
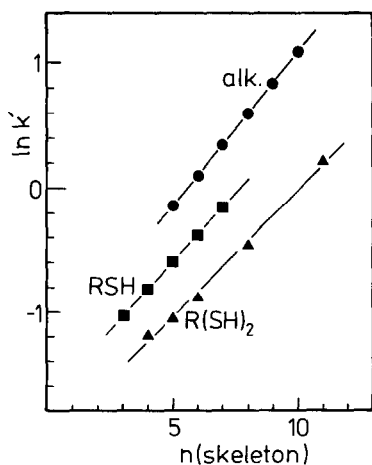

Fig. 12. Plot of $\ln k'$ *versus* skeleton atom number of n-alkanes, alkanethiols and alkanedithiols. Eluent, methanol–water (95:5); column RadPAK $5\mu C_{18}$.

TABLE II

RETENTION OF ISOMERIC THIOLS

Column, 10 cm $\times$ 3 mm I.D. CP C_{18}; eluent, methanol–water (70:30).

Solute	ln k'	I_K
n-C_3SH	0.8005	200
iso-C_3SH	0.6896	181
n-C_4SH	1.3678	298
$sec.$-C_4SH	1.2622	280
iso-C_4SH	1.3155	289
$tert.$-C_4SH	1.0814	248

retention contribution is also influenced by the presence of SH groups. In terms of the retention index, it is 88.5 units on the average for thiols and 83.3 units for the dithiols. The total retention loss in a dithiol compared with an alkane that has the same skeleton atom number is then the sum of the effects of two terminal functional groups plus a diminished retention of the methylene groups separating the centres.

(c) Isomers. Out of a group of thiols with a given composition, it is always the n-thiol that exhibits the highest retention. This is illustrated by data obtained from propane- and butanethiols (Table II). There are two reasons for the retention differences. One is the decrease of molecular surface area always observed on branching of the structure. The other is that the SH group finds somewhat different alkyl surroundings in n-butanethiol and $sec.$-butanethiol, for example.

Thioethers. (a) Monosulphides. Substitution of methylene by sulphur in an alkane yields a thioether R'SR", a special case of which is the symmetric type R_2S.

TABLE III

COEFFICIENTS OF ln $k' = a + bn_C$ AND $I_K = A + Bn_C$ FOR n-ALKANES AND SOME MONOSUBSTITUTION PRODUCTS

Eluents as indicated; column, 12.5 cm $\times$ 4 mm I.D. Nucleosil $5C_{18}$; temperature, 50°C. Correlation coefficient r for ln k' least squares fit.

| Solutes	Methanol (%)	a	b	r	A	B
n-Alkanes	60	−0.1995	0.5855	0.9999991	(0)	(100)
R_2S	60	−0.9338	0.5393	0.9991	−125.4	92.1
R_2O	60	−1.9547	0.5705	0.9997	−299.8	97.4
MeSR'	60	−0.9019	0.5550	0.997	−120.0	94.8
RSH	60	−0.7428	0.5740	0.99999	−92.8	98.0
ROH	60	−2.4478	0.5543	0.99998	−384.0	94.7
n-Alkanes	55	−0.0526	0.6442	0.99999	(0)	(100)
R_2S	55	−0.8767	0.5979	0.999	−127.9	92.8
R_2O	55	−1.9793	0.6323	0.9998	−299.1	98.2
MeSR'	55	−0.8335	0.6132	0.994	−121.2	95.2
RSH	55	−0.6484	0.6346	0.99997	−92.5	98.5
ROH	55	−2.3512	0.6024	0.999997	−356.8	93.5
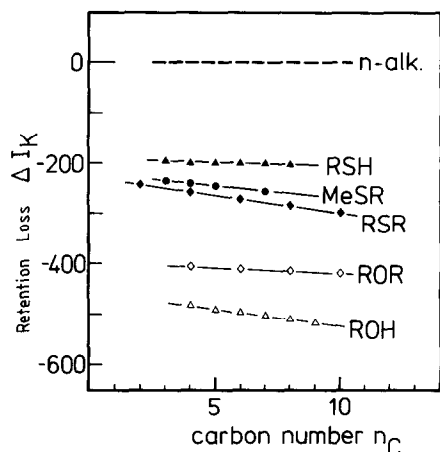
Fig. 13. Loss of retention index, ΔI_K, versus carbon atom number of thiols (RSH), methylthioalkanes (MeSR), thioethers (RSR), ethers (ROR) and alcohols (ROH). Eluent, methanol–water (55:45); column, 12.5 cm × 4 mm I.D. Nucleosil 5C$_{18}$.

