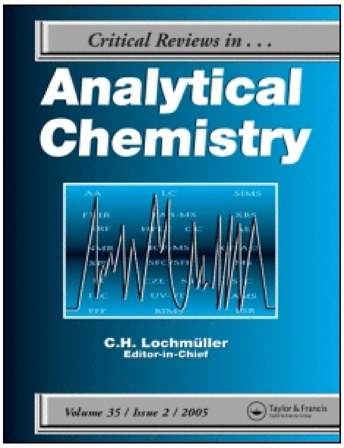

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Polarity of Nonionic Surfactants as Determined by Gas Chromatography

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Polarity of Nonionic Surfactants as Determined by Gas Chromatography

Jan Szymanowski

ABSTRACT

The use of gas chromatography to determine the polarity of model and commercial surface active agents is discussed. Various polarity parameters are presented, and their positive and negative features are discussed. Effects of chromatographic conditions upon these polarity parameters are presented. The use of the polarity index and the retention index of ethanol and methanol, and the sum of the first five McReynolds constants is favorable.

Relationships between various polarity parameters and between these parameters and the hydrophile lipophile balance (HLB) are discussed. The effect of surfactant structures upon their polarity parameters is presented.

Polarity parameters can be used to estimate the HLB of surfactants and they can be used as analytical coefficients to characterize the average structure of nonionic surfactants. Some properties of nonionic surfactants can be predicted from their polarity parameters. They can be also used to predict and interpret the behavior of extractants and surfactants at various liquid/liquid interfaces. They can be used to discuss the kinetic data and the mechanism of metal extraction by various extractants.

I. INTRODUCTION

Surface active agents usually contain one hydrophobic hydrocarbon chain and one hydrophilic group or block. They can be classified as anionic, cationic, and amphoteric surfactants. Among nonionic compounds, surfactants having one or more polyoxyethylene groups are the most important. They are usually obtained in the reaction of various alcohols, alkylphenols, alkylamines, fatty acids, and their amides, etc., with ethylene oxide according to the following reactions:

$$RXH + n\ \underset{\diagdown\ O\ \diagup}{CH_2CH_2} \xrightarrow{MOH} RX(CH_2CH_2O)_nH \qquad (1)$$

$$RNH_2 + (n+m)\ \underset{\diagdown\ O\ \diagup}{CH_2CH_2} \xrightarrow{MOH} RN\begin{cases}(CH_2CH_2O)_nH\\(CH_2CH_2O)_mH\end{cases} \qquad (2)$$

where X = O, C_6H_4–O, COO, S, etc.
C_6H_4–O

Complex polydispersed mixtures are formed that contain various homologs having different numbers of oxyethylene units. Polyoxyethylene glycols, $HO(CH_2CH_2O)_nH$, are also formed as by-products. The composition of these mixtures has been extensively studied by several authors[1] using the gas chromatography (GC) method. A number of papers were also published by us on this subject.[2-26]

Block copolymers of two different alkylene oxides, usually ethylene oxide and propylene oxide, are also manufactured and applied. Their formula can be as follows:

$$\text{EPE} \quad \text{or} \quad \text{EP} \quad \text{or} \quad \text{PEP} \qquad (3)$$

where E and P denotes polyoxyethylene and polyoxypropylene chains, respectively. Some other types of even more complex block copolymers are also manufactured.

Various esters of polyhydroxylic alcohols and carbohydrates also belong to this group of nonionic surfactants, i.e., glycerol mono- and diesters, sorbitan monoesters and their polyoxyethylene derivatives, sucrose mono- and diesters, etc.

All these compounds exhibit asymmetry and because of this, they can adsorb at different interfaces and can decrease surface and interfacial tensions. Thus, such compounds in systems containing an aqueous phase and an organic phase can (1) adsorb at the interface penetrating with their hydrophilic heads more or less deeply into the aqueous phase, or (2) dissolve better in the aqueous phase or in the organic phase (Figure 1). This behavior, as well as other properties of surfactants, depend upon their affinity for the aqueous phase, which depends upon the length and structure of a hydrophilic group and/or the length and structure of a hydrophobic group.

In 1943, Clayton[27] suggested that an appropriate balance should exist between a polar group and a hydrocarbon tail for surfactants used as emulsifiers. This hypothesis was further developed by Griffin[28,29] into a hydrophile lipophile balance (HLB) system, which has been the subject of many papers.[30-39]

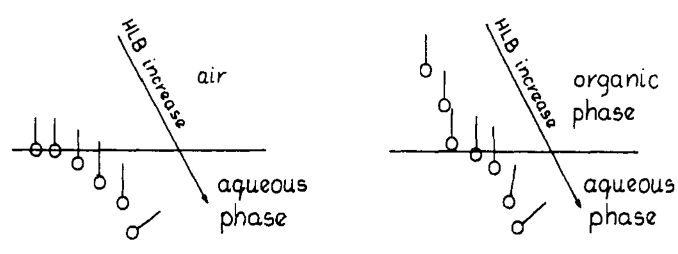

FIGURE 1. Adsorption and solubilities of surfactants and their HLB.

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Such original works usually looked for relations between HLB and the surfactants' structures, as well as relations between the HLB values and other physicochemical parameters that can be easily and precisely determined. The application of GC has been proposed for HLB determination as well and this problem was discussed by Haken.[34] However, it is necessary to state here that (1) there is no absolute scale both for the HLB and for surfactant polarity, (2) it is impossible to strictly define either considered term, (3) quite different properties are measured when different techniques are used, and (4) that even within one technique different scales may exist and the relations between selected polarity parameters and surfactant properties can be quite different. Therefore, further discussion here is concentrated upon the surfactant polarity determined by GC and upon the relations between the surfactant structures and their polarities as determined both for model pure compounds and for complex polydisperse mixtures. Polarity parameters discussed in this work are restricted only to those used for surface active agents.

II. POLARITY PARAMETERS

The determination of the liquid phase polarity in GC is a very complex problem. The use of many different polarity parameters has been proposed by several authors.[40] However, the Rohrschneider and McReynolds' systems,[41-43] which are based upon the retention indices determined for selected standard samples, are the most important ones. Rohrschneider[41,42] proposed the use of benzene, ethanol, methyl ethyl ketone, nitromethane, and pyridine as solutes to characterize various types of interactions such as electron donor, proton donor, dipole orientation, electron acceptor, and proton acceptor, respectively. The increments of these interactions into the total polarity are characterized by the difference of retention indices determined on an examined liquid phase, with squalane used as the standard nonpolar phase. McReynolds[43] used several higher homologs in place of those proposed by Rohrschneider, i.e., butanol, 2-pentanone, and nitropropane instead of ethanol, methyl ethyl ketone, and nitromethane, respectively.

The methods used for the determination of surfactant polarity are relavant for these systems, although they usually use only one standard sample (methanol or ethanol) instead of several different samples. Thus the polarity measurements are restricted only to proton donor-proton acceptor interactions. The use of squalane as a liquid nonpolar phase has also been abandoned. A surfactant is used as the liquid phase, and the retention time is determined for a selected standard sample under constant chromatographic conditions (temperature and flow of gas). Several different polarity parameters have been proposed.

A. Partition Coefficients of Water and Diisobutylene

The partition coefficient, K, defined as the ratio of the standard substance concentrations in the stationary and gas phases.[44]

$$K_i = c_i^s/c_i^g \tag{4}$$

can be calculated from

$$V_N' = K_i V_L \tag{5}$$

where V_N and V_L denote the net retention volume and the volume of the liquid phase, respectively. The net retention volume is given by

$$V_N = jF_o t_R', \tag{6}$$

where j, F_o and t_R' denote the pressure gradient correction factor, the flow rate at the column outlet and the adjusted retention time, respectively. The pressure gradient correction factor is defined by

$$j = \frac{3[(p_i/p_o)^2 - 1]}{2[(p_i/p_o)^3 - 1} \tag{7}$$

where p_i and p_o stand for the column inlet and outlet pressures, respectively.

Harva et al.[45] found the following linear relation between HLB values of sorbitan esters and their polyoxyethylene derivatives and the partition coefficient of diisobutylene:

$$HLB = 26 - K/2.6. \tag{8}$$

However, when Harva tried to use this relation to calculate the HLB values for other types of nonionic surfactants, significant deviations were sometimes observed. When water was used as a solute, different linear relations were observed for sorbitan esters and for their oxyethylene derivatives, respectively.

It seems that partition coefficients can be used to characterize surfactants, but much more data are necessary for the various types of nonionic surfactants. The main inconvenience of this parameter in comparison to the parameters, I_R, PI, and ρ, is the necessity for accurate flow rate and pressure determination. Due to this, the partition coefficient K probably was not used further by Harva or by other authors.

B. Carbon Numbers and Retention Indices of Methanol and Ethanol

The carbon number,[46]C, is the apparent number of carbon atoms in a hypothetical *n*-alkane having the same retention time as a standard alcohol. Its value is determined graphically or analytically from the relation: log retention time vs. number of carbon atoms in standard *n*-alkanes.

The retention index of standard alcohol is calculated in the typical manner, using

$$I_R = 100\ \Delta n \frac{\log t'_{ROH} - \log t'_n}{\log t'_{n+\Delta n} - \log t'_n} + 100n \qquad (9)$$

where t'_{ROH} denotes the adjusted retention time of the standard alcohol, and t'_n and $t'_{n+\Delta n}$ stand for the adjusted retention times of the standard hydrocarbons containing n and n + Δn carbon atoms whose peaks are eluted before and after the alcohol peak (usually Δn = 1).

This parameter (I_R) is equivalent to the carbon number (I_R = 100 C), although usually somewhat different values are obtained because of the use of different calculation methods. For example, for polyoxyethylene glycol dialkyl ethers,[47] somewhat higher values were obtained for the retention index in comparison to the carbon number: $I_R = 105.2\ C - 27.6$ (correlation coefficient, 0.9990). Small differences between C and I_R values were also observed for block copolymers of ethylene oxide and α-butylene oxide. For a block copolymer of BE type, the following values were reported: 6.47, 6.47, 6.49, 6.44, and 6.45, and 641, 646, 641, 641, and 642 for five independent measurements of the carbon number and retention index of methanol, respectively.[48] For a block copolymer of BEB type those parameters were equal to 6.81, 6.90, 6.90, 6.83, and 6.81, and 686, 697, 698, 693, and 692, respectively.[48] Thus, these small differences are practically unimportant.

The carbon number and the retention index of the standard alcohol (methanol or ethanol) are determined with a similar accuracy. For most of the investigated individual compounds the confidence limits at a significance level of 0.05 do not exceed 0.02 and 2 for the carbon number and the retention index, respectively.[47,49-56] Thus, they are significantly lower in comparison to the earlier values reported for block copolymers of alkylene oxides and for commercial polydisperse mixtures of nonionic surfactants.[48,57-61]

The retention index of ethanol is shifted toward higher values in comparison to this index determined for methanol by a constant value characteristic for a considered homolog series of surfactants. The following linear relations were obtained:

$$I_R^{EtOH} = 0.9038\ I_R^{MeOH} + 112.8 \qquad (10)$$

$$I_R^{EtOH} = 1.0044\ I_R^{MeOH} + 40.7 \qquad (11)$$

$$I_R^{EtOH} = 0.9076\ I_R^{MeOH} + 96.9 \qquad (12)$$

$$I_R^{EtOH} = 0.9857\ I_R^{MeOH} + 58.7 \qquad (13)$$

$$I_R^{EtOH} = 1.1261\ I_R^{MeOH} - 58.3 \qquad (14)$$

for polyoxyethylene glycols,[47] aminoether alcohols and their ethers,[50] 1,3-bis[ω-alkoxyoligo(oxyethylene)]propan-2-ols,[52] polyoxyethylene alcohols, alkylamines and thioalcohols,[55] and for α,ω-diaminooligoethers and diazapolyoxyethylene ethers,[53,54] respectively. The correlation coefficient is equal to 0.9942, 0.9980, 0,9764, 0.9862, and 0.9748, respectively.

C. Polarity Index

The polarity index of methanol, PI, proposed by Huebner,[62] is defined by the following empirical equation:

$$PI = 100 \log (C - 4.7) + 60. \qquad (15)$$

This form of Equation 13 was chosen to obtain a linear relation between the polarity index and the content of one surfactant in two-component mixtures. The factor 4.7 was determined statistically, and gave the smallest deviation from the regression line. The value log (C − 4.7) was multiplied by 100 to convert the polarity index to a whole number, and a value of 60 was added to give the polarity index a positive value. Thus, the polarity index of methanol for two-component mixtures can be calculated from the values of the polarity index determined separately for each component, or the polarity index of one component can be calculated from the polarity index of a two-component mixture and of the second surfactant. The additivity of the polarity index has been proven independently by different authors. Only small, practically nonsignificant deviations from the additivity rule have been observed in some cases.[61,63] An advantage of the polarity index over the carbon number and the relative retention of methanol (coefficient ρ discussed in Section II.D) is demonstrated in Figures 2 to 4.

In early studies, methanol was used as the standard polar agent. However, for very hydrophobic liquid phases, methanol elutes before pentane and the polarity index cannot be calculated, i.e., for C < 4.7. Due to this, the use of ethanol is preferred. Usually, linear relations are observed between polarity indices of ethanol and methanol[50-55] (Table 1). Important deviations are only observed for very hydrophobic compounds, i.e., as the polarity index of methanol is approximately 50. In this region, the polarity index of methanol is not very sensitive on the structure of surfactants used as liquid phases, and quite similar PI values are obtained for compounds having different polarities,[47] e.g., for polyoxyethylene glycols having not more than six oxyethylene groups. The regression coefficients given in Table 1 can be used to recalculate the polarity indices of methanol determined in the first works into the polarity index of ethanol.

The accuracy of the polarity index determination is high, and the confidence limits at a significance level of 0.05 do not exceed 0.5 and 1.0 U for ethanol and methanol used as the standard alcohol, respectively.[47,49-56] That accuracy is usually significantly lower, especially for individual compounds.

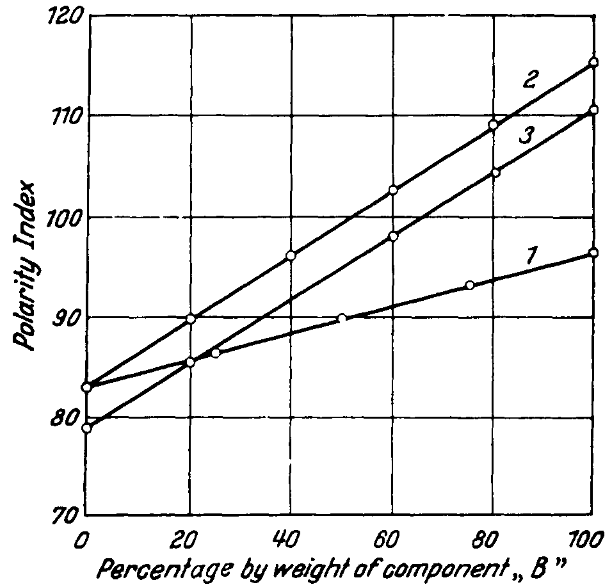


FIGURE 2. Polarity index of methanol for binary mixtures.[57] (1) Sucrose dipalmitate (A); sucrose monopalmitate (B); (2) sucrose distearate (A); Tween 20 (B); (3) mono- and diglycerides of fatty acids (A), polyoxyethylated coconut oil amine (B).

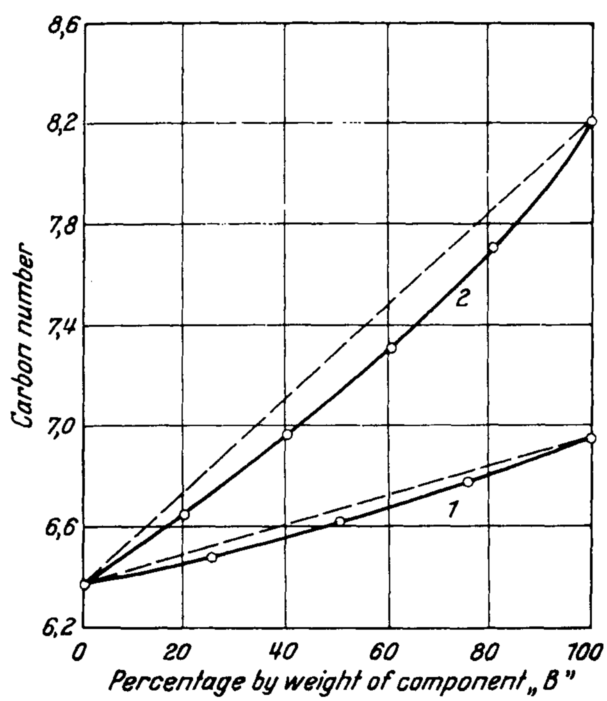


FIGURE 3. Carbon number of methanol for binary mixtures.[57] (1) Sucrose dipalmitate (A); sucrose monopalmitate (B); (2) sucrose distearate (A); Tween 20 (B).

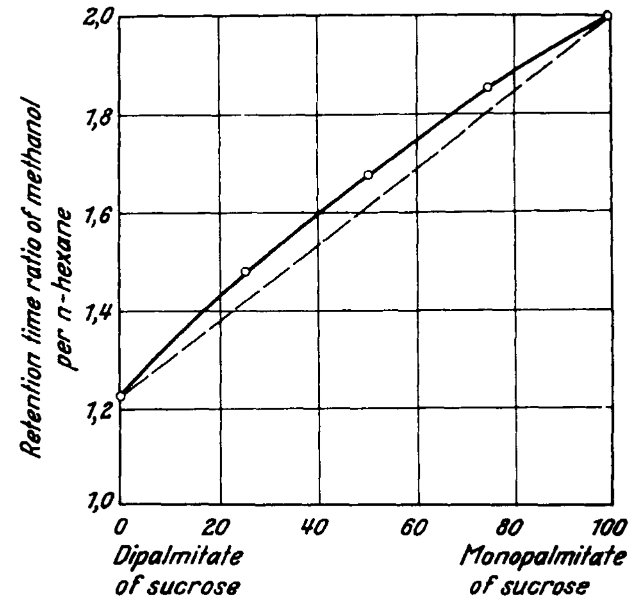


FIGURE 4. Relative retention time of methanol in comparison to *n*-hexane for binary mixtures.[57]

Table 1
Regression (a and b) and Correlation (R) Coefficients for Relation $PI^{EtOH} = a + b\, PI^{MeOH}$

Compounds	a	b	R	Ref.
Polyoxyethylene alcohols, alkylthiols, and alkylamines	30.0	0.8069	0.9826	55
Polyoxyethylene glycol dialkyl ethers	39.3	0.6695	0.9952	47,49
Aminoether alcohols and their ethers	25.2	0.8162	0.9950	50
1,3-bis[ω-Alkoxyoligo-(oxyethylene)]propan-2-ols	40.2	0.9487	0.9867	51
α,ω-Diaminooligoethers	25.5	0.9348	0.9225	53,54

Leca and Perez[64] proposed the use of the difference between the carbon numbers determined for the considered surfactant and for squalane, which was the reference nonpolar phase (methanol as polar solute):

$$C' = C_{surfactant} - C_{squalane} \qquad (16)$$

All the results were shifted toward lower values by $C_{squalane} = 3.65$ and were not discussed further.

D. Relative Retention of Alcohol

Becher and Birkmeier[65] have defined this relative retention coefficient ρ as

$$\rho = \frac{T_{EtOH}}{t_{hexane}} \qquad (17)$$

where t_{EtOH} and t_{hexane} denote the retention times of ethanol and *n*-hexane, respectively. Using this coefficient for sorbitan derivatives, they have found that, as in the case of the polarity index, some deviations from the additivity rule are observed for two-component mixtures. Similar deviations were observed by us for other groups of nonionic surfactants.[57]

Other alcohols such as methanol and isopropanol[57] and isoamyl alcohol[66] have also been used. Adjusted retention times (t′) are now used rather than uncorrected values:

$$\rho' = \frac{t'_{EtOH}}{t'_{hexane}} \tag{18}$$

As in the case of previous parameters, the relative retention of ethanol (ρ^{EtOH}) is related to the relative retention time of methanol (ρ^{MeOH}) by a linear equation, $\rho^{EtOH} = a + b\,\rho^{MeOH}$. However, deviations from this linear relation are quite important for some homolog series,[53,54] and the correlation coefficient is in the range of 0.90 to 0.99. Statistical analyses carried out for different groups of surfactants showed that the accuracy of the ρ determination is much lower than that observed for the carbon number, the retention index, and the polarity index. For example, the error of determination of the last three parameters for ethylene oxide and α-butylene oxide block copolymers is 1 to 2%, while the error of the coefficient ρ determination is 6 to 10%. Similar values were reported for other groups of nonionic surfactants, including pure individual compounds. This relates to the connection between the retention time of the polar solute and that of a single reference *n*-alkane instead of the scale constructed for several *n*-alkanes. Therefore, it was recently suggested that coefficient ρ can be calculated from the slope of Equation 19 and from the carbon number, as calculated from Equation 20.[67]

The adjusted retention time of standard alkanes is connected with the number of carbon atoms according to Equation 19:

$$\log t'_n = A + Bn. \tag{19}$$

The A and B constants can be calculated with good precision by the least square method.

The carbon number C can be calculated in a manner to that of the retention index:

$$C = \frac{\log t'_{ROH} - \log t'_n}{\log t'_{n+1} - \log t'_n} + n. \tag{20}$$

Thus:

$$C = \frac{\log t'_{ROH}/t'_n}{\log t'_{n+1}/t'_n} + n. \tag{21}$$

When Equations 18 and 19 are introduced into Equation 21 the following equation for log ρ′ is obtained:

$$\log \rho' = B(C - 6). \tag{22}$$

Using Equation 22, the coefficient ρ′ can be calculated with higher precision than directly from the values of the retention times of alcohol and *n*-hexane, especially when nonsymmetrical and/or broadened peaks are obtained on chromatograms.

In contrast to the polarity index, which has been considered in the majority of the earliest papers concerning surfactant polarity, the relative retention of alcohol to hexane considered as log ρ′ can be related to some physicochemical functions and coefficients, e.g., excess Gibbs free energy, enthalpy and entropy of mixing, and the activation coefficients of solutes in the liquid phases.[68,69] All this shows the importance of log ρ′ as a potential polarity criterion having physicochemical meaning.

Significantly different values of the polarity parameters are obtained when a large set of compounds having a different length of the hydrophilic block is considered. This is not only the result of surfactant polarity, but also reflects some small influence of the surfactants' molecular mass and their properties. Therefore, it was recently proposed that consideration be given to normalized values of log ρ′[67] defined as

$$\Delta \log \rho'_i = \log \rho'_i - \log \rho'_{st} - \Delta V^o(d_i/M_i - d_{st}/M_{st}) \tag{23}$$

where ρ'_{st}, d_{st}, and M_{st} denote the coefficient ρ′, density at column temperature, and the molecular mass, respectively, of the surfactant selected as the standard, usually the one showing the lowest polarity: ρ'_i, d_i, and M_i denote the same parameters for the considered compound "i"; and ΔV^0 is the difference of the molar volumes of methanol and hexane ($\Delta V^0 = V^o_{MeOH} - V^o_{hexane}$).

E. Retention Times of Isoamyl Alcohol and 2,4,4,-Trimethylpenten-1

Mickle et al.[66] proposed the use of the retention time of isoamyl alcohol. The chromatographic conditions were standardized at a constant temperature of 90°C, column length and diameter, the amount of liquid phase, and by adjusting for each column the flow-rate of the carrier gas to such level that the retention time of ethyl ether was constant and equal to 1.4 min. A linear relation between the retention time of isoamyl alcohol and the HLB values of Span and Tween surfactants was demonstrated. Its mathematical formula is

$$\text{HLB} = -26.0 + 3.06t, \qquad R = 0.9864. \tag{24}$$

According to Mickle, this relationship can be used to estimate the HLB values of other surfactants with an error of 0.2 to 1.5 HLB units. The HLB values for binary mixtures are obtained with similar accuracy. However, this parameter was not used in other works and for other groups of surfactants and their model compounds.

Bonadeo and Bottini[70] proposed the use of the retention time of 2,4,4-trimethylpenten-1 and demonstrated a linear relation between the HLB values of polyoxyethylated alcohols and the retention time of this solute. However, this parameter was not used in other works and for other groups of surfactants. As a result, it is impossible to predict the usefulness of this parameter as well as of the previous one.

F. Difference in the Retention Indices of *trans*-Decaline and Water

trans-Decaline and water were used as the nonpolar and polar standards, and this polarity parameter was defined as[71]

$$\Delta I_R = I_{R\ \text{decaline}} - I_{R\ \text{water}} \quad (25)$$

This criterion was not used in further works, although it was shown that for α-monoglycerides of fatty acids ΔI_R can be correlated with the HLB values on the Davies scale and with the critical micelle concentration (CMC) according to a simple linear relation. However, these relations were derived using only a few experimental data and therefore their validity should be proven after collecting more experimental data, i.e., ΔI_R, HLB, and CMC for a greater number of nonionic surfactants.

G. Sum of McReynolds Constants

Such a typical parameter was not used in the earliest works in which polarity parameters for nonionic surfactants were determined and used for the estimation of their HLB. However, our recent work[50-52] demonstrated that polarity parameters discussed previously can be correlated with the sum of McReynolds constants approximately by simple linear equations. It means that proton donor-proton acceptor interactions are the most important for the considered nonionic surfactants and their model compounds. Thus, these simple and empiric polarity parameters calculated from the retention times of a standard alcohol and standard alkanes quite well characterize the polarity of nonionic surfactants.

The sum of the first McReynolds constants,

$$\sum_{i=1}^{5} \Delta I,$$

obtained for butanol, 2-pentanone, benzene, pyridine, and nitropropane used as standard solutes and squalane as a standard nonpolar phase, is determined with the same accuracy as the retention index of alcohols and the polarity index.

