Effect of Narrowing Oxirane Adduct Distribution on Some Properties of Ethoxylated Alcohol-Based Sulfosuccinic Acid Halfesters

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Foaming and viscosity build-up properties are presented for sulfosuccinic acid derivatives of ethoxylated alcohols with broad- and narrow-range polyoxyethylene chains. Narrow-range ethoxylated alcohol-based sulfosuccinic acid halfesters show better foaming ability. The effect is especially visible at 50°C. Better viscosity build-up properties, as well as higher electrolyte resistance thereof, are also demonstrated.

KEY WORDS: **Broad- and narrow-range ethoxylates, ethoxylated alcohol-based sulfosuccinic acid halfesters.**

Recent progress in ethoxylation is reflected in a new quality of ethoxylated alcohols (1–3). Unconventional catalysts applied in ethoxylation of surfactant-range alcohols have allowed a narrow distribution of homologs to be obtained similar to alkylphenol ethoxylates and without excess of undesirable by-products [polyethylene glycols (PEG), dioxane, etc.], which are formed when acidic catalysts are used (4–6).

Emerging reports systematically provide new evidence of superior properties of narrow-range alcohol ethoxylates over conventional products, obtained with NaOH or KOH as catalysts (3,7–9). Ehoxylates are also widely used as intermediates in the manufacture of sulfates, phosphates, esters or other surfactants. For this purpose, narrow-range distributed ethoxylates (NRDE) are especially advantageous because of their intrinsic higher purity (less free alcohol, lower content of low and high molecular weight homologs).

The purpose of this work is to compare foaming and viscosity build-up properties for sulfosuccinic acid derivatives of ethoxylated alcohols with broad- and narrow-range distributed polyoxyethylene chains.

EXPERIMENTAL PROCEDURES

Materials. A mixture of primary, linear C_{12} and C_{14} alcohols (about 60% by mole of dodecanol) was used to obtain ethoxylates with broad- and narrow-range distributions of homologs with average degrees of ethoxylation of 2.2 and 2.7 (calculated from the synthesis weight balance). The homolog distributions are shown in Figure 1. Conventional products were obtained with sodium hydroxide as the catalyst, and unconventional calcium/magnesium catalyst was used to produce narrow-range ethoxylates.

Ethoxylated alcohol-based sulfosuccinic acid halfesters (EASSHE) were synthesized by esterification of the above ethoxylates with maleic anhydride at 90–95°C, molar ratio 1:1, in nitrogen atmosphere (Eq. 1), followed by sulfitation in aqueous solution of sodium sulfite at 70–75°C and molar ratio 1:1 (Eq. 2).

$$R(OC_2H_4)_nOH + \begin{array}{c} O \\ \| \\ H\text{-}C\text{-}C \\ \| \quad\;\; \rangle O \\ H\text{-}C\text{-}C \\ \| \\ O \end{array} \rightarrow \begin{array}{c} R(OC_2H_4)_nOOC\text{-}CH \\ \| \\ HOOC\text{-}CH \end{array} \qquad [1]$$

$$\begin{array}{l} H\text{-}C\text{-}COO(C_2H_4O)_nR \\ \| \\ H\text{-}C\text{-}COOH \end{array} + Na_2SO_3 \rightarrow \begin{array}{l} SO_3Na \\ \;\backslash \\ H\text{-}C\text{-}COO(C_2H_4O)_nR \\ \;/ \\ CH_2COONa \end{array} \qquad [2]$$

where n = 2.2 or 2.7. The final products were adjusted to 30% wt active substance.

Methods. Homolog distributions of ethoxylated alcohols were determined with a gas chromatograph (Perkin-Elmer Model 900, Perkin-Elmer, Norwalk, CT) with a flame-ionization detector. The separation was carried out in stainless-steel columns of 0.9 m length and 2.7 mm i.d. Chromosorb G-AW-DMCS (60–80 mesh) was used as the support, and silica resin OV-17 as the liquid phase. The weight ratio of the liquid phase to the support was 1:99. Argon was used as the carrier gas, its flow rate was 15 cm³/min. Temperatures of the injector and the detector were 330 and 340°C, respectively. The analyses were started with a column temperature of 120°C, which after 1 min was programmed for a rate of change of 4°C/min up to 320°C. All products were analyzed as acetate derivatives.

Foaming measurements were taken for 2 g/dm³ surfactant active substance solutions by the Ross-Miles method according to international standard ISO 696, with the exception that the foam height was measured after 1 and 10 min. Foaming was measured both in distilled water and in water with 3.57 mval/dm³ of total hardness. Foam stability coefficients were calculated according to the formula $X = V_{10}/V_1$, where V_1 and V_{10} denote the foam volumes after 1 and 10 min, respectively.

