Synthesis of Surfactants with Narrow-Range Distribution of the Polyoxyethylene Chain

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ABSTRACT: Ethoxylation of alcohols, alkylphenols, and alkylamines has been studied in the presence of a few catalytic systems. Distribution constants were computed. Broad-range distributed ethoxylates are formed in the presence of NaOH, and the distribution constants increase up to the homologue containing six oxyethylene units. Narrow-range distributed ethoxylates are formed in the presence of calcium-based catalysts. It is reflected in the values of the distribution constants because an increase with the growing number of oxyethylene units in successive homologue is not observed.

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KEY WORDS: Broad- and narrow-range ethoxylates, distribution constants.

Ethoxylation of hydrophobic compounds with a labile hydroxyl group is widely used in industry to manufacture nonionic surfactants and appropriate intermediates for the synthesis of ionic surface-active agents. Alkaline catalysts are used. The obtained products are polydisperse mixtures and contain less-effective components with polyoxyethylene chains that are either too short or too long.

Narrowing the oxyethylene chain distribution may be obtained by using acidic catalysts. Such products, however, contain large amounts of low-molecular weight toxic substances, including 1,4-dioxane (4). In recent years, several new catalysts for ethoxylation have been proposed, and nearly 100 patents have been issued on the subject. They are expected to permit the polyoxyethylene chain distribution to be narrowed without formation of excessive amounts of polyglycols and other undesirable molecules. Some of the new catalytic systems proposed for alcohol ethoxylation have been investigated. Such a catalyst was also proposed by the present authors (2). The aim of this work is to study the ethoxylation of various types of hydrophobes in the presence of calcium-based catalysts and to discuss the catalytic effect on the Natta–Mantica distribution coefficients (3).

EXPERIMENTAL PROCEDURES

Materials. The following substrates were used for ethoxylation: (i) lauryl alcohol containing 98% *n*-dodecanol-1 (Aldrich-Chemie; Aldrich Chemical, Milwaukee, WI); cetyl alcohol containing 95% *n*-hexadecanol-1 (Aldrich-Chemie); Alfol 1214® alcohol, a mixture of primary linear C_{12} and C_{14} alcohols containing about 60 mol% dodecanol (Ziegler alcohols; Vista Chemical Company, Austin, TX); nonylphenol (Blachownia Chemical Works, Kędzierzyn-Koźle, Poland); tallow amine containing 67% C_{18} amine and 29% C_{16} amine (Azoty Chemical Works, Kędzierzyn-Koźle, Poland); ethylene oxide (Petrochemia Mazovian Petrochemical Works, Płock, Poland); calcium-based catalyst, W7™ (Blachownia ICSO, Kędzierzyn-Koźle, Poland); and sodium hydroxide as a broad-range catalyst. Some other catalytic systems were also used. Their characteristics are given in Table 1.

Synthesis of ethoxylates. Ethoxylation was performed in a 1-L stainless-steel jacketed reactor, equipped with a driven stirrer and cooling coil. Commercial trials were performed in 2-m^3 and 6-m^3 batch reactors in Rokita Chemical Works (Brzeg Dolny, Poland). In each synthesis, the reactor was charged with a hydrophobic substrate (150 g in laboratory experiments; 930 and 1900 kg in industrial installations) and a weighed amount of catalyst (0.4% W7™ or 0.2% NaOH in respect to the hydrophobic substrate). Then the reactor was closed, vented with nitrogen, and heated to the reaction temperature (180 and 135°C for W7™ and NaOH, respectively). After preheating, ethylene oxide was admitted to the reactor from a bottle, which was pressurized with nitrogen at 0.6 MPa. Ethylene oxide pressure in e reactor was kept constant by opening and closing a micrometric valve. Samples were withdrawn at intervals and analyzed by gas chromatography.

Gas chromatography. Homologue distributions of ethoxylates were determined in a chromatograph (Perkin-Elmer model 900; Perkin-Elmer, Norwalk, CT) with a flame-ionization detector. Separation was carried out in a stainless-steel column of 0.9-m length and 2.7-mm inner diameter. Chromosorb G-AW-DMCS (60–80 mesh; Johns-Manville, Denver, CO) was used as the support, and silica resin OV-17 (Serva, Heildelberg, Germany) was used as the liquid phase. The weight ratio of liquid phase to support was 1:99. Argon was used as the carrier gas at a flow rate of 15 cm^3/min. Temperatures of the detector and injector were 330 and 340°C, respectively. Analyses were started with a column temperature of 120°C, which was programmed after 1 min at a rate of 4°C/min up to 320°C. All products were analyzed as acetate derivatives (4–6).

