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Polarity of fluorine-containing oxyethylates as determined by inverse gas chromatography

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Abstract

The polarity of fluorine-containing oxyethylates has been studied using inverse gas chromatography. Oxyethylene derivatives containing a short fluorocarbon chain (denoted as Group I) exhibit a slightly higher polarity at all temperatures than their analogues (Group II) having double-length fluorocarbon chains. The difference decreases, however, with increasing length of the oligo-oxyethylene chain. An increase in the average number of oxyethylene units increases the polarity of the products. The changes in oxyethylate polarity may be described by various parameters, i.e. the sum of the difference of the retention indices of the first five McReynolds solutes as determined on the examined liquid phase and on squalane as a reference, the polarity index, the ρ coefficient and the dispersive interaction parameters.

Introduction

The properties of surface-active agents depend, generally, on their hydrophile/lipophile balance and/or their polarity [1, 2]. Inverse gas chromatography has been proposed as a method which provides a simple procedure, and accurate and reliable quantitative parameters for the determination of the polarity of organic compounds including surfactants [3, 4], organic salts [5] and extractants [6–8].

Polarity parameters can be, generally, divided into two groups: (i) empirical polarity parameters, e.g. polarity index, retention index; and (ii) thermodynamically defined parameters (thermodynamic functions of solution, criterion A, partial molar excess Gibbs free energy of solution per methylene group).

Polarity parameters are often related to the *H*ydrophile *L*ipophile *B*alance (HLB) number – the accepted characteristic of surfactants [9–12].

Surfactants containing highly fluorinated hydrophobes exhibit unique properties associated with the low values of their free surface energy. As a

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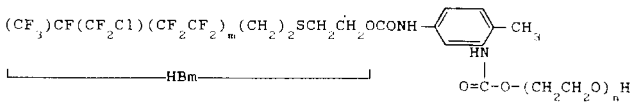
result, they are very surface active and decrease the surface tension very effectively.

The aim of this work was to determine the polarity parameters for two series of oligo-oxyethylene derivatives containing in their hydrophobic parts highly fluorinated chains. The relationship between structure (average number of EO units, presence of fluorocarbon chain of different length) and surfactant polarity are examined and discussed.

Experimental

Materials

Two groups of oxyethylene derivatives containing fluorocarbon fragments (Table 1) were used as liquid stationary phases in gas chromatographic columns. They have the following formulae:



where HB*m* denotes the hydrophobe containing '*m*' CF_2CF_2 groups, and where such hydrophobes are subdivided into groups with $m = 1$ for Group I, $m = 2$ for Group II, etc. The full symbol employed for a given compound

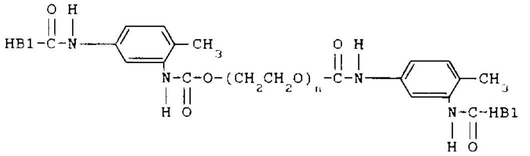
TABLE 1

Samples values of ΔI_i for McReynolds solutes and $\Sigma_{i=1}^{5}\Delta I_i$ values for fluorine-containing oxyethylates at 70 °C

Type (Group No.)	Average molecular mass of oligo-oxyethylene chain	ΔI_i value for					$\sum_{i=1}^{5} \Delta I_i$
		Bz[a] X'	Butanol Y'	MPK[a] Z'	NP[a] U'	Pyridine S'	
I	340	193.6	460.4	316.6	452.5	423.9	1846
	456	213.8	500.5	323.8	475.1	423.0	1945
	666	230.2	501.3	327.0	495.6	444.9	1999
	1005	241.8	508.4	325.9	516.8	448.6	2042
	1500	260.4	531.3	341.6	541.4	469.1	2144
	2250	274.1	552.7	348.7	567.1	487.7	2230
II	456	204.3	476.0	321.6	467.6	433.8	1903
	666	220.8	481.5	321.3	485.3	428.0	1937
	1005	236.2	499.4	325.4	507.4	441.5	2010
	1500	251.9	517.4	332.1	529.3	451.9	2083
	2250	259.7	533.3	335.0	536.4	460.8	2125
III	2000	311.8	616.9	377.1	623.1	552.5	2481

[a] Abbreviations denote the following solutes tested: Bz, benzene; MPK, pentan-2-one, Np, nitroprop-1-ane.

designates the average molecular weight of the oxyethylene chain, e.g. I-1005 denotes a compound having an oxyethylene chain of average molecular mass equal to 1005. In addition, one compound (III-2000) with the following structure was studied:



The syntheses and surface tension properties of the studied surfactants are being published separately [13].