In the same system yielding eqns. 21–24 for alkanes, thiols and dithiols, R$_2$S thio-ethers gave

$$\ln k' = -1.6797 + 0.2108 n_{(C+S)} \tag{25}$$

which is slightly less than the retention of the corresponding isomeric thiols (eqn. 23).

In water-containing eluents the difference is more pronounced (Table III). Here, it is obvious that the sulphur atom lowers the retention more effectively in a thioether position than in a thiol position. As there are no marked differences in molecular surface area values, one might say —using common terms— that a thio-ether is more polar than a thiol. As far as permanent dipole moments are concerned, this is certainly not the case, since the μ values of thiols and thioethers are almost identical. They are all of the order of 1.5–1.6 debye.

TABLE IV

THERMODYNAMIC DATA FOR THE SORPTION OF ALKANES AND SOME MONOSUBSTITUTION PRODUCTS

Eluents as indicated; column, 20 cm × 4 mm I.D. Nucleosil 5C$_{18}$; a and b data for 25°C.

Solutes	Methanol (%)	a	b	ΔH^*	$\Delta \Delta H$	ΔS^*	$\Delta \Delta S$
RSH	70	−1.4418	0.5025	−799	−471	−0.75	−0.58
ROH	70	−3.1958	0.5119	185	−456	−0.94	−0.51
RSR	70	−1.7016	0.4842	−944	−347	−1.76	−0.20
MeSR	70	−1.6386	0.4962	−217	−565	+1.91	−0.91
ROR	70	−2.5536	0.4824	481	−415	+1.33	−0.43
n-Alkanes	70	−0.8900	0.5202	−1440	−510	−0.96	−1.15
n-Alkanes	80	−1.1631	0.3990	−680	−402	+1.79	−0.95
n-Alkanes	90	−1.4368	0.2794	639	−375	+3.96	−0.70
n-Alkanes	95	−1.4981	0.2181	1019	−282	4.36	−0.51
n-Alkanes	100	−1.3450	0.1506	1080	−228	4.02	−0.46

TABLE V

SORPTION DATA FOR SOME COMPOUNDS HAVING n (skeleton) = 9

Column, 20 cm × 4 mm I.D. Nucleosil 5C$_{18}$; eluent, methanol–water (70:30).

Compound	ln k'	ΔH (cal mol^{-1})	ΔS (eu mol^{-1})
n-C$_9$	3.7918	−5740	−6.93
8-SH	2.5954	−4560	−5.35
1-S-7	2.3352	−4460	−5.53
4-S-4	2.1718	−3720	−3.37
8-OH	0.8954	−3460	−5.02
4-O-4	1.3586	−2890	−2.20

Depending on the eluent composition and the molecular size of the solute, thia substitution to produce a thioether lowers the retention by 230–300 units.

(b) Influence of the substitution site. If, within a given thioether molecule, the sulphur atom is shifted from a central position towards one end of the chain, the retention increases slightly. The change is most clearly seen if symmetric thioethers, R$_2$S, are compared with the isomeric methylthioalkanes, MeSR'. It appears that retention is greatest for the thioether containing the longest alkyl chain. This may be seen in Fig. 13, which shows ΔI_K for R$_2$S and MeSR and, for comparison, RSH, ROH, and ROR, all with 55:45 methanol–water on an ODS column. The difference between R$_2$S and MeSR retention increases with the skeleton atom number of the solute. It is seen that the retention decrease caused by the introduction of an ether oxygen far exceeds that of the thioether function. This is due to the strong electron donor properties of the oxygen, which allow the formation of effective hydrogen bonds with the eluent.

