

# Solubility parameters of broad and narrow distributed oxyethylates of fatty alcohols

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## ABSTRACT

The solubility parameter  $\delta_2$  and its components of broad and narrow distributed alcohol oxyethylates were determined by inverse gas chromatography. Corrected values of the solubility parameter  $\delta_r$  were calculated from the increments of the solubility parameter corresponding to different types of intermolecular solute–solvent interactions. The corrected value of solubility parameter is always lower than that obtained directly from Guillet and co-workers' procedure. The influence of the structure of the examined oxyethylates on the solubility parameter and its components is discussed. Narrow range distributed oxyethylates are characterized by lower values of the solubility parameters than broad range products, but the difference decreases with increase in the average oxyethylation ratio. The increase in the length of oxyethylene chain increases the solubility parameter. The solubility parameter decreases with increase in temperature. Temperature and structural dependences of the solubility parameter increments are also presented and discussed. Relationships between the solubility parameter, corrected solubility parameter, its components and polarity parameters are examined.

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## INTRODUCTION

Oxyethylene derivatives of fatty alcohols are the main, large group of non-ionic surfactants. Polarity parameters for oxyethylates with broad and narrow distributions of oxyethylene units were reported in a previous paper [1]. It was found that narrow range distributed alcohol oxyethylates exhibit higher polarity at lower temperatures than broad distributed products. This difference decreases with increasing temperature. The retention indices of the first five McReynolds products, the coefficient  $\rho$ , polarity index and criterion  $A$  properly described the changes in the polarity of oxyethylates with changes in their structure. An increase in the average number of oxyethylene units increased the polarity of the products examined.

According to Hildebrand and Scott [2], the square root of cohesive energy density is called the solubility parameter,  $\delta$ , having the units  $(\text{cal}/\text{cm}^3)^{1/2}$ ,  $(\text{J}/\text{m}^3)^{1/2}$  or  $(\text{MPa})^{1/2}$ . The solubility of any organic compound in various solvents is largely determined by its chemical structure and increases if the solubility parameters of the compound and solvent are equal. In addition to the chemical structure, the physical state also influences the solubility properties of a compound.

The solubility parameter has seldom been used for the characterization of surface-active compounds. However, the Cohesive Energy Ratio (CER) theory discussed [3] the behaviour of an emulgator in an oil–water system according to the cohesive energies of all components of the system. However, as the data required for most surfactants were not available, the CER theory has seldom been used in practical applications. Determination of the solubility parameter for

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surfactants could facilitate the description of water–surfactant–oil systems.

The solubility parameter for volatile compounds is calculated from the basic equation

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

where  $\Delta H_v$  = enthalpy of vaporization,  $R$  = gas constant,  $T$  = temperature and  $V$  = molar volume.

For low- or non-volatile species the use of eqn. 1 is impossible. There are two ways to calculate the value of the solubility parameter for this group of compounds: (i) calculation using the structural increments of cohesive energy given by Hoy [4,5] or Hoftyzer and Van Krevelen [6], which results in a *ca.* 10% relative error for the solubility parameter; and (ii) the method of Guillet and co-workers [7,8] with the use of inverse gas chromatography (IGC). Guillet and co-workers presented a procedure for the evaluation of solubility parameters under assumption that the solute–solvent interaction parameter  $\kappa^\infty$  has free energy characteristics with enthalpic ( $\kappa_H^\infty$ ) and entropic ( $\kappa_s^\infty$ ) terms:

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

In an IGC process, volatile diluent, injected on to the chromatographic column, has a tendency to be absorbed by the liquid phase, *i.e.*, examined compound (product). This tendency is a function of  $\kappa$  and is measured in terms of retention, *e.g.*, specific retention volume  $V_g$ . The interaction parameter was usually obtained in the limit of zero concentration of the solute [9–11] and calculated from the following equation:

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

where  $M_1$ ,  $P_1^0$ ,  $B_{11}$ ,  $V_1^0$ ,  $\rho_1$  and  $V_g^0$  are the molecular mass, saturated vapour pressure, second virial coefficient, molar volume and specific retention volume of the solute, respectively,  $\rho_2$

and  $V_2^0$  are the density and molar volume of polymer,  $T$  is the column temperature,  $R$  is the gas constant.

The following equation was used to calculate the solubility parameter of the stationary phase [7,8]:

$$\frac{\delta_1^2}{RT} - \frac{\kappa^\infty}{V_1^0} = \frac{2\delta_2}{RT} \cdot \delta_1 - \left( \frac{\delta_2^2}{RT} + \frac{\kappa_s^\infty}{V_1^0} \right) \quad (4)$$

where  $\delta_1$  is the solute solubility parameter. Plotting the left-hand side of eqn. 4 versus  $\delta_1$ , one obtains a straight line with slope proportional to  $\delta_2$  of the polymer [7,12,13].

