The Distribution of Compounds Formed in the Reaction between Ethylene Oxide and Alcohols

Bengt Weibull

Akzo Nobel Surface Chemistry AB, S-444 85 Stenungsund, Sweden

Weibull, B., 1995. The Distribution of Compounds Formed in the Reaction between Ethylene Oxide and Alcohols. – Acta Chem. Scand. 49: 207–216 © Acta Chemica Scandinavica 1995.
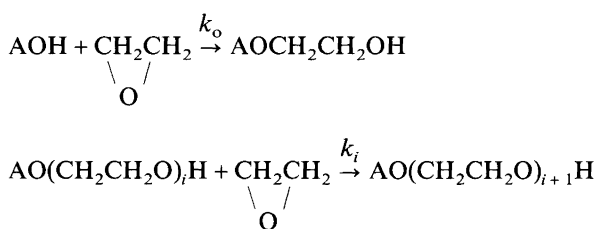
In the reaction between ethylene oxide and an alcohol in the presence of a small amount of the alkoxide, a mixture of monoalkyl ethers of oligoethylene glycols is formed. The distribution of these homologous ethers was studied with 3-phenyl-propan-1-ol as the alcohol and with the lithium, sodium or potassium as the counter-ion to the alkoxide. As a model for the distribution the formulas given by Natta are used. It is confirmed that the parameters in these formulas, called distribution constants, are not true constants but depend on the molar proportion between the ethylene oxide and the alcohol. This dependence is most pronounced with sodium and potassium and seems to be caused by the formation of complexes between the higher homologues and the cations of these metals. This is confirmed by the results of ethoxylations in the presence of an effective complexing agent for sodium and potassium, 18-crown-6. The distribution is dramatically changed with these metals but not with lithium.

Ethylene oxide reacts with alcohols to give a mixture of monoalkyl ethers of homologues of oligoethylene glycols (the simplified nomenclature used in this paper is given at the end of the paper). Surveys of published works on the reaction of ethylene oxide with compounds with an active hydrogen atom are given by Weibull.[1,2] The simplest model for the reaction with an alcohol follows Scheme 1.

These products, ethoxylates of alcohols, are of great practical importance. Those based on low molecular al-cohols are used as solvents and those based on higher alcohols form non-ionic surface active agents. Their properties depend on the alcohol, the molar proportion of the ethylene oxide to the alcohol (the degree of ethoxylation, DE) and also on the distribution of the homologues. It is therefore of practical and of theoretical importance to know the laws that determine this distribution. For the simple model in Scheme 1 it is given by the differential equation in the scheme.[3] Integration of the differential equation leads to different results depending on the relationship between the distribution constants.

For reaction steps that are kinetically identical, i.e., all distribution constants = 1, Flory[4] has shown that the result is a Poisson distribution, Scheme 2. This simple distribution applies approximately to the ethoxylation of monoethers of glycols but not to unsubstituted alcohols. Gold[5,6] and Weibull and Nycander[3] made the plausible assumption that the first step, with the reacting OH group attached to an unsubstituted alkyl group, differs kinetically from the following steps where the OH groups seem equivalently bound. The corresponding distribution is more complicated, Scheme 3. For low degrees of ethoxylation these distributions have been experimentally verified.[3]

$$AOH + CH_2CH_2 \xrightarrow{k_o} AOCH_2CH_2OH$$

(EO ring over CH$_2$CH$_2$: O)

$$AO(CH_2CH_2O)_iH + CH_2CH_2 \xrightarrow{k_i} AO(CH_2CH_2O)_{i+1}H$$

(EO ring over CH$_2$CH$_2$: O)

$$\frac{dx_i}{dx_0} = \frac{c_i x_i - c_{i-1} x_{i-1}}{x_0}$$

$$v = \Sigma\, i x_i$$

Scheme 1. Simple model for the ethoxylation of an alcohol, AOH: k_i=rate constant for ethoxylate with i moles of ethylene oxide (EO) added; x_i=mole fraction of the same; c_i = distribution constant = k_i/k_0; v = degree of ethoxylation = molar proportion of EO to AOH.

$$x_i = \exp(-v)\,\frac{v^i}{i!}$$

Scheme 2. Distribution formula according to Flory.[4]

The general case, with all steps kinetically different, was treated by Natta et al.[7-9] Scheme 4 gives the corresponding distribution.

The reactions in Scheme 1 are very slow. In practice their rate is enhanced by various means. In this work the ethoxylation of an alcohol in the presence of a small amount of its anion, the alkoxide, with cation of lithium, sodium or potassium was studied. In the literature these additives generally, but formally incorrectly, are named catalysts. Scheme 5 gives a simple model for this case. The corresponding distribution formulas have the same form as given above, but the distribution constants now include the acidity constants of the components,[3] i.e., $c_i = (k_i^- /k_0^-)*(K_i/K_0)$.

Early work to check the distribution formulas was hampered by the lack of adequate methods of quantitative analysis. Successful analyses of ethoxylates containing components with chain length (CL, number of ethyleneoxy groups) about 15 was performed by Törnquist.[10,11] He used gas chromatography on silylated ethoxylates of dodecanol. His results were used to determine, by iteration on a computer, the corresponding distribution constants according to Scheme 4.[12] It was found that the values of the distribution constants at low DE, about 2, increased with the chain length of the individual components, from ca. 2 at CL 1 to ca. 14 at CL 10. At higher DE, about 6, the order was the same but the spread was narrower: from about 2 to about 5. Thus the distribution constants are not true constants but depend on the DE. This observation was later confirmed, on less extensive material, by Sally et al.[13] and by Farkas et al.[14] Later investigations have given similar results.[15-17] Johnson et al.[16] use the designation 'oligomer reactivity coefficient' instead of 'distribution constant'.

Obviously, the simple model of Scheme 5 does not give a true picture of the ethoxylation reaction. It also ignores the fact, well known in practice, that the distribution is influenced by the choice of cation. An important paper by Orvik[18] gave a clue to a better model. He ethoxylated butanol to a low DE, about 0.18, in the presence of a small amount of lithium, sodium or potassium hydroxide, in the absence or presence of complexing agents for the alkali metals. The complexing agents used were 12-crown-4 (1,4,7,10-tetraoxacyclododecane) and 18-crown-6. In the case of LiOH these agents had no influence on the distribution of the components in the prod-

$$c = \frac{x_0 + v - 1}{x_0 - \ln(x_0) - 1}$$

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

Scheme 3. Distribution formulas according to Weibull–Nycander.[3] c = distribution constant = ratio between rate constants for the higher steps to that for the first step.

$$x_i = \sum_{j=0}^{i} a_{ij} x_0{}^{c_j}$$

$$a_{ij} = \prod_{k=0}^{i-1} c_k \Bigg/ \prod_{\substack{k=0 \\ k \neq j}}^{i} (c_k - c_j)$$

