

The solubility parameters of fluorine-containing oxyethylates

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Abstract

The solubility parameter has been used to characterize fluorine-containing oxyethylates used as stationary phases in a gas chromatographic column. The solubility parameter δ_2 and its components were determined by inverse gas chromatography. Increments of the solubility parameter correspond to different types of intermolecular solute–solvent interactions. The corrected value of solubility parameter δ_T was calculated from increments determined according to a modified Guillet procedure. Relationships existing between solubility parameter, corrected solubility parameter, its components and polarity parameters have been examined. The influence of the structure of fluorinated surfactants upon the examined parameters is presented and discussed.

Introduction

The cohesive energy E_{coh} of a substance in a condensed state is defined as the increase in internal energy U per mole of a substance if all intermolecular forces are eliminated. The cohesive energy per unit volume (E_{coh}/V) is called the cohesive energy density. According to Hildebrand and Scott [1], the square root of the cohesive energy density, i.e. the solubility parameter δ , is defined by $\delta = (E_{\text{coh}}/V)^{1/2}$ [$\text{J}^{1/2}\text{m}^{-3/2}$]. The solubility of any organic compound in various solvents is largely determined by its structure. Besides the structure, the physical state also influences the solubility properties.

The solubility parameter is seldom used for the characterization of surface-active compounds. However, the CER theory [2] discussed the behaviour of the emulsifier in oil/water systems in terms of the cohesive energies of the system's components. The data for most surfactants were unavailable and the CER theory was seldom of practical use. Hence estimations of the solubility parameter for surfactants are needed.

The solubility parameter for volatile compounds is given by

$$\delta = \left[\frac{\Delta H_v - RT}{V} \right]^{1/2} \quad (1)$$

where ΔH_v is the enthalpy of vaporization, R the gas constant, T the absolute temperature and V the molar volume. For species of low volatility, however, the use of eqn. (1) is impossible.

DiPaola-Baranyi and Guillet [3] and Guillet [4] evaluated solubility parameters using a solute–solvent interaction parameter κ^∞ separable into enthalpic (κ_H^∞) and entropic (κ_S^∞) terms:

$$\kappa^\infty = \kappa_H^\infty + \kappa_S^\infty \quad (2)$$

The quantity κ^∞ is defined as the change in the chemical potential of the solvent accompanying the formation of the actual solution less the corresponding quantity for the solvent in the formation of a reference solution. In inverse gas chromatography, a volatile diluent injected on to the column has a tendency to be absorbed by the liquid phase as a function of κ^∞ and is measured in terms of retention by a specific retention volume V_g . The interaction parameter was usually obtained by extrapolation to zero solute concentration [5–7]. Brockmeier *et al.* [8] extended the method to solvent concentrations of $0.8 < v_2 < 1$ (volume fraction units). The interaction parameter is calculated from eqn. (3)

$$\begin{aligned} \kappa_{1,2}^\infty = & \ln \left(\frac{273.15R}{P_1^0 V_g^0 M_1} \right) - \frac{P_1^0}{RT} (B_{11} - V_1^0) \\ & + \ln \left(\frac{\rho_1}{\rho_2} \right) - \left(1 - \frac{V_1^0}{V_2^0} \right) \end{aligned} \quad (3)$$

where M_1 , P_1^0 , B_{11} , V_1^0 , ρ_1 and V_g^0 are the molecular weight, saturated vapour pressure, second virial coefficient, molar volume and specific retention volume of the solute, respectively, and where ρ_2 and V_2^0 are the density and molar volume of the polymer at the column temperature T .

The enthalpic component of the interaction parameter may be expressed in terms of the solubility parameters

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of solute (1) and solvent (2) by:

$$\kappa_H^\infty = \frac{V_1^0(\delta_1 - \delta_2)^2}{RT} \quad (4)$$

Equation (2) then becomes

$$\kappa^\infty = \frac{V_1^0(\delta_1 - \delta_2)^2}{RT} + \kappa_S^\infty \quad (5)$$

On dividing this equation by V_1^0 , it may be rewritten as:

$$\frac{\delta_1^2}{RT} - \frac{\kappa^\infty}{V_1^0} = \frac{2\delta_2}{RT} \delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\kappa_S^\infty}{V_1^0} \right) \quad (6)$$

On plotting the left-hand side of eqn. (6) versus δ_1 , one obtains a straight line with a slope proportional to δ_2 of the polymer [3, 9, 10].

