

SURFACTANTS & DETERGENTS

Effect of Process Variables, Degree of Ethoxylation and Alcohol Structure on Relative Ethoxylation Rate Constants¹

Paul R. Geissler^a and Adrain E. Johnson, Jr.^b

^aExxon Chemical Company, Intermediates Technology Division, P.O. Box 241, Baton Rouge, LA 70821, and ^bDepartment of Chemical Engineering, Louisiana State University

Supercritical fluid chromatographic determinations of ethylene oxide distributions in ethoxylated alcohols with subsequent computer calculations of relative propagation to initiation ethoxylation rate constants for each ethoxylated oligomer have been carried out for normal octanol under varying reaction conditions. A number of other alcohols were also ethoxylated under essentially constant conditions. In the normal octanol studies, within an approximately fifteen-fold change in absolute ethoxylation rates due to variations in temperature, pressure, and potassium hydroxide catalyst concentration, the data indicate that such changes do not affect ethylene oxide distributions. Suggestions by earlier workers of changes in relative ethoxylation rate constants with the average degree of ethoxylation were verified. Chain length for normal alcohol feeds does not affect distributions in the C-8 to C-13 range, but branching at the carbon α to the hydroxyl carbon increases the relative propagation to initiation rate constants, and a secondary alcohol exhibits an even higher ratio.

KEY WORDS: Ethoxylated alcohols, ethoxylation process variables, ethylene oxide oligomer distributions, non-ionic surfactants, relative rate constants, and supercritical fluid chromatography.

The importance of accurately measuring and predicting ethylene oxide (EO) distributions in ethoxylated alcohol nonionic surfactants has been previously reviewed (1,2). In the base-catalyzed ethoxylation of alcohols, distributions of oligomers having different numbers of EO monomers are determined by the set of relative rates of propagation ethoxylation steps to the initial feed alcohol ethoxylation step. These relative ethoxylation rate constants are sometimes called distribution coefficients (3,4), but we have started to use the more descriptive term of "oligomer reactivity coefficients" (ORC) (5). This is being done to avoid confusion with the use of the term distribution coefficient in solution chemistry. In the first of a series of papers (2), we presented a novel, accurate, and reproducible supercritical fluid chromatographic (SFC) method for determining EO oligomer distributions in ethoxylated alcohols. The second paper (5) discusses two separate computer programs which calculate ORCs from SFC data and EO distributions in ethoxylates of single alcohols from ORCs.

The availability of precise SFC determinations of EO distributions and these two computer programs has allowed us to calculate ORCs for a variety of alco-

hols and ethoxylation conditions. Based on a limited number of ethoxylations, this paper discusses the effects of alcohol structure, temperature, EO pressure, potassium hydroxide catalyst concentration, and degree of ethoxylation on product EO distributions and ORCs. A fourth paper (to be published in the future) will apply these tools to mixtures of alcohols, resulting in a model that predicts EO distributions of their ethoxylates. An early version of such a model is already proving to be valuable in predicting EO distributions for complex alcohol mixtures whose ethoxylates cannot be easily analyzed by SFC, and for optimizing feed alcohol compositions to attain desired EO distributions.

EXPERIMENTAL

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 previously published (2). A typical SFC chromatogram for the normal octanol ethoxylates studied here and the EO distribution derived from it are shown in Figures 1 and 2. Oligomer reactivity coefficients, $ORC[i]$, defined as kinetic rate constants for ethoxylating the "i" ethoxylate divided by the kinetic rate constant for ethoxylating feed alcohol, were calculated using a second order kinetic model and computer program (5). Calculations with our two computer programs show that EO distributions are very sensitive to even small changes in EO/alcohol levels, while ORCs are not. Therefore, comparison of EO distributions in this study is very difficult because of differences in EO/alcohol ratios from run to run. Since ORCs

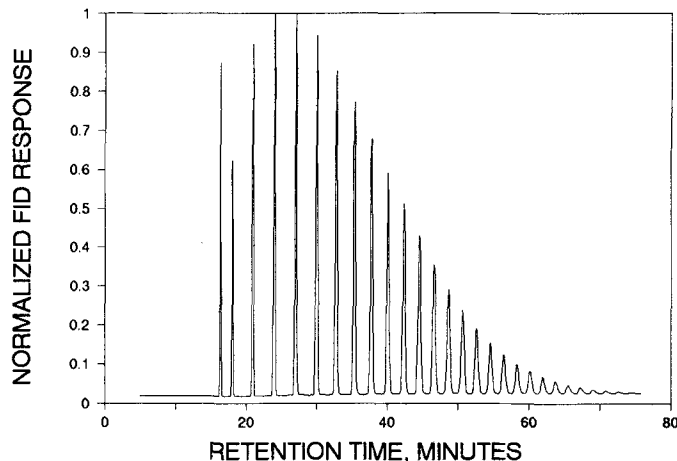


FIG. 1. Supercritical fluid chromatograph of six mole ethoxylate of normal octanol.