Scheme 4. Distribution formulas according to Natta as formulated by Weibull.[3]
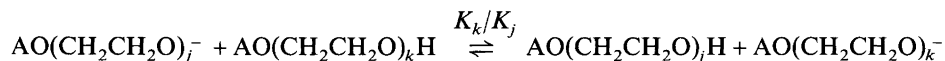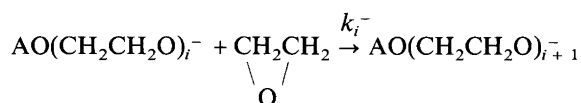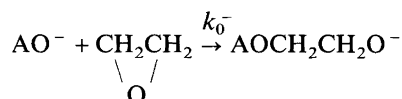
uct, which was the case with NaOH or KOH. The fraction of components of higher chain length was depressed in the presence of complexing agents and was the same as for LiOH. Orvik explained his results as follows. The anions are not free but are more or less linked to the cations as ion-pairs, Scheme 6, eqn. (1). The free anions as well as the ion-pairs react with the ethylene oxide (EO), the former are more reactive. Li^+ is highly solvated by butanol and the solvate forms ion-pairs with the anions throughout the reaction. It does not form strong complexes with crown ethers which, therefore, do not influence the distribution. On the other hand, Na^+ and K^+ are so strongly complexed by crown ethers, especially by 18-crown-6, eqn. (6), that ion-pairs are formed by these complexes, eqn. (7). The same distribution results as with Li^+. Without added complexing agents, the ethoxylates form complexes with Na^+ or K^+ (but not with Li^+), the strength of which increases with the chain length, eqn. (3). This complexing ability of monoalkyl ethers of oligoethylene glycols was noticed earlier in another connection by Ugelstad et al.[19] These complexes are stronger acids than the alcohol and uncomplexed ethers and the equilibrium with the corresponding anions, eqn. (4), is therefore shifted to the right-hand side favouring the ethoxylation of the anions of the complexes.[18]

Orvik did not study the effect at various DE values and he did not determine the amount of unchanged alcohol. It is thus not possible to calculate with any certainty his values of the distribution constants.

The aim of the present work is to find out whether the distribution constants really depend on the degree of ethoxylation (henceforth named the DE effect) and how this dependence might be explained.
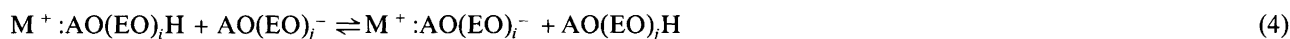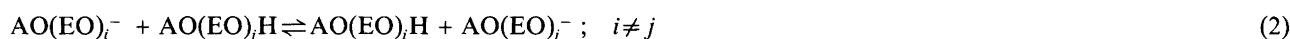
The experimental work is described in detail later on. A short survey of its scope might be useful.

An aromatic alcohol, 3-phenylpropan-1-ol, was used to make the analysis of its ethoxylates possible by high performance liquid chromatography (HPLC) with UV-detection and without derivatisation. As counter-ions to its alcoholate anion the cations of Li, Na or K were used, in all cases except seven in a concentration of 1 mol%. One series of experiments was made without further additives, another with the addition of 1 mol% 18-crown-6 as a complexing agent. The DE was varied from ca. 0.2 to ca. 8. One ethoxylation of DE ca. 1 was made of the alcohol alone without alkoxide. In all, 37 ethoxylations were performed.

$$AO^- + CH_2CH_2 \overset{k_0^-}{\rightarrow} AOCH_2CH_2O^-$$
$$\underset{O}{\underset{\diagdown \diagup}{}}$$

$$AO(CH_2CH_2O)_i^- + CH_2CH_2 \overset{k_i^-}{\rightarrow} AO(CH_2CH_2O)_{i+1}^-$$
$$\underset{O}{\underset{\diagdown \diagup}{}}$$

$$AO(CH_2CH_2O)_j^- + AO(CH_2CH_2O)_kH \overset{K_k/K_j}{\rightleftharpoons} AO(CH_2CH_2O)_jH + AO(CH_2CH_2O)_k^-$$

$$c_i = (k_i^-/k_0^-) * (K_i/K_0)$$

Scheme 5. Simple model for the ethoxylation of an alcohol in the presence of a small amount of its anion: k_i^- = rate constant for ethoxylate anion with i moles of ethylene oxide added; K_i = acidity constant for the corresponding ethoxylate; c_i = distribution constant.

$$AO(EO)_i^- : M^+ \rightleftharpoons AO(EO)_i^- + M^+ \qquad (1)$$

$$AO(EO)_i^- + AO(EO)_jH \rightleftharpoons AO(EO)_iH + AO(EO)_j^- \ ; \quad i \neq j \qquad (2)$$

$$M^+ + AO(EO)_iH \rightleftharpoons M^+ : AO(EO)_iH \qquad (3)$$

$$M^+ : AO(EO)_iH + AO(EO)_j^- \rightleftharpoons M^+ : AO(EO)_i^- + AO(EO)_jH \qquad (4)$$

$$AO(EO)_i^- : M^+ : AO(EO)_jH \rightleftharpoons AO(EO)_i^- + M^+ : AO(EO)_jH \qquad (5)$$

$$M^+ + L \rightleftharpoons M^+ : L \qquad (6)$$

$$AO(EO)_i^- : M^+ : L \rightleftharpoons AO(EO)_i^- + M^+ : L \qquad (7)$$

Scheme 6. Principal equilibria during the ethoxylation of an alcohol. $EO = CH_2CH_2O$; M = alkali metal used; L = complexing agent.

Ten ethoxylations with DE = ca. 1 were further made with the same alcohol in the presence of 1 mol% Li^+ or K^+, four of them with the addition of 2 mol% monophenylpropyl ether of hexa- or octa-ethylene glycol and six with 1, 2 or 4 mol% decanol ethoxylate of DE ca. 6 (C10–6).

Finally, five ethoxylations with DE ca. 1 were made with monophenylpropyl ethers of oligoethylene glycols of chain length 1, 2, 3, 6 and 8.

Results

As it is impossible to reproduce ethoxylations exactly it is not possible to compare their results directly. Instead the results are used to evaluate the distribution constants according to Natta's formulas, Scheme 4. One main experimental result is illustrated by Figs. 1–3 which show the dependence of the distribution constants on the DE. The dramatic effect of crown ether on the distribution in the case of Na^+ and K^+ prove that the DE effect is real and not due to analytical shortcomings, as assumed by Szymanowski,[15] or by the change of the reaction medium when the alcohol is consumed, as assumed by Johnson and Geissler et al.[16,17]

Ethoxylations with Li^+ as the cation. Fig. 1 (top) shows the dependence of the distribution constants on the DE. At low DE the values increase by and large with the chain length. With increasing DE the values decrease continuously at a given chain length, so that they approach each other and the value for the first one, c_1, which decreases only slightly. The same general results are found when crown ether is present, Fig. 1, (bottom). The effect of the addition of phenylpropyl ethers of oligoethylene glycols or of decanol ethoxylate is shown in Fig. 4. In it the distribution constants from all ethoxylations with DE close to 1 are compared. Results from Fig. 1 with Li^+ alone as well as with crown ether are included. The results are rather similar for chain lengths up to 4. At higher chain lengths the distribution constants at a given chain length differ more from each other, but not in a systematic way. With refererence to the standard deviations (SDs) given in Table 2 it seems reasonable to conclude that the additives do not significantly influence the course of the ethoxylations.

