The Effect of Reaction By-products on the Viscosities of Sodium Lauryl Sulfate Solutions

C.F. PUTNIK and **S.E. McGUIRE**, Chemicals Research Division, Continental Oil Company, Ponca City, Oklahoma 74601

ABSTRACT

The fact that free oil and inorganic salts have pronounced influence on lauryl sulfate solution viscosity is a widely recognized but little studied phenomenon. This investigation of the effects of these materials has resulted in the derivation of a correlation function which relates the concentrations of the by-products to the solution viscosity. The contributions of the reaction by-products are found to be independent additive effects which contribute exponentially to solution viscosity. The results can be explained mechanistically in terms of the micellar model for surfactant solutions.

INTRODUCTION

Sulfated "lauryl range" alcohols are remarkably versatile surface active agents. The uses of such materials range from cosmetics (1) and hair shampoos (2,3) to carpet shampoos (4,5) and emulsion polymerization (6). An important reason for this braod usage lies in the fact that the viscosity of the lauryl sulfate solution can be readily modified. This property has allowed formulators to optimize the viscometrics, as well as the performance and other properties of the surfactant solution, with respect to the requirements of a specific application.

Most alcohol sulfates are manufactured and distributed as concentrated aqueous solutions rather than as solids or slurries. The viscosities of these solutions are most commonly modified by the addition of organic solvents to reduce viscosity, or the addition of inorganic salts to increase viscosity (7). The materials added as viscosity modifiers are generally effective at low concentrations and are most often commodity materials. Thus, viscosity modification of lauryl sulfate solutions can be relatively inexpensive and straightforward.

A related and sometimes complicating factor in the control of viscosity is present in the form of by-products formed during the production of lauryl sulfate solutions. The precise nature of the by-products is dependent upon the methods of sulfation and neutralization but, in general, they consist of one or more inorganic salts and a "free oil," which is primarily composed of unreacted alcohol. These internally produced materials affect viscosity in the same manner as if they had been externally introduced.

The formation of by-products is sensitive to fluctuations in feedstocks and reaction conditions, and, therefore, some variation in lauryl sulfate solution viscosity occurs routinely. This variation, while usually small, is sufficient at times to necessitate correction by the addition of a viscosity modifier. Such corrective action may later cause difficulties to a formulator forced to deal with a new material in solution or an abnormal ratio of one by-product to the others.

All of the aforementioned factors have been recognized, utilized, and/or dealt with by the industry for a number of years. Based on this longtime awareness, however, one should not mistakenly conclude that factors affecting viscosity are well understood. Recent work in this area has centered on the effect the homolog distribution of the lauryl alcohol feedstock has on the viscosity of the derived lauryl sulfate solution (8). The results of the study clearly show that changes in the alcohol homolog distribution do result in changes in solution viscosity even when the average molecular weight is held constant. However, the measured effects due to homolog distribution changes are small when compared to the effect of reaction by-products or added salts. Furthermore, the literature is essentially devoid of any detailed information on how reaction by-products or any of the other "widely recognized" factors affect viscosity. This paucity of data has prompted us to carefully examine the effects of reaction by-products on the viscosity of lauryl sulfate solutions.

Our study is centered on sodium lauryl sulfate solutions produced from a synthetic "lauryl range" alcohol by reaction with chlorosulfonic acid and neutralization with caustic soda. This system was chosen because it represents a widely relevant case in that: the homolog distribution of the synthetic alcohol is similar to coconut-derived materials; the use of chlorosulfonic acid as the sulfating agent, rather than sulfur trioxide or oleum, introduces a chloride as well as a sulfate salt into the system as a reaction by-product; and, sodium lauryl sulfates are commonly produced.

The focus of the study on reaction by-products is prompted by the potential value of such work to producers and formulators. As some producers have the capability to adjust reaction conditions so as to alter reaction by-product concentrations, the development of quantitative information on the effects of the by-products will allow them to optimize reaction conditions with respect to desired end product properties. The potential benefit to formulators lies in the fact that two of the by-products, sodium chloride and sodium sulfate, are also commonly used as viscosity builders. Thus, information garnered about the effect of the salts as by-products may also be applicable to externally introduced salts. Finally, the development of a sound experimental understanding of these phenomena may lead to a better theoretical understanding which would benefit all.