TABLE VI

RETENTION DATA OF MULTISULPHIDES
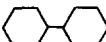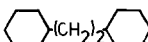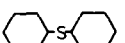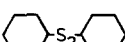
Column, RadPAK 5μC$_{18}$; eluent, methanol–water (95:5); temperature, ca. 25°C.

Solute*	ln k'	I_K	ΔI_K	$\dfrac{\Delta I_K}{n(\text{skeleton})}$ (%)
2,5-DT-6	−0.7843	215	−385	64.2
2,6-DT-7	−0.6202	282	−418	59.7
3,6-DT-8	−0.4112	368	−432	54.0
2,7-DT-8	−0.4731	343	−457	57.1
4,6-DT-9	−0.1235	486	−414	46.0
3,7-DT-9	−0.2618	429	−471	52.3
2,8-DT-9	−0.2702	426	−474	52.7
2,5,8-TT-9	−0.5760	301	−599	66.6
4,7-DT-10	+0.0187	544	−456	45.6
3,8-DT-10	−0.0545	514	−486	48.6
2,9-DT-10	−0.1122	490	−510	51.0
4,9-DT-12	+0.3073	622	−538	44.8

* DT = dithia; TT = trithia; 2,8-DT-9 = 2,8-dithianonane.

TABLE VII

RETENTION OF ALICYCLIC THIA COMPOUNDS

Nos. 1–8: column, 25 cm × 3 mm I.D. MicroPAK CH10; eluent, methanol–water (70:30). Nos. 9–12: column, RadPAK A; eluent, 100% methanol.

No.	Compound	ln k′	I_K	ΔI_K
1	cyclopentane	1.4337	431	−69
2	thiolane (S)	0.2810	201	−299
3	dithiolane (S, S)	0.0880	163	−337
4	cyclohexane	1.8671	517	−83
5	1,3-dithiane (S, S)	0.0835	162	−438
6	1,4-dithiane (S, S)	0.2659	198	−402
7	methylcyclohexane (CH$_3$)	2.2875	600	−100
8	cyclohexanethiol (SH)	1.3172	407	−293
9	bicyclohexyl	0.7239	1182	−18
10	(CH$_2$)$_2$ bridged dicyclohexyl	1.0530	1350	−50
11	dicyclohexyl sulphide (S)	0.4331	940	−360
12	dicyclohexyl disulphide (S$_2$)	0.6195	1032	−368

Some thermodynamic data relevant for sorption are given in Table IV. Since they were obtained over a narrow range of temperatures, they should be considered as fairly crude approximations. It is probably more instructive to compare the data of corresponding compounds with identical skeleton atom number. This is done in Table V for n(skeleton) = 9.

Possibly the ΔS values are all somewhat too negative, owing to an error in the phase ratio determination, but this error would be the same for all six solutes. It is seen that the sorption enthalpy is more negative for the methyl heptyl sulphide than for the dibutyl sulphide. However, the sorption entropy is also more negative. Consequently, the ln k′ difference is not large, but is nevertheless clearly evident. It should be noted that the solutes with the longest non-interrupted alkyl chain have the most negative sorption entropy. This holds even for the alcohol. The sorption enthalpy is influenced by both functionality and remaining chain length.

(c) Multisulphides. Thia compounds containing two or more non-vicinal sul-

phur atoms are called multisulphides[15] in contrast to the polysulphides, which consist of sulphur chains with organic terminal groups. Some retention data are given in Table VI. It is seen that two isolated thioether functions within one molecule lower retention roughly twice as much as a single function. In the trithianonane the retention loss is not quite triple the usual thioether value.

The retention loss, ΔI_K, obviously depends on the size of the solute molecule and on the substitution sites within it. In the series with sulphur atoms in the 2 and (ω − 1) positions, I_K goes almost linearly from − 385 for 2,5-dithiahexane to − 510 for 2,9-dithiadecane. Relative to the retention index of the parent alkane, however, it drops from 64.2% to 51%.

Within one group of compounds with the same skeleton atom number, the effect of the substitution site may be studied. For the nonanes, the retention index drops from 486 to 429 if the sulphur atoms are shifted from the 4 and 6 positions to the 3 and 7 positions. Another shift to 2 and 8 decreases the retention only slightly. Basically the same changes of retention are observed with the decanes.

