

CHROM. 17 922

## POLARITY OF POLYOXYETHYLENE GLYCOL DIALKYL ETHERS AND SOME SULPHUR ANALOGUES MEASURED BY GAS CHROMATOGRAPHY

JORG BEGER and HEIKE MERKWITZ

*Department of Chemistry, Mining Academy at Freiberg, 9200-Freiberg (G.D.R.)*

and

JAN SZYMANOWSKI\* and ADAM VOELKEL

*Institute of Chemical Technology and Engineering, Technical University of Poznań, Pl. Skłodowskiej Curie, Poznań (Poland)*

(Received May 23rd, 1985)

---

### SUMMARY

Gas-liquid chromatography was used to determine the polarity of pure model polyoxyethylene glycol dialkyl ethers and their sulphur analogues. Relationships between the polarity parameters are discussed. The polarity parameters were correlated with surfactant structure and increments for characteristic groups were determined.

---

### INTRODUCTION

Although gas-liquid chromatography (GLC) has been used by several authors<sup>1</sup> to investigate the polarity of surfactants, little information is available concerning the relationships between surfactant structure and polarity. Most studies have involved commercial mixtures or model polydisperse products; pure model products have been considered only in a few cases<sup>2-4</sup>.

The aim of this work was to study the polarity of pure model polyoxyethylene glycol dialkyl ethers and of their sulphur analogues having the following structure:  $RX(CH_2CH_2X)_nR$ , where:  $X = O$  or  $S$ . The polarity of these compounds was discussed in our previous work<sup>4</sup> in which ethanol was used as the polar agent. However, it was impossible to compare these results with those obtained previously for non-ionic surfactants containing one terminal hydrophobic chain and one polyoxyethylene chain, and to discuss the influence of the terminal hydrophobic chains upon the polarity of the surfactants. In order to obtain appropriate data for such a comparison it was necessary to carry out chromatographic measurements using methanol as the polar agent.

We also wished to investigate the influence of the surfactants' structure upon their polarity and to determine the increments in the polarity parameters of characteristic groups present in the surfactant molecules in order to predict the polarity of surfactants from their formulae.

## EXPERIMENTAL

The same 28 pure compounds were used as in our previous work<sup>4</sup>. Their formulae and the values of the determined polarity parameters are given in Table I. The numbering system is that used previously<sup>4</sup>.

Chromatographic measurements were carried out using a gas chromatograph equipped with a thermal conductivity detector. The conditions were as follows: column, 1 m × 3 mm I.D.; column and sample injector temperatures, 70 and 160°C, respectively; column packing, 25% (w/w) surfactant on Porolith (mesh size, 0.2–0.5 mm); carrier gas (nitrogen) flow-rate, 40 ml/min; polar agent, methanol; non-polar standards, mixture of C<sub>5</sub>–C<sub>9</sub> *n*-alkanes; time for column stabilization, 10 h.

For each surfactant five different measurements were made and the average values of the retention time and of the polarity parameters were calculated. The

TABLE I  
POLARITY PARAMETERS

Significance level ( $\alpha$ ) = 0.05, 70°C. Dod = C<sub>12</sub>H<sub>25</sub>; Oct = C<sub>8</sub>H<sub>17</sub>; Bu = C<sub>4</sub>H<sub>9</sub>; OE = -OCH<sub>2</sub>CH<sub>2</sub>-; EO = -CH<sub>2</sub>CH<sub>2</sub>O-; SE = -SCH<sub>2</sub>CH<sub>2</sub>-; ES = -CH<sub>2</sub>CH<sub>2</sub>S-