EXPERIMENTAL PROCEDURES

Starting Materials

The "lauryl range" alcohol used in this study was Alfol 1216-FCA alcohol produced by Continental Oil Company. An analysis of the material is given in Table I.

TABLE I

Composition of Alfol 1216-FCA Alcohol[a]

Homolog, Wt. %	
C_{10} and lower	0.3
C_{12}	58.0
C_{14}	35.6
C_{16}	5.6
C_{18} and higher	0.1
Total alcohol, wt. %	99.0
Color, APHA	5.0
Water, wt. %	0.05

[a] Determined by GLPC. A 12 ft x 1/4 in OD column packed with 20% UCW-98 silicone gum rubber on 45/60 mesh Chromosorb W-AW-DMCS was used.

TABLE II

Composition and Viscosity Data for Experimental Sodium Lauryl Sulfate Samples

Sample number	Wt. % active	Wt. % free oil	Wt. % Na_2SO_4	Wt. % NaCl	Kinematic viscosity (cSt) @ 38 C
1A	28.85	1.03	0.52	0.16	42.31
2A	28.00	1.00	0.50	0.34	36.99
3A	28.00	1.00	0.50	0.54	73.51
4A	28.80	1.03	0.77	0.14	47.16
5A	28.00	1.00	0.75	0.34	59.30
6A	28.00	1.00	0.75	0.54	127.7
7A	28.00	1.00	1.01	0.14	50.03
8A	28.00	1.00	1.02	0.35	114.9
9A	28.00	1.00	1.01	0.54	239.6
10A	28.00	1.00	1.26	0.14	94.62
11A	27.99	1.00	1.26	0.33	198.9
1B	28.00	1.30	0.50	0.13	57.71
2B	28.00	1.30	0.50	0.33	126.5
3B	28.00	1.30	0.50	0.53	256.9
4B	28.00	1.30	0.75	0.13	45.00
5B	28.00	1.30	0.75	0.33	351.1
6B	28.00	1.30	0.74	0.53	511.1
7B	28.00	1.30	1.00	0.13	171.7
8B	28.00	1.30	1.00	0.33	414.0
9B	28.06	1.31	1.00	0.53	951.1
10B	28.11	1.31	1.25	0.13	323.8
11B	28.00	1.30	1.25	0.33	664.8
12B	28.00	1.30	1.25	0.53	1792.0
1C	28.00	1.92	0.50	0.14	432.2
2C	28.00	1.92	0.50	0.54	2295.0
3C	28.00	1.92	0.75	0.34	2613.0
4C	28.00	1.92	1.00	0.14	1785.0
5C	28.00	1.92	1.00	0.54	7453.0
6C	28.00	1.92	1.26	0.34	6446.0
1D	29.47	2.37	0.53	0.15	462.1
2D	29.47	2.37	0.53	0.57	2063.0
3D	28.00	2.25	0.75	0.34	1870.0
4D	28.00	2.25	1.00	0.14	1327.0
5D	28.00	2.25	1.00	0.55	6103.0
6D	28.00	2.25	1.25	0.34	5480.0

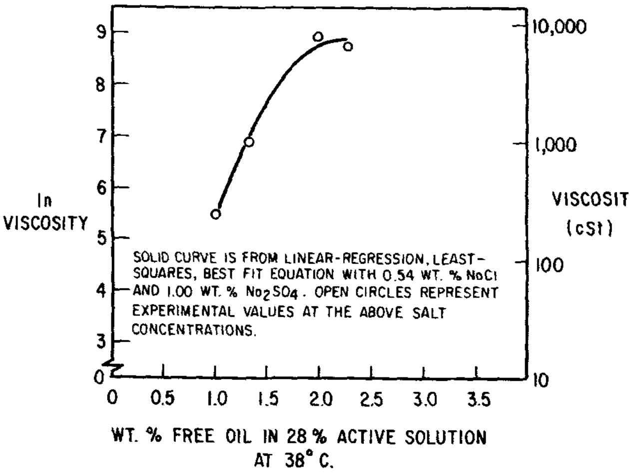

FIG. 1. Representative fit between calculated and measured viscosities of fixed composition samples.