H. Adsorption Coefficient of Iso-Octane

This coefficient, K_A, can be calculated according to Equation 26 (proposed by Martin[72,73]) by plotting V_N/V_L vs. V_L/A_L:

$$\frac{V_N}{V_L} = K_L \frac{V_L}{A_L} + K_A \quad (26)$$

where V_N denotes the net retention volume per gram of column packing; V_L and A_L stand for the volume and the surface area of the solvent per gram of column packing, respectively; and K_L and K_A are the coefficients of distribution and of adsorption which indicate, respectively, the amount of solute dissolved per unit volume and the excess of solute per unit area of the solvent surface.

The adsorption coefficient has not been widely used and its usefulness has been only shown for a few homologs of polyoxyethylene derivatives of sorbitan esters, for which the inverse proportional relation between the adsorption coefficient and the HLB has been found.[74]

Using data presented by Mysak et al.[74,75] the following relation was obtained:

$$\text{HLB} = 3.91 + \frac{290.2}{K_{A\ 100°C}}. \quad (27)$$

which is characterized by a relatively high value for the regression coefficient (R = 0.9816). The existence of similar relations has not been checked for other homolog series. The procedure used for adsorption coefficient determination is quite sophisticated and time-consuming. The surface areas for different amounts of surfactants must be experimentally determined using appropriate support. Silanized and fluorocarbon supports are not recommended. The temperature of 100°C proposed for K_A measurements seem too high because of the possible thermal degradation of nonionic surfactants, especially of block copolymer type (Figure 5).[48] Degradation temperatures for some surface active agents are given in Table 2. Quick degradation of nonionic surfactants is observed at about 150°C. However, it can also occur slowly at lower temperatures during chromatographic column stabilization and analysis.

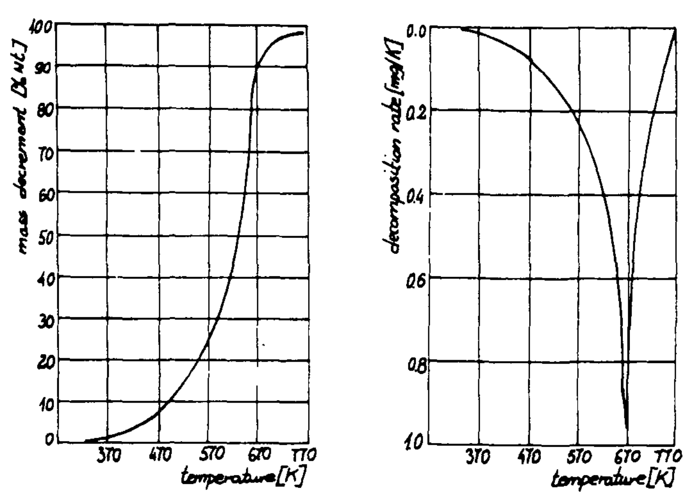


FIGURE 5. Effect of temperature upon thermal degradation of a block copolymer of EBE type (molecular mass of polyoxybutylene chain, 1500; content of polyoxyethylene chains, 75%; rate of heating, 10°C/min; furnace atmosphere, nitrogen).[48]

Taking all this into account, it seems that the proposed method is not good as a standard procedure and therefore cannot be broadly used to characterize surfactants' polarity.

I. Ratio of Partition Coefficients of Hexane and Ethanol

The parameter proposed by Mysak et al.[77] can be determined ($\alpha = K_L/K_L^o$) according to Equation 28, considering the linear relationship between V_N/V_N^o and $1/V_L$:

$$\frac{V_N}{V_N^o} = \frac{K_L}{K_L^o} + \lambda \frac{1}{V_L}, \tag{28}$$

where V_N and V_N^o denote the net retention volumes, including the adsorption of hexane and ethanol, respectively; λ is an empirical constant; and V_L stands for the volume of the liquid phase.

Taking only the four results (three of them were very close to each other) obtained for the polyoxyethylene derivatives of sorbitan esters, Mysak and associates derived the following relation correlating the HLB values with the α parameters:

$$\mathrm{HLB} = 20.3 - 20\alpha. \tag{29}$$

However, Zajceva et al.,[78] using this technique for polyoxyethylated polyamide, have found a more complex relation between α parameter and the percentage of the polyoxyethylene chain, which in some terms is equivalent to the HLB value. The explicit minimum of the α parameter was obtained for a content of the polyoxyethylene chain of about 20%. More data about the α parameter are not available in the literature. As in the case of the previous parameter, the procedure used for the determination of the partition coefficients' ratio is quite sophisticated and time-consuming.

Table 2
Susceptibility of Surfactants to Thermal Degradation

Surfactant	Degradation temp. (°C)
Sulfonated α-olefines	130
Oxyethylated fatty acids	150
Sodium sulfates of oxyethylated alcohols	150
Oxyethylated alcohols	160
Sodium alkanesulfonates	160
Sodium alkylsulfates	170
Fatty acid monoethanolamides	250
Sodium alkylbenzenesulfonates	330
Sodium soaps	380

J. Thermodynamic Functions of Solution

The specific retention volume of a solute, V_g, is connected with its partial molal enthalpy, ΔH_s^m, and the entropy of solution in a studied surfactant, ΔS_s^m, according to Equation 30:[79,80]

$$\ln V_g = -\Delta H_s^m/RT + \Delta S_s^m/R - 1000/273R. \tag{30}$$

where R stands for the gas constant and T denotes the temperature in degrees Kelvin.

By matching Equation 30 to the chromatographic data obtained at different temperatures, usually by the least squares method, the values of ΔH_s^m and ΔS_s^m for the considered solutes are obtained. Then, the partial molal free energy can be calculated according to general relation 31:

$$\Delta G_s^m = \Delta H_s^m - T\Delta S_s^m. \tag{31}$$

Assuming the additivity of the considered functions, the increments for characteristic fragments of the solutes can be calculated.[79,80] The increments for the methylene group can be obtained from the partial molal enthalpy and entropy of solution of alkanes as slopes of the linear relations correlating these functions with the number of carbon atoms, z, in the considered alkanes. The slopes of the relation $\ln V_g = az + b$, as determined at different temperatures, can also be used to calculate $\Delta H_s^m(CH_2)$, e.g., in the case of two different column temperatures by means of Equation 32:

$$\Delta H_s^m(CH_2) = \frac{R(a_{T1} - a_{T2})}{\frac{1}{T_1} - \frac{1}{T_2}}. \tag{32}$$

where a_{T1} and a_{T2} denote the slopes of the relation $\ln V_g = az + b$ at temperatures T_1 and T_2.

The partial molal enthalpy for the methyl group can then be calculated according to Equation 33:

$$\Delta H_s^m(CH_3) = \tfrac{1}{2}[\Delta H_s^m(\text{alkane}) - (z-2)\Delta H_s^m(CH_2)]. \tag{33}$$

The partial molal entropy can be similarly calculated.

The partial molal enthalpy and entropy for characteristic fragments present in the considered solutes, $\Delta H_s^m(FG)$ and $\Delta S_s^m(FG)$, can be calculated in a similar way by using the determined values of the partial molal functions for the investigated compounds and previously calculated values of these functions for the methylene and methyl groups by using Equation 34:

$$\Delta H_s^m(FG) = \Delta H_s^m(\text{solute}) - z(CH_2)\,\Delta H_s^m(CH_2) - z(CH_3)\,\Delta H_s^m(CH_3). \tag{34}$$

where $z(CH_2)$ and $z(CH_3)$ denote the numbers of methylene and methyl groups, respectively.

Partial molal free energy for characteristic fragments present in considered solutes, used as a polarity parameter, can be calculated according to general relation 31.

A more sophisticated and modern approach, which resembles the one we recently described for the calculation of increments of the arithmetic index,[12] can also be used to determine the increments of the considered thermodynamic functions. In such a case the chemical formula of the considered solutes can be expressed as

$$A_i = (G_1)_{a_{1i}} (G_2)_{a_{1i}} \ldots (G_m)_{a_{mi}}, \tag{35}$$

where $G_1, G_2, \ldots G_m$ are the characteristic groups present in the considered chemical system (in solutes used for measurements): $a_{1i}, a_{2i}, \ldots a_{mi}$ are the numbers of groups $G_1, G_2, \ldots G_m$ in the compound A_i: $i = 1, 2, \ldots n$ are the numbers of the solutes considered in the system; and $j = 1, 2, \ldots m$ are the numbers of the characteristic groups considered. It is the case that n is always greater or equal to m.

The set of subscripts $\{a_{ji}\}$, $j = 1, 2, \ldots m$, forms the formula vector, a_i, of the solute A_i:

$$a_i = [a_{1i}, a_{2i}, \ldots a_{mi}]^T. \tag{36}$$

where T donates transposition.

The formula matrix A of the chemical system, which takes into account each solute considered, is then defined as

$$A = (a_1, a_1, a_2, \ldots a_n). \tag{37}$$

Assuming the additivity of the thermodynamic functions in the system considered, the partial molal enthalpy and entropy of a solute A_i can be expressed as

$$\Delta H_s^m(A_i) = \sum_{j=1}^{m} a_{ji}\, \Delta H_s^m(G_j), \tag{38}$$

$$\Delta S_s^m(A_i) = \sum_{j=1}^{m} a_{ji}\, \Delta S_s^m(G_j), \tag{39}$$

where it is assumed that the increments of ΔH_s^m and ΔS_s^m for a group G_j are constant for all considered solutes. Thus, when the set of the partial molal enthalpy and entropy of solution obtained for all considered solutes is taken into consideration, the following sets of linear equations are obtained:

$$\underline{\Delta H_s^m} = A\, \Delta(\underline{\Delta H_s^m}) \tag{40}$$

and

$$\underline{\Delta S_s^m} = A\, \Delta(\underline{\Delta S_s^m}), \tag{41}$$

where

$$\underline{\Delta H_s^m} = [\Delta H_s^m(A_1), \Delta H_s^m(A_2), \ldots \Delta H_s^m(A_n)]^T \tag{42}$$

$$\underline{\Delta S_s^m} = [\Delta S_s^m(A_1), \Delta S_s^m(A_2), \ldots \Delta S_s^m(A_n)]^T, \tag{43}$$

$$\Delta(\underline{\Delta H_s^m}) = [\Delta H_s^m(G_1), \Delta H_s^m(G_2), \ldots \Delta H_s^m(G_n)]^T, \tag{44}$$

and

$$\Delta(\underline{\Delta S_s^m}) = [\Delta S_s^m(G_1), \Delta S_s^m(G_2), \ldots \Delta S_s^m(G_n)]^T. \tag{45}$$

The above sets of linear equations can be solved using various methods, e.g., the orthogonalization method of Gram-Schmidt.

The application of the considered thermodynamic functions is broadly discussed in GC, but up to now they have not been widely used to characterize surfactants' polarity. Although the usefulness of partial molal free energy for some functional groups (OH, C = O, and CH_2) for characterizing surfactants' polarity has been demonstrated in our works,[50-55,81-84] we think they will probably not be broadly useful in surfactant chemistry. Commercial nonionic surfactants are usually complex polydisperse mixtures and their direct analysis by GC is restricted to the products having a low molecular mass after blocking a terminal hydroxyl group(s). Using standard chromatographic liquid phases it is possible to determine the thermodynamic functions of solution in these phases for separated volatile derivatives, e.g., acetates, trimethylsilyl ethers, of the analyzed nonionic surfactants. However, the polarities of these volatile derivatives do not reflect the polarities of nonionic surfactants.

The direct determination of surfactants' thermodynamic functions of solution in standard liquid phases is only possible for the first homologs of nonionic surfactants having from one to four oxyethylene groups in their hydrophilic oligooxyethylene chain and up to six to eight carbon atoms in their hydrophobic alkyl.[83] Such products usually have no practical importance and can be considered only as models. Thus, the use of thermodynamic functions of solutions must be restricted to these functions determined for some volatile solutes dissolved in the studied surfactants.[50-55,81,82,84]

Increments of the thermodynamic functions determined for a methylene group consider only the dispersive type interactions, and because of this, they are not very sensitive upon the structure and polarity of nonionic surfactants used as liquid phases. Corresponding increments for functional groups, e.g., hydroxyl and carboxyl, depend upon the type and molecular mass of solutes[50-54] as a result of some deviations from the additivity rule. These increments can be correlated according to simple linear relations (Table 3). However, deviations from these linear relations are quite significant and, as a result, relatively low values of the correlation coefficient are obtained.

Table 3
Regression (a and b) and Correlation Coefficients (R) for Relation $P^i = a + b\,P^j$

Compounds	Parameter	a	b	R	Ref.
Polyoxyethylene alcohols, alkylthiols, and alkyamines	$\Delta G_s^m(OH)$	−0.5956	0.8597	0.9698	55
	$\Delta G_s^m(C{=}O)$	−0.5442	0.9943	0.95552	55
Aminoether alcohols and their ethers	$\Delta G_s^m(OH)$	2.12	1.0731	0.9700	55
1,3-Bis [ω-alkoxyoligo-(oxyethylene)] propan-2-ols	$\Delta G_s^m(OH)$	−4.594	0.4423	0.9333	51
	$\Delta G_s^m(C{=}O)$	0.8128	1.0333	0.9172	51
α,ω-Diamino-oligoethers	$\Delta G_s^m(OH)$	2.023	1.0391	0.9671	53, 54
	$\Delta G_s^m(C{=}O)$	−0.901	0.8645	0.9656	53, 54

Note: i and j denote ethanol and methanol or pentanone-2 and butanone-2, respectively.

They vary from 0.92 to 0.97. The errors of thermodynamic functions' determinations are significantly higher in comparison to those observed in determinations of the retention index, polarity index, and the sum of the McReynolds constants.

The determination of specific retention volume is troublesome and time-consuming. The measurements must be made at strictly constant conditions, and precise values of the carrier gas flow rate, inlet and outlet pressures, temperature, and the weight of the liquid phase are necessary. The specific retention volume is calculated according to Equation 46:

$$V_g = \frac{273\ v\ t'_R\ j}{T\ w_L}, \tag{46}$$

where v = flow rate of the carrier gas at column temperature in $cm^3\ min^{-1}$; t'_R = adjusted retention time of a solute in min; T = column temperature in K; w_L = weight of the liquid phase in g; and j = pressure-gradient correction factor, as defined by Equation 7. Some other parameters must be known to calculate appropriate correction factors needed to determine the actual flow rate.

K. Partial Molar Excess Gibbs Function of Solute Methylene Groups

This function can be determined according to Equation 47,[85] using chromatographic data for two consecutive members of a homologous series:

$$\Delta G^E(CH_2) = \frac{RT}{k} \ln \frac{(V_g\, p^o)_n}{(V_g\, p^o)_{n+k}} \tag{47}$$

where R = gas constant; T = temperature; V_g = specific retention volume of the solute; p^o = saturated vapor pressure of the solute at a given stationary phase; n and n + k = numbers of methylene groups in the solutes' molecules. Alkanes and alcohols are proposed as the standard solutes.

According to Roth and Novak,[85] linear relationships exist between $\Delta G^E(CH_2)$ and McReynolds constants. Similar relationships were observed by Voelkel[55,84] for various groups of individual compounds having an oligooxyethylene chain or chains. $\Delta G^E(CH_2)$ can be easily and precisely determined as this function is calculated from the ratio of specific retention volumes of two solutes. However, significantly different values were reported as solutes from various homologous series or even if different molecular masses from the same homologous series were used.[81,82] We believe that this function will not find broader application in characterizing surfactants. However, more data are necessary to prove this conclusion.

L. Criterion A

The importance of the dispersive forces in solute-solvent intermolecular interactions in GC has been indicated and some parameters describing these interactions have been evaluated, e.g., thermodynamic functions for a methylene group as discussed in two previous chapters.

Ševčik and Löwentap[86] proposed the use of so-called criterion A defined as

$$A = \frac{t'_{Rn+1} + t'_{Rn}}{t'_{Rn} + t'_{Rn-1}}, \tag{48}$$

where t'_{Rn+1}, t'_{Rn}, and t'_{Rn-1} are the adjusted retention times of *n*-alkanes having n + 1, n, and n − 1 carbon atoms, respectively.

The physical meaning of criterion A was also demonstrated:

$$A = \frac{\exp\left[-(\Delta G_{n+1} - \Delta G_n)\right] - 1}{1 - \exp\left[-(\Delta G_{n-1} - \Delta G_n)\right]}, \tag{49}$$

where ΔG_{n+1}, ΔG_n, and ΔG_{n-1} are the free energies of the solution of *n*-alkanes having n + 1, n, and n − 1 carbon atoms, respectively.

As in the cases of the previous two dispersive force parameters, i.e., $\Delta H_s^m(CH_2)$ and $\Delta G^E(CH_2)$, criterion A is very little sensitive upon the structure of surfactants used as liquid phases.[84] As a result, the values of criterion A for surfactants having quite different polarities change very little. Similar values of criterion A were also obtained for hydroxyoxime extractants of copper and their intermediates.[81,82] Thus, although this parameter can be calculated from simple measurements of the adjusted retention times of standard alkanes, its use in characterizing highly polar and hydrophilic nonionic surfactants is significantly limited.

M. B_S and B_N Parameters Considering Electric Intermolecular Interactions

Lamparczyk et al.[87] introduced electronic parameters into the retention index relationship:

$$I_R = \frac{(A\,\mu_{ph}^2 + \alpha_{ph})\mu_s^2 + (B_S\,\alpha_{ph} + \mu_{ph}^2)\alpha_s}{p(B_N\,\alpha_{ph} + \mu_{ph}^2)} - C, \quad (50)$$

where $A = 2/3kT$; p and C are constants; T is absolute temperature; α_{ph} and α_s denote molecular polarizability of a stationary phase and a solute, respectively; μ_{ph} and μ_s stand for dipole moments of a stationary phase and a solute, respectively; and B_S and B_N are constants for a given stationary phase and analyzed compounds. They are calculated from the first ionization potentials according to the following equations:

$$B_S = \frac{I_{ph} - I_s}{I_{ph} + I_s} \quad \text{and} \quad B_N = \frac{I_{ph}\,I_N}{I_{ph} + I_N}, \quad (51)$$

where I_{ph}, I_s, and I_N are the first ionization potentials for the stationary phase, solute, and *n*-alkane, respectively.

In most of the cases the physicochemical data present in Equation 50 are not known. The structural and electrical parameters for different liquid phases used in GC are also not available. Due to this, it is impossible to check the validity of this equation for typical chromatographic liquid phases. However, when the structure of the liquid phase is known, the calculation of the structural parameters is easy and the approximation of the electrical parameters is also possible. Equation 50 can be rearranged into Equations 52 and 53:

$$B_N[p\varkappa_{ph}(I_{Ri} + C)] + B_S\,\varkappa_{ph}\,\varkappa_{Si} + \mu_{ph}^2\,p(I_{Ri} + C)$$
$$- (A\,\mu_{ph}^2 + \varkappa_{Si})\,\mu_{Si}^2 + - \mu_{ph}^2\,\varkappa_{Si} = 0 \quad (52)$$

$$a_{1i}\,B_N + a_{2i}B_S + a_{3i} = 0 \quad (53)$$

where 1 = 1, 2, . . . n is the number of carbon atoms in alcohol,

$$a_{1i} = p\,\varkappa_{Si}(I_{Ri} + C),$$
$$a_{2i} = -\varkappa_{ph}\,\varkappa_{Si} \quad (54)$$

and

$$a_{3i} = p\,\mu_{ph}^2\,(I_{Ri} + C)$$
$$- (A\,\mu_{ph}^2 + \varkappa_{Si})\,\mu_{Si}^2 - \mu_{ph}^2\,\varkappa_{Si} \quad (54a)$$

The connectivity index, $\varkappa$, represents the molecular polarizability of both the analyzed compounds and the liquid phase.

The solution of the set of multilinear Equation 53 gives the values of B_N and B_S.

Assuming that the ionization potentials are approximately equal in both the *n*-alkane (I_N = const) and the *n*-alcohol (I_S = const) series, a set of linear equations is obtained for each stationary phase. The difference of the B_N and B_S values for different stationary phases only depends on the first ionization potential of the stationary phase. Although these values are not available, they can be approximated in the following way. Equations 55 are obtained by rearranging Equation 51:

$$I_{phi} = \frac{I_N\,B_{Ni}}{I_N + B_{Ni}} \quad \text{and} \quad I'_{phi} = \frac{I_S\,B_{Si}}{I_S + B_{Si}} \quad (55)$$

where i denotes the given liquid phase.

It is evident that I_{phi} should be equal to I'_{phi}. Thus,

$$\frac{I_N\,B_{Ni}}{I_N + B_{Ni}} = \frac{I_S\,B_{Si}}{I_S + B_{Si}} \quad \text{and} \quad I_N - p\,\frac{B_{Si}\,B_{Ni}}{B_{Ni} - B_{Si}}$$
$$= -\frac{B_{Si}B_{Ni}}{B_{Ni} - B_{Si}} \quad (56)$$

where $p = I_N/I_S$, which remains constant for a given homologs series of *n*-alkanes and alcohols.

The values of I_N, p, and I_s can be found by solving the set of linear Equations 56.

B_S and B_N parameters were used recently with success to characterize the polarity of individual polyoxyethylene glycol dialkyl ethers and some of their sulfur analogs.[88,89] However, the structural and electrical parameters needed to calculate B_S and B_N for commercial nonionic surfactants that contain several various components are not known. Thus, the use of these components is only restricted to some model compounds.

N. Conclusions

Various parameters have been proposed to characterize the polarity of surfactants. Some of these are quite empirical, e.g., the polarity index, but they can be easily and precisely determined since only the retention times of standard solutes must be measured. Other parameters have a more physical meaning, e.g., the thermodynamic functions of solution and the partial molal excess Gibbs function, or an easily evaluated physical meaning (as in the case of criterion A or relative retention time of solutes). Some physical parameters (such as partition coefficients, their ratios, and the adsorption coefficient) can be also used to characterize the polarity of surfactants. However, most of these parameters are determined according to complicated and time-consuming procedures. Simultaneously, the errors of their determinations are usually much higher in comparison to simple empirical parameters.

If a polarity parameter is recognized as a tool to solve an analytical problem or is further used to predict another parameter, then the accuracy and/or simplicity of the determination become very important. In such a case, the use of simple empirical parameters such as the polarity index and the retention index of alcohol seems best. However, if one decides to use polarity parameters to interpret some physicochemical phenomena, then appropriate parameters having such meaning seem more appropriate.

Nonionic surfactants are usually quite polar products as they contain a polyoxyethylene chain(s) and/or one or several free hydroxyl groups. Due to this, parameters that take into account only dispersive forces (e.g., thermodynamic functions of solution of a methylene group, partial molar excess Gibbs function of this group, or criterion A) are relatively insensitive to differences in structure and polarity of surfactants, and their application is limited. For contrast, parameters that take into account interactions between a polar part of the surfactant and of some polar solutes (e.g., alcohols) seem the most suitable and sensitive (e.g., retention index of alcohol) polarity index of alcohol and the sum of McReynolds constants).

III. EFFECT OF CHROMATOGRAPHIC CONDITIONS ON POLARITY PARAMETERS

The values of the considered polarity parameters are influenced by a change of chromatographic conditions, i.e., temperature, gas flow, and the content of the liquid phase. The size of the column and the type of support may also be important. The change of surfactant polarity during the measurements may be caused by its thermal degradation. It is well known that such degradation easily occurs at higher temperatures,[76] especially for nonionic surfactants having a polyoxyethylene chain. As it was presented in Table 2, the degradation of nonionic surfactants is already distinctly observed at temperatures near 150°C, e.g., at 130 to 150°C for block copolymers of ethylene oxide and α-butylene oxide.[48] Due to this, temperatures useful for polarity measurements are usually restricted to the region below 100°C. At this temperature no essential degradation is observed and the constant values of the polarity parameters are registered.

The time of column stabilization at 70°C only slightly affects the values of the empirical polarity parameters calculated from retention times of standard solutes (Table 4).[48] An increase of the temperature of column stabilization from 70° to 100°C also does not seriously affect the values of these polarity parameters (Table 5).[48] Thus, the thermal degradation of nonionic surfactants during column stabilization and analysis at 70 to 90°C can be neglected.

In the case of compounds having a low molecular mass, a bleeding of the liquid phase must be taken under consideration. However, no significant loss of the liquid phase has been observed.[56] Differences between amounts of liquid phases before and after chromatographic measurements were generally below 0.2%. Thus, if one takes into account that the initial liquid phase concentration is 25%, then the loss is so small as to be negligible.

Table 4
Effect of Time of Column Stabilization upon Polarity Parameters for Ethylene Oxide/α-Butylene Oxide Block Copolymer of BE Type[48]

	Time of column stabilization			
Parameter	1 h	3 h	7 h	10 h
C	7.27	7.22	7.21	7.20
I_R	727	724	722	722
PI	101	100	100	99.8
ρ	2.50	2.49	2.45	2.45

Note: Molecular mass of polyoxybutylene chain: 1500; content of polyoxyethylene chain: 60%; methanol as a polar agent; average values from 5 measurements.

Table 5
Effect of Temperature of Column Stabilization upon Polarity Parameters for Various Ethylene Oxide/α-Butylene Oxide Block Copolymers[48]

	C		I_R		PI		ρ	
Copolymer	I	II	I	II	I	II	I	II
BE type M_H = 500 %E = 27.1	6.36	6.35	643	642	82.1	81.6	1.40	1.37
BE type M_H = 1000 %E = 77.6	7.79	7.79	780	779	109	109	3.36	3.42
BEB type M_H = 470 %E = 25.9	6.86	6.85	688	688	93.4	93.3	2.00	2.01
BEB type M_H = 1000 %E = 79.7	8.01	8.01	801	801	112	112	3.96	3.97
EBE type M_H = 1060 %E = 56.4	7.36	7.38	738	739	102	103	2.83	2.88
EBE type M_H = 1500 %E = 75.0	7.73	7.76	779	780	110	109	3.40	3.31

Note: I: stabilization at 70°C, 10 h; II: stabilization at 100°C, 10 h; analysis at 70°C; M_H: molecular mass of polyoxybutylene chain or chains; %E: content of polyoxyethylene chains.

