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DETERMINATION OF THE OLIGOMER DISTRIBUTION IN ETHOXYLATED LINEAR AND BRANCHED ALKANOLS USING ^{13}C-NMR

LI YANG,‡ FRANK HEATLEY,* TREVOR G. BLEASE§
and ROBERT I. G. THOMPSON§
Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.

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Abstract—Short-chain ethoxylates of 1-decanol, 2-methyl-1-pentanol and 2-ethyl-1-hexanol have been prepared using anionic catalysis, and their ^{13}C-NMR spectra assigned. The oligomer distribution may be determined for ethylene oxide chain lengths of 0, 1, 2, 3, 4 and $\geqslant 5$ using the CH_2O alkanol resonance. The information from these model compounds was used to analyse commercial ethoxylates produced using an alkanol comprising several isomeric components; the distributions for various components could be determined. The oligomer distributions were comparable to those obtained from gas chromatography, and were well simulated using a simple numerical method with previously published oligomeric reactivity coefficients. The NMR technique may be particularly valuable when the alkanol consists of a mixture of isomers, or when the use of elevated temperatures is not feasible. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Short-chain ethoxylates of alkanols, R—$(OCH_2CH_2)_n$—OH, have many technological applications, for example as surfactants and functional fluids. The molecular structural parameters of these systems are the distribution of ethylene oxide (EO) chain lengths n and the structure of the alcohol. In respect of the former, the case of $n = 0$ (i.e. the unreacted alcohol) is frequently of particular importance because of its deleterious effects on the properties of the material, especially surfactant properties and chemical stability. Numerous techniques have been used to determine the distribution [1], including liquid chromatography, size exclusion chromatography, gas chromatography, thin-layer chromatography and supercritical fluid chromatography. However, in commercial practice, the alkanol is often a mixture of various chain lengths and skeletal structures [2]. Hence in these techniques, overlap may occur between the wide variety of ethoxylate structures. The object of this work was to investigate the use of high frequency ^{13}C-NMR spectroscopy for determining both the alkanol structure and the ethoxylate oligomer distribution by making use of the sensitivity of chemical shifts to chemical environment. Model oligomers of pure alcohols of different backbone structure representative of the main components of the commercial alkanol have been prepared and their spectra assigned. These results have then been used to analyse the structure of commercial ethoxylates.

EXPERIMENTAL

Materials

Molecular sieve type 4A was obtained from commercial sources (Aldrich Chemical Co. Ltd, 4–8 mesh). It was dried in an oven at over 100°C for at least 3 days, at 220°C on a vacuum line for one day and stored under dry N_2.

Ethylene oxide was obtained from commercial sources (Fluka AG, purity >99.8%). It was transferred under vacuum into a flask containing CaH_2 powder, stirred under dry ice for 24 hr, and finally evacuated under liquid N_2 to a high vacuum (10^{-4} mbar) before use.

1-Decanol was obtained from commercial sources (BDH Ltd, purity >99%). It was distilled under reduced pressure, the middle cut (126 ± 0.5°C, 30 mmHg) being collected and stored under N_2 in a flask containing dried molecular sieve.

2-Methyl-1-pentanol was obtained from commercial sources (Aldrich Chemical Co. Ltd, purity >99%). It was stirred for 3 hr with anhydrous $MgSO_4$ (Aldrich Chemical Co. Ltd, purity >97%), then filtered and distilled at atmospheric pressure, the middle cut (147 ± 0.5°C) being collected and stored under N_2 in a flask containing dried molecular sieve.

2-Ethyl-1-hexanol was obtained from commercial sources (Aldrich Chemical Co. Ltd, purity >99%). It was stirred for 3 hr with anhydrous $MgSO_4$ (Aldrich Chemical Co. Ltd, purity >97%), then filtered and distilled at atmospheric pressure, the middle cut (184 ± 1°C) being collected and stored under N_2 in a flask containing dried molecular sieve.

Potassium metal obtained from commercial sources (BDH Ltd, under liquid paraffin) was cut and weighed under dried petroleum ether.

The commercial alkanol, Synprol 135, and three commercial ethoxylates, Synperol A3, A5 and A7, were obtained from ICI Chemicals & Polymers, and were used as received.

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*To whom all correspondence should be addressed.

‡Present address: Courtaulds Coatings Ltd, North Woolwich Road, London E16 2AF, U.K.

§ICI Chemicals & Polymers Ltd, P.O. Box 90, Wilton, Cleveland TS6 8JE, U.K.

Preparation of ethoxylates

(a) Preparation of catalyst solution. The required amount of dry alkanol was injected into a dried ampoule fitted with a Teflon tap using a syringe under the protection of dry N_2. Potassium metal (ca. 3 mg) was weighed in petroleum ether, dried using tissues and then rapidly transferred into the ampoule using tweezers under dry N_2. The ampoule was placed on a vacuum line until the reaction of the alkanol with the potassium was complete and a high vacuum (10^{-4} mbar) was attained.

(b) Ethoxylation. EO (ca. 3 g) was condensed into an ampoule containing the potassium/alkanol solution cooled in a dry ice/acetone bath, evacuated under liquid N_2 and sealed using a Teflon tap under high vacuum. The ampoule was allowed to attain room temperature, and shaken gently to mix the components. The ampoule was immersed in a water bath at 50°C for about 10 days, then heated at about 50°C on a vacuum line in order to remove unreacted EO, which typically amounted to $<2\%$ of the original EO.

NMR spectroscopy

^{13}C spectra were obtained using a Varian Associates Unity 500 spectrometer operating at 125.8 MHz. Solutions in $CDCl_3$ at a concentration of ca. 200 mg cm^{-3} were employed. To ensure quantitative accuracy, a relaxation delay of 20 sec between pulses was used. To assist in the spectrum analysis, spectra were also recorded using the "Distortionless Enhancement by Polarisation Transfer" (DEPT) technique [3]. These DEPT spectra were used for two purposes: first to identify primary, secondary, tertiary and quaternary carbons, and second to clearly resolve the C-1 carbon in 2-methyl-1-alkanol ethoxylates, which is normally obscured by the solvent resonance (see below). Spectra were initially referenced by setting the alkyl terminal CH_3 signal to 14.0 ppm, but when comparing oligomeric fine structure of specific carbons in detail, spectra were referenced to a specific oligomer peak for the carbon in question; further details are given below.

