Determination of Relative Ethoxylation Rate Constants from Supercritical Fluid Chromatographic Analysis of Ethoxylated Alcohols[1]

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Based on ethylene oxide distributions in ethoxylated alcohols determined by supercritical fluid chromatography, a flexible computer model has been developed and applied to calculate relative ethoxylation rate constants for base-catalyzed ethoxylations of normal octanol. These distribution coefficients are not substantially affected by the presence of another alcohol and were found to increase with increasing ethylene oxide content of the reactant ethoxylates. Their values, however, change as the average ethylene oxide content of the ethoxylated alcohol reaction medium increases. Using distribution coefficients averaged over an ethylene oxide/alcohol molar ratio range of 2 to 10, model predictions closely match experimentally determined ethylene oxide oligomer distributions.

The distribution of oligomers, having different numbers of ethoxy groups, formed by addition of ethylene oxide (EO) to aliphatic alcohols is determined by the relative rates of the initiation and propagation ethoxylation steps. The reactions occurring during the base catalyzed ethoxylation of alcohols are discussed in Appendix I. A large amount of previous work has been carried out to determine molecular distributions of ethoxylated alcohols by various analytical procedures and to describe these distributions mathematically. A detailed review of this effort and its importance in understanding the manufacture and behavior of nonionic surfactants has been recently published (1).

An objective of our modelling effort, the first part of which is reported here, was to represent the kinetic equations for the ethoxylation of alcohols and to write very general computer programs to integrate the model numerically. Two main programs were envisioned: first, to solve by an iterative procedure for relative ethoxylation rate constants given an experimentally determined molecular distribution and second, to calculate molecular distributions given a set of relative rate constants, sometimes called distribution coefficients. To avoid confusion with the use of the latter in solution chemistry, we will use the more descriptive term, oligomer reactivity coefficients. The motivation for our effort was the development of very precise analytical determinations (2) of molecular distributions from supercritical fluid chromatography (SFC). The ultimate objective of our work is to develop a model that predicts complete and detailed EO distributions for the ethoxylation of mixed alcohol systems.

It was felt that the analytical capability of SFC would permit the discriminatory evaluation of various model alternatives, such as the use of exponents other than 1.0 for the ethoxylated alcohol concentrations, the inclusion of rate constants for ethoxylation of both alkoxide anions and ion pairs, and/or the consideration of oligomer reactivity coefficients which vary with a changing medium. Each of these possibilities, if it were included in the model, precludes the use of the equations of Natta and Mantica (3) that have been used by others (4-8) to calculate oligomer reactivity coefficients. These Natta and Mantica equations are limited to constant oligomer reactivity coefficients, an exponent of 1.0 for the ethoxylated alcohol concentration and only one forward reaction mechanism for each ethoxylation step. Therefore, a conscious decision was made to sacrifice computer calculation speed to be able to modify the model as needed to investigate alternative kinetic mechanisms.

Detailed derivation of general model equations, following the notation and methodology of Gee *et al.* (9), is given in Appendix I, and descriptions of the two computer programs that were developed (MOLDIST and RTCNST) are given in Appendix II. This paper discusses results that were obtained by applying these computer programs, using some of the model options mentioned above, to the base-catalyzed ethoxylation products of normal octanol, both in the pure state and in mixtures with other alcohols or ethoxylates.

EXPERIMENTAL

The materials, basic catalysts, standard ethoxylation procedures and determinations of EO/alcohol ratios and EO oligomer distributions from SFC peak areas used in this study have been previously reported (2).

RESULTS AND DISCUSSION

The results reported in this paper deal with experiments in which normal octanol was ethoxylated to determine oligomer reactivity coefficients for each of its ethoxylated oligomers (with respect to the initial ethoxylation rate constant of normal octanol). Since the distributions were to be measured by SFC analytical procedures, experiments were limited to ethoxylations of pure normal octanol and of its mixtures with other alcohols and ethoxylates that could be completely separated and analyzed by SFC. Three experiments

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involving separate ethoxylations of normal octanol were carried out: (i) in a pure state; (ii) in a 50/50 molar mixture with 2-ethylhexanol (2EH); (iii) in a 50/50 molar (20–80 weight) mixture with a 9 EO ethoxylate of 2EH that had been separately prepared. Samples for analysis of reaction mixtures were withdrawn from a one-liter stirred autoclave when the EO reacted amounted to approximately three and six moles per mole of total starting mixture. Each experiment was terminated at approximately nine moles of EO per mole, resulting in a total of nine molecular distributions of normal octanol ethoxylates for computerized mathematical modeling.

Oligomer reactivity coefficients (defined as the ratio of kinetic rate constants for ethoxylating the "i" ethoxylate to the kinetic rate constant for ethoxylating feed alcohol) were calculated for each ethoxylated alcohol present in the mixture. Obviously, the last ethoxylate reported in each experimental molecular distribution does not yield a distribution coefficient. The three experiments were chosen in order to test whether oligomer reactivity coefficients for pure octanol differ from those for octanol in the presence of another alcohol or of the reaction products of the ethoxylation of the other alcohol.