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*To whom correspondence should be sent.

mathematically and exactly define an EO distribution for any and all EO/alcohol ratios, they are used in the subsequent discussions to describe the effects of variables on the ethoxylation of alcohols.

RESULTS AND DISCUSSION

Effect of temperature, EO pressure, and catalyst concentration. Initial work in our laboratories (5) assumed that ethoxylation process variables (with any given catalyst) do not affect relative propagation to initiation rate constants or EO distributions in the resulting alcohol ethoxylates. Studies of the ethoxylation of primary alcohols with sodium methoxide catalyst have led others to conclude that the ratio of propagation to initiation ethoxylation rate constants (assuming all propagation steps are equal to each other) is relatively insensitive to temperature, pressure, and EO and catalyst concentrations (6). To confirm this insensitivity under the range of conditions in our study and to extend it to calculated ORC values, a fractional factorial designed set of normal octanol ethoxylations at high and low temperatures (135–165°C), EO pressures (8–30 psi), and KOH catalyst concentrations (5–21 g per 500 g alcohol) was carried out under carefully controlled conditions. Table 1 lists the average rates (based on 5–9 separate determinations made during each run) in milligrams of EO added per gram of alcohol per min for seven runs using KOH as catalyst. The absolute overall ethoxylation rates varied from 6–96 in these units.

Each ethoxylation was sampled three times, at approximately three, six, and nine moles of EO per mole of feed alcohol. Complete EO distributions for 18 samples are listed in Table 2. The calculated ORC[i] values from $i = 0$ to 12 are shown in Figures 3–8. These plots indicate that ORC values always increase between ORC[1] and ORC[6], but tend to level out thereafter. This behavior is in general agreement with earlier published results (4). However, this earlier work did not present any data for ORCs higher than ORC[4], since they were derived from gas chromatographic analyses of the ethoxylates.

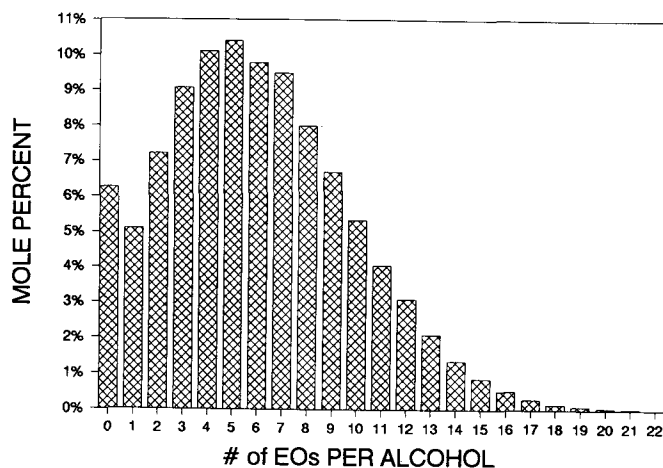


FIG. 2. Ethylene oxide distribution in six mole ethoxylate of normal octanol.

Although calculated ORC values for all three ethoxylates are shown in Figures 3–8, only the six and nine mole ethoxylate data is discussed in this section because of an observable effect of degree of ethoxylation on EO distributions (to be treated below). The ORCs for these six parameter studies are compared in these Figures with average ORC values for eight separate, normal octanol runs from our initial study (5). The previous normal octanol ORC values for six and nine mole ethoxylates are shown in Figures 3–8 as a shaded band plus and minus two σ from the mean values. The ORC values for the three, six, and nine mole ethoxylates of the appropriate parameter study are shown as symbols only. Since most of the ORC values for Runs 1–6 fall either within or close to the "old" average ORC band, we conclude that our original assumption is valid, that is, changing temperature, pressure, or KOH concentration has no measurable effect on EO distributions. Additionally, regression analysis of the six runs in this study found no effect of any of these process variables on ORC[1] at the 95% confidence limit. There appeared to be a possibility (90% confidence) of a slight effect on ORCs higher than ORC[1], due to temperature and catalyst concentration for the six mole ethoxylate, but no similar effect was found for the nine mole ethoxylate. We conclude that no statistically significant effect on ORCs exists over a fifteen-fold variation in absolute ethoxylation rates (Table 1). Therefore, any changes in these reaction parameters must affect both the initiation and propagation ethoxylation rates proportionally.