Chlorosulfonic acid was iron-free, 100% sulfating strength obtained from MCB Manufacturing Chemists. All inorganic salts were reagent grade.

Isolation of Free Oil

Free oil was isolated from a sample of lauryl sulfate commercially produced from Alfol 1216-FCA alcohol by reaction with chlorosulfonic acid. The sodium lauryl sulfate (4139g) was dissolved in 16ℓ of 50% aqueous ethanol. The resulting solution was extracted twice with 8ℓ portions of petroleum ether. The petroleum ether extracts were then combined and carefully heated on a stream bath to remove the solvent. This procedure yielded 38.1g of free oil for use in preparing alcohol sulfate solutions of specific compositions.

Preparation of Stock Alcohol Sulfate Solutions

Typically, 4.0 moles (based on average molecular weight) of the lauryl alcohol was mixed with 4.0 moles of chlorosulfonic acid at 30-40 C in a manner similar to that described previously (9). After addition of the chlorosulfonic acid, the reaction vessel was purged for 15 min with dry nitrogen, then neutralized with aqueous sodium hydroxide to give a sodium lauryl sulfate solution which was ∿29% active by weight. The solution was then carefully analyzed for active weight % by MBAS hyamine cationic titration; for free oil by petroleum ether extraction from a water-ethanol solution; for sodium sulfate by amperometric titration; and for sodium chloride by silver nitrate titration using a modified Volhard method.

Preparation of Alcohol Sulfate Solutions of Specific Composition

Appropriate amounts of distilled water, free oil, sodium sulfate, and sodium chloride were added to 35 portions of the stock solution to produce a series of 28 weight % active samples, in which the concentration of by-products varied as follows: free oil 1.00-2.25 weight %; sodium sulfate, 0.50-1.25 weight %; and sodium chloride, 0.125-0.625 weight %. The exact composition of each solution was determined to fit a three-variable, factorial experimental design. The compositions of the solutions are shown in Table II.

Viscosity Measurements

The kinematic viscosity of each sample was measured at 38 C according to ASTM method D-445.

RESULTS

The kinematic viscosities of the series of known composition samples were measured at 38 C. The samples (see the Experimental section) differed from one another in the concentrations of the reaction by-products: NaCl, Na_2SO_4, and/or free oil. The range of variation of the concentration of each by-product was chosen to encompass the majority of values encountered in commercial products.

The results of the viscosity measurements were then subjected to statistical analysis. The viscosity was treated as the dependent variable, and the concentrations (in weight percentages) of the by-products were treated as the independent variables. Multiple regression, least-squares techniques were used to obtain a correlation function relating by-product concentration and lauryl sulfate solution viscosity. The procedure included a screening of all possible cooperative interactions among the salts and free oil in addition to the individual contributions of each. Only those terms found to be significant at the 95% confidence level were retained. The "best-fit" equation resulting from this procedure is as follows:

$$\ln (\text{visc}) = 6.953 + 10.426\,(\text{FO}) - 2.366\,(\text{FO})^2 + 2.244\,(\text{SO}_4) + 3.872\,(\text{Cl})$$

where visc = kinematic viscosity at 38 C in centistokes, and (FO), (SO_4), and Cl) are the respective weight percentages of free oil, sodium sulfate, and sodium chloride on an as is basis in a 28% active solution.

