Applicability of Weimer-Cooper's Distribution Model for Ethoxylated Products

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The Natta-Mantica distribution constants characterizing the molecular mass distribution of ethoxylated product mixtures, discussed in an earlier paper, cannot be considered real constants because their values depend on the average degree of ethoxylation (Weibull-Törnquist effect). As the average degree of ethoxylation is included in the starting equation of the Weimer-Cooper's model, it was applied in an attempt to characterize the molecular mass distribution of an ethoxylated fatty alcohol. However, only a qualitative approximation of the distribution was possible with the Weimer-Cooper's constants. Consequently, the constants had to be calculated separately from measured mass distribution data. It was demonstrated that the two models predict the same constants when they are in modified form.

The catalyzed ethoxylation of dodecyl alcohol was reported in earlier papers (1-5). The subsequent studies' calculations and conclusions are based upon experimental data published in the earlier papers. Relationships were described in the above papers on the conditions of ethoxylation, and the composition of the reaction products formed. A uniform product is not obtained in the ethoxylation of a fatty alcohol. The original hydroxyl groups and those formed in the reaction are of similar reactivity, resulting in mixtures of homologues ethoxylated to different degrees.

The rate of product formation can be concluded from its composition as well as from the molar mass distribution. Different solutions of the kinetic equations have been published (6—9). The Flory-Poisson distribution (6) is the first, assuming equal rates for all the reaction steps of ethoxylation. The Weibull-Nycander-Gold type of distribution (7,8) is another, assuming that the rate of ethoxylation of the starting compound is different from that of the reaction products. The calculated molar mass distributions were compared to experimentally determined ones.

The best characterization of the reaction products is offered by the Natta-Mantica (9) type of distribution with different computed rate constants for each step of the reaction:

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

where x_i is the mole fraction of the i-th ethoxylated compound, $c_i = k_i/k_o$ is the distribution constant, and k_i and k_o are the rate coefficients of the reaction between ethylene oxide and the i-th component or the starting compound, respectively.

Based upon the work of Weibull and Törnquist (10), it was demonstrated (1) that the value of these "constants" depended on the average degree of ethoxylation, v, expressed as the number of ethylene oxide moles reacted with a single mole of the substrate. This referred to in our previous papers as the Weibull-Törnquist effect.

In order to account for this effect, we have applied the method developed by Weimer and Cooper (11) to our data.

Theoretical background. The following differential equations have been formulated by Weimer and Cooper (11) for the description of changes in the concentration of the homologues in the course of ethoxylation:

$$\frac{dx_o}{dv} = -a_o x_o \qquad [2]$$

$$\frac{dx_i}{dv} = a_{i-1} x_{i-1} - a_i x_i \qquad [3]$$

where v is the average degree of ethoxylation, x_i is the mole fraction of the i-th ethoxylated homologue, x_o is that of the untreated substrate, and a_o and a_i are proportionality constants.

Mole fractions of the components in the reaction mixture can be calculated from equations [2] and [3].

$$x_o = \exp(-a_o v) \qquad [4]$$

$$x_i = (-1)^i \prod_{j=0}^{i-1} a_j \sum_{j=0}^{i} \frac{\exp(-a_j v)}{\prod_{\substack{k=0 \\ k \neq j}}^{i} (a_k - a_j)} \qquad [5]$$

Better approximation of the measured experimental data can be achieved by introducing $z = v^{\alpha}$ and b_i as proportionality coefficients. Hence, the integrated forms of equations [6] and [7].

$$\frac{dx_o}{dz} = -b_o x_o \qquad [6]$$

$$\frac{dx_i}{dz} = b_{i-1} x_{i-1} - b_i x_i \qquad [7]$$

$$x_o = \exp(-b_o z) \qquad [8]$$

$$x_i = (-1)^i \prod_{j=0}^{i-1} b_j \sum_{j=0}^{i} \frac{\exp(-b_j \cdot v^{\alpha})}{\prod_{\substack{k=0 \\ k \neq j}}^{i} (b_k - b_j)} \qquad [9]$$

The best value for α proved to be Weimer and Cooper's (11)—0.702. The value of b_i could be calculated from equation [10].

$$b_i = 2.576 - 1.964 \exp.(-0.745i) \qquad [10]$$

In the presence of a basic catalyst, the ethoxylation of C_6-C_{18} fatty alcohols yielded reaction products of similar molar mass distribution (11). Its composition was defined by equation [9]. The reactivity of the obtained adducts increases with the increase in their ethylene oxide chain (reaching a limiting value).

A few papers refer to the practical application of the above equations. A complicated model of limited applicability was mentioned by Grossmann (12). The method was used as a comparison in the evaluation of measured data by Baumann (13).

RESULTS AND DISCUSSION

The experimental data from our earlier work (1) has been used for the calculations in this paper.

The applicability of Weimer-Cooper's distribution (valid for base catalyzed ethoxylation) has been studied for the description of the distribution of our sodium hydroxide catalyzed system.

Values for measured and calculated distributions corresponding to samples of different average degree of ethoxylation are given in Table 1. Significant differences occur between the measured and calculated molar fractions.