Gas chromatography

High resolution GC traces were obtained for the decanol ethoxylates using a Carlo Erba 4000 series instrument equipped with a Shimadzu integrator. A capillary column of length 5 m and I.D. 0.22 mm packed with a BP1 stationary phase was used, with flame ionisation detection. The flow rate of the hydrogen carrier gas was 30 cm sec^{-1}, and the column temperature was raised over the range 100–310°C at a rate of 10° min^{-1}.

RESULTS AND DISCUSSION

General features and notation

In describing the NMR spectra, it is helpful to consider first the mechanism of anionically catalysed alkanol ethoxylation. Since all the alkanols involved in this work were primary, the alkanol is denoted by $R\mathrm{CH_2OH}$. The mechanism is

$$R\mathrm{CH_2O^-} + \mathrm{C_2H_4O} \rightarrow R\mathrm{CH_2OCH_2CH_2O^-} \quad (k_0)$$

$$R\mathrm{CH_2OCH_2CH_2O^-} + \mathrm{C_2H_4O} \rightarrow R\mathrm{CH_2OCH_2CH_2OCH_2CH_2O^-} \quad (k_1)$$

the general reaction being

$$R\mathrm{CH_2(OCH_2CH_2)_nO^-} + \mathrm{C_2H_4O} \rightarrow R\mathrm{CH_2(OCH_2CH_2)_{n+1}O^-} \quad (k_n)$$

where k_n represents the rate constant for reaction of the nth oligomer. The fact that alcohol and alkoxide groups are in rapid equilibrium has two important consequences. The first is that all hydroxy species may add EO at a rate controlled by the appropriate rate constant, while the second is that only a single averaged NMR signal is observed for a particular $\mathrm{CH_2OH/CH_2O^-}$ equilibrating pair. The rate constant k_n actually represents an effective rate constant which depends on the true rate constant for reaction of the alkoxide ion and the acid dissociation constant of the alcohol (i.e. the equilibrium between alcohol and alkoxide). It has been found [4] that k_n increases with n, tending towards an asymptote at $n \approx 6$. Thus, EO units prefer to add to existing ethoxylates rather than to the alkanol, leading to a relatively high proportion of alkanol in the product.

Within the alkanol fragment, the carbon numbering scheme follows the standard method, the CH_2O carbon being designated C_1. The CH_3 side-group in 2-methylpentanol is designated $C_{3'}$ and the CH_2 and CH_3 sidegroup carbons in 2-ethylhexanol are designated $C_{3'}$ and $C_{4'}$, respectively. Within the EO fragment, the following notation is used:

$$R\mathrm{CH_2{-}O{-}}\underset{\alpha}{\mathrm{CH_2}}{-}\underbrace{\mathrm{CH_2{-}(O{-}CH_2{-}CH_2)_{n-3}{-}O{-}CH_2}}_{\text{int}}{-}\underset{\chi}{\mathrm{CH_2}}{-}\mathrm{O}{-}\underset{\psi}{\mathrm{CH_2}}{-}\underset{\omega}{\mathrm{CH_2OH}}$$

The carbons in the ethoxylates may be divided into two band groups, alkyl carbons ($C\underline{C}C$) in the R fragment appearing in the region 10–45 ppm, and alkoxy carbons ($C\underline{C}O$) in the region of 60–80 ppm. Peak assignments were made with the assistance of compilations of chemical shift data [5–7], a personal computer spectroscopy database and prediction program [7], and reported chemical shifts for poly(ethylene oxide) [8]. The alkyl region spectra depended strongly on the alkanol structure and are described further below. The chemical shifts of C_2, C_3 and $C_{3'}$ showed some sensitivity to the oligomer chain length. These carbons are designated C_jOH in the alkanol and C_jOE in the ethoxylates.

In the alkoxy region, the carbons C_1, C_ψ and C_ω were clearly distinguished in the ethoxylates of all the alkanols used in this work. The C_1 peaks could be further divided into a singlet from the unreacted alkanol, designated C_1OH, and a set of closely grouped peaks from ethoxylates, designated C_1OE. The C_1OE resonances were displaced by ca. 8 ppm to higher frequency from the C_1OH resonance. The chemical shift of C_1 depended strongly on the alkanol structure, but the shifts of the other carbons were fairly consistent in frequency. The resonances of C_1, C_2, C_α, C_χ, C_ψ and C_ω were found to be split into a number of lines from different oligomers, as described further below. The C_{int} resonance gave a complex pattern at ca. 70 ppm due to a large number of closely similar environments.

Although great care was taken to exclude water, in some preparations this was not completely achieved. The effect of water is exacerbated by its greatly enhanced reactivity compared to an alkanol. Adventitious water produced poly(ethylene oxide) (PEO), the amount of which could readily be determined