Ethoxylations with Na^+ as the cation. As shown in Fig. 2 (top) the results are similar to those with Li, but the DE effect is more pronounced. The presence of crown ether dramatically changes the picture, Fig. 2 (bottom). The
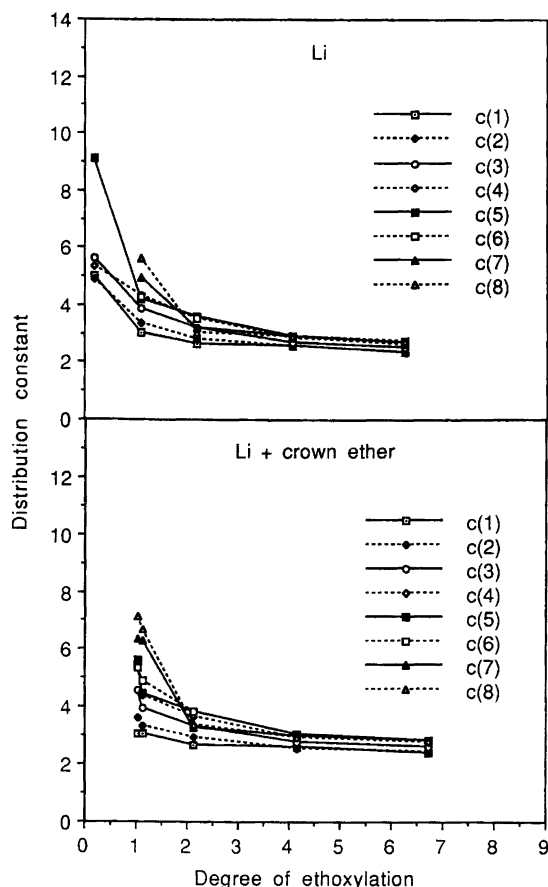
Fig. 1. Results from five ethoxylations with Li^+ alone, and five ethoxylations with added 18-crown-6, showing the dependence of the first eight distribution constants on the degree of ethoxylation. $c(1) = c_1$, etc.

Fig. 2. Results from 11 ethoxylations with Na^+. Layout as in Fig. 1.

distribution constants have values close to each other and they do not change much with DE. The two divergent values at DE ca. 2.5 correspond to the two highest chain lengths, 7 and 8, where the precision of the analysis is lower than at low chain length.

Ethoxylations with K^+ as the cation. The results with potassium as counter ion are very similar to those with sodium, Fig. 3. The effect of crown ether is, however, more pronounced. The tendency of the distribution constants to decrease with increasing DE is reduced. As they do not differ very much from each other it ought to be possible to describe the distribution by the formula in Scheme 3. Fig. 5 shows an example at DE = 4.03 with $c = 1.6$. Equally good results with the same distribution constant were obtained at DE 1.05, 2.32, and 8.29.

The effect of additions of crown ether, phenylpropyl ethers of oligoethylene glycols or decanol ethoxylate is shown in Fig. 6, DE ca. 1. The distribution constants rise sharply with increasing chain length with K^+ alone and remain almost constant in the presence of crown ether (the same points given also in Fig. 3). The results with the

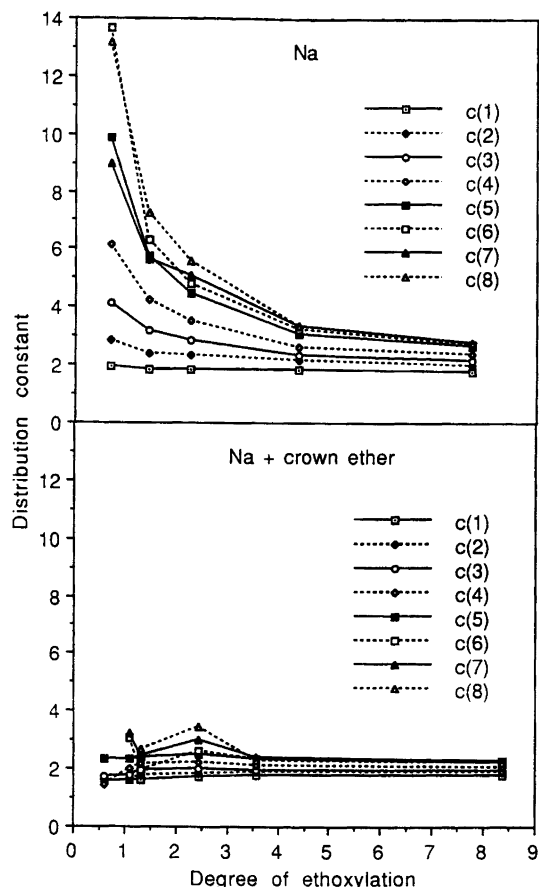five additives form a third group in between. The differences within this group do not seem significant, but the group seems to differ significantly from the other two.

The influence of the alkoxide concentration is illustrated in Fig. 7 from ethoxylations with DE ca. 1 and 0, 0.2, 1, and 5 mol% K^+. The distribution constants differ most from each other in the case of 0.2 mol%. There is no significant influence of the reaction temperature. The spread in the values of the distribution constants decreases with increasing alkoxide concentrations; at least there is a significant difference between the results at 0.2 and 5 mol%. The spread is lowest without alkoxide.

