The Prediction of Ethylene Oxide Distributions in Mixed Alcohol Ethoxylates

Paul R. Geissler[a,*], **Adrain E. Johnson, Jr.**[b] and **Larry D. Talley**[c]
[a]Exxon Chemical Company, Intermediates Technology Division, Baton Rouge, LA 70821, [b]Department of Chemical Engineering, Louisiana State University and [c]Exxon Research and Engineering, Baytown Specialty Products, Baytown, TX 77522

Supercritical fluid chromatographic analyses of ethoxylates of 2-ethylhexanol in the pure state and in mixtures were used to determine relative propagation-to-initiation ethoxylation rate constants. Earlier work with normal octanol was verified in that ethylene oxide distributions were found to be unaffected by the presence of other alcohols in the ethoxylation of mixed alcohols. An apparent decrease in the relative ethoxylation rates with increasing number of ethylene oxide monomers in ethoxylates is attributed to truncation of the measured distributions and is eliminated by adding small amounts of higher ethoxylates to the distribution. The Weibull-Tornquist effect of decreasing relative rate constants as the overall average ethylene oxide-to-alcohol ratio increases was again observed. Rate constants of the ethoxylation of 2-ethylhexanol and its ethylene oxide adducts relative to the ethoxylation of normal octanol were determined from the analysis of ethoxylates of their mixtures. A computer model using averaged relative rate constants was developed that effectively predicts the ethylene oxide distributions in ethoxylates of alcohol mixtures.

KEY WORDS: Ethoxylated alcohols, ethylene oxide oligomer distributions, non-ionic surfactants, relative rate constants, supercritical fluid chromatography, Weibull-Tornquist effect.

In the base-catalyzed ethoxylation of alcohols to produce nonionic surfactants, distributions of oligomers having different numbers of ethylene oxide (EO) monomers are determined by the rates of each propagation ethoxylation step relative to the rate of the initial feed alcohol ethoxylation. The importance of being able to measure accurately and predict EO distributions in these systems has been reviewed recently (1,2). Previous papers in this series discussed a supercritical fluid chromatographic (SFC) method of measuring EO oligomer distributions in ethoxylated alcohols (2), computer programs that calculate relative propagation-to-initiation ethoxylation rate constants from SFC data and predict EO distributions from these relative rate constants (3), and the effects of process variables, degree of ethoxylation, and alcohol structure on EO distributions (4).

The availability of precise SFC determinations of EO distributions and these two computer programs have allowed us to calculate relative propagation-to-initiation ethoxylation rate constant ratios, termed Oligomer Reactivity Coefficients (ORC), for a variety of alcohols and ethoxylation conditions. Based on a limited number of experimental ethoxylations, this paper extends the application of these tools to mixtures of alcohols, resulting in a model that predicts EO distributions of their ethoxylates. This is especially useful for complex alcohol mixtures whose ethoxylates cannot easily be analyzed by SFC and is potentially useful for optimizing feed alcohol mixture compositions to attain desired EO distributions.

EXPERIMENTAL PROCEDURES

All ethoxylations were carried out with potassium hydroxide as catalyst. Ethoxylation conditions were within ranges of temperature, EO pressure, and catalyst concentration that have been shown not to affect resulting EO distributions (4). The procedures followed in ethoxylating alcohols, in analyzing the resulting ethoxylates, and in transforming SFC peak area data into molar percentages of EO oligomers have been published (2).

RESULTS AND DISCUSSION

A previous paper (3) reported the results of calculating ORCs for the ethoxylated oligomers of normal octanol (NC8) from three experiments, one starting with pure NC8, another starting with a 50:50 mole percent mixture of 2-ethyl hexanol (2EH) and NC8, and a third starting with a 50:50 mole percent mixture of NC8 and the nine-mole ethoxylate of 2EH. New results reported in this paper deal with calculating ORCs for the ethoxylated oligomers of 2EH from two experiments, one starting with pure 2EH and the other (the second above experiment) starting with a 50:50 mixture of 2EH and NC8. In each experiment the reaction was carried out until an EO/alcohol ratio of approximately 9 was reached, with intermediate samples withdrawn at approximately 3 EO/alcohol and 6 EO/alcohol levels and a third sample withdrawn at the final 9 EO/alcohol level.

An oligomer reactivity coefficient, ORC[i], previously defined as the apparent kinetic rate constant for ethoxylating the oligomer containing i EO groups divided by the apparent kinetic rate constant for ethoxylating the feed alcohol, was calculated for each of the ethoxylated oligomers of 2EH found in the products by using a second-order kinetic model and computer program (3). It was also pointed out (3) that each ORC in the kinetic model can be considered to be a product of two ratios—one of oligomer-to-alcohol kinetic ethoxylation rate constants and a second of oligomer-to-alcohol ionization constants.

Figure 1 shows a plot of the ORCs reported previously (3) for the ethoxylated oligomers of NC8. One purpose of this paper is to compare the ORCs for the ethoxylated oligomers of 2EH with these NC8 results. A second important purpose is to demonstrate the use of these ORC values to predict molecular distributions of product mixtures obtained from ethoxylating mixtures of alcohols. A third purpose is to explain the gradual decreases in ORC values observed at ethoxylates with high EO contents.