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TABLE 1
Conditions of Alcohol Ethoxylation for Selected Catalytic Systems[a]

No.	Catalytic system	Concentration (mole/mole alc.)	Reaction temperature (°C)	Reaction rate (mole EO/mole alc • h)	Reference No.
1	$Ba(OH)_2 \cdot 8H_2O$	0.0041	170	1.5	(7)
	CaO	0.0432			
2	BaO	0.0120	170	11.0	(8)
	CH_3OH				
3	$Al(C_3H_7O)_3$	0.0166	150	1.8	(9)
	H_2SO_4	0.0082			
4	$C_{12-14}E_4OH$	0.0152	175	16.0	(10)
	H_2SO_4	0.0025			
	$Ca(OH)_2$	0.0055			
	$Al(C_3H_7O)_3$	0.0069			
5	HOC_2H_4OH		175	2.2	(11)
	$Ca(OH)_2$	0.0185			
	$MgSO_4$	0.0334			
6	W7	0.0040	180	3.5	(2)
7	NaOH	0.0093	135	4.0	—

[a] EO, Ethylene oxide.

1,4-Dioxane determination. 1,4-Dioxane content was determined by means of the headspace analysis technique with a Perkin-Elmer autosampler HS-40 and a Perkin-Elmer 8700 gas chromatograph with flame-ionization detection. The samples were thermostated for 40 min at 80°C and then transferred automatically to the gas chromatograph. A Permaphase PEG (Uberlinger, Germany) capillary column of 50-m length, 0.32-mm inner diameter, and 0.4 μm film thickness was used. Temperatures of the injector and detector were 250 and 350°C, respectively. Analyses were started at a column temperature of 40°C, which was programmed after 6 min at a rate of 10°C/min to 180°C. Helium was used as the carrier gas at an inlet pressure of 26 psig.

Polyoxyethylene glycol determination. High-performance liquid chromatography (HPLC) was used for polyoxyethylene glycol content determination. Analyses were performed on a 302-ICHF PAN chromatograph (Warsaw, Poland), with an isocratic pump and a Hewlett-Packard HP1047A refractometric detector (Avondale, PA). Separations were carried out in a stainless-steel column of 200-mm length and 2.1-mm inner diameter, filled with a reversed-phase Hypesil ODS (Avondale, PA). The mobile phase was acetonitrile/water 65:35 vol/vol with a flow rate of 0.35 cm^3/min. The detector temperature was 40°C, while analyses were performed at ambient temperature.

RESULTS AND DISCUSSION

A few catalytic systems were chosen from the patent literature for investigation. Compositions of alcohol ethoxylates obtained with the catalysts, characterized in Table 1, are presented in Table 2. The results obtained in the presence of catalyst W7™ and NaOH are also given. Narrowing the homologue distribution in comparison with the product obtained in the presence of NaOH is clearly observed. The exception is the product obtained in the presence of $CaO/Ba(OH)_2$. Considerable reduction of the unconverted alcohol is also observed.

Narrowing the homologue distribution may be quantitatively expressed by Edwards criterion E (9) or its modification proposed by us (12), called the distribution selectivity coefficient (c_s):

$$E = i \cdot (P_i)^2; \qquad [1]$$

$$c_s = [(i-1) \cdot P_{(i-1)}^2 + i \cdot P_i^2 + (i+1) \cdot P_{(i+1)}^2]/300 \qquad [2]$$

for $i > 1$;

$$c_s = [P_1^2 + 2 \cdot P_2^2]/200 \qquad [3]$$

for $i = 1$;

TABLE 2
Composition of Hexadecanol Ethoxylates Obtained with Various Catalysts[a]

Mole EO/ mole alcohol	Catalyst						
	1	2	3	4	5	NaOH	W7™
0	27.8	17.0	5.6	10.1	18.7	21.8	17.0
1	14.6	8.7	21.4	9.3	6.3	11.1	7.5
2	16.0	13.0	28.2	14.5	9.9	10.6	9.9
3	14.9	15.8	22.2	19.0	17.5	10.2	13.6
4	11.5	15.0	12.7	19.0	19.8	9.0	16.8
5	7.3	11.9	6.0	14.5	15.5	7.7	14.0
6	4.2	8.3	2.4	8.5	7.93	7.2	11.6
7	2.1	5.1	0.8	3.6	3.2	6.0	5.4
8	1.0	2.8	0.4	1.2	0.8	6.0	2.5
9	0.3	1.2	0.4	0.4	0.4	3.4	1.2
10	0.3	0.8				2.6	0.4
11		0.4				1.7	
12						1.3	
13						0.9	
14						0.4	
Average ethox. degree	2.3	3.3	2.5	3.3	3.1	3.5	3.8
E[b]	512	749	1,590	1,444	1,568	123	1,129
c_s[c]	4.6	6.6	11.8	11.9	12.3	1.7	8.9

[a] Numbers of catalytic systems are the same as in Table 1; homologue concentrations expressed in mole%; W7™ (Blachownia ICSO, Kędzierzyn-Koźle, Poland). See Table 1 for abbreviation.

