The Energetics of Surfactant Adsorption at the Air-Water Interface

A. M. MANKOWICH, U.S. Army Coating and Chemical Laboratory, Aberdeen Proving Ground, Maryland

Abstract

The standard free energy, enthalpy, and entropy changes (ΔG, ΔH, and ΔS, respectively) for the adsorption at the air-water interface of a commercial ethylene oxide (EO) adduct of straight chain nonylphenol from monomer solution at the critical micelle concentration (CMC) have been calculated from surface tension-concentration data at 21C-45C using the Gibbs equation, the standard free energy change equation $\Delta G = -RT$(ln interfacial monomer concentration/CMC), and the Gibbs-Helmholtz equation which gave ΔH directly from the slope of the (ΔG/T) vs (1/T) function. The CMC and surface tension at the CMC (γCMC) decreased, and −ΔG and molecular area increased slightly, with increasing temperature. The ΔH and ΔS values were positive, and appear explainable by the postulations applied to micellization. At ambient temperature (28C) an increase in the (EO) mol ratio of straight chain nonylphenol and C_{13} secondary alcohol ethoxylates resulted in increases of CMC, γCMC, and molecular area, and slight decreases in −ΔG. A comparison of the 9 (EO) mol ratio adducts of C_{13} straight chain primary and secondary alcohols showed that the CMC and molecular area of the secondary alcohol ethoxylate were larger, and the γCMC and −ΔG smaller, than the corresponding values of the primary alcohol ethoxylate.

Introduction

Considerable data are available in the literature on the molecular areas of adsorbed ionic and nonionic surfactants at air-water interfaces (1–9). Most of the values have been evaluated from surface tension-log concentration curves of aqueous surfactant solutions by means of the Gibbs equation, assuming complete monomolecular layer adsorption in that portion of the curve just below the critical micelle concentration (CMC) which is characterized by a straight line with a steep, negative slope. Little work has been done in estimating the standard free energy, enthalpy, and entropy changes (ΔG, ΔH, and ΔS, respectively) for this surfactant adsorption process.

This paper determines the ΔG, ΔH, and ΔS values for selected commercial surfactants. The ΔH value is calculated by the Gibbs-Helmholtz equation.

Theory

The Gibbs equation (10) is given by

$$\Gamma = -\frac{1}{2.303\ R.T.n}\ \frac{d\ (\gamma)}{d\ (\log\ c)} \qquad [1]$$

where

Γ = concentration of surface excess, in moles per cm² of interface

c = Bulk concentration, in moles/liter

γ = Surface tension, in dynes/cm.

$R = 8.317 \times 10^7$

T = Temperature in °K

n = 1, for nonionic surfactants

Since the equation is customarily applied to dilute solutions below the CMC, there is little error involved in the use of bulk concentration values instead of activities. Assuming electrical neutrality of the surface monolayer of an ionic solution, it can be shown theoretically that $n = 1$ in the presence of excess electrolyte, and $n = 2$ when no added salt is present (11–14). Experimental verification of this latter is not conclusive, several workers in the field indicating that $n = 1$ for ionic surfactants in salt-free solution (5,7,9), and Isemura calling attention to the lack of unanimity in his textbook (12). In this paper, $n = 1$ will be used for anionic surfactants (justfication for this procedure is included in a later portion of this paper).

The standard free energy of adsorption from bulk solution to the surface is given by

$$\Delta G = -\ RT\ \ln\ (\Gamma/c) \qquad [2]$$

with the thickness of the surface layer taken as the length of the molecule (Ref. 10, p 124). Harkins' treatment of the data for the adsorption of butyl alcohol at the air-water interface (15) suggests that more strictly,

$$\Delta G = -\ RT\ \ln\ (\Gamma + c/c) \qquad [3]$$

Since Γ and c must be expressed in the same units, it is proposed that in equation (3) Γ be given in molecules per cm² of interface, and that c (taken as the CMC in this study) be converted into similar units. This may be accomplished, as shown in the following example, by an approximation which obviates the need of introducing a thickness factor in Γ and c, and which does not significantly affect the estimated value of −ΔG:

Example:

Let CMC = c = 0.10 moles/liter

$0.10 \times (6.02 \times 10^{23}) \times 10^{-3} = 0.602 \times 10^{20}$ molecules/cc

