# Detergency: Micellar Relationships of an Anionic-Nonionic Surfactant Mixture[1]

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## Abstract

The micellar characteristics of the mixed micelles formed by three ratios of an anionic-nonionic surfactant mixture have been compared with the detergencies imparted by the three combinations to aqueous alkaline cleaning solutions of ca. pH 12. It was found that detergency increases with increasing charge on, and number of anionic monomers in, the mixed micelles. Improved detergency appears to be connected to a reduction in micellar dissociation.

## Introduction

Studies at this Laboratory have indicated that the detergent synergism imparted to cleaning compositions by specific anionic-nonionic surfactant mixtures can be related empirically to increasing surface tension and critical micelle concentration (CMC) of the anionic surfactant when the hydrophile-lipophile balance (HLB) of the nonionic agent lies within a specific range (1). It seems that this synergism could be connected with certain properties of the mixed micelles of the surfactant combinations, such as micellar size and charge density.

This paper is a light scattering investigation of the micellar characteristics of the mixed micelles produced by various combinations of an anionic and nonionic surfactant together with an examination of the findings for detergency correlation.

## Light Scattering and Micellar Size

Light scattering measurements of two-component systems, consisting of one solute and one solvent, are readily evaluated with Debye's equation (2). If the micellar aggregates are uncharged or carry only a small net charge, no difficulties in interpretation are presented. The equation is:

$$\frac{H\,(c - c_o)}{T - T_o} = \frac{1}{M} + 2Bc$$

where, $H = \dfrac{32\,\pi^3\,n_o^2}{3\,N\,\lambda^4}\left(\dfrac{n - n_o}{c}\right)^2$

$c$ = surfactant concn in g/ml
$c_o$ = CMC in g/ml
$T$ = solution turbidity in $cm^{-1}$
$T_o$ = solvent turbidity in $cm^{-1}$
$M$ = micellar mol wt
$n$ = refractive index of solution
$n_o$ = refractive index of solvent
$N$ = Avogadro's number
$\lambda$ = wavelength of incident light in cm
$B$ = second virial coefficient

The determination involves the extrapolation of the linear plot of $\dfrac{H\,(c - c_o)}{T - T_o}$ vs. c to the CMC, with the ordinate intercept at the CMC giving the reciprocal of the micellar mol wt. The slope of the plot, S, is related to effective micellar charge by the following function (3):

$$P = M\sqrt{2\,S\,X} = \text{charge}$$

where, X = concn of any added salt plus the CMC, in equivalents/ml. For nonionic micelles, the Debye slopes are generally very small or zero (4,5), and occassionally, slightly negative (6,7). The charge on a nonionic aggregate is therefore small. Ionic aggregates present a different picture. The surface of an anionic micelle is covered with the charges of the ionic heads of its monomer molecules (conceivably as many as 100 or more electrons), 60–80% of which are neutralized by physically-bound counterions, $Na^+$, adsorbed on the micellar surface and in the double layer (8). The effective charge of an ionic micelle may therefore be appreciable; i.e., that on a sodium lauryl sulphate micelle, with an aggregation number of 80, is 14.5 electrons (3).

Since light scattering is attributed to fluctuations of concn, and since the latter would tend to be impeded by charged aggregates, light scattering measurements of solutions of charged micelles should give reduced micellar mol wt (9), the reduction amounting to 10–20% according to the proponent of this theory (9). The later predicts nonlinearity of the Debye function for charged micelles in dilute solutions (ca. <0.8% W/V) and suggests that true micellar size is obtainable only in the presence of a small amount of electrolyte (ca. 0.02 mole/liter NaCl). Other investigators (10,11) point to the infrequent occurrence of curved $\dfrac{H\,(c - c_o)}{(T - T_o)}$ vs. c functions for ionic micelles, and suggest that the Debye equation can be used when its slope is linear (11). Nonlinearity has been related to ionic surfactants possessing a low CMC, as a result of which the concn of gegenions is insufficient to screen the micellar charges (11). This explanation must be given serious consideration because curvature of a Debye plot can usually be eliminated by the addition of a small amount of electrolyte. Representative literature data on charge effects in sodium dodecyl sulphate solutions (3) suggest that there is no simple relationship between micellar charge and micellar size, and hence Debye's conclusion (2) that micellar size is increased by electrolyte is valid. These data show in Table I.

