Saturation Adsorption at Interfaces of Surfactant Solutions

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Abstract □ Plots of the surface or interfacial tension of aqueous surfactant solutions *versus* the logarithm of the bulk concentration of the surfactant frequently become linear at concentrations from 10 to 30% of the critical micelle concentration. According to the Gibbs equation, the surface excess concentration of the surfactant in the linear region is constant; saturation adsorption is said to exist. However, the surface or interfacial tension continues to decrease considerably with increasing bulk concentration of the surfactant throughout the saturation adsorption region until the critical micelle concentration is reached. This decrease is explained as follows. While the surface excess concentration of the surfactant reaches a constant upper limit at the onset of saturation adsorption, the total surfactant concentration in the surface layer, which consists of the surface excess concentration plus the surfactant concentration present in an equivalent volume of bulk solution, continues to increase slightly with increasing bulk concentration throughout the saturation adsorption region. As the bulk concentration approaches the critical micelle concentration, the total surface concentration of the surfactant exceeds its surface excess concentration by small but increasing amounts. Because the surfactant monolayer in the saturation adsorption region is densely packed, slight increases in the total surface concentration produce disproportionately large decreases in the surface or interfacial tension. This explanation is illustrated with experimental data.

Keyphrases □ Surface tension—decrease with increasing bulk concentration of surfactant in saturation adsorption region □ Surfactants—surface tension decrease with increasing bulk concentration of surfactant in saturation adsorption region □ Saturation adsorption region—surface tension decrease with increasing bulk concentration of surfactant

The surface or interfacial tension of aqueous surfactant solutions frequently becomes a linear function of the logarithm of the surfactant concentration when that concentration comes within ~20% of the critical micelle concentration (CMC). According to the Gibbs adsorption equation, the proportionality between the surface or interfacial tension and the logarithm of the bulk concentration of the surfactant indicates that its surface excess concentration has reached a constant value. This fact must be reconciled with the continued decrease of the surface or interfacial tension with increasing surfactant concentration until the critical micelle concentration is reached.

BACKGROUND

Plots of the surface or interfacial tension, γ, of surfactant solutions *versus* the logarithm of the surfactant concentration, c_2, commonly consist of three distinct regions as shown in Fig. 1 for surface tension. Interfacial tensions have lower values, but their curves have similar shapes (1, 2). The curve initially is nearly horizontal but turns gradually steeper as c_2 increases. Eventually, between points B and D, it becomes linear. This segment is followed by another linear segment, DE, that is practically horizontal. The concentration corresponding to point D, where the plot levels off, represents the critical micelle concentration. The surfactant concentration corresponding to point B frequently is reached at concentrations as low as 10–30% of the critical micelle concentration for surfactant adsorption at both air–water and oil–water interfaces (1–3).

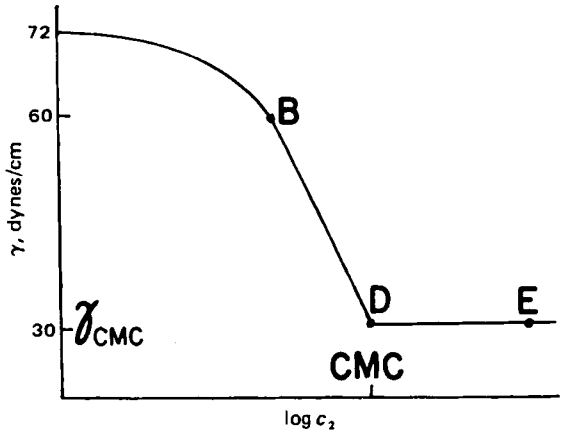

Figure 1—*Schematic plot of surface or interfacial tension* (γ) *versus logarithm of the surfactant concentration* (c_2). *The ordinate scale represents surface tension values.*

The Gibbs equation correlates the surface or interfacial tension of surfactant solutions with their bulk concentration. For nonionic surfactants, or for ionic surfactants in the presence of swamping concentrations of nonsurface-active salts with the same counterion, the equation is (1, 2):

$$\Gamma_2 = -\frac{1}{2.303RT}\frac{d\gamma}{d\log c_2} \qquad \text{(Eq. 1)}$$

where Γ_2 is the surface excess concentration, R is the gas constant (8.314×10^7 ergs/mole/°K), and T is the absolute temperature. The subscript 2 refers to the dissolved surfactant. The solution is assumed to be sufficiently dilute to use surfactant concentration instead of activity.

