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# INCREMENTS OF THE ARITHMETIC RETENTION INDEX FOR NON-IONIC SURFACTANTS WITH A POLYOXYETHYLENE CHAIN

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## SUMMARY

Arithmetic retention values were determined for successive homologues of the trimethylsilyl and acetyl derivatives of polyoxyethylene glycols, polyoxyethylene glycol monoalkyl ethers, N-polyoxyethylene alkylamines and polyoxyethylene glycol monoalkylphenyl ethers. The increments of the arithmetic retention index were calculated for the characteristic groups present in the surfactants' molecules. They can be used to estimate the arithmetic retention indices with absolute errors of 20 (0.7–0.8%) for polyoxyethylene glycols, polyoxyethylene glycol monoalkyl ethers and N-polyoxyethylene alkylamines, and with an error of 35 (0.9%) for polyoxyethylene glycol monoalkylphenyl ethers.

## INTRODUCTION

Non-ionic surfactants with a polyoxyethylene chain are usually complex mixtures with different lengths of the hydrophobic hydrocarbon chain and of the hydrophilic polyoxyethylene block. This is connected with the nature of the hydrophobic reagents used for their syntheses, *i.e.* fatty acids, alcohols, alkylamines, alkylphenols, etc., and with the possibility of ethylene oxide reacting not only with the initial hydrophobic reagent but also with the intermediates formed during the first stages of ethoxylation. Besides these main surface-active components, commercial products also contain various amounts of undesired by-products, mainly polyoxyethylene glycols with different molecular masses.

Gas–liquid chromatography has often been used to separate successive components of non-ionic surfactants and to determine their contents[1]. It is possible to separate the successive components of polyoxyethylene glycols and of their derivatives with alcohols, alkylphenols and alkylamines up to homologues with more than ten but less than twenty oxyethylene units in their molecules. Some standard well-defined samples are necessary to identify successive peaks on chromatograms, or else

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gas chromatography–mass spectrometry must be used to determine the molecular masses and the structures of the separated components[2–4]. However, this can be avoided because successive homologues differ by the number of oxyethylene groups and/or the number of methylene groups. Thus, a monotonic increase of the arithmetic retention index value is observed for homologues with a longer polyoxyethylene chain and/or a longer hydrocarbon chain. The values of the arithmetic retention index might be estimated from the values of the appropriate increments determined for the characteristic groups present in surfactant molecules; this estimation is the subject of our work.

## EXPERIMENTAL

The same model polydisperse or individual surfactants were considered as those discussed in our previous reports[2–5]. Their structures were as follows: $RO(CH_2CH_2O)_nH$, $RC_6H_4O(CH_2CH_2O)_nH$, $HO(CH_2CH_2O)_nH$, $R_2N(CH_2CH_2O)_nH$, $H(OCH_2CH_2)_m(R)N(CH_2CH_2O)_nH$ and $RNH(CH_2CH_2O)_nH$. They were analysed as trimethylsilyl derivatives and/or acetates. N,O-bis(trimethylsilyl)acetamide (Applied Science Labs, U.S.A.) and acetate chloride (Fluka, Switzerland) were used to obtain these derivatives according to standard methods. The silylation of alkylamines was described previously[5].

A gas–liquid chromatograph Perkin-Elmer Model 900 with a flame ionization detector was used. The separation was carried out in stainless-steel columns (0.6–1.8 m × 2.7 mm I.D.). Chromosorb G AW DMCS (60–80 mesh) was used as the support and silicone resin OV-17 (3%) as the liquid phase. Helium was used as the carrier gas, at a flow-rate of 50 $cm^3$/min. The temperatures of the injector and the detector were 370°C. The analyses were started with a column temperature of 130°C, which after 1 min was programmed for a rate of change of 4°C/min up to 320°C, where it was held constant. The arithmetic retention index[6] was determined for all the separated components.

## RESULTS AND DISCUSSION

The values of the arithmetic retention index ($I_R$) determined for the separated homologues of the considered surfactants are given in Tables I–V. The values of $I_R$ for the first nine to twelve homologues were only determined because of the lack of standard alkanes with higher molecular masses, although the next homologues containing up to about sixteen to eighteen oxyethylene units were separated. The values of the arithmetic retention index obtained increase as the length of the polyoxyethylene chain increases. The acetates have somewhat higher $I_R$ values than the equivalent trimethylsilyl derivatives.