No.	Compound	$I_R$	$PI$	$\rho$
1	Dod(OE) <sub>3</sub> ODod	—	—	—
2	Dod(OE) <sub>4</sub> ODod	—	—	—
3	Dod(OE) <sub>5</sub> ODod	550.1 ± 0.8	50.5 ± 0.4	0.68 ± 0.00
4	Dod(OE) <sub>6</sub> ODod	549.3 ± 0.8	50.2 ± 0.4	0.69 ± 0.01
5	Dod(OE) <sub>7</sub> ODod	558.8 ± 2.0	54.6 ± 0.9	0.72 ± 0.01
6	Dod(OE) <sub>8</sub> ODod	584.4 ± 0.9	64.9 ± 0.3	0.89 ± 0.01
7	Oct(OE) <sub>4</sub> OOct	563.0 ± 0.5	56.5 ± 0.2	0.75 ± 0.00
8	Oct(OE) <sub>7</sub> OOct	611.3 ± 0.6	73.8 ± 0.2	1.10 ± 0.01
9	Bu(OE) <sub>4</sub> OBu	607.4 ± 0.6	72.3 ± 0.2	1.06 ± 0.01
10	Bu(OE) <sub>5</sub> OBu	628.1 ± 1.4	79.0 ± 0.4	1.26 ± 0.01
11	Bu(OE) <sub>6</sub> OBu	651.4 ± 1.1	84.9 ± 0.3	1.52 ± 0.01
12	Bu(OE) <sub>7</sub> OBu	675.2 ± 0.6	90.2 ± 0.1	1.81 ± 0.01
13	Bu(OE) <sub>8</sub> OBu	692.6 ± 0.6	93.8 ± 0.1	2.07 ± 0.01
14	Bu(OE) <sub>9</sub> OBu	694.8 ± 1.2	94.3 ± 0.2	2.06 ± 0.02
15	Bu(OE)S(EO)Bu	521.0 ± 1.1	32.8 ± 0.8	0.53 ± 0.00
16	Bu(OE) <sub>2</sub> S(EO) <sub>2</sub> Bu	575.5 ± 2.4	61.5 ± 0.9	0.83 ± 0.01
17	Bu(OE) <sub>3</sub> S(EO) <sub>3</sub> Bu	630.9 ± 0.4	79.1 ± 0.1	1.28 ± 0.00
18	Bu(OE) <sub>4</sub> S(EO) <sub>4</sub> Bu	672.5 ± 0.7	89.1 ± 0.2	1.73 ± 0.01
19	Bu(OE) <sub>4</sub> SBu	604.7 ± 1.2	72.0 ± 0.4	1.04 ± 0.01
20	Bu(OE)S(EO) <sub>3</sub> Bu	599.1 ± 1.3	69.7 ± 0.3	0.99 ± 0.01
21	Bu(OE)(SE)S(ES)(EO)Bu	575.3 ± 0.7	61.3 ± 0.3	0.84 ± 0.00
22	Bu(OE) <sub>2</sub> (SE)S(ES)(EO) <sub>2</sub> Bu	658.0 ± 0.9	85.1 ± 0.2	1.53 ± 0.01
23	Bu(OE) <sub>3</sub> (SE)S(ES)(EO) <sub>3</sub> Bu	662.9 ± 1.1	87.2 ± 0.2	1.61 ± 0.01
24	Bu(OE) <sub>4</sub> (SE)S(ES)(EO) <sub>4</sub> Bu	685.5 ± 0.7	91.7 ± 0.1	1.86 ± 0.01
24	Bu(OE)(SE) <sub>2</sub> S(ES) <sub>2</sub> (EO)Bu	592.7 ± 2.3	65.7 ± 0.7	0.97 ± 0.01
26	Bu(OE) <sub>2</sub> (SE) <sub>2</sub> S(ES) <sub>2</sub> (EO) <sub>2</sub> Bu	645.1 ± 1.0	81.9 ± 0.3	1.40 ± 0.01
27	Bu(OE) <sub>3</sub> (SE) <sub>2</sub> S(ES) <sub>2</sub> (EO) <sub>3</sub> Bu	687.4 ± 0.6	92.0 ± 0.1	1.85 ± 0.01
28	Bu(OE) <sub>4</sub> (SE) <sub>2</sub> S(ES) <sub>2</sub> (EP) <sub>4</sub> Bu	697.7 ± 0.8	93.8 ± 0.2	2.03 ± 0.01

following polarity parameters were considered: carbon number,  $C$ , *i.e.*, the apparent number of carbon atoms in a standard alkane having the same retention time as methanol; retention index of methanol,  $I_R$ ; polarity index<sup>5</sup>,  $PI = 100 \log(C - 4.7) + 60$ ; coefficient  $\rho$ , defined as the ratio of the retention times of methanol and  $n$ -hexane<sup>6</sup>.