[b] E = Edwards criterion defined by Equation 1.

[c] c_s = Distribution selectivity coefficient defined by Equations 2 and 3.

where: P_i = wt% of the ith homologue, and i = polyaddition degree of the main homologue present in the largest quantity.

It was proven that, for model Poisson-type distributions, c_s values remain constant for average polyaddition degrees above 1, while Edwards criterion values change remarkably. As a result, also for real products, c_s values are less dependent on the average degree of polyaddition. Values of these coefficients are given in Table 2. The best results were obtained when calcium-based catalysts (no.s 4 and 5 and W7™) were used. Catalyst 2 shows a relatively weak effect of narrowing the homologue distribution. Moreover, barium compounds are toxic, and their presence in the ethoxylation products is not acceptable.

Products obtained in the presence of $Al(OC_3H_7)/H_2SO_4$ have high contents of toxic 1,4-dioxane and undesirable polyoxyethylene glycols. Their contents are equal to 0.4–0.1% and 5.7–8.5%, respectively. The products also contain other byproducts, which were not identified.

A strong narrowing of the homologue distribution is observed for $Ca(OH)_2Al(OC_3H_7)/H_2SO_4$ as catalyst. At the same time, excessive amounts of 1,4-dioxane and polyoxyethylene glycols were not observed. Preparation of this catalytic system is rather inconvenient however, due to its frequent gelation, which causes scorch marks to appear. Moreover, catalyst activity and product quality are not stable. This may be attributed to the use of aluminum isopropanolate, which is a readily hydrolyzed salt.

A comparable narrowing of homologue distribution is obtained in the presence of the W7™ catalyst, which can be easily prepared. It is stable during storage and leads to reproducible products. As for alkyphenol ethoxylation (13) however, the process must be carried out at higher temperatures (180°C instead of 135°C, as in the case of NaOH) and in the presence of higher catalyst quantities (0.4 wt% with respect to the hydrophobe, instead of 0.2% for NaOH).

Exemplary distributions for ethoxylates of alcohol, alkylphenol, and alkylamine, obtained in the presence of W7™ and NaOH catalysts, for selected average degrees of ethoxylation are shown in Figures 1–3. These three reagents differ significantly in their reactivities in the course of ethoxylation.

The reaction between a reactive reagent (RXH) and ethylene oxide (EO) can be described as follows:

$$\begin{array}{c} k_0 \\ \downarrow \\ \mathrm{RXH + EO \rightarrow RXEOH} \end{array} \qquad [4]$$

$$\begin{array}{c} k_1 \\ \downarrow \\ \mathrm{RXEOH + EO \rightarrow RX(EO)_2H} \end{array} \qquad [5]$$

$$\begin{array}{c} k_n \\ \downarrow \\ \mathrm{RX(EO)_{n-1}H + EO \rightarrow RX(EO)_nH} \end{array} \qquad [6]$$

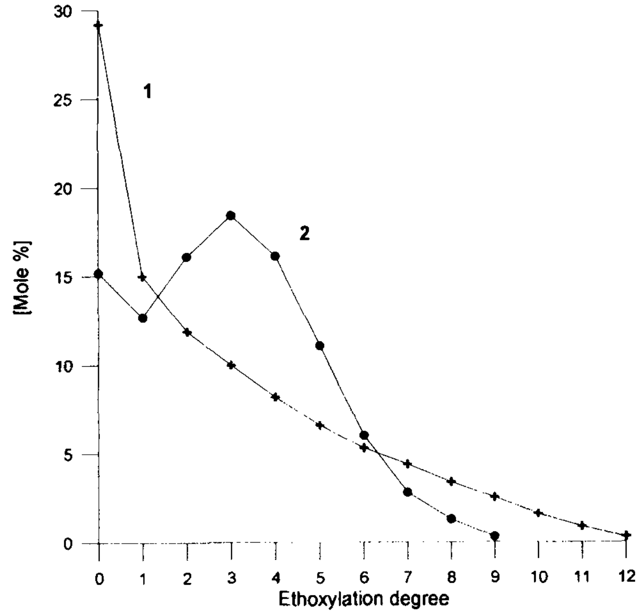


FIG. 1. Homologue distribution in ethoxylated dodecanol (average degree of ethoxylation, 2.9; 1, NaOH; 2, W7™; Blachownia ICSO, Kędzierzyn-Koźle, Poland).

