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DETERMINATION OF THE ENERGY OF INTERMOLECULAR INTERACTIONS IN GAS CHROMATOGRAPHY FROM RETENTION INDICES*

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SUMMARY

The nature of the coefficients in the linear dependence of a partial molar free energy of solution on a retention index value for all substances analyzed on a stationary phase has been ascertained. A simple procedure for estimating the difference of intermolecular interaction energies after replacement of *n*-alkyl radicals with isoalkyl or unsaturated radicals in aliphatic sulphides and disulphides has been evaluated. Variations of intermolecular interaction energies of the functional group in metameric thiatridecanes with the displacement of the S atom into the carbon chain have been determined.

INTRODUCTION

The retention of substances being analysed on various stationary phases under isothermal conditions is determined by the partial molar free energy of solution, ΔG, which depends on the molecular structure of the substance and on the stationary phase and the nature of their intermolecular interaction. The greater the value of ΔG, the greater is the polarity of the stationary phase with respect to the substance being analysed and the higher is the energy of intermolecular interaction between the stationary phase and the substance. According to this point of view, "non-polar" stationary phases do not exist[1]. To determine the polarity of the stationary phase it is necessary to obtain information on its capacity for various intermolecular interactions, primarily non-specific interactions of a physical nature, such as dispersive (d), inductive (in) and orientative (o) and specific interactions of a chemical nature, such as donor–acceptor (d–ac) including the hydrogen bond. In the general case, the partial molar free energy of solution is the sum of the energies of all kinds of intermolecular interactions:

$$\Delta G = \Delta G_d + \Delta G_{in} + \Delta G_o + \Delta G_{d-ac} \quad (1)$$

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The interpretation of polarity in gas chromatography differs from that accepted in physical chemistry. Completely "non-polar" phases do not exist, because all of them interact inductively with substances that have large dipole moments, *e.g.*, with nitropropane (dipole moment $\mu = 3.6$ D). Other examples are benzene and *p*-dinitrobenzene, which have no dipole moments but are capable of forming π-complexes with some polar stationary phases, and the polar component will account for a considerable proportion of the total free energy of solution:

$$\Delta G = \Delta G_d + (\Delta G_{in} + \Delta G_{d-ac})$$

Thus, as distinct from the concepts established in physical chemistry, from the gas chromatographic point of view *p*-dinitrobenzene and benzene are polar compounds.

In our opinion, polarity in chromatography must be determined by the capacity for various intermolecular interactions and measured quantitatively in the values of ΔG. As it is impossible to find one substance that is capable of undergoing simultaneously all of the possible kinds of intermolecular interactions with the stationary phase, six parameters have been proposed[1–3] for evaluating the polarity: the partial molar free energy of the solution of the *n*-alkane methylene group (ΔG^{CH_2}) and the ΔG values of McReynolds' five test substances. To estimate the polarity of the stationary phase, the ΔG values are calculated from the equation previously proposed by us[4]:

$$\Delta G = -2.3\,RT\left[\frac{I_x - 100n}{100} \cdot b + \log\left(\frac{V_{gn}\varrho T}{273}\right)\right] \qquad (2)$$

where I_x is the retention index of a substance, ϱ is the density of the stationary phase at the temperature of analysis (T°K); V_{gn} is the specific retention volume of an *n*-alkane with n carbon atoms, which is given by the equation

$$\log V_{gn} = a + bn \qquad (3)$$

where a and b are coefficients, with b being easily determined from

$$b = \log V_{g(n+1)} - \log V_{gn} \qquad (4)$$

It should be emphasized that polarity estimated from ΔG values, as compared with retention indices, makes it possible to obtain quantitative information on the capacity of a substance to enter into intermolecular interactions with the stationary phase. For example, the retention indices of butanol-1 on DEGA and Carbowax 1000 are almost identical (1197 and 1193, respectively), but the energies of their intermolecular interaction with these phases are different (—3080 and —3630 cal/mole, respectively)[3].