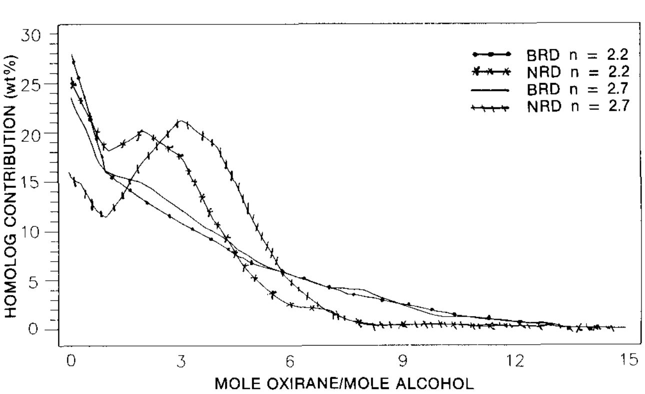

FIG. 1. Homolog distributions of alcohol ethoxylates contained in ethoxylated alcohol-based sulfosuccinic acid halfesters. BRD, broad-range distributions; NRD, narrow-range distributions.

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Viscosity was measured with the Hoppler apparatus for samples with 0, 2, 4, 6, 8 and 10% of NaCl concentration. The measurements were carried out at three temperatures, 25, 35 and 45°C. The content of active component was the same in each sample (30% wt).

RESULTS AND DISCUSSION

The studied products differed significantly in oxirane adduct distributions. Products with narrow distribution of the initial ethoxylates contained less free alcohol and lower amounts of low and high weight molecular species (Fig. 1).

Foaming. The differences in foaming abilities of distilled and hard water solutions at 25°C were not significant for narrow-range distributed (NRD) EASSHE and broad-range distributed (BRD) EASSHE with the same average ethoxylation degrees (Figs. 2a and 3a).

Perceptible foaming differences were observed at 50°C in distilled water solutions (Fig. 3b); foaming of NRD EASSHE was 15% higher for n = 2.2 and 20% higher for n = 2.7, when compared to the respective BRD EASSHE samples. For hard water solutions, foaming was comparable in each case (Fig. 2). The foam stability at 50°C was much better for NRD EASSHE (Table 1).

Another aspect of surfactant foaming properties is foam quality. Foam "uniformity" was considered to be the appropriate criterion. As "uniform" we considered an equal, thick foam, whereas "nonuniform" denoted a thin foam with visible pores. From this point of view, foams formed in hard water solutions were mostly uniform, whereas those obtained in distilled water solutions varied considerably in their appearance. The BRD EASSHE-based foams were mostly loose, with large pores. Only for n = 2.2 at 25°C did the BRD EASSHE form a uniform foam. NRD EASSHE gave a uniform, thick and stable foam at both temperatures (25 and 50°C) for both average ethoxylation degrees examined.

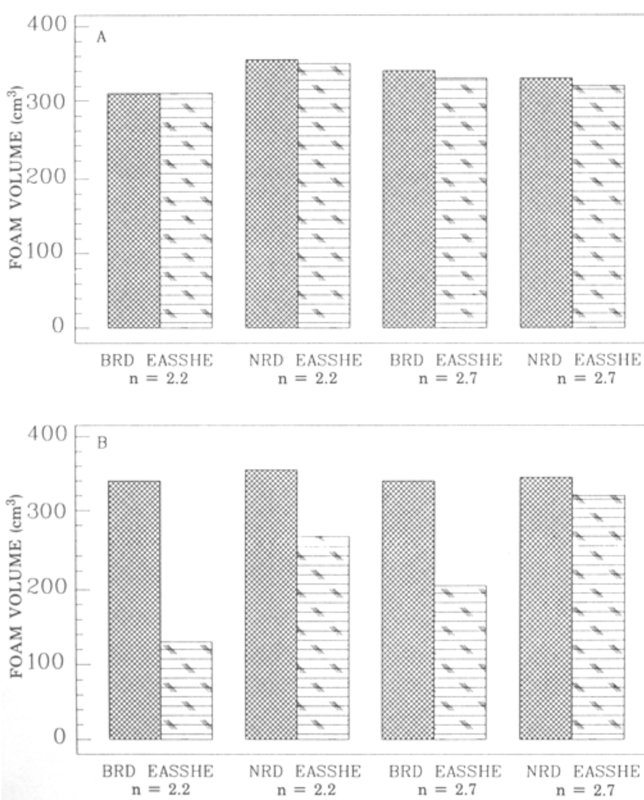

FIG. 2. Foaming in hard water solutions (A, 25°C; B, 50°C; dark columns, after 1 min, light columns, after 10 min). Abbreviations as in Figure 1. EASSHE, ethoxylated alcohol-based sulfosuccinic acid halfesters.