The expression was then compared to data from samples within the experiment. Typical agreement is shown in Figure 1. The observed agreement was to be expected, and a more meaningful comparison involving lauryl sulfate

TABLE III

Comparison of Observed and Calculated Viscosities of Uncontrolled Samples

Sample source	Wt. % active	Wt. % free oil	Wt. % Na_2SO_4	Wt. % CaCl	Kinematic viscosity (cSt) @ 38 C	Calculated viscosity (cSt) @ 38 C
Internal	29.0	1.38	0.47	0.02	43	56
Internal	29.0	1.34	0.46	0.02	37	47
Commercial	28.8	1.19	0.86	0.32	192	195
Commercial	28.1	1.13	0.31	0.23	52	34

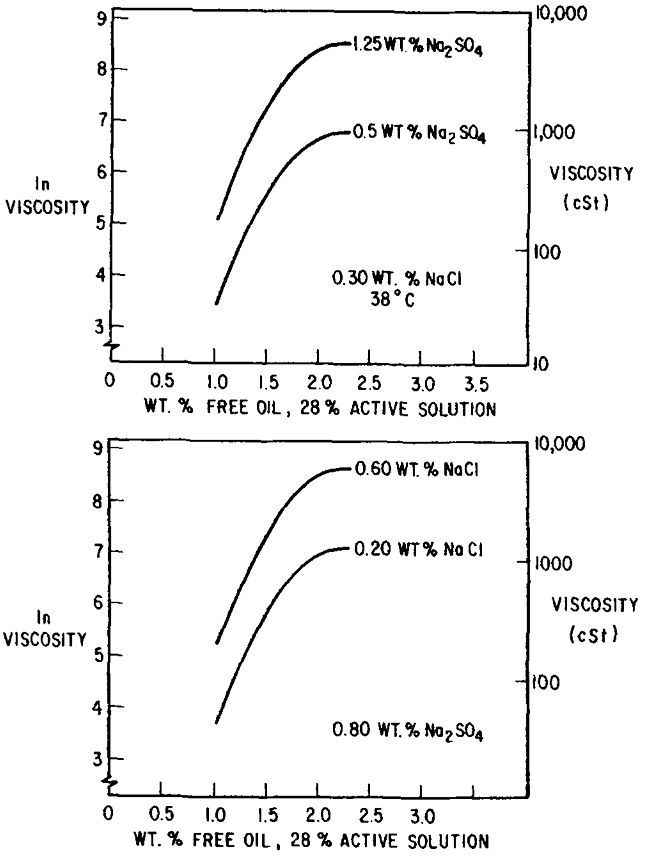

FIG. 2. Lauryl sulfate solution viscosity as a function of free oil content at several salt concentrations.

solutions from outside the original experiment was arranged.

A set of lauryl sulfate solutions was collected, which included samples prepared in our laboratories and commercially produced materials. The samples were analyzed for active percentage, by-product concentrations, and viscosity. The measured by-product concentrations were then inserted into the derived equation, and a viscosity was calculated. The calculated value was then compared with the measured viscosity. (Samples were included for comparison only if the active percentage was 28 ± 1%.)

Sample-by-sample agreement ranged from within 3 to 50%, but, overall, calculated viscosities were in "ball park" agreement with measured values, and the calculated order or magnitude was correct in every case. Representative comparisons are presented in Table III.

DISCUSSION

Analysis of the form of the derived equation provides insight to empirical and theoretical aspects of lauryl sulfate solution viscosity. First, the relationship between by-product concentration and solution viscosity is exponential; i.e., an increase in the contribution to viscosity of the by-products from some value A to value B results in an increase in solution viscosity from e^A to e^B. This is the reason relatively small changes in the concentration of one or more by-products or the addition of a small amount of salt can induce a large change in solution viscosity. For this same reason, analytical values used in the derived equation to calculate viscosities must be very accurate. A 0.1% error in the measurement of a by-product concentration can change the calculated viscosity by several hundred centistokes.