Expected results. Ideally, neither the presence of 2EH nor ethoxylated products of 2EH would affect the oligomer reactivity coefficients of normal octanol, so that essentially the same set of oligomer reactivity coefficients would result from all three experiments. Realistically, it was expected that differences in reaction media in the three experiments could cause a change not only in the absolute rate constants (overall ethoxylation speed), but also in the oligomer reactivity coefficients for each ethoxylated oligomer. This expectation was based on previous work reported by Farkas *et al.* (7), and the phenomenon is predictable based on observations of Gee *et al.* (9). They described three possible reaction mechanisms whereby EO can be added: (i) to primary alcohol and ethoxylated oligomers, a relatively slow step which can be ignored; (ii) to primary alcohol and ethoxylated oligomer alkoxide ions, presumably the fastest step; and (iii) to undissociated alkoxide-ion pairs, thought to take place at about one-tenth the rate of alkoxide ions. For different reacting media, dissociation constants of each of the alkoxide-ion pairs can be expected to be different and, more importantly as far as oligomer reactivity coefficients are concerned, ratios of these dissociation constants with respect to each other may also change.

Weibull and Nycander (10) have shown that in the presence of low concentrations of catalyst, a simple second-order reaction mechanism (first order with respect to alcohol or ethoxylated oligomer concentrations and first order with respect to EO concentrations) applies. This has been interpreted to mean that complete dissociation of alkoxide ion pairs occurs under these conditions. By neglecting the rate of reaction of alcohols in comparison to the rate of alkoxide anions, and assuming instantaneous establishment of equilibrium between ion pairs and dissociated ions, a simple kinetic expression was found to represent their data. Each oligomer reactivity coefficient Ci becomes, for this case, the product of two terms, Ci′ and Ki′, where Ci′ is the ratio of the rate constant for alkoxide anion i with respect to that of the alkoxide ion of the primary alcohol and Ki′ is the ratio of the acid-ionization constant for alkoxide ion-pair i, with respect to that of the alkoxide ion pair of the primary alcohol.

By using a rather complex but flexible numerical integration computer model in this work, it was not necessary to limit the model to either complete dissociation or complete non-dissociation assumptions, as had been done by previous investigators. It also is not necessary that the effective oligomer reactivity coefficients for each ethoxylation step be held constant during integration, if sufficient evidence is found that the changing reaction medium causes a corresponding change in the oligomer reactivity coefficients.

Experimental results. The SFC traces for all the products are similar to those shown previously (2), and one for the 2 EO ethoxylation of normal octanol in the presence of 9 EO ethoxylate of 2EH is shown in Figure 1. The results of the SFC analyses of the nine samples withdrawn from the three experimental ethoxylations are given in Table 1 as molecular distributions, expressed as normalized mole fractions, of the normal octanol and its ethoxylated oligomers.

Oligomer reactivity coefficients calculated for simple, second-order model. The results of calculating sets of oligomer reactivity coefficients for each molecular distribution in Table 1 are shown in Table 2. These oligomer reactivity coefficients were calculated by the computer program RTCNST using the simple second-order model previously described. The oligomer reactivity coefficients for all nine samples are shown in graphical form (Fig. 2) as Ci vs i, where i is the number of EO groups in the reactant ethoxylated molecule.

There are a number of pertinent observations and conclusions to be drawn from these curves: First, the relatively smooth (unscattered) appearance of the points over almost the entire range of EO groups strongly suggests that the values contain very little random measurement error, further confirming our premise of very reliable SFC analyses.

Second, the general behavior of the plots is similar to that anticipated earlier (3–5), and later reported in the literature (6,7). The oligomer reactivity coefficient

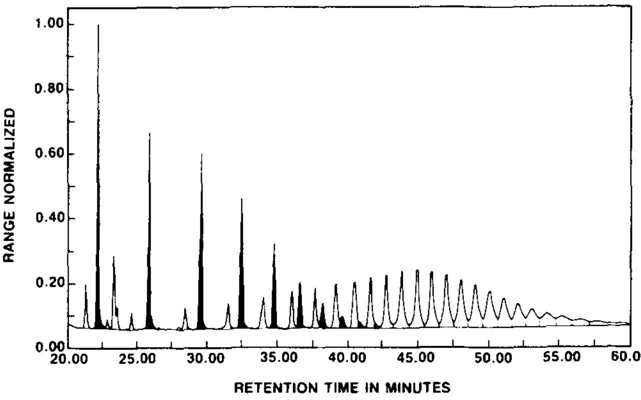

FIG. 1. SFC chromatogram of ethoxylate of equimolar mixture of normal octanol and 2-ethylhexanol (EO/Normal Octanol = 1.87). Closed peaks = normal octanol and its ethoxylates. Open peaks = 2-EH and its ethoxylates.

TABLE 1

Ethylene Oxide Distributions in Ethoxylated Normal Octanol[a]