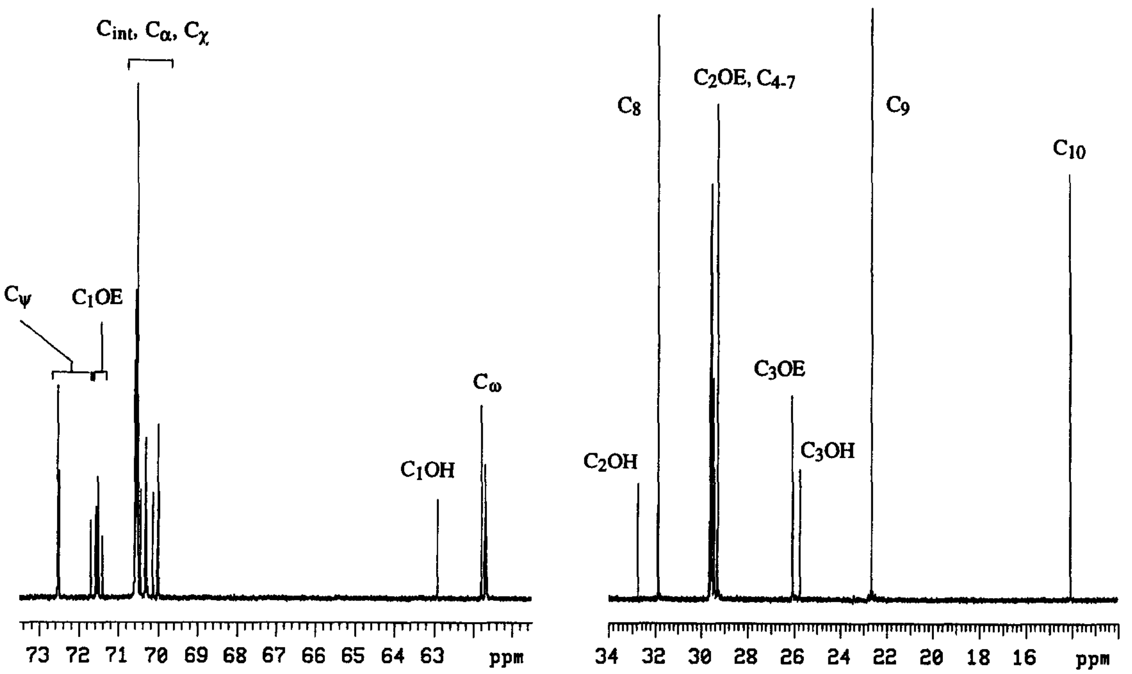


Fig. 1. The ^{13}C-NMR spectrum of a 1-decanol ethoxylate, $\langle n \rangle = 3.7$.

from the excess intensity of the C_ω peaks relative to the intensity of the C_1 peaks.

NMR spectra of decanol ethoxylates

Figure 1 shows an example of a complete decanol ethoxylate spectrum with assignments. On comparing the spectra of different ethoxylates, it was found that the C_1, C_3, C_α, C_χ, C_ψ and C_ω regions clearly showed varying degrees of oligomeric sensitivity. The C_2 carbon also showed a number of oligomer peaks, but the C_2OE peaks overlapped the C_{4-7} peaks and were not clearly resolved. Figure 2 compares the spectra of C_1OE in detail for selected samples of different degrees of ethoxylation. Up to five peaks were observed, indicating chemical shift sensitivity up to an EO chain length of five. Thus, by including the C_1OH peak at 62.5 ppm, the oligomer distribution for $n = 0, 1, 2, 3, 4$ and $\geqslant 5$ could be determined using this region.

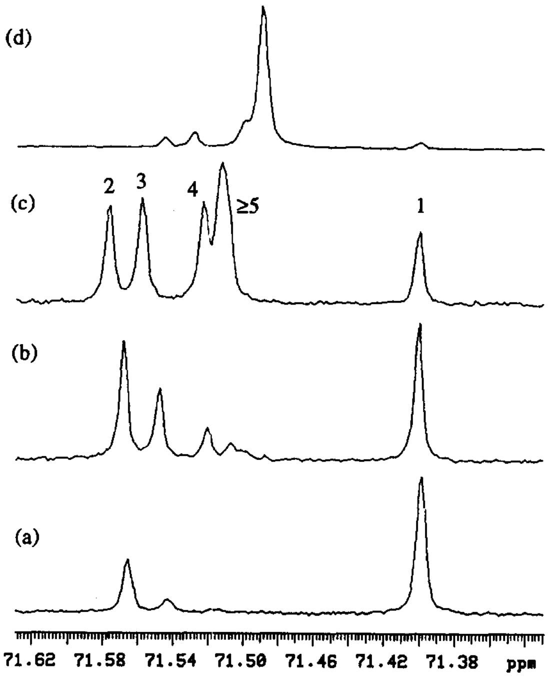


Fig. 2. Comparison of the C_1OE region of the ^{13}C-NMR spectra of 1-decanol ethoxylates: (a) $\langle n \rangle = 0.68$; (b) $\langle n \rangle = 1.9$; (c) $\langle n \rangle = 3.7$; (d) $\langle n \rangle = 7.6$. The oligomer assignment is given on spectrum (c).

Table 1. Experimental and simulated oligomer distributions (mol%) of decanol ethoxylates

	A $\langle n \rangle = 1.7$			B $\langle n \rangle = 2.5$			C $\langle n \rangle = 3.7$	
	exp.		calc.	exp.		calc.	exp.	calc.
n	NMR	GC		NMR	GC		NMR	
0	44.9	45.1	39.7	27.0	24.0	25.8	13.2	14.7
1	22.2	21.5	21.5	17.9	15.5	16.5	8.9	11.0
2	16.8	18.4	16.1	18.4	19.9	15.5	14.1	12.9
3	9.9	9.6	10.5	16.2	16.8	13.2	16.5	13.5
4	3.8	3.8	6.1	9.1	11.1	10.1	13.8	12.0
⩾5	2.4	1.6	6.1	11.4	12.7	18.9	29.3	31.9
PEO	—	—	—	—	—	—	4.2	4.0

	D $\langle n \rangle = 4.9$			E $\langle n \rangle = 5.9$			F $\langle n \rangle = 7.6$		
	exp.			calc.	exp.		calc.	exp.	calc.
n	NMR	GC		NMR	GC		NMR	GC	
0	8.6	9.3	9.4	6.1	6.4	5.9	2.5	4.4	3.7
1	5.6	6.3	7.4	3.7	4.2	4.7	2.6	3.1	3.0
2	9.9	11.3	9.4	6.4	7.3	6.4	3.8	6.0	4.2
3	12.9	14.3	11.0	9.5	10.3	8.1	6.4	8.4	5.6
4	13.4	14.9	11.2	12.9	12.4	9.0	10.1	11.1	6.9
⩾5	45.5	43.9	47.7	56.8	59.4	61.8	68.9	67.0	71.5
PEO	4.1	—	3.9	4.6	—	4.1	5.7	—	5.1

(a) Using reactivity coefficients (i) in Table 2.
(b) Using reactivity coefficients (ii) in Table 2.
(c) Using reactivity coefficients (iii) in Table 2.

