Mixed-Surfactant System of Dodecylbenzene Sulfonate and Alpha-Olefin Sulfonate: Micellar and Volumetric Studies

Satish Bharadwaj and J.C. Ahluwalia*

Department of Chemistry, Indian Institute of Technology, Hauz Khas, New Delhi 110 016, India

ABSTRACT: Critical micelle concentrations of sodium salts of dodecylbenzene sulfonate, alpha-olefin (C_{16}) sulfonate, and their mixtures have been evaluated by measuring the surface tensions of solutions at 298.15 K. Interaction parameters for mixed monolayer formation (β^{σ}) and mixed-micelle formation (β^{M}) have been calculated from the critical micelle concentration data. Densities of solutions of surfactants and their mixtures were measured with a vibrating-tube densimeter at 298.15 K. Apparent and partial molar volumes have been evaluated from solution density data. Results of the micellar properties have been explained on the basis of a nonideal multicomponent mixed-micelle model. The mixed-surfactant system exhibits synergism in all aspects when the mole fraction of alpha-olefin sulfonate in the mixture is 0.2. Volumetric properties correlate well, as the partial molar volumes also show a minimum at the same composition of the mixture. Formation of a compact mixed micelle at this composition has been envisaged.
JAOCS 73, 39–45 (1996).

KEY WORDS: Alpha-olefin sulfonate, dodecylbenzene sulfonate, interaction parameters, mixed micelle, mixed-surfactant system, partial molar volumes, synergism.

Choice of a surfactant system for many applications, from fabric detergency to tertiary oil recovery, is a critical step. In practice, mixtures of surfactants are used because a single surfactant rarely satisfies all requirements. Mixed-surfactant systems are also known to exhibit synergism, leading to enhanced performance properties. In contrast to the numerous studies of mixed-micelle formations in nonionic surfactant solutions, there have been few reports on mixtures of industrially important, nonhomologous, ionic-surfactant systems.

It would be interesting to study a mixed-surfactant system that contained two anionic surfactants with similar hydrophilic groups but different hydrophobic parts. In such systems, mixed-micelle formations should be mainly due to the hydrophobic effect of the alkyl chains and steric restrictions because there is almost no favorable interaction between the charged groups. In the present study, mixed-micelle formation by the two industrially important anionic surfactants [dodecylbenzene sulfonate–sodium salt (DBS) and alpha-olefin sulfonate–sodium salt (AOS)] has been investigated.

DBS is the main constituent of linear alkylbenzene sulfonate–sodium salt (LABS), the most commonly used active surfactant for laundry products throughout the world (1,2). LABS with alkyl chainlength in the range of 12 to 14 carbon atoms are commonly used for detergency purposes (3). The efficacy of LABS, however, is significantly diminished in hard water (4). In addition, recently, the biological breakdown (5–7) of LABS has been found to be slow and incomplete under anaerobic conditions. Due to these disadvantages, the use of LABS is being restricted, and the search is on for other, "eco-friendly" surfactants. Another alternative is to circumvent the problem to a significant extent by the use of cosurfactants.

AOS, a relatively new type of surfactant, possesses a unique set of properties not found in other surfactants (8–14). It exhibits good wetting and foaming properties, excellent detergency, good resistance to water-hardness ions, mildness to skin, low oral and dermal toxicity, and ease of biodegradability (15–17). A survey of the literature (18), however, reveals that most of the work on AOS has been patented, and to our knowledge, there is no report of studies on micellar properties of AOS, either singly or in mixture with other surfactants. The mixed-surfactant system of LABS (C_{12}–C_{14} used for detergency) and AOS has proven to be promising for detergency purposes (19,20).

Solubilization-emulsification is an important mechanism for the removal of soil from the substrate (21). This is achieved by direct solubilization of soils into the surfactant micelles or by the formation of intermediate phases, such as microemulsions, at the soil-detergent solution interface; it is governed by the volumes and compressibilities of the surfactants involved.

In an attempt to understand the basic aspects that underlie synergism in performance characteristics, a study of micellar and volumetric properties of the mixed-surfactant system, containing DBS and AOS has been undertaken.

EXPERIMENTAL PROCEDURES

DBS ($C_{12}H_{25}C_6H_4SO_3^-$, Na^+) was obtained from Sigma (St. Louis, MO) and purified according to standard procedures

---

*To whom correspondence should be addressed.

(22). The distribution of different homologues in DBS was $C_{12} = 70$; $C_{14} = 15$, and $C_{16} = 5$ parts by reversed-phase high-performance liquid chromatography (HPLC). The average molecular weight of DBS was taken to be 348.4.

AOS [$CH_3(CH_2)_{12}CH{=}CHCH_2SO_3^-$, Na^+] (>98%), obtained from Alcolac (Baltimore, MD), was used as such. Reversed-phase HPLC revealed the composition of AOS to be $C_{14} = 30$; $C_{16} = 32$, and $C_{18} = 35$ parts, and the average molecular weight was taken to be 326.