The use of Guillet's procedure gives excellent linearity for eqn. (6) [3, 9, 11–15]. Price [14] has examined a group of organic compounds of relatively low molecular mass and found a downward curvature with eqn. (6) for alkane systems, leading to low estimates of δ_2 , and an upward curvature overestimating δ_2 for other examined compounds. Price split the solubility parameter into contributions from dispersive (δ_d) and polar (δ_p) interactions to give a total (corrected) solubility parameter

$$\delta^2 = \delta_d^2 + \delta_p^2 \quad (7)$$

Although Price significantly improved predictions of the solubility parameter, he indicated that the interaction parameter κ^∞ for small molecular systems should include extra contributions which are negligible for typical polymeric systems.

We have extended the range of polar and non-polar solutes tested. Their retention data permit the calculation of further solubility parameter increments using the following procedures: (i) eqn. (6) would be used separately for three groups of solutes whose interactions with liquid stationary phases could be attributed to dispersive (alkanes), polar (aromatic hydrocarbons, ketones, nitropropane) and hydrogen-bonding (alcohols and pyridine) interactions; (ii) the total, corrected solubility parameter would be calculated from an equation similar to that proposed earlier by Hansen [16, 17]:

$$\delta_T^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (8)$$

with corresponding contributions from dispersive, polar and hydrogen-bonding forces to the cohesive energy of the molecule.

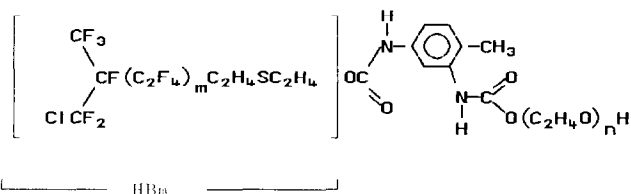
The aim of the present paper was to: (a) examine a group of oligo-oxyethylene derivatives of highly fluorinated hydrophobes by inverse gas chromatography; (b) check the applicability of the Guillet procedure for the examined oligomers and, if possible, determine their

solubility parameter δ_2 ; (c) divide the solubility parameter into contributions from dispersive, polar and hydrogen-bonding interactions; (d) calculate the corrected value of the solubility parameter from these components according to eqn. (8); and (e) examine structure–solubility parameter relationships.

Experimental

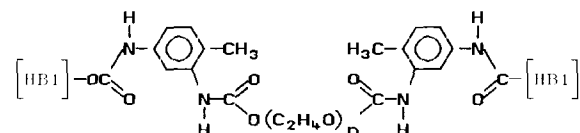
Materials

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



where HB m denotes the hydrophobic part having ' m ' C_2F_4 groups (hydrophobic part bracketed). The two groups of derivatives may be distinguished by their m value, i.e. Group I where $m=1$ and Group II where $m=2$. The full symbol for each compound also contains 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, i.e. $n^*M(C_2H_4O)$.

Additionally, one compound (III-2000) of the following structure was studied:



where HB1 denotes the hydrophobic part as in previous formulae containing one C_2F_4 group.

The synthesis and surface tensions of these surfactants [18] as well as polarity parameters have been described previously [19].

IGC experiments

The conditions for the inverse gas chromatographic experiments were as follows: column of 1 m length, 3 mm i.d.; held at 70 °C, 90 °C and 110 °C; column packing, 25% (w/w) supported on 80–120 mesh Celite; carrier gas, helium at a flow rate of 40 ml min⁻¹; detector, FID; gas chromatograph, Chrom 5 (Kovo, Czech Republic). The volatile test compounds employed were the non-polar n-alkanes with chain lengths from