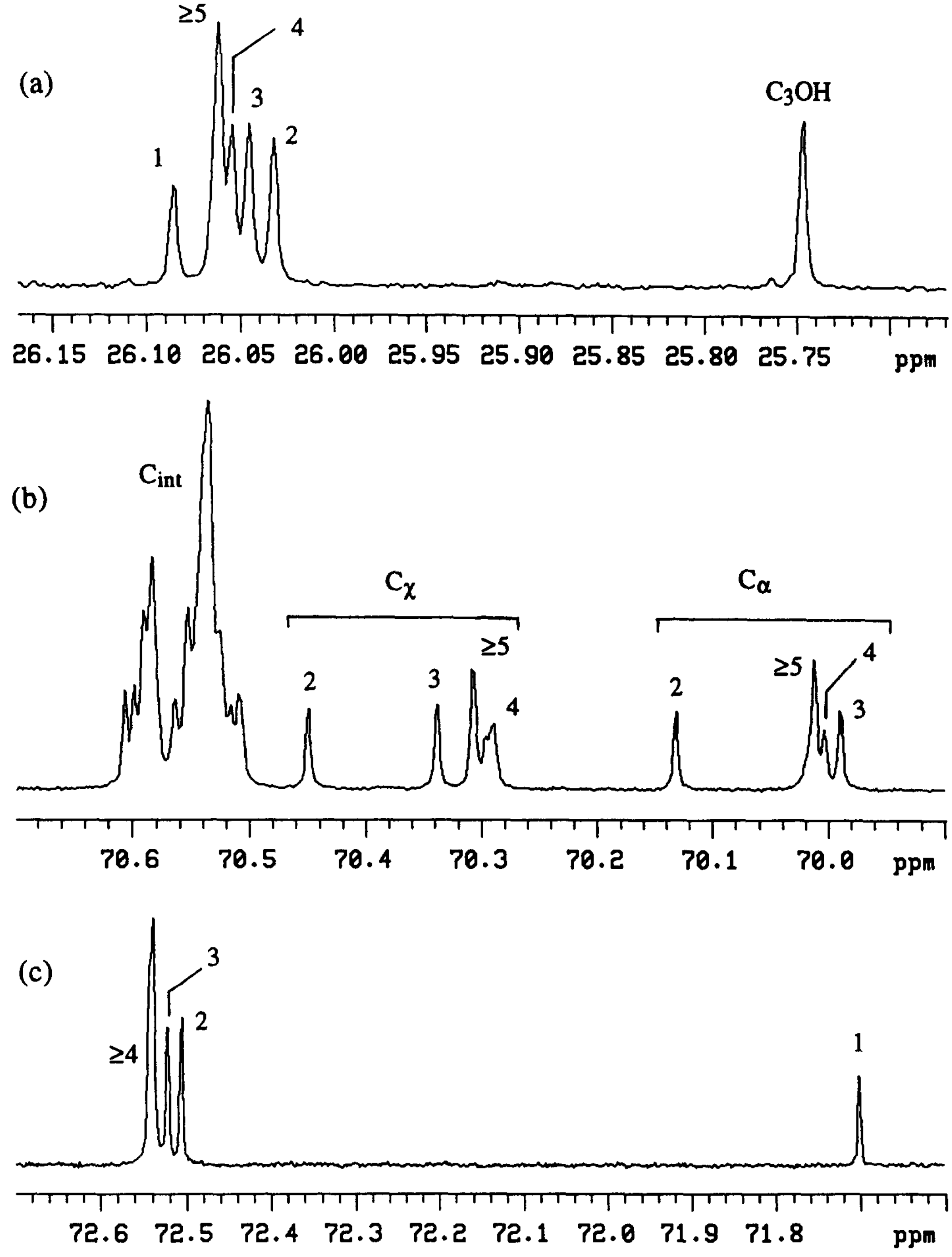


Fig. 3. Expansions of regions of the ^{13}C-NMR spectra of a 1-decanol ethoxylate with $\langle n \rangle = 3.7$: (a) C_3; (b) C_{int}, C_α and C_χ; (c) C_ψ.

At this point it should be pointed out that when spectra were referenced by setting the alkyl terminal CH_3 peak to 14.0 ppm, it was found that there were small differences of up to 0.1 ppm between the chemical shifts of C_1 in a particular oligomer in different ethoxylates. It was therefore not possible to quote the absolute chemical shifts to an accuracy of better than 0.1 ppm, though relative chemical shifts between oligomers were consistent from sample to sample. In order to accurately compare the evolution of the spectrum with degree of ethoxylation, the spectra in Fig. 2 were plotted with the peaks from the $n = 1$ oligomer aligned at 71.40 ppm. Even so, although the pattern of peaks is consistent, there are small variations in chemical shift of a particular oligomer

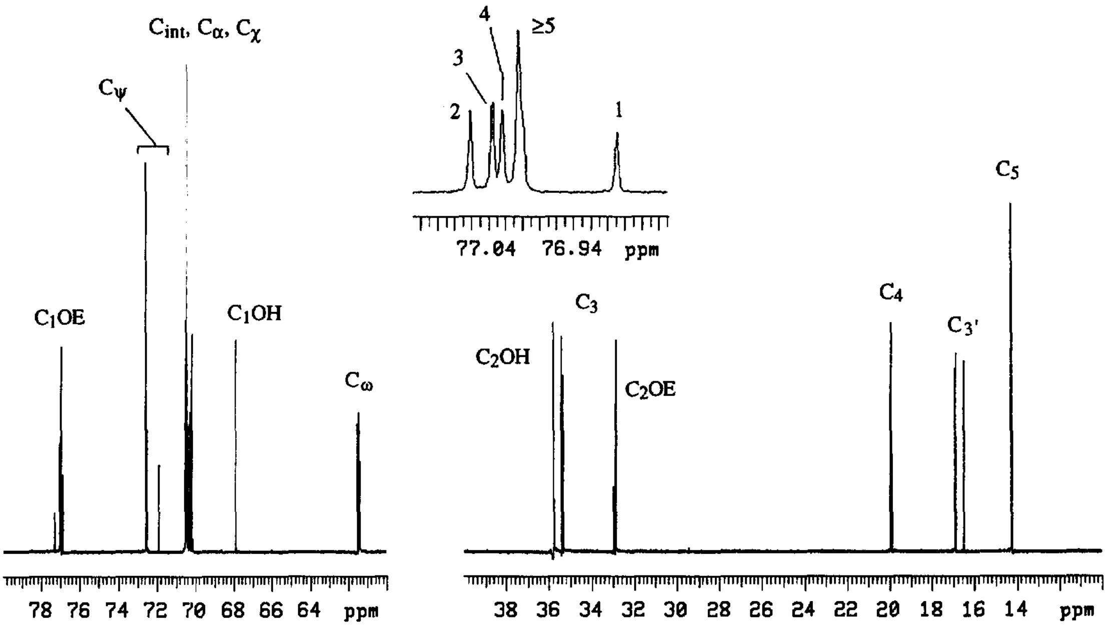


Fig. 4. The ^{13}C-NMR spectrum of a 2-methyl-1-pentanol ethoxylate, $\langle n \rangle = 4.4$. This spectrum was obtained using the DEPT technique with a final ^{1}H pulse flip angle of 45° in order to observe the C_1OE peaks at ca. 77 ppm, which were obscured by the solvent peaks in the normal spectrum. The inset expansion shows the C_1OE region.

between different ethoxylates. The origin of these differences in chemical shifts between samples probably lay in a concentration-dependent electrostatic interaction between the $CDCl_3$ solvent (which is also used as a field/frequency lock signal) and the polar EO segments. Such an interaction would affect the alkoxy carbons more than the alkyl, and its magnitude would depend on both the EO content and the ethoxylate concentration.