Critical micelle concentrations (CMC) of the surfactants and their mixtures were determined by surface-tension method at 298.15 ± 0.05 K. Surface tensions (γ) of solutions were measured in an automated drop-volume tensiometer, designed and fabricated in our laboratory. Accuracy in surface-tension measurement is within 0.05 mN m^{-1}, and the precision varies between 0.05 to 0.5 mN m^{-1}, depending on the surfactant concentration. The γ-log m plots of the two surfactants did not show a minimum, indicating the absence of impurities. CMC values of the pure surfactants are in general agreement with those reported in the literature (23,24) for similar surfactants.

Densities of the solutions of the surfactants were measured with a vibrating-tube densimeter (Anton Parr DMA 60/512; Anton Parr, Graz, Austria). Temperature was maintained at 298.15 ± 0.01 K in a thermostat (Julabo, Germany) with a proportional temperature controller (YSI, Yellow Springs, OH). The instrument was calibrated by measuring the densities of aqueous solutions of sodium chloride at 298.15 K. Operation and calibration of the densimeter are explained elsewhere (25). The accuracy of density measurement is ±0.01 to 0.1 kg m^{-3}, depending on concentration of the surfactants.

All solutions were prepared by weight with distilled, deionized, and degassed water. Surface tension and density of water at 298.15 K were taken to be 71.97 mN m^{-1} and 997.047 kg m^{-3}, respectively (5,6).

RESULTS AND DISCUSSION

The nonideal multicomponent mixed-micelle model of Holland and Rubingh (28) has been a useful model for the analysis of surface tension and CMC data. In this model, the nonideal mixing in micelles has been treated *via* a regular solution approximation, and hence this model has been referred to as regular solution theory (RST) in the present work. According to this model, CMC of the mixture of surfactants is related to those of the pure components by

$$\frac{1}{CMC_{12}} = \frac{\alpha_1}{f_1 CMC_1} + \frac{1-\alpha_1}{f_2 CMC_2} \qquad [1]$$

where f_1 and f_2 are the activity coefficients of the micelles, and CMC_1 and CMC_2 are the CMC values of surfactants 1 and 2, respectively; α_1 is the mole fraction of surfactant 1 in solution. For ideal mixing, the activity coefficients are taken to be unity. CMC values, calculated on the basis of ideal mixing as well as those determined experimentally, are plotted in Figure 1.

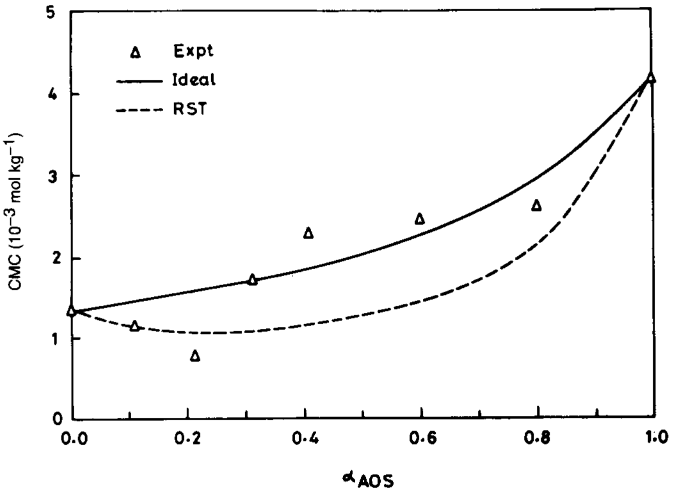

FIG. 1. Variation of critical micelle concentration (CMC) with α_{AOS} for decylbenzene sulfonate–sodium salt + alpha-olefin sulfonate–sodium (AOS) mixed-surfactant system; RST, regular solution theory.

By treating the mixed micelle as a regular solution, the activity coefficients f_1 and f_2 can be expressed as functions of mole fractions of each surfactant in the mixed micelle X_1^M and the appropriate interaction parameter β_{12}:

$$f_1 = \exp \beta_{12}(1 - X_1^M)^2 \qquad [2]$$

$$f_2 = \exp \beta_{12}(X_1^M)^2 \qquad [3]$$

The interaction parameter β_{12} is a constant related to net (pairwise) interactions in the mixed micelle of the form:

$$\beta_{12} = \frac{N_A(W_{11} + W_{22} - 2W_{12})}{RT} \qquad [4]$$

Binary mixtures of surfactants are known to exhibit synergism in three respects: (i) surface-tension reduction efficiency, (ii) mixed-micelle formation, and (iii) surface-tension reduction effectiveness. Rosen *et al.* (29,30) have derived expressions for the relevant surface properties, based on the nonideal multicomponent mixed-micelle model (30). Surface tension and CMC data for the DBS + AOS system have been analyzed according to these models.

Adsorption at aqueous solution/air interface. Surface tension and CMC data have been used to calculate the extent of interaction between the two surfactants at the solution/air interface. The mole fraction of DBS in a mixed monolayer X_1 was calculated (29) from the equation

$$\frac{X_1^2 \ln \frac{C_1}{C_1^\circ X_1}}{(1 - X_1)^2 \ln \frac{C_2}{C_2^\circ (1 - X_1)}} = 1 \qquad [5]$$

where C_1 and C_2 are the solution-phase molalities of DBS and AOS, respectively, in their mixture, to produce a given surface tension reduction, and C_1° and C_2° are the solution-phase molalities of pure DBS and AOS, respectively, to produce the same surface tension (reduction). The molecular interaction parameter β^{σ}, for mixed monolayer formation (29) at the surfactant solution/air interface, has been calculated from the following equation:

$$\beta^{\sigma} = \ln \frac{\dfrac{C_1}{C_1^{\circ} X_1}}{(1 - X_1)^2} \qquad [6]$$

The values of β^{σ} and X_1 of the surfactants and their mixtures and other parameters related to monolayer formation, at different α_{AOS}, are given in Table 1.

