

Comparison of Salt Thickening of Conventional and Peaked Alcohol Ether Sulfates

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The salt thickening properties of solutions of sodium dodecyl ether sulfate derived from alcohol ethoxylates with either peaked or conventional ethylene oxide distribution are reported. Sodium dodecyl ether sulfates with a peaked ethylene oxide distribution salt thicken more than those with a conventional ethylene oxide distribution. Rheological and light scattering studies are consistent with a model in which viscosity arises from the interaction of rod-like micelles.

KEY WORDS: Peaked ether sulfate, rheology, salt thickening.

The ability of alcohol ether sulfates to increase viscosity on addition of salt, *i.e.*, to salt thicken, can be both a boon and a bane to manufacturers of formulated products. During manufacture of consumer products, the viscosity of alcohol ether sulfate solutions must be controlled for ease of processing into a final product. Additionally, the viscosity of the final product is important. For example, consumers prefer thick shampoos to thin ones. On the other hand, the viscosity of dishwashing liquids must be limited if they are to be easily dispensed from a bottle. Understanding factors affecting salt thickening of commercial alcohol ether sulfates is therefore important. The molecular structure variables that can affect salt thickening of alcohol ether sulfate solutions are the average carbon chainlength, the carbon chainlength distribution, the average ethylene oxide content and the ethylene oxide distribution.

The distribution of ethylene oxide can be altered by the ethoxylation catalyst. Conventional ethoxylation catalysts based on NaOH give alcohol ethoxylates with a relatively broad ethylene oxide distribution. Recently, patented ethoxylation catalysts have been described that significantly narrow the ethylene oxide distribution (1,2). A typical example of the difference in ethylene oxide distribution formed by a conventional ethoxylation catalyst and a peaking ethoxylation catalyst is shown in Figure 1. Sulfation and neutralization of the alcohol ethoxylates shown in Figure 1 would give an alcohol ether sulfate with conventional ethylene oxide distribution (conventional ether sulfate) or peaked ethylene oxide distribution (peaked alcohol ether sulfate).

Peaked sodium dodecyl ether sulfate solutions salt thicken more readily than the analogous conventional sodium dodecyl ether sulfate solutions. Consequently, by using a peaked sodium dodecyl ether sulfate one may reach the same viscosity as a conventional sodium dodecyl ether sulfate, but use less salt or less surfactant. This

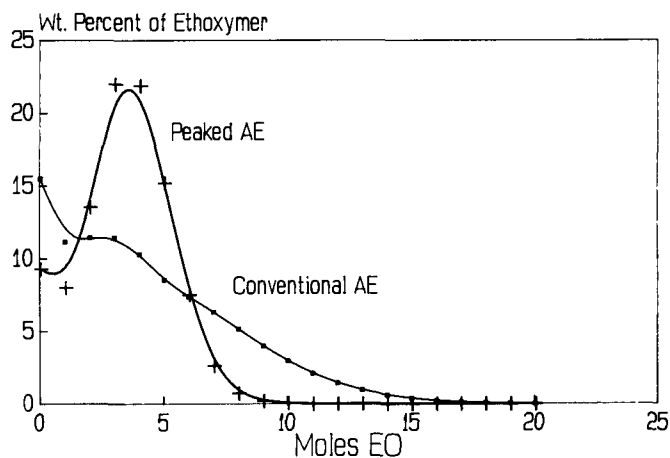


FIG. 1. Distribution of ethoxymers of dodecyl alcohol produced by a peaking and a conventional ethoxylation catalyst.

paper describes the rheology of peaked and conventional sodium dodecyl ether sulfates solutions and proposes a solution structure that is consistent with the rheological properties.

EXPERIMENTAL PROCEDURES

In this paper sodium dodecyl ether sulfate will be referenced according to the average carbon chainlength and average weight percent ethylene oxide of the alcohol ethoxylate. For example, a sodium dodecyl ether sulfate that contains 40 weight percent ethylene oxide will be designated as 12-40. All percentage figures throughout this manuscript are based on weight.