In the ethoxylations of phenylpropyl ethers of oligoethylene glycols at DE ca. 1 the distribution constants are near 1. In Fig. 8 the experimental distribution in the case of the monoether of hexaethylene glycol is compared with the Poisson distribution according to Scheme 2. Equally good consistency is obtained for the octaethylene glycol ether. For the lower homologues, mono-, di-, and tri-ethylene glycol ether, the distribution constants increase somewhat with the chain length but not as much as for the alcohol. For the monoethylene glycol ether the ratio c_7/c_1 is 2.4, for the di- and tri-ethylene glycol ether the corresponding ratios are smaller.
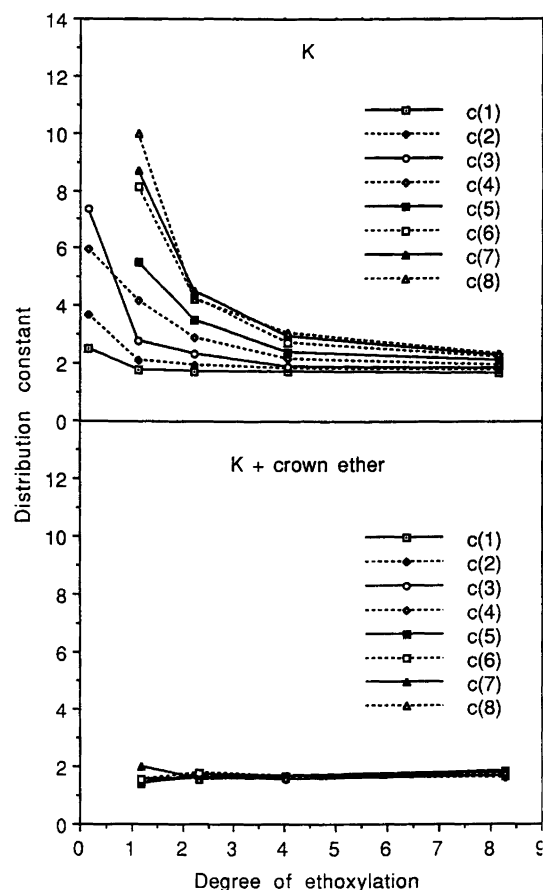
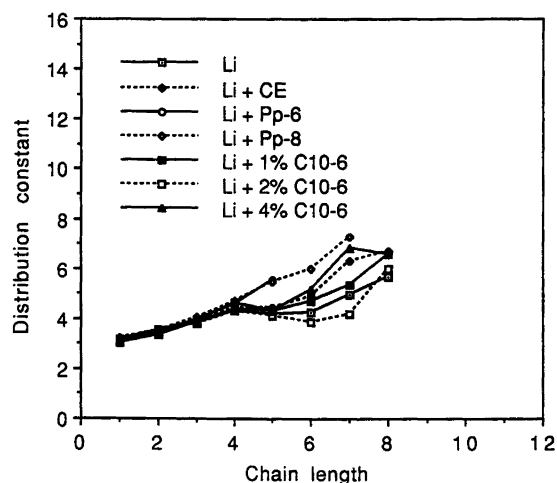*Fig. 3.* Results from 10 ethoxylations with K^+. Layout as in Fig. 1.

Fig. 4. Results from seven ethoxylations with DE ca. 1, one using Li^+ alone, and the rest with Li^+ plus additives, showing the values of the first 5–8 distribution constants against the corresponding chain lengths. For the sake of clarity, points from individual experiments are joined by lines. CE = 18-crown-6; Pp-6 = phenylpropyl ether of hexaethylene glycol; Pp-8 = phenylpropyl ether of octaethylene glycol; C10-6 = decanol ethoxylate of DE ca. 6.
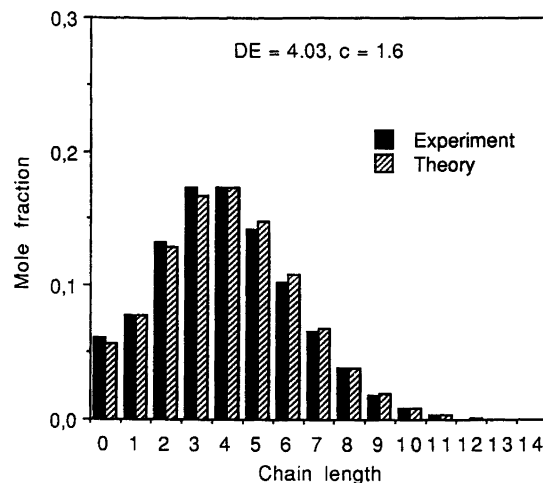

Fig. 5. Comparison of experimental distribution with distribution calculated with the formulas in Scheme 3. Distribution constant = 1.6.
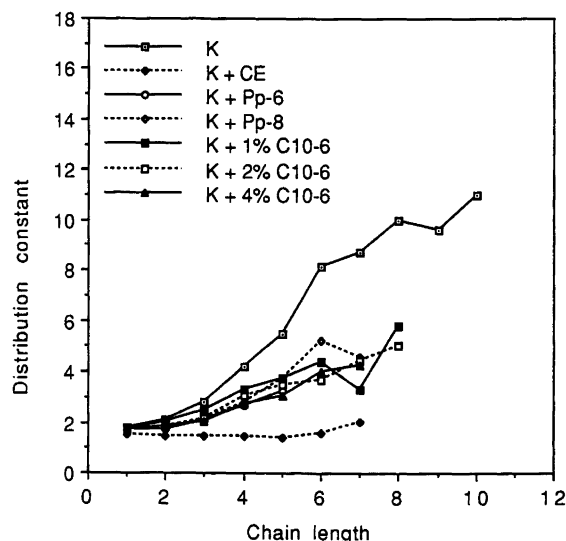

Fig. 6. Results from seven ethoxylations with DE ca. 1, one using K^+ alone, and the rest K^+ plus additives, showing the values of the first 5–10 distribution constants against the corresponding chain lengths. Layout as in Fig. 4.

Discussion

Mechanism of the ethoxylation reaction. An alcohol is a weaker acid than its ethoxylates[20] and thus its alkoxide is a stronger base and presumably more nucleophilic than the alkoxides of the ethoxylates. In the expression for the distribution constant, $c_i = (k_i^- / k_0^-) * (K_i/K_0)$, therefore the first ratio, k_i^- / k_0^- is < 1 and the second ratio, K_i/K_0, is > 1. As is known from ethoxylations of phenols, for which $k_i^- / k_0^- > 1$, $K_i/K_0 < 1$ and $c_i < 1$, and of secondary alcohols, for which $k_i^- / k_0^- < 1$, $K_i/K_0 > 1$ and $c_i > 1$ (see Refs. 1, 2) the second ratio and c_i have the same relation to unity. This relation is also assumed to hold in this investigation.
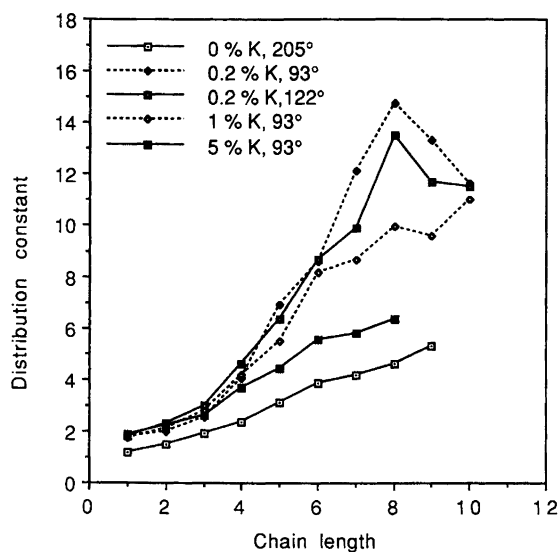
Fig. 7. Results from five ethoxylations with DE ca. 1, varying amounts of K^+ and 2 reaction temperatures.
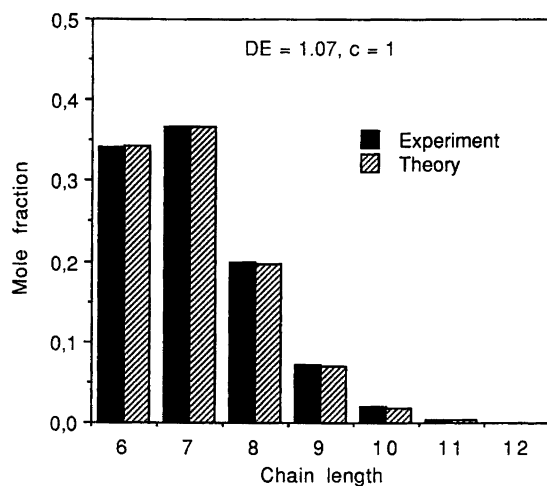