Mixed-micelle formation. The nonideal mixed-micelle model (28) has been used to calculate the interaction parameter for mixed-micelle formation β^M for the DBS + AOS system. The mole fraction of AOS in the mixed micelle X_1^M at the CMC is given by:

$$\frac{\left(X_1^M\right)^2 \ln \dfrac{\alpha_1 \mathrm{CMC}_{12}}{X_1^M \mathrm{CMC}_1}}{\left(1 - X_1^M\right)^2 \ln \dfrac{(1-\alpha_1)\mathrm{CMC}_{12}}{\left(1-X_1^M\right)\mathrm{CMC}_2}} = 1 \qquad [7]$$

where CMC_1, CMC_2, and CMC_{12} are CMC values of surfactant 1, 2, and the mixture, respectively, and α_1 is the mole fraction of surfactant 1 in solution. The interaction parameter for mixed-micelle formation β^M, is obtained from the CMC (28) by:

$$\beta^M = \frac{\ln \dfrac{\alpha_1 \mathrm{CMC}_{12}}{X_1^M \mathrm{CMC}_1}}{\left(1 - X_1^M\right)^2} \qquad [8]$$

CMC values of DBS, AOS, and their mixtures; the mole fraction of AOS in mixed micelle; and X_1^M and β^M values at different α_{AOS} are listed in Table 2. The mole fraction of AOS in the mixed micelle X_1^M, is shown as a function of α_{AOS} in Figure 2.

For ideal mixing, X_1^M has been calculated with the equation

$$X_1^M = \frac{\alpha_1 \mathrm{CMC}_2}{\alpha_1 \mathrm{CMC}_2 + (1 - \alpha_1)\mathrm{CMC}_1} \qquad [9]$$

and has also been plotted in Figure 2.

Volumetric properties. The apparent molar volumes (ϕ_V) for the pure and mixed-surfactant system have been calculated from density data with Equation 10.

TABLE 1
Parameters Related to Mixed Monolayer Formation by DBS + AOS Surfactant System[a]

α_{AOS}	$C_{12} \times 10^3$ (m)	X_1	β^{σ}	pC_{40}	γ_{CMC} (mN m^{-1})
0.0000	2.09			2.95	37.26
0.1100	1.01	0.8389	−1.6	2.99	37.21
0.2159	0.74	0.6888	−2.9	3.13	38.05
0.3142	1.31	—	—	2.88	35.97
0.4116	1.62	0.8295	0.9	2.64	35.52
0.6022	1.57	—	—	2.80	33.63
0.8013	1.58	0.3516	−0.5	2.80	31.47
1.0000	1.12			2.68	29.00

[a] DBS, decylbenzene sulfonate–sodium salt; AOS, alpha-olefin sulfonate–sodium; CMC, critical micelle concentration.

TABLE 2
Micellar Parameters of DBS + AOS Mixed-Surfactant System[a]

α_{AOS}	CMC × 10^3 (m)	$X_{\mathrm{AOS}}{}^M$	β^M
0.0000	1.3		
0.1100	1.1	0.1788	−2.6
0.2159	0.8	0.3141	−4.4
0.3142	1.7	0.1334	−0.1
0.4116	2.3	—	—
0.6022	2.4	0.3006	0.3
0.8013	2.6	0.5525	−0.5
1.0000	4.2		

[a] Abbreviations as in Table 1.

$$\phi_V = \frac{M}{\rho} - \frac{1{,}000(\rho - \rho_0)}{m \rho \rho_0} \qquad [10]$$

where ρ_0 and ρ are the densities of the solvent and the solution, respectively. M is the molecular weight of the surfactant, and m is the total surfactant molality. M is taken as the weighted average of the individual molecular weights of the two surfactants for mixtures (29), as given by:

$$M = \alpha_1 M_1 + (1 - \alpha_1) M_2 \qquad [11]$$

ϕ_V values could not be evaluated accurately for the premicellar concentrations because of the low CMC of the surfactants. The solution density, ρ, and ϕ_V at different m are given in Table 3.

Partial molar volumes ($\bar{V}_2$) of the mixed surfactant in postmicellar solutions for different compositions of the mixture have been evaluated with the following equation:

$$\bar{V}_2 = \frac{\delta m (m \phi_V)}{\delta} \qquad [12]$$

and are listed in Table 4 and plotted vs. α_{AOS} in Figure 3. Volume of mixed micellization (ΔV_m) is given by the difference between the experimental and ideal $\bar{V}_2$ as in Equation 13.