When a multi-component system of two solutes and a solvent is subjected to light scattering measurements, strict interpretation of the data is a complicated problem. A rigorous solution has been developed (12). However, its application requires the knowledge of thermodynamic interaction constants, which are not available for the anionic-nonionic surfactant

TABLE I

Micellar Charges (3)

| Solvent | Effective charge, electrons/micelle | Micellar Wt |
|---|---|---|
| Water | 14.5 | 23,050 |
| 0.02 molar NaCl | 12.8 | 27,300 |
| 0.03 molar NaCl | 12.8 | 28,700 |
| 0.10 molar NaCl | 13.4 ± 1 | 32,300 |
| 0.20 molar NaCl | 17.0 ± 2 | 34,200 |

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[1] Presented at the AOCS Meeting in New Orleans, 1964.

TABLE II
Sufactant Compositions

| Compound | % SDBS by wt | % OPE9.5 |
|---|---|---|
| "1-3" | 2.77 | 8.33 |
| "1-1" | 5.55 | 5.55 |
| "2-1" | 7.40 | 3.70 |

mixtures investigated. An approximate solution has been utilized for such mixed micelle systems (13). The procedure is based on two generally accepted assumptions concerning micellar systems: first, the completeness of the interaction of the anionic and nonionic monomers to form mixed micelles, and secondly, the monodispersity of these micelles. Hence, aqueous solutions of anionic-nonionic surfactant mixtures may be considered one solute-one solvent systems, and the mol wt of the mixed micelles may be estimated with Debye's equation. It would seem that non-additivity of the turbidities of the individual surfactants comprising the mixed aggregates would tend to confirm the validity of the assumptions. The anionic-nonionic monomer ratio in the mixed micelle is taken as equal to the ratio of the corresponding mol fractions in the surfactant mixture (13).

## Experimental

*Apparatus.* Absolute turbidity was measured with a Brice-Phoenix light scattering photometer (14), using 5460 Angstrom radiation. Refractive index increments were determined by a Rayleigh interferometer (Baird Associates, Inc.) with 5460 Angstrom light, the zero-order bands being labeled with white light.

*Procedure.* The photometer was calibrated against the opal glass diffusor supplied with the instrument. As previously reported (15), the turbidity of the water used as solvent had a value of $1.98 \times 10^{-5}$ cm$^{-1}$ based on this calibration, in good agreement with a reported value of $2.00 \times 10^{-5}$ cm$^{-1}$ (3) in the region of low turbidity where accuracy is difficult to attain. Solution for light scattering tests was prepared by pressure filtration through Selas bacteriological filters of 1.2 μ max pore size (Selas Corp. of America, Philadelphia) into a semioctagonal cell ($40 \times 40 \times 120$ mm high) using the technique described in a former report (16). Solution concn varied from 0.002–0.012 g/ml. Dissymmetries were negligible in this range. Light scattering and refractive index differences were measured at room temp (24–26C).

*Calculations.* Since the $\frac{H\ (c - c_o)}{T - T_o}$ vs. c functions were linear or very nearly so in the dilute solutions studied, indicating adequate screening of the charged aggregates and applicability of Debye's equation (11), micellar mol wt were calculated from the reciprocals of the ordinate intercepts obtained by extrapolating the plots to the corresponding CMC values. Second virial coefficients were estimated from least squares equations of the functions. Effective micellar charge was computed from the formula given previously. Degree of micellar dissociation may be estimated from the following equation (17):

