

Polarity of Broad and Narrow Distributed Ethoxylates of Fatty Alcohols

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The polarity of broad- and narrow-range alcohol ethoxylates was studied by inverse gas chromatography. The narrow-range alcohol ethoxylates (NRD) exhibit higher polarity at 70°C than the broadly distributed products (BRD). The difference in polarity between BRD and NRD products decreases, however, with increasing temperature and diminishes at 110°C, which can be predicted from structural increments. The rise of the average number of oxyethylene units increases polarity of the examined products. The changes of ethoxylate polarity are well described by examined parameters with the exception of $\Delta G_s^m(\text{CH}_2)$.

KEY WORDS: Broad- and narrow-range ethoxylates, fatty alcohol inverse gas chromatography, polarity.

Ethoxylates are the most important nonionic surfactants. They are used in the manufacturing of a wide variety of surface-active agents, e.g., cleaning and washing agents, emulsifiers. They are obtained by addition of oxirane to hydrophobic substrates having a labile hydrogen atom in their molecules. Ethoxylates of fatty alcohols, fatty acids, alkylphenols and polypropylene diols are of industrial importance. The products of ethoxylation, however, are always mixtures of adducts with different lengths of the ethoxylene chain. The following possibilities influence the properties of ethoxylates: (i) selection of the hydrophobic substrate; (ii) change of average ethoxylation degree and (iii) the distribution of oxirane adducts in the final mixture.

Competition on the surfactant market and ecological requirements cause an increasing interest in alcohol ethoxylates with confined content of homologues, which have an ethoxylation degree significantly different from the average and which are free from harmful by-products. Generally, ethoxylated fatty alcohols are biodegradable easier than, for example, ethoxylated alkylphenols (1). Furthermore, it is possible to improve the properties desired in many practical applications by using fractions with a narrow homologue distribution (2-6). The properties of surface-active agents usually depend on the hydrophile-lipophile balance (HLB) and/or on their polarity (7,8). Inverse gas chromatography is a simple procedure, which allows the definition of accurate and reliable quantitative parameters for the polarity determination of organic compounds such as surfactants (9,10), organic salts (11) and extractants (12-14).

A number of empirical relationships between the behavior of surfactants and their polarity parameters (PPs) have been applied for the prediction of their properties. The PPs can be divided into two groups: (i) empirical PPs, which include polarity index and retention index and (ii) thermodynamically defined parameters (thermodynamic functions of solution, criterion A and partial molar excess Gibbs function of solution). The PPs are related to the HLB number, which is a generally accepted characteristic of surfactants (15-18).

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The aim of this paper is the determination of the PPs for ethoxylates with broad and narrow ethoxylene distributions. It is of interest to discover how the difference in substance composition influences the polarity. A relationship between the structure [average number of ethylene oxide (EO) units, type of their distribution] and surfactant polarity is also examined and discussed.

EXPERIMENTAL PROCEDURES

Materials. Cetyl alcohol containing 94% hexadecanol was used both to prepare the conventional products [with broad-range distribution of homologue (BRD)] and the narrow-range distribution ethoxylates (NRD), in which the average degree of ethoxylation varies from 3 to 11. The conventional products were obtained by using sodium hydroxide as a catalyst, while a proprietary catalyst (19) was utilized to produce narrow-range ethoxylates.

Syntheses were performed in a 1-L stainless steel jacket reactor, equipped with a driven stirrer and a cooling coil. In each process, the reactor was charged with the alcohol substrate and an appropriate amount of the catalyst. Then the reactor was closed, vented with nitrogen and heated to the reaction temperature. After the desired temperature was achieved, ethylene oxide was admitted to the reactor from a container that had been pressurized first with nitrogen at 0.6 MPa. The pressure of EO in the reactor was kept constant by opening or closing a micrometric valve. Samples of the reaction mixtures were withdrawn at intervals and analyzed by gas chromatographic (GC) technique.

