Determination of Molar Mass Distribution of Alkyl Polyethylene Glycol Ethers

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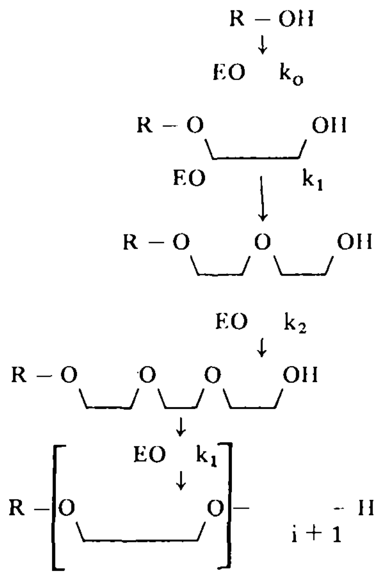
ABSTRACT

A process based on gas chromatographic separation and on the computerized evaluation of the results has been developed for the determination of the distribution and distribution coefficients of alkyl polyglycol ethers, formed in the competitive, consecutive reaction of fatty alcohol and ethylene oxide. A comparison of experimental and theoretical distributions showed that the distribution is the Weibull-Nycander-Gold type for potassium hydroxide catalyst, and the Flory type in the antimony pentachloride catalyst. The characteristic of the distribution does not change with reaction parameters in either type of distribution, though actual distribution is slightly modified by temperature. In determinations of Weibull-Nycander-Gold's c and Natta-Mantica's c_i -s distribution coefficients, the Weibull-Törnquist effect, i.e., the changing of the distribution coefficients with ethoxylation, has been experimentally proven in the example of ethoxylation catalyzed with potassium hydroxide.

INTRODUCTION

Alkyl polyglycol ethers are among the most important representatives of nonionic surfactants of industrial significance. In their production, fatty alcohols, usually $C_{12}-C_{18}$, or alkyl phenols, generally octyl or nonyl, are reacted with ethylene oxide (EO):



where k_0 is the rate constant of the starting compound and k_i, that of the compound containing the ethylene glycol unit i in the reaction with EO.

Glycol monoether that is formed at a rate constant of k_0 in the first step of the reaction can react with EO at a rate comparable to that of the starting alcohol. Thus the reaction product is not homogeneous, but a mixture of polymer homologs will be formed in a series of competitive, consecutive reactions.

Analysis of this mixture is not only a striking theoretical problem, but also an interesting practical task, because its composition affects the application technical properties of these products (1).

The composition, i.e., the concentrations, of the individual components are compared to theoretical distributions, deduced on the basis of experimental data from various hypotheses.

In the simplest case, when all the rate constants are equal, $k_0 = k_1 = \ldots = k_i$, the molar fractions of the individual components, x_i, are described by Flory's (2) relationship:

$$x_i = e^{-v} \frac{v^i}{i!} \qquad [I]$$

where v is the average degree of ethoxylation, i.e., the quantity (mol) of EO that reacted with 1 mol of the starting compound.

If the reactivity of the hydroxyl group of the starting alcohol is different from that of the glycolic hydroxyl of the individual components, the molar fractions can be calculated using the Weibull, Nycander and Gold relationship (3-5):

$$x_i = \frac{c^{i-1}}{(c-1)^i} \left\{ x_0 - x_0^c \sum_{j=0}^{i-1} \frac{1}{j!} \left[(c-1) \ln x_0 \right]^j \right\} \qquad [II]$$

$$c = \frac{x_0 + v - 1}{x_0 - \ln x_0 - 1} \qquad [III]$$

where the distribution coefficient c is according to definition of k/k_0.

Note that Flory's distribution is a special case of the Weibull-Nycander-Gold distribution, with c=1.

In general, all the reaction rate constants are different, $k_0 \neq k_1 \neq \ldots \neq k_i$. Now, the relationship between the x_i values measured is given by the relationship described by Natta and Mantica (6):

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

$$c_i = k_i/k_0 \qquad [V]$$

The aim of our work was to develop a process suitable for determination of the distribution of polymer homologs formed during ethoxylation. Our further objects were the comparison of experimental and theoretical distributions for products obtained under various reaction conditions, and the determination of the distribution coefficients.