Feed EO/Alc[b]	Pure alcohol			2EH mixture			9EO-2EH mixture		
# of EOs	2.82	5.48	8.24	3.81	6.74	9.88	1.87	4.01	5.96
0	23.09	8.10	3.25	16.48	5.45	1.80	30.95	12.33	8.08
1	15.14	6.34	2.55	11.90	4.33	1.49	19.65	9.39	5.06
2	14.90	8.24	3.52	13.39	6.19	2.19	17.73	11.64	5.88
3	13.23	9.98	4.87	12.82	7.96	3.21	13.45	13.24	7.41
4	10.56	10.81	6.20	10.85	9.11	4.40	8.32	12.67	8.65
5	7.58	10.45	7.17	8.57	9.47	5.52	4.87	11.42	9.68
6	5.46	9.79	8.12	6.58	9.12	6.40	2.65	9.37	10.05
7	3.84	8.74	8.78	5.12	8.69	7.25	1.36	7.30	10.01
8	2.62	7.47	9.11	4.14	8.06	8.00	0.67	5.37	9.56
9	1.57	5.99	8.87	3.12	7.06	8.33	0.34	3.71	8.07
10	0.91	4.55	8.17	2.30	5.96	8.23	0.00	2.34	6.57
11	0.54	3.30	7.17	1.72	4.89	7.77	0.00	0.88	5.28
12	0.29	2.31	5.99	1.25	3.88	7.03	0.00	0.33	3.33
13	0.20	1.55	4.78	0.90	2.98	6.17	0.00	0.00	1.90
14	0.05	0.96	3.58	0.52	2.15	5.22	0.00	0.00	0.46
15	0.03	0.60	2.62	0.35	1.58	4.33	0.00	0.00	0.00
16	0.00	0.36	1.84	0.00	1.12	3.49	0.00	0.00	0.00
17	0.00	0.21	1.25	0.00	0.77	2.74	0.00	0.00	0.00
18	0.00	0.12	0.83	0.00	0.48	2.11	0.00	0.00	0.00
19	0.00	0.07	0.54	0.00	0.31	1.55	0.00	0.00	0.00
20	0.00	0.04	0.34	0.00	0.19	1.08	0.00	0.00	0.00
21	0.00	0.02	0.20	0.00	0.10	0.72	0.00	0.00	0.00
22	0.00	0.00	0.12	0.00	0.05	0.48	0.00	0.00	0.00
23	0.00	0.00	0.07	0.00	0.00	0.29	0.00	0.00	0.00
24	0.00	0.00	0.04	0.00	0.00	0.15	0.00	0.00	0.00
25	0.00	0.00	0.02	0.00	0.00	0.05	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

[a] Expressed as molar percentage.

[b] EO/Octanol ratio calculated from SFC data (2).

TABLE 2

Oligomer reactivity coefficients in Ethoxylated Normal Octanol[a]

Feed EO/Alc[b]	Pure alcohol			2EH mixture			9EO-2EH mixture		
	2.82	5.48	8.24	3.81	6.74	9.88	1.87	4.01	5.96
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
1	2.297	2.218	2.257	2.236	2.223	2.198	2.181	2.208	2.566
2	2.773	2.528	2.577	2.593	2.433	2.459	2.467	2.485	3.114
3	3.167	2.739	2.731	3.025	2.642	2.590	2.663	2.626	3.268
4	3.583	2.977	2.912	3.589	2.902	2.726	3.063	2.890	3.445
5	4.181	3.308	3.164	4.260	3.212	2.914	3.316	3.025	3.529
6	4.541	3.523	3.298	4.967	3.542	3.146	3.479	3.158	3.621
7	4.718	3.684	3.394	5.501	3.801	3.288	3.411	3.148	3.594
8	4.664	3.779	3.437	5.543	3.942	3.354	2.732	2.961	3.418
9	5.014	3.898	3.504	5.871	4.131	3.448		2.501	3.378
10	5.363	4.027	3.576	6.060	4.304	3.562		2.615	3.118
11	5.199	4.149	3.635	5.810	4.428	3.682		1.370	2.417
12	5.281	4.216	3.691	5.268	4.527	3.814			1.891
13	2.481	4.258	3.739	4.069	4.596	3.919			0.774
14	4.097	4.538	3.880	3.204	4.826	4.032			
15		4.605	3.957		4.768	4.082			
16		4.698	4.056		4.658	4.100			
17		4.750	4.159		4.423	4.067			
18		4.673	4.213		4.452	3.924			
19		4.001	4.182		3.934	3.772			
20		2.597	4.098		3.099	3.622			
21			4.169		2.157	3.410			
22			3.887			3.831			
23			3.313			2.103			
24			2.098			1.127			

[a] Using 1.00 as exponent for alcohol dependency.

[b] EO/Octanol ratio calculated from SFC data (2).

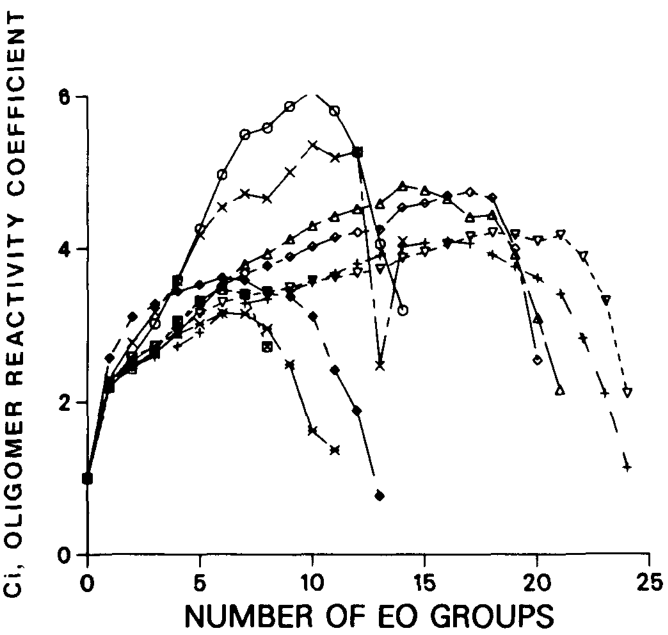

FIG. 2. Oligomer reactivity coefficients for ethoxylation of normal octanol, calculated using 1.0 alcohol exponential model. × = Pure normal octanol, EO/alcohol = 2.82, ◇ = pure normal octanol, EO/alcohol = 5.48, ▽ = pure normal octanol, EO/alcohol = 8.24, ○ = octanol in 2EH mixture, EO/alcohol = 3.81, △ = octanol in 2EH mixture, EO/alcohol = 6.74, + = octanol in 2EH mixture, EO/alcohol = 9.88, ■ = octanol in 2EH-9EOH mixture, EO/alcohol = 1.87, ✳ = octanol in 2EH-9EOH mixture, EO/alcohol = 4.01, ◆ = octanol in 2EH-9EOH mixture, EO/alcohol = 5.96.