Substantial deviations between measured and calculated data can be observed, particularly in the case of the unreacted fractions. Consequently, that causes this model of distribution to be even less applicable than expected with fatty alcohols ethoxylated in systems containing catalysts other than alkaline catalysts. (Table 2).

The next idea was the calculation of the relative rate constants a_i and b_i with the help of equations [4] and [5], as well as [8] and [9], applying the stepwise iteration method of Natta and Mantica (9). It can be concluded from data of Table 3 that rate constants of Weimer-Cooper's distribution can only be calculated as functions of the actual average degrees of ethoxylation. Decreasing relative rate constants which reach a limiting value could be obtained with an increase in the average degree of ethoxylation (Fig. 1). Therefore, the rate constants of distribution, calculated according to Weimer and Cooper (11), or with the method of Natta and Mantica (9), are similar to each other in the respect that both types exhibit the Weibull-Törnquist effect.

TABLE 1

The Calculated (According to Weimer-Cooper) and the Measured Distributions (with 5% NaOH)

v		x_0	x_1	x_2	x_3	x_4
0.64	Calculated	0.639	0.201	0.095	0.042	0.016
	Measured	0.425	0.242	0.110	0.073	0.035
0.99	Calculated	0.545	0.207	0.122	0.069	0.034
	Measured	0.315	0.207	0.155	0.095	0.055
1.48	Calculated	0.447	0.197	0.139	0.096	0.060
	Measured	0.257	0.186	0.167	0.123	0.062
2.01	Calculated	0.369	0.178	0.141	0.112	0.082
	Measured	0.233	0.167	0.184	0.143	0.088
2.54	Calculated	0.308	0.158	0.135	0.119	0.097
	Measured	0.203	0.136	0.170	0.160	0.090
3.24	Calculated	0.247	0.133	0.122	0.117	0.107
	Measured	0.140	0.098	0.152	0.170	0.114
4.05	Calculated	0.195	0.108	0.105	0.108	0.107
	Measured	0.145	0.065	0.132	0.178	0.140

x_i = mol fraction of the i-th component.
v = average degree of ethoxylation.

To scale for the effect of the average degree of ethoxylation in the change of molar fraction of the unreacted substrate (a_o and b_o)—similar to the model of Natta and Mantica (9)—new constants (c_i') have been derived from the earlier ones:

$$c_i' = \frac{a_i}{a_o} = \frac{b_i}{b_o}$$

The values of the constants (c_i') are shown in Table 4. Their values are numerically equal to the distribution constants calculated according to Natta and Mantica (9).

The numerical equality of these scaled constants occurred for ethoxylated systems prepared not only with alkaline, but also with other type of catalysts.

As the starting equations of the two calculations are very different, the exact equality of the constants (c_i-c_i') is rather surprising. To fully understand this fact comparative calculations (e.g., the determination of x_2) had to be done.

The calculation with equation [1] can be seen in equation [11] (Natta-Mantica's model):

$$x_2 = c_1 \cdot \left[\frac{x_0}{(1-c_1)\cdot(1-c_2)} + \frac{x_0^{c_1}}{(c_1-1)\cdot(c_1-c_2)} + \frac{x_0^{c_2}}{(c_2-1)\cdot(c_2-c_1)} \right] \qquad [11]$$

The calculation with Weimer-Cooper's formula is shown in equation [12]:

$$x_2 = a_0 \cdot a_1 \left[\frac{\exp(-a_0 \cdot v)}{(a_0-a_1)(a_0-a_2)} + \frac{\exp(-a_1 \cdot v)}{(a_1-a_0)(a_1-a_2)} + \frac{\exp(-a_2 \cdot v)}{(a_2-a_0)(a_2-a_1)} \right] \qquad [12]$$

Equation [4] and these equations—

$$c_1' = \frac{a_1}{a_o}, \quad c_2' = \frac{a_2}{a_o},$$

equations [11] and [12] can be rearranged as follows:

TABLE 2

The Calculated (According to Weimer-Cooper) and the Measured Distributions (with Different Catalysts)

Catalyst	Tributylamine		$SnCl_4$		$SbCl_5$	
v	1.98		2.44		4.98	
	Calculated	Measured	Calculated	Measured	Calculated	Measured
x_0	0.372	0.283	0.318	0.096	0.151	0.018
x_1	0.179	0.182	0.161	0.211	0.086	0.108
x_2	0.142	0.198	0.137	0.230	0.086	0.197
x_3	0.112	0.157	0.118	0.162	0.093	0.196
x_4	0.082	0.102	0.095	0.118	0.099	0.164

	BF_3		$HClO_4$	
	2.91		2.25	
	Calculated	Measured	Calculated	Measured
x_0	0.274	0.116	0.339	0.237
x_1	0.144	0.212	0.169	0.271
x_2	0.129	0.217	0.139	0.212
x_3	0.119	0.148	0.116	0.137
x_4	0.104	0.118	0.090	0.060