If the central methylene group in 2,8-dithianonane is also substituted by sulphur, another retention decrease from I_K = 426 to I_K = 301 is observed. It should be noted that in this case a solute molecule with nine skeleton atoms, but with neither an extraordinarily high dipole moment nor a pronounced ability to form hydrogen bonds, exhibits a retention that would be anticipated for propane.

Alicyclic systems. Within alicyclic systems, thia substitution produces retention effects very similar to those observed in alkane chains. Some examples are given in Table VII. Thia substitution in cyclopentane, to yield tetrahydrothiophene, causes a retention decrease of 230 index units, which is quite normal for a thioether. Introduction of another sulphur atom causes a further decrease of only 38 units. Similar effects are seen for the cyclohexanes. If the methyl group in methylcyclohexane is replaced to yield cyclohexanethiol, the retention loss is 193 units; this value is in the range observed for *n*-alkanethiols.

Placing a sulphur atom between the rings of bicyclohexyl lowers the retention by 242 units, and the same change is observed on going from dodecane to di-*n*-hexyl thioether. The results indicate that retention effects of thia substitution in aliphatic systems are not measurably influenced by a cyclic structure.

The influence of aromatic groups

The addition of SH to a benzene ring, yielding thiophenol, produces almost no retention change. This behaviour is entirely different from that observed with alkanes, where the addition of SH to *n*-hexane causes a retention drop from 600 to 504 units.

Table VIII shows some examples of thia substitution between aromatic groups. Going from diphenylmethane to diphenyl sulphide, one observes a retention increase of 30 index units, from fluorene to dibenzothiophene of 36 units, from dihydroanthracene to thianthrene of 33 units. A few more aromatic thia compounds, not listed in Table VIII, have been investigated, and in every case an increase of retention was observed instead of a decrease as expected from the behaviour of aliphatic compounds. It seems to be generally true that thia substitution between aromatic systems increases retention.

If the sulphur atom is bonded to one aliphatic and one aromatic group, a

TABLE VIII

RETENTION OF AROMATIC SULPHUR COMPOUNDS

Eluent, methanol–water (70:30); column, 30 cm × 3 mm I.D. MicroPAK CH10; temperature, 24°C.

Solute	t_{ms}	ln k'	I_K
Benzene	5.44	0.5048	245
Toluene	7.09	0.9050	325
Thiophenol	5.36	0.4801	241
Ethylbenzene	9.55	1.3052	405
Methylphenyl-S	7.11	0.9089	326
Benzylmercaptane	5.97	0.6512	275
Biphenyl	14.42	1.8078	505
Diphenylmethane	14.94	1.8491	513
Diphenylsulfide	17.02	1.9992	543
Diphenylethane	22.33	2.3035	604
Diphenyldisulfide	26.93	2.5083	644
Fluorene	18.94	2.1201	567
Dibenzothiophene	21.40	2.2564	594
Anthracene	25.26	2.4387	630
Dihydroanthracene	20.04	2.1834	580
Thianthrene	23.34	2.3522	613

retention decrease is observed, which, however, is less than half the loss in the case of two aliphatic groups.

Local polar centres

So far, the following observations have been stated:

(1) In sulphur rings and in the chains of polysulphanes, a sulphur atom produces more retention than a methylene group in an alkane. The excess retention depends on the eluent composition and is highest in 100% methanol.

(2) In aliphatic solutes, replacement of a methylene group by a sulphur atom produces a retention decrease that corresponds to the loss of two or three skeleton atoms. This effect is not altered by a cyclic structure of the aliphatic residues.

(3) The amount of retention loss on thia substitution depends on the location of the substitution site within the solute molecule.

(4) Multiple isolated thia substitution effects are additive as long as the sites are far apart.

(5) No retention decrease is observed if thia substitution occurs between aromatic systems.

Furthermore, it must be emphasized that thia substitution does not introduce any remarkable dipole moments. The permanent dipole moments of thioethers and thiols are all ca. 1.5–1.6 debye, far too small to cause retention changes of the observed magnitude.

The hydrogen bonding ability of thiols is very low; the bond energy does not appreciably exceed that of common Van der Waals interactions.