Homologue distribution of the ethoxylation products was analyzed with a GC (Perkin-Elmer Model 900, Norwalk, CT) equipped with a flame-ionization detector. The separation was carried out in stainless-steel columns of 0.9 m length and 2.7 mm i.d. Chromosorb G-AW-DMCS (60-80 mesh; Supelco SA, Gland, Switzerland) was used as support and silica resin OV-17 (Supelco SA) as the liquid phase. The weight ratio of the liquid phase to the support was 1:99. Argon was used as a carrier gas; its flow rate was 15 cm³/min. The injector and detector temperatures were 330 and 340°C, respectively. The analyses were started with a column temperature at 120°C, which after 1 min was programmed up to 320°C with a rate of 4°C/min. The products were analyzed as acetate derivatives.

Contents of the components with different lengths of the oligooxyethylene chain in representative pairs of ethoxylates are given in Figure 1. Comparison of the homologue distribution for the products indicates the slight shift of the maximum of the NRD products toward the homologues having a higher oxyethylene content.

Polarity parameters. The following parameters were used to express the ability of examined surfactants to interact by different intermolecular forces with the selected group of standard solutes: (i) the difference of retention indices of the first five McReynolds solutes as measured

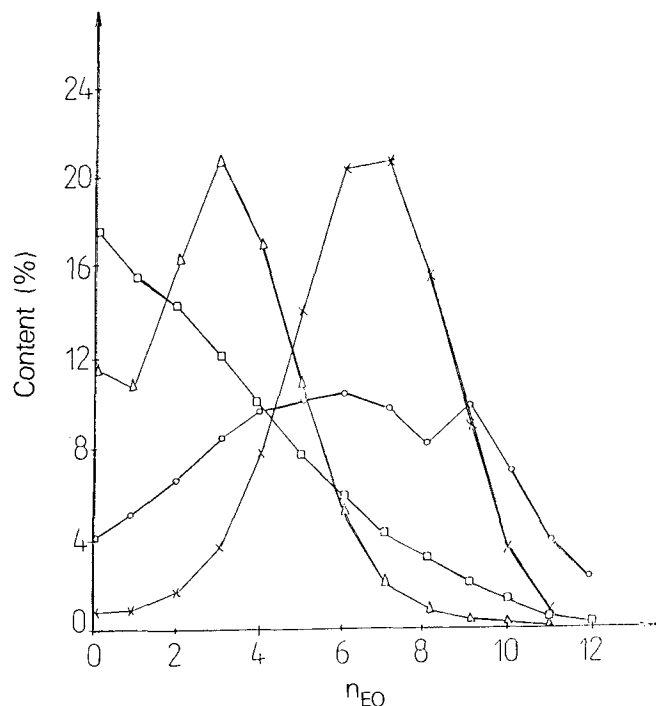


FIG. 1. Distribution of homologues in broad-range distribution (BRD) and narrow-range distribution (NRD) ethoxylates ($x = C_{16}E_7 - \text{NRD}$, $o = C_{16}E_7 - \text{BRD}$, $\Delta = C_{16}E_3 - \text{NRD}$, $\square = C_{16}E_3 - \text{BRD}$). EO, ethylene oxide.

on examined liquid phase and squalane ΔI_i , as well as their sum $\sum_{i=1}^5 \Delta I_i$ (20); (ii) coefficient ρ , defined as the ratio of adjusted retention times of standard polar solute (methanol or ethanol) to a nonpolar one (*n*-hexane) (21); (iii) polarity index (PI), defined by Huebner (22) for

characterization of surfactants by GC; (iv) criterion A (23) and partial molal Gibbs free energy of the solution per methylene group ΔG_s^m (CH_2) (24,25), which are the parameters that characterize dispersive interactions between the solute and the solvent. Criterion A was calculated from the equation:

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

where $t'_{r,n+1}$, $t'_{r,n}$ and $t'_{r,n-1}$ and $t'_{r,n-1}$ denote adjusted retention times for *n*-alkanes with *n* + 1, *n* and *n* - 1 carbon atoms, respectively.