1 molecule in the bulk solution occupies a space equal to $(1/0.602 \times 10^{20}) = 1.66113 \times 10^{-20}$ cc

Assuming the space occupied by a molecule to be cubic, each side of the cube =

$$\sqrt[3]{1.66113 \times 10^{-20}} = 25.5 \times 10^{-8}\ \text{cm}$$

The cross-sectional area per molecule in the 0.10 molar solution (bulk) =

$$(25.5 \times 10^{-8})^2 = 650.3 \times 10^{-16}\ \text{cm}^2$$

The molecules per cm² of a layer in the bulk solution parallel to the surface, and also in the surface prior to adsorption

$= (1/650.3 \times 10^{-16}) = 0.15 \times 10^{14}$ molecules/cm².

In equation (3), $R = 1.987$ and −ΔG is in calories per gram mol adsorbed surfactant.

ΔH is determined by the Gibbs-Helmholtz equation,

$$\Delta H = \Delta G - T\frac{\delta\,\Delta G}{\delta\,T} \qquad [4]$$

with the slope of the (ΔG/T) vs (1/T) function giving ΔH (16).

TABLE I

15 (EO) Adduct of Straight Chain Nonylphenol, 21C-45C

°K	CMC Molarity $\times 10^5$	$\mathring{A}^2$ Molecular Area	γ CMC Dynes/cm	ΔG Kcal/g mol	ΔH Kcal/g Mol	ΔS Cal/mol-deg
294.2	3.10	66.6	35.9	−4.5	+1.3	+20.
298	2.85	73.8	35.6	−4.5	+1.3	+19.
301	2.71	69.2	35.3	−4.6	+1.3	+20.
306.5	2.69	73.0	34.8	−4.7	+1.3	+19.
314.5	2.36	71.0	33.9	−4.9	+1.3	+20.
318	2.27	70.7	33.7	−4.9	+1.3	+20.

The change in entropy, ΔS, is given by

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad [5]$$

Experimental

Materials

Most of the experimental work was done on commercial, 100% active, nonionic surfactants, certified as biodegradable by their manufacturers. Included among these products were the 11 and 15 ethylene oxide (EO) mol ratio adducts of straight chain nonylphenol, a 9 (EO) mol ratio adduct of a C_{13} average primary alcohol, and 9 and 12 (EO) mol ratio adducts of a C_{13} average linear secondary alcohol. A branched chain anionic surfactant, sodium dodecyl benzene sulfonate (SDBS), was also tested. The agents were used as received.

Methods

Surface tensions were determined with two du-Noüy interfacial tensiometers placed adjacent each other, and calibrated by weights daily. Harkins and Jordan correction factors (17) were used. When the meters were checked against distilled water at 24.8C and reagent-grade benzene at 23.9C, the results varied from standard values (18) by −0.90% and +0.16%, respectively. All surfactant test solutions were aged 1 hr in the test dish with the ring immersed below the surface before readings were taken. Nonionic surfactant tests at 0.0005–0.032% weight to volume concentration were prepared by aliquoting 0.1% stock solutions. When necessary 0.00025% solutions were prepared by double aliquoting of the stock solution. Aliquots were diluted just before testing, using water at the test temperature. Thus the surfactant solution placed in the Petri test dish was at the test temperature. The 21C and 25C tests were carried out in a low temperature room. The 25C tests required manual temperature regulation of the atmosphere immediately surrounding the test vessels by a small electric heater placed between the instruments. Slight movement of the heater and/or variation of its power consumption, as dictated by thermometers immersed in each test solution and also placed about 3/8 in. above the center of each test vessel, provided a simple, practical means of control. Tests at 28C–45C were made at ambient temperature