C1 (for the first ethoxylated adduct) is slightly greater than 2.0, and oligomer reactivity coefficients C2 through C4 increase monotonically up to approximately 3.0. In contrast to expectations and previous conjectures, these results show that the values for C5 and higher continue to increase, but with a gradually decreasing slope.

Third, a disconcerting characteristic is exhibited by each curve in the graph. The oligomer reactivity coefficients reach a maximum and then decrease monotonically to small values as the number of EO groups in ethoxylated oligomers increase. After much thought about this phenomenon, the following explanation was postulated by us and later confirmed by a series of computer experiments: "Every set of rate constants calculated (by RTCNST) from experimentally determined molecular distributions exhibits this behavior because of the inevitable truncation of the true set of mole fractions that occurs as the minimum sensitivity limit of SFC exceeds the extremely low concentrations of the higher ethoxylated oligomers." It was found, by trial and error computer runs, that a small (usually <0.005%), fictitious amount for the ethoxylated oligomer one step higher than the last measured one can always be found that causes the "tail" of each curve to be raised. Each adjusted curve then conforms closely to those of the other experiments up to the Ci for its next-to-last, experimentally measured oligomer. Therefore, we conclude that the decrease in oligomer reactivity coefficients at high EO ethoxylates is not real, and is only a computational artifact caused by SFC's inability to completely measure total molecular distributions.

Fourth, as is readily seen from the curves of Figure 2, the oligomer reactivity coefficients calculated for normal octanol do not all fall on the same curve. Note, however, that C2 is remarkably constant, averaging 2.23, with a standard deviation of 0.036, for all molecular distributions over all three experiments, except for the one value of 2.57 calculated for the 5.96 EO sample from experiment three. The entire curve of oligomer reactivity coefficients for this sample is inconsistent with the remaining eight curves on the graph. This has been attributed to the inability (in this case only) of SFC to completely separate the higher normal alcohol ethoxylates from the 2EH ethoxylates present. This curve was, therefore, not included in our interpretation of results. Focusing on the remaining curves, we see that the values of Ci tend to spread out as i increases. Closer inspection shows that the primary cause of this apparent variation can be associated with the average moles of EO reacted per mole of feed alcohol for each curve. In general, the lower the EO reacted, the steeper the curves, whether the normal octanol was pure or in a mixture. In fact, the presence of 2EH or its ethoxylated products had very little, if any, effect upon oligomer reactivity coefficients calculated for normal octanol. There is, however, a clearly evident change in the oligomer reactivity coefficient curves for the first two experiments with an increasing amount of EO reacted. This we interpret to reflect the changing nature of the reaction medium as the average EO content of the ethoxylated alcohols increases. The third experiment was then conducted, and its oligomer reactivity coefficient curves plotted to confirm the conclusion that the observed change in oligomer reactivity coefficient curves as the reaction proceeds is caused primarily by a changing reaction medium. The curves for the first two low EO samples from experiment three provide qualitative confirmation that characteristics of the medium determine the steepness of the curves, since these two curves correspond to the curves for the high EO content samples of experiments one and two.

As might be expected, the effect of the changing medium is most rapid at the beginning of ethoxylation. There is a much smaller effect upon oligomer reactivity coefficients as the EO/alcohol molar ratio increases from six to nine than during a corresponding three to six increase in ratio. Visual extrapolation of this observation suggests that at EO/alcohol ratios greater than nine, the effect of the reaction medium does not significantly change. Most likely, this reaction medium effect is due to the relative ionization constants, Ki′, since any change in a Ki′ would have a direct, proportional effect upon the corresponding oligomer reactivity coefficient Ci. It also is very reasonable that these relative ionization constants would change with the average degree of ethoxylation. It is extremely important to realize that, since Ci's change as the reaction proceeds, the calculated Ci's using a simple second-order model are average values for the reaction that has taken place up to that point. To be more correct, the model would have to use Ci values that change as the reaction proceeds, based on average EO content of the reaction medium. Finally, it is seen that oligomer reactivity coefficients do not level off as quickly as previously anticipated, but instead continue to rise slowly and monotonically.

Comparisons of experimental molecular distributions with calculated distributions using average oligomer reactivity coefficients. Even though the above results show that a more complex model is required to account for the effect of changing reaction medium, a pragmatic approach would be to use a set of average oligomer reactivity coefficients from the values in Table 2. To test the efficacy of such a simplified second-order model for predicting molecular distributions at various EO/alcohol mole ratios, oligomer reactivity coefficients were arithmetically averaged for the six samples from experiments one and two (Table 3). Since calculated molecular distributions are not likely to be sensitive to the oligomer reactivity coefficients for the higher ethoxylated oligomers, Ci values for i higher than 10 were held constant at the C10 value. Using the experimentally determined EO/alcohol molar ratios in Table 2 and the oligomer reactivity coefficients in Table 3, MOLDIST calculated the molecular distributions for each of the nine samples. Comparisons between predicted and experimentally determined distributions are shown in Figure 3 for experiment three, the ethoxylation of normal octanol in a 50/50 molar mixture with the 9EO product from 2EH ethoxylation. Considering the SFC measurement difficulties with this sample described above, the matches between the experimental and predicted distributions are excellent, and even the high range match would have been considered good prior to this work. Although space does not permit the inclusion here of the comparisons for experiments one and two, the matches were similarly gratifying. These results show that although additional effort could probably improve the model, acceptable predictions can be achieved with the simplified second-order model based on average oligomer reactivity coefficients.