The examined ethoxylates were placed in a GC column as a liquid stationary phase coated on an inert support [Celite 80-120 mesh (25%, w/w)]. The use of such a high content of liquid phase has been suggested to eliminate adsorption effects. The other conditions of the GC experiments were as follows: a GC CHROM 5 (CSRF, Kova, Praha, Czech Republic) equipped with a flame-ionization detector; columns, 1 m length and 3 mm i.d.; column temperature, isothermally at 70, 90 and 110°C; injector and detector temperatures, 150 and 200°C, respectively; carrier gas flow rate (helium), 40 cm³/min. The C₅-C₉ *n*-alkanes and the first five McReynolds solutes (20) were used, and their adjusted retention times were determined according to the typical procedure (17,26,27).

RESULTS AND DISCUSSION

Liquid stationary phases are usually characterized by the difference in retention indices for selected solutes; ΔI_i , proposed by McReynolds, as well as by the sum of the differences for the first five solutes. It has been shown that these parameters can be used in the characterization of surface-active agents (17,25). The appropriate values of

ΔI_i and $\sum_{i=1}^5 \Delta I_i$, as determined by us, are summarized in Table 1.

TABLE 1

ΔI_i of McReynolds Solutes and $\sum_{i=1}^5 \Delta I_i$ Values for Ethoxylates Examined at 70°C^a

Type	Average number of EO units	ΔI_i for					$\sum_{i=1}^5 \Delta I_i$	
		Bz	MPK	Butanol	Pyridine	Np		
BRD	3	74.9	135.1	292.9	188.5	202.7	894.1	
	4	83.3	141.8	305.5	199.5	222.5	952.6	
	5	103.1	160.3	322.1	218.2	252.6	1056.3	
	6	104.2	162.4	323.8	219.9	257.6	1068.1	
	7	111.7	167.6	323.4	226.6	267.1	1096.5	
	8	110.4	169.1	332.3	231.7	269.4	1112.9	
	9	123.7	180.9	346.1	244.9	289.5	1185.1	
	10	130.2	186.8	346.7	246.0	297.6	1207.2	
	11	136.2	193.5	345.8	258.5	296.8	1230.8	
	NRD	3	86.0	144.4	300.0	195.9	217.5	943.9
		4	75.6	145.2	281.4	202.3	213.4	918.0
5		104.5	165.7	302.6	229.7	249.7	1052.8	
6		121.1	181.7	330.1	229.7	270.7	1132.8	
7		121.8	177.6	311.7	239.1	275.1	1125.2	
8		142.2	196.9	362.3	270.6	309.6	1281.7	
9		127.2	194.2	341.1	248.7	285.8	1197.0	
10		146.6	198.2	347.7	250.6	300.5	1243.7	
11		140.1	197.2	364.7	263.8	310.7	1276.5	

^aAbbreviations: BZ, benzene; MPK, methyl propyl ketone; Np, nitropropane-1; EO, ethylene oxide; BRD, broad-range distribution; NRD, narrow-range distribution.