In the case of pure model compounds the temperature of 70 to 90°C can be below their melting points. In such cases, the polarity must be determined for two-component mixtures made up of the considered surfactant and an additional surfactant. The polarity of the considered surfactant can then be calculated from the polarity of this mixture according to the additivity rule:

$$P_M = \sum w_i P_i, \tag{57}$$

where P_M denotes a polarity parameter for a mixture of surfactants, P_i is a polarity parameter for surfactant i, and w_i is the weight fraction of surfactant i. The error of such determination does not exceed a few percent, and is the lowest for polarity index in comparison to carbon number, retention index, and relative retention of alcohol, as a result of various deviations of these parameters from the additivity rule.

The influence of column temperature upon the polarity parameters is rather small. Huebner[62] did not find any important influence of temperature on the carbon number and the polarity index. The same conclusions were drawn by Wiśniewski et al.,[57] Leca and Perez,[64] and Krivich and Gluzman.[90] Wiśniewski et al.[57] showed that for typical nonionic surfactants the polarity index and the carbon number of methanol, ethanol, isopropanol, methyl ethyl ketone, and acetone are independent of the temperature, while coefficient ρ^{MeOH} usually decreases as the temperature increases. The decrease of ρ was also observed by Becher and Birkmeier[65] and Petrowski and Vanatta,[91] who showed the existance of a logarithmic function of retention and temperature. Wiśniewski et al.[57] showed that this relation depends upon the type of polar agent, and for acetone the ρ coefficient is almost constant, or even slightly increased, as the temperature increases (Figure 6). The strongest influence of temperature on the ρ coefficient is observed when isopropanol or methyl ethyl ketone are used as the polar agents. For methanol this effect is rather small.

In investigating the influence of column temperature upon the retention times of standard alkanes and methanol for different sorbitan esters and their polyoxyethylene derivatives and for block copolymers of ethylene oxide and α-butylene oxide, respectively, Petrowski and Vanatta[91] and Szymanowski and Voelkel,[48] observed linear relations between the logarithm of the retenton time and the reciprocal of the absolute temperature (Figure 7). The straight lines for methanol are more abrupt than those obtained for alkanes as a result of the different heats of solution of alcohol and alkanes in the considered liquid phase. Using, then, Antoine's equation:

$$\log V_g = A + \frac{\Delta H^s}{2.303\ RT}, \tag{58}$$

where V_g = specific retention volume, ΔH^s = heat of solution, T = absolute temperature, R = gas constant, and A = empirical constant, it is possible to determine the heat of solution of the considered solutes in the investigated surfactants. Due to this difference in the heat of solution for alcohols and alkanes, the influence of temperature upon the polarity parameters should be observed, although it can be different for different surfactants. For block copolymers of ethylene oxide and α-butylene oxide, the polarity parameters decrease as the column temperature decreases according to linear relations for C, I_R, and PI and a nonlinear one for the coefficient ρ. This

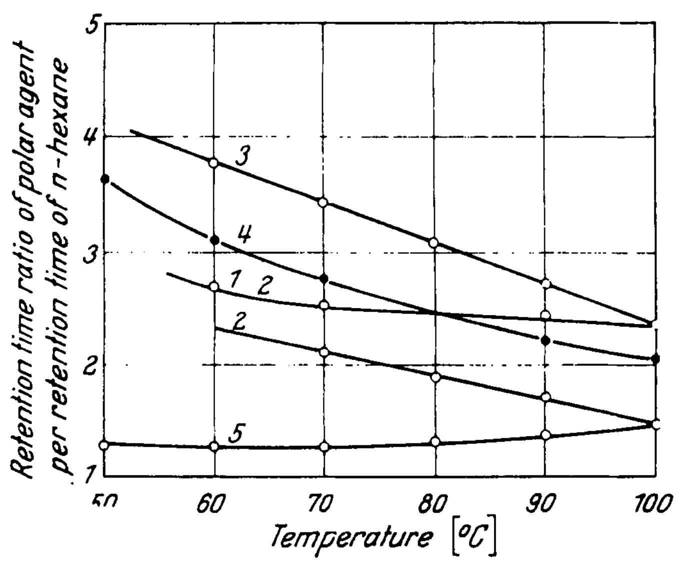


FIGURE 6. Effect of temperature on relative retention of polar solute (*n*-hexane as standard alkane; 1, methanol; 2, ethanol; 3, isopropanol; 4, methyl ethyl ketone; 5, acetone).[57]

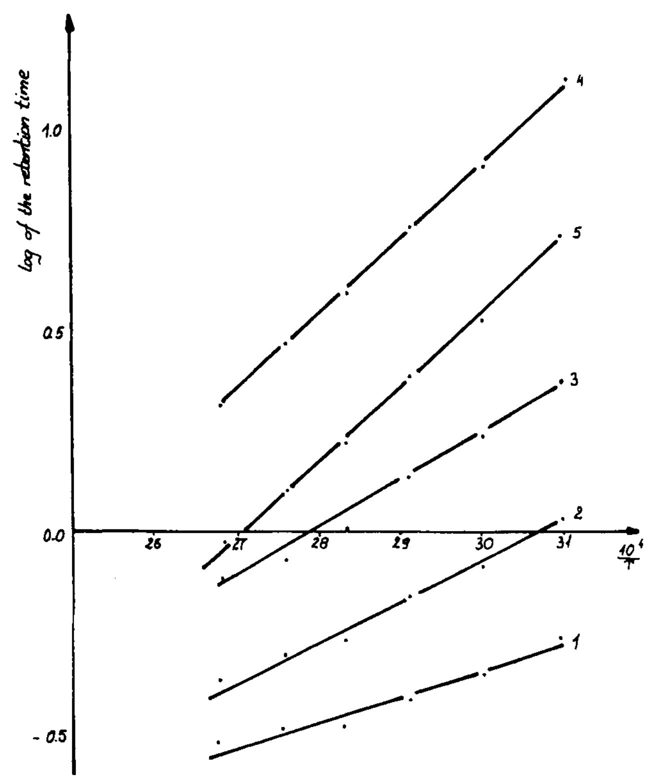


FIGURE 7. Relationship between logarithm of retention time and column temperature for ethylene oxide/α-butylene oxide block copolymer of BE type (molecular mass of polyoxybutylene chain, 1000; content of polyoxyethylene chain, 77.6%; 1, 2, 3, and 4, pentane, hexane, heptane, and nonane, respectively; 5, methanol).[48]

influence depends upon the molecular mass of the block copolymer and decreases as the molecular mass of the block copolymer increases.[48]

Similar effects of column temperature on the discussed polarity parameters were described recently by Voelkel[56] for various individual compounds having one or two short oligooxyethylene chains. Criterion A also decreases with the increase of column temperature. The dependence of the polarity parameters upon the column temperature was also observed for hydroxyoximes and hydroxyketones.[81,82] However, this dependence is rather small, and under the investigated conditions, the values of the polarity parameters decrease less than 10%. Therefore, the positions of the surfactants in their order of polarity are usually not changed if slightly different temperatures are considered (as in the case of some substances having a too high melting point, the measurements cannot be made at the standard temperature).

However, when greater changes of temperature are considered, the sequence of surfactants, according to their increased polarity measured as relative retentions, may be altered because, as was shown in works dealing with the polarity of liquid phases used in GC,[92-99] the dependence of the liquid phase polarity upon the temperature is different for various phases. According to Petsev[92] and Lapkin and Nakina,[93] the polarity may decrease or increase depending on the phase studied, while others[97-99] show that the relative retention is inversely proportional to the absolute temperature.

In the region of the used liquid phase concentration (about 25%) a small change of concentration does not influence the values of the polarity parameters.[56,62,91] Due to this large amount of the liquid phase, the type of support is also unimportant.[48,56,57,62,90] However, Petrowski and Vanatta[91] have reported significantly different values of ln ρ′ for Chromosorb W and Chromosorb P used as a support. It was also found that a change in the rate of the carrier gas (nitrogen) flow from 20 $cm^3\ min^{-1}$ to 50 $cm^3\ min^{-1}$ does not substantially affect the polarity parameters of either typical nonionic surfactants or block copolymers having a high molecular mass.[48,56,57,62,91] No significant influence of carrier gas (nitrogen or helium) upon the considered polarity parameters was observed.[56] The effect of column size upon the discussed polarity parameters is also negligible since adjusted retention times were considered.[48,56,57,62,91] Thus, the effects of column size, type of carrier and support, and the flow of the carrier gas can be ignored (Tables 6 and 7).

The considered polarity parameters are sensitive upon the sample size of the polar solute and the standard *n*-alkanes. Significantly high sensitivity upon the sample size of the polar probe is observed for the sum of the first five McReynolds probes, especially for low liquid loading and for the retention index of pyridine (Table 8).[36] Retention index of alcohols, polarity index, coefficient ρ, and thermodynamic parameters of solution decrease their values as the sample size of the polar probe increases from 0.1 to 0.3 μl. As a result, the measured polarity decreases with the increasing ratio of a polar probe to standard *n*-alkanes. Criterion A increases with an increase of the sample size of *n*-alkanes and with an increase of the stationary phase loading. The partial molal free energy of solution is much less sensitive but also slightly increases as the *n*-alkane sample size increases. Partial molar excess Gibbs free energy of solution per methylene group decreases significantly with an increase of alkanes sample size. The sample size dependence is much weaker when alcohols and ketones are used as solutes. In all cases, the influence of the solute sample size upon the considered dispersive force parameters is less significant for higher liquid loadings.

The sensitivity of the retention index to variations in column liquid loading, support activity, and sample size has been ex-

Table 6
Effect of Some Chromatographic Parameters on Measured Polarity[57]

Support	Column length (m)	Conc. of liquid phase (%)	Nitrogen flow (dm^3/h)	C	PI	ρ
Kieselguhr	1	20	2.0	7.3	101.5	2.8
70—100 mesh	1	25	2.0	7.3	101.5	2.8
	1	30	2.0	7.4	103.1	3.0
	1	25	0.5	7.3	101.5	2.8
	1	25	4.0	7.3	101.5	2.8
	2	25	2.0	7.3	101.5	2.8
Chromosorb W/NAW 60—80 mesh	1	25	2.0	7.3	105.5	2.8

Note: Temperature 70°C; Span 20 as liquid phase.

Table 7
Comparison of Polarity Parameters as Measured by Using Helium and Nitrogen as Carrier Gas

Stationary phase[a]	Carrier gas	I_R	PI	ρ	ΔG_i^m (OH)
$C_6H_{13}O(EO)_2H$	Helium	751	106.6	3.62	−10.3
	Nitrogen	750	106.2	3.60	−10.3
$C_8H_{17}O(EO)_2H$	Helium	710	97.2	1.50	−9.6
	Nitrogen	709	97.6	1.42	−9.5
$C_8H_{17}NH(EO)_2H$	Helium	810	112.3	5.66	−10.6
	Nitrogen	807	112.1	5.63	−10.5
$C_8H_{17}S(EO)_3H$	Helium	720	99.5	3.62	−9.4
	Nitrogen	723	99.6	3.55	−9.4

Note: Comparison takes place at 70°C; ethanol as solute; flow of carrier gas, 40 $cm^3\ min^{-1}$.

[a] EO = CH_2CH_2O.

Table 8
Variation of Retention Index with the Increase in Probe of Sample Size from 0.1 μl (Step 0.1 μl); ΔI_i/0.1 μl for First Five McReynolds Solutes, and Their Sum $\sum_{i=1}^{5} \Delta I_i - \Delta\left(\sum_{i=1}^{5} \Delta I_i\right)$[56]

Phase	Loading (%)	Probe: X' Benzene	Y' 1-Butanol	Z' 2-Pentanone	U' 1-Nitropropan	S' Pyridine	$\sum_{i=1}^{5} \Delta I_i$
A	10	+0.5	−0.5	+1.0	+1.2	−12.5	−10.3
	15	0.0	+0.6	+1.0	+1.3	−11.6	−8.7
	20	+2.3	−0.7	−1.0	+2.0	−8.6	−1.0
	25	+0.2	−0.1	+1.0	+0.7	−2.5	−0.7
B	10	+1.3	+0.3	0.0	+0.6	−5.8	−3.6
	15	0.0	0.0	0.0	0.0	−3.0	−3.0
	20	−0.3	−0.6	+0.3	+0.6	−3.0	−3.0
	25	0.0	0.0	0.0	0.0	−0.3	−0.3
C	10	0.0	+1.0	0.0	+0.3	−21.0	−19.7
	15	+1.0	−1.0	−0.3	+0.3	−7.7	−7.7
	20	−0.6	0.0	0.0	0.0	−2.7	−3.3
	25	+0.2	0.0	0.0	+0.3	−0.8	−0.3

Note: A: $C_4H_9O(CH_2CH_2O)_2CH_2CH(OH)CH_2(OCH_2CH_2)_4OC_4H_9$; B: $C_8H_{17}S(CH_2CH_2O)_4H$; C: $C_8H_{17}O(CH_2CH_2O)_2H$; sample size of alkanes 0.1 μl, temperature 90°C.

amined by several workers.[100-106] Vernon and Suratman[100] have pointed out that sample size and sample composition influence the retention index. These effects are much stronger on a polar than on a nonpolar phase.

Jönsson and Mathiasson[104] have concluded that in the presence of surface adsorption, both on the surface of the support and on the liquid phase, the retention volume usually varies with sample size. Accurate measurements of the retention data thus require the retention volume to be corrected for adsorption.[102-105] It was found[105] that the contribution for adsorption varies strongly with sample size. Adsorption effects decrease significantly with the increase of the stationary phase loading. Variations of the Kovats retention indices, due to adsorption effects, are the most pronounced on nonpolar stationary phases with polar solutes.[106] On polar columns, the variation in the Kovats retention index is essentially due to adsorption effects for the alkane reference compounds. Generally, both column loading and sample size ought to be high in order to keep the variation in retention index as small as possible.[106]

Examined surfactants and their model compounds are medium or strong polar and observed effects may be attributed both to the adsorption effects of polar probes and *n*-alkane reference compounds. The polarity parameters must be measured in conditions that minimize their variation due to adsorption effects, i.e., the liquid loading of 25% and the sample size of 0.2 to 0.3 μl.

Thus, although the influence of several chromatographic conditions is small or even often negligible, the polarity measurements are always carried out under constant standard conditions. They are 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 Kieselguhr (recently on Porolith, 0.2 to 0.5 mm, GDR); carrier gas (nitrogen) flow rate, 40 cm^3 min^{-1}; time for column stabilization, 10 h; and sample size, 0.2 to 0.3 μl.

Under these standard conditions, the polarity measurements are quite reproducible. The effect of column preparation is also not observed, and almost the same values are obtained for various columns prepared in the same laboratory (Table 9).[48]

As all measurements are made under the same standard parameters, broadened and skewed chromatographic peaks are also obtained, especially as pyridine is used as a polar solute.

Jönsson[107-110] studied the problem of the correct measure of retention time in linear, nonideal elution chromatography and examined relations between three different retention measures: the maximum of a peak, the median and the center of gravity, and the skew and width of the observed elution peaks. The median of the peak denotes the retention time corresponding to elution of half the molecules, i.e., as half of the elution curve emerges. The elution time of the center of gravity of the peak is determined according to the following equation:

$$t_{R\,cg} = \frac{\int t\, c(t)\, dt}{\int c(t)\, dt}, \tag{59}$$

where t denotes elution time of each point of the peak and c(t)

Table 9
Effect of Preparation of Chromatographic Columns on Values of Polarity Parameters for Ethylene Oxide/α-Butylene Oxide Block Copolymer of BE Type[48]

Polarity parameter	No. of column 1	2	3	4	5
C	6.47	6.47	6.49	6.44	6.45
I_R	641	646	641	641	641
PI	84.9	84.7	85.3	84.2	84.5
ρ	1.49	1.56	1.48	1.47	1.48

Note: 5 separately prepared columns; molecular mass of polyoxybutylene chain, 2000; content of polyoxyethylene chain, 40.3%.

Table 10
Polarity Parameters Calculated from Retention Times of Polar Solutes Estimated by Different Methods for $C_6H_{13}OCH_2CH(OH)CH_2OCH_2CH_2OC_6H_{13}$[56]

Method of calculation	Polarity parameter PI^{MeOH}	ρ^{EtOH}	I_R^{BuOH}	$I_R^{pyridine}$
Peak maximum	89.4	1.77	855	929
Peak median	89.2	1.76	853	911
Center of gravity	89.1	1.76	852	903

stands for concentration (height of the peak) at this point. For symmetrical peaks, these three measures of retention time or retention volume are identical. For skew peaks, the median is the correct measure of the retention time; however, its determination is much more complicated and time-consuming and usually much less accurate in comparison to the peak maximum.

Results obtained by Voelkel[56] have shown that chromatographic peaks of alcohols are only slightly skewed. Retention times obtained by using median, center of gravity, and maximum of the peak as retention time measures are different. Retention times of alcohols as measured at the point of the center of gravity are higher, while those obtained at peak maximum are lower in comparison to the time of the median. However, polarity parameters calculated from these three sets of retention times are generally equal to each other (Table 10).[56] The observed differences are random and statistically insignificant. Only in the case of pyridine peaks are the differences in retention time and retention index high, systematic, and significant for all stationary phases examined.

Another factor that may influence the polarity parameters is the method of the dead time estimation. Wainwright and Haken[111] pointed out that the dead time can be determined the most accurately by the method of Grobler and Balizs[112] using at least four *n*-alkanes. Other methods in which three alkanes are used are also recommended.[113]

Voelkel[56] used the Grobler and Balizs method,[112] air peak method, and the Ševčik and Löwentap method[114] for determining various polarity parameters. He obtained different values of the dead time. However, the values of the polarity parameters were practically the same. Observed small differences are random and statistically insignificant (Table 11).[56]

IV. RELATIONS BETWEEN POLARITY PARAMETERS

The polarity parameters increase as the content of the hydrophilic block increases or the content of the hydrophobic block decreases. With the increased polarity of the liquid phase, stronger interactions occur in chromatographic columns and the relative retention time of the polar agent increases. This dependence is different for the considered polarity parameters. Therefore, curves are obtained on the graphs showing the relations between different polarity parameters, i.e., PI vs. ρ, I_R vs. ρ, and I_R vs. PI (Figure 8).[47,50-52,67,81,82] Regression coefficients (a_0, a_1, and a_2) and the correlation coefficient (R) for relation:

$$P_y = a_0 + a_1P_x + a_2P_x^2, \qquad (60)$$

where P_x and P_y denote I_R, PI, and ρ, respectively, are given for various types of compounds in Table 12.[115] Correlation coefficients are in the range of 0.95 to 1.00. Regression coefficients are different for various series of considered compounds used as liquid phases and for various alcohols. Both I_R and PI increases as the coefficient ρ 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 ρ upon I_R and PI decreases as the polarity increases, and approximately straight lines are obtained for highly polar compounds.

Table 11
Polarity Parameters Calculated Using Dead Times Estimated According to Various Methods for $C_6H_{13}OCH_2CH(OH)CH_2OCH_2CH_2OC_6H_{13}$[56]

Method of dead time estimation	I_R^{EtOH}	PI^{MeOH}	$\Delta G_s^m(OH)$ (kJ mol^{-1})	Criterion A
Grobler and Balizs[112]	666.2	81.5	−8.4	2.330
Air peak	662.2	81.6	−8.4	2.330
Ševčik and Löwentap[114]	666.3	81.8	−8.3	2.331

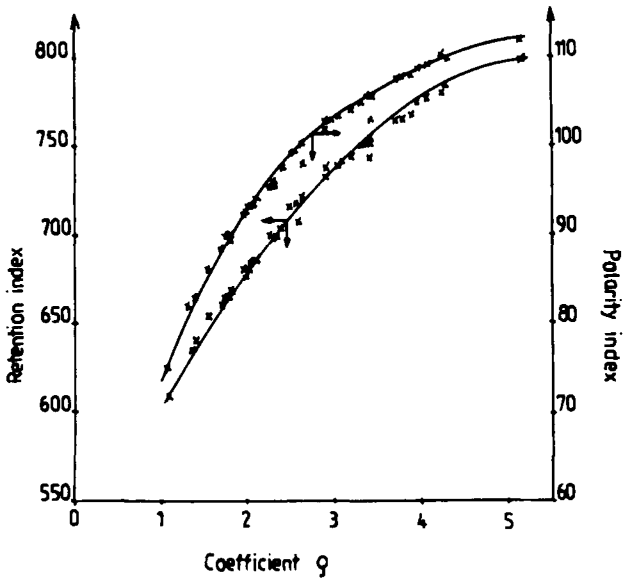


FIGURE 8. Relationships between the empirical polarity parameters (1,3-bis-[ω-alkoxyoligo(oxyethylene)]propan-2-ols; 70°C; ethanol as a polar agent).[52]

Relationships between the retention and polarity indices are usually almost linear (Figure 9).[52] As a result, regression coefficient a_2 is low in comparison to regression coefficient a_1. Thus, the retention and polarity indices of alcohol can be regarded as equivalent and the same orders of surfactants are obtained according to increasing values of the retention and polarity indices. Using these two polarity parameters, the compounds can be classified in the same order of increasing polarity. Thus, the scales of the polarity and retention indices of alcohol are quite convertible.

Similar orders can be obtained as the polarity index and coefficient ρ are considered. However, in this case, depending on the polarity parameter considered, the differences in the values of these parameters can be different and higher or lower relative polarities can be estimated in comparison to the compound having the lowest polarity. This means that the considered scales of PI and ρ as well as of I_R and ρ are not fully convertible.

Similar relationships are observed between other discussed polarity parameters, i.e., $\Delta G_s^m(OH)$ vs. PI or $\Delta G_s^m(OH)$ vs. I_R (Figure 10),[52] $\Delta G_s^m(OH)$ vs. $\Delta G_s^m(C{=}O)$ (Figure 11),[52] and $\Delta G_s^m(C{=}O)^{MPK}$ vs. $\Delta G_s^m(C{=}O)^{MEK}$ (Figure 12),[52] where MPK and MEK denote 2-pentanone and 2-butanone, respectively. However, for some compounds important deviations are observed.

In homologous series, approximately linear relations can be also observed between some dispersive force parameters, e.g., $\Delta G_s^m(CH_2)$ vs. A and $\Delta G^E(CH_2)$ vs. A reported for 1,3-bis-[ω-alkoxyoligo(oxyethylene)]propan-2-ols and aminoether alcohols and their ethers (Figure 13)[84] and between a dispersive force parameter ($\Delta G_s^m(CH_2)$, $\Delta G^E(CH_2)$, or A) and a polarity parameter obtained from the retention of a standard alcohol (PI, I_R, or $\Delta G_s^m(OH)$) (Figure 14).[55]

Relationships of the simple empirical polarity parameters determined from retention of a standard alcohol with those considering intermolecular electric interactions are more complex because various relations are observed for the same homologous series as different lengths of the alkyl groups are considered (Figure 15).[89]

The discussed polarity parameters can be also correlated with the sum of the first McReynolds constants approximately according to linear relations (Figures 16 and 17).[52] Some important deviations are observed and usually the correlation coefficient is about 0.9. Thus, it is not too high, but such an order can be still acceptable (Table 13).[115] For various homologous series, different relationships are obtained as a result of different importance of proton donor-proton acceptor interactions and their contribution to the sum of the first five McReynolds constants. However, the similar linear character of the discussed relationships demonstrates that proton donor-proton acceptor interactions make an important contribution to the total interactions occurring in the GC column during the polarity measurements. As a result, the polarity calculated only from the retention times of alcohols and alkanes can characterize the polarity of the compounds considered quite satisfactorily.

It seems that each one of the discussed polarity parameters can be used to characterize the polarity of nonionic surfactants. The scales of these parameters are quite satisfactorily convertible, although some important differences in the relative polarities are observed. The order of surfactants arranged according to their increased polarity is almost the same as various polarity parameters are considered. Small differences are only observed for compounds having similar polarities, and especially in the case of polar compounds.

However, the practical importance of various polarity parameters is different. A good parameter should be quickly and precisely determined. A procedure used for its determination should be simple and brief. These factors favor the polarity parameters obtained from the retention of the standard alcohol, i.e., the retention and polarity indices of ethanol or methanol.

A good polarity parameter should be also sensitive enough upon structural changes of compounds investigated, i.e., it should change its values with a change of the structures of the compound. This effect can be estimated by calculating relative differences of the discussed polarity parameters for various homologous series:

$$S = \frac{P_{max} - P_{min}}{P_{min}} 100\% \qquad (61)$$

where S is the sensitivity parameter and P_{max} and P_{min} are maximal and minimal values in the considered homologous series, respectively.