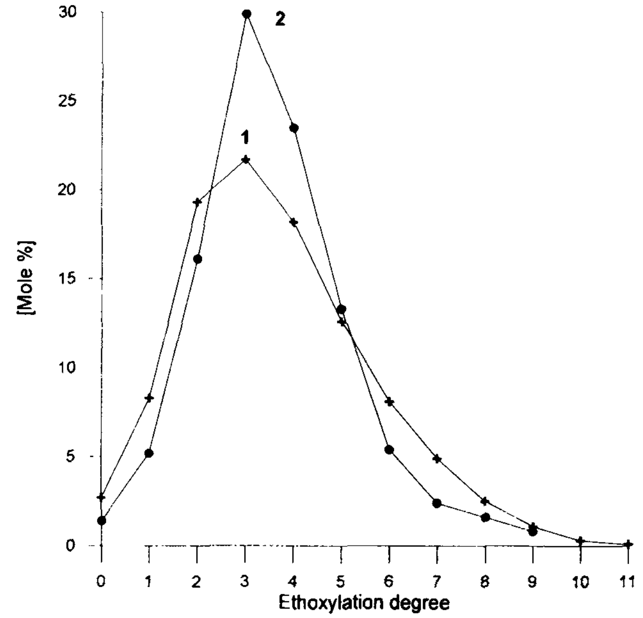


FIG. 2. Homologue distribution in ethoxylated nonylphenol (average degree of ethoxylation, 3.6; 1, NaOH; 2, W7™). See Figure 1 for company source.

where k_0, k_1, ..., k_n denote rate constants for the successive steps of the process, and X may denote oxygen, C_6H_4O, or NH. For amine, however, both hydrogen atoms are mobile and two different polyoxyethylene chains are formed. It is possible to determine the distribution of oxyethylene units in these two polyoxyethylene chains (6), but that problem will not be discussed here.

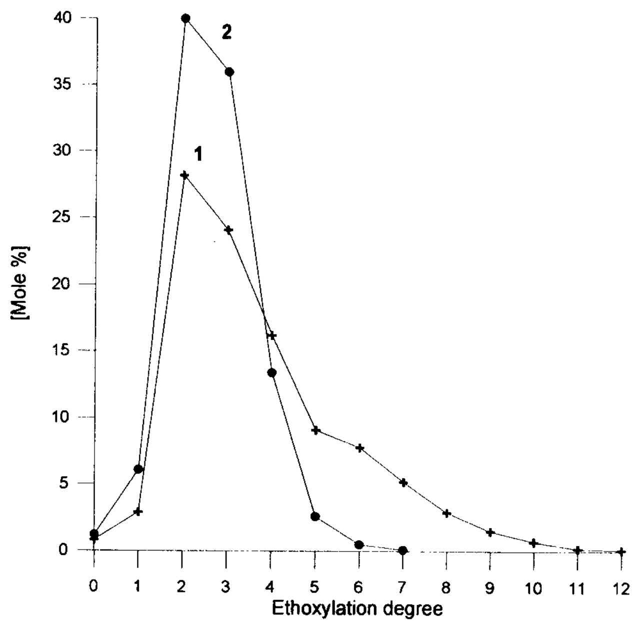


FIG. 3. Homologue distribution in ethoxylated tallow amine (average degree of ethoxylation, 4 from synthesis weight balance; 1, NaOH; 2, W7™). See Figure 1 for company source.

For alcohol ethoxylation, the reaction rate constants increase for successive steps of ethoxylation. As a result, higher homologues with more oxyethylene units are formed already at the beginning of the process, and important amounts of unconverted alcohol are present, even in products with relatively high average degrees of polyaddition.