The proposed system of polarity evaluation from eqn. 2 is universal and does not require the selection of a stationary phase with "zero polarity".

In this work, eqn. 2 has been used for the following:

(a) to ascertain the nature of the coefficients in the linear dependence of the retention index on the partial molar free energy of solution;

(b) to determine how the energy of intermolecular interactions of the functional group in metameric thiatridecanes varies with the displacement of the S atom into the carbon chain;

(c) to evaluate the change in the energy of dispersive interaction resulting

from *n*-alkyl radicals being replaced with isoalkyl radicals in aliphatic sulphides and disulphides.

EXPERIMENTAL

The gas chromatographic analysis of sulphides and disulphides with alkyl, isoalkyl and unsaturated radicals listed in Tables I–IV was performed on a Pye Unicam 104 chromatograph equipped with a flame-ionization detector. Glass columns (210 × 0.4 cm) were packed with silanized Chromosorb W AW DMCS (80–100 mesh) (Johns-Manville, Denver, Colo., U.S.A.) with 5% of stationary phase Apiezon M (Ap-M) and polyethylene glycol 1000 (PEG-1000). The columns were conditioned for 50 h at 250 °C for Ap-M and at 155 °C for PEG-1000. Samples (0.5 μl of substance vapour) were injected with a Hamilton syringe into the upper layer of the chromatographic support. The temperature of analysis was 130 °C and the flow-rate of the carrier gas (high-purity nitrogen) was varied within the range 10–100 ml/min.

The retention of sulphur-containing substances, as expressed by the Kovàts retention index relative to C_7–C_{18} *n*-alkanes, was determined. The retention indices for the investigated compounds have been published previously[5,6]. To obtain the thermodynamic functions of solution, the retention volume, V_g, for *n*-decane was determined from the equation[7]

$$V_g = \frac{273\, t' v}{w T_r} \cdot j \left(1 - \frac{P^0_{H_2O}}{P_0}\right)$$

where

t' is the corrected retention time for decane;

v is the bulk flow-rate of nitrogen carrier gas measured at room temperature with a foam flow-rate meter;

w is the mass of stationary phase in the column;

T_r is room temperature (°K);

j is a factor taking into account the pressure drop in the column:

$$j = \frac{3}{2}\left[\frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1}\right]$$

where P_i is the pressure at the column inlet and P_0 is the pressure at the column outlet; and

$$\left(1 - \frac{P^0_{H_2O}}{P_0}\right)$$

is the correction for water vapour pressure at room temperature.

Values of V_g for *n*-decane on Apiezon M and PEG-1000, the values of the b coefficients in eqn. 3 and the densities of the stationary phases at 130 °C are as follows: Apiezon M, V_g (*n*-decane) = 151.7 ml/g, $b = 0.270$ and $\varrho = 0.840$ g/cm³; PEG-1000, V_g (*n*-decane) = 21.9 ml/g, $b = 0.211$ and $\varrho = 1.086$ g/cm³. The densities were calculated from ϱ at 20 °C (ref. 8) with the coefficient of volume expansion, $\alpha = 0.001$ cm³/°C (ref. 9), taken into account.

RESULTS AND DISCUSSION

Kovàts[10,11] was the first to point out the dependence of the retention index on the free energy of solution; later this dependence was shown[12] experimentally and expressed by the equation

$$\Delta G = BI_x + A \tag{5}$$

which is valid for all substances analysed on a given stationary phase at a constant temperature and with retention indices within the linear range of *n*-alkanes, described by eqn. 3. In order to understand the physical meaning of the coefficients *A* and *B* in eqn. 5, we shall transform eqn. (2) into

$$\Delta G = -2.3\,RT \cdot \frac{b}{100} \cdot I_x - 2.3\,RT\left[\log\left(\frac{V_{gn}\varrho T}{273}\right) - b \cdot n\right] \tag{6}$$