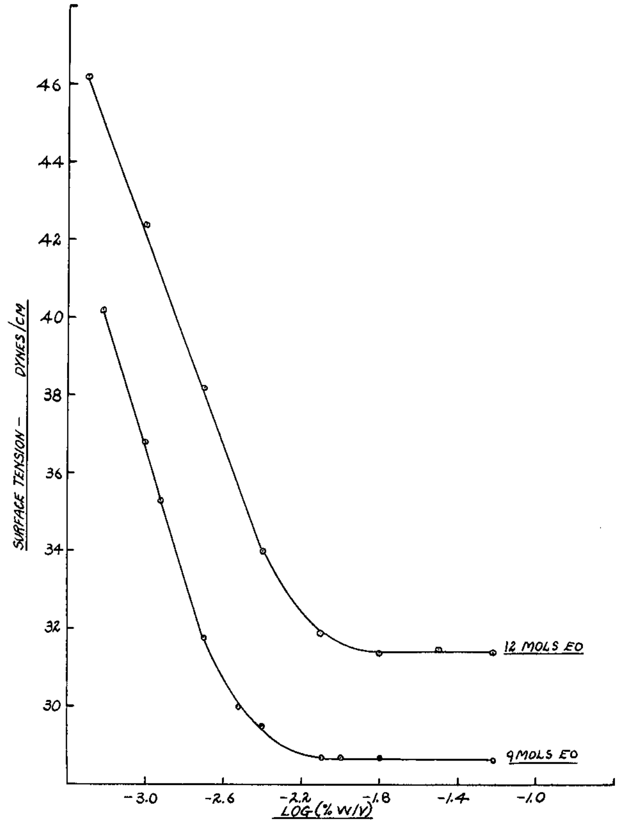

FIG. 1. Surface tension curves of ethoxylated 11–15 carbon isomeric linear secondary alcohols at 28C. EO = C_2H_4O.

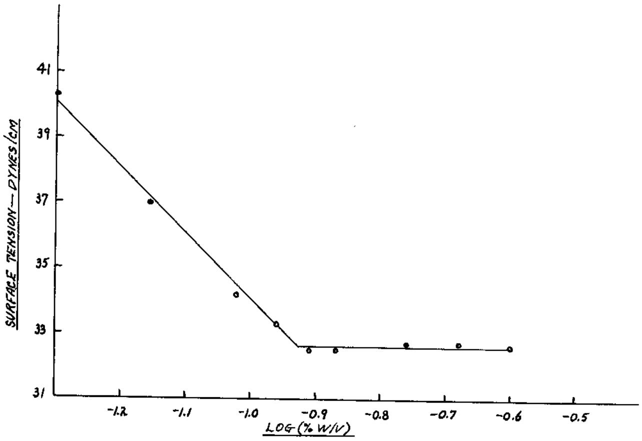

FIG. 2. Sodium dodecyl (branched) benzene sulfonate --26C.

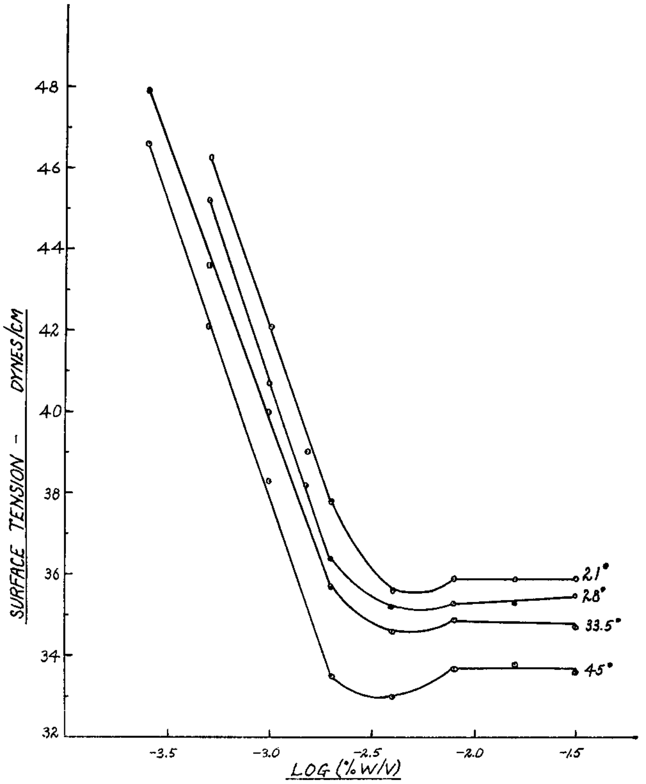

FIG. 3. 15(EO) adduct of straight chain nonyl phenol.