POLARITY OF BROAD AND NARROW DISTRIBUTED ETHOXYLATES

TABLE 2

Polarity Index for Broad- and Narrow-Range Ethoxylates of Cetyl Alcohol^a

Type	Average number of EO units	Polarity index at						
		Methanol (°C)			Ethanol (°C)			
		70	90	110	70	90	110	
BRD	3	77.4	74.0	65.8	92.4	88.8	84.2	
	4	79.5	76.1	71.5	93.3	90.7	87.1	
	5	78.7	83.9	74.6	90.3	94.9	91.3	
	6	80.7	85.0	78.0	91.7	96.0	92.9	
	7	88.3	84.7	81.2	98.6	96.3	93.7	
	8	89.4	87.7	82.8	99.6	98.4	95.0	
	9	92.9	90.2	84.9	102.1	99.8	95.4	
	10	93.3	92.7	88.6	101.7	101.7	98.2	
	11	92.7	90.4	84.0	102.9	100.0	95.5	
	NRD	3	78.6	72.0	62.8	92.7	88.8	91.9
		4	80.2	74.7	65.9	93.3	89.9	83.3
5		83.6	80.6	74.8	94.8	93.5	89.3	
6		84.1	83.5	77.6	95.6	95.3	91.6	
7		87.6	83.6	77.8	95.8	95.4	91.4	
8		93.1	87.0	81.8	103.0	97.7	94.1	
9		89.5	84.3	79.4	102.9	96.4	92.9	
10		95.5	90.2	89.2	104.5	100.6	99.1	
11		95.2	91.4	87.1	104.0	101.5	98.4	

^aSee Table 1 for abbreviations.

TABLE 3

Coefficient ρ for Broad- and Narrow-Range Ethoxylates of Cetyl Alcohol^a

Type	Average number of EO units	Coefficient ρ at						
		Methanol (°C)			Ethanol (°C)			
		70	90	110	70	90	110	
BRD	3	1.15	1.05	0.91	1.94	1.61	1.37	
	4	1.27	1.13	1.00	2.08	1.76	1.46	
	5	1.25	1.40	1.08	1.84	2.04	1.67	
	6	1.31	1.42	1.23	1.94	2.09	1.74	
	7	1.64	1.42	1.23	2.50	2.14	1.77	
	8	1.70	1.54	1.32	2.60	2.27	1.91	
	9	1.95	1.72	1.37	2.96	2.51	1.89	
	10	2.07	1.87	1.53	3.01	2.69	2.11	
	11	1.97	1.78	1.47	3.07	2.52	2.00	
	NRD	3	1.22	0.99	0.86	1.98	1.56	1.30
		4	1.33	1.14	0.98	2.10	1.77	1.41
5		1.36	1.33	1.16	2.08	1.99	1.67	
6		1.37	1.37	1.14	1.96	2.07	1.66	
7		1.76	1.43	1.25	1.98	1.93	1.78	
8		1.92	1.53	1.26	2.87	2.28	1.79	
9		1.83	1.50	1.32	2.82	2.23	1.87	
10		2.30	1.70	1.53	3.51	2.53	2.14	
11		2.28	1.84	1.60	3.38	2.62	2.22	

^aSee Table 1 for abbreviations.

The determination of ΔI_i and $\sum_{i=1}^5 \Delta I_i$ values is usually a troublesome and time-consuming procedure. It requires estimation of retention data for five selected polar solutes and the reference *n*-alkanes on two liquid phases, namely the phase to be evaluated and squalane as the nonpolar one. The use of PI and coefficient ρ as empirical measures of polarity allow surfactants to be characterized with acceptable precision (17,27). Moreover, the parameters reflect structural changes quite satisfactorily. The values of PI and coefficient ρ , which were measured with methanol and ethanol as the polar solutes, are given in Tables 2 and 3.

There is no general rule to describe the temperature dependence of $\sum_{i=1}^5 \Delta I_i$. However, for all BRD, the $\sum_{i=1}^5 \Delta I_i$ value increases with increasing temperature, while it decreases mainly for their NRD. Generally, the PI and coefficient ρ decrease with the rise of temperature.

The most interesting phenomenon we found is a relationship between the homologues' distribution and the polarity of the examined ethoxylates. The broad-range compounds exhibit lower polarity (at 70°C) than their narrow-range analogs (Fig. 2). However, the difference

