

Alkylethoxyethanesulphonates: Two Techniques for Improving Synthetic Conversions

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Alkylethoxyethanesulphonates, high-cost speciality surfactants, are most commonly synthesized from precursor ethoxyalcohols by thionyl chloride chlorination followed by sulphonation with sodium sulphite. Conversions in the sulphonation stage are only moderate with highly hydrophobic ethoxychlorides. Alkylethoxyalcohols with a novel narrow distribution of ethoxy chain lengths recently have been reported. We demonstrate how the conversion in the sulphonation of hexadecanol tetraethoxychloride increases from 65% to 80% when the traditional broad ethoxylate distribution ethoxyalcohol is replaced by narrow range ethoxyalcohol as precursor. Replacement of sodium sulphite by potassium sulphite increases conversion still further, to quantitative, in the sulphonation of the narrow range ethoxychloride. Exploitation of these two techniques in the manufacture of ethoxyethanesulphonate surfactants might be expected to improve the economics of their application.

KEY WORDS: Chlorination, ethanesulphonates, ethoxyalcohols, sulphonation, surfactant, synthesis.

The ethoxylation of long-chain fatty alcohols or the products of phenol alkylation with detergent range α -olefins provides the entry point to the two most important classes of commercial nonionic surfactants. The reaction with ethylene oxide has traditionally been performed at temperatures in excess of 120°C and pressures of 4 bar using potassium hydroxide as catalyst (1). Ethoxyalcohols manufactured with this catalyst contain a broad range of ethoxy chain lengths. The most recent advance in ethoxylation technology is the use of calcium (2), strontium (3) or barium (4) bases as catalysts, which results in substantial narrowing of ethoxylate distribution. Such peaked distribution alkylethoxyalcohols are reported to possess improved performance characteristics (5,6).

Alkyl/alkylphenylethoxyethanesulphonates are a class of anionic surfactant which is synthesized from the ethoxyalcohols according to the scheme in Figure 1. These products were first patented in 1938 by Bruson (7) who applied the Strecker sulphonation procedure to this compound series. Although ethanesulphonate surfactants are expensive to manufacture, they possess the considerable advantages over conventional surfactants of high salinity tolerance, high thermal hydrolytic stability and, by structural adjustment, widely variable HLB values. After decades of neglect, interest in these surfactants and their properties is increasing and application patents continue to appear.

One important area is their application as enhanced oil recovery surfactant flood components (8).

A number of improvements to the synthesis of ethanesulphonates have recently been reported. The

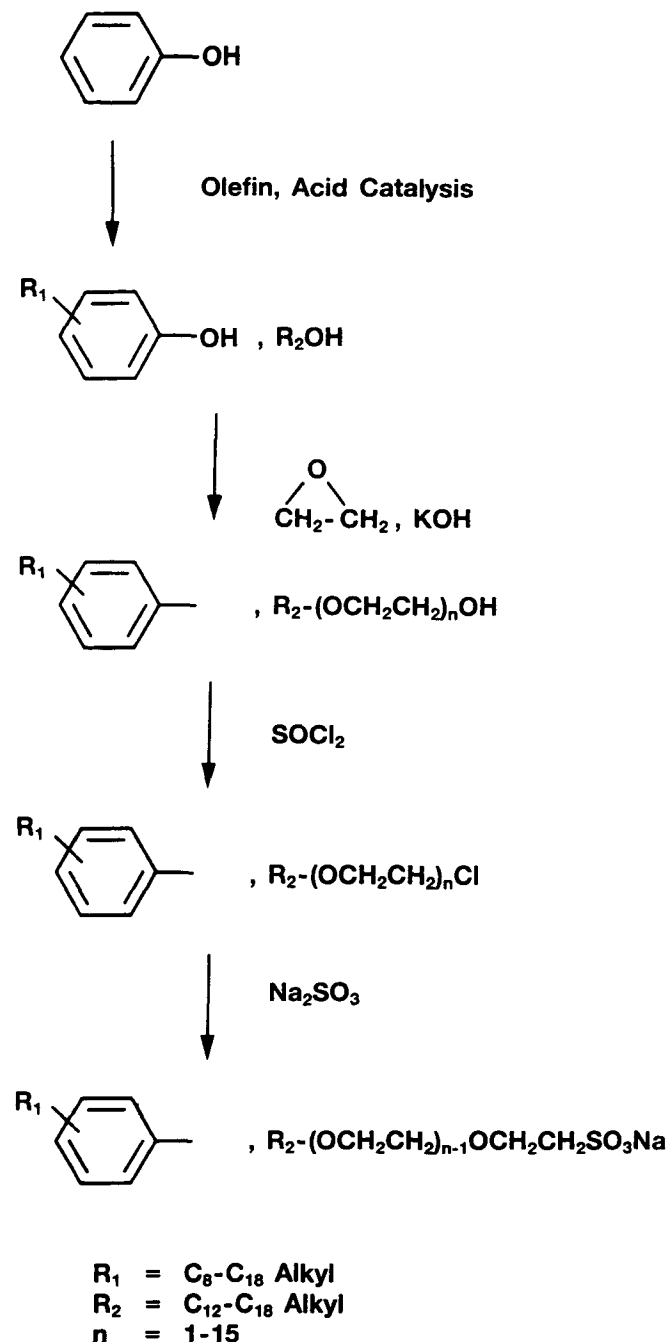


FIG. 1. Synthetic procedure for alkyl/alkylphenylethoxyethanesulphonates.