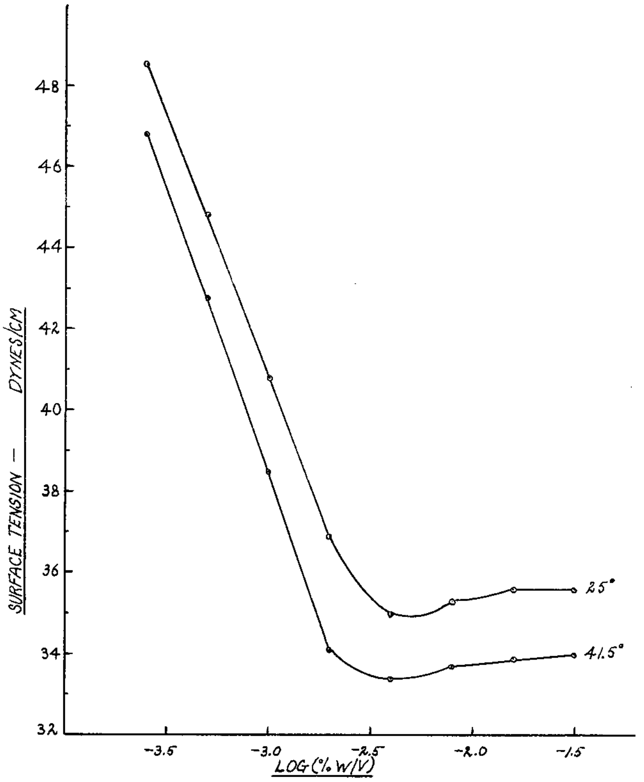

FIG. 4. 15(EO) adduct of straight chain nonylphenol.

with a manually-controlled electric heater adjacent each tensiometer. A plastic shield above the instruments limited air circulation. Solution temperatures varied not more than ±0.2C and air temperatures not more than ±0.5C from the reported test temperatures during the approximately 65 min required for a determination. To prevent evaporation during the test period, the 21C–28C tests were covered with paper cardboard and the 33.5–45C tests with sheet aluminum. Surface tension values from the two meters varying by not more than 0.2 dynes/cm were averaged and reported. When a pair of values from the two meters varied by 0.3 dynes/cm, another pair was determined; and the four values, covering a range of not more than 0.3 dynes/cm, were averaged. A pair of values showing a difference of more than 0.3 dynes/cm was discarded.

Because of the considerable amount of work involved in obtaining surface tension-concentration data at 21.2C, 25C, 28C, 33.5C, 41.5C, and 45C, ΔH and ΔS were determined only for one surfactant, the 15 (EO) adduct of straight chain nonylphenol. The value of ΔH was obtained by a least squares treatment of the (ΔG/T) vs. (1000/T) data. Surface adsorptions, molecular areas, and −ΔG for the other surfactants were determined from surface tension-concentration data at 28C. Surface tension-log concentration slopes for use in the Gibbs equation were obtained from the corresponding plots. If necessary they were calculated by least squares treatment. CMC was obtained from the surface tension-log concentration plots at the intersection of the linear negative slope (extended) and a line of zero slope drawn through the average of the nearly constant surface tensions beyond the minimum in the curve.

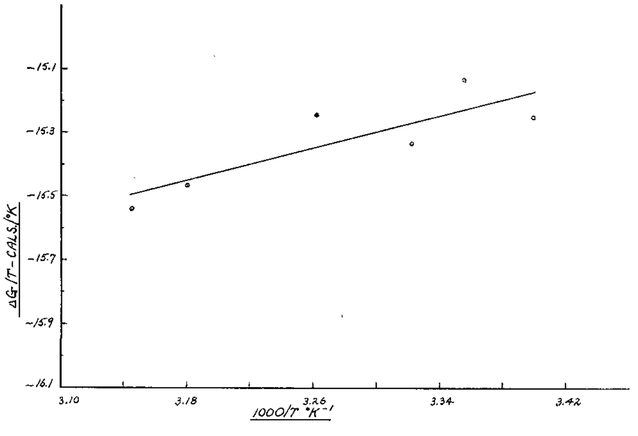

FIG. 5. Gibbs-Helmholz ΔH function for 15(EO) adduct of straight chain nonylphenol.