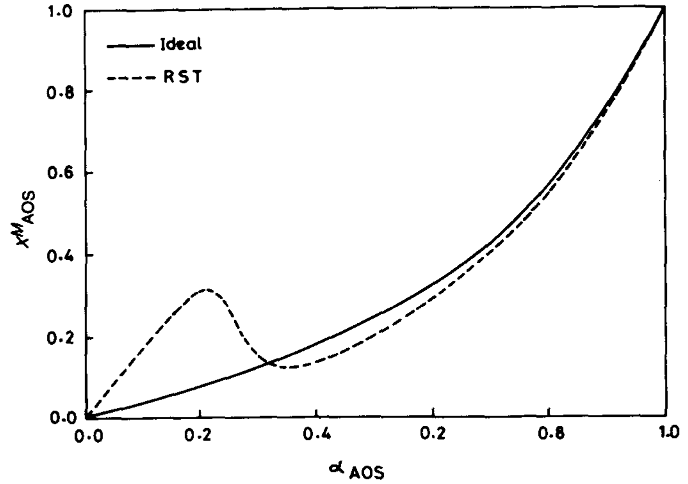

FIG. 2. Variation of micellar composition as a function of α_{AOS} for decylbenzene sulfonate–sodium salt + AOS mixed-surfactant system. Abbreviations as in Figure 1.

TABLE 3
Densities (ρ) and Apparent Molar Volumes (ϕ_V) of DBS + AOS Mixtures at 298.15 K[a]

	m mmol kg^{-1}	ρ kg m^{-3}	ϕ_V mL mol^{-1}	m mmol kg^{-1}	ρ kg m^{-3}	ϕ_V mL mol^{-1}
α_{AOS} = 0.0 (DBS)	3.4550	997.49	221.0	41.0740	1002.54	213.7
	9.7248	998.45	203.5	59.3038	1004.27	225.2
	15.0284	998.91	224.5	72.3260	1006.06	222.0
	21.7650	999.86	218.7	115.0800	1011.24	222.2
	36.1039	1001.61	221.2			
α_{AOS} = 0.1100	1.0471	997.19	212.5	45.6722	1002.84	218.2
	1.9939	997.37	184.6	51.5344	1002.96	230.3
	4.1953	997.75	178.4	58.9791	1003.95	227.8
	8.3547	998.04	227.5	82.9430	1006.80	226.6
	15.1832	999.08	212.0	93.3023	1007.98	226.8
	19.1353	999.59	213.1	122.3300	1011.27	227.0
	30.2092	1000.86	219.3	151.2659	1014.45	227.5
α_{AOS} = 0.2106	2.0340	997.29	226.1	50.3140	1002.51	234.5
	4.0454	997.48	236.1	61.6660	1003.87	232.1
	7.6750	997.83	241.4	85.1218	1006.21	234.5
	15.1698	998.55	245.1	101.3421	1007.89	234.7
	20.2096	999.08	243.4	111.5128	1009.43	230.3
	30.3977	1000.42	232.6	144.3297	1013.15	229.0
	38.6377	1001.33	232.4			
α_{AOS} = 0.3142	1.0449	997.22	178.8	40.1287	1001.40	232.5
	2.1251	997.40	175.9	46.7229	1002.09	232.9
	4.1166	997.54	223.1	54.9055	1002.86	234.9
	8.3138	997.51	286.6	79.6310	1005.50	233.9
	9.9886	998.26	220.1	97.6075	1007.20	235.6
	15.2499	998.89	220.7	112.2875	1008.67	235.8
	19.0979	999.28	224.8	147.1397	1012.59	232.8
	30.5877	1000.39	232.0			
α_{AOS} = 0.4096	2.0602	997.16	286.1	52.4989	1002.85	228.0
	4.0172	997.27	283.8	64.0590	1003.68	234.6
	8.2434	997.37	301.0	87.3109	1005.66	239.1
	9.8916	997.44	300.0	98.6070	1006.36	243.1
	15.1823	997.92	282.0	127.9660	1008.67	246.2
	19.6171	998.96	241.8	160.7890	1011.38	247.2
	39.4221	1000.92	240.6			
α_{AOS} = 0.5220	2.1157	997.43	156.8	52.5540	1001.93	243.6
	4.1261	997.59	205.5	61.5859	1002.93	240.7
	8.3054	998.04	217.8	80.9133	1004.58	242.7
	10.1041	997.96	246.6	101.0300	1006.17	245.1
	20.2807	998.91	245.3	118.4200	1007.62	246.2
	32.0680	999.95	246.5	150.3743	1010.25	246.6
	42.6942	1000.90	246.4			
α_{AOS} = 0.6149	4.1289	997.57	208.5	52.0259	1001.16	255.4
	8.1333	997.91	229.0	60.4127	1001.99	252.4
	10.0716	998.12	228.8	86.5477	1004.11	252.0
	15.2885	998.39	247.4	105.3788	1005.61	252.0
	21.0025	998.84	249.9	122.3200	1006.79	253.3
	32.0227	999.54	257.0	159.9500	1009.51	254.4
	41.3371	1000.48	251.6			
α_{AOS} = 0.8073	1.0179	997.19	189.2	40.1606	999.69	264.5
	2.0521	997.19	262.1	42.5754	999.97	261.5
	4.0194	997.25	279.3	60.8271	1001.38	258.6
	8.1035	997.54	269.8	78.2468	1002.63	258.3
	10.3334	997.65	272.1	92.9671	1003.62	258.7
	15.2647	998.06	264.6	118.4791	1005.08	261.1
	20.3051	998.28	270.0	153.3055	1007.24	261.9
	30.1526	998.70	275.9			
α_{AOS} = 1.0 (AOS)	1.7524	997.19	244.3	12.8506	997.65	279.2
	2.4042	997.22	252.6	20.5441	998.09	275.6
	4.3036	997.24	281.1	24.3404	998.40	270.7
	6.4104	997.31	285.6	50.9509	1000.05	266.9
	8.9033	997.34	294.2	77.3368	1001.49	268.0
	11.4153	997.59	278.9	169.0423	1006.39	268.9