Oligomer reactivity coefficients calculated for a model with an exponent different from 1.0 for the alcohol and ethoxylated oligomer concentrations. Gee *et al.* (9) speculated that the changing medium may cause a departure from first-order behavior. Their results indicated that the reaction was, initially at least, less than first order with respect to alcohol and ethoxylated oligomers. Although we feel that this suggestion only approximates the effect of changing ionization constants for alkoxide ion pairs, it is certainly easy to implement it in our model. Accordingly, prior to running experiment three, a series of calculations were made with RTCNST in which the exponent on the concentrations of the alcohol and its ethoxylated oligomers was changed from 1.0 to 0.9, 0.8, and finally, 0.88. When treating the data from experiments one and two only, it was found that the curves for a 0.9 exponent were indeed closer to each other than those for 1.0, as the initial steepness of low EO/alcohol curves was reduced more than for those of higher EO/alcohol ratios. The curves for an exponent of 0.8, however, were spread out further. Visual interpolation suggested that an exponential value of 0.88 would probably produce an optimal clustering of the curves. The calculated distributions coefficients for an exponent of 0.88 are listed in Table 4 and plotted in Figure 4.

As expected, the curves in Figure 4 for the various EO/alcohol ratios, ignoring those for experiment three, are initially less spread apart, up to the point at which each curve "turns down". The oligomer reactivity coefficients for experiment three, unlike those calculated with an exponent of 1.00, fell below the 0.88 exponent curves for high EO/alcohol ratio of experiments one and two. However, the "turn-down" effect was more pronounced, with the maxima at generally lower values of i than those in Figure 2. Contrary to the model with 1.0 exponent, the curves in Figure 4 could not be adjusted satisfactorily by adding small quantities of the next higher unmeasured ethoxylate to the total. As before, the "tail" could be raised, but the entire "turn-down" could not be eliminated.

Comparisons of experimental with calculated mo-

TABLE 3

Average Normal Octanol Oligomer Reactivity Coefficients[a]

i	1	2	3	4	5	6	7	8	9	10
Ci	1.000	2.238[b]	2.56	2.82	3.12	3.50	3.84	4.06	4.13	4.31

[a] Using 1.00 exponent for alcohol dependency.

[b] Standard deviation for six determinations in experiments 1 and 2 equals 0.035.

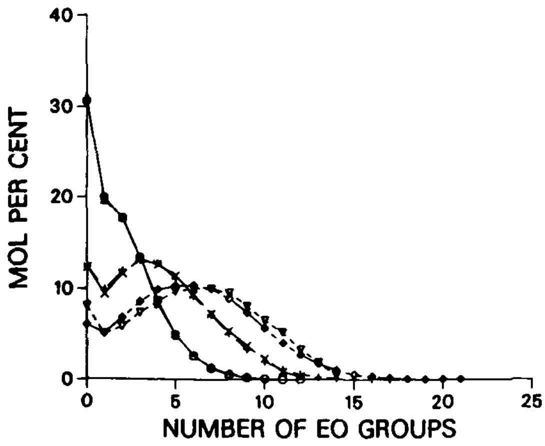

FIG. 3. Comparison of 1.0 exponential model predicted and SFC determined EO molecular distributions. ○ = EO/alcohol = 1.87, predicted; △ = EO/alcohol = 1.87, experiment 3; + = EO/alcohol = 4.01, predicted; × = EO/alcohol = 4.01, experiment 3; ◇ = EO/alcohol = 5.97, predicted; and ▽ = EO/alcohol = 5.97, experiment 3.

TABLE 4

Oligomer Reactivity Coefficients in Ethoxylated Normal Octanol[a]

Feed	Pure alcohol			2EH mixture			9EO-2EH mixture		
EO/Alc[b]	2.82	5.48	8.24	3.81	6.74	9.88	1.87	4.01	5.96
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
1	2.129	2.124	2.179	2.104	2.140	2.139	1.997	2.098	2.406
2	2.477	2.439	2.549	2.395	2.394	2.477	2.136	2.350	2.931
3	2.680	2.617	2.747	2.679	2.600	2.679	2.215	2.425	3.090
4	2.833	2.768	2.930	3.003	2.804	2.851	2.200	2.546	3.219
5	3.048	2.948	3.137	3.341	3.008	3.036	2.127	2.517	3.224
6	3.053	2.993	3.202	3.643	3.186	3.226	1.972	2.449	3.193
7	2.913	2.962	3.260	3.779	3.270	3.301	1.699	2.257	3.031
8	2.629	2.855	3.122	3.608	3.231	3.276	1.184	1.944	2.731
9	2.543	2.745	3.038	3.524	3.202	3.250		1.485	2.516
10	2.439	2.625	2.937	3.373	3.140	3.215		0.851	2.147
11	2.123	2.490	2.809	2.997	3.028	3.165		0.602	1.525
12	1.914	2.320	2.667	2.501	2.889	3.106			1.057
13	0.811	2.136	2.513	1.764	2.726	3.012			0.375
14	1.081	2.058	2.408	1.230	2.642	2.911			
15		1.891	2.262		2.412	2.762			
16		1.740	2.127		2.167	2.590			
17		1.581	1.984		1.882	3.290			
18		1.398	1.842		1.713	2.138			
19		1.069	1.664		1.372	1.892			
20		0.604	1.477		0.969	1.661			
21			1.352		0.590	1.409			
22			1.135			1.068			
23			0.859			0.759			
24			0.486			0.328			