The oligomer distributions obtained from the C_1 peaks for selected samples are given in Table 1.

Figure 3 illustrates expansions of other regions for one sample with $\langle n \rangle = 3.7$, together with the oligomer assignment derived from comparisons similar to that shown in Fig. 2. The C_ω resonance was somewhat variable in chemical shift and line width, probably due to irreproducible rates of exchange and positions of equilibrium between CH_2OH and

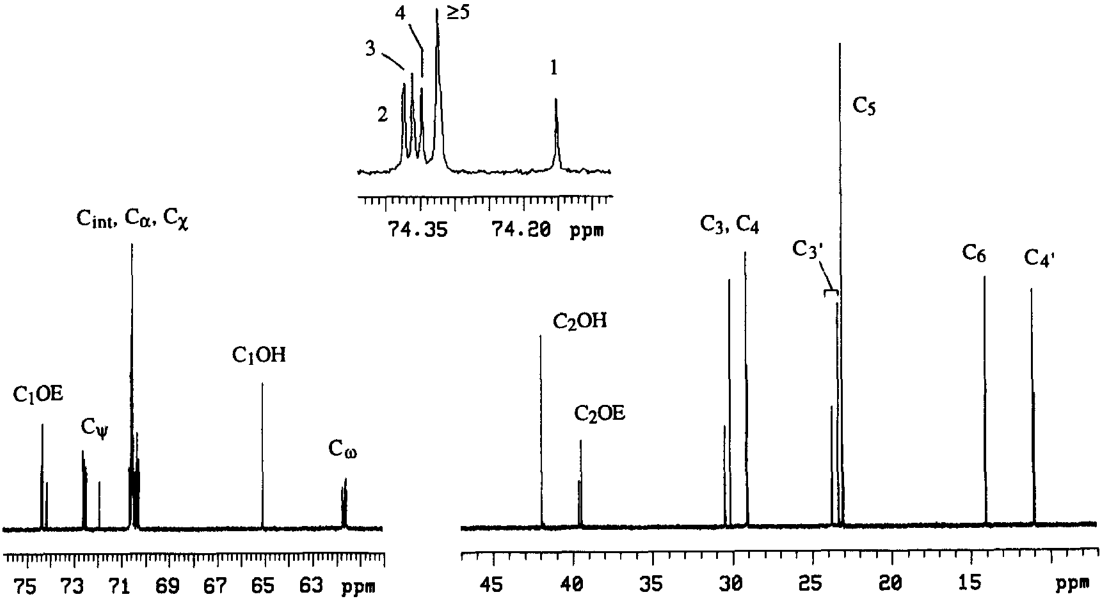


Fig. 5. The ^{13}C-NMR spectrum of a 2-ethyl-1-hexanol ethoxylate, $\langle n \rangle = 2.7$. The inset expansion shows the C_1OE region.

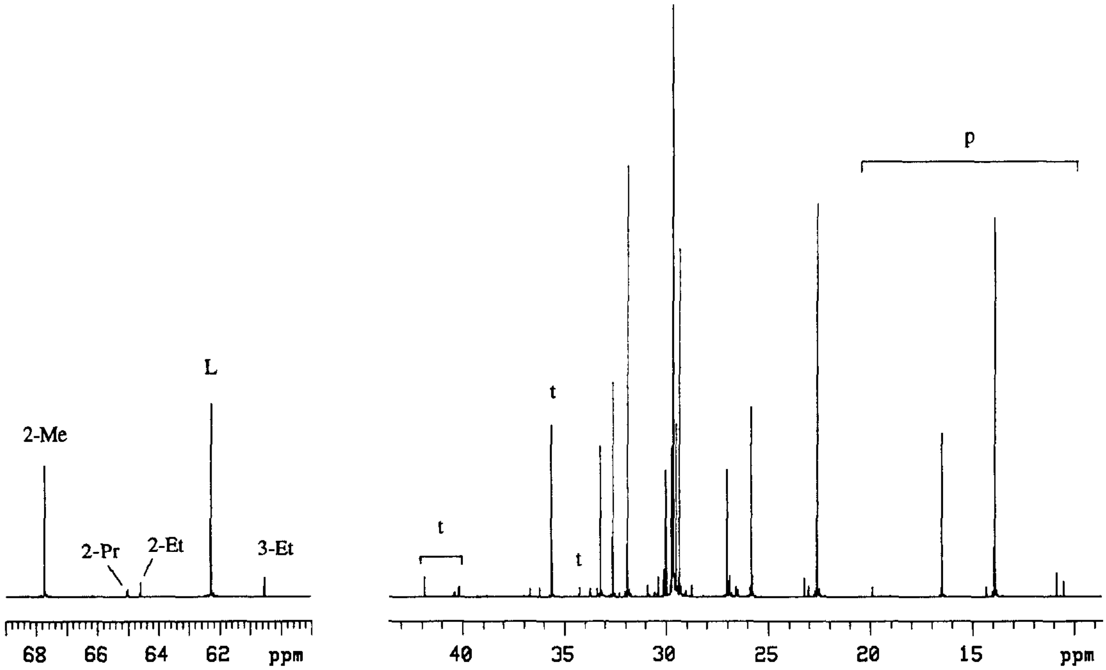


Fig. 6. The ^{13}C-NMR spectrum of a commercial alkanol, Synprol 135. In the alkyl region, the labels p and t identify CH_3 and CH carbons, respectively; all others are CH_2.

CH_2O^- species. For this reason, this region is not illustrated.