[a] Abbreviations as in Table 1.

TABLE 4
Volumetric Properties of DBS + AOS Mixed-Surfactant System at 298.15 K[a]

α_{AOS}	$\bar{V}_{2(expt)}$, mL mol^{-1}	$\bar{V}_{2(ideal)}$, mL mol^{-1}	ΔV_m mL mol^{-1}
0.0000	225.0	225.0	—
0.1100	228.9	229.8	−0.9
0.2106	229.1	234.1	−5.0
0.3140	234.5	238.5	-4.0
0.4096	250.0	242.6	7.4
0.5220	246.3	247.4	−1.1
0.6149	254.0	251.4	2.6
0.8073	259.6	259.7	−0.1
1.0000	268.0	268.0	—

[a]Abbreviations as in Table 1.

$$\Delta V_m = \bar{V}_{2(\text{expt})} - \bar{V}_{2(\text{ideal})} \qquad [13]$$

ΔV_m has been plotted vs. the mole fraction of AOS, α_{AOS}, in Figure 4 and are presented in Table 4.

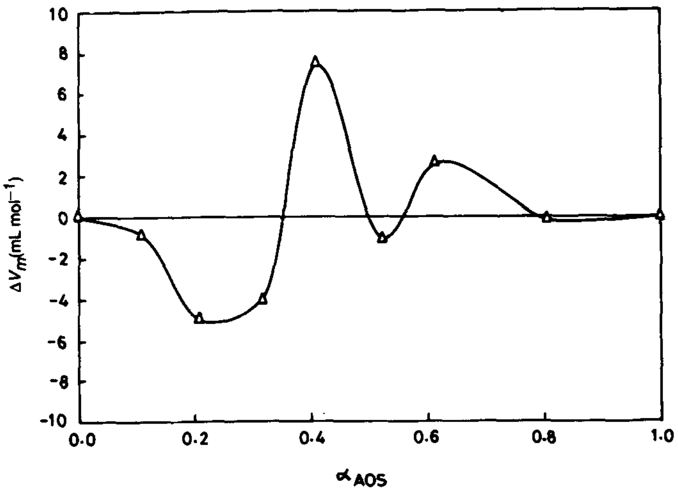

FIG. 4. Volume of mixed micellation (ΔV_m) as a function of α_{AOS} for decylbenzene sulfonate–sodium salt + AOS mixed-surfactant system. Abbreviation as in Figure 1.

Surface-tension reduction efficiency. Synergism in surface-tension reduction efficiency is present when a mixture of two surfactants can yield a given surface tension (reduction) at a concentration less than that required for the component surfactants. Conditions (29,30) for synergism in surface-tension reduction efficiency are: (i) $\beta^\sigma < 0$ and (ii) $|\ln (C^\circ_1/C^\circ_2)| < |\beta^\sigma|$, where β^σ is the interaction parameter for mixed monolayer formation at the solution/air interface. Table 1 indicates negative values of β^σ at DBS-rich compositions, the magnitudes of which are greater than the value of $|\ln (C^\circ_1/C^\circ_2)|$, i.e., 0.6487. The DBS + AOS system fulfills the condition for synergism in this respect at $\alpha_{AOS} \approx 0.21$. Surface-tension reduction efficiency is compared in terms of the total surfactant concentration C_π, required to reduce the surface tension of water by a given value, called surface pressure (π). Surface-tension reduction efficiency has been calculated for the DBS + AOS system at $\pi = 20$ and 40 mN m^{-1}. The negative logarithm of C_π is denoted by pC_π and is used as a measure of efficiency. pC_{20} and pC_{40} are plotted over the whole composition range for DBS + AOS mixtures in Figure 5. It shows that the efficiency of AOS for $\pi = 20$ is better than that of DBS, obviously due to the longer alkyl chain of AOS. To reduce the surface tension of water to 40 mN m^{-1}, more of the surfactant is required to be adsorbed at the interface, and adsorption is determined by the steric and electrostatic repulsion between the hydrophilic heads of the surfactant molecules. AOS exists both as olefin sulfonate and as 2- or 3-hydroxy sulfonate in aqueous solution. Thus the presence of a double bond or the hydroxy group in the vicinity of the sulfonate group adds to electrostatic and steric repulsions; hence pC_{40} of AOS is less than that of DBS. There is a slight increase in pC_{20} at $\alpha_{AOS} = 0.2$, which is more pronounced in pC_{40}. This is the composition at which the mixed