[a] Using 0.88 as exponent for alcohol dependency.
[b] EO/Octanol ratio calculated from SEC data (2).

lecular distributions using an exponent of 0.88 for the alcohol and oligomer concentrations. Since the use of 0.88 as the alcohol exponent had significantly decreased the spread between the six sets of oligomer reactivity coefficients of experiments one and two, a corresponding improvement in matches between calculated and experimental molecular distributions was observed for these experiments. Table 5 lists the set of rate constants averaged from experiments one and two. The average rate constants in Table 5 indicate that there is no change in oligomer reactivity coefficients at EO's higher than eight, only slightly different from the model with 1.0 exponent. Figure 5 shows the comparison of predicted and experimentally determined molecular distributions for experiment three only. The observed improvements in the matches between the sets of data for experiments one and two are not reproduced because of the poor match in oligomer reactivity coefficients between experiment three and the high EO/alcohol ratios of experiments one and two. One explanation for this poor match may lie in the fact that the 0.88 exponential model is only an artifact that ac-

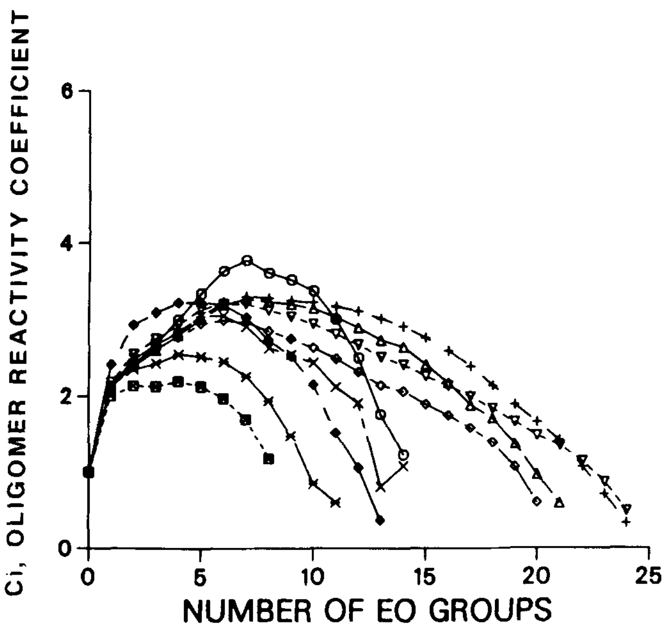

FIG. 4. Oligomer reactivity coefficients for ethoxylation of normal octanol, calculated using 0.88 alcohol exponential model. X = pure normal octanol, EO/alcohol = 2.82, ◇ = pure normal octanol, EO/alcohol = 5.48, ▽ = pure normal octanol, EO/alcohol = 8.24, ○ = octanol in 2EH mixture, EO/alcohol = 3.81, △ = octanol in 2EH mixture, EO/alcohol = 6.74, + = octanol in 2EH mixture, EO/alcohol = 9.88, ■ = octanol in 2EH-9EOH mixture, EO/alcohol = 1.87, ✳ = octanol in 2EH-9EOH mixture, EO/alcohol = 4.01, ◆ = octanol in 2EH-9EOH mixture, EO/alcohol = 5.96.

TABLE 5

Average Normal Octanol Oligomer Reactivity Coefficients[a]

i	1	2	3	4	5	6	7	8
Ci	1.000	2.135[b]	2.46	2.67	2.86	3.09	3.22	3.24

[a] Using 0.88 exponent for alcohol dependency.

[b] Standard deviation for six determinations in experiments 1 and 2 equals 0.025.

counts for changing oligomer reactivity coefficients with changing reaction medium. As suggested by Gee *et al.* (9) and supported by this work, this change is most significant at the beginning of ethoxylation, and therefore it might be expected that this 0.88 model would give a poorer fit to experimental data at the reaction conditions of experiment three. Considering the excellence of the fits shown in Figure three, further speculation concerning the unexplained "turn-down" effect of the 0.88 exponent model and trade-offs in

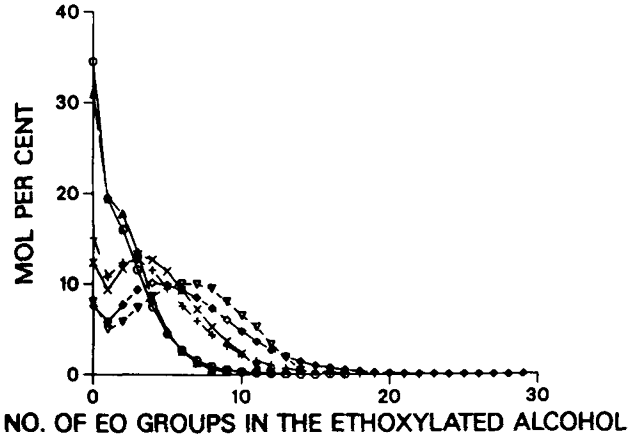

FIG. 5. Comparison of 0.88 exponential model predicted and SFC determined EO molecular distributions. ○ = EO/Alcohol = 1.87, predicted; △ = EO/alcohol = 1.87, experiment 3; + = EO/alcohol = 4.01, predicted; X = EO/alcohol = 4.01, experiment 3; ◇ = EO/alcohol = 5.97, predicted; ▽ = EO/alcohol = 5.97, experiment 3.

comparison with the 1.0 model is not warranted at this time.