## RESULTS AND DISCUSSION

The most important step in the polarity measurements carried out by GC is the determination of the retention times of selected polar agents and standard alkanes. With very hydrophobic surfactants (compounds 1 and 2), methanol is eluted very quickly and under the experimental conditions its retention time has a high error. Therefore the polarity parameters were not determined for these two compounds. For the other compounds, the values of the polarity parameters and their confidence limits are given in Table I. The ratios of the confidence limits to the average values of  $I_R$ ,  $C$ ,  $PI$  and  $\rho$  are approximately 0.15, 0.17, 0.5 and 0.8%, respectively, demonstrating the high precision of the determination of these parameters.

Theoretically, the retention index is related to the carbon number,  $I_R = 100 C$ . However, somewhat higher values were obtained, according to the relationship  $I_R = 105.2 C - 27.6$ ; correlation coefficient 0.9990. These small differences are connected with different methods of calculation and are unimportant. Therefore for further discussion the retention index will be considered.

The relationships between the retention index, polarity index and coefficient  $\rho$  are given in Fig. 1. It is seen that both  $I_R$  and  $PI$  increase as the coefficient  $\rho$  increases. The greatest changes are observed for the most hydrophobic compounds, for which  $I_R < 600$ ,  $PI < 70$  and  $\rho < 1.0$ . The influence of  $\rho$  upon  $I_R$  and  $PI$

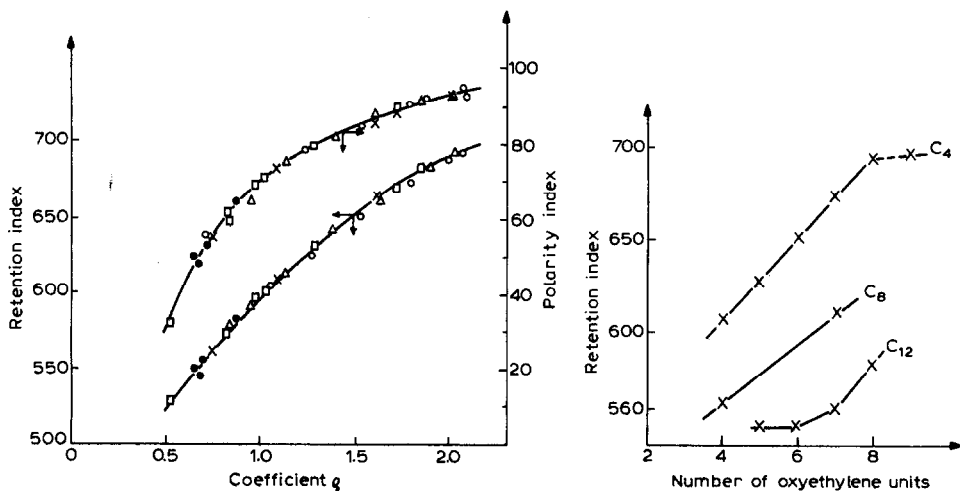


Fig. 1. Relationships between the retention and polarity indices and coefficient  $\rho$ . ●,  $\text{Dod}(\text{OE})_n\text{ODod}$ ; ×,  $\text{Oct}(\text{OE})_n\text{OOct}$ ; ○,  $\text{Bu}(\text{OE})_n\text{OBu}$ ; □,  $\text{Bu}(\text{OE})_n\text{S}(\text{EO})_m\text{Bu}$ ; △,  $\text{Bu}(\text{OE})_n(\text{SE})_m\text{S}(\text{ES})_m(\text{EO})_n\text{Bu}$ .

Fig. 2. The influence of the polyoxyethylene chain in polyoxyethylene glycol dialkyl ethers upon the retention index.

decreases as the hydrophilicity increases, and approximately straight lines are obtained for highly hydrophilic compounds.

Thus, all the considered parameters show the same trends for the investigated compounds, according to increasing polarity, but the influence of the compounds' structure upon the values of these parameters is somewhat different.