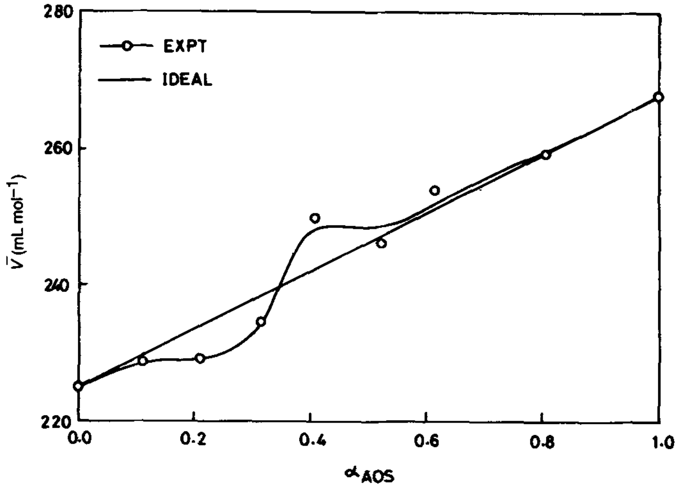

FIG. 3. Variation of partial molar volume ($\bar{V}_2$) with α_{AOS} for decylbenzene sulfonate–sodium salt + AOS mixed-surfactant system. Abbreviation as in Figure 1.

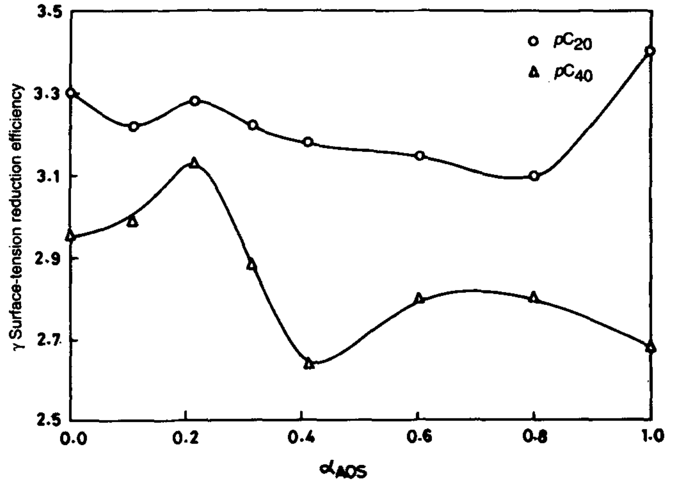

FIG. 5. Surface-tension reduction efficiency of decylbenzene sulfonate–sodium salt + AOS mixed-surfactant system. Abbreviation as in Figure 1.

monolayer is formed at the interface, as indicated by the β^σ and X_1 values in Table 1. Surface-tension reduction is related to fabric wetting and detergency, and the observed synergism is in accordance with our previous results on the detergency of DBS + AOS mixtures (20).

Surface-tension reduction effectiveness. Synergism in surface-tension reduction effectiveness exists when the mixture at its CMC reaches a surface tension lower than that attained at the CMC of the individual surfactants. This is related to the surface excess concentration Γ_{max} of the surfactants at the aqueous solution/air interface, which in turn is determined by the area of cross-section at the interface of the polar headgroup of the surfactant. The surface tension at the CMC of the mixture, γ_{CMC} values at different compositions of the mixture are presented in Table 1 and are plotted as a function of α_{AOS} in Figure 6. Conditions (29,30) for this kind of synergism are: (i) $\beta^\sigma < 0$, (ii) $\beta^\sigma - \beta^M < 0$, and (iii) $|\beta^\sigma - \beta^M| > |(\gamma^\circ_{CMC_1} - \gamma^\circ_{CMC_2})/K|$, where $\gamma^\circ_{CMC_1}$ and $\gamma^\circ_{CMC_2}$ are the surface tensions at the CMC of surfactants 1 and 2, respectively, and K is the slope of the γ vs. $\log m$ plot for the surfactant having the larger surface tension at its CMC. These conditions for synergism are not satisfied at any composition for DBS + AOS mixtures. A plot of the surface tension at the CMC of the mixtures, γ_{CMC} vs. α_{AOS}, shown in Figure 6, exhibits positive deviation from the ideal surface tension of the mixture (shown by a straight line, joining the γ°_{CMC} of DBS and AOS) at all compositions. Effectiveness of surface-tension reduction is determined by the area occupied by the polar headgroup at the solution/air interface and the repulsion between the headgroups of the surfactants at the interface. Both DBS and AOS have bulky sulfonate headgroups; in addition, DBS has a benzene ring, and AOS has a double bond next to the sulfonate groups. Steric and electrostatic repulsion due to these electron-rich groups would reduce the tendency for formation of a mixed monolayer. This is reflected in the higher value of γ°_{CMC} at all compositions of the mixture.