---

*To whom correspondence should be addressed at Exxon Chemical Company, Intermediates Technology Division, P.O. Box 241, Baton Rouge, LA 70821

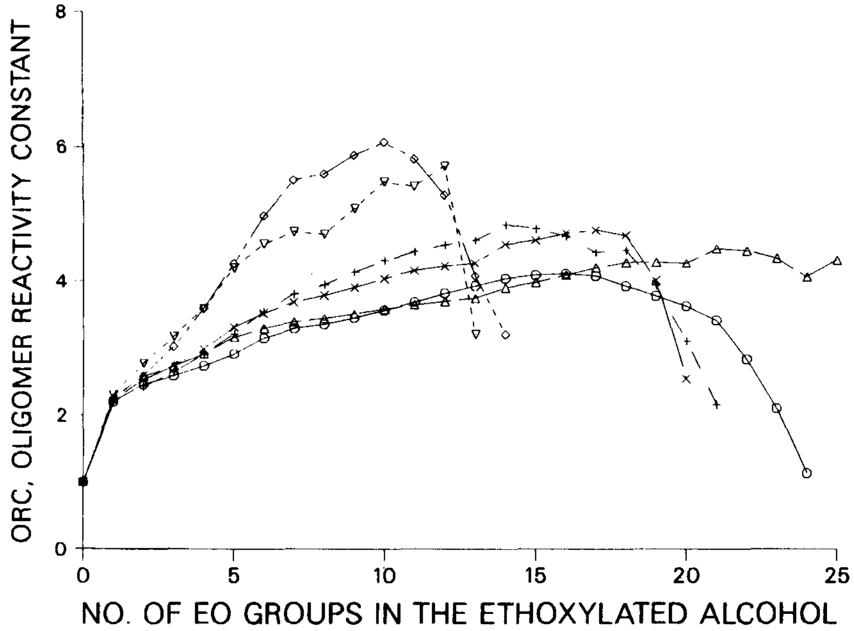

FIG. 1. Oligomer reactivity coefficients for normal octanol (3). ∇, 2.8 EO/octanol; ◊ , 3.8 EO/octanol; ×, 5.5 EO/octanol; +, 6.7 EO/octanol; △, 8.2 EO/octanol; and ○ , 9.9 EO/octanol.

The two computer programs RTCNST and MOLDIST, described in the previous paper (3), were used to calculate ORCs for 2EH and its ethoxylated oligomers from the normalized experimental SFC molecular distributions of ethoxylated 2EH obtained from the two experiments. Although it was demonstrated in the previous paper that kinetics more complex than simple second-order can be treated with these two computer programs, no change from simple second-order kinetics has been justified by the data collected to date. Accordingly, all results discussed in this paper utilize only the simple second-order kinetic model.

In order to predict molecular distributions resulting from the ethoxylation of alcohol mixtures, MDTERM (a modified version of MOLDIST) was developed. MDTERM accepts the composition of a starting mixture containing from one to ten alcohols as input. Based on given sets of ORCs for each alcohol, it calculates the molecular distribution in the product mixture that will result from the simultaneous ethoxylation of all the alcohols and their ethoxylated oligomers up to any specified overall EO/alcohol ratio. For MDTERM to calculate the competing reaction rates properly, the ORCs for the alcohols and their ethoxylated oligomers must all be relative to the reaction rate constant of only one of the alcohols in the mixture. How this was accomplished for mixtures of 2EH and NC8 is discussed later.

Experimental results. All of the SFC traces for the product mixture samples are similar to those shown previously (2). The results of the SFC analyses for the 2EH portions of the six samples of the two experiments are given in Table 1 as normalized molecular distributions of 2EH and its ethoxylated oligomers. The ORCs calculated for each of these 2EH molecular distributions are listed in Table 2 and plotted in Figure 2 as ORC[i] *vs.* i, where i is the number of EO groups in the oligomer molecule being ethoxylated.

Inspection of the curves in Figure 2 reveals the following characteristics (also exhibited by the NC8 curves in Figure 1): i) The values of ORC[1], regardless of the average EO content of the product, cluster fairly close together. They average 3.81 with a standard deviation of 0.15. ii) Each curve increases monotonically up to a maximum value before "turning down" for the final four to six ORCs. iii) The curves for the three different EO levels spread apart as i increases, exhibiting the Weibull-Tornquist effect (5) of decreasing ORCs with increasing EO/alcohol ratio that was also observed in our earlier studies (3,4). iv) The curves for pure 2EH do not differ substantially (up to the point at which they "turn down") from those for 2EH in its ethoxylates of the 50:50 2EH/NC8 mixture, showing essentially no effect upon the ORCs of one alcohol due to the presence of the other alcohol.

A comparison of the NC8 curves in Figure 1 with the 2EH curves in Figure 2 shows that the ORCs for 2EH are substantially higher than those for NC8. While for NC8 ORC[1] averaged 2.24, for 2EH ORC[1] averaged 3.81. Also, for all three EO/alcohol ratios tested, each successive ORC[i] for 2EH is higher than the corresponding ORC[i] for NC8. In other words, the ethoxylated oligomers of 2EH are more reactive relative to 2EH than the corresponding ethoxylated oligomers of NC8 are relative to NC8. Note, however, that this observation says nothing about the relative ethoxylation rate of 2EH compared to that of NC8. This important ratio is discussed later.

Explanation of "turn-down" behavior. The turn-down that is characteristic of all of the calculated ORC curves in both Figures 1 and 2 inhibits their interpretation. In a previous paper (3) we attributed the turn-down of the calculated ORC curves to the fact that all experimentally measured distributions must be truncated at some point, leaving small quantities of the highest molecular weight oligomers undetected in the product mixture. Before