The effect of the reaction parameters on absolute reaction rates was obtained from a regression analysis of the average absolute rate data of Table 1. This resulted in the equation for a simplified model shown in footnote c of Table 1. The appropriate guidelines indicate that the positive effects of all three variables on absolute ethoxylation rate are significant, as was expected. Although extreme care must be taken if this model is to be used for anything except qualitative comparisons, it was used to simulate two runs in which only temperature was varied between 135 and 165°C. The predicted rates of 143 and 511 milligrams EO/gram alcohol/min (at 20 psi and 10 grams KOH) give an activation energy of 15 kcal/mole. This agrees re-

TABLE 1

Effect of Process Variables on Ethoxylation Rate of Normal Octanol

Run #	Press	Temp. (°C)	KOH ^b	Rate EO use ^a	
				Actual	Calc ^c
1	25 psia	165	21.2	95	93
2	12	162	5.4	11	14
3	30	135	21.1	68	70
4	8	134	21.5	11	11
5	25	133	2.0	6	5
6	8	164	5.4	7	6
7 ^d	17	164	5.5	11	30

^aEO addition rate in mg per min per gram of alcohol.

^bGrams of KOH catalyst per 500 grams of alcohol.

^cCalculated from regressed equation:

Rate = $-231 + 2.69 \times \text{Press} + 1.23 \times \text{Temp.} + 2.58 \times \text{Cat wt.}$

^dNormal octanol feed diluted 1:1 with xylene.

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TABLE 2

EO Distributions in Normal Octanol Ethoxylations

Run #	1			2			3			4			5			6		
EO/Alc	2.42	5.46	8.02	3.12	5.77	8.75	2.91	5.50	8.17	3.09	5.70	8.29	3.24	6.02	9.30	3.59	5.65	8.91
# EOs																		
0	23.5	7.4	3.4	21.1	7.9	2.9	19.1	5.8	2.2	18.3	5.6	2.5	19.5	6.3	2.2	18.2	8.3	2.7
1	15.7	6.4	3.0	14.2	6.7	2.7	15.0	5.3	1.9	13.7	5.2	2.3	13.4	5.1	1.7	12.3	6.5	2.2
2	17.6	8.1	3.8	15.0	8.2	3.4	16.6	8.7	2.9	15.9	7.5	3.3	15.3	7.2	2.5	13.8	8.3	3.0
3	15.5	9.9	5.0	13.4	9.3	4.4	15.2	10.7	5.5	15.3	9.8	4.6	14.0	9.1	3.5	13.2	9.6	4.0
4	11.6	10.8	6.3	10.4	9.7	5.5	11.7	11.6	6.8	12.1	11.2	5.9	11.0	10.1	4.6	10.8	10.0	5.0
5	7.4	11.0	7.3	7.7	9.6	6.4	8.1	11.6	7.7	8.4	11.5	7.2	8.0	10.4	5.8	8.4	9.8	6.1
6	3.9	10.1	7.9	5.3	8.8	6.9	5.1	10.5	8.5	5.5	10.8	8.0	5.5	9.8	6.7	6.1	7.2	6.9
7	2.3	9.4	9.3	2.6	8.7	8.4	3.7	9.6	9.5	4.0	10.0	9.5	4.4	9.5	7.9	5.3	6.1	8.1
8	1.2	7.6	9.0	1.8	7.3	8.2	1.9	7.6	9.4	2.1	8.1	9.5	2.6	8.0	8.5	3.2	4.9	8.6
9	0.7	6.1	8.8	1.3	6.2	8.4	1.1	5.9	9.2	1.3	6.4	9.4	1.9	6.7	8.9	2.4	3.8	8.9
10	0.4	4.6	8.2	1.0	5.0	8.2	0.8	4.4	8.4	0.9	4.8	8.8	1.4	5.3	8.8	1.8	2.9	8.7
11	0.2	3.2	7.2	0.7	3.9	7.5	0.6	3.1	7.3	0.7	3.4	7.7	1.0	4.1	8.3	1.4	2.0	8.0
12	0.1	2.2	6.0	0.6	2.9	6.6	0.4	2.1	6.0	0.5	2.3	6.4	0.7	3.1	7.4	1.1	1.3	6.7
13	0.0	1.4	4.7	0.3	3.1	5.6	0.4	1.3	4.7	0.4	1.5	5.0	0.6	2.1	6.3	0.7	0.8	5.8
14	0.0	0.9	3.5	0.2	1.4	4.4	0.2	0.8	3.5	0.2	0.9	3.8	0.3	1.4	5.2	0.5	0.5	4.7
15	0.0	0.5	2.5	0.1	0.9	3.4	0.1	0.5	2.4	0.1	0.5	2.5	0.2	0.9	3.7	0.3	0.3	3.3
16	0.0	0.3	1.7	0.0	0.6	2.7	0.0	0.3	1.6	0.1	0.3	1.6	0.1	0.5	2.7	0.2	0.1	2.4
17	0.0	0.1	1.0	0.0	0.3	1.8	0.0	0.2	1.0	0.0	0.2	1.0	0.1	0.3	1.9	0.1	0.1	1.7
18	0.0	0.1	0.6	0.0	0.2	1.2	0.0	0.1	0.6	0.0	0.1	0.6	0.0	0.2	1.3	0.0	0.0	1.2
19	0.0	0.0	0.4	0.0	0.1	0.8	0.0	0.0	0.4	0.0	0.0	0.4	0.0	0.1	0.9	0.0	0.0	0.8
20	0.0	0.0	0.2	0.0	0.1	0.5	0.0	0.0	0.2	0.0	0.0	0.2	0.0	0.0	0.6	0.0	0.0	0.5
21	0.0	0.0	0.1	0.0	0.0	0.3	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.3	0.0	0.0	0.3
22	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.2
23	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.1
24	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.1