The values of the arithmetic retention index obtained were used to calculate the $I_R$ increments for the characteristic groups present in surfactant molecules. The calculations were done separately for polyoxyethylene glycols and polyoxyethylene glycol monoalkyl ethers (Tables I–III), N-polyoxyethylene alkyl- and dialkylamines (Table IV) and polyoxyethylene glycol monoalkylphenyl ethers (Table V).

The chemical formula of the separated compounds (species) in the considered group of surfactants (chemical system) can be expressed as

$$A_i = (G_1)_{a_{1i}} (G_2)_{a_{2i}} \dots (G_m)_{a_{mi}}$$

TABLE I

ARITHMETIC RETENTION INDICES FOR POLYOXYETHYLENE GLYCOLS

| *Formula** | *n* | $I_R^{exp}$ | $I_R^{calc}$ | *Error* | |
|---|---|---|---|---|---|
| | | | | *Absolute* | *Relative (%)* |
| $SilO(EO)_nSil$ | 2 | 1289 | 1265 | 24 | 1.9 |
| | 3 | 1590 | 1570 | 20 | 1.3 |
| | 4 | 1895 | 1875 | 20 | 1.1 |
| | 5 | 2194 | 2180 | 14 | 0.6 |
| | 6 | 2492 | 2485 | 7 | 0.3 |
| | 7 | 2790 | 2790 | 0 | 0.0 |
| | 8 | 3092 | 3095 | −3 | −0.1 |
| | 9 | 3392 | 3400 | −8 | −0.2 |
| | 10 | 3686 | 3705 | −19 | −0.5 |
| | 11 | 3978 | 4010 | −32 | −0.8 |
| | 12 | 4251 | 4315 | −64 | −1.5 |
| $AcO(EO)_nAc$ | 2 | 1519 | 1557 | −38 | −2.5 |
| | 3 | 1817 | 1862 | −45 | −2.5 |
| | 4 | 2129 | 2167 | −38 | −1.8 |
| | 5 | 2438 | 2472 | −34 | −1.4 |
| | 6 | 2736 | 2777 | −41 | −1.5 |
| | 7 | 3061 | 3082 | −21 | −0.7 |
| | 8 | 3371 | 3387 | −16 | −0.5 |
| | 9 | 3677 | 3692 | −15 | −0.4 |
| | 10 | 4000 | 3997 | 3 | 0.1 |
| | 11 | 4304 | 4302 | 2 | 0.0 |
| | 12 | 4658 | 4607 | 51 | 1.1 |
| Average error | | | | 23 | 0.9 |

* Sil = $Si(CH_3)_3$, Ac = $OCCH_3$, EO = $CH_2CH_2O$.

where $G_1$, $G_2$, ... $G_m$ are the characteristic groups present in the considered chemical system, $a_{1i}$, $a_{2i}$, ... $a_{mi}$ are the numbers of groups $G_1$, $G_2$, ..., $G_m$ in the compound $A_i$, $i = 1, 2, \ldots n$ are the numbers of the compounds considered in the system, and $j = 1, 2, \ldots m$ are the numbers of the characteristic groups considered. It is the case that $n$ is always greater than or equal to $m$; in our systems $n$ is much greater than $m$.

The set of subscripts $\{a_{ji}\}$, $j = 1, 2, \ldots m$, forms the formula vector, $\boldsymbol{a}_i$, of the species $A_i$

$$\boldsymbol{a}_i = \begin{bmatrix} a_{1i} \\ a_{2i} \\ \cdot \\ \cdot \\ \cdot \\ a_{mi} \end{bmatrix} = [a_{1i}, a_{2i}, \ldots a_{mi}]^T$$

where T = transposition.