Analysis of decanol ethoxylates by GC

The GC traces were similar to those reported previously [1]. For the samples prepared in this work, up to twelve peaks were shown clearly for the oligomers of decanol, though the peak separation of the higher oligomers was such that oligomers with much higher EO lengths would be resolved if they were present. The oligomer distributions of the decanol ethoxylates derived from GC are summarised in Table 1. There is excellent agreement within experimental error with the more limited distribution data from ^{13}C-NMR as described above. These results indicate that the flame ionisation detector response does not depend significantly on the oligomer size, and that there is no appreciable degradation of the

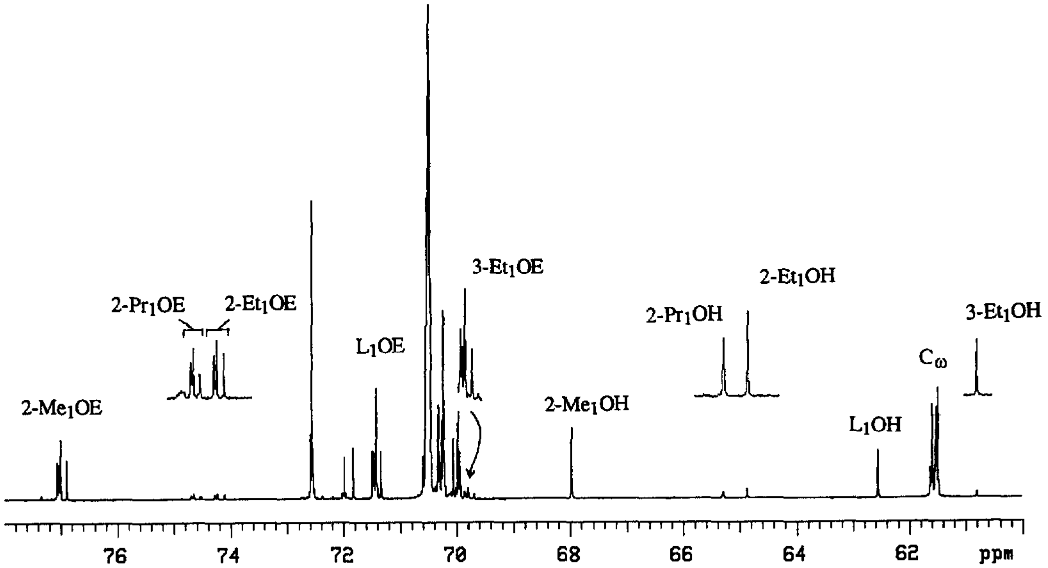


Fig. 7. The ^{13}C-NMR spectrum of a Synprol 135 ethoxylate, $\langle n \rangle = 3.2$. This spectrum was obtained using the DEPT technique with a final ^{1}H pulse flip angle of 45° in order to observe the C_1OE peaks in the 2-methyl isomer at ca. 77 ppm, which were obscured by the solvent peaks in the normal spectrum. The vertical expansions of the 2-Et$_1$, 3-Et$_1$ and 2-Pr$_1$ resonances are 10-fold.

oligomers under the more stringent thermal conditions of GC.

NMR spectra of 2-methyl-1-pentanol ethoxylates

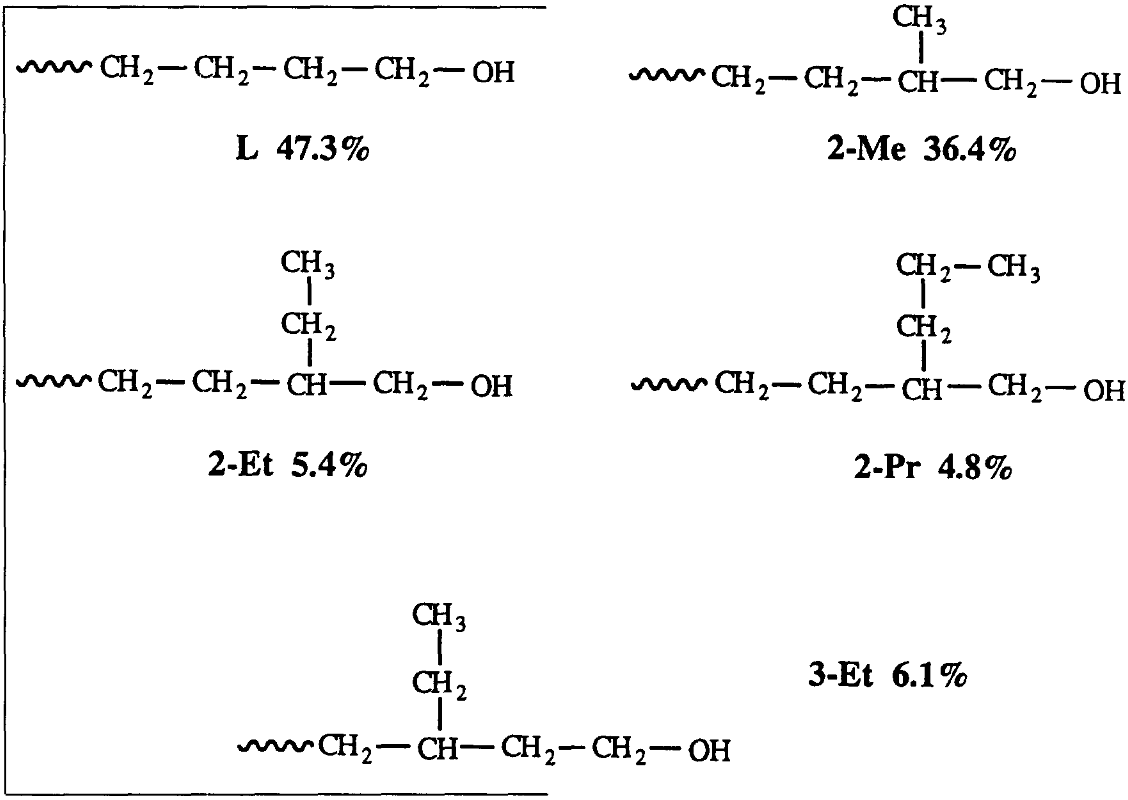
In the normal ^{13}C spectrum of these samples, the C_1OE peaks were obscured by the $CDCl_3$ solvent peaks, but they could be observed readily and clearly by using the DEPT pulse sequence with a final proton pulse of 45° to eliminate the $CDCl_3$ peaks. Figure 4 shows an example of a complete 2-methyl-1-pentanol ethoxylate spectrum with assignments. As for the decanol ethoxylates, the C_1 resonances were sensitive to the EO chain length up to $n \geqslant 5$, and the C_ψ resonances up to $n \geqslant 4$. An expansion of the C_1OE region is shown as an inset in Fig. 4 with the oligomer assignments derived from comparisons of spectra similar to that shown in Fig. 2.