$$p = \alpha A$$

where, $\alpha$ = micellar dissociation
$A$ = aggregation number

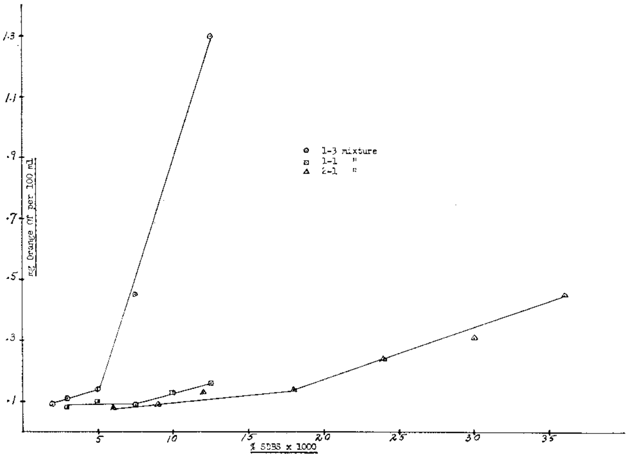

FIG. 1. Micellar solubilization-concn curves of SDBS-OPE9.5 mixtures.

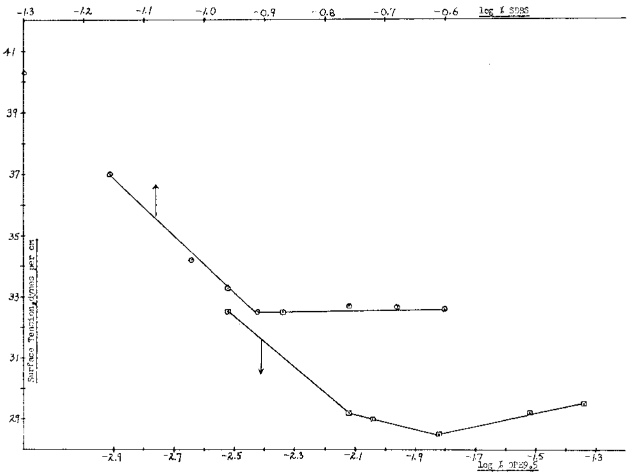

FIG. 2. Surface tension-concn curves of SDBS and OPE9.5.

*Surfactants.* The surfactants were commercial, 100% active materials. The anionic agent was a branch-chain sodium dodecyl benzene sulphonate (SDBS) different from the alkane type used in previous micellar studies (15,16). The nonionic surfactant was a 9–10 ethylene oxide mole ratio adduct (R = ca. 9.5) of octylphenol, OPE9.5, of a different batch from those previously investigated (15,16). Three SDBS–OPE9.5 surfactant mixtures were tested, 1–3, 1–1, and 2–1 ratios by wt.

*Critical Micelle Concentration.* CMC values of the individual SDBS and OPE9.5 surfactants were determined graphically from surface tension-log concn plots, placing the CMC at the intersection of the two linear portions of the plot, one nearly horizonal, adjacent to the point of maximum change in slope. Surface tensions were measured with a du Nouy interfacial tensiometer, with solutions aged one hr. Harkins-Jordan correction factors were applied (18). Values of 0.123% for SDBS and 0.015% for OPE9.5 were obtained. The dye solubilization procedure proved more suitable for use with the surfactant mixtures. Details of the solubilization of Orange OT have been reported (19). The CMC of SDBS in the 1–3, 1–1 and 2–1,SDBS-OPE9.5 surfactant mixtures was found to be 0.005%,0.0075%, and 0.018%, respectively.

*Detergency.* Asphalt and mineral oil detergencies were determined as described in Federal Specification P-C-436a, using 1600 ml boiling, 7.5% distilled water solutions of the test compounds in 2-liter beakers (1). Three test compounds, each containing one of the above-described SDBS-OPE9.5 surfactant combinations, were studied. The compounds were formulated with the same amounts of builders as the Standard Control Compound of P-C-436a. On a dry basis, these