If a surface layer of area A in square centimeters and thickness τ in centimeters contains $m_2 + n_2$ moles of surfactant while an equal volume of solution $A\tau$ in the bulk contains m_2 moles of surfactant, the surface excess or surface excess concentration of the surfactant is:

$$\Gamma_2 = n_2/A \qquad \text{(Eq. 2)}$$

The surface excess concentration and the total surface concentration of the surfactant, $(m_2 + n_2)/A$, generally are nearly identical because, by definition, surfactants are adsorbed very strongly at interfaces, making $n_2 \gg m_2$.

Along the linear portion BD, the surface excess Γ_2 is constant because the slope $d\gamma/d\log c_2$ is constant. Saturation adsorption has been reached at point B, *i.e.*, the surface excess of the surfactant does not increase further as a result of increases in its bulk concentration beyond point B. However, the surface tension of the solution continues to decrease conspicuously with increasing bulk concentration of the surfactant until point D is reached (1–3). At first glance, these two facts, namely, a constant Γ_2 accompanied by a decreasing γ resulting from an increasing c_2, seem contradictory. In an attempt to reconcile them, it was postulated that as c_2 increases, it becomes easier to bring surfactant molecules to the surface from the progressively more concentrated bulk solution despite attainment of saturation adsorption (1). Surface tension commonly is determined by measuring the resistance to increases in surface area. The continued drop in γ with increasing c_2 along BD was ascribed mainly to the increased activity of the surfactant in the bulk phase rather than at the interface (2).

The purpose of this report is to show that the specific reason for the decrease in surface or interfacial tension of the solution with increasing

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Table I—Comparison of n_2 and m_2 in the Saturation Adsorption Region at Interfaces of Aqueous Surfactant Solutions with Air or Hydrocarbons

Surfactant	Range of Saturation Adsorption, mole/liter		$n_2 \times 10^{10}$, moles	$m_2 \times 10^{13}$, moles[b], at		$\left(\frac{100\,m_2}{n_2}\right)$, %, at		Reference
	$c_{2,L}$[a]	$c_{2,U}$[a]		$c_{2,L}$	$c_{2,U}$	$c_{2,L}$	$c_{2,U}$	
$C_{12}H_{25}O(CH_2CH_2O)_{12}H$[c]	1×10^{-5}	1.4×10^{-4}	2.15	0.02	0.28	0.0009	0.013	4,5
Potassium laurate[d]	0.0016	0.0137	4.24	3.2	27	0.076	0.64	6
Dodecylamine hydrochloride[e]	0.00062	0.0035	5.20	1.2	7	0.024	0.14	6
N-Dodecyl-β-alanine[f]	0.0002	0.001	3.73	0.4	2	0.011	0.054	7
Sodium laurate[g]	0.003	0.017	3.66	6	34	0.16	0.93	3
Sodium lauryl sulfate[h]	0.00015	0.0014	3.16	0.3	2.8	0.009	0.089	3
Sodium nonyl sulfate[h]	0.010	0.043	3.04	20	86	0.66	2.83	3

[a] $c_{2,L}$ is the lower concentration limit of the saturation adsorption range, corresponding to point B; $c_{2,U}$ is the upper limit of the saturation adsorption range, corresponding to point D or the critical micelle concentration. [b] Calculated for a layer with a thickness, τ, of 2×10^{-7} cm and an area, A, of 1 cm^2. [c] Against air. [d] At a constant pH of 10.0 and a constant potassium-ion concentration of 0.1 mole/liter, against air. [e] At a constant pH of 2.0 and a constant chloride-ion concentration of 0.1 mole/liter, against air. [f] At the isoelectric point, against air. [g] At a constant pH of 10.5 and a constant sodium-ion concentration of 0.04 mole/liter, against *n*-heptane. [h] At a constant sodium-ion concentration of 0.1 mole/liter, against petroleum spirit.

bulk concentration of the surfactant in a concentration range where saturation adsorption prevails is that beyond point B, and especially close to point D, $m_2 + n_2$ can no longer be considered equal to n_2. While the surface excess concentration Γ_2 is constant along BD, the total surface concentration $(m_2 + n_2)/A$ continues to increase moderately with increasing c_2 or m_2.