Taking into account that, for the *n*-alkanes used to calculate the retention index, the partial molar free energy of solution of the methylene unit is expressed[2] by

$$\Delta G^{CH_2} = -2.3\,RTb \tag{7}$$

we shall obtain, after substituting eqn. 7 into eqn. 6,

$$\Delta G = (\Delta G^{CH_2}/100)I_x - 2.3\,RT\left[\log\left(\frac{V_{gn}\varrho T}{273}\right) - bn\right] \tag{8}$$

From eqn. 8, it follows that *A* and *B* depend on the gas chromatographic characteristics of *n*-alkanes on the investigated stationary phase:

$$B = \Delta G^{CH_2}/100 = \Delta G_{1.u.} \tag{9}$$

As can be seen from eqn. 9, *B* is the free energy corresponding to 1 retention index unit, calculated from the value of *b* determined from eqn. 3 or 4. Using eqn. 8 we shall express *A* as

$$A = -2.3\,RT\left[\log\left(\frac{V_{gn}\varrho T}{273}\right) - bn\right]$$

and eqn. 5, with eqn. 9 being taken into account, will then be written as follows:

$$\Delta G = \Delta G_{1.u.} I_x + A \tag{10}$$

If

$$\Delta G_{1.u.} I_x = \Delta G_{I_x} \tag{11}$$

we obtain

$$\Delta G = \Delta G_{I_x} + A \tag{12}$$

From eqn. 12, it follows that *A* can be found experimentally for every stationary phase by analysing *n*-alkanes only. From the specific retention volume, V_{gn}, according to the well known equation[13]

$$\Delta G = -2.3\,RT\log\left(\frac{V_{gn}\varrho T}{273}\right) \tag{13}$$

we find the value of the partial molar free energy of solution of an *n*-alkane in the stationary phase. From eqns. 7 and 9 we find $\Delta G_{1.u.}$ and calculate the partial molar free energy of solution equivalent to the retention index for an *n*-alkane (ΔG_{I_x}), and then from eqn. 12 determine *A*:

$$A = \Delta G - \Delta G_{I_x} \tag{14}$$

It can be seen from eqn. 14 that *A* in eqn. 5 represents the difference between the energy calculated from the retention index based on the energy corresponding to 1 retention index unit ($\Delta G_{1.u.}$) as obtained from *n*-alkanes and the free energy of solution determined from the specific retention volume. From eqns. 9–12 it follows that, knowing the value of I_x and that of *b* for *n*-alkanes, one can calculate the partial molar free energy of solution for any substance *x*. The value of ΔG_{I_x} is always greater than ΔG, and, therefore, *A* is always positive: it is the energy having the sign opposite to that of the free energy of solution. Experimental verification of eqn. 14 has been performed on aliphatic and cyclic sulphides, mercaptans, aromatic sulphur-containing compounds[4,14] and methyl esters of fatty acids[15]. The equations obtained for sulphur-containing compounds on Apiezon M and PEG-1000 at 130 °C and for fatty acid methyl esters on SE-30 and Silar 5CP at 200 °C have the following form:

$$\Delta G^{130}_{Ap} = -4.98\, I_x + 793 \tag{15}$$

$$\Delta G^{130}_{PEG} = -3.89\, I_x + 1052 \tag{16}$$

$$\Delta G^{200}_{SE\text{-}30} = -3.35\, I_x + 751 \tag{17}$$

$$\Delta G^{200}_{Sil.5CP} = -3.00\, I_x + 1046 \tag{18}$$

As shown by the results, coefficients *A* and *B* in eqn. 5 are therefore dependent only on the gas chromatographic characteristics of the *n*-alkanes used for the calculation of the retention index. *B* is the free energy corresponding to 1 retention index unit, but the physical meaning of *A* is not clear. Possibly, *A* is the energy expended by *n*-alkanes to overcome the surface tension of the stationary phase. In 1962 Anvaer *et al.*[16] indicated that the free energy of solution includes not only the energies of dispersive, orientative, inductive and specific interactions, but also the energy expended to move apart the solvent molecules. The magnitude of this energy depends on the shape of the molecule of the dissolved substance and the surface tension of the stationary phase. Later, a similar idea was put forward by Sakharov and co-workers[17,18]. However, for *A* to be regarded as the energy expended on the penetration of the molecule into the stationary phase layer it is necessary to conduct additional special investigations.