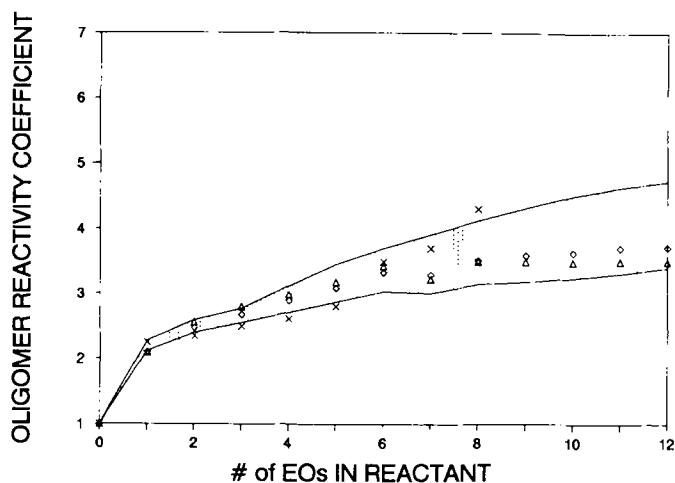


FIG. 3. Oligomer reactivity coefficients for normal octanol. Lines are \pm two σ deviation band for previous normal octanol data; X, three EO data for ethoxylation parameter run #1; \diamond , six EO data for ethoxylation parameter run #2; and \triangle , nine EO data for ethoxylation parameter run #3.

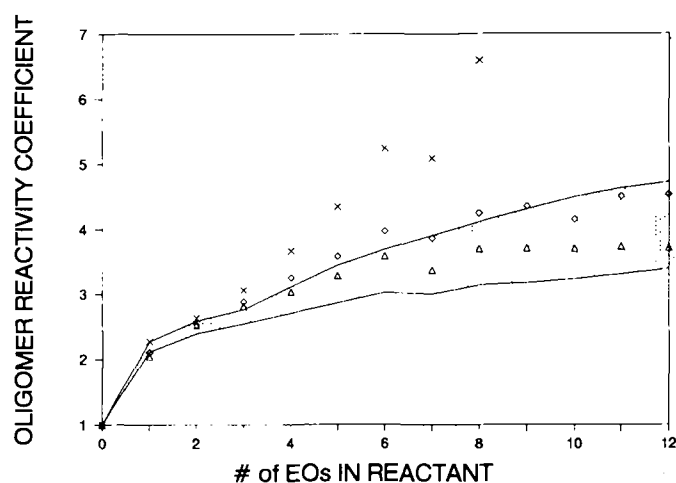


FIG. 4. Oligomer reactivity coefficients for normal octanol. Lines are \pm two σ deviation band for previous normal octanol data; X, three EO data for ethoxylation parameter run #1; \diamond , six EO data for ethoxylation parameter run #2; and \triangle , nine EO data for ethoxylation parameter run #3.

markedly well with published values of 15.8 and 16.4 kcal/mole for the first two additions of EO to phenol (7,8), and 17.8 kcal/mole for the sodium methoxide catalyzed polymerization of EO in paradioxan at 30–60°C (9).