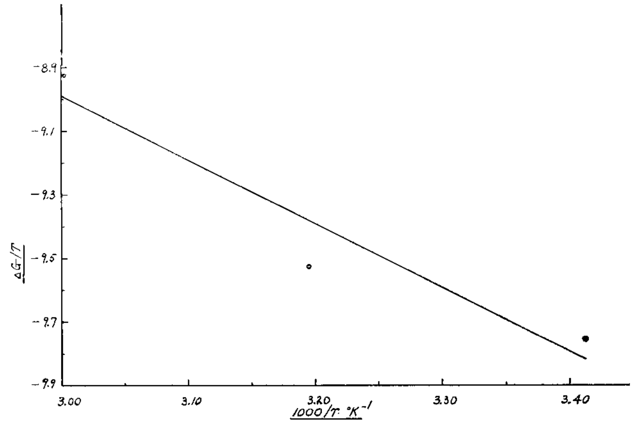

FIG. 6. Gibbs-Helmholtz ΔH function for sodium lauryl sulfate. Least squares line calculated from graphical surface tension data of Powney et al. (Ref. 20).

The details of the gravimetric detergency method have been given in previous papers (23); and the soils, 98% lauryl alcohol and ethyl stearate (mp30C–

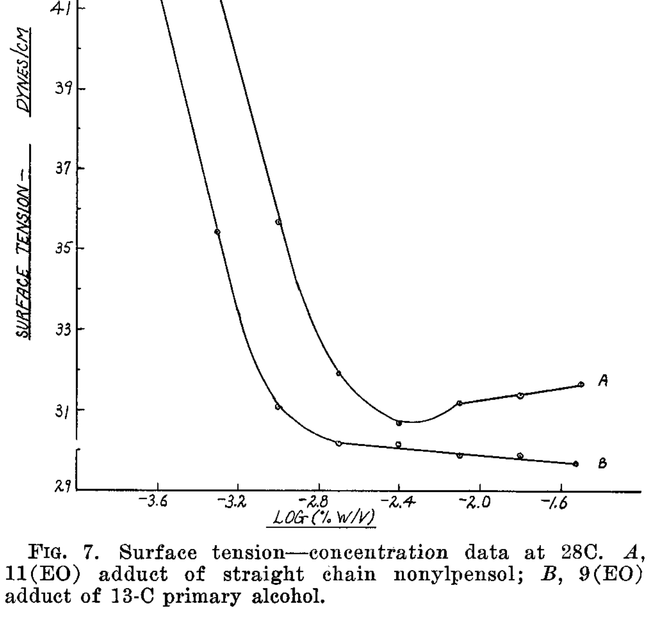

FIG. 7. Surface tension—concentration data at 28C. *A*, 11(EO) adduct of straight chain nonylpensol; *B*, 9(EO) adduct of 13-C primary alcohol.

TABLE II

—ΔG, ΔH, ΔS At Air-Water Interface Calculated From Literature Data

Literature data			Calculated values						
Ref.	Surf.	°C	CMC Molar	$\mathring{A}^2$ Molec. Area	Molec/ cm^2 $\times 10^{-14}$	Molec/ cm^2 $\times 10^{-14}$ at CMC, bulk	ΔG Kcal per mol	ΔH Kcal per mol	ΔS esu
Schick (1)	(a)	25	.000075	64	1.563	.0010	−4.4	+1.3	+19.
		50	.000040	62	1.613	.0008	−4.9	+1.3	+19.
Crook et al. (3)	(b)	15	.00034	72	1.383	.0035	−3.4	+0.3	+13.
		25	.00033	75	1.337	.0034	−3.5	+0.3	+13.
		35	.00030	77	1.302	.0032	−3.7	+0.3	+13.
		45	.00028	78	1.292	.0031	−3.8	+0.3	+13.
Powney et al. (20)	(c)	20	.0060	31.4*	3.183	.0235	−2.9	−2.0	+3.
		40	.0066	33.1*	3.026	.0251	−3.0	−2.0	+3.
		60	.0082	38.7*	2.584	.0290	−3.0	−2.0	+3.

(a) Homogeneous 10 (EO) adduct of branched chain nonylphenol.
(b) Homgeneous 10 (EO) adduct of branched chain octylphenol; literature data estimated from plots.
(c) Sodium lauryl sulfate; literature data estimated from plots.
* Calculated.