Two series of sodium dodecyl ether sulfates varying in average EO content were prepared. One series was prepared with a conventional ethoxylation catalyst. The other series was prepared with a peaking ethoxylation catalyst. The ethoxylate samples were sulfated with SO_3 and neutralized with NaOH.

The viscosity of sodium dodecyl ether sulfate solutions was measured at a shear rate of 2 sec^{-1} in a Brookfield Model DV II viscometer (Brookfield Engineering, Stoughton, MA) thermostatted to 25°C . In one series of measurements, viscosity was measured at 15% sodium alcohol ether sulfate and 2, 4, 6, 8 and 10% NaCl. In another series of measurements, viscosity was measured at 5, 10, 15, and 20% surfactant concentration and 8% NaCl.

For detailed study, peaked 12-40 sodium alcohol ether sulfate and conventional 12-40 sodium alcohol ether sulfate were chosen. These compositions correspond to an average of 2.8 moles EO and are similar to those used in commercial products, such as shampoos and dishwashing

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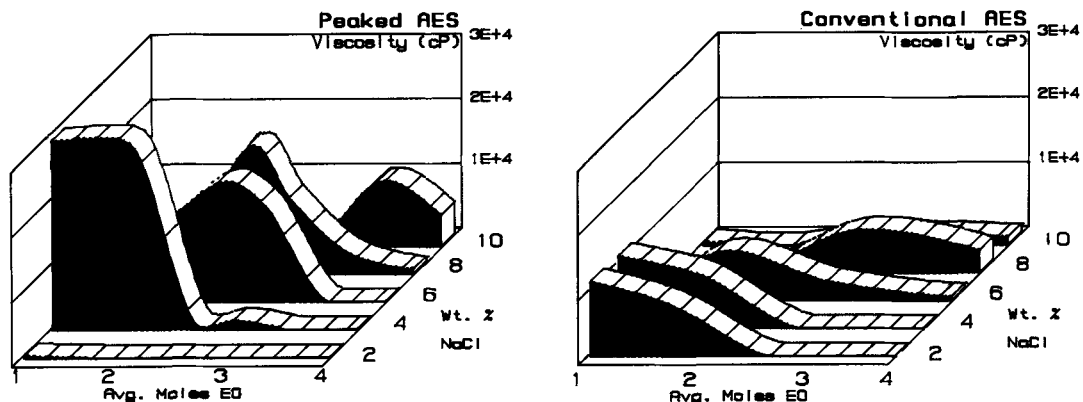


FIG. 2. Viscosity of sodium dodecyl ether sulfate vs. wt. percent NaCl and average number of moles of ethylene oxide.

liquids. Viscoelastic properties of peaked and conventional 12-40 sodium alcohol ether sulfate solutions at 8% NaCl were measured in a Carri-Med controlled stress rheometer (Carri-Med. Ltd., Surrey, England). A cone and plate configuration was used, and the storage modulus at 15°C was calculated in the frequency range 0.1-10 Hz with software provided by the manufacturer.

Solution structure was further studied with a Malvern 4700c submicron particle size analyzer (Malvern Instruments Ltd., Malvern, England). In these measurements, light from a 632.8 nm wavelength He-Ne laser irradiated 2% solutions of peaked and conventional 12-40 sodium alcohol ether sulfate solutions. The angular and time dependence of the scattered light was analyzed to probe solution structure. To detect liquid crystals in sodium dodecyl ether sulfate solutions, a Zeiss Universal Research Microscope was used. This microscope was fitted with crossed polarizers so liquid crystals could be detected.

