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RETENTION INDICES AND THERMODYNAMIC FUNCTIONS OF SOLUTION FOR MODEL NON-IONIC SURFACTANTS IN STANDARD STATIONARY PHASES DETERMINED BY GAS CHROMATOGRAPHY

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SUMMARY

Model non-ionic surfactants were analyzed on four stationary phases of different polarities. The values of the retention index and the partial molal thermodynamic parameters of solution, *i.e.*, Gibbs free energy, enthalpy and entropy, as well as of their increments for characteristic structural fragments were calculated. The influence of the surfactant structures upon the values of these parameters is discussed.

INTRODUCTION

Retention indices have been used to characterize non-ionic surfactants having a polyoxyethylene chain and the increments for appropriate characteristic fragments have been estimated[1]. Non-ionic surfactants have also been characterized as liquid phases in reversed-phase gas chromatography (GC) using methods and parameters discussed by Haken[2].

In previous papers the influence of the structure of pure model surfactants upon their retention indices[1] and partial molal thermodynamic parameters[3] has been examined. These studies have now been extended to wider range of model non-ionic surfactants.

EXPERIMENTAL

Reagents and procedure

Thirty pure model non-ionic surfactants having formula $RX(CH_2CH_2O)_nR'$, where $R = C_4H_9, C_6H_{13}, C_8H_{17}$; $R' = H, CH_3$; $X = O, NH, S$; $n = 0$–3, were used as solutes. Their structures are given in Table I.

GC measurements were carried out according to the procedure described previously[3]. The experimental conditions were as follows: gas chromatograph, Chrom 5 (Kovo, Czechoslovakia) with a thermal conductivity detector; column, stainless steel, 1 m × 3 mm I.D.; carrier gas helium, flow-rate 50 cm^3/min; temperature of analyses, 423, 443, 463 K. Chromaton N-Super (75–100 mesh ASTM) was used as the support

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TABLE I

THE STRUCTURES OF THE COMPOUNDS ANALYZED, $RX(CH_2CH_2O)_nR'$

No.	*R*	*R'*	*X*	*n*
1	C_4H_9	H	0	0
2	C_4H_9	H	0	2
3	C_4H_9	H	0	3
4	C_6H_{13}	H	S	0
5	C_6H_{13}	H	S	1
6	C_6H_{13}	H	S	2
7	C_6H_{13}	H	S	3
8	C_6H_{13}	H	0	0
9	C_6H_{13}	H	0	1
10	C_6H_{13}	H	0	2
11	C_6H_{13}	H	0	3
12	C_6H_{13}	H	NH	0
13	C_6H_{13}	H	NH	1
14	C_6H_{13}	H	NH	2
15	C_6H_{13}	H	NH	3
16	C_8H_{17}	H	S	0
17	C_8H_{17}	H	S	1
18	C_8H_{17}	H	S	2
19	C_8H_{17}	H	S	3
20	C_8H_{17}	H	0	0
21	C_8H_{17}	H	0	1
22	C_8H_{17}	H	0	2
23	C_8H_{17}	H	0	3
24	C_8H_{17}	H	NH	0
25	C_8H_{17}	H	NH	1
26	C_8H_{17}	H	NH	2
27	C_8H_{17}	H	NH	3
28	C_6H_{13}	CH_3	0	3
29	C_8H_{17}	CH_3	0	3
30	$C_{10}H_{21}$	CH_3	0	3

and SE-30, Apiezon K, OV-17 and QF-1 were used as liquid phases. The solutes dissolved in ethyl acetate were analyzed directly without conversion into volatile derivatives. Retention times were measured at the peak maximum. The retention time of air was taken as the dead time.

The retention indices were calculated in the standard way and thermodynamic functions were determined according to the method proposed by Risby[4-7]. The increments were calculated as in previous work[1,3].

RESULTS AND DISCUSSION

Retention index and increments

Exemplary values of retention indices are listed in Table II. The confidence limits do not exceed 15 units. Fig. 1 shows that the retention indices increase according to the polarity of the stationary phase in the following order: Apiezon K $\approx$ SE-30 $<$ OV-17 $<$ QF-1.