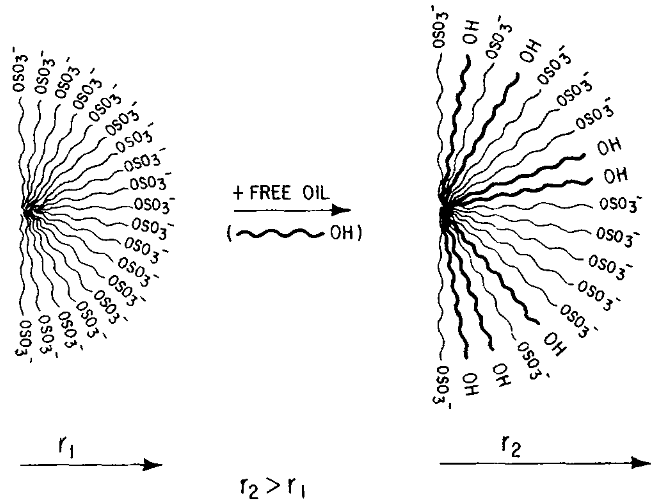

FIG. 3. Conceptual representation of the incorporation of free oil into the micellar structure. This action increases the surface area of the micelle and, therefore, solution viscosity.

A second characteristic elucidated in the equation is the effect of the free oil. The free oil is predicted to induce a rapid increase in viscosity as its concentration is increased from ∿1.0 to ∿2.0 weight % and then to reach a maximum contribution near 2.25 weight %. (Figure 2). This behavior can be understood if the micellar model for surfactant solutions is considered (10). The free oil molecules, being primarily unreacted alcohol, have a polar end consisting of the hydroxyl moiety, and therefore tend to orient at an interface such as that provided by a lauryl sulfate micelle. (Figure 3.) The inclusion of this "cosurfactant" into the micelle increases the size and surface area of the elliposidal particles and, therefore, increases the viscosity of the micellar solution.

However, the free oil molecules are not surfactants, and the energetics of the system will not indefinitely support the continued inclusion of such molecules into the micelle. At some point a transition from a micellar solution to a microemulsified system will occur. (Figure 4.) The microemulsion is energetically favored because it can accommodate the inclusion of large amounts of free oil and the commensurately large changes in particule volume with a minimum increase in surface area, since the microemulsi-

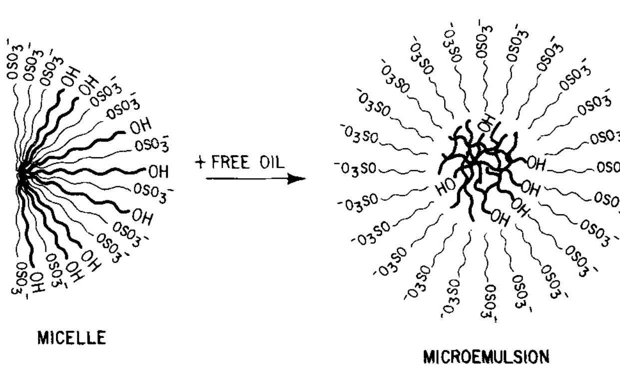

FIG. 4. Conceptual representation of the transition from a micellar solution to a microemulsified system. Note that the transition includes a geometrical transition from the ellipsoidal shape of the micelle to a near spherical particle in the microemulsion. This minimizes the surface area to volume ratio.

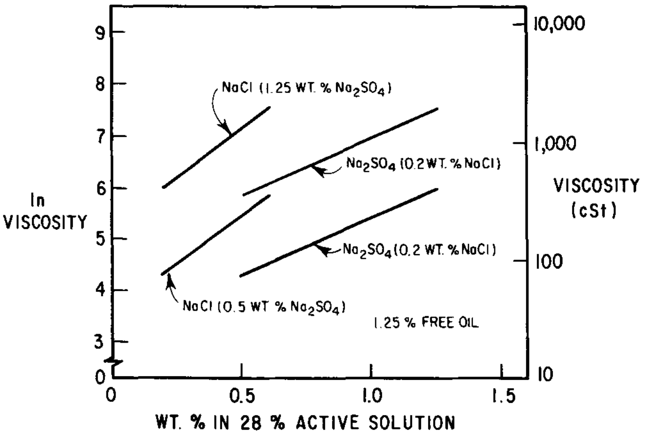

FIG. 5. Lauryl sulfate solution viscosity as a function of inorganic salt concentrations.