RESULTS AND DISCUSSION

Figure 2 shows the change in viscosity with salt concentration for 15% peaked and conventional sodium dodecyl ether sulfate solutions. The most striking feature of Figure 2 is the higher viscosity of solutions of peaked sodium dodecyl ether sulfates compared to conventional sodium dodecyl ether sulfates. For both peaked and conventional sodium dodecyl ether sulfate solutions, adding NaCl at first increased and then decreased the viscosity (Table 1). Surfactant concentration also strongly affects

viscosity of both peaked and conventional sodium dodecyl ether sulfate solutions as shown in Figure 3. Initially the viscosity increases with increasing surfactant concentration, then decreases.

The viscosity trends shown in Figures 2 and 3 must reflect differences in solution structure. Two questions arise: what causes viscosity to increase, then decrease on adding either salt or surfactant and why do peaked sodium dodecyl ether sulfate solutions exhibit higher viscosity than conventional sodium dodecyl ether sulfate solutions? To answer these questions, solution structure must be explored.

Little work has been reported on possible structures present in sodium dodecyl ether sulfate solutions in the intermediate surfactant concentration range of 15%. At approximately 1% alcohol ether sulfate, it has been assumed that spherical micelles are present (3). It is difficult, however, to explain the increase in viscosity shown in Figures 1 and 2 in terms of interacting spherical micelles. On the other hand, at 30-40% surfactant concentration, a viscous liquid crystal middle phase has been reported (4). The liquid crystal middle phase can be easily detected by polarized light microscopy (5,6). The sodium dodecyl

TABLE 1

Viscosity of 12-40 Alcohol Ether Sulfate Solutions^a

Salt concentration (wt. percent)	Conventional alcohol ether sulfate (cP)	Peaked alcohol ether sulfate (cP)
2	49.2	0
4	160	1140
6	3150	15800
8	6780	12000
10	1870	1870

^aShear rate, 2 sec⁻¹; T, 25°C.

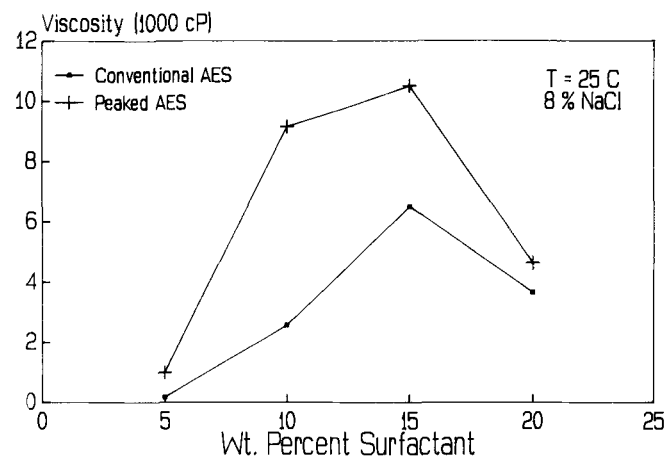


FIG. 3. Effect of sodium dodecyl ether sulfate concentration on viscosity.

ether sulfate solutions of this study were examined by polarized light microscopy to determine if liquid crystals were present. No evidence of liquid crystals was found. The viscosity trends shown in Figures 2 and 3 must reflect a structure other than spherical micelles or liquid crystals.

Sodium dodecyl sulfate solutions have been the subject of many studies, and structures proposed for these solutions are useful in suggesting structures that may be present in sodium dodecyl sulfate solutions (7,8). Like sodium alcohol ether sulfates, sodium dodecyl sulfate solutions are claimed to form spherical micelles at low surfactant concentration. At higher salt or surfactant concentration, however, it has been proposed that non-spherical micelles form. Most of the experimental evidence suggests the micelles are rod-shaped, though disk-shaped micelles are also possible. By analogy to sodium dodecyl sulfate solutions, non-spherical micelles may also form in sodium dodecyl ether sulfate solutions. The viscosity increase on increasing either salt or surfactant shown in Figures 2 and 3 may then reflect increased interaction between non-spherical micelles.