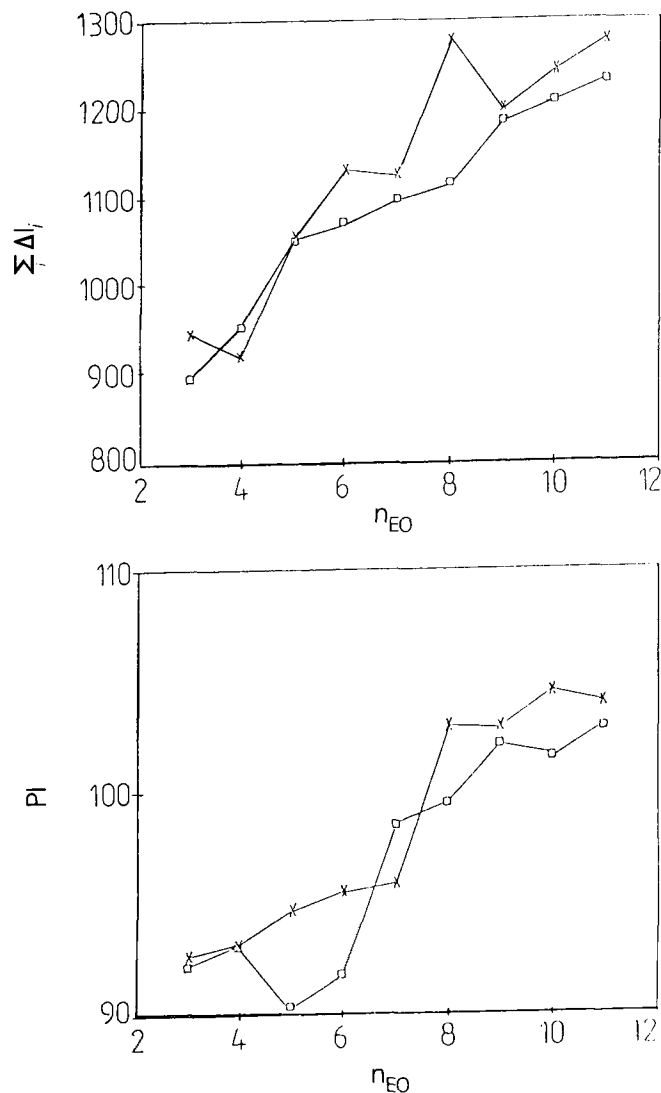


FIG. 2. $\sum_{i=1}^5 \Delta I_i$ and polarity index (PI) (ethanol as polar solute) for BRD and NRD ethoxylates (x = NRD, □ = BRD). Abbreviations as in Figure 1.

diminishes with increasing temperature. PPs for individual components can be estimated according to the following equation:

$$PP = \text{constant} + \sum a_i \Delta PP_i \quad [2]$$

by using structural increments determined previously (26). It is assumed that the increment of ΔPP_i for a group G_i is constant for all compounds. The coefficient a_i denotes the number of the G_i group in the compound under consideration.

PPs of polydisperse mixtures can be estimated from the relation:

$$PPM_M = \sum x_i \cdot PP_i \quad [3]$$

where x_i denotes the weight fraction and PP_i and PP_M are the polarity parameter of the i -th individual component and of the polydisperse mixture, respectively. The predicted PPs as well as the experimental values for the three pairs of NRD and BRD analogs are given in Table 4.

The predicted PPs are generally higher for the NRD analogs. However, the difference changes from pair to pair and seems to be negligible for $C_{16}E_6$ products. The most important difference is that observed for $C_{16}E_7$ analogs; it is probably connected to the significant shift of the maximum presented in Figure 1. It is in accordance with the experimental results shown in Figure 2.

For the BRD products, higher experimental values are obtained for PI^{MeOH} and $\sum_{i=1}^5 \Delta I_i$. However, the experimental value for PI^{EtOH} is 91.7, lower than the predicted value. Higher experimental values were also observed for NRD products. The difference was the highest for $C_{16}E_3$.