Eqn. 2 makes it possible to obtain data for thermodynamic calculations of the contributions made by the individual units or functional groups of the substances being analysed to the partial molar free energy of solution. As it follows from eqn. 2, for two substances, *i* and *j*, analysed on one stationary phase at a given temperature, the difference between their partial molar free energies of solution can be calculated[9] from the equation

$$\delta(\Delta G)_{ij} = -0.023\, RTb\delta\, I_{ij} = (\Delta G^{CH_2}/100)\, \delta\, I_{ij} \tag{19}$$

TABLE I

VARIATION OF FREE ENERGY OF SOLUTION, $\delta(\Delta G)_{n,iso}$, WITH THE REPLACEMENT OF *n*-ALKYL RADICAL WITH ISOALKYL RADICAL IN SULPHIDES AND DISULPHIDES

n-RX-*n*-R'–*n*-RX-*iso*-R'			Ap-M, 130°, $\Delta G_{t.u.} = -4.98$ cal/mole				PEG-1000, 130°, $\Delta G_{t.u.} = -3.89$ cal/mole			
n-R	*n*-R'	*iso*-R'	$\delta I_{n,iso}$		$-\delta(\Delta G)_{n,iso}$ (cal/mole)		$\delta I_{n,iso}$		$-\delta(\Delta G)_{n,iso}$ (cal/mole)	
			X = S	X = S_2	X = S	X = S_2	X = S	X = S_2	X = S	X = S_2
Ethyl	*n*-Propyl	Isopropyl	48	41	239	205	58	55	226	214
Propyl	*n*-Propyl	Isopropyl	49	44	244	219	55	60	214	234
Butyl	*n*-Propyl	Isopropyl	49	42	244	209	59	59	230	230
Amyl	*n*-Propyl	Isopropyl	49	43	244	214	62	62	242	242
Ethyl	*n*-Butyl	Isobutyl	43	45	214	224	57	64	222	249
Propyl	*n*-Butyl	Isobutyl	44	46	219	229	56	65	218	253
Butyl	*n*-Butyl	Isobutyl	44	47	219	234	57	66	222	257
Amyl	*n*-Butyl	Isobutyl	45	—	224	—	59	—	230	—
Ethyl	*n*-Butyl	*sec.*-Butyl	43	39	214	194	53	52	207	203
Propyl	*n*-Butyl	*sec.*-Butyl	44	41	219	204	56	56	218	218
Butyl	*n*-Butyl	*sec.*-Butyl	47	—	234	—	59	—	230	—
Amyl	*n*-Butyl	*sec.*-Butyl	48	—	239	—	62	—	242	—
Ethyl	*n*-Butyl	*tert.*-Butyl	101	97	503	483	128	128	498	498
Propyl	*n*-Butyl	*tert.*-Butyl	103	95	513	473	128	133	498	518
Butyl	*n*-Butyl	*tert.*-Butyl	105	99	520	495	131	134	510	522
Amyl	*n*-Butyl	*tert.*-Butyl	106	—	525	—	135	—	526	—
Ethyl	*n*-Amyl	Isoamyl	38	41	189	204	44	54	171	210
Propyl	*n*-Amyl	Isoamyl	39	40	194	199	44	55	171	214
Butyl	*n*-Amyl	Isoamyl	39	—	194	—	46	—	179	—
Amyl	*n*-Amyl	Isoamyl	39	—	194	—	46	—	179	—
Ethyl	*n*-Amyl	*sec.*-Amyl	64	62	319	309	87	83	339	323
Propyl	*n*-Amyl	*sec.*-Amyl	68	67	339	334	90	86	350	335
Butyl	*n*-Amyl	*sec.*-Amyl	71	—	354	—	94	—	362	—
Amyl	*n*-Amyl	*sec.*-Amyl	72	—	359	—	96	—	370	—
Ethyl	*n*-Amyl	*tert.*-Amyl	79	77	393	384	100	103	389	401
Propyl	*n*-Amyl	*tert.*-Amyl	83	79	413	393	105	103	409	401
Butyl	*n*-Amyl	*tert.*-Amyl	87	—	433	—	110	—	428	—
Amyl	*n*-Amyl	*tert.*-Amyl	87	—	433	—	113	—	440	—