The use of the Guillet procedure has been reported in a number of papers [7,12,14–17]. Usually excellent linearity of eqn. was found [18]. Price [17] examined organic compounds of relatively low molecular masses: two non-polar alkanes, *n*-hexadecane and squalane, two alkyl phthalates, dinonyl and di-*n*-octyl phthalate, and two compounds having polar groups, *N*-methylpyrrolidone and dibutyl-2-ethylhexamide. Price found a downward curvature of eqn. 4 for the alkane systems, *i.e.*, too low estimates of  $\delta_2$ , and upward curvature (overestimates of the solubility parameter) for the other compounds examined. Price separated the contributions to the solubility parameter attributed to dispersive ( $\delta_d$ ) and polar ( $\delta_p$ ) solute–solvent interactions. The total (corrected) solubility parameter was calculated from the equation

$$\delta^2 = \delta_d^2 + \delta_p^2 \quad (5)$$

Although Price reported a significant improvement of the prediction of the solubility parameter, he indicated that the interaction parameter  $\kappa$  for small-molecule systems should include contributions negligible for typical polymeric systems.

We extended the group of polar and non-polar test solutes. Their retention data would allow the calculation of the increments of the solubility parameter according to the following procedure: (i) eqn. 4 would be used separately for three different groups of solutes, the interactions of which with the liquid stationary phase could be attributed to dispersive (alkanes), polar non-hydrogen bonding (aromatic hydrocarbons, ketones, nitropropane) and hydrogen bonding

(alcohols and pyridine) interactions (for details, see Experimental); (ii) the total, corrected solubility parameter would be calculated from an equation similar to those proposed earlier by Hansen [19,20]:

$$\delta_T^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (6)$$

which corresponds to the contributions of interaction forces to the cohesive energy [2]:

$$E_{\text{coh}} = E_d + E_p + E_h \quad (7)$$

where  $E_d$ ,  $E_p$  and  $E_h$  denote the contributions of dispersion, polar forces and hydrogen bonding, respectively, to the cohesive energy of the molecule.

The aim of this work was to: (i) examine the group of oligomeric oligooxyethylene derivatives of cetyl alcohols by inverse gas chromatography; (ii) check the applicability of the Guillet procedure for the oligomers examined and, if possible, to determine their solubility parameter  $\delta_2$  by the Guillet procedure; (iii) separate the components of the solubility parameter which could be attributed to dispersive ( $\delta_d$ ), polar ( $\delta_p$ ) and hydrogen bonding ( $\delta_h$ ) interactions; (iv) calculate the corrected value of the solubility parameter from its components according to eqn. 6; and (v) examine structure–solubility parameter relationships for the examined group of compounds.

## EXPERIMENTAL

### Materials

Cetyl alcohol containing 94% of hexadecanol was used to obtain conventional products with a broad range distribution of homologues (BRD) and narrow range distributed ethoxylates (NRD) having average ethoxylation numbers from 3 to 11. Conventional products were obtained using sodium hydroxide as a catalyst, whereas a proprietary catalyst [18] was utilized to produce narrow range distributed ethoxylates. All products were synthesized at the Institute of Heavy Organic Synthesis “Blachownia”, Kędzierzyn-Koźle, Poland. The contents of components having different lengths of the oligooxyethylene

TABLE I

CONTENT OF COMPONENTS IN THE PAIRS OF BRD AND NRD  $C_{16}E_6$  OXYETHYLATES

Component	Content (%)	
	BRD	NRD
Light components	1.38	2.80
$C_{16}H_{33}OH$	5.86	2.28
$C_{18}H_{37}OH$	0.11	0.19
$C_{16}H_{33}O(CH_2CH_2O)_1H$	5.37	1.48
$C_{16}H_{33}O(CH_2CH_2O)_2H$	7.97	3.08
$C_{16}H_{33}O(CH_2CH_2O)_3H$	9.62	6.74
$C_{16}H_{33}O(CH_2CH_2O)_4H$	10.53	12.70
$C_{16}H_{33}O(CH_2CH_2O)_5H$	10.69	18.16
$C_{16}H_{33}O(CH_2CH_2O)_6H$	10.37	18.78
$C_{16}H_{33}O(CH_2CH_2O)_7H$	7.01	14.57
$C_{16}H_{33}O(CH_2CH_2O)_8H$	8.43	8.73
$C_{16}H_{33}O(CH_2CH_2O)_9H$	6.86	4.05
$C_{16}H_{33}O(CH_2CH_2O)_{10}H$	5.21	1.52
$C_{16}H_{33}O(CH_2CH_2O)_{11}H$	3.77	0.35
$C_{16}H_{33}O(CH_2CH_2O)_{12}H$	2.13	0.03
$C_{16}H_{33}O(CH_2CH_2O)_{13}H$	0.80	0.02
$C_{16}H_{33}O(CH_2CH_2O)_{14}H$	0.06	–
Dioxane	–	–
PEG	–	–

chain in the representative pair of oxyethylates is given in Table I. The comparison of homologue distributions for these products indicates a slight shift of the maximum in the NRD products towards the homologues having the higher content of oxyethylene groups. The exact data for GC analysis of oxyethylates were given previously [1].

