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INCREMENTS OF SOME POLARITY PARAMETERS FOR POLYOXYETHYLENE GLYCOL DIALKYL ETHERS AND FOR SOME OF THEIR SULPHUR ANALOGUES

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SUMMARY

Gas–liquid chromatography was used to determine the polarity of pure model polyoxyethylene glycol dialkyl ethers and of some their sulphur analogues. The polarity parameters were correlated with the surfactant structure and increments for characteristic groups were determined. These values can be used to estimate the polarity of surfactants using only their formulae.

INTRODUCTION

Although gas–liquid chromatography has been used by several workers[1] to investigate the polarity of surfactants, there is not much information available concerning the relationships between surfactant structure and polarity. Most work has involved commercial mixtures or model polydisperse mixtures and in only a few instances have pure model products been considered[2,3].

In all the reported work on the polarity and the hydrophilic–lipophilic balance of surfactants, simple alcohols such as methanol or ethanol have been used as solutes, and hence proton donor–proton acceptor interactions have been considered[4,5]. As polarity parameters, the so-called polarity index[6], the coefficient ρ[7] and the retention index have been considered. The polarity index (*PI*) is defined by the equation $PI = 100 \log (C - 4.7) + 60$, where C is the apparent number of carbon atoms in a standard alkane having the same retention time as the alcohol. The coefficient ρ is the ratio of the retention time of an alcohol to that of *n*-hexane.

The aim of this work was to determine the values of the above polarity parameters for polyoxyethylene glycol dialkyl ethers and of some their sulphur analogues, and to calculate the increments of the polarity parameters for characteristic groups present in the surfactant molecules, which could be used to estimate the polarity of surfactants from their formulae.

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EXPERIMENTAL

Twenty-eight pure model compounds were used for chromatographic measurements. The chromatographic measurements were carried out in the same way as in our previous work[3]. The same standard conditions for chromatographic measurements were used and the same polarity parameters were considered. Instead of Kieselguhr, Porolith (0.2–0.5 mm) (G.D.R.) was used as a support. Ethanol was used as the polar agent, and while C_5–C_9 *n*-alkanes were used as non-polar standards. The standard temperature of measurements was 70°C.

TABLE I

POLARITY PARAMETERS

t = 70°C; ethanol as the polar agent.

No.	*Compound**	I_R**	*PI***	ρ
1	$Dod(OE)_3ODod$	560.8 ± 0.4	55.7 ± 0.2	0.73 ± 0.00
2	$Dod(OE)_4ODod$	586.5 ± 0.9	66.1 ± 0.3	0.90 ± 0.01
3	$Dod(OE)_5ODod$	602.9 ± 0.2	71.2 ± 0.1	1.03 ± 0.00
4	$Dod(OE)_6ODod$	611.9 ± 0.5	73.6 ± 0.2	1.10 ± 0.00
5	$Dod(OE)_7ODod$	623.2 ± 0.4	77.6 ± 0.1	1.22 ± 0.00
6	$Dod(OE)_8ODod$	637.8 ± 0.4	81.7 ± 0.1	1.38 ± 0.00
7	$Oct(OE)_4OOct$	666.0 ± 0.3	77.0 ± 0.1	1.20 ± 0.00
8	$Oct(OE)_7OOct$	665.0 ± 0.5	88.2 ± 0.1	1.71 ± 0.01
9	$Bu(OE)_4OBu$	666.0 ± 0.3	88.4 ± 0.1	1.74 ± 0.00
10	$Bu(OE)_5OBu$	686.2 ± 1.0	92.9 ± 0.2	2.02 ± 0.02
11	$Bu(OE)_6OBu$	707.2 ± 0.8	96.9 ± 0.1	2.38 ± 0.02
12	$Bu(OE)_7OBu$	723.0 ± 0.6	99.8 ± 0.1	2.65 ± 0.01
13	$Bu(OE)_8OBu$	735.5 ± 0.5	101.9 ± 0.1	2.93 ± 0.01
14	$Bu(OE)_9OBu$	741.1 ± 0.7	102.9 ± 0.1	2.97 ± 0.02
15	Bu(OE)S(EO)Bu	572.8 ± 1.1	60.7 ± 0.4	0.80 ± 0.01
16	$Bu(OE)_2S(EO)_2Bu$	645.2 ± 1.7	83.4 ± 0.4	1.47 ± 0.02
17	$Bu(OE)_3S(EO)_3Bu$	684.9 ± 0.3	92.0 ± 0.1	1.96 ± 0.00
18	$Bu(OE)_4S(EO)_4Bu$	725.9 ± 0.3	99.9 ± 0.1	2.63 ± 0.00
19	$Bu(OE)_4SBu$	659.6 ± 0.7	87.2 ± 0.2	1.65 ± 0.01
20	$Bu(OE)S(EO)_3Bu$	653.7 ± 1.4	85.7 ± 0.3	1.57 ± 0.02
21	Bu(OE)(SE)S(ES)(EO)Bu	627.4 ± 0.4	78.5 ± 0.1	1.25 ± 0.00
22	$Bu(OE)_2(SE)S(ES)(EO)_2Bu$	669.8 ± 0.6	88.9 ± 0.1	1.72 ± 0.01
23	$Bu(OE)_3(SE)S(ES)(EO)_3Bu$	709.1 ± 0.6	96.9 ± 0.1	2.29 ± 0.02
24	$Bu(OE)_4(SE)S(ES)(EO)_4Bu$	729.7 ± 0.6	100.5 ± 0.1	2.60 ± 0.01
25***	$Bu(OE)(SE)_2S(ES)_2(EO)Bu$	654.7 ± 1.3	84.0 ± 0.3	1.42 ± 0.01
26	$Bu(OE)_2(SE)_2S(ES)_2(EO)_2Bu$	693.8 ± 0.7	93.2 ± 0.1	2.02 ± 0.01
27	$Bu(OE)_3(SE)_2S(ES)_2(EO)_3Bu$	725.0 ± 0.4	99.4 ± 0.1	2.44 ± 0.02
28	$Bu(OE)_4(SE)_2S(ES)_2(EO)_4Bu$	744.4 ± 0.4	102.9 ± 0.1	2.93 ± 0.01