Indirect evidence of non-spherical micelles is provided by the elastic response of salt-thickened sodium dodecyl ether sulfate solutions. Elastic behavior of both peaked and conventional 12-40 sodium alcohol ether sulfate solutions containing 8% NaCl is presented in Figure 4. Similar log (storage modulus) *vs.* log (frequency) plots have been reported for other surfactant solutions and have been ascribed to the time-dependent entanglement of rod-shaped micelles (9,10). If a high storage modulus reflects micelle entanglement, then the higher storage modulus of the solution of peaked 12-40 sodium alcohol ether sulfate means this solution contains more entangled micelles than the solution of conventional 12-40 sodium alcohol ether sulfate.

Though rheological measurements provide indirect evidence of non-spherical micelles, more direct evidence can be obtained from light scattering studies. Light scattering measurements can be used to deduce both micelle size and shape (7,11). Two types of experiments are typically necessary. From the dependence of the scattered

intensity on the angle of observation, it is possible to calculate the radius of gyration of the scattering particle. From dynamic light scattering measurements at a constant scattering angle, it is possible to calculate the apparent hydrodynamic radius. By comparing the radius of gyration and the apparent hydrodynamic radius, it is possible to deduce the shape of the scattering particle.

Several assumptions are necessary when using light scattering to deduce micellar shape. First, scattering particles must be sufficiently dilute to avoid multiple scattering. Secondly, data interpretation is greatly simplified if the scattering particles are non-interacting and monodisperse in size. To reduce multiple scattering, the solutions used in the light scattering studied were reduced to 2% surfactant. This concentration was chosen because sodium dodecyl sulfate solutions have been shown to contain non-spherical micelles at 2% concentration. However, high salt concentration may promote micelle growth and so increase "excluded volume" interaction. As a compromise, NaCl composition was varied from 4 to 8%. On transition from spherical to non-spherical micelles, micelles are predicted to be polydisperse and, therefore, the assumption of monodisperse population of scatterers is unlikely to hold in practice. Despite these inherent limitations, light scattering measurements have been useful in deducing micelle shape.

To calculate the radius of gyration of a scattering particle, the total scattered intensity was measured as a function of scattering angle at 25°C. The radius of gyration can be calculated from the slope of a plot $I(\theta)/I(180-\theta)$ *vs.* the $\cos(\theta)$, where $I(\theta)$ is the intensity at the scattering angle θ , n is the refractive index of the medium, λ is the wavelength of the incident light and R_g is the radius of gyration:

$$\frac{I(\theta)}{I(180-\theta)} \approx 1 + \left\{ \frac{4\pi}{\lambda n} \right\}^2 \frac{R_g^2}{3} \cos\theta \quad [1]$$

The plot is shown as Figure 5. The plot deviates from linearity at 60° scattering angle for both solutions. The

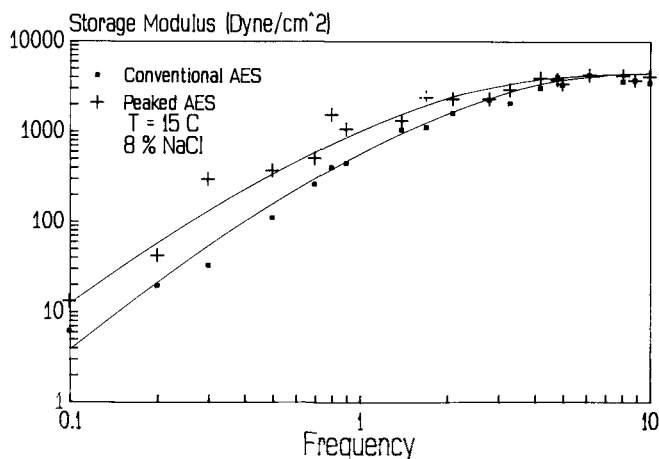


FIG. 4. Log (Storage Modulus) *vs.* Log (Frequency) for peaked and conventional sodium alcohol ether sulfate solutions.

