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Note

Increments of the arithmetic retention index for polyoxyethylene glycol monoalkyl ethers and their degradation products

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In previous work[1], arithmetic retention indices were determined for succesive homologues of non-ionic surfactants having polyoxyethylene chains. OV-17 silicone resin was used as the liquid phase. The increments of the arithmetic index were calculated for the characteristic groups present in the surfactant molecules and can be used to predict the I_R values for different homologues having various numbers of oxyethylene groups and to identify these homologues on chromatograms of commercial polydisperse mixtures.

The degradation of polyoxyethylene glycol monoalkyl ethers was recently studied and various degradation products were identified[2,3]. The aim of this work was to determine the arithmetic retention indices for polyoxyethylene glycol monoalkyl ethers and their degradation products on liquid stationary phases used for the analysis of commercial non-ionic surfactants.

EXPERIMENTAL

Polydisperse polyoxyethylene glycol monoalkyl ethers, $RO(CH_2CH_2O)_nH$, having different lengths of the alkyl group and of the polyoxyethylene chain, were used. They were analysed directly as acetates and after their degradation at 150°C in the presence of acetyl chloride[2,3].

A Perkin-Elmer Model 900 gas chromatograph with a flame ionization detector was used. The separation was carried out in stainless-steel columns filled with (I) silicone resin OV-101 (3%) on Chromosorb G AW DMCS (60–80 mesh) (0.9 m × 2.7 mm I.D.), (II) Dexsil 400 (1%), on Chromosorb G AW DMCS (80–100 mesh) (0.4 m × 2.7 mm I.D.) and (III) Carbowax 20M-TPA (12%) on Chromosorb W AW DMCS, (80-100 mesh) (1.6 m × 2.7 mm I.D.) Columns I and II were used for the direct analysis of polyoxyethylene glycol monoalkyl ethers and column III only for the analysis of their degradation products. The temperatures of columns I, II and III were 100, 130 and 100°C for 1 min and were then raised to 300, 360 and 220°C at 8, 6 and 5°C/min, respectively. Argon was used as the carrier gas at a flow-rate of 30 cm^3/min.

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The arithmetic retention index[4] was determined for all the separated components of the analysed polydisperse mixtures.

RESULTS AND DISCUSSION

The values of the arithmetic retention indices determined are given in Tables I–III. The succesive homologues of polyoxyethylene glycol monoalkyl ethers elute in order of increasing number of oxyethylene groups and increasing length of the alkyl group up to the homologues having 17 oxyethylene groups[2,3]. However, the values of

TABLE I

ARITHMETIC RETENTION INDICES FOR POLYOXYETHYLENE GLYCOL MONOALKYL ETHERS, C_mH_{2m+1}-O-$(CH_2CH_2O)_nH$, AS ACETATES, ON OV-101

m	*n*	I_R *(exp.)*	I_R *(calc.)*	*Error*	
				Absolute	*Relative (%)*
12	0	1640	1650	10	0.6
	1	1900	1912	12	0.6
	2	2173	2173	0	0.0
	3	2448	2435	−13	0.5
	4	2715	2696	−19	0.7
	5	2962	2958	−4	0.1
	6	3225	3219	−6	0.2
	7	3471	3481	10	0.3
	8	3735	3742	7	0.2
14	0	1835	1850	15	0.8
	1	2109	2112	3	0.1
	2	2364	2373	9	0.4
	3	2642	2635	−7	0.3
	4	2908	2896	−12	0.4
	5	3172	3158	−14	0.4
	6	3423	3419	−5	0.1
	7	3683	3681	−2	0.1
16	0	2045	2050	5	0.2
	1	2309	2312	3	0.1
	2	2577	2573	−4	0.2
	3	2854	2835	−19	0.7
	4	3103	3096	−7	0.2
	5	3362	3358	−4	0.1
	6	3627	3619	−8	0.2
	7	3893	3881	−12	0.3
18	0	2245	2250	5	0.2
	1	2509	2512	3	0.1
	2	2788	2773	−15	0.5
	3	3034	3035	1	0.0
	4	3294	3296	29	0.1
	5	3529	3558	29	0.8
	6	3789	3819	30	0.8
Average error				9	0.3