A different situation is observed for alkyphenol and alkylamine ethoxylation. Reactivities of the phenolic and amino groups are so high that two separate steps of the process can be considered. In the first step, only addition of one and two ethylene oxide molecules to the alkyphenol and alkylamine occurs, respectively, and higher homologues are formed in small amounts. For alkylamine, this first step can be carried out even without a catalyst. When this first step is finished, however, then propagation of the polyoxyethylene chain occurs in a way that is comparable to alcohol ethoxylation, giving a polydisperse mixture of various homologues. Thus homologues with one and two oxyethylene units are present in ethoxylated alkylphenols and alkylamines, respectively, even for high average degrees of ethoxylation. Thus differences in homologue distribution of alcohols, alkylphenols, and alkylamines ethoxylation products are significant, especially for low average degrees of ethoxylation. Nevertheless, in each case considered, a significant narrowing of the homologue distribution is observed when W7™ is used instead of NaOH. Values of E and c_s for a broad range of average degrees of ethoxylation are given in Table 3, which shows that, compared to Edwards criterion, c_s values are more stable and less sensitive to accidental labilities of its values. For narrow-range distributed (NRD) alcohol ethoxylates, they tend to increase with increasing average ethoxylation degrees and assume distinctly higher values than the coefficients calculated for the respective equivalents of the conventional broad-range distribution (BRD) ethoxylates. This reflects higher concentration of homologues near the average ethoxylation degree. For nonylphenol ethoxylates, according to the mechanism described above, at the first stage of the reaction (up to average ethoxylation degree equal to 1), no differences are confirmed in c_s calculated for equivalent ethoxylates despite the catalyst used for their synthesis. Some differences appear later in the propagation steps because only then do the kinetics of the polyaddition steps depend largely on the catalyst.

When concentrations of the successive homologues RXH, RX(EO)H, ..., RX(EO)$_n$H are denoted as x_0, x_1, ..., x_n, the kinetic equations of the second order for the subsequent reactions are considered, and distribution coefficients are defined as the ratio of the following successive rate constants: $c_1 = k_1/k_0$, $c_2 = k_2/k_0$, ..., $c_n = k_n/k_0$. Then the following set of equations is obtained:

$$-\frac{dx_1}{dx_0} = 1 - c_1 x_1 / x_0 \qquad [7]$$

$$-\frac{dx_2}{dx_0} = (c_1 x_1 - c_2 x_2 / x_0) \qquad [8]$$

$$-\frac{dx_n}{dx_0} = c_{n-1} x_n - 1 / x_0 \qquad [9]$$

which can be solved numerically, e.g., by using the numerical integration technique of the Runge–Kutta method of the fourth order and optimization algorithms of the Monte Carlo method and the simplex Nelder and Mead method (14).

The Natta–Mantica equation can also be used for distribution coefficients (3), and the same results are obtained, as follows:

$$x_i = (-1)\prod_{j=1}^{i-1} c_j \sum_{j=0}^{i} \frac{x_0^{c_j}}{\prod\limits_{\substack{k=0 \\ k \neq j}}^{i} (cj - ck)} \qquad [10]$$

Different values of the distribution coefficients are computed for increased amounts of reacted ethylene oxide. It seems, though, that the determined concentrations of the higher, extreme homologues do not reflect their exact contents, which may be caused by lack of correction coefficients, adsorption of homologues at the chromatographic column, their poor evaporation, and/or thermal degradation. Thus the obtained distribution coefficients should only be considered as a mathematical fitting of the calculated function to the initial data. Moreover, it is necessary to include only a few homologues, not more than the first eight, and to use for simultaneously computing all distributions obtained for different values of the average degree of ethoxylation.

Values of the distribution coefficients obtained for the products of alcohol ethoxylation in the presence of NaOH and W7™ catalysts are given in Figure 4. They demonstrate that, for products obtained in the presence of NaOH, the distribu-

TABLE 3
Narrowing of Homologue Distribution[a]