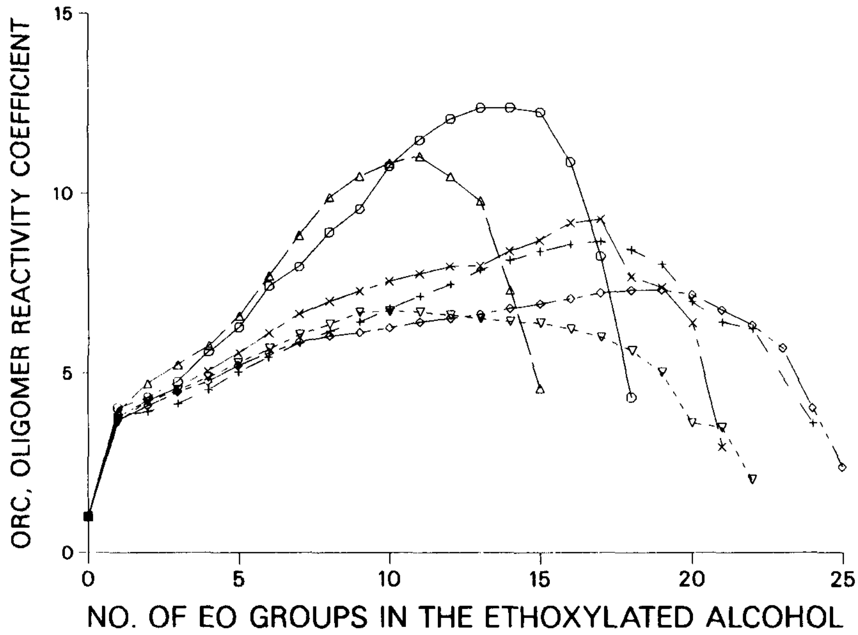

FIG. 2. Oligomer reactivity coefficients for 2EH. △, 2.5 EO/2EH; ◇ , 2.9 EO/2EH; ×, 4.4 EO/2EH; +, 6.1 EO/2EH; ▽, 7.3 EO/2EH; and ○ , 8.6 EO/2EH.

TABLE 1

Ethylene Oxide Distributions in Ethoxylated 2-Ethyl Hexanol (2EH)

Feed EO/ALC	Pure alcohol			NC_8 mixture		
# of EO's	2.9	6.1	8.9	2.5	4.4	7.3
1	32.58	13.70	8.28	37.14	21.90	11.59
2	10.40	5.12	3.09	12.01	7.78	4.36
3	11.36	6.45	3.67	11.20	8.68	4.91
4	10.86	7.51	4.26	10.20	9.34	5.71
5	8.91	8.21	4.93	8.53	9.19	6.36
6	7.15	8.41	5.36	6.41	8.51	6.78
7	5.22	7.72	5.78	4.51	7.46	6.96
8	4.01	7.38	6.11	3.15	6.30	6.93
9	2.87	6.88	6.43	2.18	5.26	6.78
10	2.08	6.02	6.65	1.55	4.26	6.39
11	1.42	5.10	6.61	1.09	3.32	6.09
12	1.00	4.05	6.33	0.75	2.51	5.62
13	0.70	3.47	5.91	0.52	1.83	5.03
14	0.49	2.70	5.33	0.34	1.31	4.31
15	0.34	2.06	4.63	0.23	0.87	3.52
16	0.23	1.54	3.91	0.13	0.57	2.73
17	0.16	1.14	3.20	0.06	0.36	2.05
18	0.11	0.81	2.54		0.23	1.47
19	0.07	0.58	1.98		0.16	1.01
20	0.03	0.42	1.51		0.09	0.66
21		0.29	1.13		0.05	0.43
22		0.18	0.84		0.03	0.19
23		0.11	0.59		0.01	0.09
24		0.07	0.40			0.03
25		0.04	0.28			
26		0.02	0.16			

TABLE 2

Oligomer Reactivity Coefficients in Ethoxylated 2-Ethyl Hexanol (2EH)

Feed EO/ALC	Pure alcohol			NC_8 mixture		
# of EO's	2.9	6.1	8.9	2.5	4.4	7.3
0	1.00	1.00	1.00	1.00	1.00	1.00
1	4.03	3.78	3.68	3.92	3.77	3.65
2	4.32	3.92	4.08	4.71	4.23	4.20
3	4.75	4.15	4.47	5.22	4.58	4.52
4	5.58	4.52	4.76	5.75	5.05	4.88
5	6.26	5.02	5.20	6.58	5.55	5.27
6	7.50	5.43	5.55	7.69	6.10	5.67
7	7.94	5.83	5.86	8.81	6.63	6.05
8	8.90	6.15	6.02	9.87	6.98	6.35
9	9.54	6.41	6.11	10.46	7.26	6.67
10	10.73	6.76	6.24	10.82	7.53	6.70
11	11.46	6.12	6.40	11.01	7.74	6.68
12	12.05	7.45	6.50	10.45	7.95	6.59
13	12.36	7.84	6.62	0.77	7.96	6.49
14	12.36	8.12	6.77	7.28	8.37	6.41
15	12.23	8.36	6.90	4.56	8.67	6.37
16	10.84	8.55	7.04		9.14	6.20
17	8.22	8.63	7.20		9.24	5.97
18	4.30	8.40	7.27		7.64	5.60
19		7.99	7.28		7.35	5.00
20		6.95	7.15		6.37	3.58
21		6.39	6.72		2.92	3.46
22		6.21	6.31			2.02
23		3.58	5.67			
24			4.01			
25			2.36			