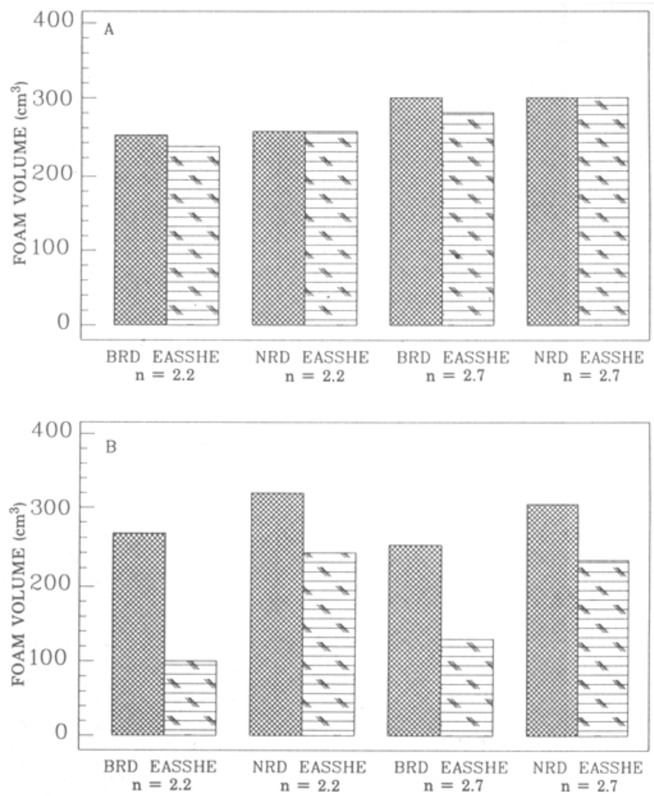

FIG. 3. Foaming in distilled water solutions (A, 25°C; B, 50°C; dark columns, after 1 min; light columns, after 10 min). Abbreviations as in Figure 2.

Viscosity build-up. Increasing the viscosity of formulations containing surfactants by NaCl addition is important for applications such as shampoos, bubble baths and dishwashing liquids. The stronger the tendency to increase viscosity with NaCl addition, the easier it is to prepare formulations with appropriate thickness. This allows for reduction of either the percentage of the active component or, alternatively, the percentage of NaCl added.

TABLE 1

Foam Stability Coefficients for BRD EASSHE and NRD EASSHE (at 50°C in distilled and hard water solutions)[a]

	Foam stability, V_{10}/V_1			
	n = 2.2		n = 2.7	
Type of distribution	dist. water	hard water	dist. water	hard water
BRD EASSHE	0.35	0.41	0.52	0.58
NRD EASSHE	0.76	0.75	0.67	0.92

[a]BRD, broad-range distributions; NRD, narrow-range distributions; EASSHE, ethoxylated alcohol-based sulfosuccinic acid halfesters.

The obtained experimental results were interpreted as a function of NaCl concentration, temperature, average ethoxylation degree and clouding phenomenon. At an NaCl concentration of 1%, both NRD EASSHE samples (with n = 2.2 and n = 2.7) had lower viscosity than their counterparts (BRD EASSHE with the same average ethoxylation degrees). Generally, the viscosity decreased slightly initially with increasing NaCl concentration (Table 2). The viscosity reached the minimum for NRD EASSHE at 2% NaCl, whereas the minimum was reached for BRD EASSHE at 4% NaCl. Afterwards, the viscosity increased to relatively high values (up to 10% NaCl concentration). However, the viscosity increase of NRD EASSHE-based solutions was much more rapid and to higher values (out of the range measurable by the Hoppler apparatus).

The viscosity's temperature dependence was similar for each sample up to 4% NaCl concentration and decreased slightly in the range of a few cP. At 6% NaCl, the tendency reversed for samples with n = 2.7, both for NRD EASSHE and for BRD EASSHE. Above 6% NaCl, viscosity increased for each sample with increasing temperature. The growing effect of temperature on viscosity was observed with increasing NaCl content in each sample. However, more remarkably, it started at lower NaCl concentration in both NRD EASSHE samples. Furthermore, the temperature effect was greater for samples containing ethoxylated alcohols with the higher average addition degree (n = 2.7), both for BRD EASSHE and for NRD EASSHE.