Specification		N_a	Ethoxylation degree																	
Hydrophobe	Catalyst	(GC)	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	E	c_s
Dodecanol	W7™	1.1	46.8	22.6	16.1	9.0	3.7	1.2	0.2										520	5.1
	NaOH	1.1	53.4	20.7	11.1	6.4	3.8	2.1	1.2	0.7	0.5	0.2							428	3.4
	W7™	1.9	27.4	19.9	19.6	16.1	9.9	4.6	1.6	0.5	0.3								396	5.8
	NaOH	1.9	40.7	17.8	12.4	8.9	6.5	4.3	3.2	2.4	1.6	1.1	0.5	0.3					317	3.1
	W7™	2.9	15.2	12.7	16.1	18.4	16.1	11.1	6.0	2.8	1.3	0.3							1,016	8.6
	NaOH	2.9	29.2	15.0	11.9	10.0	8.2	6.6	5.3	4.4	3.4	2.5	1.6	0.9	0.3				225	2.5
	W7™	4.1	7.9	6.7	9.7	15.0	16.9	15.7	12.4	8.2	4.5	1.9	0.7	0.4					1,142	10.2
	NaOH	4.1	22.5	10.6	9.3	8.8	8.4	7.5	6.6	6.2	5.3	4.4	3.5	2.6	1.8	1.3	0.9	0.4	112	1.4
	W7™	5.4	3.4	4.2	5.9	9.3	13.1	15.3	15.3	12.7	8.9	5.5	3.0	1.7	0.8	0.4	0.4		1,404	12.4
	NaOH	5.4	16.4	7.9	7.2	7.2	7.2	7.2	7.2	7.2	6.6	6.6	5.3	4.6	3.3	2.6	2.0	1.3	311	2.9
ALFOL® 1214	W7™	1.6	33.5	19.4	18.6	14.9	8.5	3.7	1.1	0.3									376	5.3
(Ziegler alcoh.)	NaOH	1.5	46.3	16.5	13.4	9.2	5.6	3.4	2.2	1.7	0.9	0.6	0.3	0.3					272	3.2
	W7™	2.5	22.6	12.7	15.7	17.5	14.5	9.7	4.5	2.1	0.6								919	7.5
	NaOH	2.4	31.9	16.8	13.6	10.4	8.0	5.6	4.1	3.3	2.4	1.8	1.2	0.6	0.3	0.3			282	3.3
	W7™	4.1	9.3	5.6	9.0	13.8	18.0	17.6	10.4	7.1	4.1	3.0	1.1	0.4	0.4				1,296	11.4
	NaOH	4.3	17.7	12.0	10.8	9.6	8.4	7.4	6.6	5.8	5.4	4.7	3.9	2.7	1.9	1.6	0.8	0.8	144	1.9
	W7™	6.8	2.0	0.7	0.7	5.4	6.0	10.7	14.6	16.8	16.1	11.4	8.0	4.7	2.0	0.7			1,976	17.8
	NaOH	6.4	10.3	6.0	6.0	6.7	7.3	7.9	7.3	7.9	7.9	6.7	6.7	6.1	4.2	3.6	2.4	3.0	499	4.5
Nonylphenol	W7™	1.1	4.8	84	10.7	0.5													7,056	36.4
	NaOH	1.2	0.8	82.6	15.8	0.8													6,823	36.6
	W7™	2.0	1.2	32.9	42.7	17.4	4.3	0.9	0.3	0.3									3,647	18.8
	NaOH	2.1	1.3	34.0	33.6	18.2	8.2	3.1	1.3	0.3									1,156	17.1
	W7™	2.7	0.7	10.5	34.7	32.3	14.6	5.4	1.0	0.7									2,408	18.8
	NaOH	2.6	1.7	21.0	31.0	23.3	13.0	6.0	2.7	1.0	0.3								1,922	13.3
	W7™	3.6	1.5	5.3	16.0	30.0	23.6	13.3	5.3	2.3	1.5	0.8	0.4						2,700	18.1
	NaOH	3.7	2.7	8.4	19.4	21.7	18.3	12.5	8.0	4.9	2.7	1.1	0.4						1,413	11.7
	W7™	4.8	3.9	2.6	5.2	14.2	22.7	21.0	13.3	6.9	3.4	2.6	1.7	1.3	0.9	0.4			2,061	16.2
	NaOH	5.1	4.4	6.2	9.7	12.3	13.2	12.3	11.0	10.1	7.5	5.7	3.5	2.2	1.3	0.4			696	6.4

[a]Homologue concentrations expressed in mole%, N_{av}: average degree of ethoxylation determined by gas chromatography (GC); ALFOL® 1214 (Vista Chemical Company, Austin, TX). See Table 2 for other company source.