NMR spectra of 2-ethyl-1-hexanol ethoxylates

Figure 5 shows an example of a complete 2-ethyl-1-hexanol ethoxylate spectrum with assignments. The C_1OE resonances were clearly resolved. As for the previous ethoxylates, the C_1 resonances were sensitive to the EO chain length up to $n \geqslant 5$, and the C_ψ resonances up to $n \geqslant 4$. An expansion of the C_1OE region is shown as an inset in Fig. 5 with the oligomer assignments derived from comparisons of spectra similar to that shown in Fig. 2.

NMR spectra of commercial synperonic ethoxylates

The alkanol component of these materials is a mixture designated Synprol 135, the ^{13}C-NMR spectra of which is shown in Fig. 6. All the peaks in the region 60–68 ppm were found to be CH_2 carbons, so the material contained only primary alcohols. There are five CH_2OH peaks, two major and three minor. The alkyl region, 10–42 ppm, was complex, comprising CH, CH_2 and CH_3 peaks as indicated in Fig. 6. The empirical formula of the mixture was determined as $(CH_3)_{1.4}(CH_2)_{11.1}(CH)_{0.4}CH_2OH$. Using the chemical shifts of the pure alkanols used in this work, literature data [5–7], and chemical shift prediction software [7], the CH_2OH, CH and CH_3 peaks were assigned to the following alcohol structures, with their designations and molar abundances determined from the intensities of the CH_2OH peaks:



$\sim CH_2-CH_2-CH_2-CH_2-OH$

L 47.3%

$\sim CH_2-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-OH$

2-Me 36.4%

$\sim CH_2-CH_2-\overset{\displaystyle CH_3-CH_2}{\overset{|}{CH}}-CH_2-OH$

2-Et 5.4%

$\sim CH_2-CH_2-\overset{\displaystyle CH_3-CH_2-CH_2}{\overset{|}{CH}}-CH_2-OH$

2-Pr 4.8%

$\sim CH_2-\overset{\displaystyle CH_3-CH_2}{\overset{|}{CH}}-CH_2-CH_2-OH$

3-Et 6.1%

The structure of the remainder of the alkyl chain was not elucidated.

For the determination of the oligomer distribution in ethoxylates of this composite alkanol, attention was focussed on the C_1 resonances, since the spectra described above showed that the resonances of this carbon in the various components were well separated. Figure 7 shows the ^{13}C-NMR spectrum of Synperonic A3 obtained using the DEPT technique with a final ^1H pulse flip angle of 45° in order to observe the C_1OE peaks in the 2-methyl isomer at ca. 77 ppm which were obscured by the solvent peaks in the normal spectrum. Using the spectra of the model ethoxylates described above as guides, the regions corresponding to the C_1OE carbons in the ethoxylates of the Synprol components were clearly differentiated, as indicated on the figure. The resolution of the spectra of these more complex materials was worse than the model ethoxylates, with the consequence that the oligomer distribution could only be determined up to $n \geqslant 4$ for each component. Numerical data for the oligomer distribution in these commercial materials is presented at the end of the following section.

Analysis of oligomer distribution

The following kinetic analysis follows a scheme developed in Ref. [4], with modifications to allow a simplified numerical calculation of the oligomer distribution and to include a mixture of alkanols with different reactivities.

From the general reaction scheme outlined above, the rate equations for an alkanol *R*OH are

$$\frac{d[RE_0]}{dt} = -k_0^R[RE_0][E] \tag{1}$$

$$\frac{d[RE_i]}{dt} = -k_i^R[RE_i][E] + k_{i-1}^R[RE_{i-1}][E] \quad (i \geqslant 1) \tag{2}$$

$$\frac{d[E]}{dt} = -\sum_R \sum_{i=0}^{\infty} k_i^R[RE_i][E] \tag{3}$$

where E denotes ethylene oxide and RE_i denotes the *i*th oligomer. In regard to the oligomer distribution, it is the relative rates of reaction which are of significance. For this purpose, the above equations may be simplified as follows.

The probability of occurrence of oligomer *i* of component *R*OH, P_i^R, is given by

$$P_i^R = \frac{[RE_i]}{\sum_R [RE_0]_0} \tag{4}$$

where $[RE_0]_0$ is the initial concentration of component *R*OH. Dividing equations (1), (2) and (3) by $\Sigma_R\,[RE_0]_0$, and defining the quantity *M* as

$$M = \frac{[E]}{\sum_R [RE_0]_0} \tag{5}$$

we obtain

$$\frac{dP_0^R}{dt} = -k_0^R P_0^R[E] \tag{6}$$

$$\frac{dP_i^R}{dt} = -k_i^R P_i^R[E] + k_{i-1}^R P_{i-1}^R[E] \quad (i \geqslant 1) \tag{7}$$

$$\frac{dM}{dt} = -\sum_R \sum_{i=0}^{\infty} k_i^R P_i^R[E] \tag{8}$$

Dividing equations (6) and (7) by equation (8), and defining oligomeric reactivity coefficients C_i^R referred to one of the alkanol components according to

$$C_i^R = \frac{k_i^R}{k_0^R} \tag{9}$$

gives the following equations which express the change in the oligomer probabilities as *M* decreases, i.e. as the ethylene oxide reacts:

$$\frac{dP_0^R}{dM} = \frac{C_0^R P_0^R}{S} \tag{10}$$

$$\frac{dP_i^R}{dM} = \frac{C_i^R P_i^R - C_{i-1}^R P_{i-1}^R}{S} \quad (i \geqslant 1) \tag{11}$$

with *S* defined by

$$S = \sum_R \sum_{i=0}^{\infty} C_i^R P_i^R \tag{12}$$

Note that this scheme can readily incorporate adventitious water by treating it as an "alkanol" component.