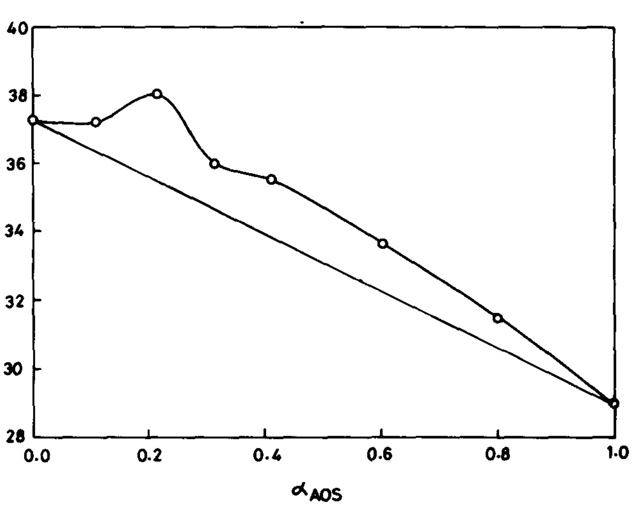

FIG. 6. Surface-tension reduction effectiveness of decylbenzene sulfonate–sodium salt + AOS mixed-surfactant system. Abbreviation as in Figure 1.

Mixed-micelle formation. The mixture of surfactants shows synergism in mixed-micelle formation when the CMC is lower than those of individual surfactants. In Figure 1, comparison of experimental CMC with that calculated on the basis of ideal mixing indicates interaction between the two surfactants, leading to mixed-micelle formation. Conditions (29,30) for this type of synergism are: (i) $\beta^M < 0$ and (ii) $|\ln(CMC_1/CMC_2)| < |\beta^M|$. The DBS + AOS system exhibits synergism in mixed-micelle formation when $\alpha_{AOS} \leq 0.2$. The nonideal mixed-micelle model gives an average β^M of −1.4 (Table 2). Addition of more AOS increases repulsive interactions, which lead to a positive deviation from ideality. Consequently, the CMC values in the region $\alpha_{AOS} = 0.3$ to 0.6 are high.

In the absence of any favorable electrostatic interaction for the formation of mixed micelles, the hydrophobic interaction between the "tails" of the two surfactants and the favored configuration attained by rearrangement of the surfactants is due to incorporation of AOS seem to be the main driving force for the formation of mixed micelles by the DBS + AOS system.

Mixed-micellar composition and volume of micellization. The variation of mixed-micellar composition X_1^M with the bulk composition α_{AOS} of the DBS + AOS mixture, calculated according to the ideal solution theory, and RST are shown in Figure 4. According to RST, the mole fraction of AOS in mixed micelles is larger than that in bulk solution at $\alpha_{AOS} \leq 0.3$. At other compositions of the mixtures, the mixed-micellar composition is almost the same as that predicted by ideal behavior of the two surfactants. From the structure of the two molecules, it appears that incorporation of AOS into DBS micelles is favored over incorporation of DBS into AOS micelles.

The $\bar{V}_2$ values show deviation from ideal behavior at the same compositions where there is synergism in mixed-micelle formation in Figure 5 ($\alpha_{AOS} \leq 0.3$). These deviations are more clearly represented in Figure 6, where the volume change on mixed micelle formation ΔV_m is plotted vs. α_{AOS}. There is a decrease in the volume of the mixed micelle at $\alpha_{AOS} \leq 0.3$. A reorganization of the monomers in the mixed micelle takes place on incorporation of AOS into DBS micelles, leading to a more compact packing of monomers within the mixed micelle. At higher mole fractions of AOS in the mixture, the increasing repulsions between the headgroups lead to an increase in size of the mixed micelle; in fact at $\alpha_{AOS} = 0.4$, ΔV_m is large and positive. Further increase in AOS content leads to generally ideal behavior, without significant change in ΔV_m.

The mixed-surfactant system of DBS + AOS exhibits synergism in surface-tension reduction efficiency and mixed-micelle formation, when the mole fraction of AOS in the mixture is 0.20. The partial molar volumes also show a minimum at the same composition of the mixture. The volume change on mixed micellization of this mixture indicates that the two surfactants interact favorably to form a compact mixed micelled at $\alpha_{AOS} = 0.2$. Volume behavior correlates well with the CMC data. Calculations based on RST of nonideal mixed-micelle formation yield β^M and X_1^M, which are consistent with molar volume data.