IGC measurements

Oxyethylates were placed in a GC column as a liquid stationary phase coated on an inert support, i.e. Celite 80–120 mesh (25% w/w). The use of such a high content of liquid phase was considered necessary to eliminate adsorption effects. Other details of the GC experiments were as follows: chromatograph, CHROM 5 (Kovo, CSRF) equipped with FID; columns, 1 m length, 3 mm i.d.; column temperature, isothermal at 70, 90 and 110 °C; injector temperature, 150 °C; detector temperature, 200 °C; carrier gas flow rate (helium), 40 cm^3 min^{-1}. The first five McReynolds solutes [14] were used together with C_5–C_9 n-alkanes and their adjusted retention times were determined according to normal procedures [10, 15, 16].

Polarity parameters

The following parameters were used to express the ability of the surfactants to interact with the selected group of standard solutes:

1. The difference in retention indices of the first five McReynolds solutes (as measured on the examined liquid phase and squalane) ΔI_i, as well as their sum $\Sigma_{i=1}^{5}\Delta I_i$ [14].
2. The ρ coefficient defined as the ratio of the adjusted retention times of the standard polar solute (methanol or ethanol) to the non-polar solute (n-hexane) [17].
3. The polarity index *PI* defined by Huebner [18] for the characterization of surfactants by GC methods.
4. Criterion *A* [19] and the partial molal Gibbs free energy of solution per methylene group, $\Delta G_s^m(CH_2)$ [20, 21], parameters which characterize the dispersive interactions between the solute and the solvent. Criterion A was calculated from the equation

   $$A=(t'_{r,n+1}-t'_{r,n})/(t'_{r,n}-t'_{r,n-1}) \qquad (1)$$

   where $t'_{r,n+1}$, $t'_{r,n}$ and $t'_{r,n-1}$ denote the adjusted retention times for n-alkanes having $n+1$, n and $n-1$ carbon atoms, respectively.
5. The partial molar excess Gibbs free energy of solution per methylene group $\Delta G^E(CH_2)$ introduced by Roth and Novak [22] and calculated

according to the equation

$$\Delta G^{E}(CH_2)=RT\ln[(V_g p^0)_{i_N}/(V_g p^0)_{i_{N+1}}] \qquad (2)$$

where p^0 and V_g denote the saturated vapour pressure and the specific retention volume for two homologous testing solutes, $i_N=(CH_3)_m(CH_2)_nX$ and $i_{N+1}=(CH_3)_m(CH_2)_{n+1}X$.

Results and discussion

Fluorine-containing compounds were placed onto the chromatographic column and their properties examined at temperature conditions which maintained them in the liquid state so that the surfactants studied acted as stationary phases in the gas chromatographic process. Liquid stationary phases are commonly characterized by the difference between the retention indices of selected solutes as proposed by McReynolds, as well as by the sum of these differences for the first five solutes. It has been shown that these parameters may be used in the characterization of surface-active agents [10, 16]. The appropriate values of ΔI_i and $\Sigma_{i=1}^{5}\Delta I_i$ are summarized in Table 1. The sum of the differences in retention indices for the first five McReynolds standards increased with the increase in the oxyethylation ratio. Values of ΔI_i for the test solutes also increased for all stationary liquid phases examined. Slightly higher values were observed for Group I hydrophobes in comparison to their analogues from Group II. This means that the presence of the second $-CF_2CF_2-$ group decreases the polarity of the compound. The difference between the maximum and minimum $\Sigma_{i=1}^{5}\Delta I_i$ values was significantly higher, 285 i.u. at 70 °C for Group I surfactants compared with 222 i.u. for Group II. The addition of one oxyethylene group to a surfactant molecule increased the $\Sigma_{i=1}^{5}\Delta I_i$ value by 12.8 i.u. for Group I surfactants and by 5.4 i.u. for Group II. These values are significantly lower than those calculated for typical surface-active agents having hydrocarbon chains where the increment for one oxyethylene group was 57 i.u. [23].

Determination of the ΔI_i and $\Sigma_{i=1}^{5}\Delta I_i$ values requires the estimation of retention data for five selected polar solutes and the reference n-alkanes on two liquid phases, i.e. the examined phase and non-polar squalane. The use of the polarity index *PI* and the ρ coefficient as empirical polarity measures allows the surfactant to be characterized with an acceptable precision [10, 16], but the procedure is shorter in length than that in the case of previous parameters employed. These parameters are also sufficiently sensitive to reflect structural changes. The polarity index and values of the ρ coefficient measured using methanol and ethanol as polar solutes are listed in Tables 2 and 3.