TABLE 1. Solubility parameters for fluorine-containing oxyethylates at 70 °C

Group	Average molecular mass of oligo-oxyethylene chain	Solubility parameters [$10^3 \text{J}^{1/2} \text{m}^{-3/2}$]				
		δ_2	δ_p	δ_h	δ_d	δ_T
I	340	19.12	6.91	8.67	13.12	17.18
	456	19.24	6.51	8.34	13.35	17.03
	666	19.30	6.74	8.76	13.16	17.19
	1005	19.46	7.32	9.68	12.74	17.06
	1500	19.55	6.91	9.41	13.11	17.56
	2250	19.67	7.50	9.97	12.63	17.75
II	456	19.05	6.70	8.56	13.13	17.04
	666	18.91	5.09	6.97	14.42	16.81
	1005	19.23	6.91	9.13	12.91	17.25
	1500	19.76	8.01	10.64	12.32	18.14
	2250	19.83	7.88	10.68	12.32	18.11
III	2000	20.17	8.62	11.03	12.12	18.51

C_5 to C_{10} ; the aromatic hydrocarbons, benzene, toluene, xylene and ethyl benzene; the polar n-alkanols with chain lengths from C_1 to C_4 ; butan-2-one and pentan-2-one; nitropropane and pyridine.

Solubility parameter and its components

The solubility parameter δ_1 for the test solutes was calculated from eqn. (1) using recorded ΔH_v values [20, 21]. The Flory–Huggins parameter κ_{12}^∞ was calculated from eqn. (3) using recorded [22] or calculated [3, 23] values for B_{11} . Vapour pressures were obtained from the literature [17, 24, 25]. The solubility parameter δ_2 was calculated initially from relationship (6). The increments of solubility parameter corresponding to the different solute–solvent interactions were determined as follows. Firstly, eqn. (6) was used separately for the three groups of solutes listed above. It was assumed that the slope for the n-alkanes was proportional to the dispersive component, i.e.

$$\delta_d = \frac{\text{slope}_{\text{n-alkanes}} \times R \times T}{2} \quad (9)$$

The polar increment of δ_p was then calculated from the difference between the slopes for the polar solutes and the n-alkanes, i.e.

$$\delta_p = \frac{[\text{slope}_{\text{polar}} - \text{slope}_{\text{n-alkanes}}] \times R \times T}{2} \quad (10)$$

and, finally, the hydrogen-bonding component was obtained from the corresponding relationship for n-alcohols and n-alkanes

$$\delta_h = \frac{[\text{slope}_{\text{alcohols}} - \text{slope}_{\text{n-alkanes}}] \times R \times T}{2} \quad (11)$$

New values of the solubility parameter were calculated from eqn. (8).

Results and discussion

The important question was the applicability of Guillet's procedure and eqn. (6) for estimating the solubility parameters of relatively low molecular mass oligomers. The slight deviations from linearity expected from eqn. (6) were observed but the correlation coefficients were always higher than 0.93. Thus Guillet's procedure may be used for evaluating δ_2 for this group of organic compounds.

However, the deviations from linearity for all the test solutes were sufficiently significant to warrant correction using the method of increments outlined in the Experimental section (Fig. 1). Values of the solubility parameter δ_2 determined according to Guillet's procedure, the increments of the solubility parameter (δ_d ,

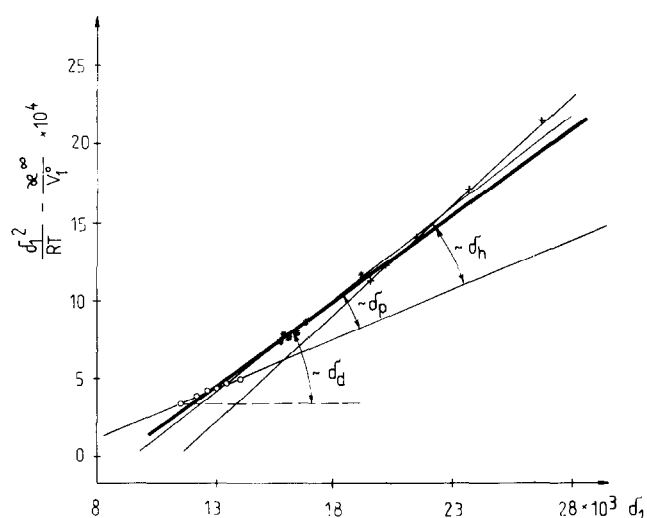


Fig. 1. Determination of increments of solubility parameters. The points depicted relate to the various compounds as follows: O, alkanes; *, aromatic solutes; and +, alcohols and pyridine.

δ_p and δ_h) and the corrected solubility parameter δ_T are listed in Tables 1–3.