* Dod = $C_{12}H_{25}$; Oct = C_8H_{17}; Bu = C_4H_9; EO = $-CH_2CH_2O-$; ES = $-CH_2CH_2S-$.

** I_R = Retention index; *PI* = polarity index.

*** Column temperature, 90°C.

RESULTS AND DISCUSSION

The formulae of the surfactants and the average values of the determined polarity parameters and their confidence limits at the significance level of 0.05 are given in Table I.

The results indicate the high precision of the determination of the polarity parameters. The precisions of the determination of the retention index and the polarity index are equivalent, while the coefficient ρ is determined with lower precision. For the retention index and the polarity index the ratios of the confidence limits to the average values of the polarity parameters are about 0.1%, while for the coefficient ρ they do not exceed 1%.

This statistical analysis demonstrates that the parameters under consideration can be used to discuss the influence of the structure of the compounds on their polarity, and even the influence of small changes in structure on polarity can be observed.

The influence of the number of oxyethylene units on the values of the polarity parameters is shown in Figs. 1–3. The effect of the length of the polyoxyethylene chain on polarity depends on the number of oxyethylene units and on the number of carbon atoms in the alkyl group. As the number of oxyethylene groups increases, the polarity of the compounds also increases but straight lines are observed only for 4–8 oxyethylene units. This means that the first oxyethylene groups influence the polarity of the surfactants more strongly than subsequent groups. Thus, a greater increase in polarity is observed for compounds 1 and 2, containing three and four oxyethylene groups, whereas a much smaller increase is observed for compounds 13

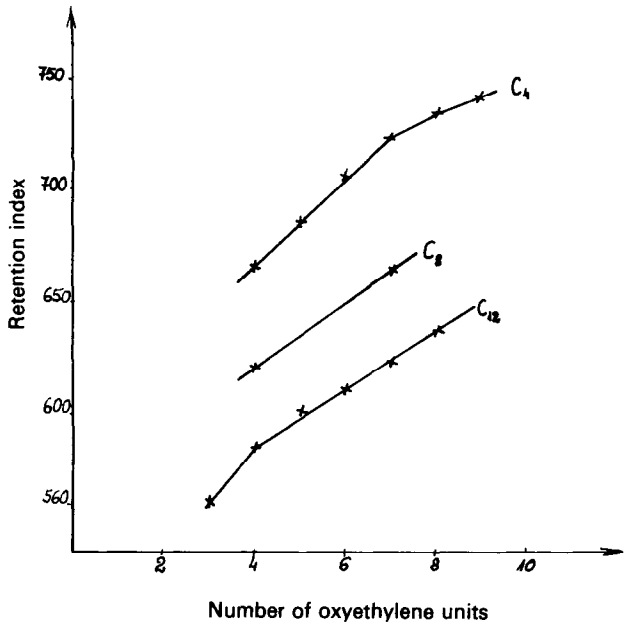

Fig. 1. Influence of the polyoxyethylene chain in polyoxyethylene glycol dialkyl ethers on the retention index of ethanol.