The results for the 0.88 exponent show that further improvements in understanding ethoxylation mechanisms may be achieved with more complex models. A next step could be to incorporate two forward reaction rates, for alkoxide ions and for ion pairs of the alcohol and each ethoxylated oligomer. This would include both Ci′ and Ki′ in the equations, permitting each Ki′ to vary with a changing medium. Such modifications are under consideration, but at present no results are available. Work is currently underway to develop a model that simultaneously predicts all of the molecular distributions resulting from ethoxylating mixtures of various alcohols. This application will be able to predict distributions that cannot be determined experimentally because of overlap problems in some SFC analyses. More importantly, it will be able to optimize, with respect to desired EO distributions, alcohol blend compositions before their ethoxylation.

APPENDIX I

In this section the equations for the simplified second-order kinetic model are developed. They are based on assumptions of negligible ethoxylation rates for alcohols and their ethoxylated oligomers compared to the rates for alkoxides of these species, and of instantaneous and complete dissociation of alkoxide-ion pairs, thereby neglecting the reaction rates of the ion pairs. Since the concentration of EO is present in every term of every rate expression, it is convenient to divide all equations by it, as well as by various other quantities that also are present in every term. All of these quantities are then incorporated into a pseudo-time variable for integration purposes. The use of pseudo-time presents no difficulty because, for all integrations of the model equations, the criterion for stopping the integration was the achievement of either a desired EO/alcohol mole ratio or a desired fraction reacted of the feed alcohol.

The reaction for the ethoxylation of an alcohol in the absence of a catalyst is:

$$\mathrm{ROH + C_2H_4O \rightarrow ROC_2H_4OH} \qquad [1]$$

For convenience, using EO for C_2H_4O in [1] gives:

$$\mathrm{ROH + EO \rightarrow RO(EO)H} \qquad [2]$$

Similarly, the reaction for the ethoxylation of any subsequent ethoxylated oligomer is:

$$\mathrm{RO(EO)_iH + EO \rightarrow RO(EO)_{i+1}H} \qquad [3]$$

In the presence of KOH catalyst each alcohol and ethoxylated oligomer combines with the catalyst to form alkoxide anions and ion pairs. Neglecting the reactions both of ion pairs (assuming complete dissociation) and of uncombined alcohol and its oligomers leaves the following as the controlling reactions:

$$\mathrm{RO^- + EO \rightarrow RO(EO)^-} \qquad [4]$$

$$\text{and, } \mathrm{RO(EO)_i^- + EO \rightarrow RO(EO)^-_{i+1}} \qquad [5]$$

Instantaneous equilibrium is assumed for the following proton transfer reaction between the alkoxide anion of each ethoxylated alcohol and alcohol:

$$\mathrm{RO(EO)^-_i + ROH \rightleftharpoons RO(EO)_iH + RO^-} \qquad [6]$$

It can be shown that the equilibrium constant for reaction [6] is equal to Ko/Ki, the reciprocal of the relative ionization constant of the ethoxylated alcohol oligomer with respect to the feed alcohol. This is based on the fact that the potassium alkoxides are distributed in proportion to the concentrations of the feed alcohol and its oligomers. Replacing Ki/Ko by K′i, an expression for the concentration of the alkoxide anion of each ethoxylated oligomer can be written:

$$\mathrm{[RO(EO)^-_i] = K'i[RO(EO)_iH][RO^-]/[ROH]} \qquad [7]$$

Assuming each reaction is first order with respect to the concentrations of both the EO and the alkoxide ion, the resulting reaction rate expressions are:

$$\mathrm{-r_{ROH} = -d[ROH]/dt = k_o[RO^-][EO]} \qquad [8]$$

$$\begin{aligned} \mathrm{-r_{RO(EO)_iH}} &= \mathrm{-d[RO(EO)_iH]/dt} \\ &= \mathrm{k_i[RO(EO)_i^-][EO]} \\ &\quad \mathrm{-k_{i-1}[RO(EO)^-_{i-1}][EO]} \end{aligned} \qquad [9]$$

$$\text{and, } \quad \mathrm{-r_{EO} = \sum_{i=0}^{N}\{k_i[RO(EO)^-_i][EO]\}} \qquad [10]$$

To transform these expressions into more tractable form, a series of manipulations are performed: First, divide all three equations by k_o and [EO], and substitute Ci′ for k_i/k_o:

$$\mathrm{-d[ROH]/\{k_o[EO]\}dt = Co'[RO^-]} \qquad [11]$$

$$\begin{aligned} \mathrm{-d[RO(EO)_iH]/\{k_o[EO]\}dt} &= \mathrm{Ci'[RO(EO)^-_i]} \\ &\quad \mathrm{-(C_{i\text{-}1}')[RO(EO)^-_{i-1}]} \end{aligned} \qquad [12]$$

$$\text{and, } \mathrm{-r_{EO}/\{k_o[EO]\} = \sum_{i=0}^{N}\{Ci'[RO(EO)^-_i]\}} \qquad [13]$$