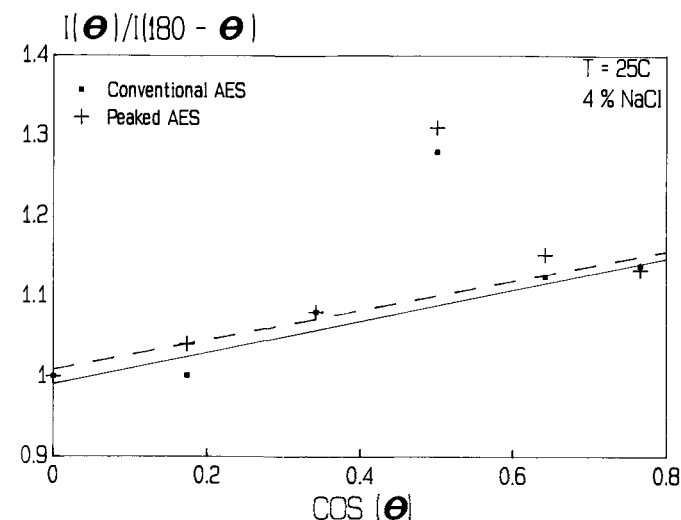


FIG. 5. Intensity (θ)/Intensity ($180 - \theta$) *vs.* $\cos(\theta)$ for conventional and peaked 2% sodium dodecyl sulfate solutions.

reason for this deviation is unknown. Omitting the point at 60° , the slope is approximately the same for both conventional and peaked sodium dodecyl ether sulfate solutions. From equation 1, the radius of gyration is estimated to be 290 angstroms (\AA).

To calculate the apparent hydrodynamic radius, dynamic light scattering measurements were done on 2% surfactant solutions. For these measurements, the NaCl

concentration was increased from 4 to 8%. For the peaked dodecyl ether sulfate solution, a coacervate formed at 8% NaCl, and so, light scattering data were not taken on this solution. The scattered light was analyzed by the method of cumulants and the results are shown in Figures 6 and 7.

For both conventional and peaked sodium dodecyl ether sulfate solutions, the distribution of apparent hydrodynamic radii is bimodal. The population representing larger particles may represent incipient coacervate formation. Consequently, the peak corresponding to the smaller scatterers was taken as representing micelles. At 4% NaCl, the apparent hydrodynamic radius is estimated as 166 \AA and 157 \AA for peaked and conventional sodium dodecyl ether sulfate solutions, respectively. To deduce micellar shape, it is necessary to make an assumption about the radius of the micelle. For sodium dodecyl sulfate solutions, the radius has been taken as the length of a fully extended sodium dodecyl sulfate molecule, 25 \AA (7). The radius of micelles formed by the molecules of this study must be somewhat larger. This is because the molecule contains, on average, 2.8 moles of EO. I assumed the average molecular length of sodium dodecyl ether sulfate was 35 \AA .

Equations relating to the radius of gyration to micellar dimensions for spherical, rod-shaped and disk-shaped micelles are shown in Table 2 (11). Assuming a short axis