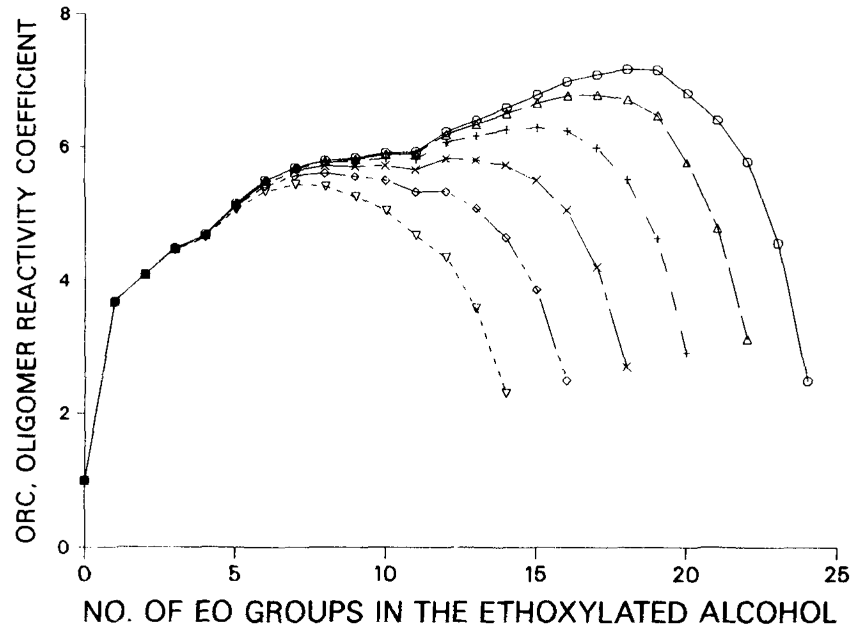

FIG. 3. Effect of truncating oligomer distribution on oligomer reactivity coefficients for 8.6-mole ethoxylate of 2EH. ○, No truncation; △, 2 moles truncated; +, 4 moles truncated; ×, 6 moles truncated; ◇, 8 moles truncated; and ▽, 10 moles truncated.

completing the primary discussion of this paper, further analysis of this behavior and its explanation are presented here.

It is clear that normalization of the reported mole fractions causes each reported mole fraction to be slightly too high by a factor dependent on the unknown sum of the mole fractions of the undetected oligomers. This very small, and unknown, positive bias in all of the reported mole fractions may not seem a likely cause of the substantial turn-downs that are observed in every set of ORCs calculated from molecular distributions. However, it is easily demonstrated that truncation of the measured distributions, followed by renormalization of the distribution, results in the always-present turn-down behavior. For example, Figure 3 shows the effect upon the calculated ORCs of artificially truncating the SFC-measured distribution of the nine-mole ethoxylate of pure 2EH by omitting, one at a time, each mole fraction, starting with the last (highest EO content) oligomer reported by the SFC analysis procedure. As each ethoxylated oligomer in turn is dropped out of the distribution, the turn-down behavior of the remaining calculated ORCs gradually moves to the left, affecting ORCs of oligomers with lower and lower EO content. Accordingly, it appears that the original turn-down behavior of the calculated ORCs was due to the missing high molecular weight ethoxylated oligomers that were not measured by SFC.

To grasp why this is true one must realize that each ORC is calculated by RTCNST so that its corresponding oligomer leaves unreacted exactly that quantity (mole fraction) of itself needed to match the SFC distribution. Simultaneously, it must produce enough of the next higher EO oligomer to equal exactly the total quantity (mole fraction) of all of the higher EO oligomers. When the last oligomer is reached in the ORC calculations, its calculated ORC must always be zero, since there are no higher oligomers present in the truncated distribution. Obviously, it is then in substantial error compared to its true value. Therefore, in this work, the computer program was terminated prior to calculating the ORC for the last reported oligomer in the normalized distribution.

It was not realized at first, however, that not only is there always a substantial negative error in the ORC calculated for the last oligomer, but there also is a substantial, but smaller, negative error in the ORC calculated for the next-to-last oligomer, because it is required to react only enough to supply the last oligomer in the distribution, but not the missing higher oligomers. Similarly, on moving to next lower molecular weights in the distribution, the calculated ORCs for each oligomer in turn also contain negative errors because of the missing higher oligomers. However, the relative magnitude of this error rapidly decreases as the mole fraction of the missing (truncated) oligomers becomes an ever-smaller portion of the total oligomers that contain more EO than the one being considered. This process results in what we have referred to as the turn-down behavior of the calculated ORCs.

Elimination of turn-down behavior. Based on the above analysis, a procedure has been developed whereby consistent ORC values can be calculated for the affected ORCs by the elimination of the turn-down behavior. This is accomplished by adding to the measured molecular distribution at the next higher EO oligomer a proper estimate of the total of the missing (truncated) mole fractions, renormalizing the distribution, and recalculating the ORCs for this revised distribution. Furthermore, we have found that a straight-forward, trial-and-error procedure can be very effective in determining a proper estimate of the truncated mole fractions. First, starting with a very small estimate of the total of the missing (truncated) mole fractions and gradually increasing this estimate in small steps, revised ORCs are calculated for each estimate. Second, by