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standard conditions for the conversion of ethoxyalcohols into ethoxychlorides (thionyl chloride, 80–100°C, 4–18 hr) results in ethoxylate group loss as 1,4-dioxan (9). We recently demonstrated that this chlorination stage is catalyzed by soluble alkali and alkaline earth metal bases/salts (10). Dramatic rate acceleration and suppression of ethoxylate group loss result. Catalysis by such inorganic compounds was then extended to include the ethoxylation stage so that a single catalyst could be employed for both ethoxylation and chlorination stages (11). Lithium hydroxide was identified as the most effective catalyst for the conversion of alcohols/alkylphenols into conventional broad distribution ethoxychlorides. In addition, strontium hydroxide is suitable to catalyze both stages for the production of the newer narrow distribution ethoxylates.

The original process for conversion of ethoxychlorides into the ethoxysulphonate surfactants involved heating with sodium sulphite and water (70% by weight of total reaction mixture) in an autoclave at 150–160°C for 4–8 hr (7). Depending upon the substrate structure, the viscosity of such reaction mixtures can become so high that inefficient stirring/heat transfer results and yields are consequently reduced. Recent advances in the technique of sulphonation include the use of added sulphonate surfactant product and low M.W. alcohols to reduce viscosity/increase conversions (12). Furthermore, the replacement of sodium sulphite by potassium sulphite allows the reduction of the water content to a low level, thus increasing throughput in addition to yield and, as a consequence, reducing viscosity problems (13,14).

The present paper reports that the sodium sulphite sulphonation of ethoxychlorides derived from the recent narrow ethoxylate distribution ethoxyalcohols results in higher conversions than in comparable sulphonation with conventional broad distribution substrates. We also illustrate how a further increment in conversion may be achieved in the preparation of sulphonates based on narrow distribution ethoxyalcohols by using potassium sulphite instead of sodium sulphite. These two techniques should improve the economics of production and application of ethoxyethanesulphonate surfactants.

EXPERIMENTAL PROCEDURES

Ethoxylation was performed in a two-liter, stainless steel autoclave equipped with anchor and turbine agitators connected through a magnetic drive to an electric motor. Potassium hydroxide (0.3%, w/w) or strontium hydroxide (1%, w/w)-phenol promoter (1.5%, w/w) (3) were used as catalysts. Hexadecanol was purchased from Aldrich Chemical Co. (Milwaukee, WI). After mixing of substrate and catalyst, water was removed under vacuum at 100°C prior to ethoxylation with four moles of ethylene oxide at 125°C and 4 bar pressure over 5 hr. ^1H and ^{13}C NMR spectroscopy were performed on a Jeol FX270 spectrometer at 270 and 67.78 MHz, respectively. The average ethoxylate value was determined from the ^1H NMR spectrum (CDCl_3) and from the ^{13}C NMR spectrum, the ratio of CH_2OH peaks at 61.7 and 62.7 ppm gave the ratio of ethoxylated to free hexadecanol in the ethoxyalcohol products. Fast

atom bombardment mass spectroscopy (FAB-MS) was performed on a Kratos MS-50 spectrometer (Kratos Analytical, Ramsey, NJ). Samples were dissolved in a glycerol matrix and ionized by bombardment with argon atoms. FAB-MS was used to determine relative ethoxylate distributions for the ethoxyalcohols.

Chlorination of ethoxyalcohols was performed on a 0.4 kg scale by slowly adding (without cooling) thionyl chloride (1.2 equivalents) to the stirred ethoxyalcohol at room temperature. Acidic gases were vigorously evolved and an exotherm to 50–60°C was obtained. The mixture was heated at 80°C until chlorination was complete. ^{13}C NMR spectroscopy was used to monitor reaction progress. CH_2Cl peaks appeared at 42.7 and 44.8 ppm, and CH_2OH peaks at 61.7 and 62.7 ppm, and CH_2OSOCl peak 65.7 ppm had disappeared at 100% chlorination. Acidic gases were removed from the ethoxychlorides by pumping under vacuum (0.1 mm, 80°C, 2 hr).