EXPERIMENTAL PROCEDURES

Alkyl polyglycol ethers were synthesized in the semimicro variant of the apparatus described earlier (7-8), based on the measurement of volumetric flow. Dodecyl alcohol ("Alfol 12," produced by Condea) (0.02 mol) was used for our experiments, to which 0.8-10 mol% potassium hydroxide (Reanal) or 0.5-1.7 mol% antimony pentachloride (Merck) was added. (Antimony pentachloride, difficult to weigh, was added in the following way: a stock solution was prepared from the starting alcohol and the catalyst, and this solution was diluted in the desired measure with the starting alcohol.)

Characteristic parameters of the ethoxylation reactions are summarized in Table I.

TABLE I

Parameters of the Ethoxylation Reaction

Serial no.	Catalyst (mol%)	Reaction Time (min)	Reaction Temperature (C)	v
1	$SbCl_5$ 0.86	13	78	2.50
2	1.36	8.5	78	2.49
3	1.69	7	78	2.48
4	0.88	5	30	1.36
5	0.86	6	30	1.96
6	0.87	7	30	2.56
7	0.86	9	30	3.81
8	0.85	11	30	4.98
9	0.54	15	30	2.55
10	1.36	4.7	30	2.63
11	0.86	10	50	2.80
12	KOH 0.80	288	140	2.49
13	2.69	60	140	2.54
14	4.91	30	140	2.63
15	10.25	17	140	2.68
16	2.97	20	140	1.02
17	2.99	40	140	2.13
18	2.96	80	140	3.75
19	2.96	245	100	2.40
20	3.20	31	180	2.55

Product composition was determined by gas chromatography (GC) directly from the sample without chemical modification. It is to be expected that alkyl polyglycol ethers, similar to other low-volatile compounds with a tendency to tailing, can be more easily separated by GC in the form of their derivatives. However, in all the chemical modifications facilitating GC investigation, even in the very mild acetylation with ketene (9), by-products are formed, which in the present case, make the quantitative evaluation of the gas chromatograms impossible.

The analyses were done on a gas chromatograph model Chrom 31 (Kovo), and temperature was programmed with the electronic integrator Digint 21 (Chinoin). A 1.4 m length with LD 6 mm stainless steel column was used packed with 10% SE 301 (Carlo Erba) on 30-60 mesh Chromosorb W AW DMCS (Johns-Manville).

The conditions of analysis are as follows: 190 C starting temperature, 10 C/min program rate, and 290 C maximal temperature. Carrier gas was nitrogen (50 cm^3/min)/hydrogen (60 cm^3/min)/air (950 cm^3/min). Injection point temperature was 305 C. Figure 1 shows the gas chromatogram of an ethoxylated reaction mixture.

It can be seen from the gas chromatogram that the first five members of the alkyl polyglycol ether series can be analyzed without chemical modification. Homogeneous surfactants synthesized by us earlier (10) have been used for quantitative analysis.

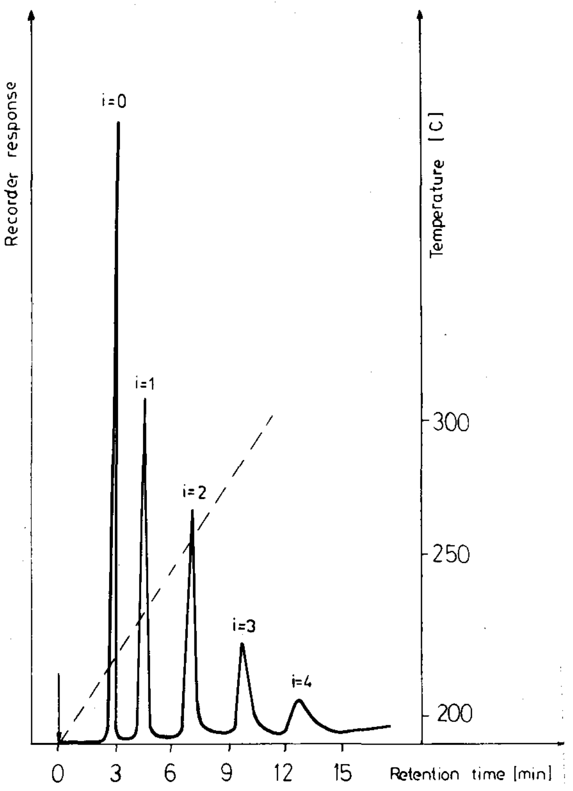


FIG. 1. Gas chromatogram of ethoxylated dodecyl alcohol 2.69 mol% KOH, 140 C.