The HLB numbers were calculated according to the definition equation from an average content of oxyethylene units, $HLB = 20 \cdot M_H/M$, where M_H and M denote molecular weights of the hydrophile part and of the whole molecule, respectively. The HLB numbers were also obtained from the following relation (17,28):

$$HLB^G = 0.213 \cdot PI - 7.05 \quad [4]$$

TABLE 4

Predicted and Measured Polarity Parameters for $C_{16}E_n$ NRD and BRD Analogs (70°C)^a

Ethoxylate	Parameter	PI^{MeOH}		PI^{EtOH}		Total ΔI_i		HLB	
		pred.	exp.	pred.	exp.	pred.	exp.	$HLB^G{}^b$	$HLB^G{}^c$
$C_{16}E_3$	NRD	67.3	78.6	80.9	92.7	616	944	6.0	9.7
	BRD	66.4	77.3	79.9	92.3	599	894	5.7	9.4
$C_{16}E_6$	NRD	79.0	84.1	89.7	95.6	898	1132	8.9	10.8
	BRD	79.3	80.7	90.4	91.7	894	1068	8.4	10.1
$C_{16}E_7$	NRD	89.1	87.6	99.8	99.9	1073	1125	10.3	11.6
	BRD	83.2	88.3	94.0	91.7	965	1056	9.1	11.8

^aAbbreviations: PI, polarity index; pred., predicted; exp., experimental; HLB, hydrophile-lipophile balance. Also see Table 1 for abbreviations.

^b HLB^G predicted from definition (see text).

^cCalculated according to Equation 4.

POLARITY OF BROAD AND NARROW DISTRIBUTED ETHOXYLATES

TABLE 5

Criterion A for Broad- and Narrow-Range Distribution of C₁₆E_n Products and Its Temperature Dependence^a

Type	Average number of EO units	Criterion A (°C)			A = * exp (b/T)			
		70	90	110	a	b	R ^b	
BRD	3	2.343	2.147	2.002	0.518	517.1	0.9999	
	4	2.324	2.157	1.971	0.484	539.6	0.9960	
	5	2.307	2.132	1.948	0.460	554.3	0.9980	
	6	2.313	2.126	1.973	0.505	522.2	1.0000	
	7	2.253	2.130	1.942	0.551	485.2	0.9850	
	8	2.261	2.118	1.976	0.625	441.8	0.9990	
	9	2.299	2.150	1.922	0.421	584.9	0.9850	
	10	2.299	2.150	1.941	0.599	453.2	0.9840	
	11	2.230	2.118	1.934	0.480	533.5	0.9999	
	NRD	3	2.256	2.177	1.984	0.674	418.1	0.9600
		4	2.320	2.160	1.990	0.537	502.8	0.9970
5		2.270	2.128	1.977	0.608	452.9	0.9980	
6		2.221	2.149	1.957	0.676	411.5	0.9550	
7		2.210	2.108	1.970	0.742	375.9	0.9910	
8		2.188	2.159	1.935	0.698	397.4	0.9110	
9		2.184	2.111	1.965	0.806	344.4	0.9730	
10		2.145	2.095	1.944	0.852	319.7	0.9480	
11		2.163	2.067	1.938	0.762	359.2	0.9910	

^aSee Table 1 for abbreviations.

^bCorrelation coefficient.

TABLE 6

$\Delta G_s^m(\text{CH}_2)$ for Broad- and Narrow-Range Distribution of C₁₆E_n Products^a

Type	Average number of EO units	$\Delta G_s^m(\text{CH}_2)$ [kJ/mol] (°C)			
		70	90	110	
BRD	3	-2.42	-2.31	-2.20	
	4	-2.43	-2.29	-2.17	
	5	-2.40	-2.26	-2.13	
	6	-2.39	-2.27	-2.14	
	7	-2.37	-2.25	-2.13	
	8	-2.33	-2.24	-2.16	
	9	-2.41	-2.26	-2.11	
	10	-2.32	-2.23	-2.13	
	11	-2.27	-2.14	-2.01	
	NRD	3	-2.36	-2.29	-2.22
		4	-2.39	-2.27	-2.14
5		-2.20	-2.17	-2.13	
6		-2.28	-2.21	-2.11	
7		-2.24	-2.18	-2.12	
8		-2.30	-2.17	-2.15	
9		-2.34	-2.20	-2.06	
10		-2.38	-2.25	-2.10	
11		-2.28	-2.13	-1.97	

^aFor abbreviations see Table 1.

where HLB^G denotes the HLB number in the Griffin scale and PI is the polarity index determined experimentally (with methanol as a polar solute). The above equation is valid for ethoxylated fatty alcohols. The predicted values of HLB are always lower than those obtained from experimental data. In each case, the higher values of HLB are observed for narrow-range products, both for predicted and experimental data.