Sulphonation was performed in a one-liter glass Buchi autoclave with ethoxychloride (100 g) and sodium or potassium sulphite (3 equivalents) in aqueous ethanol (1:1, 400 mL) at 155–160°C for 6 hr with a pressure of 10 bar. ^{13}C NMR spectroscopy indicated absence of CH_2Cl peaks after this time, and conversion to sulphonate vs hydrolysis was recorded from the $\text{CH}_2\text{SO}_3\text{M}$ to CH_2OH ratio at 50.6 and 61.7 ppm.

RESULTS AND DISCUSSION

Ethoxylation of hexadecanol proceeded smoothly under identical conditions with both the broad ethoxylate range (KOH) and the narrow range [$\text{Sr}(\text{OH})_2$ -promoter] catalysts. Product analytical data (Table 1) confirm the narrowing effect of strontium catalysis (3) together with the reduction of unethoxylated alcohol. FAB-MS data is only comparative as relative response factors of different ethoxylate homologues are unknown. The FAB-MS response factor of unethoxylated hexadecanol is anticipated to be considerably different from those of the ethoxylates so that relative molar percentage is taken from the ^{13}C NMR spectrum.

The behavior of the hexadecylethoxyalcohols to chlorination followed by sulphonation is detailed in Table 2. As expected, the narrow range ethoxyalcohol is chlorinated rapidly through catalysis by *in situ*, solubilized strontium ions (10,11). Chlorination of the broad range ethoxyalcohol required considerably longer for completion, as potassium ions are not catalytic for this substrate because of an absence of a necessary crown ether type solubilizing effect. Previous data (11) indicate the production of 1,4-dioxan through ethoxylate group cleavage of 0.02 and greater than 0.2 moles per mole ethoxyalcohol for the chlorination of these narrow and broad range ethoxyalcohols, respectively. Loss of yield and an overall shortening of ethoxylate chain length (by at least 0.4 units) for the broad range ethoxyalcohol thus occurs on chlorination.

Standard sulphonation of the broad range ethoxychloride with sodium sulphite results in 65% sulphonation and 35% hydrolysis to ethoxyalcohol. With the narrow range ethoxychloride, sulphonation is increased to 80%. With sulphonation reactions we have generally observed increased hydrolysis of ethoxychloride and a lower rate

TABLE 1

Compositional Comparison of Hexadecylethoxyalcohols

Ethoxylate number n	Molar percentage (FAB-MS)	
	Broad	Narrow
0	8.93 ^a	7.69 ^a
1	3.20	2.38
2	14.16	12.52
3	15.39	17.71
4	20.65	26.47
5	15.16	17.97
6	9.06	9.18
7	5.33	3.89
8	3.28	1.49
9	1.94	0.53
10	1.09	0.18
11	0.80	0
12	0.49	0
13	0.31	0
14	0.21	0
Average ethoxylate number	4.4 ^b	4.1 ^b

^aDetermined from ¹³C NMR spectrum.^bDetermined from ¹H NMR Spectrum.

TABLE 2

Chlorination and Sulphonation of Broad and Narrow Ethoxylates of Hexadecanol

Ethoxylate distribution	Chlorination	Sulphonation ratio CH ₂ SO ₃ M:CH ₂ OH ^a
	time to completion ^a (hr)	
Broad	8	65:35 ^b
Narrow	2	80:20 ^b
Narrow	2	100:0 ^c

^aDetermined from ¹³C NMR spectrum.^bSulphonation with Na₂SO₃.^cSulphonation with K₂SO₃.

of reaction for the more hydrophobic ethoxychlorides, i.e., those with longer alkyl groups or lower degree of ethoxylation. This implies increased hydrolysis for the shorter ethoxychloride chains in a single ethoxychloride distribution and we advance this as a possible explanation for the improved sulphonation characteristics of ethoxychlorides derived from narrow range ethoxyalcohols. This effect is presumably magnified through increased ethoxy group loss in the uncatalyzed chlorination of the broad range ethoxyalcohol.

We have observed in our laboratories that the highest conversions to sulphonate are obtained using potassium sulphite rather than sodium sulphite as the sulphonating agent (13,14). Application of potassium sulphite to the narrow range ethoxychloride dramatically results in quantitative conversion to sulphonate. This is related to the inverted solubility ratio of potassium sulphite:chloride as compared to sodium sulphite:chloride (14). High conversion in the sulphonation of ethoxyalcohols is important, not only because ethanesulphonates are inherently expensive surfactants, but also because it ensures close matching of ethoxylate distribution with that of the ethoxyalcohol precursor. In addition, the lower levels of ethoxyalcohol in the ethanesulphonate products could improve performance characteristics.

ACKNOWLEDGMENTS

We thank the British Petroleum Company plc for permission to publish this work. Mr. M. Lancaster (BP Chemicals) performed the ethoxylations, Dr. J.R. Bales recorded the NMR spectra, and Mr. K.J. Bare performed FAB-MS.

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[Received August 15, 1988; accepted May 13, 1990]