### IGC experiments

The conditions for the IGC experiments were the same as reported previously [1]. To facilitate the determination of the components of solubility parameters, the number of test solutes was significantly increased. The following volatile compounds were used as test probes: *n*-alkanes from *n*-pentane to *n*-decane, the aromatic hydrocarbons benzene, toluene, xylene and ethylbenzene, *n*-alkanols from methanol to 1-butanol, the ketones 2-butanone and 2-pentanone, nitropropane and pyridine.

### Solubility parameter and its components

Solubility parameters for the test solutes,  $\delta_1$ , were calculated from eqn. 1 using the values of the enthalpy of evaporation [21,22]. These values are presented in Table II. The Flory–Huggins interaction parameter  $\kappa_{12}^\infty$  was calculated from eqn. 3 using the values of the second virial coefficient,  $B_{11}$  (Table II), taken from ref. 23 or calculated by the procedure given in refs. 7 and 24. Vapour pressures were taken or compiled from literature data [20,25,26]. The solubility parameter  $\delta_2$ , in the first step, was calculated from eqn. 4. The increments of the solubility parameter corresponding to different types of solute–solvent interactions were determined as follows: eqn. 4 was used separately for three groups of solutes, (i) *n*-alkanes, (ii) polar non-hydrogen bonding compounds (aromatic hydrocarbons, ketones and nitropropane) and (iii) alcohols and pyridine; it was assumed that the slope of eqn. 4 for *n*-alkanes is proportional to the dispersive component of the solubility parameter:

$$\delta_d = \frac{\text{slope}_{n\text{-alkanes}} \cdot RT}{2} \quad (8)$$

the polar increment of the solubility parameter,  $\delta_p$ , was calculated from the difference in the slopes for polar solutes and *n*-alkanes:

$$\delta_p = \frac{(\text{slope}_{\text{polar}} - \text{slope}_{n\text{-alkanes}})RT}{2} \quad (9)$$

and the hydrogen bonding component,  $\delta_h$ , from the corresponding relationship for *n*-alkanols, pyridine and *n*-alkanes:

$$\delta_h = \frac{(\text{slope}_{\text{alcohols}} - \text{slope}_{n\text{-alkanes}})RT}{2} \quad (10)$$

The corrected value of solubility parameter was calculated from eqn. 6.

### RESULTS AND DISCUSSION

The main problem was the applicability of the Guillet procedure for the determination of the solubility parameter of surface-active agents of

TABLE II  
SOLUBILITY PARAMETERS,  $\delta_1$ , AND VIRIAL COEFFICIENTS,  $B_{11}$ , FOR THE TEST SOLUTES

Test solute	Solubility parameter, $\delta_1$ [(J/m <sup>3</sup> ) <sup>1/2</sup> ]			Virial coefficient, $B_{11}$ (cm <sup>3</sup> /mol)		
	70°C	80°C	90°C	70°C	80°C	90°C
<i>n</i> -Pentane	12076	11768	11433	-836	-733	-629
<i>n</i> -Hexane	12722	12299	12199	-1275	-1111	-947
<i>n</i> -Heptane	13266	13039	12799	-1899	-1650	-1401
<i>n</i> -Octane	13610	13399	13176	-2660	-2301	-1943
<i>n</i> -Nonane	13953	13746	13548	-3500	-3000	-2570
<i>n</i> -Decane	14229	14035	13841	-4600	-3900	-3300
Methanol	27483	27022	26524	-1157	-944	-731
Ethanol	24043	23664	23542	-1708	-1174	-640
1-Propanol	22064	21741	21370	-1619	-1278	-937
1-Butanol	20504	20262	20019	-1770	-1484	-1199
2-Butanone	17223	16919	16613	-1527	-1239	-952
2-Pentanone	16399	16126	15840	-2450	-1997	-1543
1-Nitropropane	19589	19541	19493	-3272	-2611	-2118
Pyridine	19535	19285	19035	-1303	-1171	-1039
Benzene	17176	16884	16601	-1036	-902	-768
Toluene	16518	16292	16035	-2041	-1681	-1408
Xylene	16183	15955	15715	-3214	-2616	-2164
Ethylbenzene	16483	16441	16400	-2706	-2228	-1863

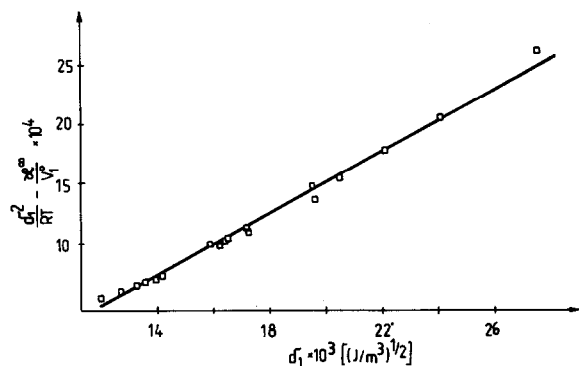


Fig. 1. Example of relationship of  $(\delta_1^2/RT - \kappa^\infty/V_1^0)$  vs.  $\delta_1$  for  $C_{16}E_3$  (BRD type).