All these observations indicate that around the site of thia substitution a local polar centre is created, most probably under the polarizing influence of the surrounding polar eluent. Since a strong retention decrease is observed only (and always) when

aliphatic protons are found in the immediate vicinity of the sulphur atom, one has to assume that the local polar centres consist of the sulphur atom and, at least, one neighbouring group carrying aliphatic hydrogen, plus several solvating eluent molecules. The creation of such localized "solvation patches" would shield the covered part of the solute molecule against any solvophobic expulsion forces, making that part quasi-solvophilic. Besides an increased direct solute–solvent interaction, the loss of free energy of cavity formation for the respective parts of the solute molecule would also counteract solvophobicity, thus decreasing retention.

The ΔI_K values of thiols and dithiols indicate that a terminal polar centre comprises *ca.* two skeleton atoms:

$$HS-CH_2-CH_2-CH_2-R \quad HS-CH_2-CH_2-R'-CH_2-CH_2SH$$
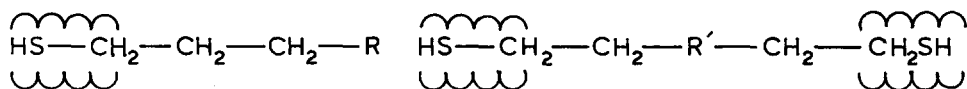
where the wavy lines symbolize the "solvation patches". In thioethers the solvation patch covers two to three skeleton atoms:

$$R-CH_2-CH_2-S-CH_2-CH_2-R$$
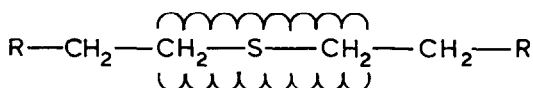
This is consistent with the observed retention decrease of $\Delta I_K = 200\text{--}300$.

The effect of solvation patch formation is not strictly localized. It also has some influence on the retention increment of methylene groups farther away. This is to be expected, for two reasons. One is that the local polar centre will have an inductive effect on neighbouring methylene groups, as a result of which they will experience a slightly stronger interaction with the eluent. The other is thought to be some orientation of adjacent eluent molecules by the solvation patches, which will decrease their ability to exert the solvophobic effect. Both effects together decrease the retention contribution of methylene groups non-vicinal to the sulphur atom.
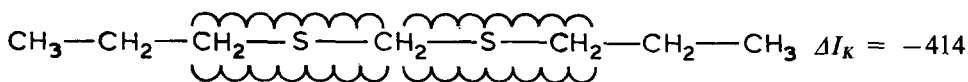
The extent to which methylene retention is lowered depends on the water content of the eluent. In 95% methanol $I_K(CH_2)$ is 83.3 for dithiols and 88.5 for terminal monothiols. The thioether value lies in between. In 55:45 methanol–water the respective values are 98.5 for RSH, 95.2 for meSR, and 92.8 for R_2S. Here it is clearly seen that the effect on $I_K(CH_2)$ is lowest when the remaining alkyl chain is longest.

Obviously the methylene retention approaches the alkane value of 100 if the eluent composition approaches 100% water. The overall retention decrease, ΔI_K, of thia-alkane solutes does not change much in the region from 100% methanol to 55% methanol. This indicates that considerable amounts of water can be involved in solvation patch formation.

The influence of the relative location of substitution sites can be seen in the dithianonanes, for example. In 2,8-dithianonane the local polar centres are as far apart as possible and do not interfere

$$CH_3-S-CH_2-CH_2-CH_2-CH_2-CH_2-S-CH_3 \quad \Delta I_K = -471$$
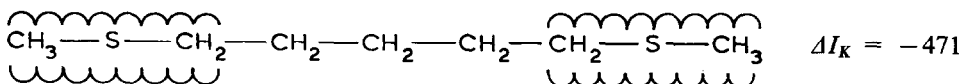
In 4,6-dithiahexane there is some interference

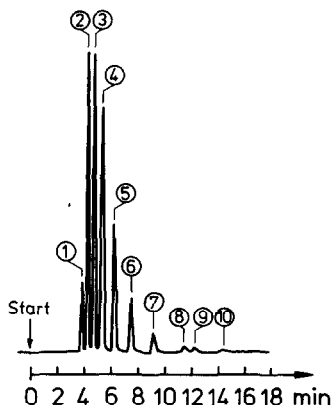$$CH_3-CH_2-CH_2-S-CH_2-S-CH_2-CH_2-CH_3 \quad \Delta I_K = -414$$