TABLE III
Light Scattering Data

| $\frac{\text{Anionic}}{\text{Nonionic}}$ ratio | $c \times 10^3$ g/ml | $(c - c_0) \times 10^3$ g/ml | $T - T_0$ $cm^{-1} \times 10^5$ | $\frac{n - n_0}{c}$ | $H \times 10^5$ | $\frac{H(c - c_0)}{T - T_0} \times 10^5$ |
|---|---|---|---|---|---|---|
| 0.333 | 12.0 | 11.8 | 31.40 | 0.164 | 0.2957 | 11.11 |
| | 8.00 | 7.80 | 23.94 | 0.161 | 0.2847 | 9.28 |
| | 4.00 | 3.80 | 12.72 | 0.155 | 0.2642 | 7.89 |
| 1 | 8.00 | 7.85 | 26.19 | 0.169 | 0.3126 | 9.37 |
| | 4.00 | 3.85 | 15.10 | 0.159 | 0.2773 | 7.07 |
| | 2.00 | 1.85 | 8.18 | 0.157 | 0.2711 | 6.13 |
| 2 | 9.00 | 8.73 | 29.78 | 0.171 | 0.3215 | 9.42 |
| | 6.00 | 5.73 | 24.34 | 0.175 | 0.3356 | 7.90 |
| | 3.00 | 2.73 | 12.91 | 0.165 | 0.2994 | 6.33 |
| SDBS alone | 8.00 | 6.77 | 35.86 | 0.187 | 0.3833 | 7.24 |
| | 6.00 | 4.77 | 29.55 | 0.187 | 0.3833 | 6.19 |
| | 4.80 | 3.57 | 26.00 | 0.187 | 0.3833 | 5.26 |
| OPE-9.5 alone | 10.0 | 9.85 | 196.52 | 0.151 | 0.2501 | 1.254 |
| | 8.00 | 7.85 | 152.97 | 0.151 | 0.2501 | 1.283 |
| | 4.00 | 3.85 | 72.87 | 0.151 | 0.2501 | 1.321 |
| | 2.00 | 1.85 | 34.56 | 0.151 | 0.2501 | 1.339 |

percentages by wt were as follows:

| | |
|---|---|
| $Na_2SiO_3 \cdot 5H_2O$ . . . . | 34.5% |
| $NaH_2PO_4 \cdot H_2O$ . . . . | 12.0% |
| $Na_3PO_4 \cdot 12H_2O$ . . . . | 33.5% |
| $Na_2SO_4$ . . . . . . . . | 8.9% |

Hence, 11.1% of each test compound consisted of the anionic-nonionic surfactant mixture as given in Table II. The "1–1" test compound is substantially the P-C-436a Standard Control Compound (the anionic-nonionic surfactant ratio of which equals 1.13–1).

## Results and Discussion

*Critical Micelle Concentration.* Figure 1 shows the micellar solubilization-concn curves of the various SDBS-OPE9.5 mixtures, and indicates the CMC of SDBS for each mixture. The surface tension-log concn curves of SDBS and OPE9.5 are given in Figure 2.