relatively low molecular mass. As an example, for the group of surfactants examined the relationship between the left-hand side of eqn. 4 and  $\delta_1$  is shown in Fig. 1. Only slight deviations from the straight line are observed and the correlation coefficients are relatively high ( $>0.9$ ). The deviations are significantly smaller than those reported by Price [17]. Values of the solubility

parameter  $\delta_2$  determined directly from eqn. 4 are presented in Tables III–V. However, the deviations from the straight line described by eqn. 4 are large enough to allow the determination of increments of the solubility parameter (Fig. 2). Estimated increments of the solubility parameter are also given in Tables III–V. The experimental error in the determination of  $\delta_2$ , increments of the solubility parameter ( $\delta_d$ ,  $\delta_p$ ,  $\delta_h$ ) and corrected solubility parameter never exceeded  $0.05 \cdot 10^3$   $(J/m^3)^{1/2}$  and generally was in the range 0.01–0.02 units. They were used for the calculation of corrected solubility parameter  $\delta_T$  by the use of eqn. 6, values for which are also given in Tables III–V. The values of the corrected solubility parameter  $\delta_T$  are lower than those calculated directly from eqn. 4. The difference changes from  $1 \cdot 10^3$  to  $3 \cdot 10^3$   $(J/m^3)^{1/2}$  depending on the type of compound examined and the average number of oxyethylene units in its molecule.

The solubility parameter  $\delta_2$  increases with increase in the average oxyethylation rate of cetyl alcohol for compounds containing up to

TABLE III

SOLUBILITY PARAMETER ( $\delta_2$ ), ITS COMPONENTS ( $\delta_d$ ,  $\delta_p$ ,  $\delta_h$ ) AND CORRECTED SOLUBILITY PARAMETER ( $\delta_T$ ) FOR BROAD AND NARROW DISTRIBUTED OXYETHYLATES [ $10^3(J/m^3)^{1/2}$ ] AT 70°C

Type	Average number of EO units	$\delta_2$	$\delta_d$	$\delta_p$	$\delta_h$	$\delta_T$	
BRD	3	16.14	14.88	0.41	0.99	14.92	
	4	16.83	14.68	1.62	3.48	15.17	
	5	16.79	14.92	1.88	2.62	15.26	
	6	16.88	14.86	2.94	1.75	15.25	
	7	17.24	13.30	5.18	6.14	15.54	
	8	18.00	13.17	4.51	7.21	15.67	
	9	17.83	13.85	3.77	6.01	15.56	
	10	17.57	14.08	4.31	5.87	15.84	
	11	17.83	13.68	4.27	8.10	16.46	
	NRD	3	16.64	14.12	2.79	5.76	15.16
		4	17.22	14.12	3.12	5.39	15.20
5		17.06	13.74	3.62	5.78	15.34	
6		17.24	13.24	4.10	6.47	15.30	
7		17.03	13.47	4.10	6.14	15.36	
8		17.40	13.44	4.02	6.69	15.54	
9		17.75	14.46	2.93	5.17	15.63	
10		18.12	14.81	4.21	4.31	15.99	
11		18.40	13.90	6.70	4.10	15.97	

TABLE IV

SOLUBILITY PARAMETER ( $\delta_2$ ), ITS COMPONENTS ( $\delta_d$ ,  $\delta_p$ ,  $\delta_h$ ) AND CORRECTED SOLUBILITY PARAMETER ( $\delta_T$ ) FOR BROAD AND NARROW DISTRIBUTED OXYETHYLATES [ $10^3(\text{J}/\text{m}^3)^{1/2}$ ] AT 90°C

Type	Average number of EO units	$\delta_2$	$\delta_d$	$\delta_p$	$\delta_h$	$\delta_T$	
BRD	3	15.81	14.43	0.22	2.31	14.61	
	4	16.58	14.21	1.77	3.58	14.76	
	5	16.83	14.28	2.11	3.84	14.94	
	6	16.82	14.43	1.96	3.73	15.04	
	7	17.12	14.25	2.32	4.13	15.02	
	8	17.13	14.27	2.39	4.38	15.12	
	9	17.37	13.73	3.36	5.28	15.09	
	10	17.26	14.10	2.70	4.75	15.12	
	11	17.81	13.34	4.09	6.49	15.39	
	NRD	3	16.89	13.94	2.60	4.36	14.84
		4	17.01	13.90	2.55	4.59	14.85
5		17.41	13.46	3.47	5.79	15.06	
6		17.44	13.48	3.42	6.04	15.03	
7		17.38	13.49	3.56	5.67	15.06	
8		17.74	13.33	4.58	5.83	15.25	
9		17.25	13.79	3.17	5.24	15.09	
10		17.50	13.39	4.13	5.82	15.17	
11		17.79	13.13	4.39	6.86	15.45	