The results of the "simulation procedure" indicate that slightly higher polarity of the narrow-range products at 70°C is to be expected.

The increase of the average number of ethoxylene units causes a rise of the considered polarity parameters (Fig. 2). The deviations from the hypothetical straight lines are probably caused by the dispersed composition of the examined products.

The dispersive interaction parameters also have been used for evaluation of the physicochemical properties of organic compounds (10,29). According to Poole and Poole (10), $\Delta G_s^m(\text{CH}_2)$ —the partial molal Gibbs free energy of a solution for a methylene group—can be treated as one of the most reasonable and acceptable measures of the solvent strength. Poole and Poole (10) showed that the solvent strength is synonymous with the polarity term. However, it is not easy to define both terms in a totally unambiguous manner. In the case under consideration, ethoxylates play the role of a solvent. The appropriate values of criterion A and $\Delta G_s^m(\text{CH}_2)$ are given in Tables 5 and 6, respectively. Criterion A is, according to Sevcik and Löwentap (23), a measure of the reluctance of a stationary phase to dissolve a hydrocarbon chain. An increase of the stationary phase polarity reflects in a decrease of criterion A. Criterion A lowers with an increase of the EO unit number, both for BRD and NRD products, thus showing the increasing polarity of the liquid phases. The higher values of criterion A obtained for BRD products indicate their lower polarity in comparison with the NRD analogs.

The same results are obtained when $\sum_{i=1}^5 \Delta I_i$, PI and coefficient ρ are used as the PPs. The differences in values determined for the two sets of ethoxylates diminish when the temperature rises. However, even at 110°C the values of criterion A indicate a slightly higher polarity of NRD products.

The temperature dependence of criterion A has been described (23,29) as follows:

$$A = a \cdot \exp(b/T) \quad [5]$$

This relation is also fulfilled in the case under consideration. The appropriate regression and correlation coefficients are given in Table 6. Correlation coefficients are high and exceed 0.95 in most cases.

The use of ΔG_s^m (CH_2) as a PP requires appropriate experimental precision; it is useful for compounds with well-defined structure. The sensitivity of ΔG_s^m (CH_2) upon the compound's structure is much lower than that of PI, I_R or coefficient ρ (30). The observed increase of ΔG_s^m (CH_2) with temperature is related to the decreasing polarity of the ethoxylates.

Our studies demonstrate that the retention indices of the first five McReynolds solutes, the ratio of adjusted retention times of a standard alcohol (methanol or ethanol) to *n*-hexane, the PI and criterion A can be used to study the polarity of NBD and BRD ethoxylates of fatty alcohols. Narrow-range alcohol ethoxylates exhibit higher polarity at 70°C than the broad-range products. The difference decreases, however, with increasing temperature and then diminishes at 110°C. The difference in polarity between the BRD and NRD products can be predicted from structural increments. The rise of the average number of ethoxylene units increases the polarity of the examined products.

Our results confirm the differences in polarity between NRD and BRD counterparts. As a consequence, different effective HLB numbers of the products are expected, despite the corresponding average ethoxylation degrees. This is also the reason for the existing differences in some properties between NRD and BRD ethoxylates, e.g., their different solubilities in water.

Thus, the observed improvement of several properties of NRD ethoxylates (2-6) is in agreement with our independent polarity measurements of NRD and BRD ethoxylates, carried out by inverse GC.

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