Table 12
Regression (a_0, a_1, and a_2) and Correlation Coefficients for Relation $P_y = a_0 + a_1 \cdot P_x + a_2 \cdot P_x^2$ [115]

Compounds	P_y	P_x	Solute	Regression coefficients a_0	a_1	a_2	Correlation coefficient
A	I_R	PI	Methanol	617.9	−3.595	0.046	0.9867
			Ethanol	821.1	−7.94	0.069	0.9761
	I_R	ρ	Methanol	536.9	72.46	−3.644	0.9768
			Ethanol	564.5	54.12	−1.944	0.9700
	PI	ρ	Methanol	56.6	17.5	−1.089	0.9443
			Ethanol	67.11	11.27	−0.523	0.9464
B	I_R	PI	Methanol	483.5	−0.035	0.024	0.9923
			Ethanol	539.1	−1.384	0.032	0.9867
	I_R	ρ	Methanol	422.1	216.3	−40.78	0.9988
			Ethanol	471.1	150.7	−20.35	0.9830
	PI	ρ	Methanol	−5.529	98.86	−25.02	0.9911
			Ethanol	27.15	50.69	−8.65	0.9945
C	I_R	PI	Methanol	825.2	−7.537	0.065	0.9929
			Ethanol	328.4	2.135	0.018	0.9951
	I_R	ρ	Methanol	436.2	153.4	−17.79	0.9917
			Ethanol	518.3	99.82	−8.85	0.9971
	PI	ρ	Methanol	34.22	37.01	−4.74	0.9726
			Ethanol	63.20	18.25	−1.70	0.9982
D	I_R	PI	Methanol	1028.8	−13.09	0.100	0.9565
			Ethanol	1435.6	−21.29	0.141	0.9796
	I_R	ρ	Methanol	521.2	92.43	−6.39	0.9165
			Ethanol	533.4	101.11	−5.83	0.9223
	PI	ρ	Methanol	41.33	42.08	−3.25	0.9553
			Ethanol	52.18	47.83	−1.88	0.9718
E	I_R	PI	Methanol	589.9	−2.870	0.042	0.9998
	I_R	ρ	Methanol	374.2	270.1	−49.13	0.9933
	PI	ρ	Methanol	8.60	75.16	−14.64	0.9932

Note: A: polyoxyethylene alcohols, alkylthiols, and alkylamines;[55] B: polyoxyethylene glycol dialkyl ethers;[47,49] C: aminoether alchols and their ethers[50] and 1,3-bis-[ω-alkoxyoligo-(oxyethylene)]-propan-2-ols;[51] D: α,ω-diaminooligoethers;[53,54] and E: hydroxyoximes.[81,82]

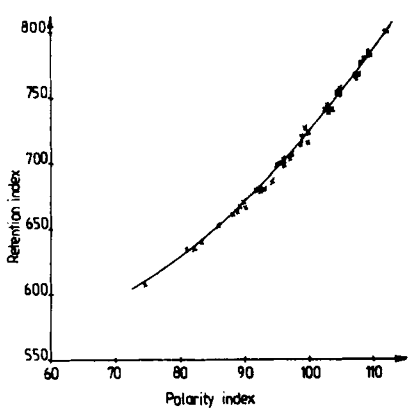


FIGURE 9. Relationship between the retention index and the polarity index (1,3-bis-[ω-alkoxyoligo(oxyethylene)]propan-2-ols; 70°C; ethanol as a polar agent).[52]

The data presented in Table 14 demonstrate that the sensitivity of each polarity parameter upon structural changes depends on the type of compounds considered, e.g., quite different S values were obtained for various homologous series.[55,84] The effect of a solute (methanol or ethanol) is relatively small and can be neglected. The most sensitive parameter is the coefficient ρ, however, the accuracy of its determination is very low (the lowest among the polarity parameters calculated from appropriate retention times). Sensitivities of criterion A and the partial molal free energy of solution of methylene group are very low. Thus, if used, they must be determined with very high precision. The sensitivities of the sum of the first five McReynolds constants and of the partial molar excess Gibbs function of the solute methylene group are of a similar order and higher in comparison to the retention and polarity indices of the standard alcohol. Although these two last polarity parameters are not very sensitive upon structural changes, they reflect quite well changes in compound structure, including the increase of a hydrocarbon and/or a polyoxyethylene chain, the

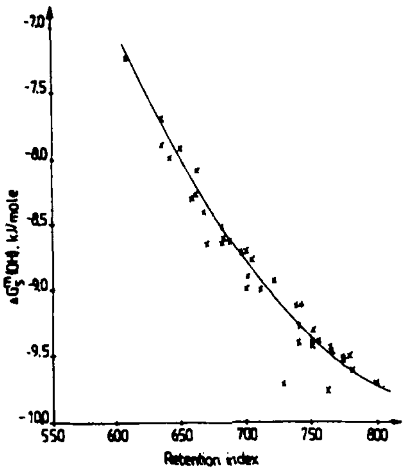


FIGURE 10. Relationship between the partial molal free energy of hydroxyl group solution and the retention index of ethanol (1,3-bis-[ω-alkoxy-oligo(oxyethylene)]propan-2-ols; 70 to 90°C).[52]

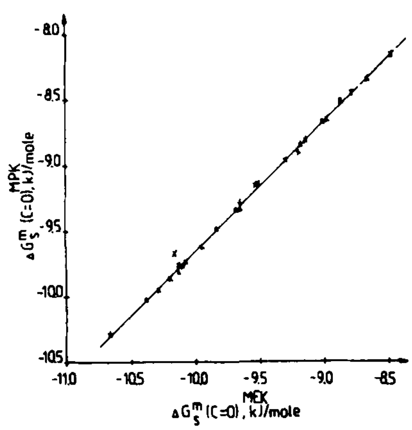


FIGURE 11. Relationship between the partial molal free energies of solution of hydroxyl and carbonyl groups (1,3-bis-[ω-alkoxyoligo-(oxyethylene)]propan-2-ols; 70 to 90°C; ethanol and 2-butanone as polar agents).[52]

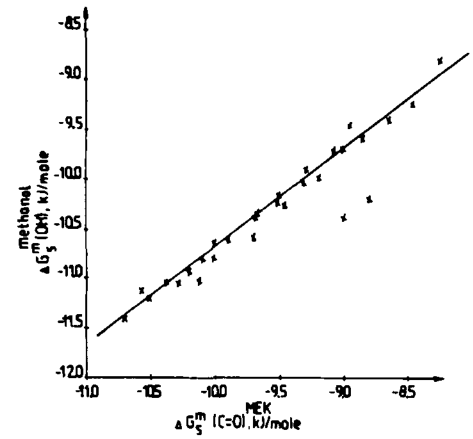


FIGURE 12. Relationship between the partial molal free energies of solution of carbonyl groups (1,3-bis-[ω-alkoxyoligo(oxyethylene)]propan-2-ols; MEK, 2-butanone: MPK, 2-pentanone).[52]

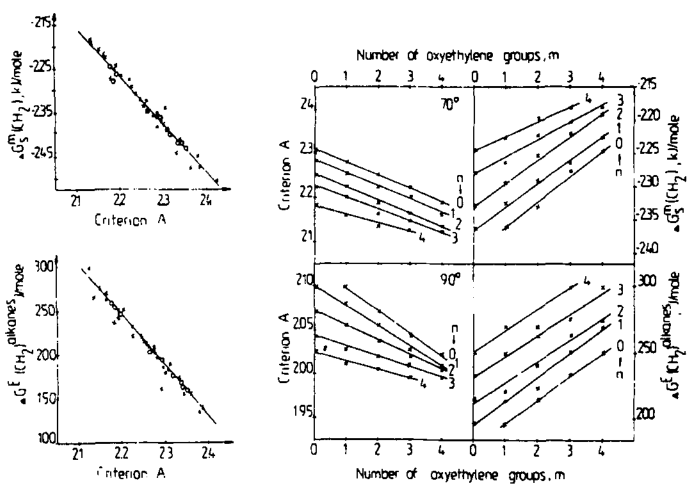


FIGURE 13. Relationships between dispersive force parameters (x, 1,3-bis-[ω-alkoxyoligo(oxyethylene)]propan-2-ols; ○, aminoether alcohols and their ethers).[84]

presence of various heteroatoms, and the changes in the symmetries of the compound (discussed in Section VI). These two parameters, I_A and PI, can be precisely determined according to the routine standard procedure. As a result, they can be used to characterize the polarity of various surface active agents and different model compounds. They can also be used to study the effects of structural changes in surfactant molecules on their polarities and/or their HLB, and their surface active and usage properties.

V. POLARITY PARAMETERS AND HYDROPHILE LIPOPHILE BALANCE

Polarity data have been used by several authors[27-39] to determine the HLB of nonionic surfactants. Linear relations are provided in the literature between the HLB and the polarity parameters determined by GC, although not always in the form of mathematical equations (Tables 15 to 17). These relations are usually proposed for the determination of HLB values. However, they are valid only for the homologous series of surfactants having the same structure, but different lengths of the polyoxyethylene and/or the hydrophobic chain. No general relations exist, as is shown in Figures 18 and 19. However, Becher and Birkmeier[65] pointed out that the different relations observed for the different groups of nonionic surfactants can be caused by the presence of impurities in commercial surfactants. By extracting nonreacted polyol from sorbitan derivatives they obtained corrected values for the ρ coefficient, which were in agreement with those obtained for polyoxyethylene fatty alcohols. Because of this, the so-called general relation

$$HLB^G = 8.55\ \rho^{EtOH} - 6.36 \qquad (62)$$

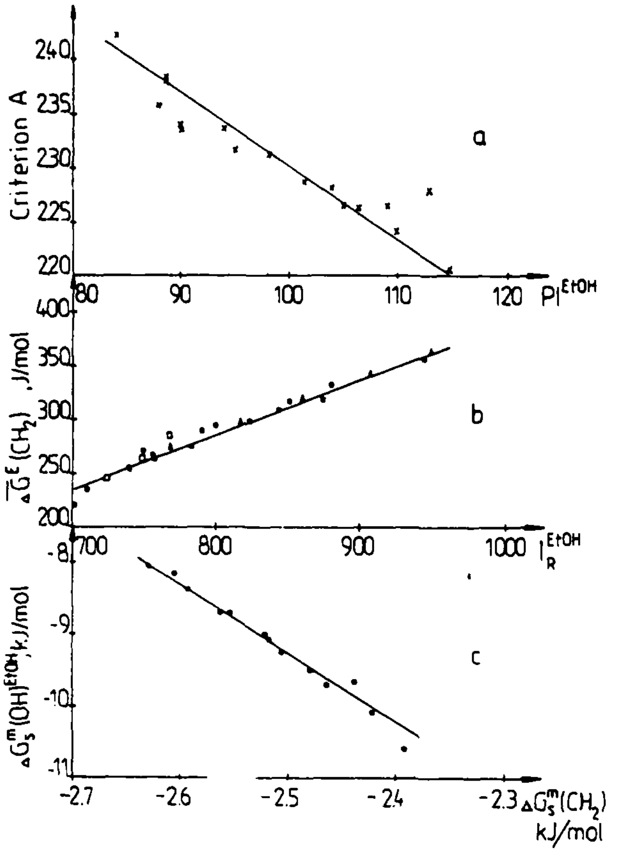


FIGURE 14. Relationships between polarity parameters for polyoxyethylene glycol dialky ethers (a), polyoxyethylene alkylamines (b), and polyoxyethylene thioalcohols (c).[55]

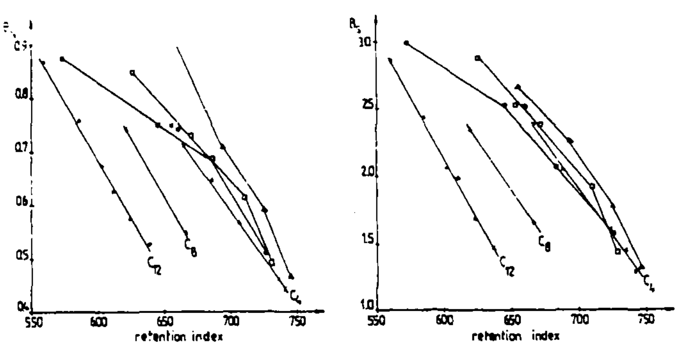


FIGURE 15. Relationships between B_N and B_S and the retention index of ethanol (x, $RO(CH_2CH_2O)_nR$; O, $Bu(OCH_2CH_2)_mS(CH_2CH_2O)_mBu$; □, $Bu(OCH_2CH_2)_mSCH_2CH_2SCH_2CH_2S(CH_2CH_2O)_mBu$; Δ, $Bu(OCH_2CH_2)_m(SCH_2CH_2)_2S(CH_2CH_2S)_2(CH_2CH_2O)_mBu$; n = 3 to 9; m = 1 to 4).[89]

was obtained for the considered groups of surfactants. The influence of the impurities on the values of the polarity index was also demonstrated by Krivich and Gluzman.[90] However, using pure model compounds having different structures, we have found that such a generalization is impossible.[47,49-55]

Another drawback to the relations cited in the literature and

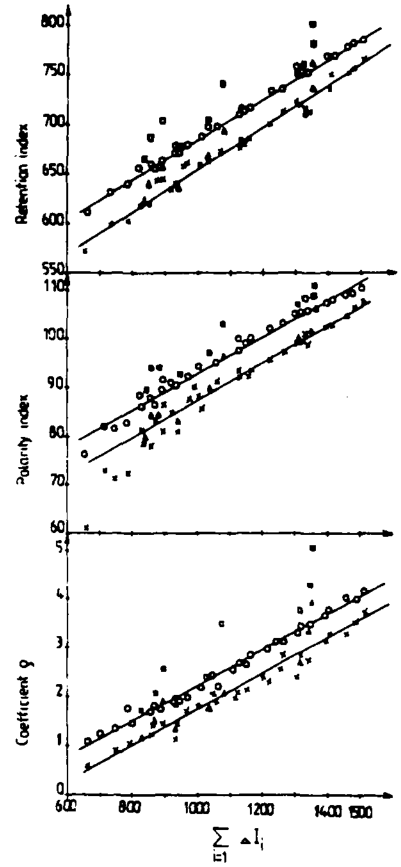


FIGURE 16. Relationships between the empirical polarity parameters and the sum of the first five McReynolds constants (x, Δ, methanol; O, □, ethanol; Δ, □, aminoether alcohols and their ethers; x, O, 1,3-bis[ω-alkoxyoligo-(oxyethylene)] propan-2-ols).[52]

presented in Tables 15 to 17 is connected to the omission of the procedure used for the HLB determination.

Two different scales of HLB exist, i.e., Griffin and Davies. In the case of the Griffin scale, the HLB can be determined from appropriate emulsion tests, or in some cases for typical nonionic surfactants having one short hydrophobic hydrocarbon chain and a polyoxyethylene chain. The HLB can be estimated according to one of the equivalent Equations 63:[2-9]

$$HLB^G = 20\,\frac{M_H}{M} \quad \text{and} \quad HLB^G = \frac{E}{5}, \tag{63}$$

where M and M_H denote the molecular mass of a surfactant and the molecular mass of its hydrophilic polyoxyethylene chain, respectively, and E stands for the content (%) of the polyoxyethylene chain. Some other equations are cited in the literature.[2-9] The authors usually use the calculation procedure (Equations 63), but they do not mention it because it causes a great deal of confusion. Moreover, such calculations give only

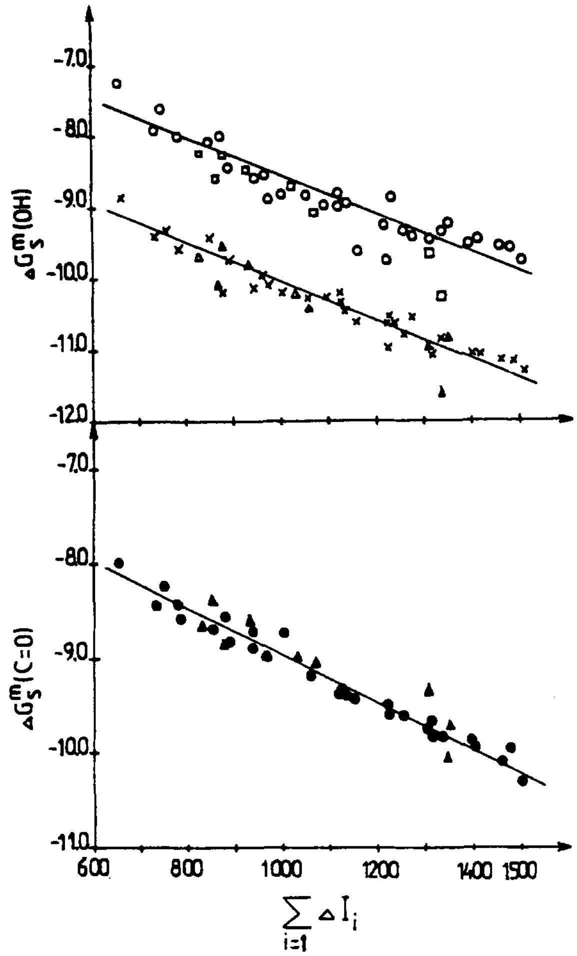


FIGURE 17. Relationships between the partial molal free energy of solution of a functional group and the sum of the first five McReynolds constants (x, △, methanol; ○, □, ethanol; ●, ▲, 2-pentanone; △, □, ▲, aminoether alcohols and their ethers; x, ○, ●, 1,3-bis[ω-alkoxyoligo(oxyethylene)]-propan-2-ols).[52]

very rough estimation because they do not reflect the influence of the surroundings. It is well known that the HLB can change, and one constant value cannot be attributed to the considered surfactant or to a surfactant's mixture.

In the case of the Davies scale, the HLB^D is calculated from appropriate increments (Table 18) according to the following relation:[128,129]

$$HLB^D = 7 + \Sigma \Delta HLB_i^D \qquad (64)$$

where ΔHLB_i^D are increments of HLB for characteristic groups present in a surfactant molecule. This procedure also gives only rough estimation of the HLB, and HLB^D values are usually significantly different in comparison to HLB^G values. Moreover, HLB^D values for various homologous series change by an appropriate increment, while HLB^G changes with different rate, finally achieving a constant value of an appropriate asymptote.

Table 13
Regression (a and b) and Correlation Coefficients (R) for Relation $P = a + b \sum_{i=1}^{5} \Delta I_i$[115]

Liquid phase	Polarity parameter	Solute	a	b	R
A	I_R	Methanol	390.98	0.2575	0.9479
		Ethanol	443.03	0.2548	0.9384
	PI	Methanol	30.707	0.0484	0.9824
		Ethanol	55.447	0.0387	0.9584
	ρ	Methanol	−4.888	$6.589 \cdot 10^{-3}$	0.9308
		Ethanol	−5.808	$8.584 \cdot 10^{-3}$	0.9470
	A	At 70°C	2.542	$-2.078 \cdot 10^{-4}$	0.8932
		At 90°C	2.376	$-2.022 \cdot 10^{-4}$	0.9175
	ΔG_s^m (OH)	Methanol	−6.363	$-3.731 \cdot 10^{-3}$	0.8673
		Ethanol	−5.589	$-3.272 \cdot 10^{-3}$	0.8577
	ΔG_s^m (C=O)	2-Butanone	−4.421	$-3.676 \cdot 10^{-3}$	0.8776
		2-Pentanone	−3.643	$-3.837 \cdot 10^{-3}$	0.8577
	ΔG^E (CH_2)	Alkanes	95.36	0.0692	0.8592
		Alcohols	30.73	0.0596	0.8700
		Ketones	413.78	0.1474	0.8668
	ΔG_s^m (CH_2)	Alkanes	−2.892	$4.124 \cdot 10^{-4}$	0.9008
B	I_R	Methanol	439.62	0.2132	0.9595
		Ethanol	469.49	0.2086	0.9673
	PI	Methanol	38.067	0.0469	0.9653
		Ethanol	49.147	0.0418	0.9536
	ρ	Methanol	−1.211	$2.80 \cdot 10^{-3}$	0.9521
		Ethanol	−1.162	$3.07 \cdot 10^{-3}$	0.9422
	A	At 70°C	2.361	$-3.349 \cdot 10^{-4}$	0.9712
		At 90°C	2.291	$-1.970 \cdot 10^{-4}$	0.9355
	ΔG_s^m (OH)	Methanol	−7.180	$-2.620 \cdot 10^{-3}$	0.9361
		Ethanol	−5.689	$-2.688 \cdot 10^{-3}$	0.9785
	ΔG_s^m (C=O)	2-Butanone	−6.576	$-2.633 \cdot 10^{-3}$	0.9361
		2-Pentanone	−6.598	$-2.355 \cdot 10^{-3}$	0.9647
	ΔG^E (CH_2)	Alkanes	3.878	0.1850	0.9897
		Alcohols	−49.45	0.1631	0.9834
		Ketones	214.57	0.3982	0.9908
	$\overline{\Delta G^E}$ (CH_2)	—	52.04	0.2540	0.9869
	ΔG_s^m (CH_2)	Alkanes	−2.371	$3.614 \cdot 10^{-4}$	0.9758
C[53]	I_R	Methanol	393.7	0.308	0.8953
		Ethanol	427.8	0.296	0.9185
	PI	Methanol	42.004	0.0533	0.8526
		Ethanol	55.700	0.0422	0.9244
	ρ	Methanol	−4.18	$6.670 \cdot 10^{-3}$	0.9378
		Ethanol	−4.70	$7.611 \cdot 10^{-3}$	0.9466
	ΔG_s^m (OH)	Methanol	−7.316	$-3.641 \cdot 10^{-3}$	0.7688
		Ethanol	−5.587	$-3.692 \cdot 10^{-3}$	0.7632
	ΔG_s^m (C=O)	2-Butanone	−6.737	$-2.091 \cdot 10^{-3}$	0.8812
		2-Pentanone	−6.649	$-1.890 \cdot 10^{-3}$	0.8651
C[54]	I_R	Methanol	452.1	0.2340	0.9071
		Ethanol	463.7	0.2551	0.9472
	PI	Methanol	45.53	0.0470	0.8725
		Ethanol	56.25	0.0428	0.9165
	ρ	Methanol	−2.53	$4.73 \cdot 10^{-3}$	0.8995
		Ethanol	−3.73	$6.66 \cdot 10^{-3}$	0.9186
	ΔG_s^m (OH)	Methanol	−7.005	$-3.781 \cdot 10^{-3}$	0.8428
		Ethanol	−4.879	$-4.381 \cdot 10^{-3}$	0.8804
	ΔG_s^m (OH)	2-Butanone	−5.723	$-3.113 \cdot 10^{-3}$	0.8414
		2-Pentanone	−5.518	$-2.991 \cdot 10^{-3}$	0.8260

Note: A: polyoxyethylene alcohols, alkylthiols, and alkylamines;[55] B: 1,3-bis[ω-alkoxyoligo(oxyethylene)]propan-2-ols;[51] and C: α,ω-diaminooligoethers.[53,54]

Table 14
Sensitivity of Polarity Parameters $\frac{P_{max} - P_{min}}{P_{min}} \cdot$ 100%[115]

Polarity parameter	Solute	Group of compounds used as liquid phases						
		A	B	C	D	E[53]	E[54]	F
I_R	Methanol	74	27	22	35	42	20	79
	Ethanol	75	23	18	28	56	20	—
PI	Methanol	165	87	35	79	34	38	117
	Ethanol	120	44	25	48	27	29	—
ρ	Methanol	1957	198	224	393	225	171	356
	Ethanol	1162	184	191	292	416	171	—
ΔG_s^m (OH)	Methanol	76	—	16	23	28	30	—
	Ethanol	91	—	20	25	32	21	—
ΔG_s^m (C=O)	2-Butanone	105	—	—	—	31	23	—
	2-Pentanone	160	—	14	22	25	22	—
$\sum_{i=1}^{5} \Delta I_i$	—	331	—	62	128	172	67	—
A	Alkanes	24	—	8	17	—	—	10
ΔG_s^m (CH_2)	Alkanes	37	—	8	13	—	—	—
Δ^E (CH_2)	Alkanes	86	—	55	109	—	—	43

Note: A: polyoxyethylene alcohols, alkylthiols, and alkylamines;[55] B: polyoxyethylene glycol dialkyl ethers;[47,49] C: aminoether alcohols and their ethers;[50] D: 1,3-bis-[ω-alkoxyoligo-(oxyethylene)]-propan-2-ols;[51] E: α,ω-diaminooligoethers;[53,54] and F: hydroxyoximes.[81,82]

When the structure of a surfactant is not known, its approximate HLB value can be estimated from the polarity index according to Equation 65:[58]

$$HLB^G = 0.309\ PI^{MeOH} - 18.3. \tag{65}$$

This equation was obtained using the calculated HLB^G values and the polarity index of methanol experimentally determined for the following groups of surfactants: sorbitan esters and their polyoxyethylene ethers (Span and Tween surfactants), polyoxyethylene derivatives of alkylphenols, dinonylphenol, alcohols and fatty acids, and sucrose esters of fatty acids.[58] However, the error in such an estimation can be great and even for typical surfactants can be equal to 2 HLB units. The use of specific relations obtained, e.g., for sorbitan esters and their polyoxyethylene ethers or for polyoxyethylene alcohols, to determine the HLB values for other groups of surfactants from their polarity parameters has been proposed.[45,122,123] However, such calculations often lead to great errors in HLB estimation. Therefore, two special procedures have been recently developed to more accurately obtain HLB.

The first procedure for HLB calculation is as follows.[133] An appropriate homologous series of surfactants for which the relation between HLB and a polarity parameter, e.g., PI, is known, as in the case of polyoxyethylene nonylphenols (Equation 66):

$$HLB_{si} = 0.435\ PI_{si} - 31.4, \tag{66}$$

is selected as the standard series of surfactants. For a new series of surfactants, it is necessary to determine the HLB and PI for two homologs: HLB_{m1}, PI_{m1}, and HLB_{m2} and PI_{m2}. Then, introducing HLB_{m1} and HBL_{m2} into Equation 66, appropriate values of the polarity index PI_{s1} and PI_{s2} are calculated. These values of the polarity index are shown by standard surfactants exhibiting the same HLB values as the investigated surfactants. The values of PI_{si} and PI_{mi} are connected according to Equation 67:

$$\frac{PI_{mi} - PI_{m1}}{PI_{si} - PI_{s1}} = A \tag{67}$$

Introducing into this equation the values of PI_{m1}, PI_{m2}, PI_{s1}, and PI_{s2}, the constant A is obtained. At this point the HLB for another homolog can be determined from the value of its polarity index. Introducing PI_{mi} into Equation 67, an appropriate value of PI_{si} is obtained. Placing, then, PI_{si} into Equation 66, the HLB for a standard surfactant having the same HLB as the considered surfactant is obtained. The idea of this method is presented in Figure 20.

As linear relations between HLB and PI are considered for both series of surfactants, then:

$$HLB_{mi} = a_m + b_m\ PI_{mi} \tag{68}$$

and

$$HLB_{si} = a_s + b_s\ PI_{si}. \tag{69}$$

Thus, as $HLB_{mi} = HLB_{si}$ then

$$PI_{si} = D + E\ PI_{mi}, \tag{70}$$

where D and E are regression coefficients.

By introducing Equation 70 into Equation 69, the appropriate linear equation for HLB is obtained:

$$HLB_{si} = HLB_{mi} = a_s + b_s(D + E\ PI_{mi}). \tag{71}$$

The values of D and E regression coefficients for some practically important groups of nonionic surfactants are given in Table 19; a_s and b_s are equal to 0.435 and −31.4, respectively, as polyoxyethylene nonylphenols were selected as standard surfactants.