TABLE V

SOLUBILITY PARAMETER ( $\delta_2$ ), ITS COMPONENTS ( $\delta_d$ ,  $\delta_p$ ,  $\delta_h$ ) AND CORRECTED SOLUBILITY PARAMETER ( $\delta_T$ ) FOR BROAD AND NARROW DISTRIBUTED OXYETHYLATES [ $10^3(\text{J}/\text{m}^3)^{1/2}$ ] AT 110°C

Type	Average number of EO units	$\delta_2$	$\delta_d$	$\delta_p$	$\delta_h$	$\delta_T$	
BRD	3	15.54	14.51	0.15	1.19	14.26	
	4	16.28	14.19	0.91	2.54	14.28	
	5	16.29	13.92	1.88	2.62	14.28	
	6	16.29	13.76	1.96	3.39	14.30	
	7	16.77	13.04	3.52	5.08	14.43	
	8	16.57	12.83	4.58	5.50	14.41	
	9	16.99	12.68	3.58	6.02	14.49	
	10	16.88	13.07	3.34	5.30	14.49	
	11	17.52	12.59	4.60	6.78	14.99	
	NRD	3	16.21	12.92	2.85	5.53	14.34
		4	16.62	13.28	2.73	4.61	14.32
5		17.13	12.90	3.58	5.95	14.65	
6		17.18	12.54	4.20	6.37	14.68	
7		17.05	13.01	3.49	5.60	14.59	
8		17.09	12.96	3.89	5.58	14.64	
9		17.06	13.12	3.42	5.47	14.62	
10		17.25	12.66	4.10	6.39	14.76	
11		17.57	12.59	4.50	6.78	15.07	

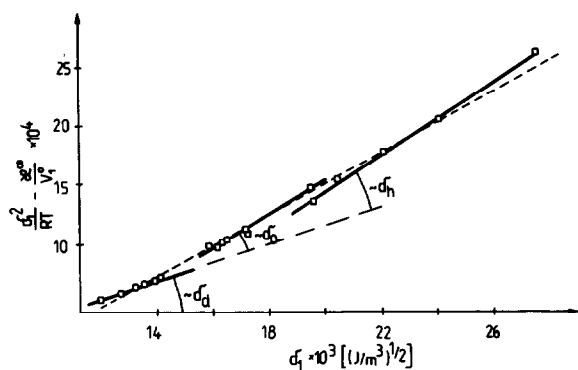


Fig. 2. Determination of increments of the solubility parameter.

7–8 oxyethylene units in both the BRD and NRD groups of surfactants. For BRD compounds having more than 7–8 oxyethylene units some decrease in  $\delta_2$  is observed. This effect is observed only at 70°C. The influence of the number of oxyethylene chain length on the solubility parameter  $\delta_2$  is less significant (Fig. 3) than for BRD analogues. Values of the solubility parameter  $\delta_2$  are higher for NRD products, but the difference decreases with increase in the oxyethylation ratio.

The examined parameters are characterized by  $\delta_2$  values ranging from  $16 \cdot 10^3$  to  $18 \cdot 10^3$   $(J/m^3)^{1/2}$  at 70°C, which correspond to 7.8–9  $(cal/cm^3)^{1/2}$  [note that  $10^3 (J/m^3)^{1/2} = (MPa)^{1/2} =$

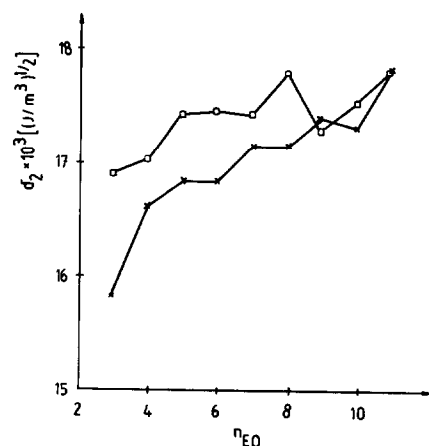


Fig. 3. Influence of the number of oxyethylene units on the values of the solubility parameter  $\delta_2$  for (x) BRD and (□) NRD oxyethylates.

$0.4888 (cal/cm^3)^{1/2}$ . These values are higher than or equal to those reported for polystyrene of  $7.6 (cal/cm^3)^{1/2}$  [7], poly(methyl acrylate) of  $8.7 (cal/cm^3)^{1/2}$  [7] and silicone stationary phases, OV-101 of  $6.49 (cal/cm^3)^{1/2}$  and OV-105 of  $6.83 (cal/cm^3)^{1/2}$  [15]. Sanetra *et al.* [27] reported  $\delta_2$  values for poly(styrene–divinylbenzene) copolymers containing 5, 10 and 20% of divinylbenzene of 14.8, 15.7 and 17.8  $(MPa)^{1/2}$ , respectively. Becerra *et al.* [15] explained the increase in the solubility parameter by the presence of 5% of cyanopropyl groups in the molecule of a dimethylsilicone. Hence the increase in the content of polar groups increases the solubility parameter. Therefore, we could discuss the increase in the solubility parameter for BRD and NRD cetyl alcohol oxyethylates as being due to an increase in their polarity.