*Micellar Size.* Tables III and IV give the light scattering data and summary of micellar calculations of the surfactants and their mixtures. A micellar wt of 73,500 was obtained for OPE9.5. It is interesting to note that if the OPE9.5 $\frac{H\ (c - c_0)}{T - T_0}$ vs. c data of Kushner et al. (6) is extrapolated to the accepted CMC value of this detergent [0.015% was obtained herein; Fowkes (20) reported the same value; and Hsiao (21) found an average value of 0.012% for the related 8.5 mole ratio ethylene oxide adduct of octyl phenol], a micellar wt of ca. 77,000 is obtained. The wt of the 1–1 and 2–1 SDBS-OPE9.5 mixtures were substantially the same—19800 and 20300, respectively while that of the 1–3 system was 15900. The monomers/micelle differed in all three systems. These results suggest that the formation of mixed micelles in an anionic-nonionic surfactant mixture involves more than the solubilization of nonionic molecules by anionic micelles, but consists of a reconstitution of the micelles, as suggested recently for the interaction of nonionic micelles with either hydrocarbons or alcohols (22). Reconstitution of the micelles in the SDBS-OPE9.5 mixtures is due to a number of opposing forces with a consequent balance between corresponding decreases and increases in free energy in each system. Factors contributing to micellar growth are the van der Waals attractions of the hydrocarbon chains of both monomers, and the neutralization of the micellar charge by the gegenions ($Na^+$) furnished by the SDBS monomer. Factors opposing micellar growth are electrostatic repulsion of the charged heads of the SDBS molecules, the hydrocarbon-covering efficiency of the ethoxy groups of the OPE9.5 monomer (23), and the decrease in entropy of the system caused by aggregation. In view of the small values obtained for the mixed aggregates, it is reasonable to assume that the ethoxy screening effect of the OPE9.5 molecules has considerably more influence on micellar size than reduced charge density in these salt-free systems. The similarity of aggregate size of the 1–1 and 2–1 mixtures is fortuitous. Table IV does show a connection between reduction of micellar charge and nonionic content of the mixed micelle. The effective charge of only 6.6 electrons per SDBS micelle indicates substantial screening of the micellar charge by the gegenions originating in the free monomer. This is confirmed by the fairly small Debye slope for SDBS ($60.9 \times 10^{-4}$), which approximate slopes of detergent solutions containing swamping electrolyte. For example, the slope for sodium dodecyl sulphate in 0.02M NaCl has been reported (3) as $47.3 \times 10^{-4}$. However, the charge on the SDBS micelle is not unusually low. If the formula for micellar charge ($p = M\sqrt{2SX}$) is applied to the data and $\frac{H\ (c - c_0)}{T - T_0}$ vs. c plots given by Debye (2) and Tarter (11), the following charge values are obtained:

| | |
|---|---|
| dodecylamine hydrochloride . . . . | 7.8 |
| sodium tetradecane sulphonate . . . | 6.1 |

*Non-Additivitivity of Surfactant Turbidities.* Table V shows the non-additivity of the surfactant turbidities in the three SDBS-OPE9.5 mixtures. A few of the individual surfactant values were obtained by

TABLE IV
Micellar Summary

| Ratio of $\frac{\text{Anionic}}{\text{Nonionic}}$ | $c_0 \times 10^3$, g/ml | | M | monomers/micelle | | $B \times 10^2$ | Debye slope, $S \times 10^4$ | P |
|---|---|---|---|---|---|---|---|---|
| | SDBS | surfactant mix | | SDBS | OPE-9.5 | | | |
| 0.333 | 0.05 | .20 | 15,900 | 11 | 19 | .20 | 40.3 | 0.9 |
| 1 | 0.075 | .15 | 19,800 | 28 | 16 | .27 | 54.5 | 1.2 |
| 2 | 0.18 | .27 | 20,300 | 39 | 11 | .26 | 51.5 | 1.7 |
| SDBS alone | 1.23 | .... | 31,600 | 91 | .... | .31 | 60.9 | 6.6 |
| OPE-9.5 alone | ...... | * | 73,500 | .... | 118 | −.005 | −1.06 | +0.5 |

* ($c_0 \times 10^3$) of OPE-9.5 = 0.15 g/ml.

TABLE V
Non-Additivity of SDBS and OPE9.5 Turbidities

| $\frac{\text{Anionic}}{\text{Nonionic}}$ ratio | $c \times 10^3$ g/ml | $T - T_0$, $cm^{-1} \times 10^5$ | | |
|---|---|---|---|---|
| | | SDBS + OPE9.5 | SDBS alone | OPE9.5 alone |
| 0.333 | 12.0 | 31.40 | 20.30 | 175.0 |
| 1 | 8.00 | 26.19 | 23.40 | 72.87 |
| 2 | 9.00 | 29.78 | 29.55 | 53.40 |

interpolation in, and one by a small extrapolation of, the corresponding $(T - T_0)$ vs. c functions of SDBS and OPE9.5, both of which are linear in the ranges covered. Considerable interaction is indicated, since otherwise the turbidities of the surfactants in each mixture would be additive.