The solubility parameter δ_2 at 70 °C for Group I surfactants increased from 19.12 to 19.67 [$10^3 J^{1/2} m^{-3/2}$] with increasing length of oxyethylene chain. Similar increase was observed for Group II surfactants. Generally, δ_2 was slightly higher for the first group of surfactants having shorter fluorocarbon chains, but the difference decreased with an increase in oxyethylene content (Fig. 2). The presence of additional $-CF_2CF_2-$ groups in the molecules led to a decrease in the δ_2 values but was less significant for compounds having a longer oxyethylene chain. Recently, the significant influence of the urethane segment in compound III-2000 on the polarity has been discussed [19]. In this case, as well, a much higher δ_2 value for III-2000 was observed.

These values are higher than those reported for broad and narrow distribution oxyethylates of cetyl alcohol

[26] and 1,3-bis[ω -hexoxy-oligo(oxyethylene)]-propan-2-ols which are typically from 17.1 to 18.6 [$10^3 J^{1/2} m^{-3/2}$] [27].

The dispersive component of the solubility parameter δ_d decreased with increasing oxyethylation ratio and was slightly higher for Group II surfactants. It varied from 13.35 to 12.68 [$10^3 J^{1/2} m^{-3/2}$] for Group I and from 14.4 to 12.32 [$10^3 J^{1/2} m^{-3/2}$] for Group II compounds (at 70 °C). A much lower value for the dispersive component δ_d was found for compound III-2000 (12.12 [$10^3 J^{1/2} m^{-3/2}$]).

The polar increment of the solubility parameter increased with increasing oxyethylation ratio and varied from 6.91 to 7.50 and from 6.70 to 7.88 [$10^3 J^{1/2} m^{-3/2}$] for Group I and II compounds, respectively. For compounds from Group II having an oxyethylene chain with >30 oxyethylene units, the values of δ_p were all approximately 8 [$10^3 J^{1/2} m^{-3/2}$] (at 70 °C) (Fig. 3). The δ_p value of III-2000 was greater (8.62 [$10^3 J^{1/2} m^{-3/2}$]).

TABLE 2. Solubility parameters for fluorine-containing oxyethylates at 90 °C

Group	Average molecular mass of oligo-oxyethylene chain	Solubility parameters [$10^3 J^{1/2} m^{-3/2}$]				
		δ_2	δ_p	δ_h	δ_d	δ_T
I	340	18.73	7.55	9.63	11.77	16.97
	456	18.91	6.74	8.66	12.52	16.65
	666	18.92	7.62	9.78	11.78	17.10
	1005	19.09	7.82	10.50	11.57	17.47
	1500	19.55	7.51	9.94	12.05	17.34
	2250	19.67	8.63	11.69	11.01	17.23
II	456	19.02	7.80	10.21	11.73	17.40
	666	18.56	6.02	7.98	12.97	16.38
	1005	19.03	7.06	9.85	12.25	17.24
	1500	19.43	8.59	11.24	11.39	18.16
	2250	19.33	8.37	10.90	11.49	17.91
III	2000	20.17	9.15	11.75	11.22	18.65

TABLE 3. Solubility parameters for fluorine-containing oxyethylates at 110 °C

Group	Average molecular mass of oligo-oxyethylene chain	Solubility parameters [$10^3 J^{1/2} m^{-3/2}$]				
		δ_2	δ_p	δ_h	δ_d	δ_T
I	340	18.44	7.99	10.57	10.60	16.97
	456	18.50	7.16	9.40	11.36	16.39
	666	18.64	7.45	10.08	11.25	16.84
	1005	18.83	7.65	10.80	11.11	17.28
	1500	18.78	7.88	10.54	10.95	17.12
	2250	19.02	8.58	11.62	10.43	17.81
II	456	18.75	8.28	11.25	10.48	17.47
	666	18.19	6.65	8.96	11.62	16.11
	1005	18.70	7.66	10.93	10.97	17.28
	1500	19.29	8.71	12.02	10.56	18.22
	2250	18.88	7.82	10.63	11.06	17.21
III	2000	19.41	9.23	12.25	10.18	18.41