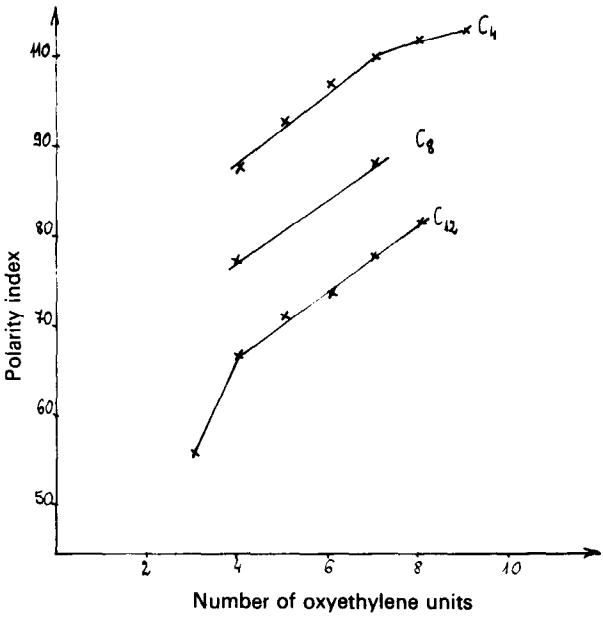

Fig. 2. Influence of the polyoxyethylene chain in polyoxyethylene glycol dialkyl ethers on the polarity index of ethanol.

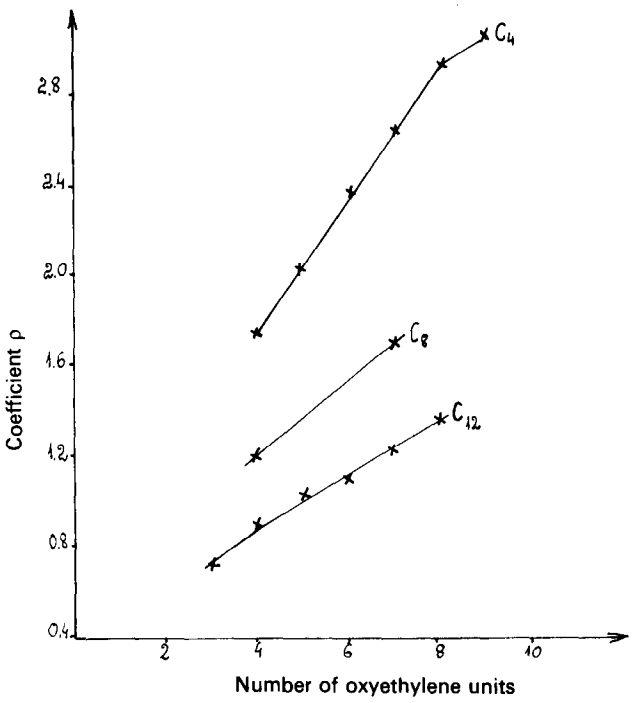

Fig. 3. Influence of the polyoxyethylene chain in polyoxyethylene glycol dialkyl ethers on the coefficient ρ of ethanol.

and 14, containing eight and nine oxyethylene groups. In the region from four to eight oxyethylene groups in the polyoxyethylene chain, appropriate constant increments of the polarity parameters can be atributed to each oxyethylene group. The values of the regression coefficients for the determined straight lines are given in Table II. The slopes of the derived straight lines give the values of the increments per oxyethylene group. The effect of the polyoxyethylene chain on the polarity of the surfactants depends on the length of the alkyl chains and increases as the length of the hydrophobes decreases. Higher slopes are obtained for shorter alkyl chains. Hence the calculation of only one average increment for an oxyethylene group, as has been done previously[3], is a simplification.

TABLE II

REGRESSION COEFFICIENTS OF THE RELATIONSHIP $PP_i = A_i n + B_i$

PP_i = Polarity parameters; n = number of oxyethylene groups; A_i, B_i = contants.