Fig. 8. Distribution results from ethoxylation of phenylpropyl ether of hexaethylene glycol, DE ca. 1, compared with the Poisson distribution calculated with the formula of Scheme 2.

The simplest cases are those with Na^+ or K^+ as counter ions and a crown ether present as a complexing agent. The cations are then well defined throughout the reaction, eqn. (6), Scheme 6, and also the ion-pairs with the anions, eqn. (7). As the alcohol is a weaker acid than its ethoxylates [the equilibrium (2) shifted to the right with $i = 0$] the first step should be kinetically unfavourable compared with the following, kinetically identical poly-addition steps. This expectation is confirmed by the results: the approximately constant distribution constant is > 1.

With N^+ or K^+ as counter ions but without crown ether all the distribution constants should be > 1 for the same reason as above. This is confirmed by the experimental results, which, however, also show that the distribution constants increase with the chain length at a

given DE. At the beginning of the ethoxylation, with low DE, the concentration of the ethoxylates is smaller than that of the cation. The ethoxylates are complexed by the cation, more completely for higher chain lengths, eqn. (3), Scheme 6. The complexed, higher ethoxylates are more acidic than the uncomplexed ethoxylates [equilibrium (4) shifted to the right] and therefore the distribution constants should increase with the chain length, which is found to be the case. The major, uncomplexed part of the cation is solvated by the alcohol. The solvate forms ion-pairs of low reactivity with the anions of the alcohol and the lower ethoxylates, eqn. (1), accentuating the differences between the distribution constants. At higher DE all the cations will be complexed by the ethoxylates, eqn. (3) and ion-pairs of these of high reactivity will be formed with all anions, eqn. (5). The conditions are reminiscent of those with crown ether present and the distribution constants of the ethoxylates will become more similar. This is confirmed by the results with added phenylpropyl ether of hexa- or octa-ethylene glycol or decanol ethoxylate which forms complexes with the cation, and therefore makes the distribution more uniform.

Increased alkoxide concentration also makes the distribution more uniform. At low DE the reaction rate of the higher ethoxylates already have near maximal reactivity (see above) but the reaction rates of the alcohol and of the lower ethoxylates is increased through their higher anion concentration. A larger proportion of them is formed at a given DE. In the application of the distribution formulas, Scheme 4, in which the concentration of the alkoxide is neglected,[3] this leads to lower values for the distribution constants.

Ethoxylates of oligoethylene glycol ethers have distribution constants closer to each other than ethoxylates of the alcohol. The hexa- and octa-ethylene glycol ethers and their ethoxylates should have near identical complexing and acidity properties. The ethoxylates of these ethers should therefore, as found, show a Poisson distribution, Scheme 2. The mono-, di- and tri-ethylene glycol ethers form less stable complexes and the distribution constants of their ethoxylates should increase with the chain length. For the monoethylene glycol ether the ratio c_7/c_1 is found to be 2.4. However, the results in Fig. 3 (DE ca. 1) give a value of 4.9 for the corresponding ratio. In the latter case K^+ is solvated by the alcohol, in the former by the glycol ether. The ion-pairs with the glycol ether might be looser, thereby equalising the reactivities of the anions of different chain length.

The ethoxylation with L^+ as the counter-ion also shows a DE effect, although somewhat weaker than that with Na^+ or K^+. As Li^+ does not give strong complexes with crown ether or, presumably, with oligoethylene glycol ethers another explanation must be sought. Li^+ is strongly solvated[18] by the alcohol at low DE and thus may be assumed to behave uniformly in the ion-pair formation with the various anions. Distribution according to the formulas in Scheme 3, with $c > 1$, would have been expected. Perhaps the alkoxide and anions of low chain

length form tighter ion-pairs than do anions of high chain length, giving the latter anions increased reactivity and, consequently, larger distribution constants.

In the single ethoxylation experiment without catalyst with DE = 1 the values of the distribution constants also increased with the chain length. In the absence of further experimental results it seems premature to speculate on the mechanism involved.

Experimental

Materials. 3-Phenylpropan-1-ol was from Merck (*zur Synthese, Gehalt* > 98%). GC showed it to be > 99%. It was used without further purification. Ethylene oxide was the product of Berol Nobel AB, > 99.9%. Ethylene glycol was from Merck, (*p.a.*); diethylene glycol, (*puriss p.a.*), and triethylene glycol (anhydrous, *puriss* > 99%) were from Fluka; tetraethylene glycol (*zur Synthese 97%*) was from Merck and 18-crown-6, (*purum* > 97%) and decanol, (ca. 97%) were from Fluka.

Apparatus. A schematic diagram of the ethoxylation apparatus is shown in Fig. 9. Most of its components are standard equipment for HPLC. Two pressure vessels were prepared by cutting a 1″ preparative HPLC column of 250 mm length and 23 mm inner diameter into two pieces, one 70 mm, the other 180 mm long. Both were closed at one end with non-magnetic Swagelock end caps, and at the other end with Valco fittings for 1/16″ tubing. The reaction vessel proper, RV, was a cylinder of non-magnetic stainless steel with wall and bottom ca. 1 mm thick. Its lid was made of Teflon and had a small, central hole. It fitted tightly in the smaller pressure vessel, PV1, and both were tightly closed when the Valco fitting
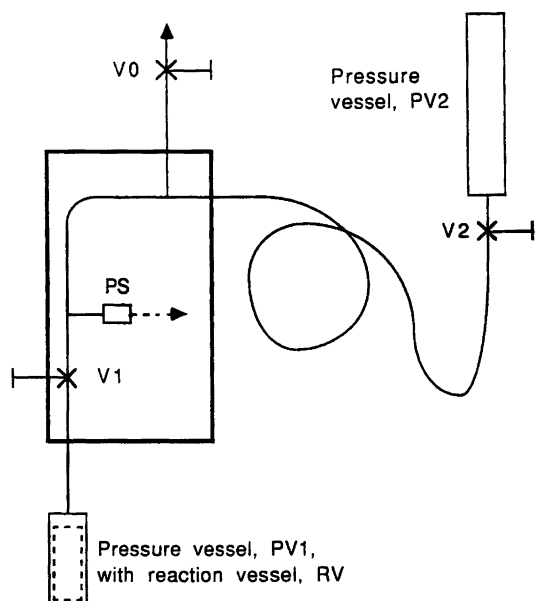

Fig. 9. Schematic diagram of ethoxylation equipment.

was drawn. A folded Teflon band, nearly as long as the reaction vessel, was placed in it, with a small stirring magnet in its fold. The larger pressure vessel, PV2, was used as container for ethylene oxide.