The formula matrix $\boldsymbol{A}$ of the chemical system is then defined as:

TABLE II

ARITHMETIC RETENTION INDICES FOR POLYOXYETHYLENE GLYCOL MONOALKYL ETHERS

| *Formula* | *n* | $I_R^{exp}$ | $I_R^{calc}$ | *Error* | |
|---|---|---|---|---|---|
| | | | | *Absolute* | *Relative (%)* |
| $C_{10}H_{21}O(EO)_nSil$ | 0 | 1383 | 1380 | 3 | 0.2 |
| | 1 | 1733 | 1685 | 48 | 2.8 |
| | 2 | 2020 | 1990 | 30 | 1.5 |
| | 3 | 2308 | 2295 | 13 | 0.6 |
| | 4 | 2614 | 2600 | 14 | 0.5 |
| | 5 | 2910 | 2905 | 5 | 0.2 |
| | 6 | 3200 | 3210 | −10 | −0.3 |
| | 7 | 3510 | 3515 | −5 | −0.1 |
| | 8 | 3810 | 3820 | −10 | −0.3 |
| | 9 | 4081 | 4125 | −44 | −1.1 |
| | 10 | 4413 | 4430 | −17 | −0.4 |
| $C_{12}H_{25}O(EO)_nSil$ | 0 | 1583 | 1580 | 3 | 0.2 |
| | 1 | 1894 | 1885 | 9 | 0.5 |
| | 2 | 2200 | 2190 | 10 | 0.5 |
| | 3 | 2498 | 2495 | 3 | 0.1 |
| | 4 | 2802 | 2800 | 2 | 0.1 |
| | 5 | 3095 | 3105 | −10 | −0.3 |
| | 6 | 3399 | 3410 | −11 | −0.3 |
| | 7 | 3699 | 3715 | −16 | −0.4 |
| | 8 | 3987 | 4020 | −33 | −0.8 |
| | 9 | 4255 | 4325 | −70 | −1.6 |
| $C_{14}H_{29}O(EO)_nSil$ | 0 | 1773 | 1780 | −7 | −0.4 |
| | 1 | 2100 | 2085 | 15 | 0.7 |
| | 2 | 2410 | 2390 | 20 | 0.8 |
| | 3 | 2707 | 2695 | 12 | 0.4 |
| | 4 | 3003 | 3000 | 3 | 0.1 |
| | 5 | 3300 | 3305 | −5 | −0.2 |
| | 6 | 3600 | 3610 | −10 | −0.3 |
| | 7 | 3895 | 3915 | −20 | −0.5 |
| | 8 | 4163 | 4220 | −57 | −1.4 |
| | 9 | 4555 | 4525 | 30 | 0.7 |
| Average error | | | | 18 | 0.6 |

$$\boldsymbol{A} = (\boldsymbol{a}_1, \boldsymbol{a}_2, \ldots, \boldsymbol{a}_n).$$

Thus, if only three successive homologues of polyoxyethylene glycols in the form of their trimethylsilyl and acetyl derivatives are considered: $(CH_3)_3SiO(CH_2CH_2O)_2Si(CH_3)_3$, $(CH_3)_3SiO(CH_2CH_2O)_3Si(CH_3)_3$, $(CH_3)_3SiO(CH_2CH_2O)_4Si(CH_3)_3$, $CH_3COO(CH_2CH_2O)_2OCCH_3$, $CH_3COO(CH_2CH_2O)_3OCCH_3$ and $CH_3COO(CH_2CH_2O)_4OCCH_3$, and the following characteristic groupps, $CH_2$, O, $(CH_3)_3SiO$ and $CH_3COO$, are chosen as the components of the compounds considered, the formula matrix of the system is:

TABLE III

ARITHMETIC RETENTION INDICES FOR POLYOXYETHYLENE GLYCOL MONOALKYL ETHERS

| *Formula* | *n* | $I_R^{exp}$ | $I_R^{calc}$ | *Error* | |
|---|---|---|---|---|---|
| | | | | *Absolute* | *Relative (%)* |
| $C_{10}H_{21}O(EO)_nAc$ | 0 | 1484 | 1526 | −42 | −2.8 |
| | 1 | 1810 | 1831 | −21 | −1.2 |
| | 2 | 2148 | 2136 | 12 | 0.6 |
| | 3 | 2461 | 2441 | 20 | 0.8 |
| | 4 | 2772 | 2746 | 26 | 0.9 |
| | 5 | 3081 | 3051 | 30 | 1.0 |
| | 6 | 3387 | 3356 | 31 | 0.9 |
| | 7 | 3685 | 3661 | 24 | 0.7 |
| | 8 | 3960 | 3966 | −6 | −0.2 |
| | 9 | 4307 | 4271 | 36 | 0.8 |
| $C_{12}H_{25}O(EO)_nAc$ | 0 | 1707 | 2027 | 1726 | −16 | −1.1 |
| | 1 | 2342 | 2031 | −4 | −0.2 |
| | 2 | 2658 | 2336 | 6 | 0.3 |
| | 3 | 2972 | 2641 | 17 | 0.6 |
| | 4 | 3277 | 2946 | 26 | 0.9 |
| | 5 | 3576 | 3251 | 26 | 0.8 |
| | 6 | 3887 | 3556 | 20 | 0.6 |
| | 7 | 4153 | 3861 | 26 | 0.7 |
| | 8 | 4454 | 4166 | −13 | −0.3 |
| | 9 | | 4471 | −17 | −0.4 |
| $C_{14}H_{29}O(EO)_nAc$ | 0 | 1907 | 1926 | −19 | −1.0 |
| | 1 | 2225 | 2231 | −6 | −0.3 |
| | 2 | 2535 | 2536 | −1 | 0.0 |
| | 3 | 2837 | 2841 | −4 | −0.1 |
| | 4 | 3138 | 3146 | −8 | −0.3 |
| | 5 | 3439 | 3451 | −12 | −0.3 |
| | 6 | 3739 | 3756 | −17 | −0.5 |
| | 7 | 4025 | 4061 | −36 | −0.9 |
| | 8 | 4338 | 4366 | −28 | −0.6 |
| Average error | | | | 19 | 0.7 |

$$A = \begin{bmatrix} 4 & 6 & 8 & 4 & 6 & 8 \\ 1 & 2 & 3 & 1 & 2 & 2 \\ 2 & 2 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & 2 & 2 \end{bmatrix}$$

In our case the number of homologues of the polyoxyethylene glycols and the polyoxyethylene glycol monoalkyl ethers was 82, and the number of characteristic groups was 4. In the case of N-polyoxyethylene alkylamines these numbers were 40 and 7, respectively; the following characteristic groups were considerred: O, OH, $OSi(CH_3)_3$, N, NH and $NSi(CH_3)_3$. For polyoxyethylene glycol monoalkylphenyl

TABLE IV

ARITHMETIC RETENTION INDICES FOR N-POLYOXYETHYLENE ALKYL- AND DIALKYI AMINES

| *Formula* | *n* | $I_R^{exp}$ | $I_R^{calc}$ | *Error* | |
|---|---|---|---|---|---|
| | | | | *Absolute* | *Relative (%)* |
| $C_6H_{13}N$ with $(EO)_mSil$ and $(EO)_1Sil$; $m+1=n$ | 2 | 1659 | 1676 | −17 | −1.0 |
| | 3 | 1969 | 1975 | − 6 | −0.3 |
| | 4 | 2266 | 2274 | − 8 | −0.4 |
| | 5 | 2559 | 2573 | −14 | −0.5 |
| | 6 | 2841 | 2872 | −31 | −1.1 |
| | 7 | 3129 | 3171 | −42 | −1.3 |
| | 8 | 3433 | 3470 | −37 | −1.1 |
| | 9 | 3717 | 3769 | −52 | −1.4 |
| $C_6H_{17}N$ with (EO)H and (EO)H | 2 | 1695 | 1664 | 31 | 1.8 |
| $C_{10}H_{21}NH(EO)_nSil$ | 1 | 1750 | 1762 | −12 | −0.7 |
| | 2 | 2071 | 2061 | 10 | 0.5 |
| | 3 | 2372 | 2360 | 12 | 0.5 |
| | 4 | 2670 | 2659 | 11 | 0.4 |
| | 5 | 2975 | 2958 | 17 | 0.6 |
| | 6 | 3280 | 3257 | 23 | 0.7 |
| $C_6H_{13}NH(EO)_nSil$ | 1 | 1356 | 1362 | − 6 | −0.4 |
| $C_{10}H_{21}N(EO)_nSil$ / Sil | 1 | 1823 | 1818 | 5 | 0.3 |
| | 2 | 2125 | 2117 | 8 | 0.4 |
| | 3 | 2411 | 2416 | − 5 | −0.2 |
| | 4 | 2687 | 2715 | −28 | −1.0 |
| $C_6H_{13}N(EO)_nSil$ / Sil | 1 | 1439 | 1418 | 21 | 1.5 |
| $C_{10}H_{21}NH(EO)_nH$ | 1 | 1750 | 1556 | − 6 | −0.3 |
| | 2 | 2047 | 2055 | − 8 | −0.4 |
| | 3 | 2353 | 2354 | − 1 | 0.0 |
| | 4 | 2668 | 2653 | 15 | 0.6 |
| | 5 | 2998 | 2952 | 46 | 1.5 |
| | 6 | 3313 | 3251 | 62 | 1.9 |
| $C_6H_{13}NH(EO)_nH$ | 1 | 1335 | 1356 | −21 | −1.6 |
| Bu, Bu, $N(EO)_nSil$ | 1 | 1361 | 1351 | 10 | 0.7 |
| | 2 | 1660 | 1650 | 10 | 0.6 |
| | 3 | 1966 | 1949 | 17 | 0.9 |
| | 4 | 2270 | 2248 | 22 | 1.0 |
| | 5 | 2570 | 2547 | 23 | 0.9 |
| | 6 | 2870 | 2846 | 24 | 0.8 |
| Bu, Bu, $N(EO)_nH$ | 1 | 1337 | 1345 | − 8 | −0.6 |
| | 2 | 1609 | 1644 | −35 | −2.2 |
| | 3 | 1924 | 1943 | −19 | −1.0 |
| | 4 | 2244 | 2242 | 2 | 0.1 |
| | 5 | 2564 | 2541 | 23 | 0.9 |
| | 6 | 2888 | 2840 | 48 | 1.7 |
| Average error | | | | 20 | 0.8 |