As indicated previously, corrected values of the solubility parameter  $\delta_T$  are always lower than those predicted directly by the Guillet procedure. The difference varies from  $1 \cdot 10^3$  to  $3 \cdot 10^3$   $(J/m^3)^{1/2}$  depending on the type of oxyethylate (BRD or NRD product), the number of oxyethylene units in the molecule and the temperature of GC experiment. Values of the corrected solubility parameter  $\delta_T$  increase with increase in the oxyethylene chain length but the differences between the two groups of compounds examined are very small. Slightly higher values are observed for NRD products (by 0.2–1.0 units), but the differences diminish for homologues containing more than 7–8 oxyethylene units in their molecules (Fig. 4).

The corrected solubility parameter  $\delta_T$  is calculated from increments corresponding to different types of intermolecular interactions. These increments depend also on the composition of the materials examined. The dispersive component of the solubility parameter  $\delta_d$  tends to decrease with increasing oxyethylation ratio for both groups of compounds examined. However, the relationships are not monotonic, *e.g.*, linear (Fig. 5a). Generally, for a lower content of oxyethylene units  $\delta_d$  is higher for BRD products, whereas for  $n_{EO} \geq 7-8$  these values are similar for both groups of oxyethylates or, in some instances, higher for NRD analogues.

The polar component of the solubility parameter  $\delta_p$  increases with increase in the length of the

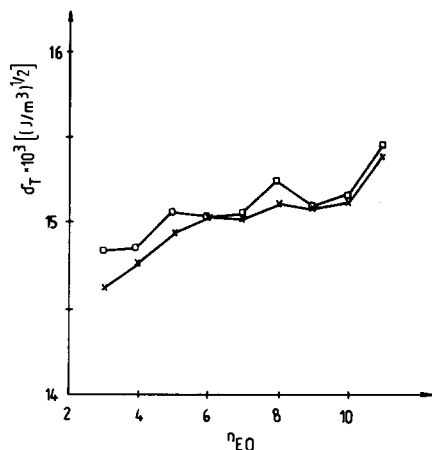


Fig. 4. Influence of the number of oxyethylene units on corrected values of solubility parameter  $\delta_f$  for (x) BRD and (□) NRD oxyethylates.

oxyethylene chain. Generally,  $\delta_p$  is higher for NRD products. However, for  $n_{EO} \geq 7-8$   $\delta_p$  is higher for BRD oxyethylates (at 70°C, Fig. 5b). At higher temperatures, i.e. 90 and 110°C, this effect disappears and the  $\delta_p$  values are very similar for both series of compounds.

The same behaviour is observed for the hydrogen bonding component of the solubility parameter  $\delta_h$ . Significantly higher  $\delta_h$  values are observed for compounds having a short oxyethylene chain (Fig. 5c). Higher homologues are characterized by similar values of this parameter.

In each instance large and significant changes in the values of the solubility parameter components are observed for BRD products, whereas the changes for the NRD analogues are much lower. As an example, the difference between the maximum and minimum values of  $\delta_p$  (at 70°C) for BRD products is  $4.5 \cdot 10^3 \text{ (J/m}^3)^{1/2}$ , whereas the difference for NRD oxyethylates is  $1.42 \cdot 10^3 \text{ (J/m}^3)^{1/2}$ . Moreover, for higher contents of oxyethylene units the values for all types of solubility parameter increments are similar. As a result, the corrected values of the solubility parameter  $\delta_T$  are similar for both groups of oxyethylates and slightly higher values for NRD products are observed only for  $n_{EO} \leq 5$ . In this region the  $\delta_d$  component is much higher for BRD products, but it does not compensate for the

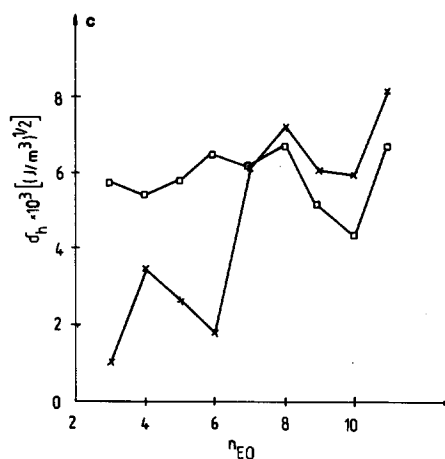
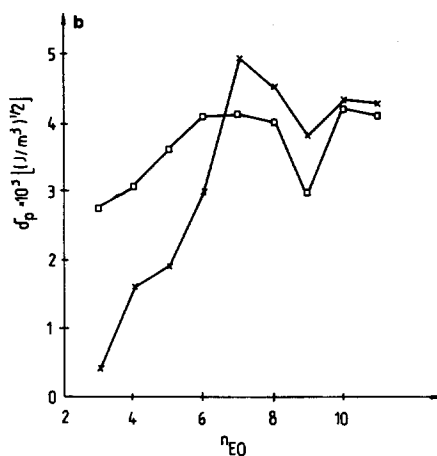
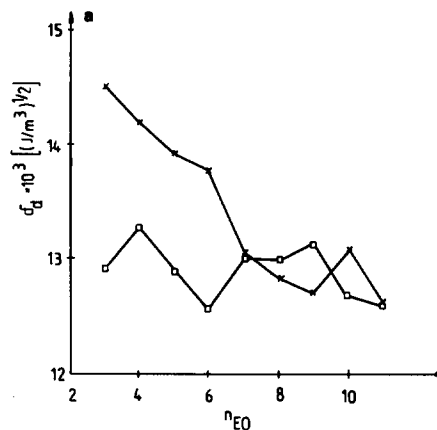