Effect of degree of ethoxylation (Weibull-Tornquist effect). It has been previously reported by others (4) that ORC[i]s between $i = 2$ and $i = 4$ decrease as the

average degree of ethoxylation increases from 1 to 4. The decreases observed were greater as [i] increased, with little or no change in ORC[1] over the same ethoxylation range. Data also has been presented, but not discussed extensively, indicating that ORC[i > 4] values calculated from SFC data of three EO/alcohol samples are significantly higher than those for six and nine ethoxylates (5). This decrease, termed the Weibull-

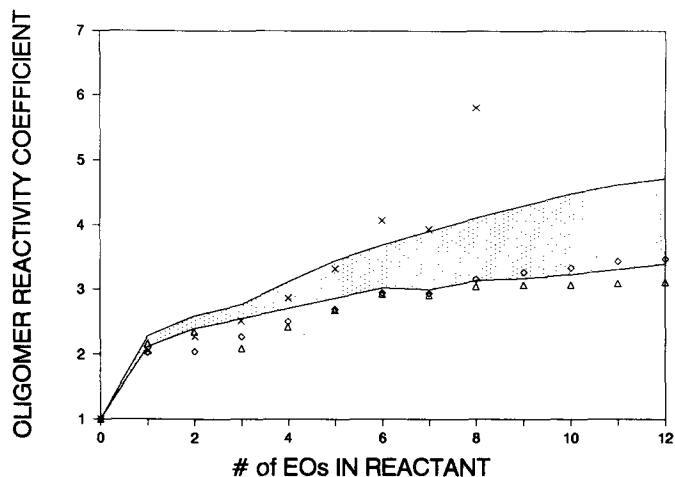


FIG. 5. Oligomer reactivity coefficients for normal octanol. Lines are $\pm \sigma$ deviation band for previous normal octanol data; X, three EO data for ethoxylation parameter run #3; \diamond , six EO data for ethoxylation parameter run #3; Δ , nine EO data for ethoxylation parameter run #3.

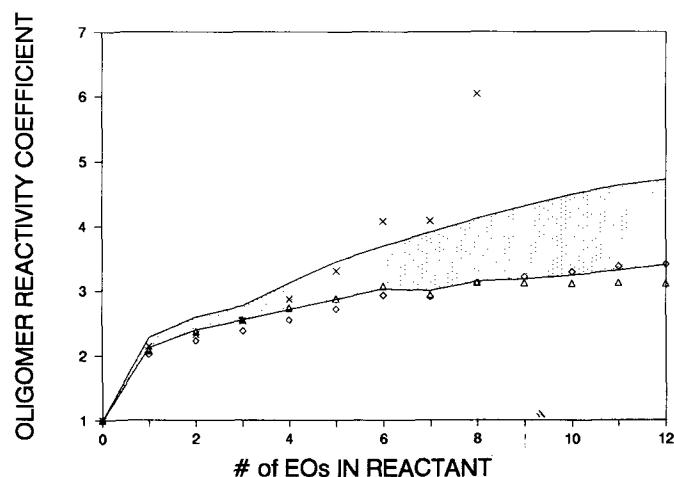


FIG. 6. Oligomer reactivity coefficients for normal octanol. Lines are $\pm 2\sigma$ deviation band for previous normal octanol data; X, three EO data for ethoxylation parameter run #4; \diamond , six EO data for ethoxylation parameter run #4; and Δ , nine EO data for ethoxylation parameter run #4.