TABLE V

ARITHMETIC RETENTION INDICES FOR POLYOXYETHYLENE GLYCOL MONOALKYLPHENYL ETHERS

| *Formula* | *n* | $I_R^{exp}$ | $I_R^{calc}$ | *Error* | |
|---|---|---|---|---|---|
| | | | | *Absolute* | *Relative (%)* |
| O (EO)$_n$Sil | 0 | 1697 | 1797 | −100 | −5.9 |
| \| | 1 | 2050 | 2102 | − 52 | −2.5 |
| $C_6H_4$ | 2 | 2393 | 2407 | − 14 | −0.6 |
| \| | 3 | 2729 | 2712 | 17 | 0.6 |
| $H_3C$–C–$CH_3$ | 4 | 3045 | 3017 | 28 | 0.9 |
| \| | 5 | 3366 | 3322 | 44 | 1.3 |
| $CH_2$ | 6 | 3666 | 3627 | 39 | 1.1 |
| \| | 7 | 3973 | 3932 | 41 | 1.0 |
| $H_3C$–C–$CH_3$ | 8 | 4283 | 4237 | 46 | 1.1 |
| \| | 9 | 4592 | 4542 | 50 | 1.1 |
| $CH_3$ | | | | | |
| O (EO)$_n$Sil | 0 | 1968 | 1895 | 73 | 3.7 |
| \| | 1 | 2152 | 2200 | − 48 | 2.2 |
| $C_6H_4$ | 2 | 2459 | 2505 | − 46 | 1.9 |
| \| | 3 | 2783 | 2810 | − 27 | 1.0 |
| $CH_2$ | 4 | 3095 | 3115 | − 20 | 0.6 |
| \| | 5 | 3401 | 3420 | − 19 | 0.6 |
| CH–$C_2H_5$ | 6 | 3708 | 3725 | − 17 | 0.5 |
| \| | 7 | 4006 | 4030 | − 24 | 0.6 |
| $(CH_2)_3$ | 8 | 4326 | 4335 | − 9 | 0.2 |
| \| | 9 | 4639 | 4640 | − 1 | 0.0 |
| $CH_3$ | | | | | |
| O (EO)$_n$OAc | 1 | 2175 | 2248 | − 73 | −3.4 |
| \| | 2 | 2525 | 2553 | − 28 | −1.1 |
| $C_6H_4$ | 3 | 2854 | 2858 | − 4 | −0.1 |
| \| | 4 | 3156 | 3163 | − 7 | −0.2 |
| $H_3C$–C–$CH_3$ | 5 | 3486 | 3468 | 18 | 0.5 |
| \| | 6 | 3812 | 3773 | 39 | 1.0 |
| $CH_2$ | 7 | 4125 | 4078 | 47 | 1.1 |
| \| | 8 | 4437 | 4383 | 54 | 1.2 |
| $H_3C$–C–$CH_3$ | | | | | |
| \| | | | | | |
| $CH_3$ | | | | | |
| Average error | | | | 35 | 0.9 |

ethers the numbers of the species in the system and of the considered groups $CH_2$ = $CH_3$, a branched alkyl, O, $OSi(CH_3)_3$, $OOCH_3$ and $C_6H_4$ were 28 and 6, respectively.