The mass of the individual homologs has been determined from the gas chromatogram of the test sample, and from this, the mol number of the individual homologs has been calculated using known mol masses. The total mol number cannot be determined by the summation of mol numbers, because not all the components of the sample are eluted from the column.

$$\sum_{i=0}^{4} x_i \neq 1$$

Weibull and Törnquist (11), while processing data measured by other authors, calculated mol fractions under the simplifying assumption that the logarithm of the molar fractions of higher homologs changes linearly with the number of EO units. Molar fractions also can be determined exactly, without approximation methods, considering that the total mol number fraction, x_i, can be calculated when the volume and the density of the test sample are known:

$$x_i = \frac{n_i m_o}{n_k \rho_o V}$$

where n_i is the mol number determined on the basis of the gas chromatogram; ρ_o is the density of the ethoxylated reaction mixture; m_o is the mass of the ethoxylated reaction mixture; V is the volume of the sample investigated by gas chromatography. The accuracy of the gas chromatographic determination of the molar fractions is ca. 3-5%.

TABLE II

Relative Errors (S) of the Simulated x_i and Calculated c_i Values (%)

	S_{x_0}	S_{x_1}	S_{c_1}	S_{x_2}	S_{c_2}	S_{x_3}	S_{c_3}	S_{x_4}	S_{c_4}
W[a]	4.5	4.0	4.9	4.9	7.6	6.2	5.7	4.0	4.9
F	4.5	4.0	4.5	7.4	6.3	5.6	6.1	4.2	10.6

[a] W = distribution of Weibull-Nycander-Gold type; F = distribution of Flory type.

TABLE III

Distribution and Distribution Coefficients of the Products Obtained in Ethoxylation Catalyzed with Antimony Pentachloride

Serial no.	x_0	x_1	x_2	x_3	x_4	v	c	c_1	c_2	c_3	c_4
1	0.077	0.227	0.280	0.193	0.094	2.50	0.96	0.89	0.86	1.01	1.52
2	0.070	0.119	0.190	0.183	0.135	2.49	0.90	1.37	1.31	1.51	1.93
3	0.073	0.220	0.233	0.170	0.115	2.48	0.92	0.89	1.06	1.38	1.68
4	0.283	0.291	0.187	0.085	0.043	1.36	1.18	1.34	1.85	2.48	2.78
5	0.191	0.264	0.214	0.131	0.085	1.96	1.34	1.22	1.54	2.11	2.43
6	0.103	0.211	0.230	0.165	0.120	2.58	1.21	1.09	1.22	1.59	1.72
7	0.039	0.158	0.222	0.179	0.146	3.81	1.25	0.87	0.93	0.93	0.93
8	0.018	0.108	0.197	0.196	0.164	4.98	1.32	0.81	0.82	0.96	1.07
9	0.098	0.259	0.260	0.172	0.110	2.55	1.16	0.90	0.97	1.20	1.00
10	0.097	0.226	0.231	0.177	0.125	2.63	1.21	1.00	1.17	1.36	1.24
11	0.085	0.218	0.252	0.288	0.110	2.80	1.22	0.97	1.02	0.54	0.58

$x_0 - x_4$ = Measured distribution; $c_1 - c_4$ = distribution coefficients according to Natta and Mantica; c = distribution coefficient according to Weibull, Nycander and Gold; v = average degree of ethoxylation.

RESULTS AND DISCUSSION

The average degree of ethoxylation, v, was measured and the molar fractions, x_i, were determined from the gas chromatograms as already described. Since v was known the theoretical Flory distribution was calculated using Equation I. Using x_o and v, the Weibull-Nycander-Gold distribution coefficient c was calculated with Equation III and with x_o and c, theoretical Weibull-Nycander-Gold distribution was calculated with Equation II. The Natta-Mantica distribution coefficients c_1, c_2, ... c_4 were calculated by Equation IV from molar fractions x_0, x_1, ... x_4 according to the approximate interval bisection method.

Calculations were performed on a Videoton 1010 (R10) computer with a FORTRAN program.