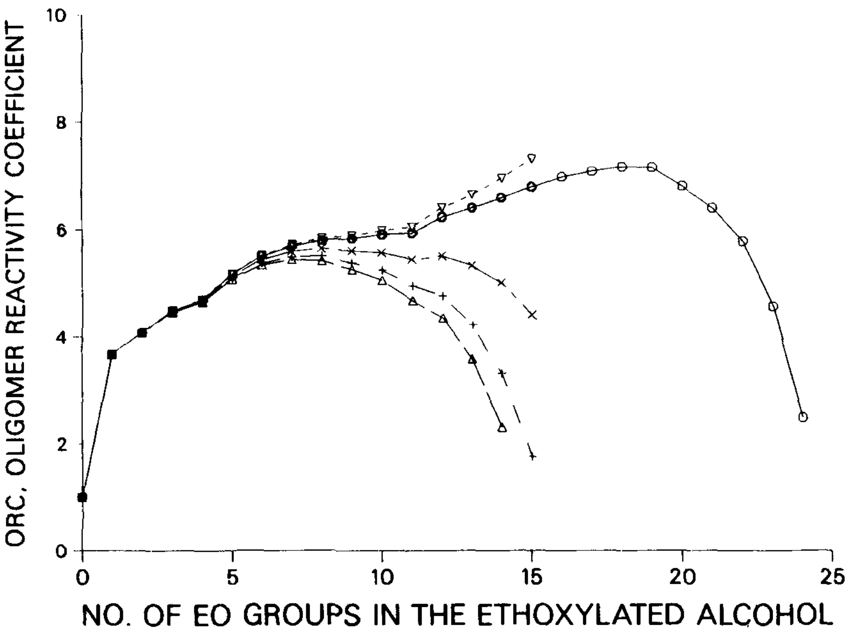

FIG. 4. Effect of adding higher molecular weight oligomers to truncated distribution of 8.6-mole ethoxylate of 2EH. △, 10 Moles truncated; +, 0.02 mole % added; ×, 0.06 mole % added; ○ , 0.11 mole % added; and ▽, 0.12 mole % added.

plotting the resulting "family" of ORC curves, it can be observed that the turn-down behavior is gradually eliminated, until it is finally replaced with the opposite "turn-up" behavior, when the estimate of the missing mole fraction becomes too large. A "best" truncation estimate is then selected, that is, the one that most nearly eliminates the "turn-down" completely without resulting in any noticeable "turn-up" in the tail of the ORC curve.

To illustrate that this procedure does result in correct values for the "turned-down" ORCs, we applied it to the severely truncated SFC distribution in Figure 3, which was generated by omitting the highest ten of the twenty-five measured oligomers of the 9-mole ethoxylate of pure 2EH. The values of the ORCs calculated from the original SFC distribution and from this artificially truncated distribution are both shown in Figure 4, along with several curves generated by applying the elimination procedure. The artificial truncation induces a severe characteristic turn-down behavior in the remaining calculated ORCs. However, the above-discussed procedure for determining the total truncated mole fraction successfully eliminates the artificially induced turn-down behavior. Moreover, the calculated ORCs for the first 15 EO oligomers remaining in the truncated distribution are restored to the identical values calculated for them from the original distribution.

In Figure 5 the procedure to find the truncated mole fraction was applied to the original distribution of the same 9-EO ethoxylate of pure 2EH. The truncation error estimates ranged from 0.001 to 0.003 mole fraction. The curve for 0.0025 was selected as the one which effectively eliminates the truncation error without introducing any substantial amount of "turn-up" behavior. Clearly, this selection is somewhat subjective, but not exceptionally so, as there appears to be a definite upward inflection in the curve introduced by the 0.003 error estimate.

Revised ORCs for ethoxylated oligomers of 2EH. The procedure described above for determining truncated mole fractions was applied to all six of the molecular distributions in Table 1, resulting in the revised set of ORCs in Figure 6. As expected, the main effect of the revision was to eliminate completely the turn-down behavior of virtually every curve, except for the 9-EO sample of the 50-50 NC8-2EH starting mixture, which continues to exhibit an anomalous gradual decline above ORC[11]. It also can be seen that the revised ORC curves for the 3-EO samples do not level out, but continue to increase slightly, up to the last calculated coefficient, ORC[15]. On the other hand, the revised 6-EO and 9-EO curves appear to level out at about ORC[18], which is much higher than might be expected based on simple molecular considerations. Thus, the capability of the SFC technique to measure mole fractions precisely of the higher molecular weight oligomers has revealed that the calculated ORCs do not become insensitive to the EO content of the ethoxylated oligomer until many EO groups have been added to the feed alcohol.

Weibull-Tornquist effect. The Weibull-Tornquist effect (5–7) of the changing reaction medium on the ORCs of the oligomers of 2EH is clearly evident in Figure 6. As the average EO/alcohol level of the product mixture increases from 3 to 9, each revised ORC[i] declines in value. This effect becomes more pronounced with increasing EO content of the oligomer, as indicated by divergence of the curves. The ORCs of the oligomers of NC8 in Figure 1 also exhibit this Weibull-Tornquist effect, but it is somewhat obscured by the turn-down behavior of the unrevised curves.

In both Figures 1 and 6, the decline in each ORC[i] with increasing EO/alcohol ratio is greater from 3 to 6 than for the increase from 6 to 9, suggesting that there may be little effect on the ORCs with further increases above the 9-EO/alcohol level. When analyzing the behavior of the calculated ORCs with a changing medium (as indicated by the EO/alcohol ratio), an important point must be remembered. The ORCs calculated by RTCNST to match each sampled SFC distribution were held constant in the model throughout the entire course of the ethoxylation. Consequently, they do not represent instantaneous values of the changing ORCs corresponding to the EO/alcohol ratio when the sample was taken, but instead represent "average" ORCs over the entire course of the reaction.

As previously explained, each calculated ORC[i] may be considered to be the product of two ratios, k_i/k_0 and K_i/K_0, the ratio of the kinetic rate constants and the ratio of the ionization equilibrium constants, respectively, of oligomer [i] to that of the starting or feed alcohol. Accordingly, for this mechanism, the change that is observed in each ORC[i] as the medium changes with increasing EO/alcohol ratio (Weibull-Tornquist effect) can be