Table 15
Relations between HLB Values, as Expressed on Griffin (HLB^G) and Davies (HLB^D) Scales, and Polarity Index (Methanol as a Polar Agent)[116]

No.	Equation	Temp (°C)	Surfactants and comments	Ref.
1	$HLB^G = 0.248\ PI - 14.37$	70	Sorbitan esters	58, 117
2	$HLB^G = 0.201\ PI - 6.35$	70	Polyoxyethylene sorbitan esters	58, 117
3	$HLB^G = 0.435\ PI - 31.43$	70	Polyoxyethylene alkylphenols	58, 117
4	$HLB^G = 0.237\ PI - 8.84$	70	Polyoxyethylene dinonylphenols	58, 117
5	$HLB^G = 0.213\ PI - 7.05$	70	Polyoxyethylene alcohols	58, 117
6	$HLB^G = 0.350\ PI - 21.96$	70	Polyoxyethylene alkylamines	58, 117
7	$HLB^G = 0.282\ PI - 16.92$	70	Sucrose esters	58, 117—119
8	$HLB^G = a\ PI + b$	65	Polyoxyethylene nonylphenols; equations were not given; deviations for low HLB values	63
9	$HLB^G = 0.154\ PI - 7.56$	65	Polyoxyethylene monoglicerides	120
10	$HLB^G = 0.154\ PI - 2.97$	—	Polyoxyethylene fatty acids	121
11	$HLB^G = 0.332\ PI - 21.0$	60—95	Sorbitan esters and their polyoxyethylene derivatives; equation was not given	64
12	$HLB^G = 0.376\ PI - 24.9$	60—95	Sorbitan esters	64
13	$HLB^G = 0.325\ PI - 19.5$	60—95	Polyoxyethylene sorbitan esters	64
14	$HLB^G = 45.45 \log PI - 71.14$	70	Purified sorbitan esters and their polyoxyethylene ethers, polyoxyethylene fatty alcohols, and pentaerythritol	122—125
15	$HLB^G = 0.3251\ PI - 24.1$	70	Pluronic surfactants; only 4 products: PL-68, PL-64, PL-61 and PL-44	126
16	$HLB^G = 109.89 \log PI - 211.7$	70	Polyoxyethylene fatty alcohols	127
17	$HLB^D = 0.192\ PI - 12.6$	65	Polyoxyethylene monoglycerides	120

The error of the HLB determination using this procedure does not exceed 0.5 HLB units, while the average error is 0.2 HLB units (Table 20). The method is generally valid and accurate, but accurate values of HLB for a standard series and for two homologs of the new surfactant series are necessary.

The HLB of nonionic surfactants can also be estimated according to modified Equation 72:[134-136]

$$HLB = \frac{HI^E\ E}{5}, \tag{72}$$

where HI^E denotes the hydrophilicity index. This equation can be used for surfactants containing various heteroatoms (nitrogen, sulfur) and for block copolymers for which Equation 63 is not valid. It can be also used for typical polydisperse mixtures of nonionic surfactants as well as for various model individual compounds.

The hydrophilicity index can be defined similarly to the hydrophobicity index,[137-140] which has been defined as the ratio of the effective number of methylene groups in a hydrophobic chain to the actual number in it. Thus, the hydrophilicity index can be defined as the ratio of the effective content or the effective length of a hydrophilic polyoxyethylene chain to the actual content or the actual length of this chain (Equation 73):

$$HI^E = E_{eff}/E. \tag{73}$$

Instead of the actual content of the polyoxyethylene chain, the use of the effective content of the polyoxyethylene chain is proposed for HLB calculations. This effective content of the hydrophilic chain is defined by the actual content of the polyoxyethylene chain in a hypothetical surfactant from the standard series, having the same polarity as the considered surfactant. Knowing the relation between the content of the polyoxyethylene chain and the polarity for the standard series of surfactants, which in this case is characterized by the polarity index, e.g.,

$$E = 1.065\ PI^{MeOH} - 35.25 \tag{74}$$

for polyoxyethylene alcohols, the effective content of the hydrophilic block in a considered surfactant can be estimated by introducing its experimentally determined polarity index in Equation 74.

The values of the effective content of the hydrophilic block

Table 16
Relations between HLB Values, as Expressed on Griffin (HLB^G) and Davies (HLB^D) Scales, and Coefficient ρ[116]

No.	Equation	Temp (°C)	Polar agent	Surfactants	Ref.
1	$HLB^G = 8.55\,\rho - 6.36$	80	EtOH	Polyoxyethylene alcohols	65
2	$HLB^G = 31.2\,\rho - 30.7$	80	EtOH	Sorbitan esters and their polyoxyethylene ethers	91
3	$HLB^G = 3.37\,\rho' + 0.58$	80	EtOH	Sorbitan esters and their polyoxyethylene ethers	91
4	$HLB^G = 8.21\,\rho + 3.93$	65	MeOH	Polyoxyethylene monoglycerides	75
5	$HLB^G = 8.08 \ln \rho' - 0.36$	40	EtOH	Sorbitan esters and their polyoxyethylene ethers	91
6	$HLB^G = 8.78 \ln \rho' + 0.24$	60	EtOH	Sorbitan esters and their polyoxyethylene ethers	91
7	$HLB^G = 10.2 \ln \rho' + 0.45$	80	EtOH	Sorbitan esters and their polyoxyethylene ethers	91
8	$HLB^G = a\,\rho' + b$	iso-PeOH	pentane	Sorbitan esters and their polyoxyethylene ethers; equations are not given	
9	$HLB^G = 5.83\,\rho - 7.72$	80	EtOH	Ethylene oxide/α-butylene oxide block copolymers	121
10	$HLB^G = 1.78\,\rho + 0.23$	80	EtOH pentane	Polyoxyethylene fatty alcohols	127
11	$HLB^D = 10.25 \log \rho + 1.90$	65	MeOH	Polyoxyethylene monoglycerides	120

Table 17
Relations between HLB Values, as Expressed on Griffin (HLB^G) and Davies (HLB^D) Scales, and Polarity Parameters Determined by GC[116]

Equation	Temp (°C)	Surfactants and comments	Ref.
$HLB^G = 26 - K/2.6$	80	Sorbitan esters and their polyoxyethylene ethers; K: partition coefficient of diisobutylene	45
$HBL^G = 21.3 - t/6.4$	80	Polyoxyethylene fatty alcohols; retention of 2,4,4-trimethylpentene, mm	70
$HLB^G = 20.3 - 20\alpha$	100	Polyoxyethylene sorbitan esters; α: ratio of partition coefficients of hexane and ethanol	76
$HBL^G = 3.91 + 290.2/K_A$	100	Polyoxyethylene sorbitan esters; K_A: adsorption coefficeint of isooctane	74
$HLB^G = 9.091\,C^{MeOH} - 52.3$	60—90	Sorbitan esters; C^{MeOH}: carbon number of MeOH	64
$HLB^G = 5.405\,C^{MeOH} - 26.0$	60—95	Polyoxyethylene sorbitan esters	64
$HLB^D = 19.4 - 0.045\,\Delta I$	100	α-Monoglicerides; $\Delta I = I_{R\,decaline} - I_{R\,water}$	71
$HLB^D = 0.0133\,\Delta I - 1.33$	100	α-Monoglicerides of octadecenoic acids	71
$HLB^D = 0.0179\,\Delta I - 3.46$	100	α-Monoglicerides of octadecenoic acids	71

depend in some way upon the polarity parameter (Figure 21)[136] and on the polar solute used as the standard (Figure 22).[136] These two effects are relatively small and are caused by different interactions between the surfactant considered and standard alcohols. However, somewhat different sets of HLB are estimated using various polarity parameters and polar solutes, respectively. Other groups of surfactants can also be used as the standards, i.e., polyoxyethylene nonylphenols for which appropriate data were determined (Figure 23).[134] Using this data, somewhat different HLB values are obtained in comparison to those estimated from the polarity data of polyoxyethylene alcohols.

The choice of an appropriate standard group of surfactants is not always easy because these standard surfactants should

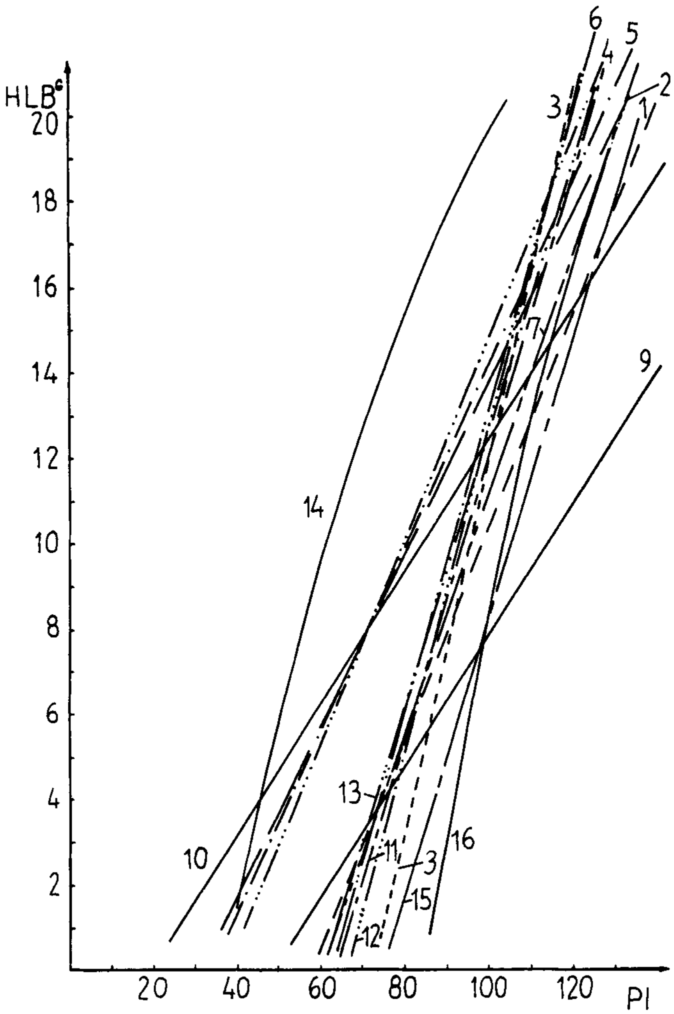


FIGURE 18. Relations between the HLB values and the polarity index (relations' numbers are the same as in Table 15).[116]

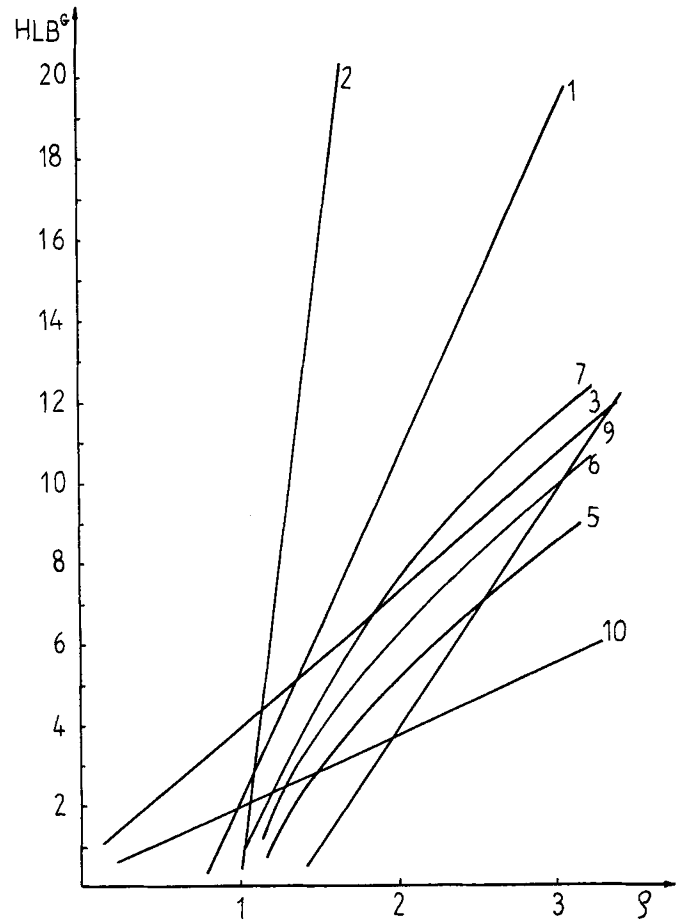


FIGURE 19. Relations between the HLB values and the coefficient ρ (relations' numbers are the same as in Table 16).[116]

exhibit similar polarities and HLB as studied surfactants. The proposed method of HLB estimation is quite general, and other parameters of surfactant polarity or hydrophilicity, taking into account the influence of the surfactants' surroundings, can be used as polarity criteria.

VI. RELATIONS BETWEEN SURFACTANTS' STRUCTURES AND THEIR POLARITY PARAMETERS

The formula of a nonionic surfactant having one hydrocarbon chain and one polyoxyethylene chain can be presented as follows:

$$RX(CH_2CH_2O)_nH, \text{ abbreviated as } L(EO)_nH \text{ and } LH \quad (75)$$

where X denotes O, S, etc., depending upon the class of compounds considered, and L stands for the hydrophobic part of the surfactant molecule. If we also assume the additivity of the polarity and neglect the influence of the terminal hydroxyl group, which is quite reliable for surfactants having a high enough molecular mass, the following equation for the surfactant polarity can be written:

$$P = \Delta P_H f + \Delta P_L(1 - f), \quad (76)$$

where ΔP_H and ΔP_L denote the polarities of the hydrophilic chain and the hydrophobic group, respectively, and f stands for the weight fraction of the polyoxyethylene chain content. ΔP_H and ΔP_L are constant, and the straight lines are obtained when the relations between the polarity parameters and the weight fractions of the oxyethylene group content are considered:

$$P = \Delta P_L + f(\Delta P_H - \Delta P_L), \quad (77)$$

which is fully supported by our experimental results (Figure 24).[61,136] The same results were obtained by Fineman,[63] who divided surfactants into three parts: a hydrophobic group, a

Table 18
Davies HLB Increments for Molecule Characteristic Fragments[128–132]

Molecular characteristic fragment	ΔHLB_i
Hydrophilic groups	
$—SO_4Na$	38.7
—COOK	21.1
—COONa	19.1
—N< (tertially amine)	9.4
—COOR (sorbitan esters)	6.8
—COOR	2.4
—COOH	2.1
—OH	1.9
—O—	1.3
—OH (sorbitan ring)	0.5
$—CH_2HC_2O—$	0.33
Hydrophobic groups	
$—CH_3$	−0.475
$—CH_2—$	−0.475
—CH<	−0.475
$—CF_3$	−0.870
$—CF_2—$	−0.870
$—C_3H_7O—$	−0.15

polyoxyethylene chain and a terminal $—CH_2CH_2OH$ group. Assuming a constant influence of the terminal $—CH_2CH_2OH$ group upon the surfactant polarity, he pointed out that the hydrophobe and $—CH_2CH_2OH$ group can be considered together as one term. As a result, Equation 77 was obtained in which ΔP_L denotes the sum of both the hydrophobe and the hydrophilic $—CH_2CH_2OH$ group.

Thus, by extrapolating the polarity of surfactants to the content of the polyoxyethylene chain of 100%, the polarity of this hydrophilic chain can be determined. Quite the same values of the polarity index are obtained when data determined for different classes of surfactants are considered (Table 21).[47,58,61,63,117,136] These values are also in agreement with the values determined for polyoxyethylene glycols having an appropriate high molecular mass for which the influence of the terminal hydroxyl group can be neglected.

It is interesting that quite similar values were obtained as ethanol was used as the polar solute. In this case, ΔP_H values reported for symmetrical 1,3-bis-[ω-alkoxyoligo(oxyethylene)]-propan-2-ols having 4 and 6 carbon atoms in their each terminal alkyl were 122 and 123, respectively.[136] The value of 123.5 was obtained for polyoxyethylene alcohols, alkylphenols, and fatty acids.[136]

Such a simple approximation of the hydrophilic block polarity is not always possible. The polarity parameters of asymmetric 1,3-bis-[ω-alkoxyoligo(oxyethylene)]-propan-2-ols having two terminal alkyls, $R^1(OCH_2CH_2)_nOCH_2CH(OH)CH_2O(CH_2CH_2O)_mR^2$, where n and m and R^1 and R^2 are different, respectively, also increase as the content of the hydrophilic

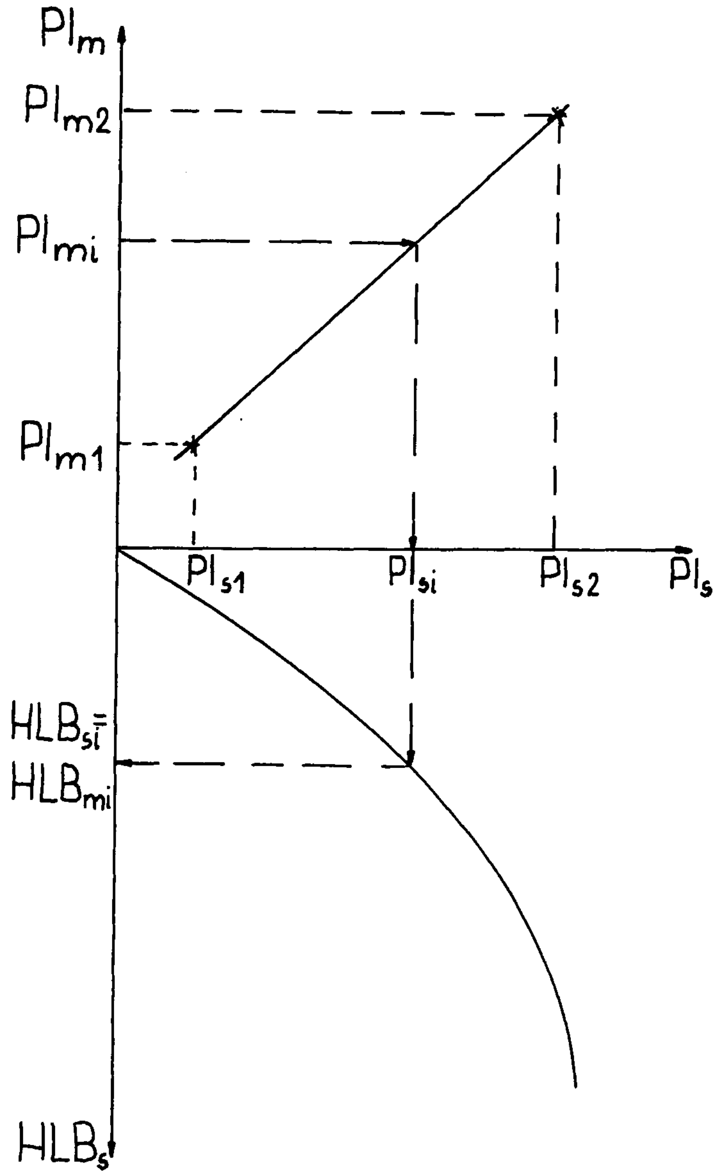


FIGURE 20. HLB estimation using standard group of surfactants.

Table 19
Regression Coefficients for Relation $PI_{si} = D + E\,PI_{mi}$ (Polyoxyethylene Nonylphenols as Standards)[133]

Group of surfactants	D	E
Span	39.1	0.570
Tween	57.7	0.462
Polyoxyethylene dinonylphenols	52.0	0.545
Polyoxyethylene fatty alcohols	56.1	0.487
Polyoxyethylene fatty acids	21.6	0.805
Sucrose esters of fatty acids	33.3	0.648

Table 20
Calculated HLB Values (Polyoxyethylene Nonylphenols as Standards)[133]

Surfactant	Producer	PI[58]	HLB	HLB_{calc}	ΔHLB
Span 80	Koch-Light Lab	73.9	4.3	3.9	−4.3
Span 60		77.6	4.7	4.8	+0.1
Span 40		86.0	6.7	6.9	+0.2
Span 20		93.0	8.6	8.7	+0.1
Tween 80	Schuchardt	107.0	15.0	15.1	+0.1
Tween 60		107.0	14.9	15.1	+0.2
Tween 40		108.4	15.6	15.5	−0.1
Tween 20		114.8	16.7	16.8	+0.1
Serdox NES 8	N. V. Servo	96.9	13.5	13.0	+0.5
Serdox NES 12		101.0	14.4	14.4	0.0
Serdox NKS 25		109.4	16.2	16.2	0.0
Serdox NSG 200		86.3	8.6	8.2	−0.4
Serdox NSG 264		91.8	9.8	10.1	+0.3
Serdox NSG 400		97.7	12.0	12.2	+0.2
Serdox NSG 600		101.5	13.8	13.5	−0.3

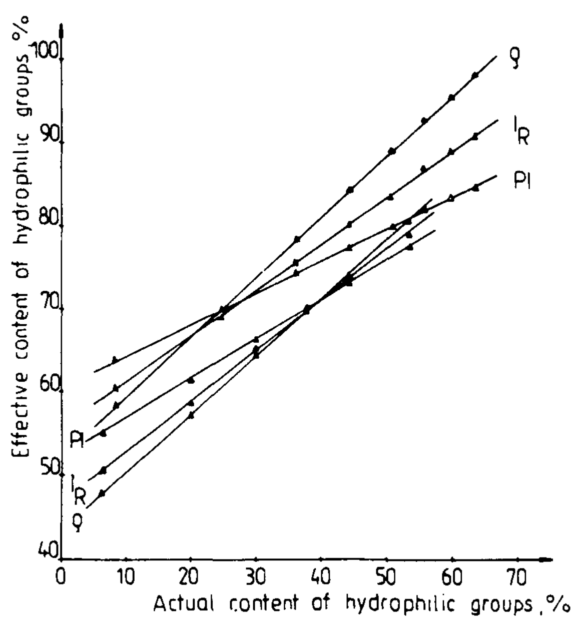


FIGURE 21. Effect of polarity parameters on relationship between effective and actual contents of hydrophilic groups for 1,3-bis-[ω-alkoxyoligo(oxyethylene)]propan-2-ols, $R(OCH_2CH_2)_n\ OCH_2CH(OH)CH_2O(CH_2CH_2O)_mR$ (△, R = C_4H_9; ▲, R = C_6H_{13}).[136]

group increases, but the derivation of a linear relation is impossible. Experimental data are too scattered and a new parameter for characterizing the symmetry of compounds should be considered.[136] Such simple linear relations for approximation to the hydrophilic group content of 100% give constant values for the hydrophilic block polarity were also not obtained for polyoxyethylene 4-alkylphenylamines.[140]

The extrapolation of the hydrophilic group content to 0%

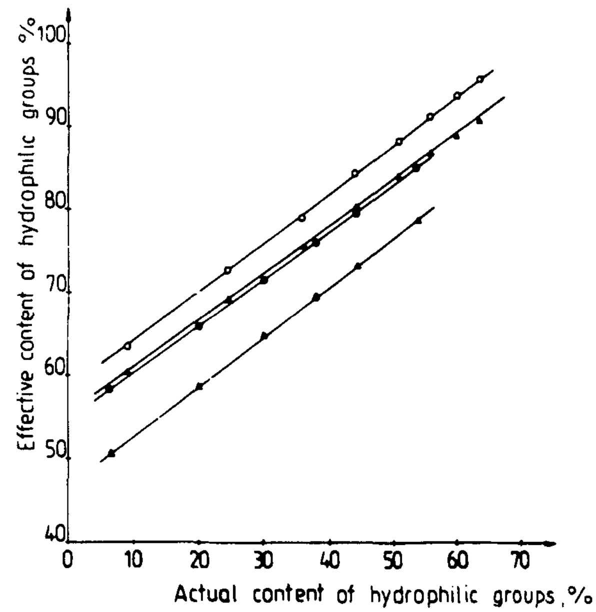


FIGURE 22. Effect of polar agent on relationship between effective and actual contents of hydrophilic groups for 1,3-bis-[ω-alkoxyoligo(oxyethylene)] propan-2-ols, $R(OCH_2CH_2)_nOCH_2CH(OH)CH_2O(CH_2CH_2O)_mR$; (○, △, R = C_4H_9; ●, ▲, R = C_6H_{13}; ○, ●, methanol; △, ▲, ethanol).[136]

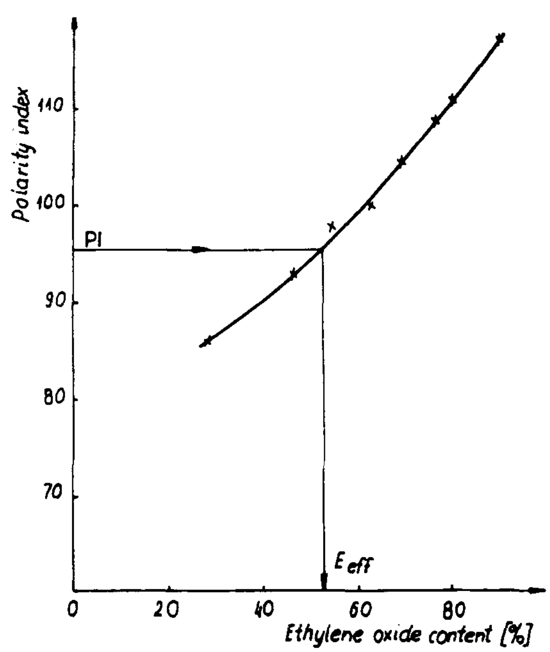


FIGURE 23. Polarity index of polyoxyethylene nonylphenols and determination of the effective content of polyoxyethylene chain.[134]

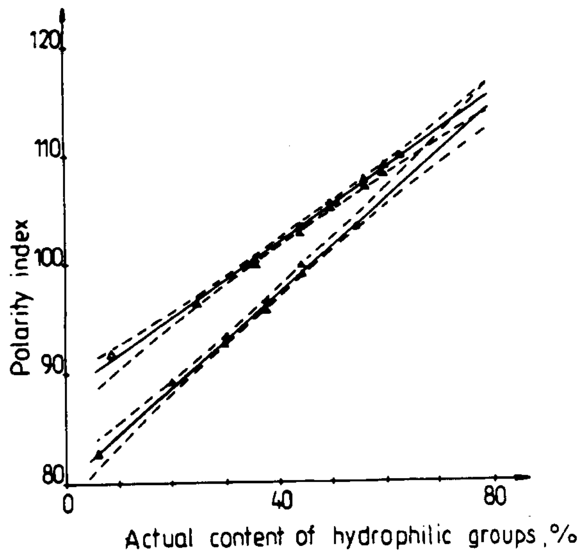


FIGURE 24. Polarity index for symmetrical 1,3-bis-[ω-alkoxyoligo-(oxyethylene)]propan-2-ols, $R(OCH_2CH_2)_nOCH_2CH(OH)CH_2O(CH_2CH_2O)_mR$ (△, R = C_4H_9; ▲, R = C_6H_{13}; ethanol as the solute; dashed lines denote the confidence limits for significance level of 0.05).[136]

Table 21
Polarity Index for Polyoxyethylene Chain

No.	Surfactants	ΔPI_H	Ref.
1	Polyoxyethylene monoalkylphenols	118	58, 117
2	Polyoxyethylene dinonylphenols	122	58, 117
3	*N,N*-di-polyoxyethylene alkylamines	120	58, 117
4	Polyoxyethylene alcohols	127	58, 17
5	Surfactants of groups 1, 2, 3, and 4	121	58, 17
6	Polyoxyethylene glycol dialkyl ethers	123	47
7	Ethylene oxide/α-butylene oxide block copolymers	122	61
8	Symmetrical 1,3-bis-[ω-alkoxyoligo-(oxyethylene)]-propan-2-ols	122	61
	R = C_4H_9	126	136
	R = C_6H_{13}	123	136
9	Sorbitan esters and their polyoxyethylene ethers	122	58, 117
10	Polyoxyethylene glycols		
	200	139	61
	400	133	61
	600	131	61
	1000	130	61
	2000	128	61
	4000	123.5	61
	Carbowax 20 M	126	63

gives appropriate polarities of hydrophobic chains. The following values of this increment were obtained: approximately 60 for hydrocarbon chains present in polyoxyethylene alcohols, alkylphenols, fatty acids, and polyoxyethylene glycol dialkyl ethers;[136] 70 to 75 for short terminal hydrocarbon chains in symmetrical 1,3-bis-[ω-alkoxyoligo(oxyethylene)]-propan-2-ols;[136] and 70 to 85 for polyoxyethylene glycols having various molecular masses.[61] Thus, the polarity of these hydrophobic chains increases in the following order: a long carbon chain < two short terminal hydrocarbon chains < a polyoxybutylene chain. The polarity of the polyoxybutylene chain decreases as the molecular mass of the polyoxybutylene chain increases, both in polyoxybutylene glycols and in various types of ethylene oxide/α-butylene oxide block copolymers.