The question arose in the analysis of the Natta-Mantica relationship of whether measuring errors are summarized in the error of the single distribution coefficients, because the previously calculated c_k values ($k = 1, ... i - 1$) and the molar fractions are used in the calculation of each c_i. Because of the complexity of Equation IV, analysis of errors was performed by simulation calculations, i.e., the data of a given distribution were varied at random, according to the standard deviation of measurement, and the change in the standard deviation of the distribution coefficients has been determined.

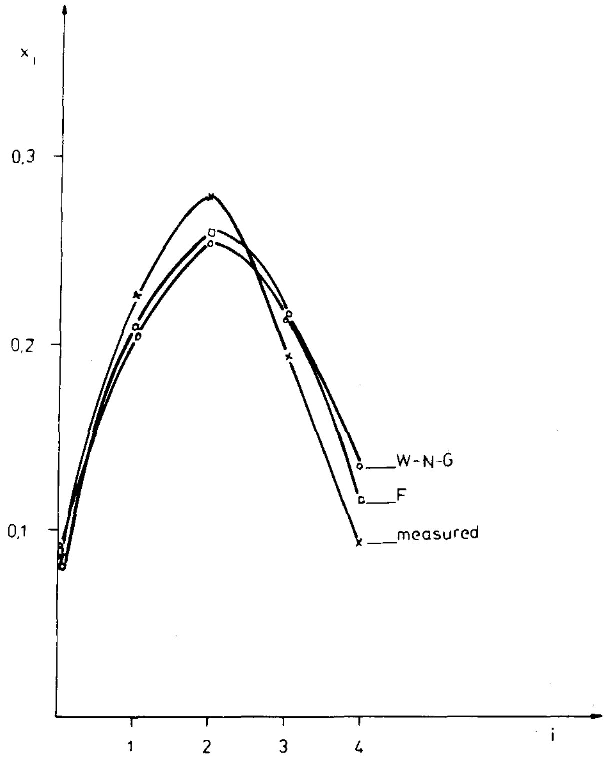


FIG. 2. **Distribution of ethoxylated product catalyzed by antimony pentachloride.**

We used given x_o, x_1, ... x_4 values of a distribution of Weibull-Nycander-Gold type and, to the given values of the molar fractions, stochastic values from a normal distribution with zero expected value and with standard deviation 0.05 were added. Thus, simulated x_o, x_1, ... x_4 values were obtained. The relative errors of the simulated x_o, x_1, ... x_4 are in Table II. The corresponding c_1, c_2, ... c_4 values were calculated according to Natta-Mantica's model (Equation IV) with the simulated x_o, x_1, ... x_4 values. The relative error of the calculated c_1, c_2, ... c_4 can be seen in Table II.

It can be concluded that the measuring error of molar fractions x_o, x_1, ... x_4, i.e., the standard deviation of the molar fractions, does not accumulate in the deviation of the distribution coefficients c_1, c_2, ... c_4.

Similar investigations were also made with a distribution of Flory type (Table II). The relative errors show that the standard deviation of the determination increases with increasing i, so that, in the Flory-type distribution the reliability of the increasing c_i values is lower.

ETHOXYLATIONS CATALYZED WITH ANTIMONY PENTACHLORIDE

Characteristic data of ethoxylations catalyzed with antimony pentachloride are summarized in Table III. Serial numbers are identical to those in Table I. Upon comparing Weibull-Nycander-Gold's c and Natta-Mantica's c_i distribution coefficients, it can be established that their values vary close to one, so that ethoxylation catalyzed with antimony pentachloride gives a Flory distribution according to expected values (12).

Figure 2 shows the measured and calculated distribution curves of an ethoxylation catalyzed with antimony pentachloride. It can be seen that the Flory and Weibull-Nycander-Gold distributions are nearly identical. This is not surprising, because if the value of the distribution coefficient calculated according to Weibull-Nycander-Gold is about 1, the Weibull-Nycander-Gold distribution becomes a Flory distribution. The character of the Flory distribution does not