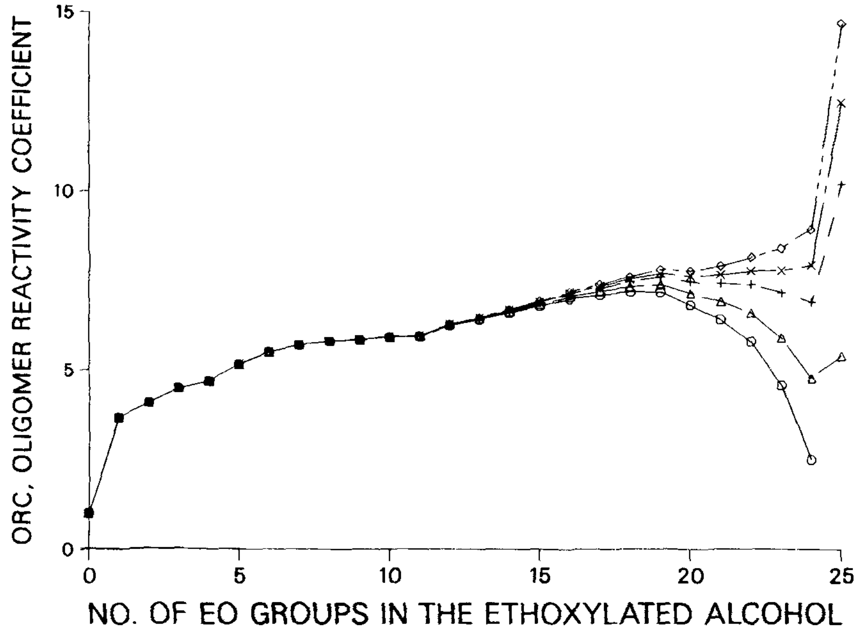

FIG. 5. Effect of adding higher molecular weight oligomers to original distribution of 8.6-mole ethoxylate of 2EH. ○ , SFC determined distribution; △, 0.001 mole % added; +, 0.002 mole % added; ×, 0.0025 mole % added; and ◇ , 0.003 mole % added.

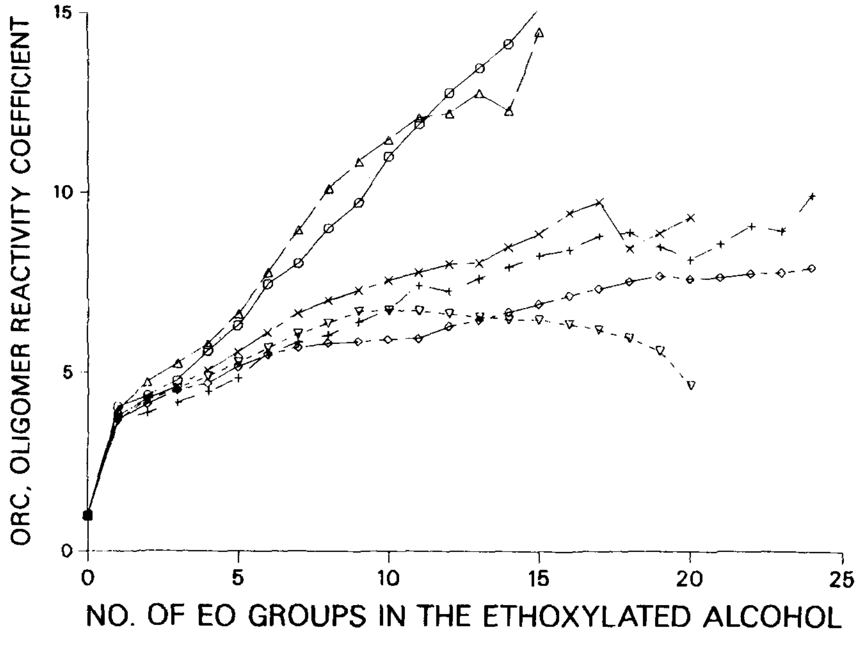

FIG. 6. Revised oligomer reactivity coefficients for 2EH. △, 2.5 EO/2EH; ○ , 2.9 EO/2EH; ×, 4.4 EO/2EH; +, 6.1 EO/2EH; ∇, 7.3 EO/2EH; and ◇ , 8.6 EO/2EH.

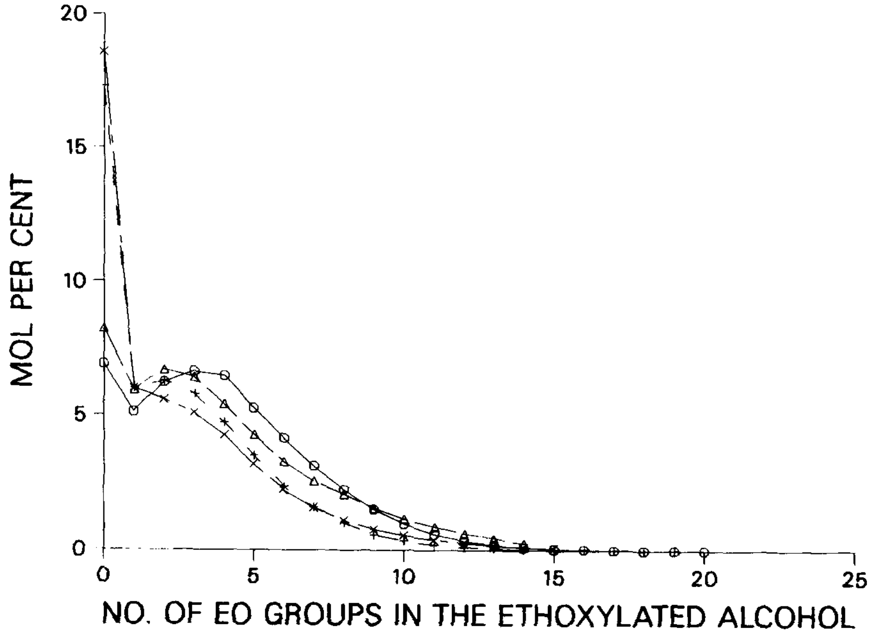

FIG. 7. Comparison of EO distributions for 50:50 mixture of octanol and 2EH at 3.0 EO/alcohol. ○ , Predicted NC8, 3.9 EO/NC8; △, SFC determined NC8, 3.8 EO/NC8; +, predicted 2EH, 2.4 EO/2EH; and X, SFC determined 2EH, 2.5 EO/2EH.