Pressure was measured by means of an electronic minisensor, PS, type BHL 4700 from Transamerica Instruments Ltd.

The various parts of the apparatus were fixed on a plywood board which was held vertically by a strong stand. The EO pressure vessel was fixed upside-down in a stand placed on a balance. The parts were connected by 1/16″ stainless steel HPLC tubing. The valve V0 was a Whitey '40' series Ball Valve, SS-42F2, the valves V1 and V2 were Nupro SS-2JB.

Ethoxylation. The general procedure was as follows. For a series of experiments in which the mixture to be ethoxylated was to be the same, the mixture was prepared in sufficient quantity for the whole series. The amount of metal to be used was reacted, under nitrogen, with phenylpropanol, Li and Na with careful warming, K at room temperature. To the clear solution was added 18-crown-6, when required. For an individual experiment the quantity of reaction mixture depended on the DE intended and varied from ca. 4 g to ca. 15 g. It, as well as eventual additives, was weighed into the RV that was then placed in PV1. The Valco fitting was drawn and the vessel placed in a juice bottle of aluminium. The narrow space between was filled with creased strips of aluminium foil to improve the heat conduction. The tubing of the vessel was coupled to the fitting of the valve V1. A heating bath was applied from below to the bottle. A stirrer hotplate was placed under the bath. With the valve V1 open and the valve V2 closed the apparatus was evacuated. When a vacuum had been attained the valve V0 was closed. When the vacuum remained steady, the valve V1 was closed and heating and stirring were started. When the desired temperature was reached it was held for another half hour and the valve V2 was then opened. The ethylene oxide in PV2 stood under nitrogen pressure, ca. 6 atm. After some minutes the weight became stable and the valve V1 was opened slightly. The change in weight with time was followed. The two valves were closed when the intended amount of EO, between ca. 1 and ca. 11 g, had been added. Heating and stirring were continued for another hour to complete the reaction. The valves V1 and V0 were opened and vacuum applied to evaporate traces of unchanged EO. The apparatus was then dismantled and the reaction vessel weighed after being cooled. The DE was calculated.

The ethoxylations with Li$^+$ were carried out at 115–120°C, those with Na$^+$ at 120–125°C and those with K$^+$, which proceed more rapidly, at about 100°C. One ethoxylation was carried out with no alkoxide. It was very slow and was performed at 205°C.

The supply of phenylpropyl ethers of ethylene glycols was limited. Therefore, in the experiments with them they had to be weighed in individually in the RV for each

ethoxylation. The quantities of K were then too small to be weighed in directly. Instead it was added as a solution of potassium methylate in methanol. The methanol was evaporated off under vacuum before the ethoxylation was started.

Syntheses of monophenylpropyl ethers of oligoethylene glycols. These were all synthesised by a modification of a method described by Björe, Strandlund, and Lamm.[21] The principle was as follows. Phenylpropanol was reacted with methanesulphonyl chloride in the presence of triethylamine to give phenylpropyl mesylate. This was reacted with a surplus of the alcoholate of the glycol. The raw product, mainly the desired monoether, was purified by reaction with maleic anhydride to give the monoester of maleic acid. This was neutralised with sodium hydroxide, the salt was purified, and the final product recovered after saponification of the ester. As an example, the details of the synthesis of diethyleneglycol monophenylpropyl ether is described.

Phenylpropanol (0.1 mol, 13.6 g), dichloromethane (60 ml), and triethylamine (0.12 mol, 12.1 g) were mixed in a three-necked flask equipped with a thermometer, drying tube with calcium chloride, and magnetic stirrer. The flask was cooled and held at $-10\,^\circ$C. Mesyl chloride (0.11 mol, 12.6 g) was slowly added. When the addition was completed and the mixture had reached room temperature it was extracted, first with dilute HCl, then with a dilute solution of sodium carbonate. The organic layer was dried (MgSO$_4$), filtered, and evaporated to dryness, yield 21.6 g (94%).

Diethylene glycol (ca. 2 mol, 209 g) was placed in a 500 ml three-necked flask equipped with a thermometer, magnetic stirrer, and outlet to the fume cupboard vent. It was filled with nitrogen and at ca. 100$\,^\circ$C sodium was added in small pieces (0.3 mol, 6.9 g). When all the sodium had reacted the mesylate was dropped into the stirred mixture at 80$\,^\circ$C over half an hour. It was left at 80$\,^\circ$C for another 2 h and was then, after cooling, diluted with ca. double its volume of water. The mixture was extracted with 3×50 ml of dichloromethane, and the combined organic layers were washed twice with an equal volume of water. The organic layer was worked up, yield 21.2 g (94.5%).

The yellow–brown product (0.092 mol, 20.6 g) was mixed with maleic anhydride (Merck, *zur Synthese*, 99%, 0.185 mol, 18.2 g). The mixture was kept at ca. 100$\,^\circ$C. To follow the reaction small samples were titrated potentiometrically with 0.1 M KOH. The reaction was almost complete after 1 h, but was continued for a further 2 h. The cooled mixture was dissolved in dichloromethane (100 ml) and the solution then extracted with 3×100 ml of water to remove most of the surplus of maleic acid. The organic layer was then neutralised, in the separatory funnel, against phenolphthalein with 1 M sodium hydroxide, added in decreasing portions, total amount 110 ml. A thick emulsion resulted whose separation was facilitated by addition of 20 ml of ethanol. The

aqueous layer was extracted with 50 ml of dichloromethane. The organic layers yielded 1.15 g of a yellow liquid that was not further investigated. To the neutral aqueous layer were added 150 ml of 1 M NaOH. It rapidly became turbid and was left overnight. It was then extracted with 3×50 ml of dichloromethane. The aqueous layer was discarded and the combined organic layers were washed twice with 20 ml of water. The light yellow organic layer yielded a viscous liquid, 18.1 g, 83% based on the phenylpropanol used. UV (abs. ethanol, ε): 267 (151), 258 (207) nm. The peak at 267 nm was sharp and narrow on the shoulder of the main peak at 258 nm.