Fig. 5. Influence of the number of oxyethylene units on increments of the solubility parameter for (x) BRD and (□) NRD oxyethylates: (a)  $\delta_d$  vs.  $n_{EO}$  at 110°C; (b)  $\delta_p$  vs.  $n_{EO}$  at 70°C; (c)  $\delta_h$  vs.  $n_{EO}$  at 70°C.



differences in  $\delta_p$  and  $\delta_h$  between the two series of compounds.

The solubility parameter  $\delta_2$  and its corrected value  $\delta_T$  decrease with increasing column temperature. It is contradiction with statements by Becerra *et al.* [15] but agrees with the findings of Fernandez-Sanchez *et al.* [16]. The decrease in the solubility parameter seems to be approximately linear (Fig. 6a), but the evaluation of statistically significant relationships requires more experimental data than are available. Similar behaviour was observed with typical polarity parameters determined previously for the examined oxyethylates [1]. The polarity index, *PI*, the coefficient  $\rho$  and the retention indices of polar test solutes also decreased with increasing temperature. A detailed analysis of the temperature dependence of the solubility parameter's

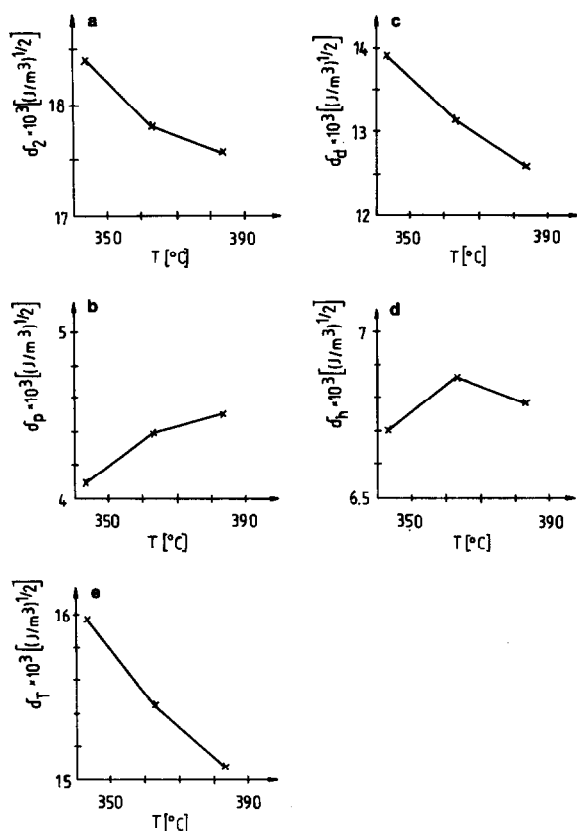


Fig. 6. Temperature dependence of (a) the solubility parameter  $\delta_2$ , (b) dispersive component  $\delta_d$ , (c) polar component  $\delta_p$ , (d) hydrogen bonding component  $\delta_h$  and (e) corrected solubility parameter  $\delta_T$  for  $C_{16}\bar{E}_{11}$  narrow range distributed oxyethylate.

components should answer the question of what the reason is for the decrease in a compound's polarity. The most significant changes are observed for the dispersive components of the solubility parameter  $\delta_d$  (Fig. 6b). The decrease in this increment varies from  $0.24 \cdot 10^3$  to  $1.31 \cdot 10^3$   $(J/m^3)^{1/2}$ , depending on the type of oxyethylate and the length of the oxyethylene chain. The polar component  $\delta_p$  varies or increases with increasing temperature. There is no general rule that could describe the temperature behaviour of this increment of the solubility parameter (Fig. 6c). For BRD having  $n_{EO} = 11$  the lowest value of  $\delta_p$  is observed at  $90^\circ\text{C}$  and increases at  $110^\circ\text{C}$ . In contrast, for  $C_{16}\bar{E}_4$  BRD oxyethylate ( $\bar{E}_n$  denotes average number of oxyethylene units) the maximum value is measured at  $90^\circ\text{C}$ . A monotonic decrease in  $\delta_p$  was found, *e.g.*, for  $C_{16}\bar{E}_7$  NRD oxyethylate. However, a monotonic increase was observed for the  $C_{16}\bar{E}_{11}$  NRD analogue.

The hydrogen bonding increment of the solubility parameter also varies with increasing temperature. A representative example is given in Fig. 6d for an NRD homologue having  $n_{EO} = 11$ . Only in a few instances does the change in  $\delta_h$  have a monotonic character, as for  $C_{16}\bar{E}_7$  NRD oxyethylate.