TABLE II

THE RETENTION INDICES OF THE COMPOUNDS EXAMINED AT 443 K ($\alpha = 0.05$)

No.	*Apiezon K*	*SE-30*	*OV-17*	*QF-1*
1	675 ± 4	675 ± 4	740 ± 1	867 ± 1
2	1150 ± 1	1193 ± 1	1340 ± 2	1469 ± 4
3	1437 ± 2	1479 ± 2	1653 ± 1	1797 ± 2
4	931 ± 4	918 ± 6	994 ± 6	1043 ± 14
5	1318 ± 4	1317 ± 1	1520 ± 1	1621 ± 1
6	1564 ± 1	1578 ± 1	1825 ± 1	1952 ± 1
7	1829 ± 3	1844 ± 1	2149 ± 1	2273 ± 1
8	815 ± 8	822 ± 8	966 ± 6	1003 ± 14
9	1054 ± 14	1090 ± 1	1234 ± 2	1534 ± 4
10	1325 ± 4	1363 ± 1	1515 ± 1	1662 ± 1
11	1576 ± 1	1631 ± 1	1844 ± 1	1983 ± 1
12	815 ± 8	829 ± 9	911 ± 7	993 ± 13
13	1183 ± 1	1197 ± 2	1333 ± 1	1475 ± 2
14	1424 ± 1	1443 ± 1	1592 ± 1	1757 ± 1
15	1656 ± 2	1703 ± 1	1896 ± 7	2082 ± 2
16	1200 ± 1	1140 ± 1	1231 ± 3	1298 ± 8
17	1603 ± 2	1562 ± 2	1740 ± 5	1918 ± 11
18	1791 ± 2	1830 ± 2	2050 ± 2	2277 ± 8
19	2045 ± 2	2123 ± 3	2361 ± 4	2604 ± 7
20	1044 ± 5	999 ± 6	1180 ± 7	1299 ± 16
21	1274 ± 1	1282 ± 3	1452 ± 3	1569 ± 2
22	1552 ± 2	1568 ± 1	1782 ± 4	1928 ± 6
23	1822 ± 1	1855 ± 1	2019 ± 6	2272 ± 4
24	1091 ± 8	993 ± 5	1066 ± 8	1230 ± 11
25	1408 ± 3	1333 ± 2	1533 ± 4	1711 ± 9
26	1645 ± 1	1608 ± 3	1834 ± 3	2062 ± 5
27	1913 ± 2	1917 ± 2	2128 ± 1	2355 ± 5
28	1592 ± 1	1660 ± 3	1847 ± 1	1903 ± 6
29	1837 ± 1	1880 ± 1	2088 ± 1	2175 ± 3
30	2028 ± 1	2121 ± 1	2261 ± 1	2435 ± 1

The presence of different heteroatoms in the surfactant molecules influences the retention index of the examined oxyethylates in the following order: $RS(CH_2CH_2O)_nH > RNH(CH_2CH_2O)_nH \geqslant RO(CH_2CH_2O)_nH$. As expected, was equivalent to about 100 retention index units (Fig. 2).

The influence of the liquid phase polarity and the surfactant structure upon the retention index is particularly explicit for derivatives having an oxyethylene chain terminated by a free hydroxyl group (–OH) or by a methoxyl group ($-OCH_3$) (Table III). On the apolar phases (Apiezon K, SE-30), compounds having a methoxyl group exhibit higher retention indices than their analogues having an hydroxyl group. An increase in the stationary phase polarity reverses this relationship, and compounds having a free hydroxyl group show higher retention indices on QF-1. Dispersive interactions between the liquid phase and the solute molecules are predominant on apolar phases. This type of intermolecular interactions increases with increasing number of methylene groups in the solutes. The loss of the mobile hydrogen atom does not compensate for the increase in dispersive interactions. With an increase in the