According to Equation 75, the polarity of nonionic surfactants can be also described as

$$P = m\,\Delta P_{CH_2} + \Delta P_X + n\,\Delta P_{EO}, \qquad (78)$$

where ΔP_{CH_2}, ΔP_X, and ΔP_{EO} denote the increments of the polarity parameters for the considered groups, while m and n represent the numbers of the methylene (the methyl group is recognized as equivalent to the methylene group) and the oxyethylene groups, respectively. In reality, ΔP_X is the sum of the constituent value typical for the considered group of surfactants and of the increment for the characteristic group considered. However, it is not always possible to find the values of both these components, and therefore they can be calculated as a sum. However, in this case it is impossible to attribute any physical meaning to such determined increments.

The values obtained for some structural fragments of surfactants having Equation 75 are given in Table 22. Using these increments, it is possible to estimate the polarity index of the individual surfactants having a low number of oxyethylene groups with absolute and relative errors of 1.5 PI units and 1.6%, respectively.[141] The absolute and relative errors of such estimation for polydisperse mixtures are equal to 3.8 PI units and 1.6%, respectively.[141]

Polarity increments having a physical meaning can be obtained as constituent values characteristic for various homologous series, and appropriate increments for structural fragments of surfactant molecules are computed assuming a constant constituent value characteristic for the considered group of

Table 22
Increments of Polarity Index of Methanol for Structural Fragments of Surfactants $RX(CH_2CH_2O)_nH$[141]

Structural fragments	Increments
—CH_2—, —CH_3	−2.985
—O—	103.058
—S—	102.212
—NH—	119.238
—CH_2CH_2O—, —CH_2CH_2OH	3.838

compounds and positive and negative values for polar and nonpolar groups, respectively. Thus, the polarity of a compound A_i (P_{Ai}) can be expressed as

$$P_{Ai} = \text{constant} + \sum a_{ji}\,\Delta P_{Gj}, \tag{79}$$

where it is assumed that the increment of ΔP for a group G_j is constant for all compounds present in the system, and the coefficient a_{ji} denotes the number of G_j group in a compound A_j.

The values of these increments for the polarity index, retention index, and the sum of McReynolds constants are given in Table 23.[115] Various increments were obtained for different homologous series. They can be used to predict the polarity parameters for the compounds considered and their homologs only from their formulas. The accuracies of such predictions are good and the errors are below 3% and 4 to 5% for the retention and polarity indices of alcohol, respectively. The sum of the McReynolds constants is estimated with the higher relative error of 4 to 9%.

Although different increments were obtained for the same structural fragments present in various homologous series, it was possible to compute the average increments (group D in Table 23), which can be used to predict the polarity parameters of different groups of surfactants and model compounds. The errors of such predictions are then about 4, 5 to 7, and 10% for the retention index, polarity index, and the sum of McReynolds constants, respectively.

Appropriate increments for other polarity parameters, i.e., $\Delta G_s^m(OH)$, $\Delta G_s^m(C{=}O)$, ρ, A, $\Delta G_s^m(CH_2)$ and $\Delta G^E(CH_2)$, are also given in the literature,[50-52,84,89] and can be used to predict appropriate polarity parameters. They can also be estimated using relations between various polarity parameters, as presented in Section IV.

Hydroxyl groups and nitrogen atoms have the most significant effect on the polarity of the examined compounds. The relative polarities of the structural fragments depend both upon the type of the compounds and the polarity parameter (Tables 24 and 25)[119] as a result of different structures of compounds considered and various interactions measured by different parameters. However, the considered polarity parameters can be arranged in the following order of their decreasing polarity: $-OH > -N\langle\ > -NH- > -Cl > -O- > -S-$. Only in the case of 1,3-bis-[ω-alkoxyoligo(oxyethylene)]-propan-2-ols, $R(OCH_2CH_2)_nOCH_2CH(OH)CH_2O(CH_2CH_2O)_MR$, were somewhat higher increments obtained for nitrogen atoms in comparison to hydroxyl groups. However, in this case, the hydroxyl group is the secondary one and it is screened by oligooxyethylene chains.

A linear effect of the polyoxyethylene chain length upon the

Table 23
Increments of Polarity Parameters for Characteristic Fragments[115]

			Increments								Error	
P	Solute	Liquid phase	—CH₂—	—O—	—NH—	—N=	—S—	—OH	—Cl	Const	Abs	Rel. %
I_R	MeOH	A	−17.5	72.9	164.6	166.7	55.8	197.0	135.0	530.9	19	2.7
		B	−5.8	31.5	—	—	22.6	—	—	538.1	11	2.7
		C	−8.9	36.0	—	55.4	—	25.1	—	643.7	12	1.8
		D	−10.1	37.9	124.4	128.2	27.8	110.1	62.7	590.6	27	4.0
	EtOH	A	−17.4	70.2	152.7	156.8	48.2	183.9	105.1	610.9	21	2.8
		B	−5.1	27.8	—	—	18.0	—	—	604.2	9	1.9
		C	−9.0	34.6	—	68.1	—	21.9	—	690.4	7	1.0
		D	−9.7	32.9	105.1	121.8	22.2	84.1	53.9	672.1	32	4.5
PI	MeOH	A	−3.11	12.3	28.81	30.01	8.82	42.82	19.55	58.73	3.8	4.7
		B	−1.77	9.68	—	—	6.70	—	—	48.32	4.1	6.9
		C	−1.86	7.93	—	12.75	—	21.97	—	81.42	3.0	3.2
		D	−2.05	8.06	27.86	29.65	6.33	27.51	8.66	65.40	5.3	6.6
	EtOH	A	−2.67	10.4	21.85	22.85	5.03	30.54	14.26	81.26	3.5	3.7
		B	−1.27	6.91	—	—	4.46	—	—	70.78	2.4	3.0
		C	−1.69	6.48	—	12.85	—	13.87	—	93.98	1.6	1.6
		D	−1.66	5.94	19.26	20.51	4.34	17.87	9.39	85.84	4.7	4.9
$\sum_{i=1}^{5}\Delta I_i$	—	A	−78	289	523	549	212	632	453	853	105	8.6
		C	−38	163	—	221	—	194	—	848	34	3.2
		D	−57	171	419	495	168	346	253	1040	118	10.5

Note: A; polyoxyethylene alcohols, alkylthiols, and alkylamines;[55] B: polyoxyethylene glycol dialkyl ethers;[47–49] C: aminoether alcohols and their ethers[50] and 1,3-bis-[ω-alkoxy-oligo(oxyethylene)]-propan-2-ols;[51] D: weight average for groups A, B, C, and α-ω-diaminooligoethers.

Table 24
Realtive Polarities of Structural Fragments for 1,3-bis-[ω-alkoxyoligo(oxyethylene)]-propan-2-ols[115]

Parameter	Polar solute	—N=	—OH	—O—
I_R	Methanol	1.54	0.69	1
	Ethanol	1.97	0.63	1
PI	Methanol	1.61	1.77	1
	Ethanol	1.98	0.59	1
ρ	Methanol	1.37	0.24	1
	Ethanol	2.12	0.37	1
ΔG_s^m (OH)	Methanol	1.85	1.23	1
	Ethanol	2.29	1.16	1
ΔG_s^m (C=O)	2-Butanone	1.32	0.97	1
	2-Pentanone	2.21	1.19	1
$\sum_{i=1}^{5} I_i$	McReynolds solutes	1.35	1.18	1
A	Alkanes	1.33	1.20	1
ΔG_s^m (CH_2)	Alkanes	1.77	1.42	1
$\overline{\Delta G^E}$ (CH_2)	—	1.36	1.23	1
ΔG^E (CH_2)	Alkanes	1.33	1.16	1
	Alcohols	1.34	1.33	1
	Ketones	1.34	1.25	1

Table 25
Relative Polarities of Structural Fragments for Polyoxyethylene Alcohols, Alkylthiols, and Alkylamines[115]

Parameter	Polar solute	—OH—	—N=	—NH—	—Cl	—O—	—S—
I_R	Methanol	2.69	2.28	2.26	1.85	1	0.76
	Ethanol	2.62	2.24	2.17	1.50	1	0.69
PI	Methanol	3.47	2.43	2.33	1.58	1	0.71
	Ethanol	2.95	2.21	2.11	1.38	1	0.48
ρ	Methanol	2.35	2.43	2.23	1.90	1	0.71
	Ethanol	2.36	2.41	2.28	1.56	1	0.85
ΔG_s^m (OH)	Methanol	2.65	2.24	2.19	1.39	1	0.35
	Ethanol	2.85	1.79	1.62	1.48	1	0.13
ΔG_s^m (C=O)	2-Butanone	2.68	2.24	2.07	1.47	1	0.22
	2-Pentanone	3.15	2.60	2.01	2.00	1	0.35
$\sum_{i=1}^{5} I_i$	McReynolds solutes	2.19	1.90	1.81	1.57	1	0.74
A	Alkanes	1.64	1.34	1.29	1.27	1	0.88
ΔG_s^m (CH_2)	Alkanes	2.43	2.61	2.29	2.28	1	0.45
$\overline{\Delta G^E}$ (CH_2)	—	1.49	1.24	1.06	0.95	1	0.83
ΔG^E (CH_2)	Alkanes	1.63	1.25	1.01	1.14	1	0.84
	Ketones	1.52	1.23	1.05	0.83	1	0.84
	Alcohols	1.42	1.24	1.07	0.92	1	0.82

polarity index of polydisperse mixtures of nonionic surfactants has been also demonstrated by Krivich and Bakholdina,[122] who have derived the following relation between the polarity index of polydisperse polyoxyethylene derivatives of the thioalcohols, the number of carbon atoms in the hydrophobe (n), and the number of oxyethylene groups (m):

$$PI^{MeOH\ 70°C} = (0.12\ n^2 - 2.25\ n + 14.9)m + 81.8. \quad (80)$$

Similar relationships are probably valid for other groups of nonionic surfactants having a low number of oxyethylene groups in their molecules.

For polyoxyethylene derivatives of pentaerythritol esters, the following relation was obtained:[122]

$$\log PI = 2.07 + 0.002m - (0.013 - 0.0004m)n, \quad (81)$$

where n denotes the number of carbon atoms in the acyl group and m stands for the number of oxyethylene groups.

Shilov and Molova,[142] investigating the polarity of three different sodium alkylsulfates, have demonstrated the following linear relation between the polarity index and the number of the carbon atoms (n):

$$PI^{MeOH\ 80°C} = 139.6 - 2.68\ n. \quad (82)$$

Similar linear relations were presented by us[47,49-55] for various homologous series and different polarity parameters.

For α,ω-diaminoethers derivatives, $RNHCH_2(CH_2OCH_2)_n CH_2NHR$, linear relations of P vs. $1/C_n$ and P vs. 1/M were found, where P denotes the polarity parameter, C_n is the number of carbon atoms in the alkyl group, and M is the molecular weight (Figure 25).[53] The following linear relations having high correlation coefficients (R) were obtained:

$$PI^{MeOH} = 93.33 + 7790/M, \quad R = 0.9950, \quad (83)$$

$$PI^{EtOH} = 79.39 + 6408/M, \quad R = 0.9874. \quad (84)$$

However, such approaches are only valid when the change in the number of the oxyethylene or methylene groups is rather small, and only for the first homologs having a short polyoxyethylene chain. Only for the first homologs of nonionic surfactants is the measured polarity proportional to the number of oxyethylene units,[90,124,125] e.g., up to the homologs containing 8 and 16 oxyethylene groups for polyoxyethylene alcohols containing 6 and 14 carbon atoms in their alkyl, respectively. A similar situation occurs for other groups or surfactants.[123,143] This means that constant increments for structural fragments of surfactants can be determined only for the first homologs having an appropriate short polyoxyethylene chain, but a longer chain for surfactants having more methylene groups in their

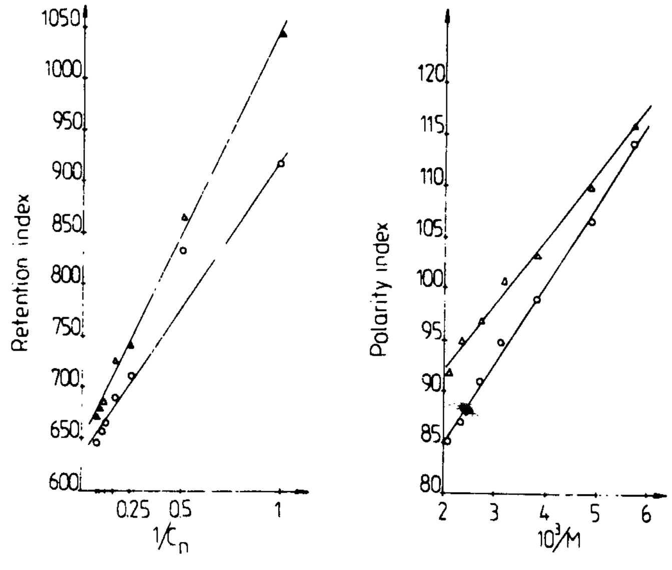


FIGURE 25. Polarity vs. reciprocal of alkyl chain length and of molecular mass for α,ω-diaminooligoether derivatives, $RNH(CH_2CH_2O)_nCH_2CH_2NHR$ (○, methanol; △, ethanol).[53]

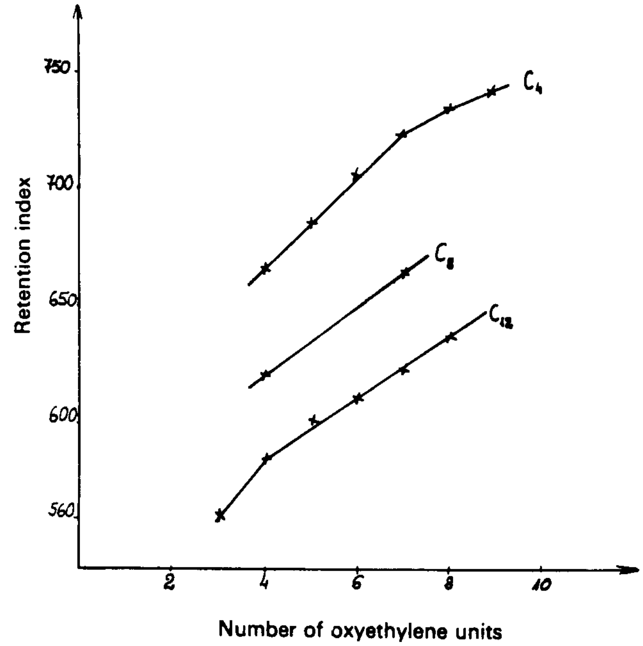


FIGURE 26. Influence of polyoxyethylene chain in polyoxyethylene glycol dialkyl ethers, $RO(CH_2CH_2O)_nR$, on retention index of ethanol.[49]

hydrophobic hydrocarbon chains. However, when surfactants having a longer polyoxyethylene chain are considered, each oxyethylene group that follows causes a smaller increase of the measured polarity, which tends to the constant value characteristic for the polyoxyethylene chain. Thus, in this region, the additivity of the polarity for structural fragments cannot be considered. Moreover, the influence of the polyoxyethylene chain upon surfactant polarity also depends upon the alkyl length.

For polyoxyethylene glycol dialkyl ethers, $RO(CH_2CH_2O)_nR$, having from four to eight oxyethylene groups, the polarity of considered compounds,[47,49] measured by the retention index of methanol and ethanol, the polarity index, and the coefficient ρ, is proportional to the number of oxyethylene groups (Figure 26). Because of this, the additivity rule is satisfied. However, the increments for the oxyethylene group are not constant and their values depend upon the length of the alkyl, decreasing for longer alkyls.[47,49]

Polyoxyethylene glycol dialkyl ethers are significantly less polar than polyoxyethylene alcohols, $R(CH_2CH_2O)_nH$, due to the blocking of the terminal hydroxyl group and the screening of the polyoxyethylene chain by terminal alkyls. This difference in polarities of the considered homologous series diminishes as the length of the polyoxyethylene chain increases and disappears for compounds containing above 12 oxyethylene groups (Figure 27).[144] This suggests that the first oxyethylene groups in the polyoxyethylene glycol dialkyl ethers act as hydrophobes under the experimental conditions of GC.

The replacement of the oxygen atom by sulfur atoms causes decreased polarity. For symmetrical compounds having one

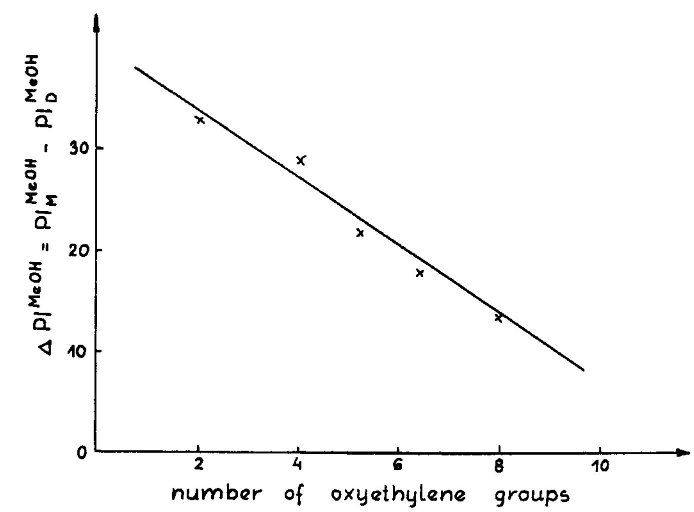


FIGURE 27. Effect of polyoxyethylene chain upon decrease of polarity index for polyoxyethylene glycol dibutyl ethers in comparison to polyoxyethylene alocohols.[144]

central sulfur atom, $R(OCH_2CH_2)_nS(CH_2CH_2O)_nR$, straight line relations between the polarity parameters and the sum of the numbers of oxyethylene and thioethylene groups have been obtained, and they are shifted in a parallel manner toward lower values of the polarity parameters as compared to analogs containing oxygen (Figure 28).[49] This replacement of the central oxygen by a sulfur atom is approximately equivalent to a de-

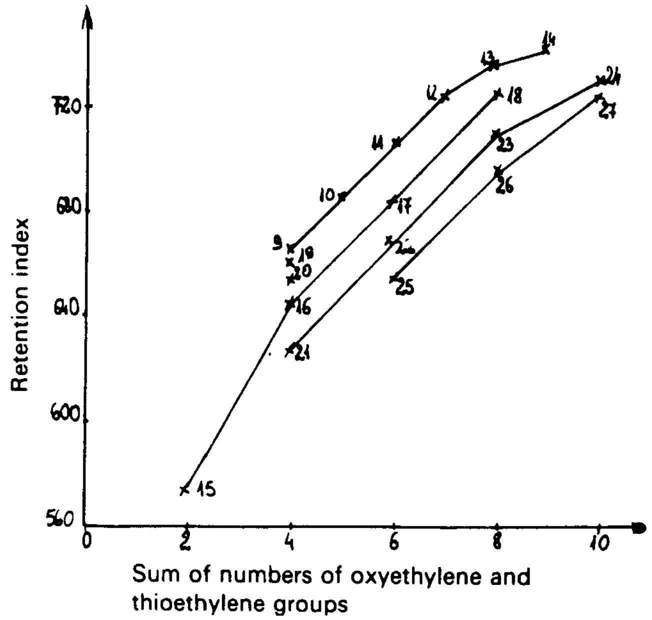


FIGURE 24. Polarity index for symmetrical 1,3-bis-[ω-alkoxyoligo-(oxyethylene)]propan-2-ols, $R(OCH_2CH_2)_nOCH_2CH(OH)CH_2O(CH_2CH_2O)_mR$ (Δ, R = C_4H_9; ▲, R = C_6H_{13}; ethanol as the solute; dashed lines denote the confidence limits for significance level of 0.05).[136]

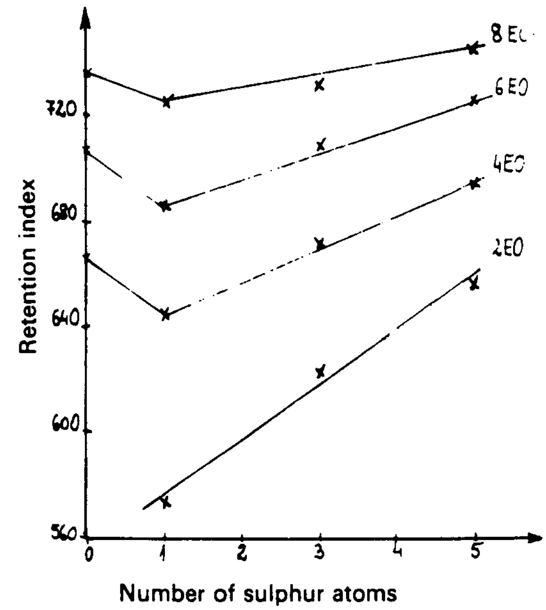


FIGURE 29. Influence of the number of sulfur atoms on retention index of ethanol for polyoxyethylene glycol dialkyl ethers and their sulfur analogs.[49]

crease in the length of the polyoxyethylene chain by one oxyethylene group. Hence, the effective length of a hydrophilic chain for such sulfur analogs is lower than for the appropriate oxygen homologs by about one oxyethylene group. The polarity of sulfur analogs depends on the location of the sulfur atom in the surfactant molecule, and when the asymmetry increases the polarity increases. Thus, the following order of the polarity is observed: $Bu(OE)_2O(EO)_2Bu > BuS(EO)_4Bu > Bu(OE)S(EO)_3Bu > Bu(OE)_2S(EO)_2Bu$ (compounds 9, 19, 20, and 16 in Figure 28), where EO means CH_2CH_2O.

When the next oxygen atoms in the neighborhood of the central sulfur atom are replaced by sulfur atoms, i.e., as the number of thioethylene groups increases, the polarity of such compounds, $R(OE)_n(SE)_mS(ES)_m(EO)_nR$, is lower than appropriate oxygen analogs, but increases proportionally for compounds having a constant number of oxyethylene units (Figure 29).[47,49]

The polarity of compounds having the same alkyls and the same polyoxyethylene groups depends significantly upon the type of the end group bonded with the polyoxyethylene chain. Derivatives of alcohols having a polyoxyethylene chain terminated by methoxyl group, CH_3O, exhibit higher retention indices on apolar phases (Apiezon K, SE-30) than their analogs having a hydroxyl group.[145] An increase of the stationary phase polarity reverses this relationship.

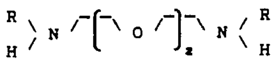
The change of the polarity caused by the introduction of the chlorine atom, as measured by GC, is lower than that of the hydroxyl group but higher in comparison to the methoxy group.[55] As a result, the polarity changes in the following order of compounds considered:[55] $RO(CH_2CH_2O)_nCH_2CH_2OH > RO(CH_2CH_2O)_nCH_2CH_2Cl > RO(CH_2CH_2O)_nCH_2CH_2OCH_3 > RO(CH_2CH_2O)_nCH_2CH_2OR$.

An important factor influencing the polarities of compounds is the type of heteroatom linked to the alkyl group. The highest polarities are exhibited by alkylamine derivatives, while the lowest, by derivatives of alkylthiols. Polyoxyethylene dialkylamines exhibit higher polarities than polyoxyethylene monoalkylamines containing the same numbers of carbon atoms in their alkyls. As a result, the polarity of appropriate polyoxyethylene ethers changes in the following order:[55] $R^1(R^2)N(CH_2CH_2O)_nH > RNH(CH_2CH_2O)_nH > RO(CH_2CH_2O)_nH > RS(CH_2CH_2O)_nH$, where $R^1 + R^2 = R$.