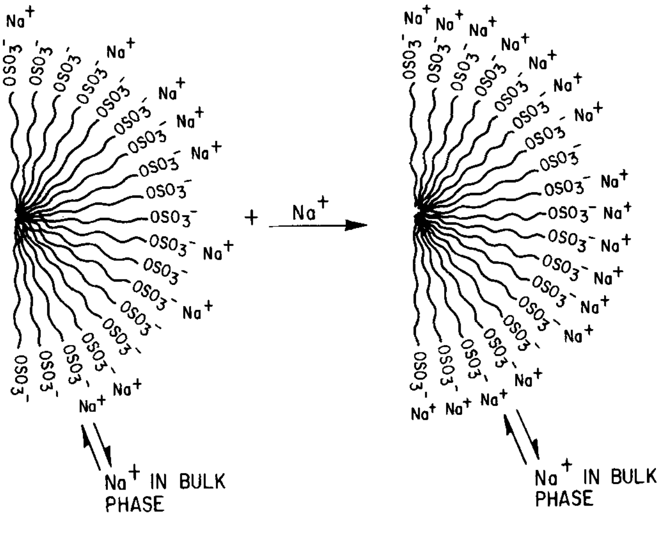

FIG. 6. Cationic association at the micellar surface. The increased degree of association at higher salt concentrations increases the "effective" size of the particle.

fied droplets are spherical. Thus, the viscosity change with increasing free oil concentration will not be as pronounced in this phase, which apparently occurs between 2.0 and 2.5 weight % free oil in the lauryl sulfate systems.

A third characteristic of the system elucidated by the equation is the linear correlation between ℓn (viscosity) and the concentration of both salts. (Figure 5.) Based on the coefficients (which define the slopes of the linear relationships), sodium chloride has a more pronounced effect that sodium sulfate on a weight basis, while the inverse is true on a mole basis. The effect of these two salts appears to be dependent on the number of sodium cations added to the system.

The salt effect is also consistent with the micellar solution model. In the case of salts, however, the observed effect on viscosity is the result of interaction between the cations from the salt(s) and the micelle at the micelle/bulk solution interface rather than in the micelle itself, as was the case with free oil. Viewed from outside, a micelle would appear as an ellipsoidal particle with a highly charged surface. The bulk solution immediately adjacent to the surface contains a relatively high concentration of "semibound" cations in equilibria with cations in bulk solution. The addition of salt increases the concentrations of both "semibound" and bulk phase cations. The increase in "semibound" cations increases the *effective* size of the micellar particle, Figure 6; the increased salt concentration in the bulk phase changes the ionic strength and viscosity of the bulk phase. Both effects contribute to the observed increase in solution viscosity.

Lastly, the derivation of the equation showed that no cooperative or synergistic interactions among by-products make a statistically significant contribution to viscosity and that the effects of the individual by-products are additive. The significance of this result is that each by-product may be considered separately and that the equation is applicable to solutions produced via SO_3 or oleum sulfation by simply dropping the sodium chloride term.

It is necessary to comment, at this point, on the use of the micellar model in analyzing the effect of by-products on viscosity. Concentrations in the range of 28-30 weight % represent the solubility limit for most lauryl sulfates in water. At these concentrations, the system is probably more accurately described as an aqueous agglomeration of micelles rather than as a true micellar solution. However, the preceeding arguments apply as well to the aqueous agglomeration as to the individual micelles. We have used the individual micelle as the model to simplify the mechanistic framework and not to imply that it precisely represents the actual solution.

The work reported herein and the equation derived from it provide an at least semiquantitative characterization of some of the "well known" factors which affect the viscosity of sodium lauryl sulfate solutions. Further experiments may lead to refinements in the coefficients of the individual terms in the equation, but the signs, magnitudes, and relative order of the terms appear to be correct. This is evidenced by the agreement found between calculated and measured viscosities of samples from outside the experiment. The applicability of the equation is limited only by the scope of the data from which it was generated and by the accuracy of by-product analyses. Thus, the derived correlation function, when combined with analytical data, can be useful as a tool for predicting and understanding changes in lauryl sulfate solution viscosity.

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