However, it was necessary to set the values of the increment of the arithmetic index for the methylene group and for the methyl group as being 100. Therefore standard alkanes were considered in the numbers equivalent to the numbers of the surfactants present in the system. In this case the formula vectors are very simple because the formula of the alkane can be expressed as: $A_i = (CH_2)_{a_{CH_2,i}}$ (the methyl

group is considered equivalent to the methylene group). Thus, the formula vector is; $\boldsymbol{a}_i = [a_{CH_2,i}, O, \ldots, O]^T$. An exemplary formula matrix for a system containing hexane, heptane and octane is:

$$\boldsymbol{A} = \begin{bmatrix} 6 & 7 & 8 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

The whole matrix of the system considers all the formula vectors determined both for the considered surfactants and for the standard alkanes: $\boldsymbol{A} = [\boldsymbol{a}_1, \boldsymbol{a}_2, \ldots, \boldsymbol{a}_n, \boldsymbol{a}_{i+1}, \ldots, \boldsymbol{a}_{2n}]$, where $\boldsymbol{a}_1, \ldots, \boldsymbol{a}_n$ denote the formula vectors for the separated homologues of the considered surfactants, while $\boldsymbol{a}_{n1}, \ldots, \boldsymbol{a}_{2n}$ denote the formula vectors for additionally considered standard alkanes.

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

$$I_{R,A_i} = \sum_{j=1}^{m} a_{ji} \cdot \Delta I_{R,G_j}$$

where it is assumed that the increment of $I_R$ for a group $G_j$ is constant for all compounds present in the considered system. Thus, when the set of the arithmetic retention index obtained for all compounds present in the system is taken into consideration, the following set of linear equations is obtained:

$$I_{R,A_1} = \sum_{j=1}^{m} a_{j1} \cdot \Delta I_{R,G_j}$$

$$I_{R,A_2} = \sum_{j=1}^{m} a_{j2} \cdot \Delta I_{R,G_j}$$

$$\vdots$$

$$I_{R,A_n} = \sum_{j=1}^{m} a_{jn} \cdot \Delta I_{R,G_j}$$

which can be presented as:

$$\boldsymbol{I}_R = \boldsymbol{A} \cdot \Delta \boldsymbol{I}_R$$

where

$$\boldsymbol{I}_R = [I_{R,A_1}, I_{R,A_2}, \ldots, I_{R,A_n}]^T$$

$$\Delta \boldsymbol{I}_R = [\Delta I_{R,G_2}, \ldots, \Delta I_{R,G_n}]^T$$

The above set of linear equations was solved by the orthogonalization method of

Gram-Schmidt[7]. The values of the increments for the arithmetic retention index obtained for polyoxyethylene glycols and polyoxyethylene glycol monoalkyl ethers and for N-polyoxyethylene alkylamines are given in Table VI. The increments for polyoxyethylene glycol monoalkylphenyl ethers are also given in this table, but they were calculated in a somewhat different way that will be discussed later.

The increments obtained can be used to estimate the values of the arithmetic retention index of the surfactants (Table I–V). The average absolute errors of $I_R$ estimation for polyoxyethylene glycols, polyoxyethylene glycol monoalkyl ethers and N-polyoxyethylene alkylamines are *ca.* 20 units, which corresponds to a relative error of *ca.* 0.7–0.8%. This proves the validity of the applied calculation method and the accuracry of $I_R$ determination. Thus, for the groups of surfactants considered the arithmetic retention index of the successive homologues can be estimated from the increments obtained, which may be useful for the identification of succesive peaks on the chromatograms.