where δI_{ij} is the difference between the retention indices of substances i and j and b is determined from eqn. 3 or 4.

Eqn. 19 enables one to determine the energy difference in the forces of intermolecular interactions of the two compared substances, which makes it possible to evaluate the energy contributions of different structural units of a molecule or of a functional group to the free energy of solution.

Eqn. 19 was used by us to ascertain the differences in the energy of dispersive interaction with the polar and non-polar stationary phases of alkyl radicals with normal and iso structures, as exemplified by aliphatic sulphides and disulphides.

Table I shows the values calculated for the partial molar free energies of solution, $\delta(\Delta G)_{n,iso}$, for di-*n*-alkyl sulphides and their isomeric *n*-alkyl isoalkyl sulphides in Apiezon M and PEG-1000. If we compare the variation of the $\delta I_{n,iso}$ values on Apiezon M and PEG-1000 it appears that the contribution of the radicals is different and depends on the polarity of the stationary phase. In fact, this is not so. If the energy corresponding to 1 retention index unit is taken into account, it turns out that a change in the free energies of solution caused by the iso radical replacing the normal radical, $\delta(\Delta G)_{n,iso}$, is virtually the same on both the polar and the non-polar stationary phase in sulphides and disulphides (see Table I).

Similar results were obtained by the analysis of di-*n*-alkyl disulphides and their isomeric *n*-alkyl isoalkyl disulphides. With the replacement of the normal radical with the iso radical in disulphides, as well as in sulphides, the value of $\delta(\Delta G)_{n,iso}$ is seen to be specific for each radical and to be virtually the same on both the polar and the non-polar stationary phases (see Table I).

Comparison of the data in Table I makes it possible to draw the conclusion that $\delta(\Delta G)_{n,iso}$ represents mainly the change in the energy of dispersive interaction of iso radicals (as compared with normal radicals) with the polar and the non-polar stationary phase, which does not depend on the nature of the functional group, –S– and $-S_2-$. It should also be noted that the energy of dispersive interaction decreases with increasing branching of the radical. For example, for both sulphides and disulphides, the replacement of *n*-butyl with *tert.*-butyl results in a reduction in the free energy of solution of 473–525 cal/mole in Apiezon M and 498–526 cal/mole in PEG-1000. The less branched is the radical, the lower is the value of $\delta(\Delta G)_{n,iso}$, *e.g.*, when *n*-amyl is replaced with isoamyl, the observed change in the intermolecular interaction is only 189–204 cal/mole with Apiezon M and 171–214 cal/mole with PEG-1000. This may be associated with the formation of a greater number of contacts of the normal radicals with the stationary phase molecules than of the more compact iso radical, which reduces the energy of intermolecular interaction of the latter with the stationary phase. It is extremely interesting to study the nature of the variations of $\delta(\Delta G)_{n,iso}$ and, in our opinion, this will be useful in elaborating the theory of solutions.