*Detergency and Detergency Correlation.* Remembering that asphalt soil removal by aqueous cleaning solutions may be considered an index of detergent efficiency (1), the data of Table VI show that the detergency of Federal Specification P-C-436a type alkaline cleaners increases considerably with increasing SDBS content of the SDBS-OPE9.5 surfactant mixture, from poor detergency with 25% SDBS, to good 15–16 min detergency with 50% SDBS, to excellent 9 min detergency with 67% SDBS in the surfactant mixture. Comparing the detergency and micellar data of Tables VI and IV, respectively, it can be seen that detergency increases with increasing charge on, and number of SDBS monomers in, the mixed micelle. It is of interest that SDBS alone and the 1–3 anionic-nonionic mixture, both of which do not impart improved detergency to alkaline cleaners of the type studied, have micellar dissociation values of .07–.08, while the 1–1 and 2–1 surfactant mixtures, which give these cleaners asphalt-removing power, have a micellar dissociation of .04.

TABLE VI
Detergency Summary

| Compound | % SDBS in surfactant mixture | Detergent Efficiency | |
|---|---|---|---|
| | | mineral oil 3 min cleaning | asphalt min for removal |
| "1-3" | 25 | good * | 243 mg; 284 mg ** |
| "1-1" | 50 | good | 15–16 min |
| "2-1" | 67 | good | 9–9 min |

* "good" denotes no water breaks nor residue-pattern stains.
** mg residual asphalt soil after 21 min cleaning; original asphalt soil = 330 mg.

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# 46th Annual Report of the Smalley Committee 1963-1964

THE SMALLEY COMMITTEE, through six subcommittees, distributed over 4200 samples and tabulated and graded over 18,000 test results during the past season. Each subcommittee has furnished its collaborators with a final report summarizing the work done and showing final relative performance. Table I lists the types of samples furnished and the extent of participation.

TABLE I

| Series | Number of collaborators | Number of samples | Graded tests per sample |
|---|---|---|---|
| Cottonseed | 37 | 10 | 5 |
| Soybean | 33 | 10 | 2 |
| Peanut | 13 | 7 | 4 |
| Meal | 129 | 15 | 3–4 |
| Cottonseed oil | 77 | 4 | 3 |
| Soybean oil | 84 | 4 | 3 |
| Tallow and grease | 76 | 5 | 6 |
| Glycerine | 24 | 5 | 6 |
| Drying oil | 19 | 6 | 4 |
| Edible fat | 58 | 5 | 7–10 |

As of March 31, 1964, the AOCS Smalley account showed the following:

| | |
|---|---|
| Receipts | $7512.45 |
| Expenses paid | 3581.98 |
| Expenses to be paid | 2423.24 |
| Balance | $1507.23 |

A detailed accounting will be given to the Governing Board.

A rotary countercurrent mixer has been purchased by Law & Co. for use in preparing next season's meal samples. It will also be used for the preparation of the Magruder Fertilizer Samples as well as the Check Feed Samples of the Association of American Feed Control Officials. The mixer will be depreciated over a period of five years and the cost to the Smalley Committee will be only slightly over $100 per year for the next five years. Sample uniformity should be improved considerably.

Grading this year was handled as for the 1962–63 season. The Baumann method was used to grade all but the Drying Oil, Tallow and Grease and the two Vegetable Oil series. An explanation of the method may be found in last year's Smalley Report. Details of the procedure are given in the August 1963 issue of the Journal.

Certificates are awarded this year to 29 collaborators.

*Drying Oils.* With 19 chemists participating, first place was won by: Warren Chapin, The Sherwin-Williams Co., Cleveland, Ohio, with a grade of 97.75%; Vern Bloomquist, The Minnesota Linseed Oil Co., Minneapolis, Minnesota, was second with a grade of 97.25%.

*Soybean Oil.* With 84 chemists participating, the following were tied for first place with grades of 100.0%: P. R. Gibson, The Procter & Gamble Mfg. Co., Macon, Ga.; F. M. Tindall, Humko Products,