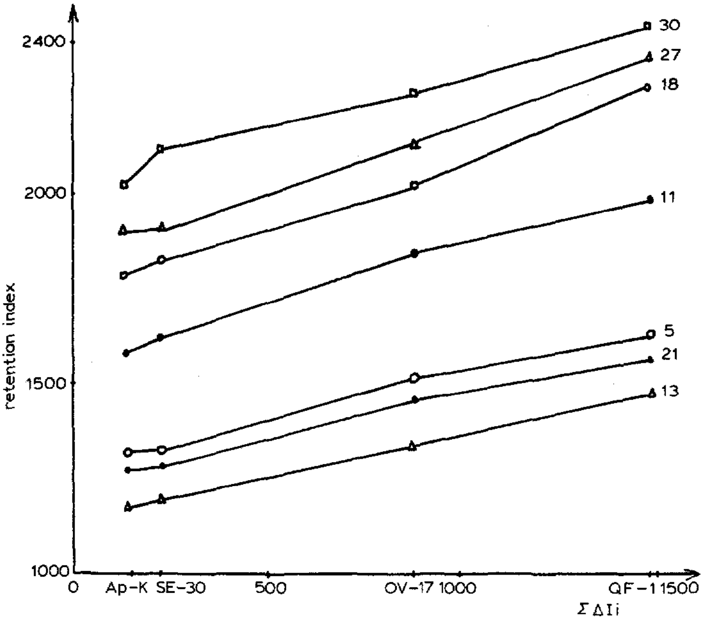

Fig. 1. The influence of the stationary phase polarity upon the retention index at 443 K. ●, X = O, R′ = H; ○, X = S, R′ = H; △, X = NH, R′ = H; □, X = O, R′ = CH_3. $\Sigma \Delta I_i$ is the sum of differences of retention indices for McReynolds probes measured on a given stationary phase and squalane.

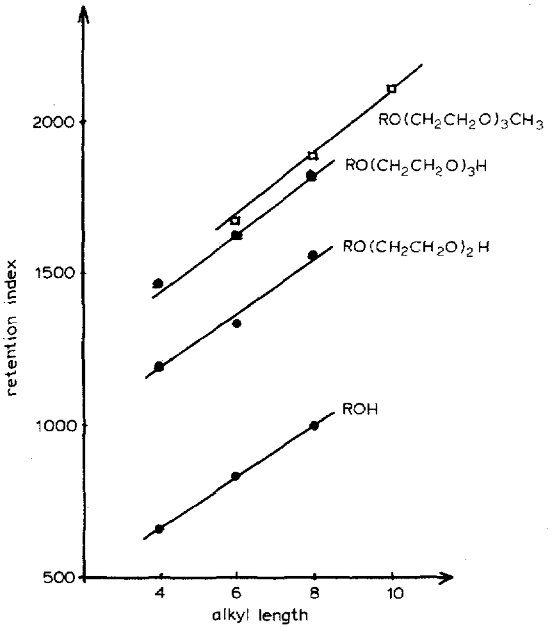

Fig. 2. The influence of the alkyl chain length upon the retention index on SE-30.

TABLE III

COMPARISON OF THE RETENTION PARAMETERS FOR COMPOUNDS TERMINATED BY AN HYDROXYL GROUP AND A METHOXYL GROUP

R	*Phase*	I_R		ΔG_s^m *(kJ/mol)*	
		-OH	*-OCH₃*	*-OH*	*-OCH₃*
C_6H_{13}	Apiezon K	1576	1592	−19.9	−21.0
	SE-30	1631	1660	−18.1	−21.8
	OV-17	1844	1847	−21.3	−19.6
	QF-1	1983	1903	−15.9	−14.7
C_8H_{17}	Apiezon K	1822	1837	−23.3	−24.9
	SE-30	1855	1880	−20.8	−21.7
	OV-17	2019	2088	−23.2	−23.4
	QF-1	2272	2175	−19.9	−17.6

liquid phase polarity, interactions of the proton donor–proton acceptor type prevail over dispersive interactions. So, significant differences in the values of the retention index are observed. Interactions specific to other molecular fragments are not important, because they are identical for both homologous series.

There is a statistically significant relationship between the retention index and the number of oxyethylene units the straight lines obtained being characterized by a correlation coefficient greater than 0.9990 (Fig. 3).