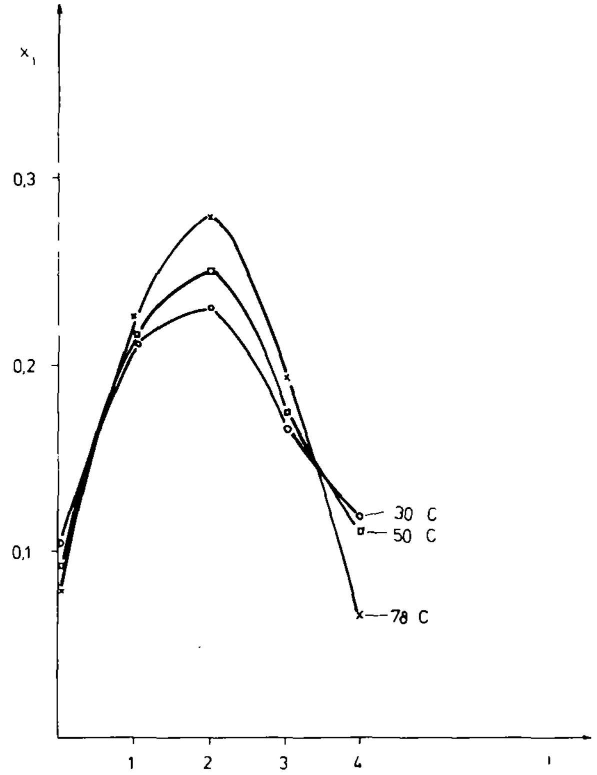


FIG. 3. The change of distribution with temperature 0.8 mol% $SbCl_5$, v = 2.5.

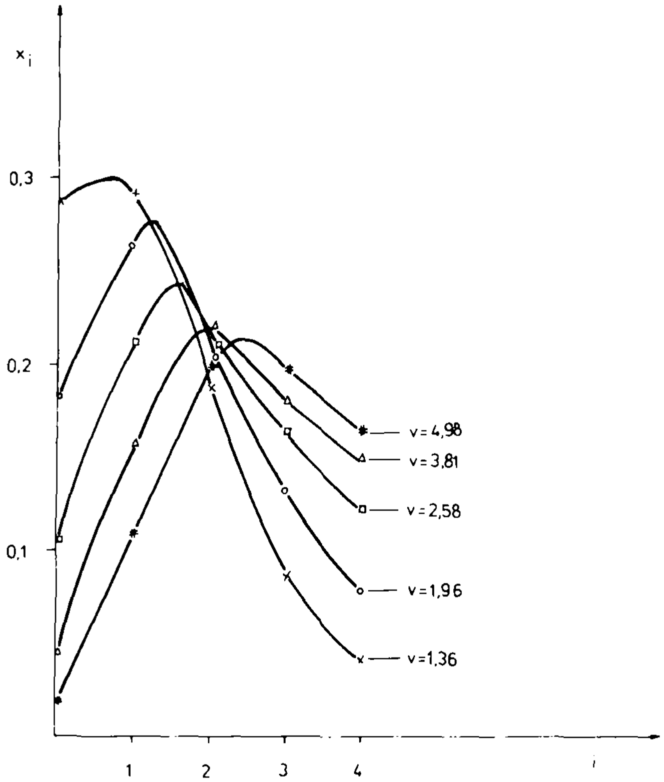


FIG. 4. The change of distribution with the average number of *ethylene oxide groups* 0.8 mol% $SbCl_5$, 30C.

change with catalyst concentration or with temperature, but the actual distribution becomes narrower with increasing temperature and its maximum increases (Fig. 3).

Upon investigation of the relationship between average degree of ethoxylation (v) and distribution, it can be established that the character of the Flory distribution does not change here, either (Fig. 4), but the value of the maximum of the distribution diminishes with increasing degree of ethoxylation, and its location is shifted under broadening of the distribution toward a higher degree of ethoxylation.

ETHOXYLATIONS CATALYZED WITH POTASSIUM HYDROXIDE

Distribution data of ethoxylation catalyzed with potassium hydroxide are summarized in Table IV. Serial numbers are identical to those in Table I. It can be seen from data in the table that in catalyses with potassium hydroxide, there is always a distribution of the Weibull-Nycander-Gold type. In the catalyst concentration range of 1-10 mol% customary in industrial processes, distributions measured are identical within the limits of experimental error, so that distribution can be considered to be independent of catalyst concentration. Distribution becomes broader and somewhat flatter with increasing temperature (Fig. 5).