TABLE 3

Calculated Weimer-Cooper's Constants

	0.64		0.99		1.48		2.01		2.54		3.24		4.05	
x_i/v	a_i	b_i	a_i	b_i	a_i	b_i	a_i	b_i	a_i	b_i	a_i	b_i	a_i	b_i
0	1.34	1.17	1.17	1.16	0.76	1.03	0.72	0.98	0.62	0.82	0.55	0.78	0.48	0.72
1	2.71	2.37	2.44	2.43	1.61	2.11	1.53	1.90	1.43	1.89	1.44	2.05	1.52	2.31
2	5.60	4.91	3.35	3.34	1.70	2.60	1.60	1.97	1.45	1.92	1.27	1.80	1.11	1.68
3	7.33	6.42	5.07	5.06	2.09	3.33	1.93	2.38	1.47	1.94	1.24	1.76	0.99	1.50
4	13.64	11.96	7.97	7.95	3.14	6.10	2.72	3.35	2.67	3.52	1.77	2.52	1.25	1.89

$$x_2 = \frac{a_1}{a_0}\left[\frac{x_0}{\left(\frac{a_0}{a_0}-\frac{a_1}{a_0}\right)\cdot\left(\frac{a_0}{a_0}-\frac{a_2}{a_0}\right)}+\frac{\exp(-a_0\cdot v\cdot c_1')}{\left(\frac{a_1}{a_0}-\frac{a_0}{a_0}\right)\cdot\left(\frac{a_1}{a_0}-\frac{a_2}{a_0}\right)}+\frac{\exp(a_0\cdot v\cdot c_2')}{\left(\frac{a_2}{a_0}-\frac{a_0}{a_0}\right)\cdot\left(\frac{a_2}{a_0}-\frac{a_1}{a_0}\right)}\right] \quad [13]$$

$$x_2 = c_1'\left[\frac{x_0}{(1-c_1')\cdot(1-c_2')}+\frac{x_0^{c'}1}{(c_1'-1)\cdot(c_1'-c_2')}+\frac{x_0^{c'}2}{(c_2'-1)\cdot(c_2'-c_1')}\right] \quad [14]$$

provided $c_i = c_i'$ in equation [14] can be replaced by equation [11].

Consequently, the molar mass distribution functions elaborated by Weimer and Cooper (11) or Natta and Mantica (9), respectively, are not completely independent of one another. Equivalency can be demonstrated between the two equations if

$$c_i = \frac{a_i}{a_o} \text{ and } c_i = \frac{b_i}{b_o},$$

respectively. The a and b constants are calculated from the corresponding experimental data. Therefore, simple division leads from the Weimer-Cooper's (11) constants to those obtained by Natta and Mantica (9).

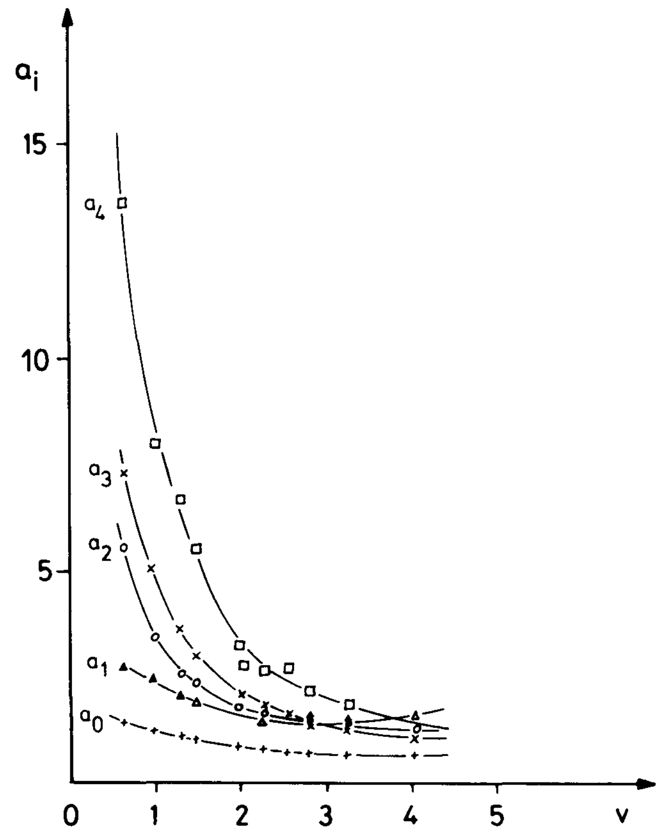

FIG. 1. The effect of the average degree of ethoxylation on the calculated Weimer-Cooper's constant.

TABLE 4

c_i' Constant of Different Reactions

v	0.64	0.99	1.48	2.01	2.54	3.24	4.05
c_1'	2.03	2.09	2.05	2.12	2.31	2.64	3.19
c_2'	4.19	2.87	2.53	2.21	3.34	2.31	2.32
c_3'	5.49	4.35	3.24	2.66	2.37	2.27	2.07
c_4'	10.22	6.83	5.93	3.75	4.30	3.25	2.61

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[Received December 7, 1988; accepted December 26, 1989]
[JS/D5618]