In the case of amine and thioalcohol derivatives, the first oxyethylene group

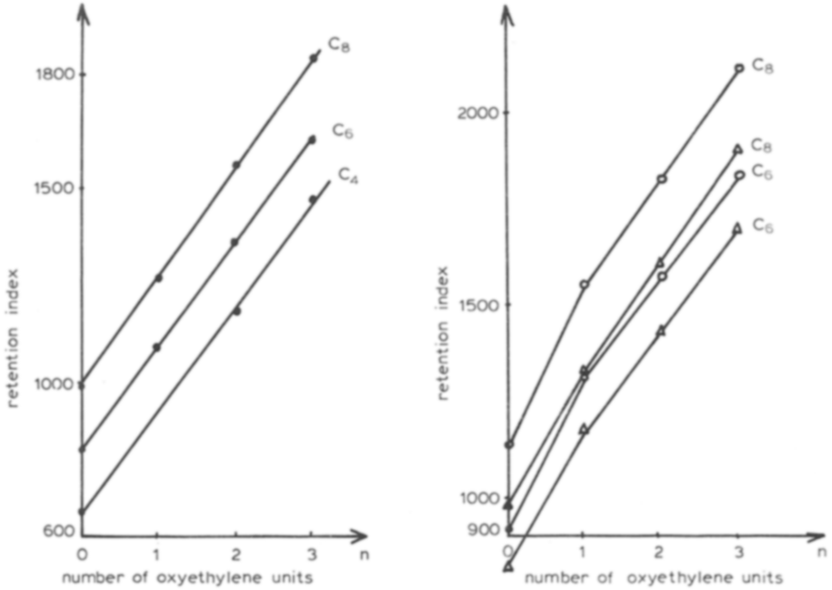

Fig. 3. The influence of the number of oxyethylene units upon the retention index on SE-30. Symbols as in Fig. 1.

changes the retention index in a somewhat different way from that of subsequent oxyethylene groups. The change in slope caused by the first oxyethylene group is connected with the introduction of the terminal hydroxyl group into the molecule.

The observed linear relationships were used to calculate the retention index increments for $-CH_2CH_2O-$, $-CH_2-$, $-NH_2$, $-OH$ and $-SH$. The increments for the central $-S-$,$-O-$ and $-NH-$ groups were obtained from the total retention indices and appropriate increments for the alkyl and the oxyethylene chain. (Table IV).

The second method of calculation enables the estimation of the increments for all fragments present in the surfactant molecules and, for example, allows the distinction between a terminal hydroxyl group connected to an alkyl ($-OH$) or an oxyethylene chain ($-OH^E$).

In general, the increments increase with increasing polarity of the stationary liquid phase. Only increments calculated for the ether and thioether groups exhibit smaller values on Apiezon K in comparison with those on SE-30.

Both groups of increments can be used to predict the retention indices for the surfactants. For the first set of increments the relative error of such estimations does not exceed 4%, while for the second set this error is 1.6, 1.9, 1.8 and 2.9% for SE-30, Apiezon K, OV-17 and QF-1, respectively.

Thermodynamic parameters of solution and their increments

The partial molal thermodynamic parameters, *i.e*, the enthalpy, entropy and Gibbs free energy of solution, calculated for a chosen group of solutes have been used to select liguid stationary phases according to their polarities[4–7]. These parameters also be considered as a measure of the different types of intermolecular interactions between a solute and a stationary phase. For homologous series the interaction forces should increase with increasing polarity, due to the increasing length of the oligooxyethylene chain. This effect should be much more evident on polar or medium polar phases, *e.g.*, QF-1, OV-17 than on non-polar ones (SE-30, Apiezon K) and is confirmed by the experimental results given in Figs. 4–6. An increase in the surfactant polarity results in a decrease in the partial molal enthalphy and Gibbs free energy of solution.

An increase in the alkyl chain length gives an opposite effect. The replacement of an oxygen atom connected to the alkyl chain by an NH group has little influence on the values of the considered parameters. However, much lower values of ΔH_s^m

TABLE IV

RETENTION INDEX INCREMENTS

Group	*Apiezon K*	*SE-30*	*OV-17*	*QF-1*
$-CH_2CH_2O-$	247	272	297	322
$-SH$	365	329	412	443
$-OH$	245	232	362	456
$-NH_2$	253	211	289	411
$-O-$	47	73	97	122
$-S-$	275	306	365	364
$-NH-$	152	132	165	232