Polarity parameter	*Alkyl*	A_i	B_i	*Correlation coefficient*
I_R	C_4	19.2	590.0	0.9982
	C_8	14.7	562.0	1.0000
	C_{12}	12.3	538.7	0.9958
PI	C_4	3.80	73.5	0.9955
	C_8	3.73	62.1	0.9999
	C_{12}	3.76	51.5	0.9955
ρ	C_4	0.301	0.54	0.9988
	C_8	0.170	0.52	1.0000
	C_{12}	0.115	0.44	0.9923

The values of the B_i coefficients given in Table II determine the values of the polarity parameters for the sum of the alkoxy and alkyl groups. Assuming additivity also in this instance, the following relationship can be considered:

$$B_i = \Delta PP_{RO} + \Delta PP_R = 2\,\Delta PP_R + \Delta PP_O$$

where ΔPP_{RO}, ΔPP_R and ΔPP_O denote appropriate increments of the polarity parameters for the alkoxy and alkyl groups and the ethereal oxygen, respectively. Assuming that $\Delta PP_{CH_2} = \Delta PP_{CH_3}$, the following relationship is obtained:

$$B_i = 2m\Delta PP_{CH_2} + \Delta PP_O$$

where m denotes the number of carbon atoms in the alkyl group.

Using the values of the B_i coefficients obtained, the appropriate increments for the methylene and methyl groups present in the hydrophobes and for the ethereal oxygen bonded with one alkyl group were calculated and are given in Table III. These values can be used to predict the polarity parameters for the group of compounds discussed. For other alkyl chains, interpolation or even extrapolation of in-

TABLE III

INCREMENTS FOR THE ESTIMATION OF POLARITY PARAMETERS

Group	*Alkyl*	ΔI_R	ΔPI	$\Delta\rho$
$-OCH_2CH_2-$	C_4	19.2	3.80	0.301
	C_8	14.7	3.73	0.170
	C_{12}	12.3	3.76	0.115
$-O-$	–	614.1	84.5	0.58
$-CH_2-$, $-CH_3$	–	−3.21	−1.375	−0.00625

crement values for the oxyethylene group is possible. Comparison of the predicted values of the polarity parameters with those obtained experimentally shows fairly good agreement. The average absolute errors of the determination of the polarity parameters are about 1.9, 0.6 and 0.02 for the retention index, polarity index and ρ, respectively, corresponding to approximate percentage of 0.3%, 0.8% and 1%, respectively.

The replacement of one oxygen atom by a sulphur atom causes a decrease in polarity. The data presented in Figs. 4–6 show that straight lines obtained for symmetrical compounds having one central sulphur atom are shifted in a parallel manner towards lower values of the polarity parameters compared with analogues containing oxygen. These results indicate that replacement of the central oxygen by a sulphur atom is approximately equivalent to a decrease in the length of the polyoxyethylene chain by one oxyethylene group. Hence the effective length of a hydrophilic chain for such sulphur analogues is lower than that for the appropriate oxygen homologues by about one oxyethylene group. However, the decrease in polarity observed for sulphur analogues depends on the location of the sulphur atom in the surfactant

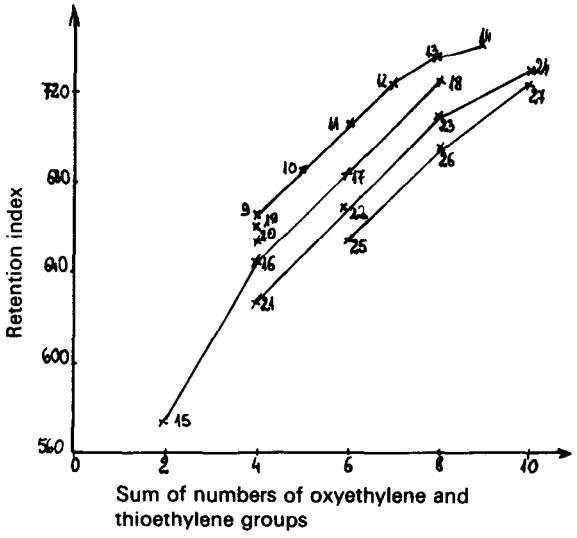

Fig. 4. Retention index of polyoxyethylene glycol dialkyl ethers and their sulphur analogues.