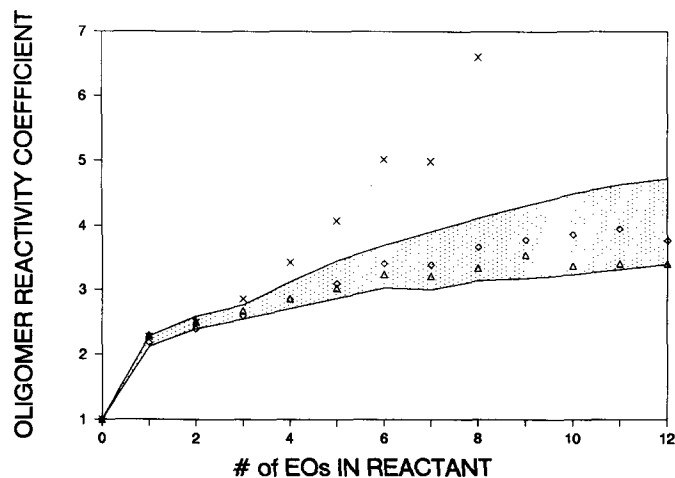


FIG. 7. Oligomer reactivity coefficients for normal octanol. Lines are $\pm 2\sigma$ deviation band for previous normal octanol data; X, three EO data for ethoxylation parameter run #5; \diamond , six EO data for ethoxylation parameter run #5; and Δ , nine EO data for ethoxylation parameter run #5.

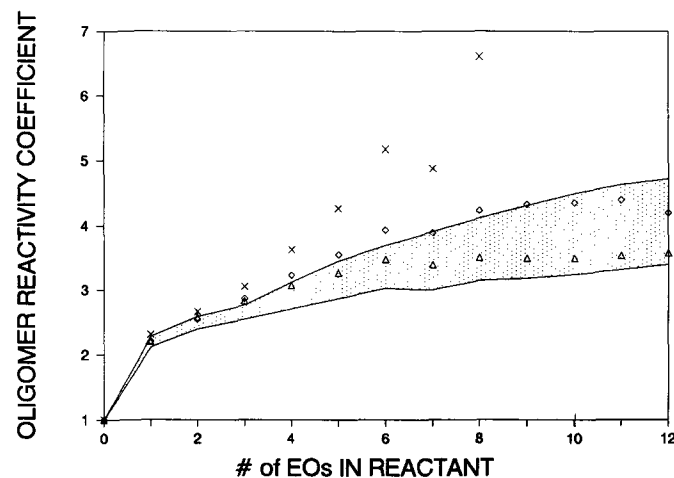


FIG. 8. Oligomer reactivity coefficients for normal octanol. Lines are $\pm 2\sigma$ deviation band for previous normal octanol data; X, three EO data for ethoxylation parameter run #6; \diamond , six EO data for ethoxylation parameter run #6; and Δ , nine EO data for ethoxylation parameter run #6.

Tornquist effect (4), was also observed in five of the six runs of this study. Figures 4-8 show that ORC[i] values for three EO samples in Runs 2-6 increase more rapidly with increasing [i] than do those for the six and nine EO samples, and that they are definitely higher than the corresponding values of the six and nine EO samples. Based on SFC analyses of low EO ethoxylates of a mixture of normal octanol and nine EO 2-ethylhexanol (2-EH) ethoxylate, we attributed this Weibull-Tornquist effect to the changing nature of the

reaction media as ethoxylation proceeds. The results reported here show that the effect occurs under a wide range of reaction conditions.

Effect of alcohol chain length. ORC[i]s for a series of ethoxylations of pure, single component alcohol feeds using KOH catalyst concentrations, temperatures, and EO pressures within the variability range cited above are shown in Figures 9-11. In those cases where the number of runs was more than one, the average values shown have relative standard deviations of less than

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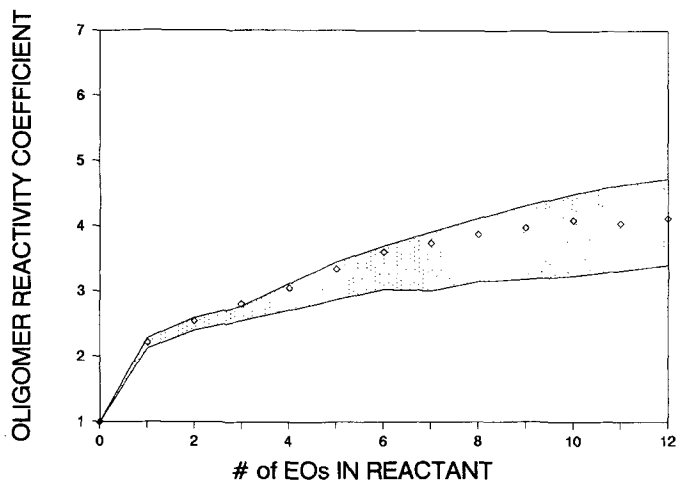


FIG. 9. Oligomer reactivity coefficients for normal tridecanol. Lines are \pm two σ deviation band for previous normal octanol data; \diamond , data for seven mole ethoxylate of n-tridecanol.