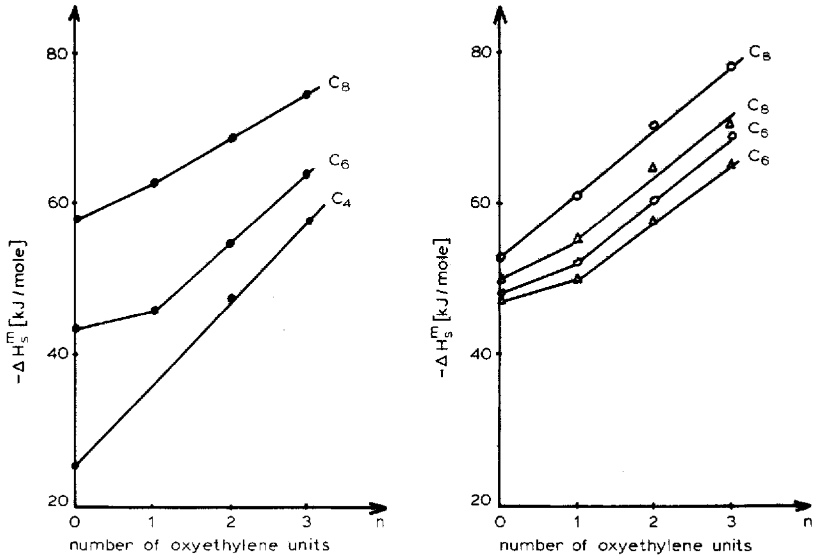

Fig. 4. The influence of the surfactant structure upon the partial molal enthalpy of solution on QF-1. Symbols as in Fig. 1.

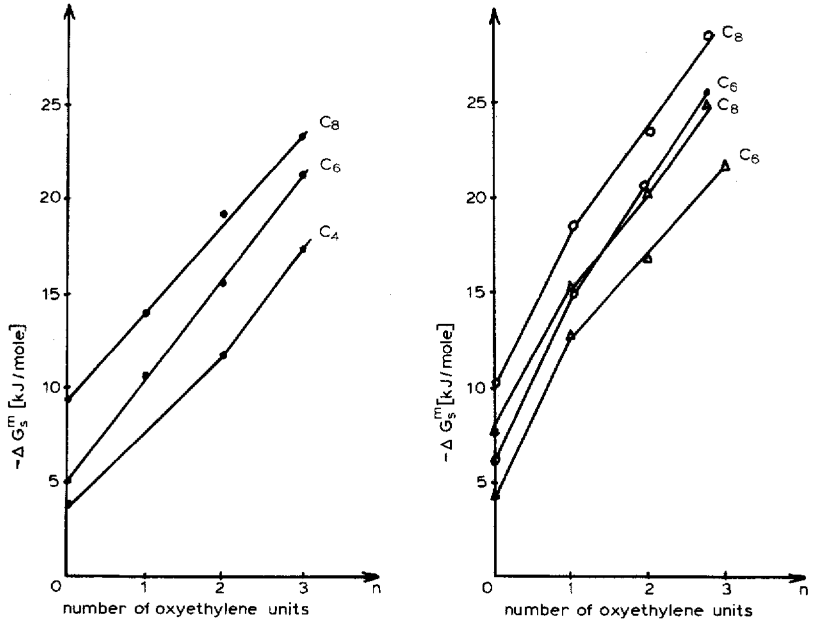

Fig. 5. The influence of the surfactant structure upon the partial molal Gibbs free energy of solution on OV-17. Symbols as in Fig. 1.

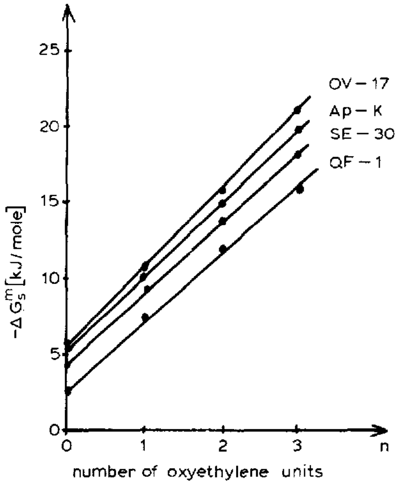

Fig. 6. The Gibbs free energy of $C_8H_{17}O(CH_2CH_2O)_nH$ solution in different stationary phases.

and ΔG_s^m were obtained for thioalcohol derivatives. This means that these compounds can be considered as more polar, in accord with the conclusion drawn from retention index values. So, the values of the partial molal thermodynamic parameters depend upon the polarities of the non-ionic surfactants, *i.e.*, the length of the polyoxyethylene chain and of the hydrophobic alkyl group, the presence of the heteroatom and the polarity of the liquid phase.

The values of ΔG_s^m are much higher than ΔH_s^m values, indicating a significant influence of the entropy factor upon the intermolecular interactions.

The increments for the thermodynamic parameters are presented in Tables V–VII. These increments can be used to predict the discussed thermodynamic param-

TABLE V

RETENTION INDEX INCREMENTS AT 443 K

R = Regression coefficient; F = Snedecor test value.