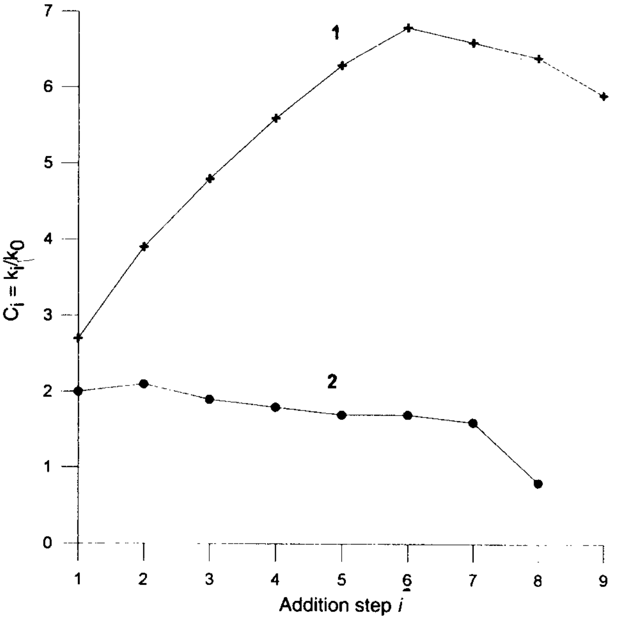
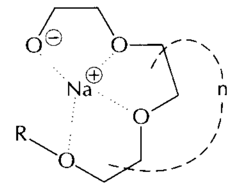


FIG. 4. Distribution constants for ethoxylated dodecanol (1, NaOH; 2, W7™). See Figure 1 for company source.

tion coefficients increase up to the homologue with six oxyethylene units and then decrease above ten oxyethylene units in the polyoxyethylene chain. This is the Weibull–Tornquist effect (15), also confirmed by others (14,16,17). It was established that growing oligoethoxy chains can surround a catalyst cation, forming alkoxylate-metallic ion complexes, as can be seen in Scheme 1.



SCHEME 1

This complexation weakens the catalyst metal and alkoxylate ion pair bonds, causing the alkoxylates to be more reactive with ethylene oxide. The reactivity increase of the crownlike complexes is reflected by an appropriate rise of reaction-rate constants (distribution constants). As a result, broadening of the homologue distribution occurs, which is easy to confirm by a simple mathematical simulation with the Weibull-Nycander-Gold model (18), where $k_0 \neq k_1 = k_2 = \ldots = k_n$.

The distribution constants do not increase for products obtained in the presence of the W7™ catalyst, and, as a result, products of narrower distribution of homologues are obtained. Most probably, when a polyvalent metal cation is part

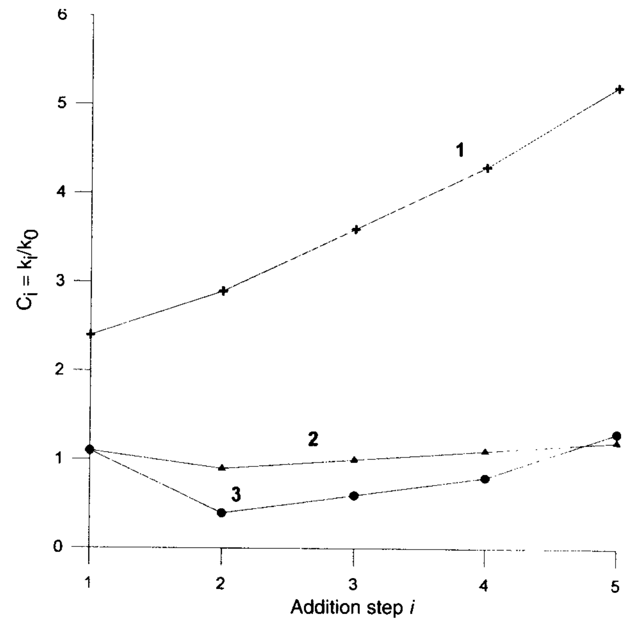


FIG. 5. Distribution constants for nonionic surfactants obtained in the presence of NaOH [1, Alfol® 1214 (Vista Chemical Co., Austin, TX), industrial scale; 2, nonylphenol; 3, tallow amine].

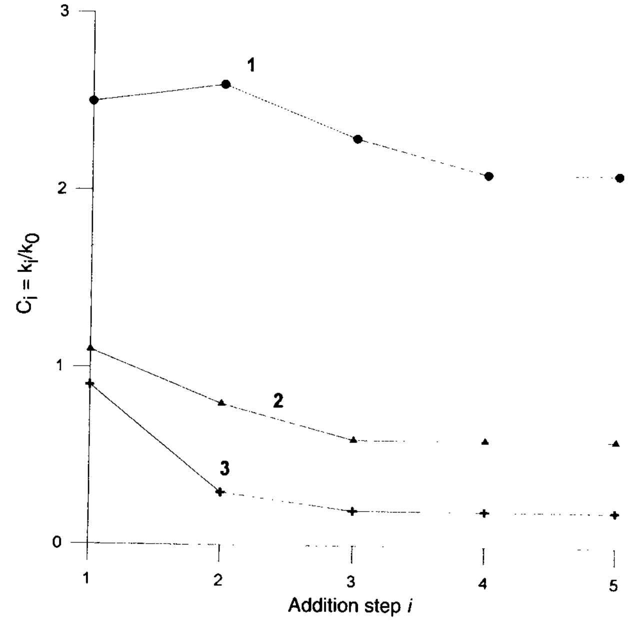


FIG. 6. Distribution constants for nonionic surfactants obtained in the presence of W7™ (1, Alfol 1214®, industrial scale; 2, nonylphenol; 3, tallow amine). See Figures 1 and 5 for company sources, respectively.