A remarkable effect of the average ethoxylation degree on viscosity was observed at higher NaCl concentrations (at 6% for NRD EASSHE and at 8% for BRD EASSHE). For NRD EASSHE, the viscosity decreased strongly for the higher ethoxylation degree. At 8% NaCl, the aqueous solution of NRD EASSHEs became pasty. For BRD EASSHE with n = 2.2, the viscosity increase was moderate, up to 10% NaCl. Contrary to the relation observed for NRD EASSHE, BRD EASSHE with n = 2.7 showed a much more rapid viscosity increase (compared with n = 2.2), but it was still smaller than both NRD EASSHE samples.

There is a well-known clouding phenomenon that occurs with increasing NaCl content. Both samples of BRD EASSHE, with n = 2.2 and n = 2.7, began clouding at 4% NaCl at 25 and 35°C but it cleared up at 45°C. For 6, 8 and 10% NaCl content, all BRD EASSHE solutions were milky. NRD EASSHE solutions were much more electrolyte resistant. NRD EASSHE with n = 2.2 began clouding in 6% NaCl at 25 and 35°C, afterwards clearing at 45°C. It also formed a white paste in 8% NaCl at all experimental temperatures. Surprisingly, the solutions of NRD EASSHE with n = 2.7 were clear at all concentrations of NaCl and at all temperatures investigated.

Generally, NRD EASSHE, compared to BRD EASSHE, provided better foaming ability, higher foam stability and superior foam quality. These effects are especially visible at 50°C. Although this may be a hint for use for many applications, an appropriate theoretical explanation needs more systhematical studies.

NRD EASSHE also exhibited better viscosity build-up properties, as well as higher electrolyte resistance. Many reports confirm the better viscosity build-up properties of peaked alcohol ether sulfates in comparison to their conventional counterparts (8–10). This was also achieved in our investigations with ethoxylate-based sulfosuccinic acid derivatives. We consider a similar mechanism to be responsible for the existing differences in both cases. Smith postulated (9) that, at higher surfactant or salt concentrations, viscosity increases may reflect increased interaction among enlarged micelles. Chiu *et al.* (7) stated that in case of alcohol ethoxylates the micelle

TABLE 2

Effect of NaCl Concentration on the Dynamic Viscosity of NRD and BRD EASSHE[a]

NaCl content (%)	Temperature (°C)	Viscosity (cP) BRD, n = 2.2	NRD, n = 2.2	BRD, n = 2.7	NRD, n = 2.7
1	25	10.77	7.35	13.82	11.90
	35	8.47	6.16	11.54	9.64
	45	7.15	5.14	9.52	8.03
2	25	8.37	7.20	11.69	9.41
	35	6.78	5.85	8.42	7.53
	45	5.56	4.86	6.88	6.15
4	25	8.24[b]	13.56	10.12[b]	11.92
	35	6.11[b]	11.83	7.78[b]	10.22
	45	4.82	9.77	6.36	9.61
6	25	9.97[b]	267.96[b]	11.99[b]	48.88
	35	6.91[b]	265.85[b]	12.72[b]	68.46
	45	5.49[b]	203.68	13.22[b]	78.33
8	25	14.68[b]	p[b]	79.79[b]	p
	35	14.93[b]	p[b]	101.25[b]	p
	45	16.15[b]	p[b]	125.79[b]	p
10	25	29.78	p[b]	840.0[b]	p
	35	45.69	p[b]	1646.4[b]	p
	45	75.39	p[b]	2755.2[b]	p

[a]Abbreviations as in Table 1. p, Paste (out of range measurable by Hoppler method).
[b]Milky solution.

aggregation number of a $C_{12}E_x$ surfactant increases with a decrease of ethylene oxide number in the molecule. Supposing that it is still valid for ethoxy derivatives, the strictly reduced amounts of highly ethoxylated homologs in NRD products and their derivatives may result in the formation of micelles that are bigger and more entangled than the solutions of their conventional counterparts.

The content of homologs containing more than 6 oxyethylene groups in NRDE, used in our investigation, was about 1%, whereas BRDE contain 8.6 and 12.5% of these high molecular weight species. Furthermore, the reduced amount of higher ethoxylated homologs and unreacted alcohol increases the concentration of homologs with the desired, narrow range of ethoxylation degrees and limits the contribution of compounds with undesirable surface activity.

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[Received May 7, 1992; accepted March 19, 1993]