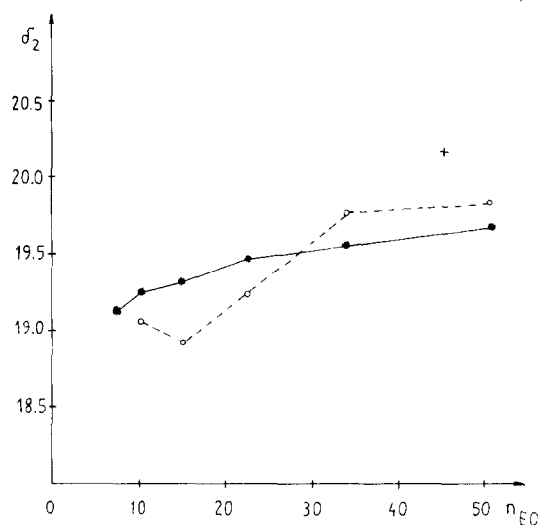


Fig. 2. Solubility parameter δ_2 for two series of fluorine-containing oxyethylates.

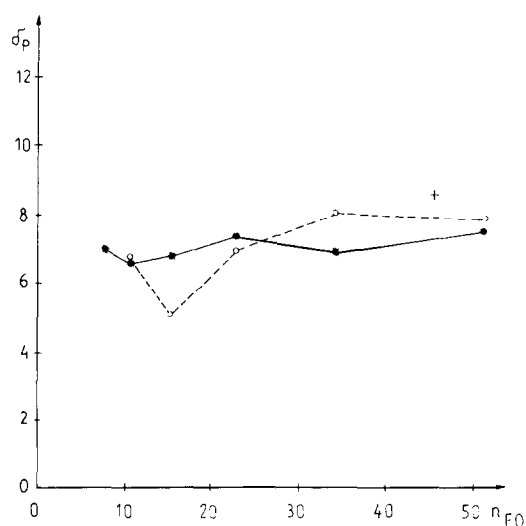


Fig. 3. Polar component of solubility parameter for fluorine-containing oxyethylates.

The hydrogen-bonding component δ_h was greater than δ_p and varied from 8.67 to 9.97 [$10^3 \text{J}^{1/2} \text{m}^{-3/2}$] for Group I and from 8.56 to 10.68 [$10^3 \text{J}^{1/2} \text{m}^{-3/2}$] for Group II compounds. Again, the highest values were observed for compound III-2000.

The presence of an additional $-\text{CF}_2\text{CF}_2-$ group led to a slight decrease in the values of δ_p and δ_h for compounds having less than 30 oxyethylene units. For higher homologues, higher δ_p and δ_h values were observed for surfactants from Group II.

The solubility parameter increments for compound III-2000 were significantly different from those of the other surfactants, i.e. δ_d lower; δ_p and δ_h higher.

Values of the corrected solubility parameter δ_T were always lower than those of δ_2 by *c.* 1.4–2.5 units depending on the type of surfactant, the length of the

oxyethylene chain and the column temperature. The relationship between the δ_T values for compounds of Groups I and II was similar to those observed for δ_2 values obtained directly.

An increase in the temperature of the chromatographic column caused a decrease of δ_2 from 19.3 at 70 °C to 18.64 [$10^3 \text{J}^{1/2} \text{m}^{-3/2}$] at 110 °C for I-666. The greatest decrease of 0.95 units was observed for compound II-2250. The values of δ_T also decreased with increasing temperature but the change was smaller than that of δ_2 . This results from a decrease in the dispersive component and a slight increase in the polar and hydrogen-bonding increments.

Fluorine-containing surfactants have recently been characterized by the use of polarity parameters [19]. Well-accepted parameters such as the polarity index *PI* [28], the McReynolds' value $\Sigma_{i=1}^5 \Delta I_i$ [29], criterion *A* [30] and partial molar Gibbs excess free energy of one methylene group $\Delta G^E(\text{CH}_2)$ [31] were used. The relationships between the polarity parameters and the solubility parameter δ_2 and its increments are presented in Table 4. The highest statistical significance was observed for the relationship between the solubility parameter δ_2 and $\Sigma_{i=1}^5 \Delta I_i$, i.e. the sum of the differences of the retention indices determined on the examined stationary phase and squalane for the first five McReynolds' solutes. Significantly lower correlation coefficients were obtained for the relationship between δ_p and $\Sigma_{i=1}^5 \Delta I_i$. The dispersive component δ_d correlated well with the dispersive interaction parameters used previously, i.e. partial molar Gibbs excess free energy of one methylene group $\Delta G^E(\text{CH}_2)$ and criterion *A*. The value of the corrected solubility parameter δ_T increased with increasing $\Sigma_{i=1}^5 \Delta I_i$ value (Fig. 4) and the correlation coefficients of this relationship were