A gas chromatographic study of sulphides and disulphides with alkyl radicals containing a double and a triple carbon–carbon bond made it possible to obtain data on the variation of the energy of intermolecular interaction of unsaturated radicals with polar and non-polar stationary phases. Table II gives the values of $\delta(\Delta G)_{n,unsat.}$ for sulphides and disulphides. The replacement of *n*-ethyl and *n*-propyl with vinyl and allyl radicals, respectively, results in a very slight change in the energy of intermolecular interaction with the non-polar stationary phase. The picture changes

TABLE II

VARIATION OF FREE ENERGY OF SOLUTION, $\delta(\Delta G)_{n,unsat.}$, WITH THE REPLACEMENT OF *n*-ALKYL RADICAL BY UNSATURATED RADICAL IN SULPHIDES AND DISULPHIDES

n-RX-*n*-R′–*n*-RX-*unsat.*-R′			Ap-M, 130°, $\Delta G_{t.u.} = -4.98$ cal/mole				PEG-1000, 130°, $\Delta G_{t.u.} = -3.89$ cal/mole			
n-R	*n*-R′	*unsat.*-R′	$\delta I_{n,unsat.}$		$-\delta(\Delta G)_{n,unsat.}$ (cal/mole)		$\delta I_{n,unsat.}$		$-\delta(\Delta G)_{n,unsat.}$ (cal/mole)	
			X = S	$X = S_2$	X = S	$X = S_2$	X = S	$X = S_2$	X = S	$X = S_2$
Methyl	Ethyl	Vinyl	8		40		−53		−207	
Ethyl	Ethyl	Vinyl	2		10		−54		−211	
Propyl	Ethyl	Vinyl	0		0		−52		−203	
Butyl	Ethyl	Vinyl	0		0		−50		−195	
Amyl	Ethyl	Vinyl	0		0		−49		−191	
Methyl	Propyl	Allyl	18	18	90	90	−50	−48	−195	−187
Ethyl	Propyl	Allyl	17	18	85	90	−50	−45	−195	−175
Propyl	Propyl	Allyl	18	17	90	85	−51	−42	−199	−163
Butyl	Propyl	Allyl	18		90		−50		−195	
Amyl	Propyl	Allyl	18		90		−49		−191	
Methyl	Propyl	Propargyl	10		50		−253		−984	
Ethyl	Propyl	Propargyl	12		60		−253		−984	
Propyl	Propyl	Propargyl	11		55		−251		−976	
Butyl	Propyl	Propargyl	11		55		−251		−976	
Amyl	Propyl	Propargyl	10		50		−250		−972	

sharply on the polar PEG-1000 stationary phase: unsaturated sulphides and disulphides are retained in the column longer than the saturated compounds, *i.e.*, the sequence of elution of substances changes in comparison with Apiezon M. As can be seen from Table II, the energy of intermolecular interaction with PEG-1000, when a double bond is inserted into the normal radical, increases on average by 191–211 cal/mole, and the insertion of a triple bond results in a 5-fold increase in the energy of intermolecular interaction with the stationary phase. In this instance we are probably dealing with a specific donor–acceptor interaction of the unsaturated radical with the polar PEG-1000. It is of interest that, as with the iso radical, variation of the intermolecular interaction energy is specific to the unsaturated radical and depends only slightly on the nature of the –S– and $-S_2-$ functional groups.

Using McReynolds' tables[19] we calculated the values of $\delta(\Delta G)_{n,iso}$ and $\delta(\Delta G)_{n,unsat.}$ for ethers and esters. As can be seen from Table III, the characteristics obtained for isoaliphatic and unsaturated radicals are the same as those observed for sulphides and disulphides in this work, taking into account the difference in the analysis temperatures. If intramolecular interaction of a functional group with a double or triple bond of the radical is possible in the molecule investigated, the value of $\delta(\Delta G)_{n,unsat.}$ will, of course, also depend on the nature of the functional group.