TABLE II

ARITHMETIC RETENTION INDICES FOR POLYOXYETHYLENE GLYCOL MONODODECYL ETHERS, $C_{12}H_{25}O(CH_1CH_2O)_nH$, AS ACETATES ON DEXSIL 400

n	I_R *(exp.)*	I_R *(calc.)*	*Error*	
			Absolute	*Relative (%)*
0	1686	1653	−33	2.0
1	1929	1930	1	0.1
2	2196	2208	12	0.5
3	2475	2485	10	0.4
4	2750	2762	12	0.4
5	3020	3040	20	0.7
6	3312	3317	5	0.2
7	3600	3594	−6	0.2
8	3876	3871	−5	0.1
9	4167	4149	−18	0.4
Average error			12	0.5

I_R for only the first seven to nine homologues were determined because of the lack of standard alkanes with higher molecular masses.

The values of the arithmetic retention indices follow linear relationships correlating I_R with the number of oxyethylene groups. Hence the slopes determine the I_R increments for one oxyethylene group. Similar values were obtained for various homologous series of polyoxyethylene glycol monoalkyl ethers containing different

TABLE III

ARITHMETIC RETENTION INDICES FOR THE DEGRADATION PRODUCTS OF POLYOXYETHYLENE GLYCOL MONOALKYL ETHERS ON CARBOWAX 20M-TPA

Compound	I_R *(exp.)*	I_R *(calc.)*	*Error*	
			Absolute	*Relative (%)*
$CH_3COOCH_2CH_2Cl$	1318	1352	34	2.6
$CH_3COOCH_2CH_2OCH_2CH_2Cl$	1757	1747	−10	0.6
$CH_3COOCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$	2157	2142	−15	0.7
$C_{10}H_{21}Cl$	1470	1467	−3	0.1
$C_{10}H_{21}OCH_2CH_2Cl$	1838	1862	24	1.3
$C_{12}H_{25}Cl$	1684	1667	−17	1.0
$C_{12}H_{25}OCH_2CH_2Cl$	2064	2062	−2	0.1
$ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$	1935	1924	−11	0.6
$ClCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$	2330	2319	−11	0.5
$CH_3COOC_{10}H_{21}$	1684	1685	1	0.1
$CH_3COOCH_2CH_2OC_{10}H_{21}$	2068	2080	12	0.6
$CH_3COOC_{12}H_{25}$	1893	1885	8	0.4
$CH_3COOCH_2CH_2OC_{12}H_{25}$	2278	2280	2	0.1
$CH_3COOCH_2CH_2OCH_2CH_2OOCCH_3$	1970	1965	−5	0.3
$CH_3COOCH_2CH_2OCH_2CH_2OCH_2CH_2OOCCH_3$	2375	2360	−15	0.6
Average error			10	0.7

TABLE IV

REGRESSION AND CORRELATION COEFFICIENTS FOR THE LINEAR RELATIONSHIP $I_R = A + Bn$, WHERE n DENOTES THE NUMBER OF OXYETHYLENE GROUPS

Liquid stationary phase	*Alkyl group*	*A*	*B*	*Correlation coefficient*
OV-101	$C_{12}H_{25}$	1649	261.9	0.99988
	$C_{14}H_{29}$	1842	264.2	0.99993
	$C_{16}H_{33}$	2049	263.5	0.99995
	$C_{18}H_{37}$	2258	256.4	0.99977
Dexsil 400	$C_{12}H_{25}$	1653	277.3	0.99984

numbers of carbon atoms in their alkyl groups (Table IV). The correlation coefficients are high (*ca.* 1.0) and demonstrate the statistical validity of the equations derived.

The chemical formulae of the separated components in the group of surfactants considered can be expressed as

$$A_i = (G_1)_{a_{1i}}, (G_2)_{a_{2i}}, \ldots, (G_l)_{a_{li}}$$

where $G_1, G_2, \ldots, G_l$ are the characteristic groups present in the system considered, a_{1a}, $a_{2i}, \ldots, a_{li}$ are the numbers of groups $G_1, G_2, \ldots, G_l$ in compound A_i, $i = 1, 2, \ldots, k$ are the numbers of compounds considered in the system and $j = 1, 2, \ldots, l$ are the numbers of the characteristic groups considered.