Similar results were observed as in the case of the $\Sigma_{i=1}^{5}\Delta I_i$ values when the polarity index *PI* (Fig. 1) and the ρ coefficient were used as polarity parameters. Once again, the relatively small influence of the oxyethylene group upon the polarity of the surfactant may be observed. The following

TABLE 2

Polarity index (*PI*) for fluorine-containing oxyethylates

Type (Group No.)	Average molecular mass of oligo-oxyethylene chain	Measured polarity index					
		With methanol at			With ethanol at		
		70 °C	90 °C	110 °C	70 °C	90 °C	110 °C
I	340	109.9	107.7	102.7	116.0	114.0	110.4
	456	114.4	112.8	110.0	120.0	119.0	116.6
	666	114.1	111.5	109.0	119.3	117.4	114.9
	1005	115.9	113.4	111.5	120.1	117.9	115.6
	1500	119.2	116.7	113.2	122.2	120.9	118.2
	2250	120.0	118.7	113.8	124.1	121.7	118.8
II	456	111.1	109.3	106.1	116.6	114.7	111.9
	666	113.9	112.3	109.4	117.8	116.5	114.4
	1005	115.1	115.1	112.9	119.7	117.6	115.0
	1500	117.4	115.0	113.8	120.9	118.4	117.7
	2250	118.4	115.4	114.0	122.4	118.9	118.6
III	2000	125.7	124.7	123.2	129.4	128.5	126.8

TABLE 3

Coefficient ρ for fluorine-containing oxyethylates

Type (Group No.)	Average molecular mass of oligo-oxyethylene chain	Measured ρ coefficient					
		With methanol at			With ethanol at		
		70 °C	90 °C	110 °C	70 °C	90 °C	110 °C
I	340	4.23	3.10	2.35	5.81	4.03	2.97
	456	5.12	4.05	2.99	6.98	5.45	3.81
	666	5.17	3.63	3.12	6.91	4.71	3.84
	1005	5.45	3.91	3.35	6.86	4.78	3.89
	1500	6.64	4.63	3.36	7.92	5.69	4.04
	2250	6.58	4.41	3.32	8.40	5.10	3.99
II	456	4.41	3.46	2.68	5.88	4.35	3.22
	666	5.56	4.03	2.95	6.92	4.91	3.52
	1005	5.10	4.47	3.28	6.59	5.05	3.55
	1500	5.72	4.16	3.52	7.02	4.89	4.07
	2250	6.10	4.19	3.53	7.69	4.96	4.21
III	2000	8.34	6.12	4.38	10.55	7.53	5.11

increments were calculated for the $-CH_2CH_2O-$ group: (i) polarity index *PI* (methanol as the testing solute), 0.14 i.u. and 0.18 i.u. for Group I and Group II hydrophobes, respectively; (ii) polarity index *PI* (ethanol as the testing solute), 0.11 i.u. and 0.14 i.u. for Group I and Group II hydrophobes, respectively; (iii) ρ coefficient (methanol as the testing solute), 0.079 i.u.

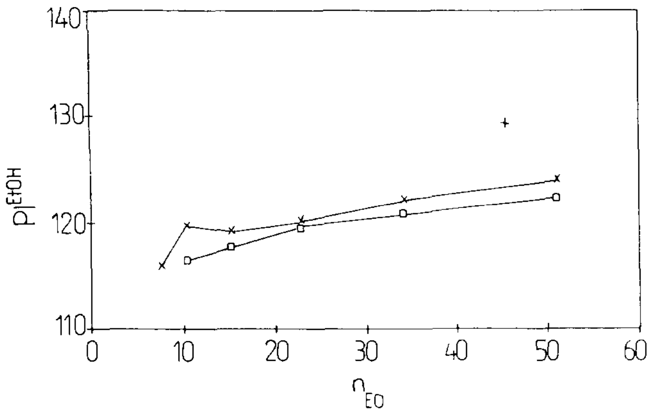
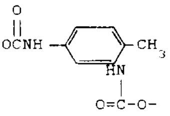


Fig. 1. Influence of the length of the oligo-oxyethylene chain, n_{EO}, upon the polarity index *PI* (ethanol employed as the polar solute at 70 °C): ×, Group I hydrophobes; □, Group II hydrophobes; +, compound III-2000.

and 0.039 for Group I and Group II hydrophobes, respectively; (iv) ρ coefficient (ethanol as the testing solute), 0.083 i.u. and 0.044 i.u. for Group I and Group II hydrophobes, respectively.