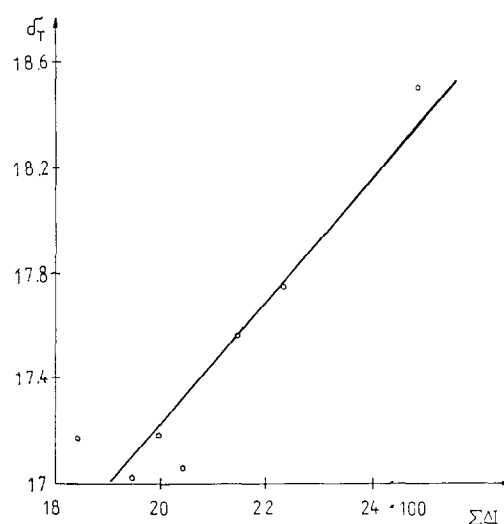


Fig. 4. Relationship between corrected solubility parameter δ_T and $\Sigma_{i=1}^5 \Delta I_i$ for fluorine-containing oxyethylates from Group I.

TABLE 4. Relationships between solubility and polarity parameters for fluorine-containing surfactants

Group	Polarity parameter	Solubility parameter	$Y = a \cdot X + b$			
			a	b	R	F -ratio
I	$\sum_{i=1}^5 \Delta J_i$	δ_2	1.65×10^{-3}	16.04	0.993	368.63
		δ_p	2.96×10^{-3}	1.00	0.885	18.10
		δ_h	4.11×10^{-3}	0.78	0.937	35.72
		δ_T	2.37×10^{-3}	12.50	0.939	37.68
	PI	δ_2	0.0663	11.74	0.998	108.25
		δ_p	0.1126	-5.95	0.823	10.65
		δ_h	0.1611	-9.46	0.899	21.24
		δ_T	0.0925	6.64	0.899	20.95
	$\Delta G^E(\text{CH}_2)$ Criterion A	δ_d	-3.88×10^{-3}	15.91	-0.958	56.55
		δ_d	8.929	-5.77	0.903	22.15
II	$\sum_{i=1}^5 \Delta J_i$	δ_2	4.23×10^{-3}	10.85	0.952	29.05
		δ_p	9.83×10^{-3}	-12.85	0.787	4.88
		δ_h	9.02×10^{-3}	-8.12	0.866	2.39
		δ_T	6.13×10^{-3}	5.13	0.933	20.16
	PI	δ_2	0.1267	4.75	0.876	9.89
		δ_p	0.2602	-23.05	0.899	2.07
		δ_h	0.4000	-36.88	0.842	3.68
		δ_T	0.1836	-3.68	0.857	8.27
	$\Delta G^E(\text{CH}_2)$ Criterion A	δ_d	-7.26×10^{-3}	19.10	-0.853	8.01
		δ_d	18.22	-25.21	0.930	19.33

also satisfactory. The correlation coefficients of the polarity parameter-solubility parameter relationships were slightly worse when the polarity index PI was used instead of the $\sum_{i=1}^5 \Delta J_i$ value. However, the correlation coefficient of the PI versus δ_2 relationship (Group I) was very high, i.e. 0.998. Similar relationships were observed for both groups of fluorine-containing surfactants, but the statistical characteristics were better for Group I compounds.

Conclusions

The solubility parameters δ_2 and δ_T increased with increasing oxyethylation ratio in the examined surfactants. The corrected parameter δ_T was always smaller than δ_2 . A similar behaviour was observed for the increments δ_p and δ_h , while the dispersive component δ_d decreased with increasing length of the oligo-oxyethylene chain.

Increase in temperature led to a decrease in the δ_2 , δ_T and δ_d values and to an increase in the δ_p and δ_h values.

Statistically significant relationships were found between the solubility parameter, its increments, the corrected solubility parameter and the polarity parameters. The solubility parameter, corrected solubility parameter

and its polar components increased with increasing polarity of the surfactants.

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