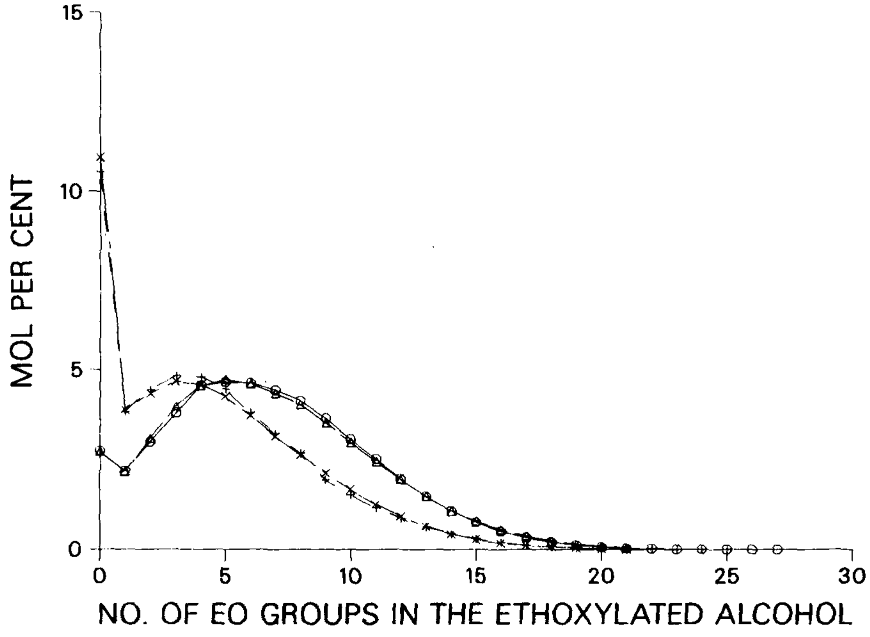

FIG. 8. Comparison of EO distributions for 50:50 mixture of octanol and 2EH at 6.0-EO/alcohol. ○ , Predicted NC8, 6.7 EO/NC8; △, SFC determined NC8, 6.7 EO/NC8; +, predicted 2EH, 4.4 EO/2EH; and X, SFC determined 2EH, 4.4 EO/2EH.

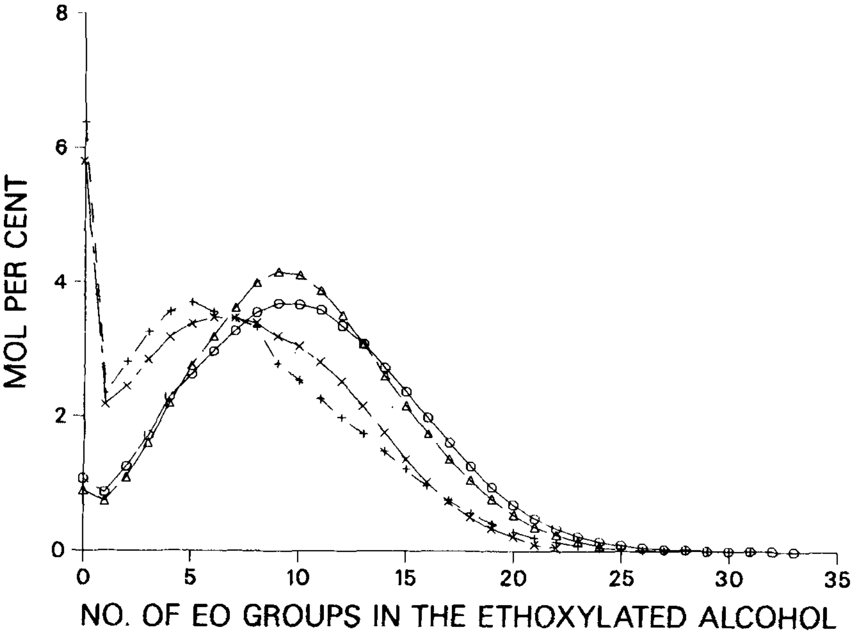

FIG. 9. Comparison of EO distributions for 50:50 mixture of octanol and 2EH at 9.0-EO/alcohol. ○ , Predicted NC8, 10.2 EO/NC8; △, SFC determined NC8, 9.9 EO/NC8; +, predicted 2EH, 7.0 EO/2EH; and ×, SFC determined 2EH, 7.3 EO/2EH.

attributed to a change in the K_i/K_0 ratio for that oligomer, since the k_i/k_0 kinetic ratio should be dependent only on the reaction temperature.

Prediction of molecular distributions in ethoxylated mixed alcohols. An original goal of our work was to develop a means of predicting (computing) molecular oligomer distributions of ethoxylated products not only when the feed is a pure alcohol, but also when the feed is a complex mixture of isomers such as typically is present in commercial alcohols. To accomplish this, a new program, MDTERM, was developed by revising MOLDIST, the program for pure alcohols. MDTERM is capable of predicting the overall distribution resulting from the ethoxylation of a mixture containing up to ten different alcohol types. As ORC data are accumulated, they are added to a "library" of ORC data sets contained in the program, one for each alcohol type that is found to exhibit an ORC data set uniquely different from the others. Our earlier studies (4) found that there is little or no effect of varying chain length of alcohols on their ORCs, therefore only one set of ORCs is used for linear primary alcohols. However, branching in the alcohol molecule has been found to cause significant differences. For example, a methyl group attached to the carbon alpha to the hydroxyl carbon produces a different set of ORCs than does an ethyl group. The library presently includes, among others, sets of ORCs for linear primary alcohols, for 2-methyl 1-alcohols, for ethyl and higher alpha-branched primary alcohols, and for 3-alkyl branched 1-alcohols.