31C), have been characterized (24,25). Approximately 60 mg soil, accurately weighed, is applied to a 2½ × 2½ in. WD-1020, 18–20 gauge, cold-rolled steel panel, polished and cleaned in a standardized way, the lauryl alcohol by dipping and the ethyl stearate by melting the weighed sample on one face of the test panel. The panel is cleaned for 2 min without agitation in a distilled water solution of the surfactant at 180F ± 1F. It is then given two distilled water rinses at 83F without agitation, dried, cooled and weighed. Next it is degreased with solvent, alcohol rinsed, dried and reweighed.

Results and Discussion

15 (EO) Adduct of Straight Chain Nonylphenol at 21C–45C

Plots of the surface tension-log % concentration (W/V) data at the various temperatures are given in Figures 3 and 4. In Table I are listed CMC, γCMC, molecular area, and ΔG determined from these data, as well as ΔH which was determined by a least squares treatment of the (ΔG/T) vs. (1000/T) data plotted in Figure 5, and ΔS which was calculated by equation (5). The CMC and γCMC decreased, and molecular area and −ΔG increased slightly, with increasing temperature. The ΔH and ΔS values were positive. The temperature dependence of the CMC, γCMC, and molecular area, of this commercial, biodegradable nonionic surfactant is in general similar to results reported for both commercial and homogeneous branched chain alkylphenol ethoxylates (1,3). The positvie ΔH and ΔS values appear reasonable from the conventional concept of adsorption at the air-water interface. In an aqueous detergent solution, adsorption of detergent monomers at the surface is accompanied by the simultaneous expulsion of water molecules therefrom. Schick's conclusion concerning the positive ΔH and ΔS of micellization of nonionic surfactants seems applicable here; namely, the positive ΔS due to desolvation of water molecules predominates over the negative ΔS involved in the formation of an ordered adsorbed monolayer (19). Moreover, if amphipathic molecules equilibrate at the air-water interface with their hydrophobic groups above the interface (1), then one can speculate that the disorder of the dangling, unrestricted hydrophobic groups also contributes to the positive ΔS.

In the absence of reported results on ΔG, ΔH, and ΔS for the adsorption of surfactants at the air-water interface, it is informative to utilize related literature data to calculate these parameters. When the data are in the form of surface tension-concentration curves at several temperatures, the treatment is as already described in this paper. When CMC-molecular area-temperature data are reported, the surface excess (molecules/cm^2) is determined from molecular area, and molecules/cm^2 in bulk solution follows from the CMC; ΔG is then calculated by equation (3), and ΔH and ΔS follow as already described. Table II gives the results of treatments of representative literature data. It is to be noted that Schick's data for a homogeneous, 10 (EO) adduct of branched chain nonylphenol (1) yield positive ΔH and ΔS values of +1.3 kcal/g mol and 19. cal/mol degree, respectively. These results are the same as those obtained herein for the commercial, 15 (EO) adduct of straight chain nonylphenol (Table I). The data of Crook et al. (3) for the homogeneous, 10 (EO) adduct of branched chain octylphenol also yield positive ΔH and ΔS values. Significantly, the surface tension-concentration data of Powney et al. (20) for anionic sodium lauryl sulfate give positive CMC and molecular area temperature coefficients, together with negative ΔH (See Fig. 6) and small, positive ΔS values. The latter seem to indicate that the desolvation effect and/or increased configurational entropy of the monomers is only slightly greater than the restrictive effect of the adsorbed monomers.

11 (EO) and 15 (EO) Adducts of Straight Chain Nonylphenol at 28C

Figures 3 and 7 give the plots of the surface tension-log (% concentration) data of 11 (EO) and 15 (EO) adducts of straight chain nonylphenol at 28C. Table III lists the values of the slopes below the CMC. γCMC, CMC, molecular area, and −ΔG calculated from these data. It is noted that CMC. γCMC, and molecular area increase, while −ΔG decreases

TABLE III

Commercial Ethylene oxide Adducts of Straight Chain Hydrophobes, 28C

Hydrophobe	No. of (EO)	CMC Molarity	γ CMC Dynes/cm.	Slope below CMC Dynes/cm	$\mathring{A}^2$ Molecular area	ΔG Kcal/ g mol
Nonylphenol	11	.0000247	31.5	−18.50	51.8	−4.8
	15	.0000271	35.3	−13.84	69.2	−4.6
C_{13} Average Secondary alcohol	9	.0000515	28.7	−16.07	59.6	−4.6
	12	.0000867	31.4	−13.55	70.6	−4.1
C_{13} Average Primary alcohol	9	.0000149	30.2	−20.60	46.5	−5.1

Note: Alkyl groups of hydrophobes are linear.