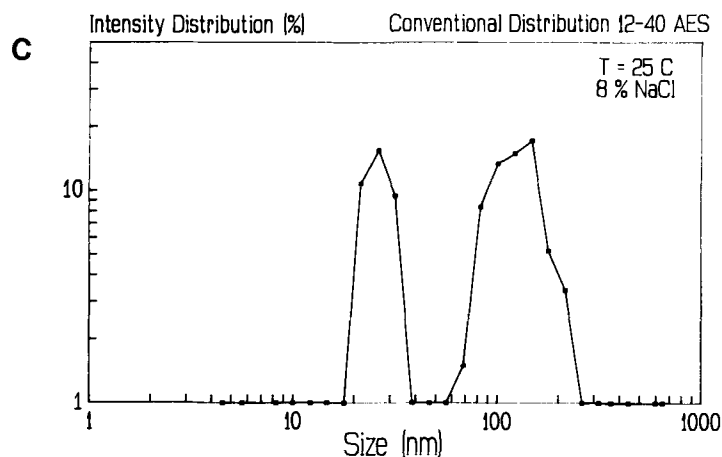
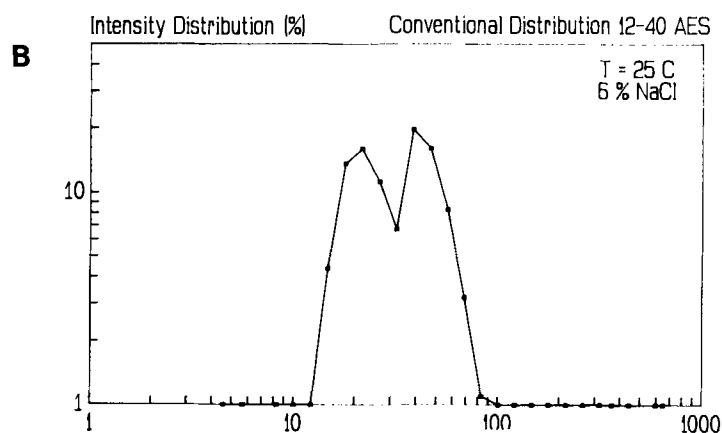
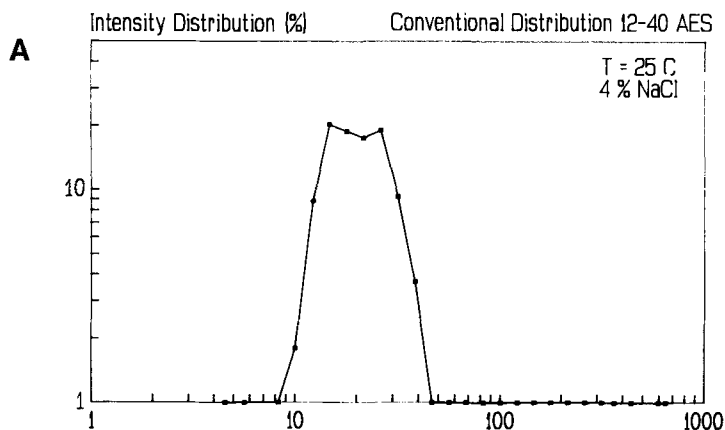


FIG. 6. Apparent hydrodynamic diameter distribution for 2% conventional 12-40 alcohol ether sulfate solutions at A, 4; B, 6; and C, 8% NaCl.

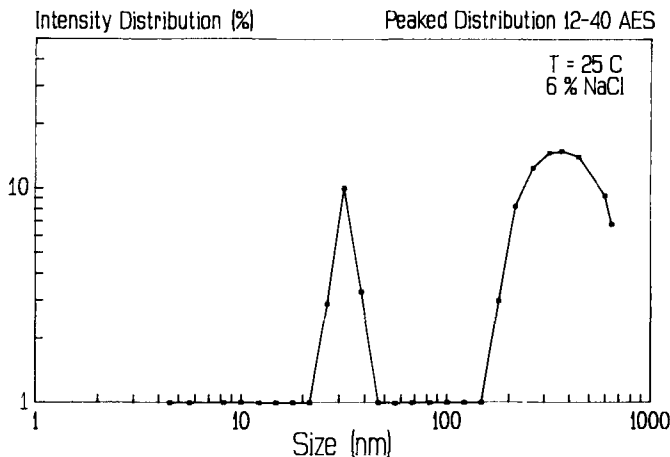
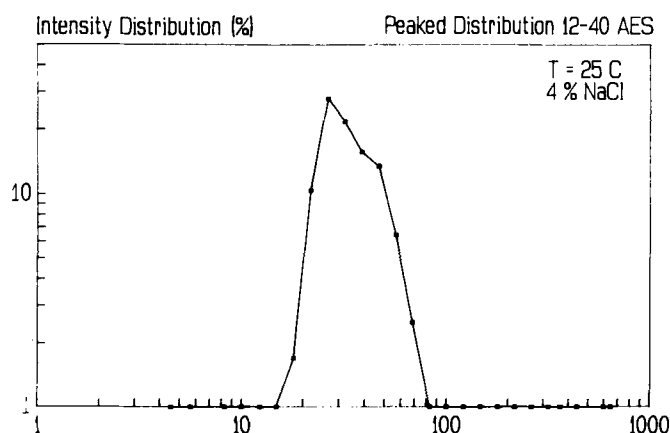