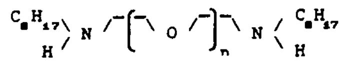
The polarity of 1,3-bis-[ω-alkoxyoligo(oxyethylene)]-propan-2-ols depends significantly upon their symmetry. Compounds having symmetrical oligooxyethylene chains exhibit lower polarity than those having two different oligooxyethylene groups:[51] $RO(CH_2CH_2O)_nCH_2CH(OH)CH_2\ (OCH_2CH_2)_mOR > RO(CH_2CH_2O)_nCH_2CH(OH)CH_2\ (OCH_2CH_2)_nOR$, where n and m are different.

The effect of alkoxy groups is quite opposite of that of the oligooxyethylene chains, and compounds having the same terminal alkoxy groups exhibit higher polarities than those having two different alkoxy groups:[52] $RO(CH_2CH_2O)_nCH_2CH(OH)CH_2\ (OCH_2CH_2)_nOR > R^1O(CH_2CH_2O)_nCH_2CH(OH)CH_2\ (OCH_2CH_2)_nOR^2$, where $R^1 + R^2 = 2R$.

The polarity of α,ω-diaminooligoether derivatives of the following types:[53]



1



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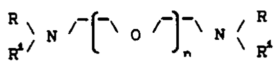

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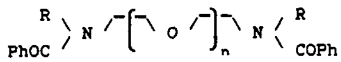

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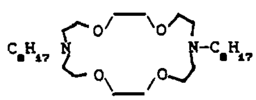


5

where R and R^1 denote alkyl groups (CH_3 to $C_{12}H_{25}$), a cyclohexyl, or a benzoyl group and n equals 2, 3, and 4 depends significantly upon their structures, and increases as the lengths of the alkyl groups and of the oligooxyethylene chain decrease and increase, respectively. These compounds contain two nitrogen atoms bridged by an oligooxyethylene chain, and each linked to combinations of hydrogen atoms and alkyl and acyl groups.

For the first homologs having short alkyls (methyl, ethyl, and butyl) their polarity decreases rapidly as the alkyl length increases (Figure 30). However, a further increase of the alkyl length causes a much weaker decrease in polarity, and approximately linear relations are observed for compounds having from 4 to 12 carbon atoms in each alkyl group. The different

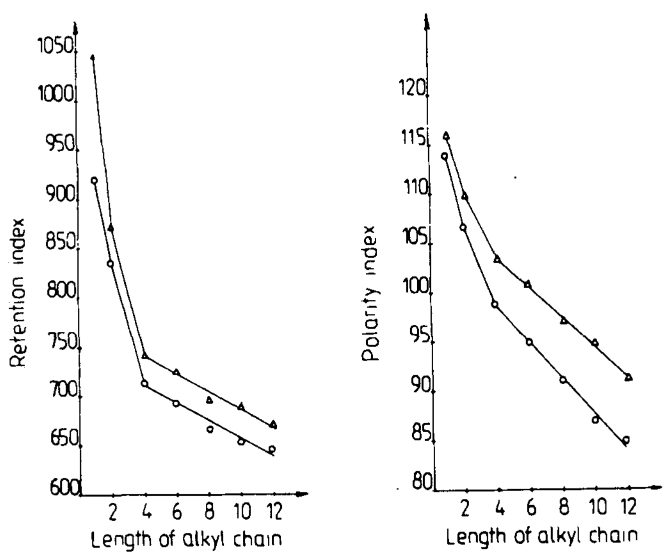
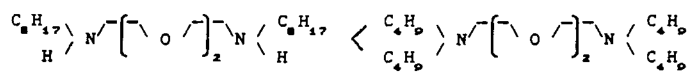


FIGURE 30. Effect of the length of alkyl chain on the polarity of α,ω-diaminooligoethers of the following type, $RNHCH_2(CH_2OCH_2)_2CH_2NHR$ (compounds 1).[53]

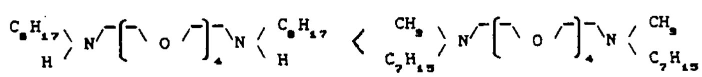
gradients of these relations for each polarity parameter do not significantly depend upon the type of the polar solute and they are similar for methanol and ethanol and for 2-butanone and 2-pentanone, respectively. The effect of the number of oxyethylene groups upon the polarities of the compounds is also approximately linear.[53]

Isomers having each nitrogen atom linked with two short alkyls are much more polar than isomers, in which each nitrogen atom is linked with only one, but a long alkyl group, as in the case of compounds 1e and 3a.

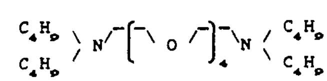


1e 3a

The polarity parameters for compound 3a are higher than for compound 1e by about 100 U for I_R and $\sum_{i=1}^{5} \Delta I_i$, 15 U for PI, and 2 U for coefficient ρ and $\Delta G_s^m(OH)$. This effect is therefore very strong and much more important than the effect of the lengths of the nonpolar alkyl groups and of the polar oligooxyethylene chain. The same effect becomes even stronger as the length of the polar oligooxyethylene chain increases. As compounds 2b and 3b are compared for which n = 4, then the observed increase of the polarity parameters is about 50% higher than in the case of compounds 1e and 3a. This increase is already observed as the hydrogen atoms are replaced by the methyl groups (compound 3c). This replacement causes a similar increase of the polarity parameters with a further change from methyl to butyl group (compounds 3c and 3b).

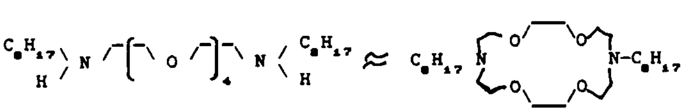


2b ⋧ 3c



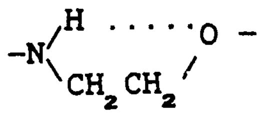
3b

The effect of the oligooxyethylene chain length is also much stronger for compounds having two short alkyls linked with each nitrogen atom (for compounds 3 in comparison to compounds 1 and 2), e.g., for compounds 3a and 3b in comparison to compounds 1e and 2b. In this case, P_i (3b) − P_i (3a) >> P_i(2b) − P_i(1e), where P_i denotes the polarity parameters considered (PI, I_R, ρ, $\Delta G_s^m(OH)$, $\Delta G_s^m(CO)$, and ΣΔI). It is interesting that the linear compound 2b exhibits the same polarity as the cyclic compound 5. The same values of the polarity parameters, including the contributions for the McReynolds constants, were obtained for these two compounds.

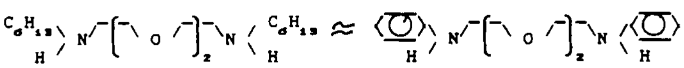


2b ≈ 5

This is probably a result of hydrogen bonding in compound 2b between hydrogen atoms bonded with nitrogen atoms and oxygen atoms present in the oxyethylene groups linked with nitrogen atoms.



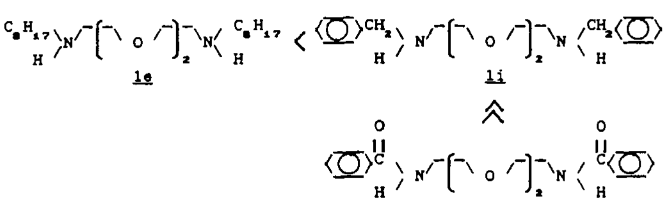
The comparison of the polarity parameters obtained for compounds 1d and 1h demonstrates that these compounds exhibit similar polarities as retention times of alcohols and ketones are considered. Retention indices of alcohols, polarity indices, coefficients ρ, and partial molal Gibbs free energies of solution are almost the same for both these two compounds. However,



1d ≈ 1h

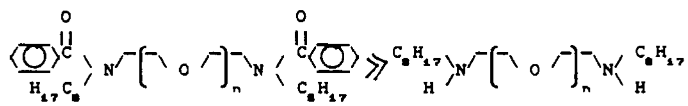
as more complex McReynolds constants are considered, a higher $\sum_{i=1}^{5} \Delta I_i$ is obtained for compound 1d.

The replacement of the octyl group by the benzyl group results in only a small polarity increase (compounds 1e and 1i), which rapidly increases as the octyl group is replaced by the benzoyl group (compounds 1e and 4a). Thus,



1e < 1i ⋀ 4a

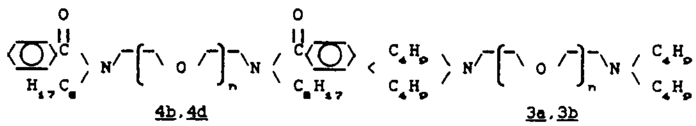
This effect is so strong that compounds 4b, 4c, and 4d are much more polar than compounds 1e, 2a, and 2b, respectively, and they exhibit the polarity near the polarities of compounds 3a and 3b in which each nitrogen atom is bonded with two short butyl groups. Thus,



4b, 4c, 4d ≫ 1e, 2a, 2b

n = 2, 3 and 4, respectively

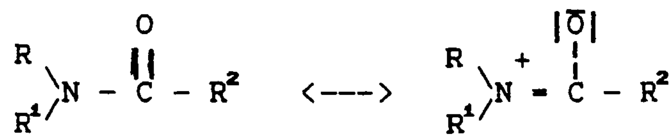
and



4b, 4d < 3a, 3b

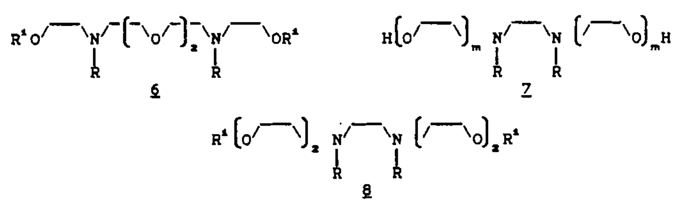
n = 2 and 4, respectively

Compounds 4 have slightly acidic nitrogen atoms and they form two mesomer structures:



As a result, they are more polar than appropriate compounds 1, 2, 3, and 5, in which nitrogen atoms are strongly basic due to the free electron pairs.

The polarity of various isomers of α,ω-diaminooligoether derivatives that contain two nitrogen atoms bridged by an oligooxyethylene chain or by two methylene groups as also considered.[54] Their structures are as follows:



6 7 8

where R and R^1 denote alkyl groups (CH_3 to C_8H_{17}) or hydrogen (R^1) and m is equal 0, 1, or 2.

As demonstrated in Figure 31,[54] the polarity of these compounds depends to a great extent upon the distribution of oxyethylene groups and alkyl chains in the molecule. For compounds 2c, 6a, and 7c having heteroatom bonded protons (=N—H; —O—H), the polarity increases as the oxyethylene groups are shifted from the molecule center into terminal positions (left side of the scheme). The analogous effect is observed for compounds 1e and 7b:

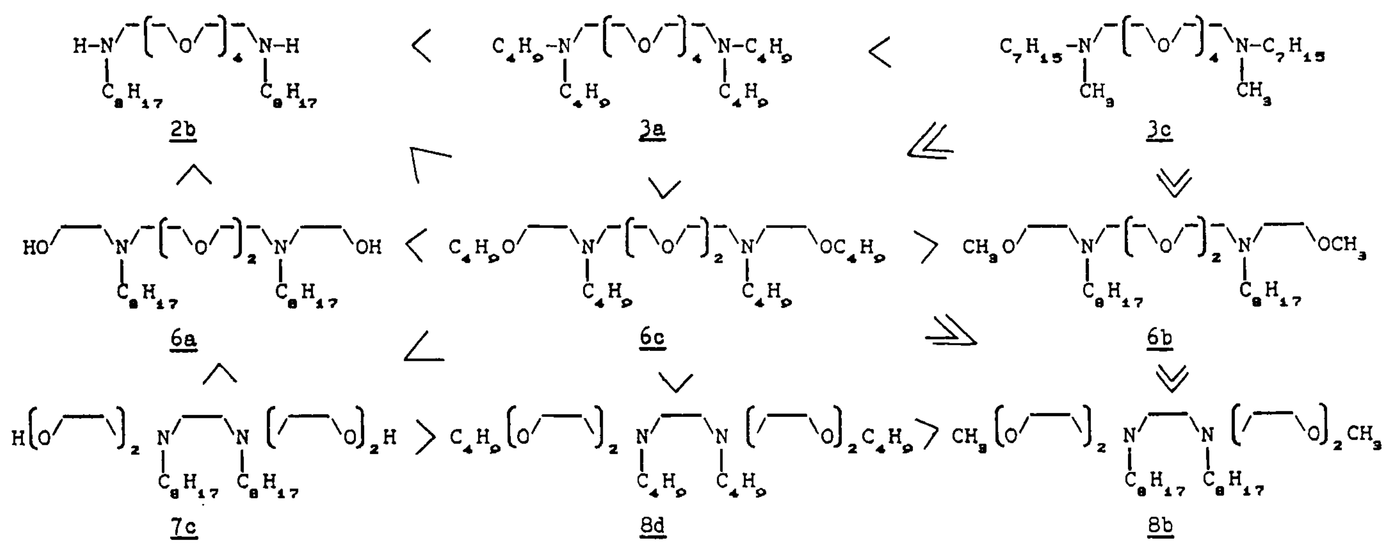
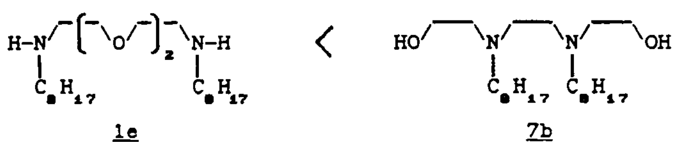
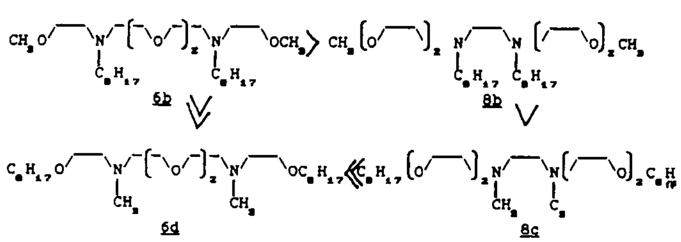


FIGURE 31. Polarity of isomeric α,ω-diaminooligoethers.[54]

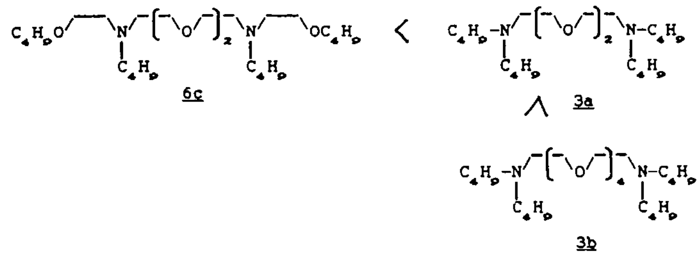


Quite opposite effects are observed for compounds 3c, 6b, and 8b and compounds 3a, 6c, and 8d (the middle and right columns in Figure 31) having four alkyl substituents. The effect is stronger for compounds having four butyl groups (3a, 6c, and 8d) than for compounds having two heptyl or nonyl groups and two methyl groups (compounds 3c, 6b, and 8b). For α,ω-bis-aminooligoethers having two nitrogen atoms bridged by an oligooxyethylene chain it was demonstrated that compounds having four short butyl groups exhibit higher polarities in comparison to those compounds having two octyl groups (first line in Figure 31).[53] As a result, compounds 7c and 8b are more polar than compound 8d. The decrease of the polarity of compounds 6c and 8d is probably caused by the diminishing of the length of the oligooxyethylene chain present in the molecule center and by the screening of the terminal oxygens by hydrophobic alkyl groups. Because of this, oxyethylene groups linked with nitrogen and butyl groups become less polar or even act as nonpolar groups. Such a supposition is confirmed by the comparison of the polarities of compounds 6b, 6d, 8b, and 8c.



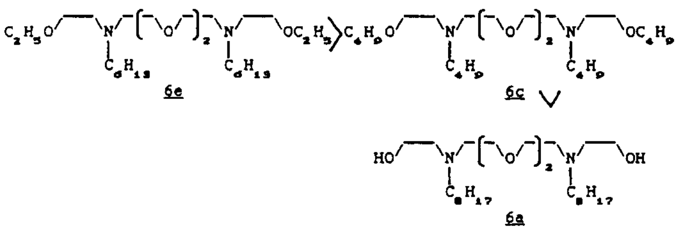
The lowest and highest polarities are shown by compounds 6d and 6b, respectively, having two oxyethylene groups in the centers of the molecules and two oxyethylene groups at the outskirts of the molecules. The screening of the oxygen atom by the bulk octyl group is so effective that the polar character of this oxyethylene group disappears and compound 6d shows such low polarity. The methyl group is small and its effect is relatively weak. Compounds 8b and 8c are only slightly less polar than compound 6b, but much more polar than compound 6d. It means that the presence of two oxyethylene groups on each side of the molecule decreases significantly the screening effect of the terminal alkyl groups. Moreover, the polarities of compounds 8b and 8c, having the bulk octyl group linked with nitrogen and oxygen, respectively, are almost the same. It means also that all compounds with the ethylene diamine structure exhibit only a weak influence over the number of oxyethylene chains and the distribution of alkyl chains in the molecule upon their polarity, as shown for compounds 7 and 8.

The effect of the screening of oxygen atoms by alkyl groups is clearly observed as the polarity of compound 6c is compared to the polarities of 3a and 3b.

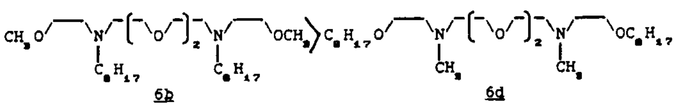


Compound 6c is not only less polar then compound 3b, having four oxyethylene units, but is also somewhat less polar than compound 3a, having only two oxyethylene groups in the molecule center. It means that the polar character of the oxygen atoms diminishes so significantly that the oxyethylene groups linked with the terminal butyls become even somewhat nonpolar.

Compounds 6a, 6c, and 6e are isomers having different distributions of carbon atoms in their alkyls while the number and the distribution of the oxyethylene groups are the same. Their polarities change in the following order:

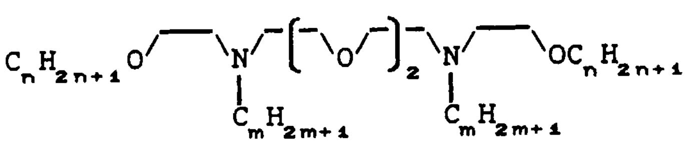


In this case, compounds having short alkyls linked with each nitrogen atom and each terminal oxygen are more polar than compounds having the long alkyl linked with each nitrogen atom. Thus, the conclusion is similar to that reported previously,[53] where it was demonstrated that compounds having two short alkyls connected with the nitrogen atom are more polar than compounds having only one long alkyl group. This effect is even more important than the screening of the oxygen atoms by short alkyl groups. However, the polarity decreases as the length of this alkyl increases. As a result, compound 6c is less polar than compound 6e. Similarly, compound 6d is less polar than compound 6b.



The latter compounds are also less polar than compounds 6a, 6c, and 6e as a result of two additional methylene groups present in their molecules.

The effect of the lengths of the alkyl groups bonded with nitrogen and oxygen atoms, respectively, can be described quantitatively (Figure 32) as the differences between carbon numbers in the alkyls and taken under consideration;[54] for $\Delta n = m—n$



For low and high Δn values, low polarity is observed and it increases as the differences between the numbers of carbon atoms in both alkyls diminish. However, the maximal polarity is not obtained for $\Delta n = 0$, but is somewhat shifted to positive Δn values. As the relation I_R vs. n is considered, where n denotes the number of carbon atoms in the alkyl group bonded with the oxygen atom, the maximal polarity is observed for $n = 2$. It means that the polarity increases only as the alkyl group increases up to the ethyl group. The further increase of this group length results in the decrease of the polarities of the compound.

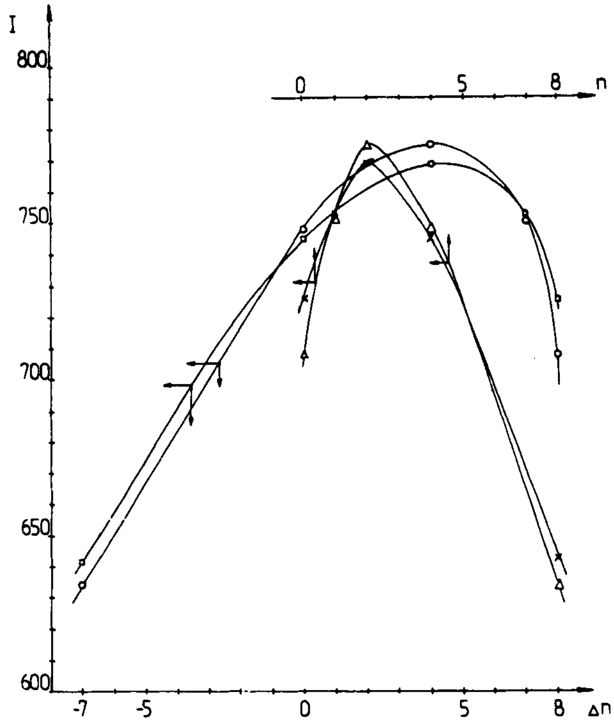
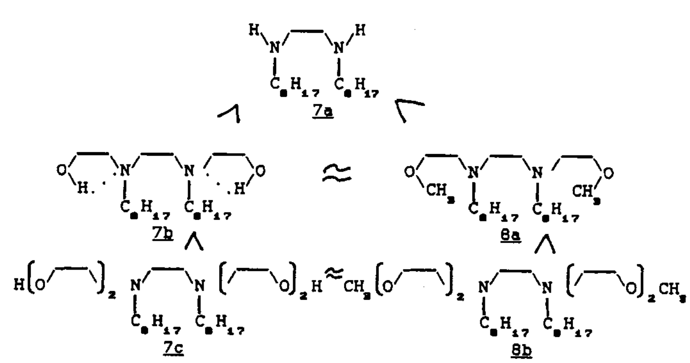


FIGURE 32. Influence of distribution of carbon atoms in alkyl chains upon retention index of alcohol for compounds 6, $R^1OCH_2CH_2N(R)CH_2(CH_2OCH_2)_2CH_2N(R)CH_2CH_2OR^1$ (x, △, methanol; □, ○, ethanol; x, □, 70°C; △, ○, 90°C).[54]

The screening effect of the small methyl group is weak and almost negligible. As a result, compounds having free hydroxyl groups exhibit polarity similar to that observed for compounds having terminal methyl groups, i.e., the polarities of compounds 7b and 7c are similar to those compounds 8a and 8b. The limited decrease in polarity for compound 6a may be attributed to the internal hydrogen bonding which is much weaker for compounds 7b and 7c.



Thus, the effects of the methoxy and hydroxyl groups upon compound polarities are quite similar. Similar relations are observed for compounds of types $RNH(CH_2CH_2O)_nH$ and $RNH(CH_2CH_2O)_nCH_3$, although differences in their polarities are somewhat higher than for compounds having two nitrogen atoms.

For block copolymers of alkylene oxides, which are very complex fragments, calculation of the polarity increments for structural fragments is impossible. However, for three different types of block copolymers of ethylene oxide and α-butylene oxide having a polyoxyethylene chain (E) and a polyoxybutylene chain (B) in the center or at the terminal positions of the molecule, i.e., for block copolymers of the following type: EBE,[146] BEB,[147] and BE,[148] empirical polynomials correlating the polarity parameters with the content of the polyoxyethylene chain (E) and the molecular mass of the polyoxybutylene chain (M_B) were determined,[61,135,149] e.g., for PI:

$$PI = a_0 + a_1E + a_2M_B + a_3E^2 + a_4M_B^2 + a_5EM_B, \quad (85)$$

where E and M_B are in coded forms.

For each group of the considered block copolymers the particular form of Equation 85 is a little different (Table 26),[61] but in each case the polarity depends mainly upon the content of the polyoxyethylene chain, and the influence of the molecular mass of the polyoxybutylene block is much less important. Thus, the polarity of the block copolymers significantly increases as the content of the polyoxyethylene chain increases, but an increase of the molecular mass of the polyoxybutylene chain causes only a small decrease in the polarity. Using equations presented in Table 26, the polarity parameters of ethylene oxide/α-butylene oxide block copolymers can be estimated with satisfactory errors. They are usually below 2% for the carbon atom, retention index, and the polarity index, and about 6% for coefficient ρ.

The column temperature influences the values of the polarity parameters. This influence largely depends upon the molecular mass of the block copolymers, and the differences between the values of the polarity parameters at two standard temperatures, 50 and 100°C, decrease almost proportionally as the molecular mass of the block copolymer increases (Figure 33).[48] This relationship can be used to estimate the molecular mass of the considered block copolymers.

The content of the polyoxyethylene chains can be estimated from the polarity index and the effective length of the hydrophilic blocks according to empirical relations presented in Table 27.[61] The effective length of the polyoxyethylene chain can be calculated according to the following relation:

$$E_{eff} = 1.545\ PI^{MeOH} - 91.5, \quad (86)$$

obtained by rearrangement of Equation 65, or according to Equation 74, discussed in Section V. The relative errors of

Table 26
Relations Correlating Polarity of Ethylene Oxide/α-Butylene Oxide Block Copolymers with Considered Structural Parameters[61]

No.	Copolymer type	Correlation
1	BE	$C = 6.84 + 0.9012\,x_1 + 0.210675\,x_1^2 - 0.03581\,x_2$
2	BE	$PI = 92.23 + 17.5712\,x_1 - 0.80919\,x_2$
3	BE	$I_R = 688.17 + 86.8497\,x_1 + 18.8216\,x_1^2 - 5.59099\,x_2$??
4	BE	$\rho = 1.923 + 1.27482\,x_1 + 0.530991\,x_1^2 - 0.06296\,x_2$
5	BEB	$C = 7.07 + 0.7821\,x_1 - 0.11195\,x_2 + 0.109326\,x_1^2 + 0.129732\,x_2^2 + 0.150231\,x_1x_2$
6	BEB	$PI = 97.53 + 14.4014\,x_1 - 2.0379\,x_2 + 4.18135\,x_1x_2 + 2.56784\,X_2^2$
7	BEB	$I_R = 711.25 + 76.5223\,x_1 - 10.5966\,x_2 + 13.7053\,x_2^2$
8	BEB	$\rho = 2.204 + 1.11297\,x_1 - 0.109368\,x_2 + 0.316016\,x_1^2 + 0.215989\,x_1x_2 + 0.175525\,x_2^2$
9	EBE	$C = 6.96 + 0.744032\,x_1 - 0.181925\,x_2$
10	EBE	$PI = 96.69 + 13.939\,x_1 - 4.014\,x_2 - 3.1377\,x_1^2 + 3.6757\,x_1x_2$
11	EBE	$I_R = 701.12 + 69.7832\,x_1 - 21.3767\,x_2$
12	EBE	$\rho = 2.094 + 0.78035\,x_1 - 0.25216\,x_2$

Codes for correlations:

No. 1—4: $x_1 = \frac{E - 47.6}{27.5}$, $x_2 = \frac{M_H - 1216.5}{618.5}$; No. 5—8: $x_1 = \frac{E - 153.3}{27.4}$, $x_2 = \frac{M_H - 1308.5}{840.5}$; No. 9—12: $x_1 = \frac{E - 51.8}{27.5}$, $x_2 = \frac{M_H - 1256}{758}$.