In our systems k is much greater than l; $k = 46$, 10 and 15 for OV-101, Dexsil 400 and Carbowax 20M-TPA, respectively, whereas $l = 3$ or 4. The following groups are considered: the methylene group equivalent to the methyl group ($-CH_2-$, $-CH_3$), the etheric oxygen $-O-$, the $-OOCCH_3$ group and the chlorine atom ($-Cl$). The oxyethylene group is considered as the sum of two methylene groups and the etheric oxygen.

The set of subscripts $\{a_{ji}\}$, $j = 1, 2, \ldots, l$, forms the formula vector, a_i, of the compound A_i:

$$a_i = [a_{1i}, a_{2i}, \ldots, a_{li}]^T$$

where T denotes transposition.

The formula matrix **A** of the system considered is then defined as $\mathbf{A} = \mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_n$. Hence, if the products of degradation of polyoxyethylene glycol monoalkyl ethers are considered (Table III), this formula matrix is

$$\mathbf{A} = \begin{bmatrix} 2 & 4 & 6 & 10 & 12 & 12 & 14 & 5 & 7 & 10 & 12 & 12 & 14 \\ 0 & 1 & 2 & 0 & 1 & 0 & 1 & 2 & 3 & 0 & 1 & 0 & 1 \\ 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 \end{bmatrix}$$

where the order of compounds is the same as that in Table III. The groups considered, $-CH_2-$, $-CH_3$, $-O-$, $-OOCCH_3$ and $-Cl$, are numbered 1, 2, 3 and 4, respectively.

TABLE V
INCREMENTS OF THE ARITHMETIC RETENTION INDEX

Group	*OV-101*	*Dexil 400*	*Carbowax 20M-TPA*
$-CH_2-$, $-CH_3$	100	100	100
$-OCH_2CH_2-$	261.5	277	395
$-O-$	61.5	77	195
$-OOCCH_3$	450	453	685
$-Cl$	–	–	467

However, if the above formula matrix were considered, the increments of the arithmetic index would not be equal to 100. Therefore, the standard *n*-alkanes were also considered. Their formula can be expressed as $A_i = (CH_2)_{a_{CH_2 i}}$ (the methyl group is considered equivalent to the methylene group) and their formula vector is $\mathbf{a}_i = [a_{CH_2 i}, 0,0,0]$. The whole matrix of the system considers the formula vectors of all compounds present in the system, including standard alkanes.

Assuming additivity, the arithmetic retention index of a compound A_i can be expressed as:

$$I_{RA_i} = \sum_{j=1}^{k} a_{ji} \Delta I_{RG_j}$$

where it is assumed that the increment of I_R for a group G_j is constant for all compounds considered. Thus, for all compounds present in the system, the following set of linear equations is obtained:

$$\mathbf{I}_R = \mathbf{A}\Delta\mathbf{I}_R$$

where

$$I_R = [I_{RA_1}, I_{RA_2}, \ldots, I_{RA_k}]^T$$

$$\Delta I_R = [\Delta I_{RG_1}, \Delta I_{RG_2}, \ldots, \Delta I_{RG_k}]^T$$

The increments of the arithmetic retention index obtained by solving the above set of linear equations are given in Table V. These increments can be used to calculate the retention indices of the compounds considered (Table I–III). The errors in such predictions are relatively low and equal to about 10 units of the arithmetic retention index for polyoxyethylene glycol monoalkyl ethers and their degradation products. Hence the increments obtained can be used to predict the arithmetic retention index for different homologues of the groups of compounds considered.

CONCLUSIONS

The arithmetic retention index calculated from the increments determined for characteristic groups present in polyoxyethylene glycol monoalkyl ethers and their

degradation products can be used to identify peaks on chromatograms. The average absolute and relative errors of the arithmetic retention index calculation are 10 and 0.5%, respectively.

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