The polarity parameters calculated from the data obtained for methanol (MeOH) are shifted towards lower values in comparison to the corresponding parameters calculated for ethanol (EtOH)<sup>4</sup>. The following statistically significant relationships were obtained:

$$\begin{aligned} I_R^{\text{EtOH}} &= 0.9038 I_R^{\text{MeOH}} + 112.80 & R &= 0.9942 \\ \text{PI}^{\text{EtOH}} &= 0.6695 \text{PI}^{\text{MeOH}} + 39.27 & R &= 0.9952 \\ \rho^{\text{EtOH}} &= 1.3204 \rho^{\text{MeOH}} + 0.22 & R &= 0.9898 \end{aligned}$$

The highest deviations are observed in the case of the coefficients, which is a result of the greater errors in determination of the parameters.

The influence of the number of oxyethylene units upon the values of the polarity parameters is shown in Figs. 2-4. As the number of oxyethylene groups increases the polarity of the compounds also increases, but straight lines are observed only for compounds having four and eight carbon atoms in each alkyl group. For compounds having 12 carbon atoms in the terminal alkyls, the length of the polyoxyethylene chain influences the polarity parameters only for compounds containing more than six or seven oxyethylene units. This means that the first few oxyethylene groups are so well screened by the hydrophobic alkyls that their polar character is not observed. The values of the regression coefficients for the determined straight lines are given in Table II.

The slopes of the straight lines yield the increments in the polarity parameters per oxyethylene group, while the intercepts  $B_i$  determine the values of the polarity

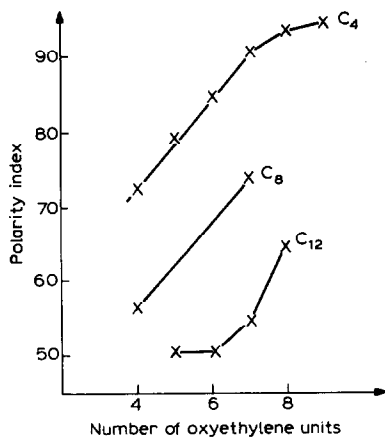


Fig. 3. The influence of the polyoxyethylene chain in polyoxyethylene glycol dialkyl ethers upon the polarity index.

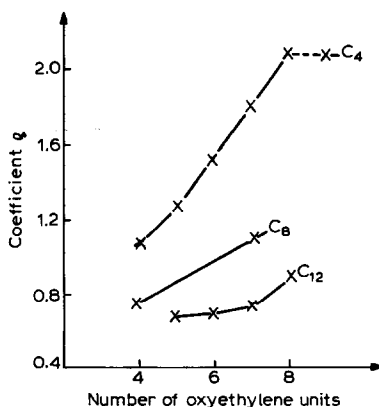


Fig. 4. The influence of the polyoxyethylene chain in polyoxyethylene glycol dialkyl ethers upon the coefficient  $\rho$ .

TABLE II

REGRESSION COEFFICIENTS OF THE RELATIONSHIP  $PP_i = A_i n + B_i$ PP<sub>i</sub> = Polarity parameter; *n* = number of oxyethylene groups; *A<sub>i</sub>*, *B<sub>i</sub>* = constants; *R* = correlation coefficient.

Polarity parameter	Alkyl	<i>A<sub>i</sub></i>	<i>B<sub>i</sub></i>	<i>R</i>
<i>I<sub>R</sub></i>	C <sub>4</sub>	21.7	520.4	0.9988
	C <sub>8</sub>	16.1	498.6	1.0000
	C <sub>12</sub>	11.3	486.9	0.8834
PI	C <sub>4</sub>	5.42	51.8	0.9942
	C <sub>8</sub>	5.77	33.4	1.0000
	C <sub>12</sub>	4.76	24.1	0.8949
$\rho$	C <sub>4</sub>	0.257	0.002	0.9981
	C <sub>8</sub>	0.117	0.283	1.0000
	C <sub>12</sub>	0.066	0.316	0.8622