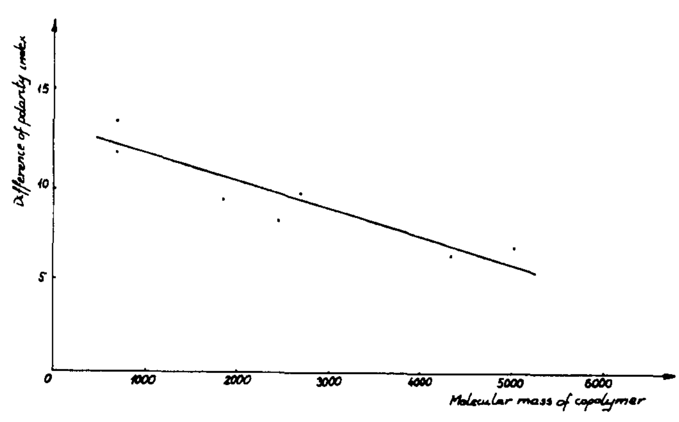


FIGURE 33. Relationship between difference of polarity index of methanol ($\Delta PI^{MeOH} = PI^{50} - PI^{100}$, and molecular mass of ethylene oxide/α-butylene oxide block copolymers.[48]

Table 27
Relations Correlating Polarity Index with Content of Polyoxyethylene Chain[61]

Type of copolymer	Correlation	Correlation coefficient
BE	$\frac{PI}{E_{eff}} = \exp 3.15017 - 0.64995 \ln E$	0.99
BEB	$\frac{PI}{E_{eff}(100 - E_{eff})} = \frac{1}{20.0825 - 2.51252\ 10^{-3}\ E^2}$	0.98
EBE	$\frac{PI}{E_{eff}} = \frac{1}{0.852743 - 12.422/E}$	0.99
	$E_{eff} = 1.545\ PI - 91.5$	

such estimations are 4, 11.5, and 14% for block copolymers for BE, BEB, and EBE types, respectively.[61]

Ethylene oxide/α-butylene oxide block copolymers exhibit somewhat higher hydrophilicity than nonionic surfactants having one hydrophobic hydrocarbon chain and one short polyoxyethylene chain. This is connected with the presence of a polyoxybutylene block in the copolymer.

To quantitatively determine the influence of the polyoxybutylene chain on the polarity of block copolymers, the hydrophilicity index (HI^E, Equation 73) and the hydrophobicity index (HI^P) were used:[61]

$$HI^P = \frac{100 - E_{eff}}{100 - E_{act}}, \tag{87}$$

where E_{eff} and E_{act}, respectively, denote the effective and actual content of the polyoxyethylene chain.

It has been found that both the hydrophilicity and hydrophobicity indices do not undergo greater changes for block copolymers of BE type. However, for other groups of copolymers, i.e., of EBE and BEB type, the influence of the molecular mass of the hydrophobic block and the content of the polyoxyethylene chain are important. The hydrophilicity index decreases and the hydrophobicity index increases with the increase of the molecular mass of hydrophobe, and with the increase of the polyoxyethylene block content (Figure 34).[61] The highest changes are observed for compounds having a low molecular mass of the hydrophobe and a low polyoxyethylene chain content.

The polarity of block copolymers can also be characterized by other parameters such as the water value (WV)[150] and the emulsion inversion point (EIP).[151] Other parameters can also be considered.[151] It has been found that the molecular mass of the block copolymers (M), the content of the polyoxyethylene chains (E), and the molecular mass of the polyoxybutylene chains can be correlated with the polarity parameters according to empirical polynomial equations, which can be used to estimate the considered parameters.[152] Statistical analysis of different relations has shown that the most convenient for estimations are the following relations: M vs. EIP and PI (Figure 35). M_B vs. EIP and PI (Figure 36), and E vs. EIP and PI (Figure 37).[152] Some other relations can be also considered.

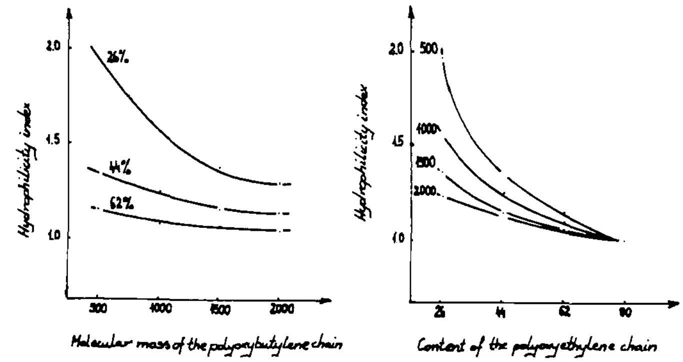


FIGURE 34. Influence of molecular mass of polyoxybutylene block and of polyoxyethylene block content upon hydrophilicity index of ethylene oxide/α-butylene oxide block copolymers of BEB type.[61]

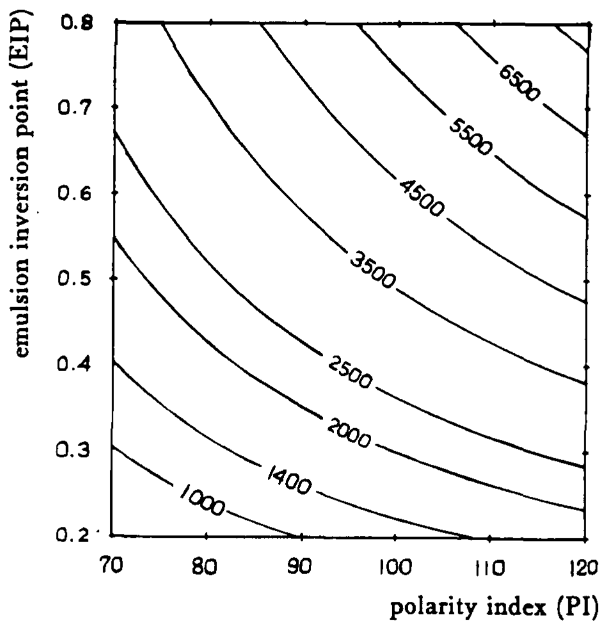


FIGURE 35. Contour lines of constant molecular mass for ethylene oxide/α-butylene oxide block copolymers of EBE type.[152]

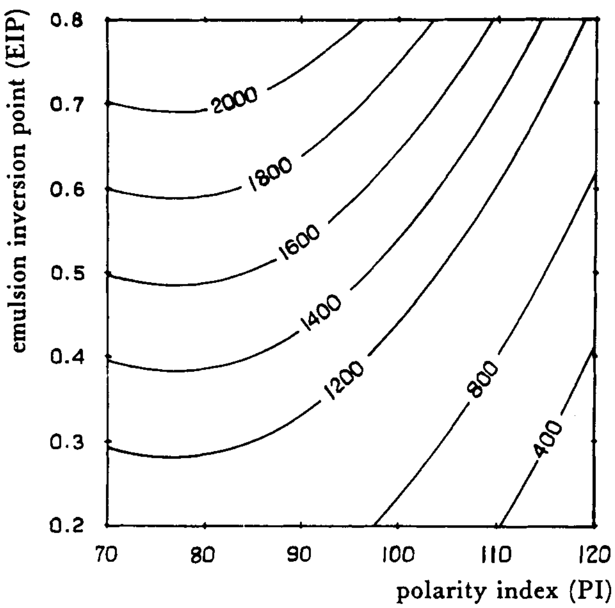


FIGURE 36. Contour lines of constant polyoxybutylene group molecular mass for ethylene oxide/α-butylene oxide block copolymers of EBE type.[152]

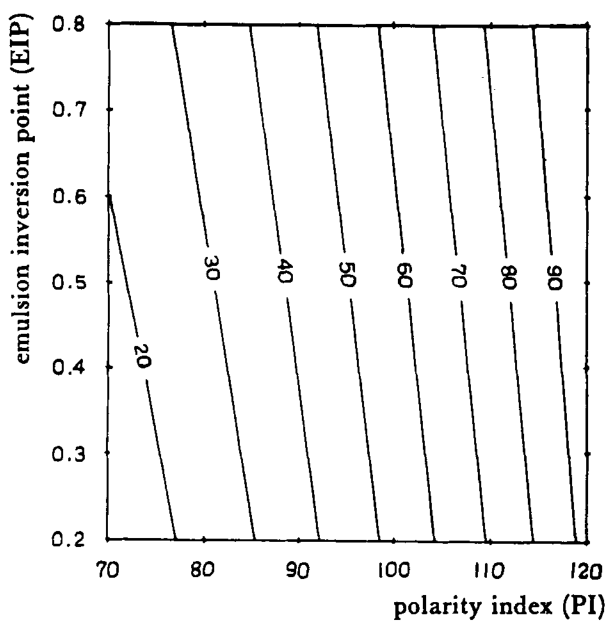


FIGURE 37. Contour lines of constant polyoxyethylene chain content for ethylene oxide/ α-butylene oxide block copolymers of EBE type.[152]

VII. RELATIONS BETWEEN PROPERTIES OF NONIONIC SURFACTANTS AND THEIR POLARITY PARAMETERS

It has been accepted that some properties of nonionic surfactants are connected with their HLB.[27-39] This concerns the solubility of surfactants, their capacity for emulsion formation, and their applications. Thus, if HLB is correlated with the polarity parameters determined by GC, an appropriate modification of Griffin's traditional tables is possible, and some properties and applications of surfactants can be predicted from their polarity parameters, e.g., from the polarity index of methanol (Table 28).

As already mentioned, the block copolymers of ethylene oxide and α-butylene oxide can be characterized by a set of two different polarity parameters; the first determined by GC, and the second characterizing the behavior of block copolymers in an aqueous solution, e.g., the emulsion inversion point (EIP), the point of temperature inversion (PIT), or the water value (WV). Statistically valid polynomial equations were derived to correlate the surface tension of aqueous solutions, foaming, wetting, washing abilities, and emulsion formation for block copolymers with the considered structural and polarity parameters.[153,154] Thus, it is possible to correlate properties of block copolymers both with parameters characterizing their average structure, i.e., E, M_B, and M, and with parameters characterizing their polarity according to the following types of relations:

$$Y_i = a_o + \sum_{i=1}^{n} a_i x_i + \sum_{i=1}^{n} \sum_{j=1}^{n} a_{ij} x_i x_j \qquad (88)$$

or

$$\ln Y_i = a_o + \sum_{i=1}^{n} a_i x_i + \sum_{i=1}^{n} \sum_{j=1}^{n} a_{ij} x_i x_j \qquad (89)$$

where Y_i denotes properties of surfactants considered, x_i and x_j are structural and polarity parameters taken under consideration (E, M, M_B, PI, EIP, PIT, and WV), and a_o, a_i, and a_{ij} are appropriate regression coefficients. These equations were further used to estimate the appropriate optimal polarity parameters for block copolymers exhibiting different properties and to determine the optimal ratios between the content of the polyoxyethylene blocks and the molecular mass of the polyoxybutylene chains (Figures 38 and 39).[146,154]

Good surface, foaming, wetting, and washing properties are exhibited by block copolymers of the EBE type, having the following values for the parameters considered:[146,154] (1) decreasing surface tension: $800 < M_B < 1300$, $20\% < E < 50\%$, $80 < PI < 100$, $7 < WV < 22$; (2) foaming properties: $1000 < M_B < 1600$, $E > 70\%$, $PI > 105$, $WV > 13$; (3) wetting: $1000 < M_B < 1500$, $30\% < E < 60\%$, $85 < PI < 100$, $7 < WV < 16$; (4) washing: $1000 < M_B < 1600$, $E > 50\%$, $PI > 95$, $WV > 9$; and (5) emulsion stability: $800 < M_B < 1600$, $E < 50\%$, $80 < PI < 90$, $8 < WV < 12$, $EIP < 0.5$. The optimal states of the HLB are as follows: (1) decreasing surface tension: $E = 0.048\ M_B - 10.1$ or WV =

Table 28
Polarity Index and Properties of Nonionic Surfactants

PI^{MeOH}	Application	PI^{MeOH}	Emulsion formation	PI^{MeOH}	Solubility in aqueous phase
54—60	Antifoaming agent	52—68	Emulsifier is soluble in oil phase; emulsion is not formed	58—68	Compound does not disperse in water
60—76	Emulsifier W/O	68—76	Emulsion W/O	60—76	Wrong dispersion
80—88	Wetting agent	84—91	Inversion point	76—84	Milky dispersion after stirring
103—111	Detergent	99—111	Emulsion O/W	84—91	Stable milky dispersion
111—123	Solubilization agent	115—130	Emulsifier is soluble in water phase; emulsion is formed	103	Clear solution

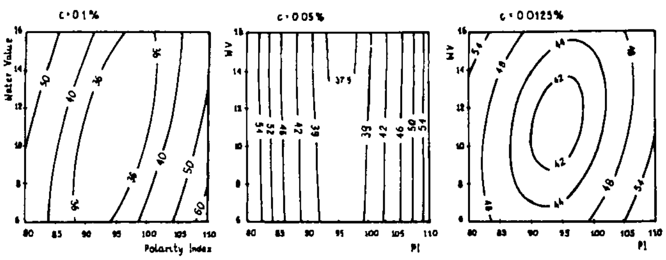


FIGURE 38. Influence of molecular mass and polarity index on surface tension of water solutions of ethylene oxide/α-butylene oxide block copolymers of EBE type (contour lines of constant surface tension of water solutions).[154]

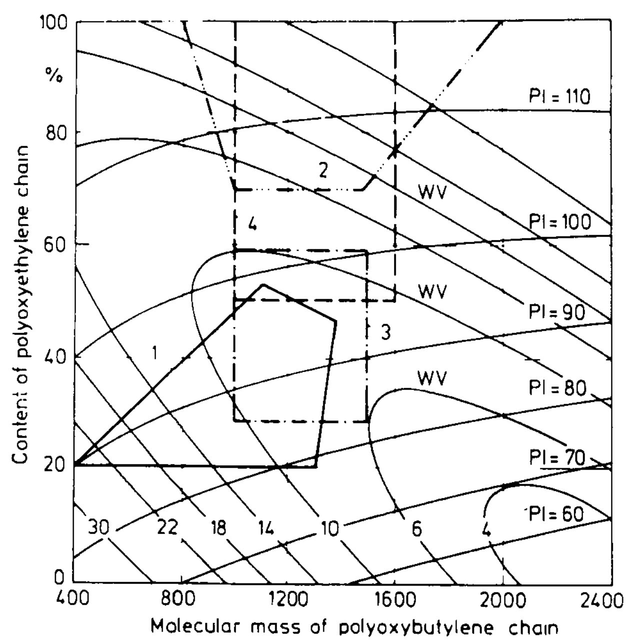
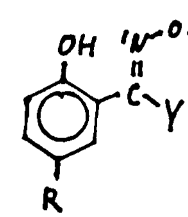


FIGURE 39. Optimal regions of surface activity and usage properties of ethylene oxide/α-butylene oxide block copolymers of EBE type (1, surface activity; 2, foaming; 3, wetting; 4, washing).[146]

$1.277\ PI - 110.5$; (2) foaming properties: $E = 0.258\ M_B - 240.2$; (3) wetting: $E = 0.32\ M_B - 285$; and (4) washing: $M_B = 1200$ for WFK Krefeld standard fabric, and $E = 60\%$ for EMPA 101 standard fabric.[146,154]

VIII. HYDROPHILE LIPOPHILE BALANCE OF HYDROXYOXIME EXTRACTANTS AND KINETICS AND MECHANISM OF COPPER EXTRACTION

Hydroxyoximes of the following general formula:



where R denotes a long alkyl and Y stands for the hydrogen, a short alkyl, or the phenyl, have two slightly hydrophilic groups, i.e., phenolic and oximino groups, and a hydrophobic alkyl.[81,82,155-165] Depending upon the length of the alkyl these oximes can exhibit higher affinity for the aqueous or for the organic phase, or they can adsorb at the interface, thus decreasing the interfacial tension.

It has been found that the polarity parameters determined by GC are proportional to the content of the hydrophilic groups in the oxime molecule (Figure 40), and that the phenolic group shows a contribution to hydroxyoxime polarity which is two times higher than that of the oximino group.[81,82,100] The effective molecular mass of the oximino group as used to calculate the HLB is 8.7, while its ΔHLB^D increment amounts to 1.0.

The HLB on the Griffin and Davies scales are correlated

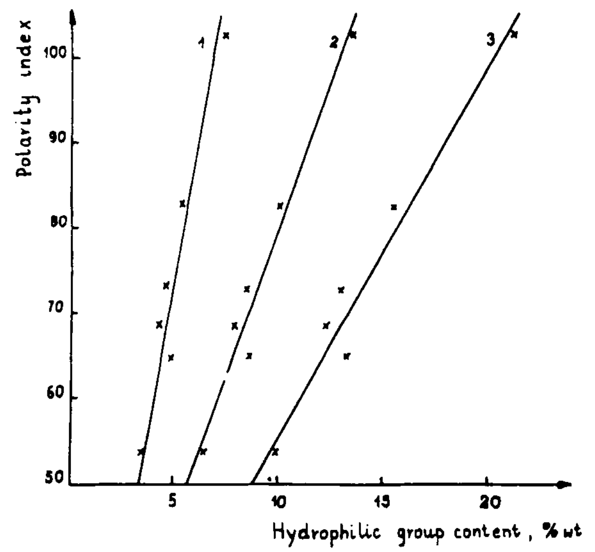


FIGURE 40. Influence of hydrophilic group contents in hydroxyoximes upon polarity index of methanol (1, OH; 2, NOH; 3, OH + NOH).[162]

with the number of carbon atoms in the R and Y groups according to Equations 90 and 91, respectively:[158]

$$HLB^G = \frac{514}{137 + 14n}, \tag{90}$$

$$HLB^D = 9.9 - 0.475(7 + n), \tag{91}$$

where n denotes the sum of the carbon atoms in the R and Y groups. Thus, the relation between the considered HLB coefficients is as follows:

$$HLB^G = \frac{514}{331 - 29.5\ HLB^D}. \tag{92}$$

The solubility of the hydroxyoximes in the aqueous solutions depends upon the hydroxyoxime HLB, and the logarithm of the oxime solubility in the aqueous phase increases proportionally to its HLB value on the Griffin scale.[158]

The rate of copper extraction under constant extraction conditions can be correlated with hydroxyoxime HLB values, and depending upon the method used for kinetic studies, somewhat different relations are obtained. When the interface is constant, the extraction rate increases as the HLB of oximes increases.[158,162]

For hydroxyoximes considered HLB^G values vary in the range of 1.5 to 3.5, and HLB^D values vary from 1 to 6. Such high hydrophobicity of hydroxyoximes supports the interfacial mechanism for the oxime reaction with copper. The largest part of the hydroxyoxime molecule should be within the organic region of the interphase as the weakly hydrophilic groups cannot penetrate deeply into the aqueous phase. However, due to the very low hydrophilicity of hydroxyoximes having a large alkyl group, the decrease in the length of the hydrocarbon chain causes a sharp increase in the polarity, although the hydrophobic part of the molecule always dominates the hydrophilic groups. As a result, the oxime molecule may penetrate more deeply into the aqueous layers in the direct neighborhood of the interface, and eventually a change in the extraction mechanism occurs. In the homogeneous phase, the reaction proceeds more quickly than in the heterogeneous system with a small interfacial area.

In the region of low HLB values (below $HLB^G = 2.2$ and $HLB^D = 3$), the extraction rate depends strongly upon the oxime structure, and some deviations of the experimental data are observed (Figure 41).[162] Thus, this effect is observed in the region where extraction proceeds at the interface, or the interfacial reaction dominates the volume reaction in the aqueous phase. It is assumed that depending upon the HLB values complexing can proceed in the bulk of the aqueous phase (for oximes having $HLB^G > 2.8$), at the interface (for oximes having $HLB^G < 1.7$), or simultaneously in the bulk of the aqueous phase and at the interface (for oximes having $1.7 < HLB^G < 2.8$).[162] Thus, the extraction of copper by hydroxyoximes proceeds at the interface or in the bulk of the aqueous phase when the number of carbon atoms in both R and Y groups is not less than 11 or not greater than 3, respectively. For oximes having a total of from 3 to 11 carbon atoms in these two groups, the extraction occurs at the interface as well as in the bulk of the aqueous phase. The mechanism of these processes is discussed elsewhere.[159-165]

This critical number of carbon atoms can change slightly

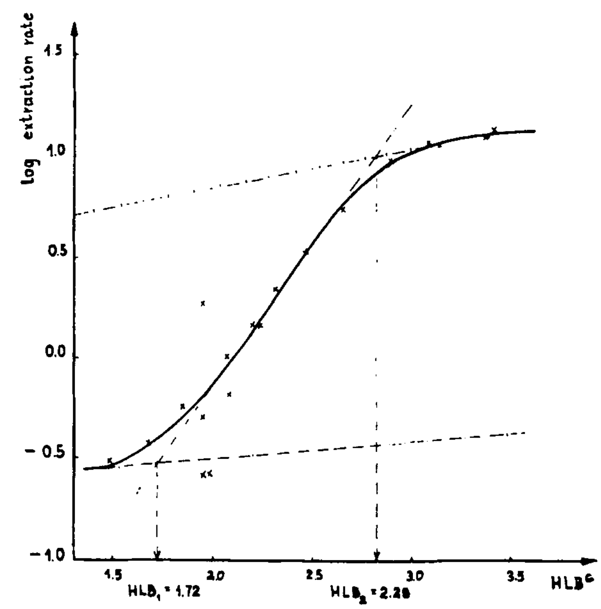


FIGURE 41. Influence of hydrophilic lipophilic balance upon copper extraction by hydroxyoximes.[162]

depending upon the experimental conditions and upon the method used for the extraction rate determination. This is due to different hydrodynamic conditions and different physicochemical parameters describing the extraction system; in particular, the influence of the diluent type should be quite substantial.

The contribution (β) of the volume reaction to the measured reaction rate (v) can be expressed by Equation 93:

$$v = v_v \beta + v_s (1 - \beta). \tag{93}$$

Thus,

$$\beta = \frac{v - v_s}{v_v - v_s} 100\%. \tag{94}$$

The results presented in Figure 42[162] show that for oximes having a total of not less than 11 carbon atoms in the alkyl groups the contribution of the volume reaction is less than 10%, while for oximes having a total of not more than 3 carbon atoms the contribution is above 90%. A contribution of 50% is obtained for oximes containing 6 to 7 carbon atoms both in the R and Y groups. Thus, the contributions of the volume reaction for some commercial extractants can be estimated as 5, 15, and 20% for Lix 65N, SME 529, and P 50, respectively.

IX. CONCLUSIONS

In the published literature concerning surfactants, measurements of the surfactants' polarities by means of GC are considered as the measurements of the HLB, and appropriate empirical relations between these parameters have been derived. Certain polarity parameters can also be used as analytical coefficients to characterize the average structure of nonionic surfactants. It is also possible to correlate the properties of surfactants and extractants with their polarity parameters, which can be precisely and accurately determined. These relationships can be used to predict the properties of surfactants from their polarity parameters. The use of polarity and the retention indices of ethanol or methanol and the sum of the first five McReynolds constants is favorable. These parameters can be estimated with reasonable accuracy from structural increments determined for characteristic fragments of surfactants. The polarity parameters can also be used to describe the behavior of extractants and surfactants at various liquid/liquid interfaces; as a result, they can be used to assess kinetic data and the mechanism of metal extraction by various extractants. Some new applications of polarity parameters for surfactants and extractants will continue to be examined in the future.

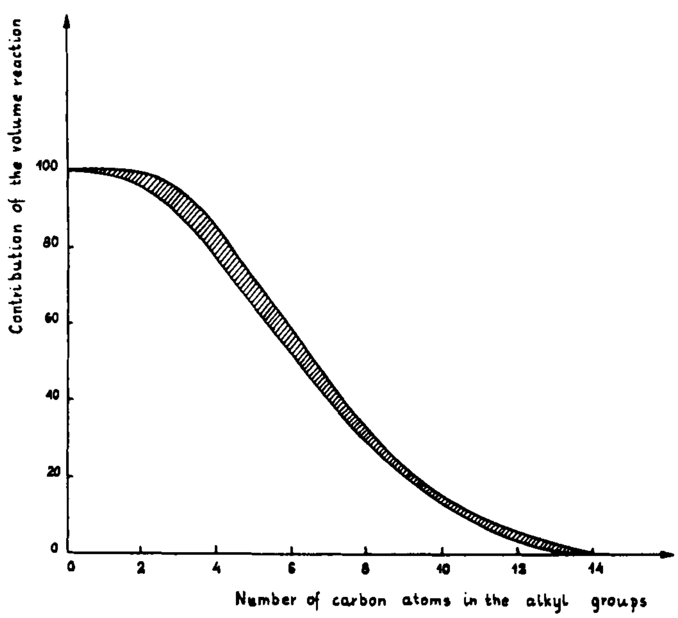


FIGURE 42. Influence of number of carbon atoms in R and Y groups upon contribution of volume reaction.[162]

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