of the ethoxylation catalyst, formation of a crownlike complex is not observed, and the activity of the closely bonded metal cation-alkoxylate anion ion pair remains uninfluenced by the change in polyoxyethylene chainlength.

The kinetics of alkaline ethoxylation of alcohols were recently studied by Santacesaria *et al.* (19,20), who concluded that, for KOH, oxyethylene chainlength seems to have little or no influence on stability of the ionic couple, and, consequently, on its reactivity toward ethylene oxide. From the data presented, the Weibull-Tornquist effect is one of the main factors responsible for broadening the homologues' distribution with alkaline catalysts, especially for alcohol ethoxylates. Furthermore, the differences between the two catalytic systems, attributed to different bonding strengths of the corresponding ionic couples, are significantly dependent on the complexation effect of the growing polyethylene chain in the presence of alkaline catalysts, which, however, is not determined for the other polyvalent catalysts.

Similar results are obtained when the syntheses are carried out on an industrial scale, and when nonylphenol and alkylamine are used as reagents. The Weibull-Tornquist effect is observed for products obtained in the presence of NaOH, but it is not reported for products obtained in the presence of W7™ (Figs. 5 and 6). The same relationship was observed for the other catalysts considered. For nonylphenol and alkylamine ethoxylation, however, the estimated distribution coefficients have only qualitative character because of the significant error in the determination of small near-zero, amounts of unreacted nonylphenol and alkylamine needed for computing.

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REFERENCES

1. Bailey, Jr., F.E., and J.V. Koleske, *Alkylene Oxides and Their Polymers*, Marcel Dekker, Inc., New York, 1991, p. 39.
2. Hreczuch, W., Z. Krasnodębski, G. Bekierz, J. Szymanowski, and G. Bekierz, Polish Patent appl. P-300743, 1993.
3. Natta, G., and E. Mantica, *J. Am. Chem. Soc. 74:*3152 (1952).
4. Szymanowski, J., H. Szewczyk, and B. Atamańczuk, *Tenside Surfactants Deterg. 21:*139 (1984).
5. Szymanowski, J., H. Szewczyk, and J. Hetper, *Ibid. 18:*333 (1981).
6. Szymanowski, J., H. Szewczyk, and W. Jerzykiewicz, *Ibid. 18:*130 (1981).
7. Kang, Y., G.L. Nield, and P.H. Washecheck, U.S. Patent 4,302,613, 1981.
8. McCain, J.H., and F.L. Theiling, European Patent 0026544, 1980.
9. Edwards, C.L., European Patent 0228121, 1986.
10. Leach, B.E., M.L. Shanon, and D.L. Wharry, U.S. Patent 4,775,653, 1988.
11. King, S.W., and D.W. Scott, European Patent 0361617, 1989.
12. Hreczuch, W., *Przem. Chem. 69:*314 (1990).
13. Barhoum, R., E. Meissner, W. Hreczuch, and J. Szymanowski, *J. Chem. Techn. Biotechnol. 61:*215 (1994).
14. Szymanowski, J., B. Atamańczuk, and H. Szewczyk, *Ibid. 40:*1 (1987).
15. Weibull, B., and J. Tornquist, *Intern. Kongr. fur Grenzflachenaktive Stoffe*, Zurich, 1972.
16. Sallay, P., J. Morgos, L. Farkas, I. Rusznak, G. Veress, and B. Bartha, *Tenside Surfactants Deterg. 17:*298 (1980).
17. Hirao, A., S. Nakachama, M. Takashi, and N. Yamazuki, *Macromol. Chem. 179:*1735 (1978).
18. Farkas, L., J. Morgos, P. Sallay, and I. Rusznak, *J. Am. Oil Chem. Soc. 58:*650 (1981).
19. Santacesaria, E., M.D. Serio, R. Garaffa, and G. Addino, *Ind. Eng. Chem. Res. 31:*2413 (1992).
20. Santacesaria, E., *Proceedings of the Third International Surfactant Congress*, London, 1992, pp. 2281–2291.

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