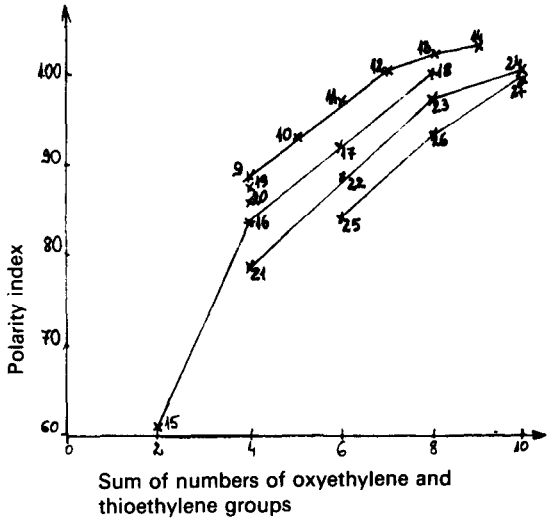

Fig. 5. Polarity index of polyoxyethylene glycol dialkyl ethers and their sulphur analogues.

molecule, and when the asymmetry increases the decrease in polarity is less. Hence the following order of polarity is observed: $Bu(OE)_2O(EO)_2Bu$ > $BuS(EO)_4Bu$ > $Bu(OE)S(EO)_3Bu$ > $Bu(OE)_2S(EO)_2Bu$. The values of the appropriate increments for sulphur atoms are given in Table IV. The average errors of the predicted values of the retention index, the polarity index and ρ are about 1.1, 1.4 and 0.1, respectively,

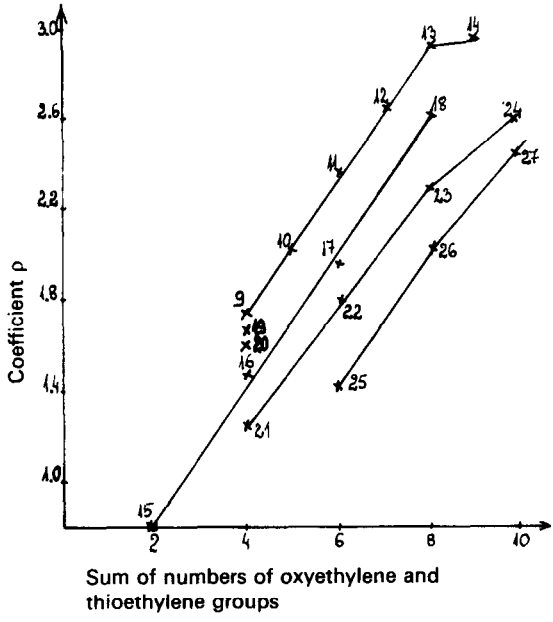

Fig. 6. Coefficient ρ of polyoxyethylene glycol dialkyl ethers and their sulphur analogues.

TABLE IV

INCREMENTS OF POLARITY PARAMETERS FOR SULPHUR ATOMS

Sulphur position	ΔI_R	ΔPI	$\Delta\rho$
Central: $Bu(OE)_nS(EO)_nBu$	598.0	76.8	0.383
Bonded with one EO: $Bu(OE)S(EO)_3Bu$	605.7	78.6	0.666
Bonded with alkyl: $BuS(EO)_4Bu$	611.6	80.1	0.674

corresponding to approximate percentage errors of 0.2%, 1.5% and 5.5%, respectively.

When the next oxygen atoms in the neighbourhood of the central sulphur are replaced by sulphur, a further decrease in polarity is observed in comparison with the appropriate oxygen analogues. However, this decrease is smaller than for the introduction of the first sulphur atom. The polarity of sulphur analogues increases as the length of the polythioethylene chain increases (Figs. 7–9). Depending on the length of the polyoxyethylene chain, the effect of the polythioethylene chain on surfactant polarity is quantitively different. This effect of the polythioethylene chain diminishes as the length of the polyoxyethylene chain increases. This influence can be determined from the slopes of the straight lines in Figs. 7–9. The values of the estimated increments are given in Table IV. The average errors of the predicted polarity parameters are 2.8, 1.0 and 0.05 for the retention index, the polarity index and ρ, respectively, corresponding to percentage errors of about 0.5%, 1.2% and 2.8%, respectively. Thus, the increments determined can be used for the compounds studied to estimate polarity parameters on the basis only of their formulae.

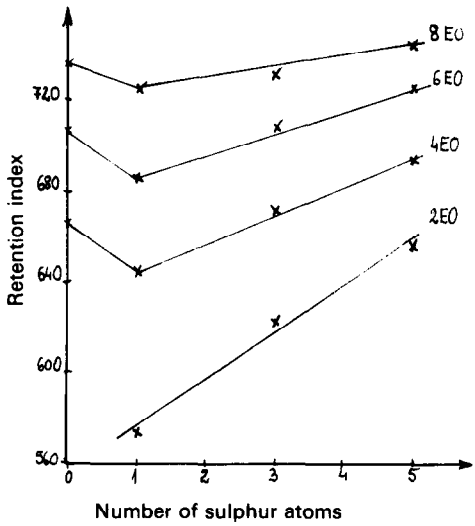

Fig. 7. Influence of the number of sulphur atoms on the retention index of ethanol.