In gas chromatography the total free energy of solution is often regarded as being the sum of the energy contributions from the individual groups of a molecule. The principle of the additivity of thermodynamic functions has been used[20–23] to classify stationary phases proceeding from the free energy of solution of functional

TABLE III

CALCULATED VALUES OF $\delta(\Delta G)_{n,iso}$ AND $\delta(\Delta G)_{n,unsat.}$ FOR ETHERS AND ESTERS AT 120°[19]

No.	*Compounds compared*	*Ap-M*, $\Delta G_{i.a.} = -5.17$ cal/mole		*PEG-1000*, $\Delta G_{i.a.} = -4.08$ cal/mole	
		$\delta I_{n,iso}$	$(-\Delta G)_{n,iso}$ (cal/mole)	$\delta I_{n,iso}$	$-\delta(\Delta G)_{n,iso}$ (cal/mole)
	Ethers				
1	PrOPr–PrOiPr	47	243	65	265
2	MeOBu–MeOiBu	41	212	64	261
3	AmOAm–AmOiAm	37	191	51	208
4	EtOBu–EtO*tert.*-Bu	79	408	107	437
	Esters				
5	MeC(O)OBu–MeC(O)OiBu	43	222	61	249
6	EtC(O)OBu–EtO(O)iBu	45	233	57	232
7	PrC(O)OBu–PrC(O)OiBu	43	222	59	241
8	MeC(O)OAm–MeC(O)OiAm	35	181	51	208
9	EtC(O)OAm–EtC(O)OiAm	32	165	45	184
10*	EtOEt–EtOVin	−3	−16	−61	−249
11*	EtC(O)OEt–VinC(O)OEt	4	21	−36	−147
12*	EtC(O)OBu–VinC(O)OBu	3	16	−41	−167
13*	HC(O)OPr–HC(O)OA11	16	83	−49	−200
14*	MeC(O)OPr–MeC(O)OA11	15	78	−52	−212

* δI and $\delta(\Delta G)$ values for compounds 10–14 are the differences in indices and free energies resulting from the replacement of *n*-radical by unsaturated radical, *i.e.*, $\delta I_{n,unsat.}$ and $\delta(\Delta G)_{n,unsat.}$.

TABLE IV

VALUES OF RETENTION INDICES (I), FREE ENERGIES OF SOLUTION (ΔG) AND ENERGY CONTRIBUTIONS OF -S- GROUP FOR METAMERIC THIATRIDECANES ON APIEZON M AND PEG-1000

K, position of sulphur in metameric sulphides ($C_{12}H_{24}S$)	Apiezon M, 130°, $\Delta G_{l.u.} = -4.98$ cal/mole				PEG-1000, 130°, $\Delta G_{l.u.} = -3.98$ cal/mole			
	I (metamer)	$-\Delta G^{**}$ (metamer) (cal/mole)	$-\delta(\Delta G)_{2,K>2}^{*}$ (cal/mole)	Energy contribution of -S- group (cal/mole)	I (metamer)	$-\Delta G^{**}$ (metamer) (cal/mole)	$-\delta(\Delta G)_{2,K>2}^{*}$ (cal/mole)	Energy contribution of -S- group (cal/mole)
2	1520	6831	0	1595	1757	5783	0	2173
3	1493	6696	135	1460	1710	5600	183	1990
4	1481	6636	195	1400	1692	5530	253	1920
5	1477	6616	215	1380	1684	5499	284	1889
6	1475	6606	225	1370	1681	5487	296	1877
7	1473	6597	234	1360	1678	5475	308	1865

* $\delta(\Delta G)_{2,K>2}$ is the difference between the free energies of solution of 2-thiatridecane and the metamer with the position of sulphur atom $K > 2$ ($K < 7$); determined from eqn. 19.