These values are significantly lower than those observed for surfactants possessing a typical hydrocarbon chain, for which the appropriate increments in the polarity index PI for one oxyethylene group were 3.96 i.u. and 2.62 for methanol and ethanol as the testing solutes, respectively [23]. Increments for the ρ coefficient were not listed in this case. This limited influence of an increase in the oxyethylene chain length upon a compound's polarity relative to the situation with hydrocarbon surfactants may be explained as follows. The compounds examined contained oligo-oxyethylene groups which had 10 to *c.* 50 oxyethylene, $-CH_2CH_2O-$ (EO), units whereas typical surfactants possessing a hydrocarbon hydrophobe as previously reported contained 13–14 EO units. Thus, the increments for such typical surfactants were calculated under conditions where each added oxyethylene unit strongly influenced the compound's polarity. However, for the fluorocarbon surfactants examined in the present work, the polyoxyethylene chain was much longer and hence the effect of its length upon the polarity of the compound was significantly diminished.

The polarity parameters were always lower for Group II surfactants. This means that the presence of an additional $-CF_2CF_2-$ group (see Materials section above) in such molecules decreases their polarity. The differences between the various indices measured for appropriate homologues from both series of compounds were as follows: $\Sigma_{i=1}^{5}\Delta I_i$, 32–105 i.u.; PI^{MeOH}, 0.5–2.6 i.u.; PI^{EtOH}, 0.5–3.2 i.u.; ρ^{MeOH} coefficient, 0.5–0.8 i.u., ρ^{EtOH} coefficient, 0.07–0.9 i.u. However, it is important to point out that oligo-oxyethylene and fluorocarbon chains are not the only elements capable of influencing the measured polarity. Each of the examined compounds contained the urethane segment (A), i.e.



(A)

and the significant influence of this structural element is demonstrated by the high polarity of compound III-2000. This compound contained two HB1 elements together with an oligo-oxyethylene chain which was shorter in length than that in the I-2250 analogue. Whereas the presence of the additional fluorocarbon chain length should decrease the polarity, the second urethane segment (A) caused a significant increase in the polarity parameters. Values of $\Sigma_{i=1}^{5}\Delta I_i$, PI^{EtOH} and ρ^{EtOH} (at 70 °C) determined for III-2000 were higher by 251 i.u., 5.3 i.u. and 2.15 i.u., respectively, than for I-2250.

The most important component of solute–solvent intermolecular interactions are dispersive forces, and it has been shown that dispersive interaction parameters may be used successfully for the description of a compound's polarity [3, 4, 24]. Values of criterion A calculated for the surfactants examined are listed in Table 4, from which it is seen that higher values were found for Group II surfactants (Fig. 2). Values of criterion A decrease with increasing number of oxyethylene units in the compounds examined and with an increasing temperature for the chromatographic column. The temperature dependence may be described via the equation proposed by Ševčik and Löwentap [19]:

$$A = a\,\exp(b/T) \qquad (3)$$

TABLE 4

Criterion A and its temperature dependence

Type (Group No.)	Average molecular mass of oligo-oxyethylene chain	Criterion A at			$A = a\,\exp(b/T)$		
		70 °C	90 °C	110 °C	a	b	R^{a}
I	340	2.136	1.937	1.804	0.421	555.5	0.998
	456	2.106	1.974	1.817	0.517	483.2	0.995
	666	2.124	1.941	1.903	0.726	364.7	0.949
	1005	2.094	1.929	1.878	0.726	360.5	0.968
	1500	2.098	1.938	1.837	0.584	437.4	0.997
	2250	2.069	1.842	1.804	0.541	455.4	0.939
II	456	2.117	1.971	1.834	0.537	470.8	0.999
	666	2.167	1.981	1.815	0.398	581.7	1.000
	1005	2.065	1.965	1.806	0.580	437.6	0.984
	1500	2.069	1.922	1.853	0.712	364.0	0.987
	2250	2.072	1.906	1.846	0.675	382.0	0.976
III	2000	2.007	1.877	1.764	0.584	423.7	1.000

[a] R = correlation coefficient.