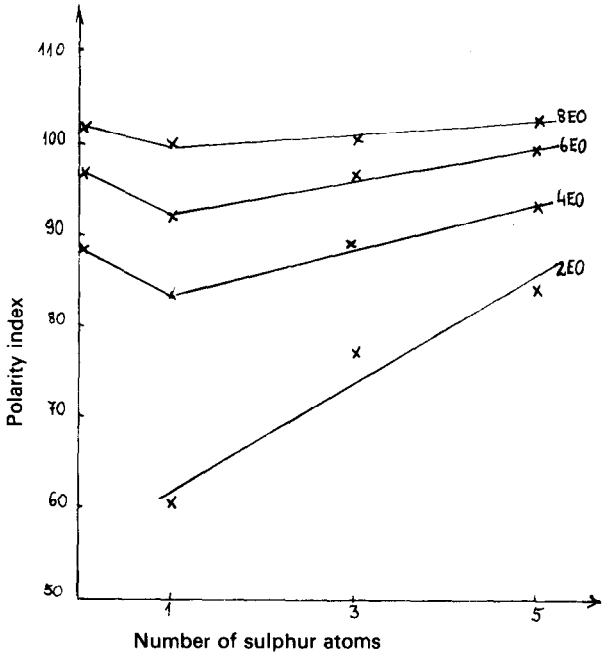

Fig. 8. Influence of the number of sulphur atoms on the polarity index of ethanol.

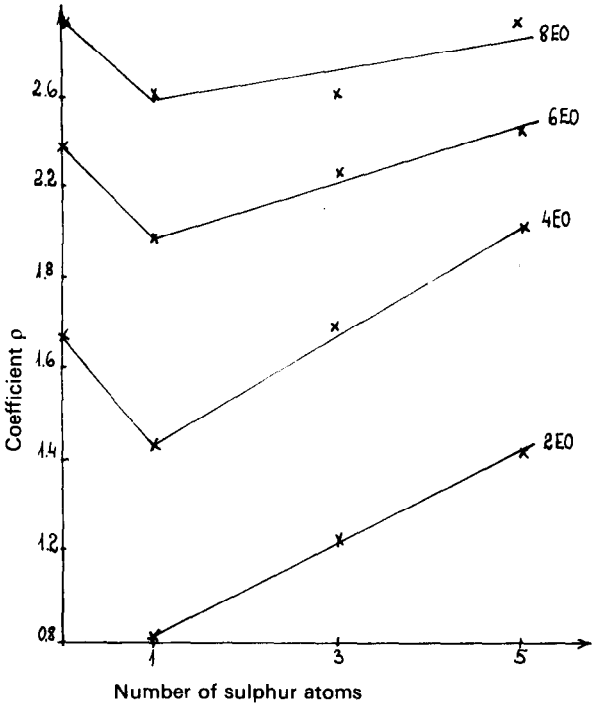

Fig. 9. Influence of the number of sulphur atoms on the coefficient ρ of ethanol.

TABLE V

INCREMENTS OF POLARITY PARAMETERS FOR THE THIOETHYLENE GROUP

Number of oxyethylene groups	ΔI_R	ΔPI	$\Delta\rho$
2	20.5	5.8	0.15
4	12.1	2.5	0.14
6	10.0	1.85	0.12
8	4.6	0.75	0.075

CONCLUSIONS

Gas–liquid chromatography can be used to determine the influence of the structure of non-ionic surfactants on their polarity. The retention index and polarity index of ethanol were determined with high precision, and were correlated with the structure of the surfactants. The results reflect small structural changes. The additivity of these two parameters can be assumed, and the increments determined for the characteristic groups present in a surfactant molecule can be used to estimate the polarity of surfactants using only their formulae. Depending on the structure of the surfactants considered their polarity can be estimated with errors in the range 0.2–1.5%. The replacement of oxygen atoms in the polyoxyethylene chain by sulphur atoms decreases the surfactant polarity. The polythioethylene chain shows polar character, but its influence on the surfactant polarity is weak and depends on the length of the polyoxyethylene chain.

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