The syntheses of phenylpropyl ethers of mono-, tri-, and tetra-ethylene glycol were carried out in the same way described using the corresponding glycols. The ether of hexaethylene (octaethylene) glycol was made in an analogous way from triethylene (tetraethylene) glycol phenylpropyl ether and triethylene (tetraethylene) glycol. In the latter cases the solutions of the salts of the maleic acid half-esters formed inseparable emulsions with dichloromethane, so diethyl ether was used as the solvent instead. The position of the UV maxima was the same as above, the extinction coefficients varied somewhat, which made determination of response factors necessary in HPLC (see later). The compounds were further characterised as follows (Pp-1 = phenylpropyl ether of monoethylene glycol etc.). The NMR spectra were recorded on a Varian VXR 300 instrument.

Phenylpropanol. Anal. found: OH 13.20 wt %, calc: 13.23. n_D^{20} 1.5263. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.88 (2 H, m), 2.70 (2 H, t), 3.66 (2 H, dd), 7.24 (5 H, m). *Pp-1.* Anal. found: OH 9.92, calc: 10.00. n_D^{20} 1.5128. *Pp-2.* Anal. found: OH 8.01, calc: 8.03. n_D^{20} 1.5053. ^{1}H NMR: δ 1.93 (2 H, m), 2.69 (2 H, t), 3.48 (2 H, t), 3.66 (8 H, m), 7.24 (5 H, m). *Pp-3.* Anal. found: OH 6.81, calc: 6.71. n_D^{20} 1.5005. ^{1}H NMR: δ 1.91 (2 H, m), 2.69 (2 H, t), 3.48 (2 H, t), 3.65 (12 H, m), 7.23 (5 H, m). *Pp-4.* Anal. found: OH 5.80, calc: 5.77. n_D^{20} 1.4967. ^{1}H NMR: δ 1.91 (2 H, m), 2.69 (2 H, t), 3.47 (2 H, t), 3.65 (16 H, m), 7.24 (5 H, m). *Pp-6.* n_D^{20} 1.4915. ^{1}H NMR: δ 1.91 (2 H, m), 2.69 (2 H, t), 3.47 (2 H, t), 3.65 (24 H, m), 7.24 (5 H, m). *Pp-8.* ^{1}H NMR: δ 1.91 (2 H, m), 2.68 (2 H, t), 3.47 (2 H, t), 3.65 (32 H, m), 7.24 (5 H, m).

Analyses HPLC. The pump unit was a Merck Hitachi 655-11 Liquid Chromatograph, for gradient elution coupled to a Merck Hitachi L-5000 LC Controller. The detector was a Merck Hitachi 655A Variable Wavelength UV Monitor. The volume of the sample loop was 20 µl. The chromatograms were taken on a Spectra Physics SP4270 Integrator and were also registered on a disc file for final evaluation on a Spectra Physics LABNET-AT System.

Several columns were tested. The best and most satisfactory results were obtained with ChromTech CT-sil 100 5 µm AMINO, 250×4.6 mm (Catalog No: CN 5A6; ChromTech AB, Box 512, S-145 63, Norsborg, Sweden).

Two solvent mixtures were used. S1: *tert*-butyl methyl ether–isooctane (2,2,4-trimethylpentane) 50:50 (v:v) and 0.1% acetic acid. S2: acetonitrile–methanol 95:5 (v:v) and 0.1% acetic acid. A typical elution scheme at 267 nm: 100% S1 for 10 min, linear gradient elution for 40 min to 100% S2. Flow rate 1 ml min^{-1}. Fig. 10 shows a typical chromatogram, DE = 7.73. Some chromatograms were taken at the broad maximum at 258 nm. The same solvents were used, but the elution scheme was modified to improve the base line: 100% S1 for 10 min, linear gradient elution for 25 min to 50% S1 + 50% S2, 15 min with this mixture.

Response factors (RF) were determined relative to phenylpropanol for the first four oligoethylene glycol ethers in the following way. Their HPLC diagrams showed them to be >97% pure (counted with RF = 1) with small amounts of phenylpropanol and of their near homologues as contaminants. Three mixtures of different composition were made with the five compounds and the approximate composition of the latter ones determined with RF = 1. Linear regression of the areas from the HPLC diagrams of the mixtures on the corresponding concentrations was carried out and the values of the specific areas of the individual homologues used to calculate new RF-values. These were then used to correct the composition of the ethers and the procedure was repeated until the two sets of RF-values became identical. At 267 nm the successive RFs were 1, 1.122, 1.101, 1.048, 1.030, SD 0.006; at 258 nm they were 1, 1.070, 1.034, 1.020, and 1.014, SD 0.006. It was assumed that the RF for higher homologues remained constant and identical with the RF for the tetra glycol. For practical reasons this constant value was taken as unity in the evaluation of the chromatograms of the ethoxylates and the other ones referred to it: 0.971, 1.090, 1.069, 1.018 and 0.986, 1.055, 1.020, 1.006.

In all, 52 ethoxylates were analysed with at least two chromatograms each, 99 at 267 nm, 16 at 258 nm. The sum of the areas, corrected by their RF-values, of the peaks in a chromatogram corresponding to 1 mmol l^{-1}
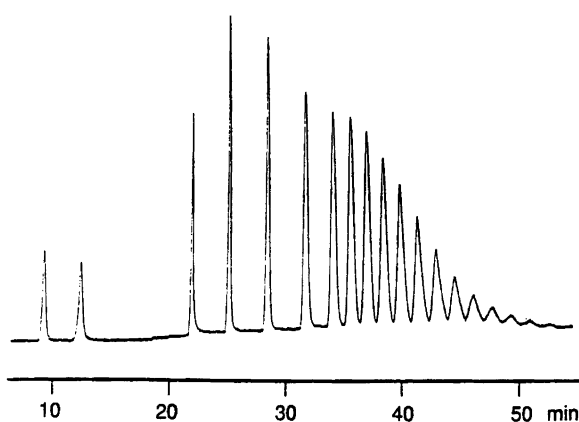

Fig. 10. An example of a raw chromatogram. DE = 7.73. The peak furthest to the left corresponds to phenylpropanol, the following correspond in order to ethoxylates of increasing chain length.

of the phenylpropanol used in the ethoxylation, called specific area, should be a characteristic constant. This was tested on 19 chromatograms of nine ethoxylates of DE ca. 1 and on 14 of six of DE ca. 8. In the former case the mean value was 131.9, SD within ethoxylates 0.94, between ethoxylates 1.46, in the latter case 131.1, 4.56, and 5.51.

Methods of evaluation

Evaluation of simple ethoxylation experiments. The chromatograms of the ethoxylates give an estimate of their composition. However, the limited sensitivity of HPLC precludes the estimation of higher components beyond a certain, low concentration. As described earlier[12] their amounts may be estimated by extrapolation in a linear logarithmic diagram. The corrected, experimental amounts of the components shown in the chromatograms were then used to determine the distribution constants, c_i, in Natta's formulas, Scheme 4. This was made by an iterative method by means of a BASIC program on a PC with double precision. In principle it works as follows. In the first iterative cycle the value of c_1 is systematically varied until the two formulas in Scheme 4 reproduce the experimental value of x_1 corresponding to the experimental value of x_0. In the next cycle the value of c_2 is analogously estimated with the value of c_1 just obtained. The procedure is repeated until all c_i have been estimated. An example is given in Table 1. Evaluation was made of all individual chromatograms as well as of the means of the chromatograms of individual ethoxylates.