REFERENCES

1. Rosen, M.J., *Surfactant and Interfacial Phenomena*, Wiley Interscience, New York, 1978.
2. de Almeida, J.L.G., M. Dufaux, Y. Ben Taarit, and C. Naccache, Linear Alkylbenzenes, *J. Am. Oil Chem. Soc. 71:*675–694 (1994).
3. Ainsworth, S.J., Soaps and Detergents—Product Report, *Chem. Eng. News*, Vol. 27, Jan. 24, 1994, p. 34.
4. Matheson, K.L., M.F. Cox, and D.L. Smith, Interactions Between Linear Alkylbenzene Sulfonates and Water Hardness Ions I. Effect of Calcium Ion on Surfactant Solubility and Implications for Detergency Performance, *J. Am. Oil Chem. Soc. 62:*1391–1396 (1985).
5. Hinds, G.E., in *Anionic Surfactants*, Vol. 1, edited by W.M. Linfield, Marcel Dekker, Inc., New York, 1976, p. 17.
6. Swesher, R.D., *Surfactant Biodegradation*, Marcel Dekker, Inc., New York, 1970.
7. Ogoshi, T., and Y. Miyawaki, Soap and Related Products: Palm and Lauric Oils, *J. Am. Oil Chem. Soc. 62:*331–335 (1985).
8. Tuvell, M.E., G.O. Kuehnhanss, G.D. Heidebrecht, P.C. Hu, and A.D. Zielinksi, AOS—An Anionic Surfactant System: Its Manufacture, Composition, Properties and Potential Application, *Ibid. 55:*70–80 (1978).
9. *Aliphatic Surfactants*, Stanford Research Institute Report Nos. 59 and 59A, Menlo Park, Dec. 1969 and Mar. 1974.
10. Suri, S.K., N. Homendra, and S. Bharadwaj, Versatility of Alpha-Olefin Sulfonate in Indian Soap and Detergent Industry, *Chemical Business 4:*45–59 (1991).
11. Dewitt, W.J., Performance of Alpha-Olefin Sulfonates Derived from Ziegler Olefins in Light-Duty Liquid Detergents, *J. Am. Oil Chem. Soc. 49:*361–365 (1972).
12. Suri, S.K., H. Naorem, and S. Bharadwaj, Versatility of Alpha-Olefin Sulfonates in Indian Synthetic Detergent Industry, in *Chemical Weekly*, Oct. 15, 1991, pp. 113–123.
13. Kessler, A., and E.P. Phillip, U.S. Patent 3,332,880 (1969) to Procter and Gamble, CA, 68, 4243.
14. Pueschel, F., Industrial Uses of Surface-Active Agents, in *Tenside 4:*1 (1967).
15. Green, H.A., in *Anionic Surfactants*, Vol. 7, Part II, edited by W.M. Linfield, Surfactant Science Series, Marcel Dekker, Inc., New York, 1976.
16. F.A. Knaggs, M.I. Nassbaum, and A. Schulz, *Kirk Othmer Encyclopedia of Chemical Technology*, Vol. 22, Wiley Interscience, 1983, p. 1.
17. Gulf Oil Technical Literature on Alpha Olefin Sulfonate, Gulf Oil Chemicals Department, New York, 1968.
18. Nishikido, N., and G. Sugihara, in *Mixed Surfactant Systems*, edited by K. Ogino and M. Abe, Marcel Dekker, Inc., New York, 1993, pp. 393–444.
19. Cox, M.F., T.P. Matson, J.L. Berna, A. Moreno, S. Kawakami, and M. Suzuki, Worldwide Studies of Mixed Active Laundry Detergency, *J. Am. Oil Chem. Soc. 61:*330–339 (1984).
20. Suri, S.K., M.S. Thakur, and S. Bharadwaj, The Mixed Surfactant System of Linear Alkylbenzene Sulfonate and Alpha-Olefin Sulfonate, *Ibid. 70:*59–64 (1993).
21. Miller, C.A., and K.H. Raney, Solubilization-Emulsification Mechanisms of Detergency, *Colloids Surfaces A: Physicochem. Eng. Aspects 74:*169–215 (1993).
22. Rosen, M.J., and H.A. Goldsmith, *Systematic Analysis of Surface-Active Agents,* 2nd edn.,Wiley Interscience, New York, 1972.
23. Mukerjee, P., and K.J. Mysels, *Critical Micelle Concentrations of Aqueous Surfactant Systems*, NSRDS-NBS 36, National Bureau of Standards, Washington, 1971.
24. Lysogor, N.A., N.G. Kurilova, V.G. Matashkin, and A.P. Rudoi, Surface-Active Properties of Sodium α-Olefin Sulfonates, *Maslo-Zhir Prom-st 10:*35–37 (1982):CA 98 (1983) 18475s.
25. Kumar, S., Thermodynamic Studies of Some Industrially Important Liquids and Their Mixtures, Ph.D. Thesis, Indian Institute of Technology, Delhi, 1994.
26. Lide, D.R. (ed.), *CRC Handbook of Chemistry and Physics*, 75th edn., CRC Press, London, 1994, pp. 6–10.
27. Kell, G.S., Precise Representation of Volume Properties of Water at One Atmosphere, *J. Chem. Eng. Data 12:*66–69 (1967).
28. Holland, P.M., and D.N. Rubingh, Nonideal Multicomponent Mixed Micelle Model, *J. Phys. Chem. 87:*1984–1990 (1983).
29. Rosen, M.J., and X.Y. Hua, Synergism in Binary Mixtures of Surfactants: II. Some Experimental Data, *J. Am. Oil Chem. Soc. 59:*582–585 (1982).
30. Rosen, M.J., and R.Y. Zhu, Synergism in Binary Mixtures of Surfactants IV: Effectiveness of Surface Tension Reduction, *J. Colloid & Interface Sci. 99:*435–442 (1984).
31. Desnoyers, J.E., G. Perron and A. Roux, in *Surfactant Solutions: New Methods of Investigation*, Vol. 22, edited by R. Zana, Surfactant Science Series, Marcel Dekker, Inc., New York, 1987, pp. 1–55.

[Received August 1, 1995; accepted November 6, 1995]