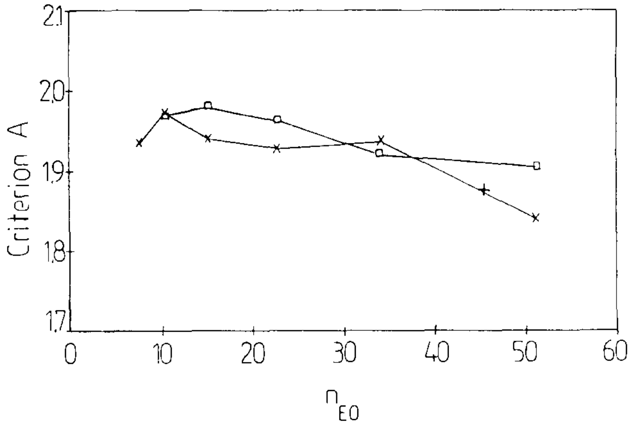


Fig. 2. Relationship between values of criterion A and the number of oxyethylene units, n_{EO}, at 90 °C: ×, Group I hydrophobes; □, Group II hydrophobes; +, compound III-2000.

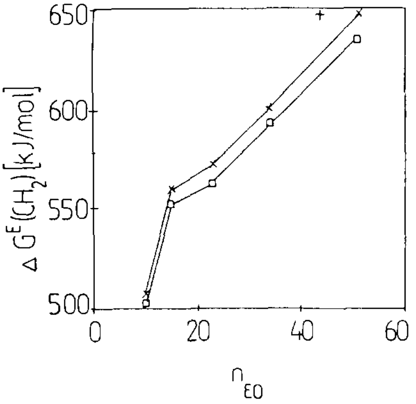


Fig. 3. Influence of the number of oxyethylene units, n_{EO}, upon the partial molar excess Gibbs free energy of solution per methylene group, $\Delta G^E(CH_2)$ (ketones employed as testing solutes at 70 °C): ×, Group I hydrophobes; □, Group II hydrophobes; +, compound III-2000.

Values for the regression and correlation coefficients in eqn. (3) are also listed in Table 4. Since the value of criterion A decreases with increasing polarity of the stationary phase, conclusions drawn from an analysis of this parameter are in agreement with those for $\Sigma_{i=1}^{5}\Delta I_i$, the polarity index PI or the ρ coefficient.

The partial molar excess Gibbs free energy per methylene group, $\Delta G^E(CH_2)$, increased with increasing numbers of oxyethylene units and values were somewhat higher for Group I surfactants (Fig. 3). This parameter is a measure of the resistance of the liquid phase to solution of the apolar methylene group. Its value increased with increasing polarity of the stationary phase, a trend which was in accord with conclusions drawn from the analyses of the previous parameters.

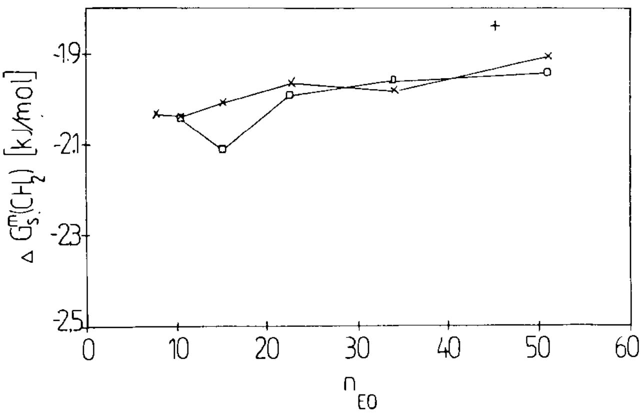


Fig. 4. Influence of the number of oxyethylene units, n_{EO}, upon the partial molal Gibbs free energy of solution per methylene group, $\Delta G_s^m(CH_2)$, at 70 °C: ×, Group I hydrophobes; □, Group II hydrophobes; +, compound III-2000.

The partial molal Gibbs free energy of solution per methylene group, $\Delta G_s^m(CH_2)$, also increased with increasing length of the oligo-oxyethylene chain and was slightly higher for Group I surfactants than for their analogues from Group II (Fig. 4).

Conclusions

Two groups of oxyethylene derivatives containing fluorocarbon hydrophobes have been examined by inverse gas chromatography. The surfactants examined were characterized via their polarity parameters. Thus, the polarity of the examined compounds increased with increasing length of the oligo-oxyethylene chain and decreased with an increase in the fluorocarbon content of the hydrophobe, i.e. the addition of a $-CF_2CF_2-$ group. All the polarity parameters examined describe the structure–polarity relationships in a similar fashion. The influence of an oxyethylene unit upon the polarity of a given compound was found to be significantly smaller than for the corresponding hydrocarbon surfactants.

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