Fig. 14. Chromatogram of dimethyl polysulphides. Peaks 1 to 8 are Me_2S_2 to Me_2S_9, peak 9 is S_8 (impurity), peak 10 is Me_2S_{10}. Eluent, methanol–water (95:5); column, RadPAK $5\mu C_{18}$ (taken from ref. 17).

and the retention loss per centre drops to 207 units.

This trend is continued in 4,5-dithianonane (propyl butyl disulphide):

$$CH_3\text{—}CH_2\text{—}CH_2\text{—}S\text{—}S\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_3 \quad \Delta I_K = -285$$
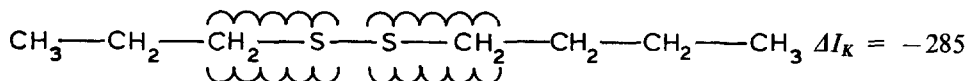
It is obvious that the retention-decreasing effect of this substitution is less the closer the sulphur atoms are located, because their spheres of influence within the alkyl chain are mutually diminished.

In 2,5,8-trithianonane

$$CH_3\text{—}S\text{—}CH_2\text{—}CH_2\text{—}S\text{—}CH_2\text{—}CH_2\text{—}S\text{—}CH_3 \quad \Delta I_K = -599$$
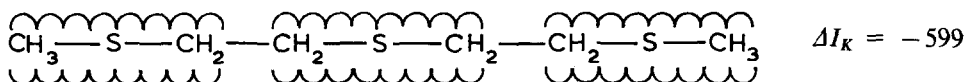
the solute molecule is completely solvated. The sorption enthalpy is very small, even positive, in 100% methanol. The surprisingly low retention (corresponding to that of propane) is mainly supported by the positive sorption entropy.

Polysulphides

Polysulphides, RS_nR' ($n \geq 2$) consist of sulphur chains with organic terminal groups. The longest chain identified by RPLC is the $nC_3S_{21}nC_3$, but we are sure that even longer chains exist.
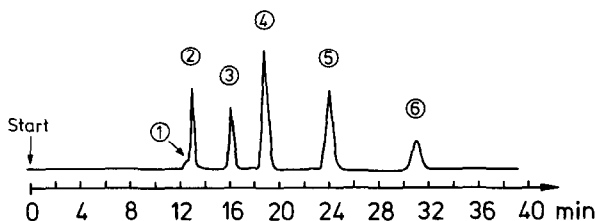

Fig. 15. Chromatogram of di-*n*-hexyl polysulphides. Peaks 1 and 3–6 are Hex_2S_2 to Hex_2S_6, peak 2 is S_8 (impurity). Eluent, methanol–water (95:5); column RadPAK $5\mu C_{18}$ (taken from ref. 17).

TABLE IX

OBSERVED RETENTION INDICES, I_K, OF ALKYL POLYSULPHIDES R_2S_n

Eluent, methanol–water (95:5); column, 10 cm × 8 cm, RadPAK $5\mu C_{18}$; temperature, 26°C.

n_S	R group					
	Me	Et	n-Pr	n-Bu	n-Pe	n-Hex
2	153	338	529	721	899	1077
3	312	477	670	848	1025	1206
4	422	582	763	935	1106	1283
5	552	713	888	1056	1225	1400
6	679	839	1010	1178	1345	1516
7	807	967	1136	1301	1466	1637
8	934	–	1259	1425	–	–
9	1058	–	1385	–	–	–
10	1182	–	–	–	–	–

The retention of polysulphides is determined by the lengths of both the sulphur chain and the terminal alkyl chains. Basically, it can be deduced from the retention effects of alkanes, polysulphanes, and local polar centres.

Fig. 14 shows a chromatogram of the dimethyl polysulphides from Me_2S_2 to Me_2S_{10}. The peak sequence looks like a homologous series, except for peak No. 9 which is due to S_8. A chromatogram of a polysulphide with longer terminal groups, di-n-hexyl polysulphide, is shown in Fig. 15. Owing to the hexyl groups, retention times are much longer. The S_8 impurity peak is now found just behind that of the disulphide.