One basic requirement in our approach to predicting molecular distributions of mixed alcohol ethoxylates is that, although the ORCs of the ethoxylated oligomers of an alcohol are affected by the overall degree of ethoxylation of an alcohol mixture, they are not affected by the presence of another alcohol and/or its oligomers. This has been shown to be true for all alcohol mixtures that we have investigated to date. A second basic requirement is that all the ORCs in the library must be relative to one of the alcohol types. Linear primary alcohol was arbitrarily chosen as the reference alcohol type. The calculated ORCs for the other alcohol data sets in the library, including their ORC[0], have been multiplied by a correction factor to make them relative to the ORCs for linear primary alcohols. These new ORC values have been termed comparative oligomer reactivity coefficients (CORCs) to differentiate them from the ORC values for a given alcohol relative to itself. In this terminology, the only CORC value that is exactly 1.0 by definition is the CORC[0] for linear alcohols.

The CORC correction factor (to convert ORCs into CORCs) for a given alcohol can be determined from an experiment in which it is ethoxylated as part of a mixture containing either NC8 or some other alcohol for which the CORC correction factor has previously been determined. As an example, to determine the CORC correction factor for 2EH, the experiment reported here starting with a 50:50 mixture of 2EH and NC8 was used. An iterative search procedure was incorporated into MDTERM to find that value of the CORC correction factor required for the quantity (mole fraction) of 2EH remaining in the calculated product mixture to match that measured by SFC at each EO/alcohol level sampled. This automatically forces the mole fractions of all the other ethoxylated oligomers in the mixture to match the SFC measured quantities, since the ORCs of each ethoxylated oligomer with respect to its starting alcohol had previously been calculated by RTCNST to achieve this. The three calculated CORC correction factors for 2EH, based on the three samples withdrawn at 3-, 6-, and 9-EO/alcohol levels are 0.549, 0.522, and 0.537, respectively. Thus, while the ORCs for

2EH were found to be higher than those for NC8, the initial ethoxylation of 2EH itself is a little more than half the rate of the initial ethoxylation of NC8 in a competitive reaction.

The following is an illustration of how the model can be used to predict product distributions that result from the ethoxylation of alcohol mixtures. The 2EH ORC set for 6-EO/alcohol was transformed into a CORC set by multiplying it by 0.536, the average of the three correction factors calculated above for 3-, 6-, and 9-EO. It is important to point out that this CORC set for 2EH becomes constant at a value of 4.5 for oligomers with high EO levels, a value exactly equal to the constant value of ORC reached with increasing EO oligomer contents in the 6-mole ethoxylation of NC8. Remembering that CORC[i] = ORC[i] for NC8, this is consistent with the suggestion that ethoxylation rates should be equal at high EO oligomer contents, independent of the feed alcohol.

Separate work, not reported here, using "peaked" ethoxylation catalysts has shown that the ORCs reach a maximum value near the ethoxylate that has the highest concentration and gradually decrease with increasing EO contents. The application of the techniques of adding small amounts of higher ethoxylates to the "truncated" distribution did not cause the ORC values to become constant at high EO levels for these peaked distributions, as it did with distributions from conventional KOH catalysts.

These two CORC sets for 2EH and for NC8 were used in MDTERM to predict the molecular distributions resulting from the ethoxylation of an equimolar mixture of 2EH and NC8 at 3-, 6-, and 9-EO. Since changing CORC values with increasing overall EO-to-alcohol ratios were not used, the Weibull-Tornquist effect on reaction rate constants due to changing reaction medium is not included in predictions of molecular distributions with this data set. The predicted distributions for NC8 and 2EH at 3-, 6-, and 9-EO/alcohol ratios are shown in Figures 7–9, compared with their respective experimentally determined distributions.

In spite of the above described simplifications in the CORC data sets used for these two alcohols, the predicted molecular distribution of the mixed alcohol ethoxylate is a good match of the experimentally measured distribution for the 9-EO case. It is not surprising that only a fair match is "predicted" for the 3-EO case, since the Weibull-Tornquist effect is more pronounced at lower EO/alcohol ratios. It is also not surprising that the best match is for the 6-EO case, since the average CORC values at that level were used in the data sets. This example illustrates that acceptable predictions of molecular distributions for alcohol mixtures can be achieved by using constant (average) CORC data sets. If desired, more data sets, or interpolations between data sets, can easily be used to account for the effect of EO/alcohol ratio within a single computer prediction to yield even better matches of predicted and experimental distributions at all EO-to-alcohol ratios.

ACKNOWLEDGMENTS

D. Henderson carried out ethoxylation experiments. R. McAndrew and C. Brown performed SFC analyses of ethoxylates. E. Green provided SFC column and separation expertise.

REFERENCES

1. Cross, J. (ed.), *Nonionic Surfactants Chemical Analysis*, Marcel Dekker, New York, 1987.
2. Geissler, P.R., *J. Am. Oil Chem. Soc. 66*:685 (1989).
3. Johnson, A.E., P.R. Geissler and L.D. Talley, *Ibid. 67*:123 (1990).
4. Geissler, P.R., and A.E. Johnson, *Ibid. 67*:541 (1990).
5. Weibull, B., and J. Tornquist, *VI Intern. Kongr. für Grenzflachenactive Stoffe*, Zurich, September 11-15, 1972.
6. Farkas, L., J. Morgos, P. Sallay, I. Rusznak, B. Bartha and G. Veress, *J. Am. Oil Chem. Soc. 58*:650 (1981).
7. Sallay, P., L. Farkas and Rusznak, *Ibid. 67*:209 (1990).

[Received November 8, 1990; accepted April 9, 1991]