Neither Weibull-Nycander-Gold's c nor Natta-Mantica's c_i distribution coefficients change considerably with temperature, because the reactivities of the alcoholic and glycolic hydroxyl groups to EO vary equally with the change in temperature.

With increasing average degree of ethoxylation, distribution becomes broader and its maximum diminishes (Fig. 6). The difference between the theoretical Weibull-Nycander-Gold and practical distributions becomes important with the triethylene glycol ether. Thus, the reactivities of the glycolic hydroxyl groups are not identical, as has been

TABLE IV

Distribution and Distribution Coefficients of the Products Obtained in Ethoxylation Catalyzed with Potassium Hydroxide

Serial no.	x_0	x_1	x_2	x_3	x_4	v	c	c_1	c_2	c_3	c_4
12	0.220	0.147	0.170	0.137	0.102	2.49	2.33	2.28	2.37	2.94	3.54
13	0.209	0.137	0.160	0.130	0.098	2.54	2.26	2.34	2.47	3.15	3.95
14	0.216	0.146	0.164	0.136	0.104	2.63	2.47	2.26	2.44	2.98	3.53
15	0.202	0.146	0.167	0.144	0.111	2.68	2.35	2.17	2.32	2.73	3.16
16	0.364	0.207	0.142	0.070	0.033	1.02	1.02	2.27	3.30	6.32	12.81
17	0.235	0.164	0.168	0.130	0.095	2.13	2.00	2.17	2.46	3.10	3.77
18	0.119	0.172	0.131	0.139	0.132	3.75	2.30	2.60	2.15	2.47	2.74
19	0.218	0.151	0.177	0.150	0.105	2.40	2.18	2.22	2.26	2.59	3.19
20	0.245	0.156	0.155	0.126	0.097	2.55	2.76	2.32	2.74	3.35	3.92

x_0-x_4 = measured distribution; c_1-c_4 = distribution coefficients according to Natta and Mantica; c = distribution coefficient according to Weibull, Nycander and Gold; v = average degree of ethoxylation.

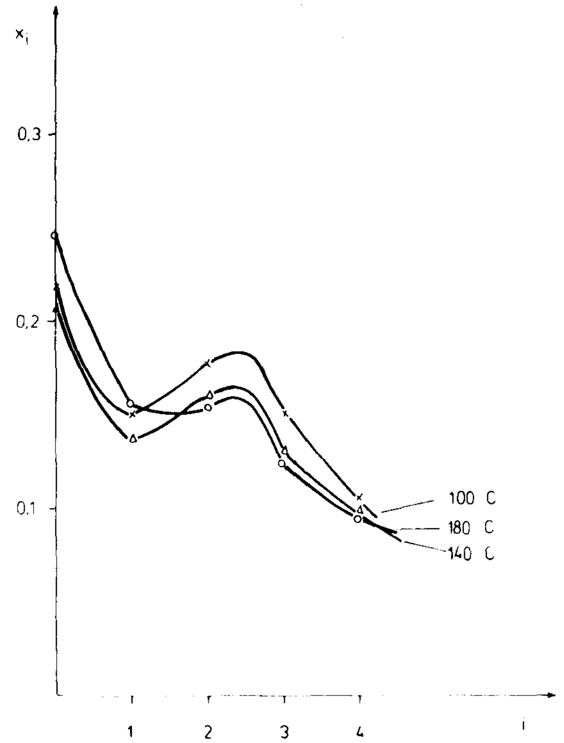


FIG. 5. Effect of temperature on the distribution, 3 mol% KOH, v = 2.5.