Group	*SE-30*	*Apiezon K*	*OV-17*	*QF-1*
CH_3–	100	100	100	100
–CH_2–	100	100	100	100
–SH	329	365	411	468
–OH	232	244	361	455
–NH_2	211	252	287	409
–S–	330	326	434	469
–O–	92	74	132	145
–NH–	155	173	213	268
–OH^E	186	191	273	390
R	0.9990	0.9993	0.9990	0.9990
F	2534.9	3517.6	2624.3	647.4
Abs. error	25	21	28	52
Rel. error	1.6	1.9	1.8	2.9

TABLE VI

INCREMENTS OF PARTIAL MOLAL ENTHALPY OF SOLUTION (kJ/mol)

Group	*SE-30*	*Apiezon K*	*OV-17*	*QF-1*
CH_3–	−16.3	−11.5	−13.9	−13.2
–CH_2–	−2.2	−2.9	−2.7	−2.2
–SH	−19.0	−22.6	−16.3	−18.5
–OH	−13.2	−14.6	−20.4	−19.4
–NH_2	−13.9	−24.6	−14.8	−24.9
–S–	−12.1	−7.9	−11.5	−11.3
–O–	−3.4	−6.5	−5.3	−1.9
–NH–	−0.2	−9.0	−7.4	−7.0
–OH^E	−10.3	−12.6	−9.1	−17.0
R	0.9748	0.9506	0.9366	0.9117
F	10.881	6.827	18.764	9.054
Abs. error	5.8	4.6	3.7	4.0
Rel. error	8.8	8.8	6.1	9.0

eters with a quite good precision, as demonstrated by the low absolute and relative errors.

These increments can be also used to predict the specific retention volumes of the examined compounds, *e.g.*, the values of ΔH_s^m and ΔS_s^m on Apiezon K calculated for $C_6H_{13}S(CH_2CH_2O)_2H$ are equal to −60.9 kJ/mol and −93 J/K mole, respectively. By introducing these values into the following equation

$$\ln V_g = -\frac{\Delta H_s^m}{RT} + \frac{\Delta S_s^m}{R} + \ln (1000/273\ R) \tag{1}$$

the V_g is calculated to be 452, while the experimental values is 463. The absolute and relative errors are 11 and 2.4%, respectively.

TABLE VII

INCREMENTS OF PARTIAL MOLAL GIBBS FREE ENERGY OF SOLUTION (kJ/mol)

Group	*SE-30*	*Apiezon K*	*OV-17*	*QF-1*
CH_3–	2.4	3.1	3.5	4.1
–CH_2–	−1.6	−1.9	−1.7	−1.4
–SH	−0.5	−1.3	−1.4	−1.0
–OH	0.7	−0.6	−1.4	−1.9
–NH_2	1.4	1.3	0.7	0.1
–S–	−5.0	−5.5	−6.7	−5.9
–O–	−1.3	−1.4	−1.9	−1.8
–NH–	−2.1	−2.8	−3.4	−3.3
–OH^E	1.0	1.7	0.1	−0.2
R	0.9778	0.9933	0.9942	0.9855
F	161.257	540.363	625.614	248.693
Abs. error	0.4	0.8	0.4	0.6
Rel. error	4.4	6.4	5.0	11.3

TABLE VIII

CORRELATION COEFFICIENTS FOR THE RELATIONSHIPS $\Delta G_s^m = A \cdot I_R + B$ ($\alpha = 0.05$)

Parameter	*SE-30*	*Apiezon K*	*OV-17*	*QF-1*
$A \cdot 10^2$	-1.6 ± 0.1	-1.8 ± 0.1	-1.6 ± 0.1	-1.2 ± 0.1
B	8.3 ± 0.8	9.1 ± 1.2	9.5 ± 0.9	8.7 ± 1.0
R	0.9952	0.9911	0.9954	0.9911
F	3420	1884	3650	1884
Abs. error	5	7	4	5
Rel. error	4.4	5.8	4.8	8.4

The conclusions drawn from the retention index values for the terminal OH and OCH_3 groups are in agreement with the partial molal Gibbs free energy of solution because higher retention indices are equivalent to lower values of ΔG_s^m (Table II).

Following the idea of Golovnya and Misharina[8], the linear relationships between ΔG_s^m and the retention index were calculated (Table VIII). The slopes of these straight lines give ΔG_s^m for a methylene group.

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