parameters for the sum of the alkoxy and alkyl groups. From these data, assuming the additivity of the polarity parameters, the increments for the methylene,  $\Delta PP_{CH_2}$ , and methyl groups present in the hydrophobes and for ethereal oxygen bonded to one alkyl,  $\Delta PP_0$ , were calculated:  $B_i = 2m \Delta PP_{CH_2} + \Delta PP_0$ , where *m* denotes the number of carbon atoms in the alkyl group. It was assumed that  $\Delta PP_{CH_2} = \Delta PP_{CH_3}$ . The values of the increments are given in Table III. They can be used to estimate the retention index and the polarity index for the group of compounds discussed. A comparison of the estimated polarity parameters with those obtained experimentally shows satisfactory agreement. The average absolute and percentage errors are 4.1 and 0.7% for the retention index and 2.5 and 4.9% for the polarity index. Calculations of the increments in the  $\rho$  coefficient did not give satisfactory results.

According to the predicted values of the average polarity increments for the methylene and methyl groups, the polarity of the investigated compounds decreases with increasing number of carbon atoms in the alkyl groups. The increments in the polarity parameters for the homologues containing four and seven oxyethylene units are in Table IV. Unlike the previous set (Table III), this one contains average increments for the oxyethylene group and different values for the methylene groups, which

TABLE III

INCREMENTS FOR THE ESTIMATION OF POLARITY PARAMETERS

Group	Alkyl	$\Delta I_R$	$\Delta PI$
-OCH <sub>2</sub> CH <sub>2</sub> -	C <sub>4</sub>	21.7	5.42
	C <sub>8</sub>	16.1	5.77
	C <sub>12</sub>	11.3	4.76
-O-	-	535.5	63.7
-CH <sub>2</sub> -, -CH <sub>3</sub>	-	-2.094	-1.713

TABLE IV  
INCREMENTS FOR THE ESTIMATION OF POLARITY PARAMETERS

Group	Polyoxyethylene chain	$\Delta I_r$	$\Delta PI$	$\Delta \rho$
-CH <sub>2</sub> -, -CH <sub>3</sub>	(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>7</sub>	-7.27	-2.22	-0.068
	(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>4</sub>	-5.55	-1.975	-0.0387
-OCH <sub>2</sub> CH <sub>2</sub> -	-	26.5	6.8	0.31
-O-	-	545.9	60.9	0.13

depend upon the length of the polyoxyethylene chain. However, the errors in the determination of the polarity parameters are higher in this case, the average absolute errors being 10.9, 1.3 and 0.05 for  $I_R$ , PI and  $\rho$ , corresponding to percentage errors of 1.9, 2.1 and 11.1%. Thus, the first set of increments is preferable and we propose to use this set (Table III) for estimating the values of the polarity parameters from the general formulae of the surfactants under consideration.

The substitution of one oxygen by a sulphur atom in these compounds results in a decrease in polarity. The data presented in Fig. 5 show that the straight lines obtained for symmetrical compounds having one central sulphur atom are shifted towards lower values of the polarity parameters in comparison to the analogues containing oxygen. However, this decrease in polarity depends upon the location of the sulphur atom in the surfactant molecule, and when the asymmetry increases the decrease in polarity is less. The values of the increments for sulphur atoms are given in Table V. The absolute and percentage errors are 3.1 and 0.5% for  $I_R$ , 3.6 and 9.4% for PI and 0.02 and 4.7% for coefficient  $\rho$ .

When the next oxygen atoms in the neighbourhood of the central sulphur atom are substituted by sulphur a further decrease in polarity is observed in comparison to the oxygen analogues. However, this decrease is smaller than in the case of the introduction of the first sulphur atom. This means that a polythioethylene chain is

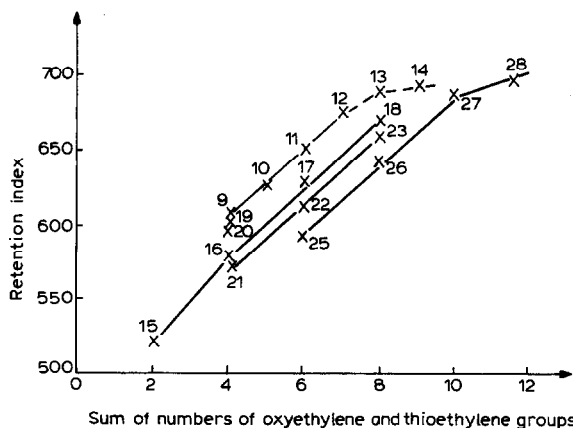


Fig. 5. The retention index of polyoxyethylene glycol dialkyl ethers and their sulphur analogues. Compound numbers refer to Table I.