The simplest way of calculating the oligomer probabilities for given initial composition, degree of reaction and reactivity coefficients is a numerical method in which the variable *M* is allowed to change in tiny steps d*M* from its initial value to its final value, and the corresponding changes in the probabilities dP_i^R on each step are evaluated using equations (10) and (11). Initially, the probabilities P_0^R are set equal to the initial mole fraction of component *R*OH and all other probabilities are set to zero. After each step the values of P_i^R are adjusted by the values of dP_i^R and the process is repeated until the final value of *M* is reached. If the steps are sufficiently small, the simulation approaches a continuous process; trial calculations showed that this limit was attained for practical purposes with a value of d*M* of 0.01. In addition, these trials showed that for the largest degree of ethoxylation encountered in this work, evaluation of the oligomer probabilities up to $n = 50$ was more than sufficient to encompass all oligomers.

Simulations were carried out first for several decanol ethoxylates using reactivity coefficients based on values obtained for octanol ethoxylates using super-fluid liquid chromatography [4]. Experimental and calculated distributions are compared in Table 1 and the reactivity coefficients used are reported in Table 2. In Ref. [4], it was found that the reactivity coefficients depended not only on the oligomer but also on the EO/alcohol mole ratio. The coefficients for samples A and B follow those given in Ref. [4] for a system with an initial EO/octanol ratio of 2.82, the coefficients for samples C, D and E follow those found for a system with an EO/octanol ratio of 5.48, while the coefficients for sample F follow those found for a system with an EO/octanol ratio of 8.24. In the cases of samples C, D, E and F, there was some polymerisation by EO by adventitious water but the water reactivity coefficients do not appear to have

Table 2. Reactivity coefficients used to calculate the oligomer distributions of 1-decanol ethoxylates in Table 1. C_n^D and C_n^w denote reactivity coefficients for decanol and water, respectively

n	C_n^D (i)	C_n^D (ii)	C_n^D (iii)	C_n^w (ii)	C_n^w (iii)
0	(1)	(1)	(1)	10	10
1	2.3	2.2	2.2	8	8
2	2.8	2.5	2.5	6	6
3	3.2	2.7	2.7	5	5
4	3.6	3.0	2.9	5	4
5	4.2	3.3	3.2	5	4
6	4.5	3.5	3.4	5	4
7	4.7	3.7	3.6	5	4
$\geqslant 8$	5.0	4.0	3.8	5	4

(i) Used for $(\mathrm{EO}/R\mathrm{OH}) \leqslant 3$.
(ii) Used for $3 < (\mathrm{EO}/R\mathrm{OH}) \leqslant 7$.
(iii) Used for $(\mathrm{EO}/R\mathrm{OH}) > 7$.

Table 3. Experimental (NMR) and simulated oligomer distributions (mol%) for commercial Synprol 135 ethoxylates

	$\langle n \rangle = 3$		$\langle n \rangle = 5$		$\langle n \rangle = 7$	
n	exp.	calc. (i)	exp.	calc. (ii)	exp.	calc. (iii)
L isomer						
0	9.1	10.5	4.0	4.7	2.1	1.8
1	6.5	7.2	4.7	3.7	1.2	1.4
2	8.0	7.5	4.8	4.9	2.4	2.0
3	7.6	7.2	6.0	5.9	3.2	2.8
⩾4	22.4	24.5	34.6	37.9	46.4	48.9
S isomer						
0	15.8	13.2	11.7	7.5	5.8	4.8
1	6.1	5.4	6.3	3.4	1.9	1.8
2	6.7	5.1	6.1	3.9	4.1	3.1
3	7.6	4.7	4.5	4.3	4.5	3.5
⩾4	10.2	14.7	17.3	23.8	28.4	29.9
PEO						

(i), (ii) and (iii) as in Table 2.

been determined. The values given in Table 2 are somewhat arbitrary estimates, but they were included in the calculation to make some allowance for their effect on the alkanol oligomer distribution. The rationale for the water coefficients chosen was as follows:

(i) the rate constant for reaction of water is significantly greater than that for the reaction of a CH_2OH group;

(ii) for long PEO chains the rate constant will not differ significantly from that for a long alkanol ethoxylate.

There is satisfactory agreement between the experimental and calculated distributions.

As described earlier, Synprol 135 is a mixture of several isomers, the most important being linear (L, 47.3%) and 2-methyl (2-Me, 36.4%) alcohols. The other components detected, 2-ethyl, 2-propyl and 3-ethyl, were presented in much smaller amounts (⩾6%); their oligomers, although detectable by NMR, were difficult to quantify with the accuracy required to determine their reactivity coefficients reliably. For the purposes of verifying the general validity of the simulation method presented here and the consistency of the NMR oligomer distributions with previously published reactivity coefficients, the 3-Et isomer was assumed to have the same reactivity as the L isomer, and the 2-Et and 2-Pr isomers were assumed to have the same reactivity as the 2-Me isomer. Synprol 135 was assumed to comprise only two distinct alcohols, designated *L* (linear, L + 3-Et, 57%) and *S* (substituted, 2-Me + 2-Et + 2-Pr, 43%). The rate constant for ethoxylation of the *L* component was taken as the reference for the reactivity coefficients. The reactivity coefficients for the oligomers of the *L* component were taken to be the same as for the simulation of decanol above, i.e. they were assumed to vary with the EO content as in Ref. [4] (Table 2). Furthermore, it was assumed that the reactivity coefficients for the oligomers of the *S* component would rapidly approach those of the *L* oligomers (of the same length) as the size of the oligomer increased. Attention was focussed on adjusting the reactivity coefficients of the *S* component and its lower oligomers to achieve a satisfactory agreement between simulation and experiment. In fact, it was found that this objective could be substantially obtained simply by setting the reactivity coefficient C_0^S of the *S* component to 0.7, without significantly altering the reactivity coefficients of its oligomers, i.e. taking $C_n^S = C_n^L$ for $n \geqslant 1$. The simulated and experimental (NMR) distributions for the commercial ethoxylates are compared in Table 3. Again, there is satisfactory agreement between the experimental and calculated distributions.

CONCLUSIONS

This work shows that useful information on the oligomer distribution of alkanol ethoxylates may be obtained from ^{13}C-NMR spectroscopy. The NMR technique may be particularly valuable when the alkanol consists of a mixture of isomers, or when the use of elevated temperatures in chromatographic techniques is not desirable.

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