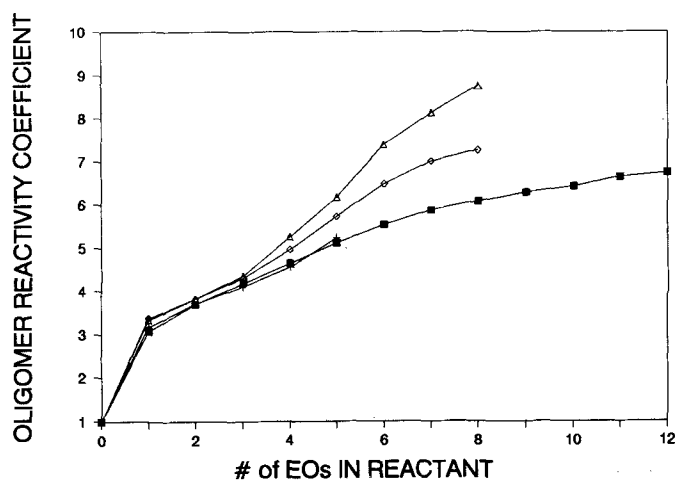


FIG. 10. Oligomer reactivity coefficients for 2-alkyl branched alcohols. \square , data for seven mole ethoxylate for 2-methyldodecanol; +, data for two mole ethoxylate of 2-ethyl-dodecanol; \diamond , data for two mole ethoxylate of 2-butyl-dodecanol; and Δ , data for two mole ethoxylate of 2-hexyloctanol.

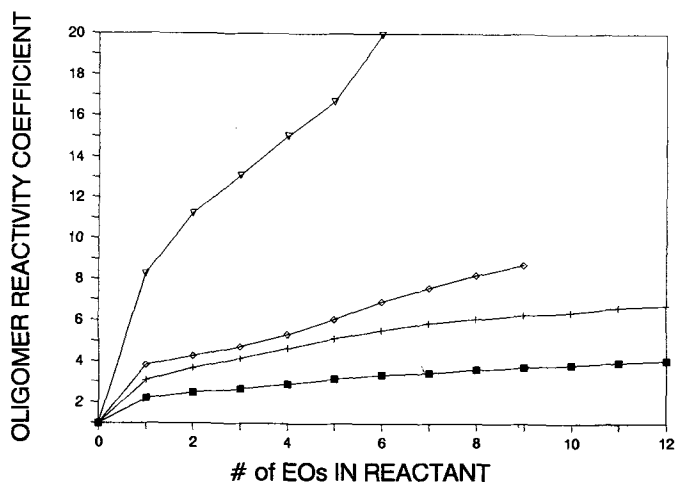


FIG. 11. Oligomer reactivity coefficients for various alcohols. \square , normal octanol (average of eight runs); +, seven mole ethoxylate of 2-methyldodecanol (1 run); \diamond , 2-ethylhexanol (average of eight runs); and ∇ , seven mole ethoxylate of cyclic secondary alcohol (1 run).

10%. Comparison in Figure 9 of the ORC values for normal tridecanol (symbols) and normal octanol (band of average six and nine EO plus and minus two sigma) shows, as expected, that alcohol carbon length does not affect EO distributions at these lengths.

Effect of 2-alkyl branching. ORC values for a series of C-14 alcohols (2-ethyl-dodecanol, 2-butyl-dodecanol, and 2-hexyloctanol) were calculated from analyses of their two mole ethoxylates. Also included in Figure 10 (for comparison) is data for a seven mole ethoxylate of 2-methyldodecanol. Note that the higher values of ORCs for these branched alcohols as compared with normal

alcohols is not due to their higher propagation rates, but is actually caused by lower initiation rates of the branched alcohols. Since each set of ORCs are values relative to the ethoxylation of that particular feed alcohol, competitive ethoxylation experiments are required to determine relative ethoxylation rates of one alcohol vs another. From these and from defining $ORC'[i]$ as $k(i)/k(0\text{-octanol})$, arbitrarily choosing normal octanol for a basis, ORC' values can be determined for all alcohols relative to the initial ethoxylation rate constant of normal octanol. It is expected that variations in $ORC'[i]$ will be greatest for this branched alcohol series at $ORC'[0]$, and this variation will decrease with increasing $[i]$. At sufficiently high $[i]$, ORCs should be independent of the feed alcohol used. Work of this competitive ethoxylation type is currently underway to completely determine the net effect of mixed alcohol feeds on EO distributions.