TABLE IV

Sodium Dodecyl (Branched) Benzene Sulfonate at 26C

CMC Molarity	γ CMC Dynes/cm	$\overset{\circ}{A}^2$ Molecular area	$\Gamma \times 10^{-14}$ Molecules cm^2	(Molecules/cm^2) $\times 10^{-14}$ at CMC, bulk	ΔG, Kcal per g mol
.00353	32.6	47.1[a]	2.108[a]	.0162	—2.9

[a] Based on "n" = 1 in Gibbs equation.

slightly, as the (EO) mole ratio increases. The changes in CMC, γCMC, and molecular area are similar to results reported for commercial and homogeneous branched chain octylphenol and nonylphenol ethoxylates (1,3,6,21).

9 (EO) and (12 EO) Adducts of A C_{13} Linear Secondary Alcohol at 28C

Table III also shows that increasing the (EO) mole ratio of a C_{13} average linear secondary alcohol ethoxylate from 9 to 12 results in increased values of CMC, γCMC, and molecular area, with $-\Delta G$ decreasing. These values are based on surface tension data plotted in Figure 1.

9 (EO) Adducts of C_{13} Straight Chain Primary and Secondary Alcohols at 28C

A comparison of the 9 (EO) adducts of C_{13} straight chain primary and secondary alcohols given in Table III indicates that the CMC and molecular area of the secondary alcohol ethoxylate are larger, and the γCMC and $-\Delta G$ smaller, than the corresponding values of the primary alcohol ethoxylate. Surface tension data of the latter are plotted in Figure 7.

Sodium Dodecyl (Branched) Benzene Sulfonate at 26C

Figure 2 and Table IV contain the surface tension-concentration data and the parameters determined from the latter with the Gibbs and free energy equations. The surface excess has been calculated using "n" = 1 in the Gibbs equation. We have already referred to the lack of unanimity among workers in the field concerning "n" when the equation is applied to salt-free ionic surfactants. It is informative to compute the molecular area of sodium dodecyl sulfate (SDS) from literature surface tension data using both "n" = 1 and "n" = 2, and then to compare these results with the generally-accepted value. Using the graphical, 25C surface tension-concentration data of Rosano and Karg (5) and the accepted CMC of 0.00813M (8), the Gibbs equation gives SDS molecular areas of 51 Å^2 ("n" = 1) and 101 Å^2 ("n" = 2) at the CMC. The accepted value appears to lie between 38 Å^2 and 40 $=^2$ at the CMC. The latter figure was obtained by direct measurement of the concentration decrease involved in the formation of a large surface area by foam generation (8). The 38 Å^2 value was calculated by the Gibbs equation using activities (22). It is obvious that the use of "n" = 2 with salt-free anionic SDS yields a molecular area approximately twice the actual value. Pethica made a similar observation (14) when he pointed out that molecular adsorptions of ionic surfactants from electrolyte-free solution calculated with "n" = 2 were approximately one-half of the surface concentrations measured by a radiotracer technique.

Conclusions

A comparison of the air-water interfacial adsorption parameters of the surfactants studied herein reveals that the $-\Delta G$ values of nonionics (-4.1 to -5.1 kcal/g mol) are considerably larger than those of anionics (-2.5 to -2.9 kcal/g mol, with the first value calculated from the sodium lauryl sulfate surface tension-concentration data of Rosano et al.). Since the larger the value of $-\Delta G$, the greater the tendency for the corresponding surface adsorption to occur, it follows that $-\Delta G$ is directly proportional to surfactant surface activity. It is to be noted that with the surfactants studied, $-\Delta G$ is inversely proportional to CMC. Hence, these results indicate that the smaller the CMC of a surfactant, the greater its surface activity. The CMC of the 15(EO) adduct of branched chain nonylphenol is four times larger than that of the 15 (EO) adduct of straight chain nonylphenol, indicating that the van der Waals attractive forces between branched hydrocarbon chains are considerably less than those between linear hydrocarbon chains.

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