FIG. 7. Apparent hydrodynamic diameter distribution for 2% peaked 12-40 sodium alcohol ether sulfate solutions at A, 4; and B, 6% NaCl.

SURFACTANTS & DETERGENTS

TABLE 2
Calculation of Micellar Dimensions

Model	R_g	R_h	Dimensions (Å)	$R_{h \text{ predict}}$ (Å)
Sphere	$(3/5)^{1/2}R$	R	a = b = 35	374
Disk	$(2a^2/5 + b^2/5)^{1/2}$	$(b(a^2/b^2-1)^{1/2}/\tan^{-1}\{(a^2/b^2-1)^{1/2}\})$	a = 458, b = 35	305
Rod	$(a^2/12 + b^2/2)^{1/2}$	$a/(2\ln(a/b)-0.19-8.24/(\ln(a/b)+12(\ln(a/b))^2))$	a = 1000, b = 35	195

length of 35 Å, it is possible to calculate the long axis dimension for rod- or disk-shaped micelles consistent with a radius of gyration of 290 Å. These micellar dimensions then can be used to calculate an apparent hydrodynamic radius. This calculation has also been done and the results appear in Table 2.

The experimentally measured apparent hydrodynamic radius is approximately 160 Å. As seen in Table 2, the predicted apparent hydrodynamic radius is 374 Å for spherical micelles, 298 Å for disk-shaped micelles and 195 Å for rod-shaped micelles. The rod-shaped micelle model most closely predicts the observed apparent hydrodynamic radius. The prediction can be made closer to the experimental value by assuming a smaller rod radius. The important conclusion is that the light scattering data are consistent with a sodium dodecyl ether sulfate solution containing rod-shaped micelles.

If sodium dodecyl ether sulfate solutions contain interacting rod-shaped micelles, the main features of Figures 2 and 3 now can be explained. In Figure 2, the initial increase in viscosity with increase in salt concentration can be attributed to an increase in the length of the rod-shaped micelles. The growth of rod-shaped micelles with increasing salt concentration has been proposed to occur in sodium dodecyl sulfate solutions (7). It is plausible that micelles of sodium dodecyl ether sulfate also grow with increased NaCl concentration. The decrease in viscosity seen in Figure 2 at higher salt concentrations has been observed for other surfactant solutions and has been attributed to an increase in the flexibility of rod-shaped micelles (12,13). In Figure 3, the initial increase in viscosity with increasing surfactant concentration can also be attributed to an increase in length of rod-shaped micelles. The decrease in viscosity observed at higher surfactant concentration is more difficult to understand. It has been suggested that when rod-shaped micelles become long enough, they align in the direction of flow and so the

viscosity decreases (12). If this explanation is correct, then sodium dodecyl ether sulfate solutions should show flow birefringence at higher surfactant concentration.

In summary, peaked sodium dodecyl ether sulfates salt thicken more readily than their conventional counterparts. The thickened solutions exhibit elasticity. Light scattering studies suggest that nonspherical micelles, likely to be rod-shaped, are present in these solutions. Differences in salt thickening behavior must depend on differences in the solution structure. Further study of the growth and interaction of nonspherical micelles will be necessary to explain these differences.

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