It is evident that in the group of all n-aliphatic polysulphides, R_2S_n, two different kinds of homology can be found. First, with a constant sulphur chain length, n_S, the length of the alkyl chains, n_C, can be varied —what we call C-homology. Second, for a constant n_C of the terminal groups, the sulphur chain length, n_S, can be varied— what we call S-homology.

In Table IX, a set of experimentally determined retention indices of dialkyl polysulphides is shown. They are based on the alkane retention equation for the chromatographic system in use

$$\ln k'(\text{alk}) = -1.3606 + 0.2406 n_C \quad (r = 0.999995) \tag{26}$$

The C-homologous series can be described as

$$I_K = A_C + B_C n_C \tag{27}$$

where A_C and B_C are linear functions of the sulphur atom number, n_S. The corresponding expression for the S-homologues is

$$I_K = A_S + B_S n_S \tag{28}$$

with A_S and B_S being linear functions of the carbon atom number, n_C. A simultaneous regression of the data in Table IX after n_C and n_S, yields for this particular chromatographic system,

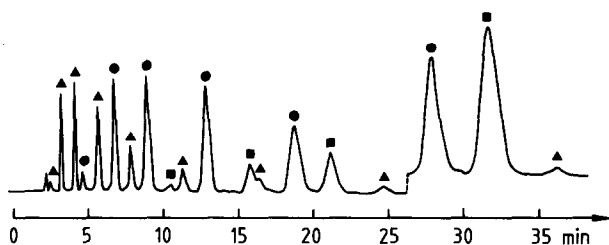$$I_K = -227 + 121.2 n_S + 86.0 n_C \quad (r = 0.999) \tag{29}$$

Fig. 16. Chromatogram of dimethyl polysulphides (▲), methyl butyl polysulphides (●) and dibutyl poly-sulphides (■). Eluent methanol–water (85:15); flow-rate, 1.5 μl/min; column, RadPAK $5\mu C_{18}$ (taken from ref. 18).

This equation allows us to calculate the retention of any arbitrary dialkyl polysul-phide within 1% relative standard deviation. The dimethyl compounds show some-what larger deviations, as is usual for the first member of a series.

Polysulphides with different end-groups, RS_nR', can also be separated. This is demonstrated in Fig. 16 for a mixture of Me_2S_n, $MeBuS_n$, and Bu_2S_n.

The effect of an increasing degree of vicinal thia substitution within a molecule of given skeleton atom number can be seen in Fig. 17. The I_K values of tetradecane and various substitution products are shown as a function of the sulphur atom num-ber, n_S. Tetradecane itself has an I_K of 1400, by definition. In going to the hexyl heptyl sulphide, a large drop of retention to ca. 1060 is observed, owing to the crea-tion of a local polar centre. The polar centre in dihexyl disulphide
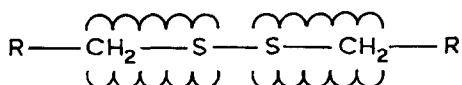
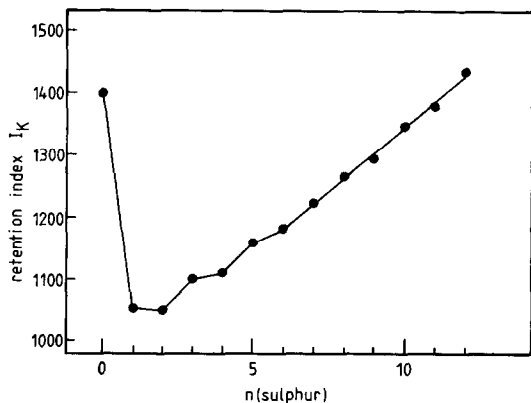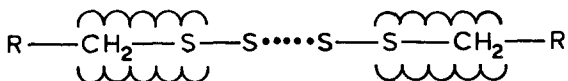has virtually the same effect. When more sulphur atoms are introduced, the centre is split:

Fig. 17. Retention index, I_K, versus sulphur atom number of tetradecane, heptyl hexyl thioether and polysulphides with skeleton atom number 14. Eluent, methanol–water (95:5); column, RadPAK $5\mu C_{18}$.
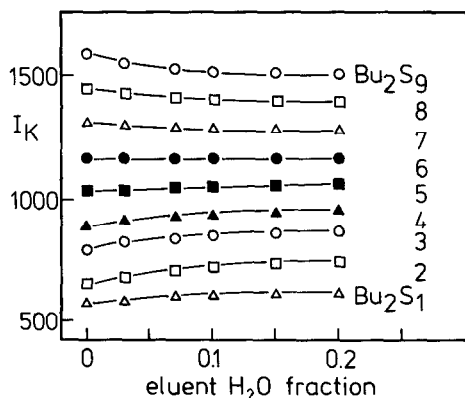
Fig. 18. Retention index of dibutyl sulphide to dibutyl nonasulphide *versus* water content of aqueous methanol. Column, RadPAK $5\mu C_{18}$.

The extent of solvation patch formation does not increase. Instead, the sulphur atoms between the local polar centres, being fairly undisturbed, contribute some additional retention. Consequently, retention is again increased. Between $EtS_{11}Me$ and $MeS_{12}Me$ the excess retention introduced by the sulphur atoms overcompensates for the initial retention loss, and I_K exceeds the value of 1400.

A closer look at the retention of the lower polysulphides reveals a distinct alternation, the I_K values of even n_S solutes being low, and those of odd n_S solutes being high. This is caused by the alternation of the permanent dipole moments of dialkyl polysulphides, which are high for even n_S and low for odd n_S:

$$\mu(S_1) = 1.5, \; \mu(S_2) = 1.96, \; \mu(S_3) = 1.65, \; \mu(S_4) = 2.16$$

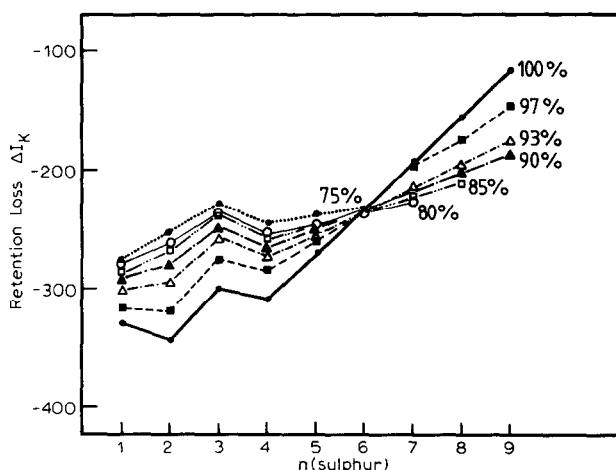The higher dipole moments of disulphides and tetrasulphides strengthen the

Fig. 19. Retention loss, ΔI_K, *versus* sulphur atom number of dibutyl polysulphides for some eluent compositions from 100% methanol to methanol-water (75:25); column, RadPAK $5\mu C_{18}$.

interaction with the polar eluent, thus decreasing retention. It is obvious that changes in the permanent dipole moment do not have very marked consequences for retention. For $n_S > 5$ the dipole moment effect vanishes, owing to the helical shape of polysulphide chains.

The influence of eluent composition on polysulphide retention can be seen in Fig. 18, which shows the retention indices of di-n-butyl polysulphides as a function of the water percentage of the eluent. From monosulphide to pentasulphide there is an increase of I_K with increasing water content of the eluent. The hexasulphide I_K is unaffected by the eluent composition. The I_K values of the higher sulphides decrease with increasing water content, indicating a similarity with sulphur rings or polysulphanes.

The combined influence of eluent composition and dipole moment changes is evident from Fig. 19. The ΔI_K values of di-n-butyl polysulfide are shown as a function of the sulphur atom number, n_S, with the methanol percentage of the eluent as an additional parameter. The strongest ΔI_K changes are seen with 100% methanol as eluent. The ΔI_K change from mono- to disulphide is negative for 100% to 95% methanol, and positive for smaller percentages. At 95% methanol the change is zero. At Bu_2S_6 all the curves intersect.

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