The influence of temperature on the corrected solubility parameter is a result of temperature variations of its components. The sum of these variations gives an almost linear decrease in  $\delta_T$  with increasing temperature (Fig. 6e). This decrease in  $\delta_T$  is mainly caused by the significant decrease in the dispersive component  $\delta_d$  with increase in temperature.

It was mentioned previously that one may discuss the solubility parameter and/or corrected solubility parameter as a measure of a compound's polarity. The polarity of surfactants is often expressed with the use of parameters determined by GC [18,28]. These parameters determined for broad and narrow range distributed oxyethylates of cetyl alcohol have been reported previously [1].

Both the solubility parameter  $\delta_2$  and corrected solubility parameter  $\delta_T$  increase with increase in representative polarity parameters such as the

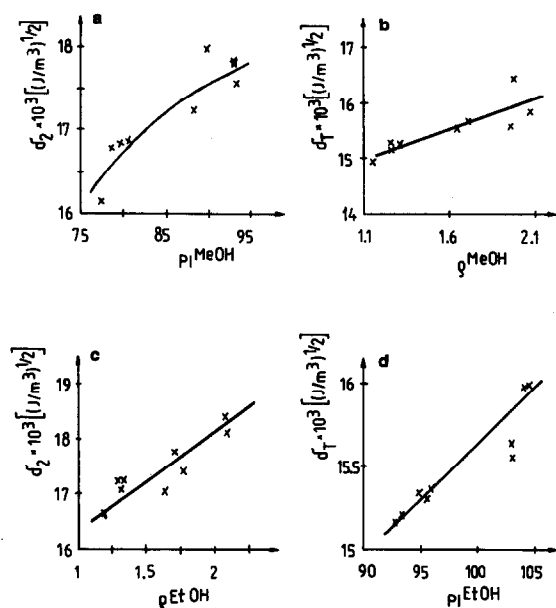


Fig. 7. Relationships between solubility and polarity parameters: (a) solubility parameter  $\delta_2$  vs. polarity index (methanol as polar solute); (b)  $\delta_T$  vs. coefficient  $\rho$  (methanol as polar solute); (c)  $\delta_2$  vs. coefficient  $\rho$  (methanol as polar solute); (d)  $\delta_T$  vs. polarity index (ethanol as polar solute).

polarity index  $PI$  and coefficient  $\rho$  (Fig. 7). However, these relationships are not linear. The relationship between polar ( $\delta_p$ ) and hydrogen bonding ( $\delta_h$ ) components of the solubility parameters and previously determined polarity parameters are presented in Fig. 8. Both increments of the solubility parameter increase with increasing polarity of the compounds examined. In other

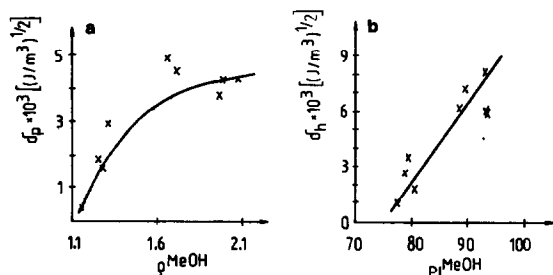


Fig. 8. Relationships between increments of solubility parameter and polarity parameters: (a)  $\delta_p$  vs. coefficient  $\rho$  (methanol as polar solute); (b)  $\delta_h$  vs. polarity index (methanol as polar solute).

words, the observed and measured increases in polarity are a result of increasing polar and hydrogen bonding interactions between the liquid stationary phase and test solutes in IGC.

## CONCLUSIONS

Two series of cetyl alcohol oxyethylates with broad and narrow range distributions of oxyethylene units were characterized in terms of solubility parameters. The values of the solubility parameters were determined by IGC. It was found that the Guillet procedure is applicable also for compounds having relatively low molecular masses. However, some deviations from the straight line described by eqn. 4 were observed. This allows a procedure for the determination of the solubility parameter increments from IGC data to be proposed. Dispersive, polar and hydrogen bonding components were calculated and their structural dependence was examined. Corrected solubility parameters were calculated from these increments. Generally, the solubility parameter  $\delta_2$ , the corrected solubility parameter  $\delta_T$  and the polar and hydrogen bonding components increase with increasing oxyethylation ratio. The dispersive component decreases with increase in the number of oxyethylene units. The increase in the corrected solubility parameter is a result of increases in the polar and hydrogen bonding components. Although both solubility and corrected solubility parameters describe the compounds examined in a similar way, the use of the corrected solubility parameter  $\delta_T$  is suggested. This parameter is calculated according to the accepted Hansen's equation using the increments determined from IGC experiments. A significant temperature dependence was found for all the parameters examined. Both the solubility parameter and corrected solubility parameter decrease with increasing temperature. It seems that this decrease is mainly caused by a decrease in the dispersive increment of the solubility parameter with increasing column temperature in IGC. The increase in the solubility parameters is accompanied by an increase in the polarity parameters, e.g., the polarity index and the coefficient  $\rho$ .

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