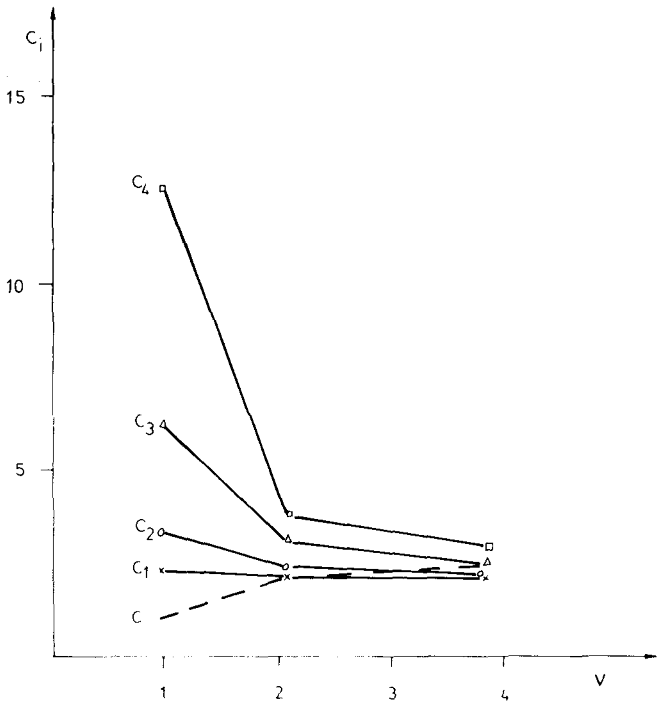


FIG. 7. Dependence of constant of distribution from average number of ethylene oxide groups 3 mol% KOH, 140 C.

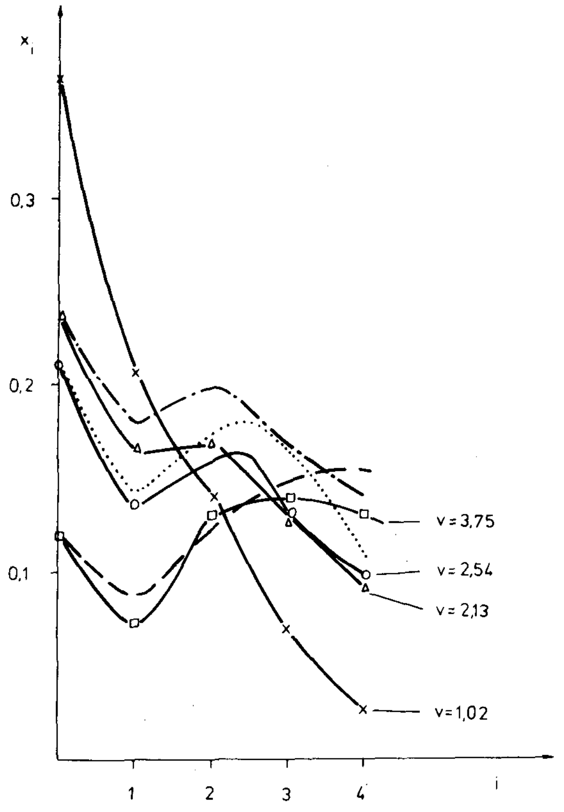


FIG. 6. The change of distribution with the average number of ethylene oxide groups measured = solid line; theoretical Weibull-Nycander-Gold = dotted line; 3 mol% KOH, 140 C.

assumed by Weibull and Nycander (3) and by Gold (4, 5).

Weibull and Törnquist (11) determined the distribution coefficients with the Natta-Mantica relationship from the results of ethoxylation reactions obtained by 10 authors, using different bases as catalyst. Contrary to expectation, distribution coefficients were found to change with the degree of ethoxylation. We shall call this effect the Weibull-Törnquist effect.

As Weibull and Törnquist (11) processed data of 10 authors measured in different ways, the possibility could not be excluded that the change in distribution coefficients is just apparent, and is to be attributed only to the measuring errors of the different experiments.

Upon investigation of the relationship between distribution coefficients and average degree of ethoxylation (Fig. 7), it can be established that both Weibull-Nycander-Gold's c and Natta-Mantica's c_i distribution coefficients approach a limiting value with increasing degree of ethoxylation. This limiting value of $c = 2-3$ is approached by c from lower, and by the c_i-s from higher values.

Our measured results, which can be considered as the experimental proof of the Weibull-Törnquist effect, unequivocally prove that the distribution coefficients are not true constants, but change during the oxyethylation reaction both in absolute value and as related to one another.

This effect explains the fact that literature data related to ethoxylation are different. If the parameters of reaction are the same, a given concentration of the catalyst is expected to give equal distribution coefficients for equal, average degrees of ethoxylation. The knowledge of Weibull-Nycander-Gold's c is important for the technical application of a nonionic surfactant, because the amount of the starting compound in an ethoxylated product can be characterized by it.

The unreacted starting compound can influence the application properties, e.g., by foaming. The knowledge of the Natta-Mantica distribution coefficients, c_i, make it possible to examine the complex mechanism of ethoxylation.

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