Now the concentration of the alkoxide anion in the above three equations can be replaced with its equivalent expression from equation [7]:

$$\begin{aligned} &\mathrm{-d[ROH]/\{k_o[EO]\}dt =} \\ &\qquad \mathrm{(Co')(Ko')[ROH][RO^-]/[ROH]} \end{aligned} \qquad [14]$$

$$\begin{aligned} &\mathrm{-d[RO(EO)_iH]/\{k_o[EO]\,\}dt =} \\ &\qquad \mathrm{(Ci')(Ki')[RO(EO)_i\,H][RO^-]/[ROH]} \\ &\qquad \mathrm{(C_{i\text{-}1}')(K_{i\text{-}1}')[RO(EO)_{i\text{-}1}H][RO^-]/[ROH]} \end{aligned} \qquad [15]$$

$$\begin{aligned} &\text{and, } \mathrm{-r_{EO}/\{k_o[EO]\} =} \\ &\qquad \mathrm{\sum_{i=0}^{N}\{Ci'(Ki')[\,RO(EO)_iH][RO\ ]/[ROH]\}} \end{aligned} \qquad [16]$$

At this point, the ratio [RO⁻]/[ROH], which appears in all three equations, is also transferred to the left hand side by division:

$$\begin{aligned} &\mathrm{-d[ROH]/\{k_o[EO][RO^-]/[ROH]\}dt =} \\ &\qquad \mathrm{(C_o')(Ko')[ROH]} \end{aligned} \qquad [17]$$

$$\begin{aligned}-d[RO(EO)_iH]/\{k_o[EO][RO^-]/[ROH]\}\,dt = {} & (Ci')(Ki')[RO(EO)_iH] \\ & - (C_{i-1}')(K_{i-1}')[RO(EO)_iH]\end{aligned} \qquad [18]$$

$$\text{and, } -r_{EO}/\{k_o[EO][RO^-]/[ROH]\} = \sum_{i=0}^{N} \{Ci'(Ki')[RO(EO)_iH]\} \qquad [19]$$

The final step is to set the rate of consumption of EO in equation [19] equal to dXEO/dt, where XEO is defined to be the amount of EO consumed; and to define a psuedo-time, $dT = \{k_o[\,EO][\,RO^-]/[\,ROH]\}dt$ and an oligomer reactivity coefficient, $Ci = Ci'Ki'$, and substitute them into the three differential equations: (Note that Co and K′o are both equal to one)

$$-d[ROH]/dT = [ROH]$$

$$-d[RO(EO)_iH]/dt = (Ci)[RO(EO)_iH] \qquad [20]$$

$$- (C_{i-1})[RO(EO)_iH] \qquad [21]$$

$$dXEO/dT = \sum_{i=0}^{N} Ci[RO(EO)_iH] \qquad [22]$$

Equations [20–22] are the final working equations that were integrated within the two programs, RTCNST and MOLDIST, to calculate the results reported in this paper.

APPENDIX II

In this section, brief descriptions are provided of the two FORTRAN computer programs that were developed to perform the calculations reported here.

MOLDIST. This program uses a desired final EO/alcohol mole ratio as input and computes the molecular distribution of the ethoxylated product that will result, based upon a given set of oligomer reactivity coefficients. To facilitate the use of more complex models in the future, a function subroutine is used to calculate the oligomer reactivity coefficients each time they are needed. The version used in this work returns one value of Ci for the combined product Ci′Ki′ for each value of i, as shown in Tables 3 and 5, depending upon whether the model exponent selected is 1.0 or 0.88, regardless of the degree of ethoxylation that has occurred.

Numerical integration is performed by a subroutine which can be either the one provided in MOLDIST (RK2) or one from any ODE package that may be available on the computer system being used. As usual, the kinetic model itself is included in subroutine DER, which calculates derivatives for the feed alcohol and each of the ethoxylated oligomers (up to a maximum of 100 oligomers) when called by the integration routine. MOLDIST communicates with DER via the labeled COMMON feature of FORTRAN.

Upon completion of its calculations, if requested by the user, MOLDIST calls a plotting subroutine MPLOT, which writes a file containing instructions to an in-house plotting package. This package can then be invoked to produce a graph of the molecular distributions on a laser-graphics printer. The graphs in this paper were produced in this manner.

RTCNST. This subroutine uses an experimentally-determined (SFC) molecular distribution of the product from ethoxylation of an alcohol as input data. The feed material is assumed to be pure alcohol, so that molecular distributions of products from the ethoxylation of mixtures must first be partitioned and normalized into separate distributions, each containing only one alcohol and its ethoxylated oligomers. By an iterative search procedure, RTCNST determines the numerical values of each combined oligomer reactivity coefficient required to match exactly the given molecular distribution, first finding the value of C1 required to match the experimentally-measured mole fraction of $RO(EO)_1H$ when the mole fraction of ROH has declined from its initial value of 1.0 to its experimentally-determined final value, then finding the value of C2 required to match the mole fraction of the second ethoxylated oligomer, etc. On each step, the program integrates the kinetic model by calling the same subroutine called by MOLDIST, using all of the previously calculated oligomer reactivity coefficients and the current trial value for the oligomer reactivity coefficient that is being found by the iterative search procedure.

RTCNST takes its data from an input file provided by the user, containing a title record followed by as many records as needed to provide the experimental molecular distribution in free-format. RTCNST will process all problems in the input file in sequence, stopping when an end-of-file is reached. It then calls a plotting subroutine KPLOT, which creates a file of the calculated oligomer reactivity coefficients for an in-house plotting routine. As with MOLDIST, the plotting routine can then be used to produce graphs of the oligomer reactivity coefficients such as those included in this paper.

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