** ΔG values of metamers were calculated from eqns. 15 and 16.

groups in a stationary phase. According to the views of Novák and co-workers[14–26], for the $(CH_3)_n(CH_2)_mX$ homologous series, where X is the functional group, the following equality is valid:

$$\Delta G_{(CH_3)_n(CH_2)_mX} = n\Delta G^{CH_3} + m\Delta G^{CH_2} + \Delta G^{X} \qquad (20)$$

from which it follows that the contribution of a functional group to the free energy of solution does not depend on its position in the molecule and is the same in different homologous series, being described by eqn. 20.

Viewing the retention of a substance in gas chromatography as being determined by the energy of intermolecular interactions with the stationary phase, one would expect the characteristics of the interactions, of both physical and chemical nature, to depend not only on the number of atoms in the functional group and its valency, but also on its position in the molecule. The place of the functional group in the molecule determines its accessibility as regards interaction with the stationary phase. It should also not be excluded that surrounding groups exert a mutual effect on the capability of the functional group to enter into intermolecular interactions. From this point of view, it would be wrong to assert *a priori* that the energy contribution of the carboxyl group will be the same in the homologous series of *n*-alkyl acetates and methyl esters of fatty acids, although, formally, these homologous series are both described by eqn. 20.

To check this assumption, we studied the gas chromatographic behaviour of metameric compounds, *i.e.*, isomers belonging to the same class with the same number of carbon atoms but with different positions of the functional group. This makes it possible to answer the question of whether it is correct, knowing the magnitude of the functional group's contribution to the free energy of solution of one homologous series, to regard this contribution as remaining unchanged in another homologous series. In our study we chose the –S– sulphide group for which, as was previously established[14], the energy of intermolecular interaction with polar and non-polar stationary phases is determined by the energy of Van der Waals physical forces.

We followed the variation of the –S– group energy contribution in thiatridecane metamers as –S– moves into the aliphatic chain. Comparison of the retention indices of the homologous series methyl *n*-alkyl, ethyl *n*-alkyl, propyl *n*-alkyl and butyl *n*-alkyl sulphides[5] has shown that the energy contributions of ΔG^{CH_3} and ΔG^{CH_2} are the same in the metamers studied and are equal to the energy contributions of these groups in *n*-alkanes. The functional group's energy contribution in the series of metamers decreases with the migration of the sulphur atom along the chain. This can be clearly seen from the data in Table IV, which gives the values of the difference between the free energies of solution for thiatridecane metamers and thiatridecane-2. It can be seen from Table IV that, when the sulphur atom moves from position 2, *i.e.*, at $K = 2$, to position 7, at $K = 7$, the partial molar free energy of solution decreases by 234 cal/mole with Apiezon M and by 308 cal/mole with PEG-1000. From this, the important conclusion is inferred that one can use additive equations similar to eqn. 20 only for given homologous series. In designating the contribution of a functional group, ΔG^{X}, it is necessary to indicate its position in the molecule.

The energy contribution of the functional group, as well as that of the

methylene group, depends on the homologous series and on the nature of the stationary nary phase. That is why one cannot use the ΔH or ΔG values for individual functional groups, –O–, >C=O, –OH, –CHO or –O–C$\langle^{O}_{CH_3}$, to classify stationary phases, as some workers have proposed[20–23]. The data obtained by us show that in order to use additivity schemes to assess the contributions to the ΔG value it is necessary to indicate precisely the functional group's position and to take into account the possibility of the energy contributions from the CH_2 and CH_3 groups not being equivalent to the corresponding values for *n*-alkanes.

The previously proposed eqn. 2 has thus been successfully used not only to give a universal system of polarity and selectivity in gas chromatography[2,3], but also to ascertain the nature of coefficients A and B in equation describing the dependence of the free energy of solution on retention index, and to evaluate the energy of intermolecular interactions between the functional groups and individual units of a molecule and the stationary phase. Further studies of the variation of the energy of intermolecular interaction between functional groups and individual units of a molecule and different stationary phases will make it possible to obtain useful data for the development of the theory of solutions.

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