The $ORC[1]$ values are only slightly different from each other within this series. They do, however, increase very slightly in the expected order with increasing branching from ethyl (3.18) to butyl (3.38), but with no further increase to hexyl (3.35). The differences between them become more striking at higher $ORC[i]$ levels, increasing at $ORC[4]$ from 4.6 to 5.0 to 5.3 as branching size increases. Since these are ORC values for low overall EO content ethoxylates, and since presently we do not have sufficient data to determine if these small differences are real, care should be taken in drawing too many conclusions from this observation. In any case, it is obvious that branching at the carbon α to the hydroxyl carbon causes higher $ORC[1]$ values than those of normal alcohols and that any effect of increased branching size decreases at greater than two carbons. However, when considering ORC' values relative to normal octanol for these branched alcohols, $ORC'[0]$ will be less than 1 and

ORC[1] will be lower than ORC[1] for normal octanol.

Effect of alcohol structure. For ease of comparison, the ORC data at high EO levels for alcohols with different structures are shown in Figure 11. In terms of relative propagation to initiation rates, the following order is readily observed and, as discussed previously, can be attributed to steric hindrance effects at the hydroxyl group in the feed alcohol being ethoxylated: normal < 2-methyl < 2-alkyl branched << secondary. Since curves for the 2-alkyl branched C-14 alcohols (Fig. 10) would differ from an average 2-EH curve, it is vital to again recognize that the former curves are determined from low (2EO) samples, while the latter curve is based on high ethoxylates. For this reason, the curve for 2-EH only is shown in Figure 11. The curve for 2-methyldodecanol fits smoothly between the normal and 2-EH curves. A difficult-to-ethoxylate cyclic secondary alcohol, hydroxy-di-methyl-tricyclo (5,3,1,0^{2,6}) decane, lies well above all of the primary alcohols curves.

Effect of reaction dilution. Figure 12 compares ORCs for the ethoxylation of normal octanol in a 1:1 orthoxy-lene weight mixture with average, normal octanol values. The data clearly indicates that dilution of feed alcohols with inert solvent does not alter the resulting EO distribution, even though there is a two-three-fold decrease in absolute ethoxylation rate (comparing actual ethoxylation rate with rate predicted from regression model for Run 7 in Table 1). Since dilution of feed alcohols could be expected to affect only absolute and not relative propagation to initiation ethoxylation rates (ORCs), this result is somewhat gratifying. But, at dilution, where no reaction media effects may be possible, it might also be expected that the Weibull-Tornquist effect would not be observed. However, at the 1:1 dilution of this test the effect is again clearly observed.

Conclusion. SFC has been shown to be an easy to use method for determining EO distributions in ethoxylated alcohols, generating self consistent and logical data as ethoxylation reaction parameters are varied.

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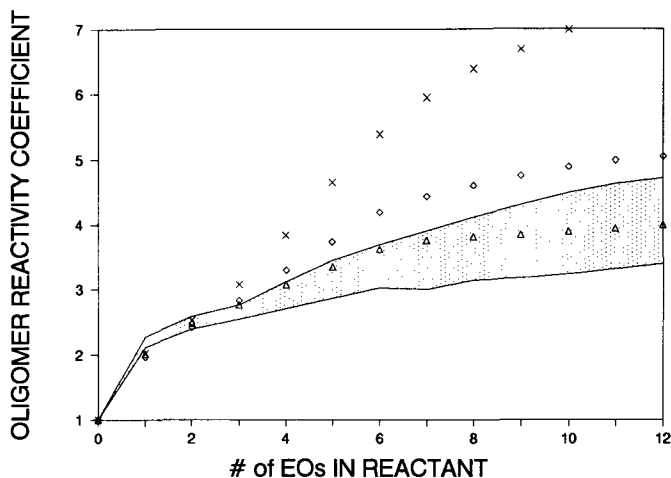


FIG. 12. Effect of dilution on oligomer reactivity coefficients. Lines are \pm two σ deviation band for previous normal octanol data (undiluted); \times , three data for ethoxylation parameter run #7; \diamond , six EO data for ethoxylation parameter run #7; and Δ , nine EO data for ethoxylation parameter run #7.

respect to ethoxylation kinetics, and K. Webber, K. Colle, J. Jung, and M. Keenan provided ethoxylated alcohol samples.

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