In the case of polyoxyethylene glycol monoalkylphenyl ethers it is necessary to take into account the fact that the alkyl chain is branched, and hence that successive homologues elute earlier than equivalent isomers with the straight-chain octyl group. Thus, lower values of the arithmetic retention index are obtained for homologues with a more branched alkyl chain. The $I_R$ increment for a branched octyl group is then lower than 800, and the increment per statistical carbon atom in a branched alkyl is lower than 100. A linear relation is observed between the arithmetic retention index and the connectivity index[8] (Fig. 1). Using the least-squares method the following equation was obtained: $I_R = 197.64 + 208.25$, which is characterized by a high value for the determination coefficient ($R^2 = 0.9987$). The connectivity indices for *n*-octyl, 2-ethylhexyl and 1,1,3,3-tetramethylbutyl are 4.0607, 3.9545 and 3.4571, respectively. Assuming that the $I_R$ increment is proportional to the increment of the connectivity index, the following values of $I_R$ for 2-ethylhexyl and 1,1,3,3-tetramethylbutyl were obtained: $800 \cdot 3.9545/4.0607 = 779$ and $800 \cdot 3.4571/4.0607 = 681$, respectively. These values correspond to $\Delta I_R$ values of 97.375 and 85.125 for

TABLE VI

INCREMENTS OF THE ARITHMETIC RETENTION INDEX

| *Group* | *A** | *B*** | *C**** |
|---|---|---|---|
| $-CH_2-$, $-CH_3$ | 100 | 100 | 100 |
| 2-Ethylhexyl | – | – | 779 |
| 1,1,3,3-Tetramethylbutyl | – | – | 681 |
| –O– | 105 | 99 | 105 |
| –OH | – | 319 | – |
| –OSil | 380 | 325 | 380 |
| –OAc | 526 | – | 526 |
| $-C_6H_4-$ | – | – | 736 |
| =N– | – | 26 | – |
| =NH | – | 237 | – |
| =NSil | – | 293 | – |

* A = polyoxyethylene glycols and polyoxyethylene glycol monoalkyl ethers.
** B = N-polyoxyethylene alkylamines.
*** C = polyoxyethylene glycol monoalkylphenyl ethers.

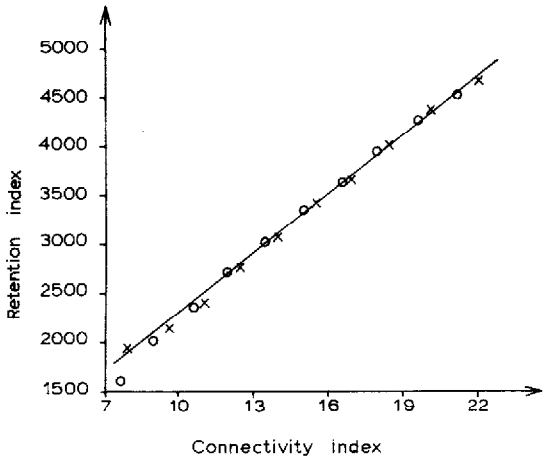


Fig. 1. The relation between the arithmetic retention index and the connectivity index; × = polyoxyethylene glycol 2-ethylhexylphenyl ethers; ○ = polyoxyethylene glycol 1,1,3,3-tetramethylbutylphenyl ethers.

each statistical carbon atom in 2-ethylhexyl and 1,1,3,3-tetramethylbutyl, respectively, compared with 100 in the *n*-octyl group. The increments for other characteristic groups present in polyoxyethylene glycol monoalkylphenyl ethers were similarly calculated. These values are given in Table VI, and the comparison of the estimated $I_R$ values with those determined experimentally is shown in Table V. Te average absolute and relative errors are 35 and 0.9%, respectively, which is almost twice as large on the $I_R$ scale than in the case of the previous groups of compounds considered.

## CONCLUSIONS

The arithmetic retention index estimated from the increments determined for characeristic groups present in the surfactant molecules of the polyoxyethylene glycols and their derivatives can be used to identify peaks on the chromatograms. The average absolute and relative errors of the arithmetic retention index estimation are 20 and 0.7–0.8%, respectively, for polyoxyethylene glycols, polyoxyethylene glycol monoalkyl ethers and N-polyoxyethylene alkylamines, and 35 and 0.9%, respectively, for polyoxyethylene glycol monoalkylphenyl ethers.

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