An alternative method is numeric integration of the differential equation in Scheme 1. Such a method was used by Szymanowski[15] and by Johnson et al.[16,17] As a check an integration program using Euler's method with re-

Table 1. Example of evaluation of distribution constants from a chromatogram. Degree of ethoxylation = 1.127, determined from weighed amounts of reactants. Column 1: mole fractions, calculated from the raw chromatogram, corresponding DE = 1.045. Column 2: mole fractions after correction for response, corresponding DE = 1.070. Column 3: mole fractions after correction by extrapolation, corresponding DE = 1.069.

Chain length, i	1	2	3	c_i
0	0.4710	0.4481	0.4478	1.000
1	0.2513	0.2684	0.2682	1.770
2	0.1509	0.1581	0.1580	2.095
3	0.0707	0.0705	0.0704	2.817
4	0.0287	0.0281	0.0281	4.328
5	0.0137	0.0135	0.0134	5.505
6	0.0058	0.0057	0.0057	8.746
7	0.0040	0.0039	0.0039	7.747
8	0.0022	0.0022	0.0022	8.069
9	0.0012	0.0012	0.0012	8.175
10	0.0005	0.0005	0.0005	12.048
	1.0000	1.0000	0.9994	

peated Richardson extrapolation was worked out. It gave the same results as the above method.

Evaluation of ethoxylation experiments based on mixtures. In mixtures of phenylpropanol with another alcohol both compounds react with EO. A decanol ethoxylate does not absorb UV and the above method of evaluation was used. With added oligoethylene glycol monophenylpropyl ether, however, only the contributions in the chromatogram from phenylpropanol should be used. This was made by the extrapolation method, using points below the chain length of the added ether.

Reliability of values for distribution constants. Analytical errors in the chromatograms of course influence the values of the calculated distribution constants. To estimate this influence experimental values for three ethoxylates of DE 0.16, 1.1, and 8.1 were given random errors, 0–5% and 0–20%, with 10 replicates in each series. All distribution constants were calculated and then the mean and SD of the distribution constant of every chain length. Of course the SDs were much larger in the second series than in the first. In the three ethoxylates and in both series the SD increased with the magnitude of the distribution constant.

The same tendency was observed among the distribution constant values calculated from the chromatograms. They were divided into five groups: $c_i < 2$, $2 < c_i < 4$, $4 < c_i < 5$, $5 < c_i < 6$, $c_i > 6$. Each group thus contained distribution constants from many ethoxylates. For each group the variance within analyses was estimated. Table 2 gives a summary of the results. The SDs given are based only on analytical errors and do not include other sources of error, but give a rough estimate of the reliability of the calculated values of the distribution constants.

Nomenclature. The strict IUPAC nomenclature is very cumbersome and even unclear to use for some of the compounds in this study. The example given below will illustrate the nomenclature used. Some other definitions are also clarified.

Formula: $HO(CH_2CH_2O)_4OH$; IUPAC: 3,6,9-Trioxaundecane-1,11-diol; Name used here: Tetraethylene glycol.

Ethoxylation: the reaction of ethylene oxide (EO, oxirane) with compounds with active hydrogen atoms. *Degree of ethoxylation* (DE): the molar proportion between the ethylene oxide reacted and the compound to be ethoxylated. *Ethoxylate:* either the mixture of homologue compounds formed by ethoxylation or an individual compound in this mixture. *Chain length* (CL): the number of ethyleneoxy groups $(-CH_2CH_2O-)$ in an individual compound.

References

1. Weibull, B. In: Schönfeldt, N., *Grenzflächenaktive Äthylenoxid-Addukte*, Wissenschaftliche Verlagsgesellschaft, Stuttgart 1976, Ch. II.a.
2. Weibull, B. In: Schönfeldt, N., *Grenzflächenaktive Äthylenoxid-Addukte. Ergänzungsband 1984*, Wissenschaftliche Verlagsgesellschaft, Stuttgart 1984, Ch. II.a.
3. Weibull, B. and Nycander, B. *Acta Chem Scand. 8* (1954) 847.
4. Flory, P. J. *J. Am. Chem. Soc. 62* (1940) 1561.
5. Gold, L. *J. Chem. Phys. 20* (1952) 1651.
6. Gold, L. *J. Chem. Phys. 28* (1958) 91.
7. Natta, G. *Rend. Ist. Lombardo Sci. 78*, No. 1 (1945) 307.
8. Natta, G. and Simonetta, M. *Rend. Ist. Lombardo Sci. 78*, No. 1 (1945) 336.
9. Natta, G. and Mantica, E. *J. Am. Chem. Soc. 74* (1952) 3152.
10. Törnquist, J. *Acta Chem. Scand. 20* (1966) 572.
11. Törnquist, J. *Acta Chem. Scand. 23* (1969) 1935.
12. Weibull, B. and Törnquist, J. *Chem., Phys. Chem. Anwendungstech. Grenzflächenaktiven Stoffe, Ber. VI. Int. Kongr. 1972*, Carl Hanser Verlag, München 1973, Vol. 1, p. 125.
13. Sallay, P., Morgós, J., Farkas, L., Rusznák, I., Veress, G. and Bartha, B. *Tenside Deterg. 17* (1980) 298.
14. Farkas, L., Morgós, J., Sallay, P., Rusznák, I., Bartha, B. and Veress, G. *J. Am. Oil Chem. Soc. 58* (1981) 650.
15. Szymanowski, J. *J. Chem. Tech. Biotechnol. 40* (1987) 1.
16. Johnson, A. E., Jr., Geissler, P. R. and Talley, L. D. *J. Am. Oil Chem. Soc. 67* (1990) 123.
17. Geissler, P. R. and Johnson, A. E. Jr. *J. Am. Oil Chem. Soc. 67* (1990) 541.
18. Orvik, J. A. *J. Am. Chem. Soc. 98* (1976) 3322.
19. Ugelstad, J., Mörk, P. B. and Jenssen, B. *Acta Chem. Scand. 17* (1963) 1455.
20. Hine, J. and Hine, M. *J. Am. Chem. Soc. 74* (1952) 5266.
21. Björe, A., Strandlund, G. and Lamm, B. *Personal communication.*

Table 2. Statistical evaluation of values of distribution constants.

Range of values of constants	Number of constants	Number of analyses	Standard deviation
0–2	106	243	0.058
2–4	189	406	0.171
4–5	46	97	0.336
5–6	22	50	0.528
>6	42	89	1.611