TABLE V  
INCREMENTS FOR THE SULPHUR ATOM

Sulphur position	$\Delta I_R$	$\Delta PI$	$\Delta \rho$
Central Bu(OE) <sub>n</sub> S(OE) <sub>n</sub> Bu	525	51	0.24
Bonded to one oxyethylene group Bu(OE)S(OE) <sub>3</sub> Bu	546	58	0.40
Bonded to alkyl BuS(OE) <sub>4</sub> Bu	552	60	0.45

polar, but weaker in comparison to a polyoxyethylene chain. The polarity of the sulphur analogues increases as the length of the polythioethylene chain increases (Fig. 6). Depending on the length of the polyoxyethylene chain, the effect of the polythioethylene block upon surfactant polarity is quantitatively different, and diminishes as the length of the polyoxyethylene chain increases. The increments for the thioethylene group, calculated as the slopes of the straight lines correlating the polarity parameters with the number of thioethylene groups, are given in Table VI. The av-

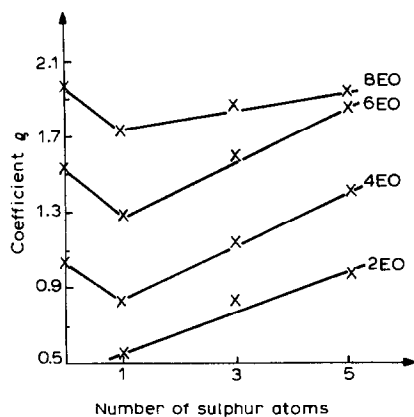


Fig. 6. The influence of the number of sulphur atoms upon the coefficient  $\rho$  of methanol.

TABLE VI  
INCREMENTS FOR THE THIOETHYLENE GROUP

Number of oxyethylene groups	$\Delta I_R$	$\Delta PI$	$\Delta \rho$
2	17.9	8.2	0.11
4	17.4	5.1	0.14
6	14.1	3.2	0.14
8	6.3	1.2	0.075

erage absolute and percentage errors of approximation of the polarity parameters by means of calculated increments are 3.3 and 0.5% for  $I_R$ , 1.9 and 3.3% for PI and 0.02 and 1.8% for coefficient  $\rho$ .

## CONCLUSIONS

Gas-liquid chromatography can be used to measure the influence of the structure of non-ionic surfactants upon their polarity. For this purpose, the retention index of methanol is the most appropriate parameter among those investigated. It is determined with satisfactory precision and can be correlated with the surfactants' structure. The additivity of this parameter 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 by using only their formulae. Depending upon the structure of the considered surfactants, their polarities can be estimated with errors in the range of 0.5–2.0%. The errors in the estimation of the polarity index are higher and, depending upon the surfactants' structure, are in the range of 3–9.4%. However, only these data (the polarity index of methanol) can be used to compare the polarity of the studied surfactants having two terminal hydrophobic groups with the polarity of typical non-ionic surfactants having one terminal hydrophobic group and one terminal polyoxyethylene group, and to estimate the hydrophile-lipophile balance of the surfactants studied in this work.

## REFERENCES

- 1 J. K. Haken, *Advan. Chromatogr.*, 17 (1979) 163.
- 2 A. Olano and I. Martinez, *Tenside Deterg.*, 12 (1975) 334.
- 3 J. Szymanowski, A. Voelkel, J. Beger and C. Pöschmann, *Tenside Deterg.*, 20 (1983) 173.
- 4 J. Szymanowski, A. Voelkel, J. Beger and H. Merkwitz, *J. Chromatogr.*, 330 (1985) 61.
- 5 V. R. Huebner, *Anal. Chem.*, 34 (1962) 488.
- 6 P. Becher and R. L. Birkmeir, *J. Amer. Oil Chem. Soc.*, 41 (1964) 169.