THEORETICAL

Rearrangement of Eq. 1 and integration between the limits γ, c_2 and γ_{CMC},CMC, where γ_{CMC} is the plateau surface tension along DE, yields:

$$\gamma - \gamma_{CMC} = 2.303RT\Gamma_2 \log \text{CMC} - 2.303RT\Gamma_2 \log c_2 \quad \text{(Eq. 3)}$$

The number of moles of surfactant, m_2, contained in $A\tau$ cm^3 of bulk solution is directly proportional to the bulk concentration c_2. If c_2 is expressed in moles per liter:

$$c_2 = 1000m_2/A\tau \quad \text{(Eq. 4)}$$

After substituting and transposing γ_{CMC}, Eq. 3 becomes:

$$\gamma = a - b \log m_2 \quad \text{(Eq. 5)}$$

for the region (BD) of saturation adsorption, where Γ_2 is constant. The constants a and b are equal to $\gamma_{CMC} + 2.303RT\Gamma_2 \log \text{CMC} - 2.303RT\Gamma_2 \log (1000/A\tau)$ and $2.303RT\Gamma_2$, respectively. According to Eq. 5, γ continues to decrease with increasing bulk concentration even after saturation adsorption is reached because c_2 and m_2 increase while Γ_2 and n_2 remain constant.

RESULTS

The values of m_2 at the lower and upper limits of the saturation adsorption range are compared here with the corresponding n_2 values for seven surfactants. Calculations are shown for the nonionic surfactant $C_{12}H_{25}O(CH_2CH_2O)_{12}H$. At 23° (296 °K), $d\gamma/d \log c_2$ in the region of saturation adsorption below the critical micelle concentration was reported as −12.2 dynes/cm (4, 5). Application of the Gibbs equation results in $\Gamma_2 = 2.15 \times 10^{-10}$ mole/cm^2. Hence, $n_2 = A\Gamma_2 = 2.15 \times 10^{-10}$ mole of surfactant for a surface area, A, of 1 cm^2. Saturation adsorption, shown by the linearity of the γ *versus* log c_2 plot, prevailed from the critical micelle concentration of 1.45×10^{-4} mole/liter down to at least $c_2 = 1 \times 10^{-5}$. A surface layer with a thickness, τ, of 20 Å (2×10^{-7} cm) and an area, A, of 1 cm^2 contains $m_2 = c_2A\tau/1000 = 2.0 \times 10^{-15}$ mole of surfactant if the bulk concentration, c_2, is 1×10^{-5} mole/liter but contains 2.8×10^{-14} mole if c_2 is 1.4×10^{-4}. Since $n_2 = 2.15 \times 10^{-10}$ mole, these two m_2 values represent 0.0009 and 0.013% of n_2, respectively. The increase in m_2 from point B to point D amounts to 0.013 − 0.0009 = 0.012% of n_2.

These numerical values and the corresponding data for six additional surfactant systems are listed in Table I. The lower concentration limits of the saturation adsorption range for the three oil–water interfaces probably are smaller than the values shown in the $c_{2,L}$ column since Ref. 3 listed interfacial tension values only at three or four concentrations. The values of m_2 increase by almost an order of magnitude from the lower to the upper concentration limit of the saturation adsorption region, *i.e.*, from point B to point D in Fig. 1. However, most of the m_2 values amount to <1% of n_2. Likewise, the increases in m_2 from the lower to the upper concentration limit of the saturation adsorption region represent <1% of n_2 in most cases. Systems with higher critical micelle concentration values have higher absolute values of m_2 and also higher percentage values of m_2 with respect to n_2 since all seven n_2 values are of the same order of magnitude.

The value of 20 Å for the thickness of the surface region used in the calculations was selected arbitrarily as corresponding approximately to the length of a fully extended surfactant molecule. According to Eq. 4, larger τ values would produce proportionally larger m_2 values for a given bulk concentration, thereby also increasing the percentage of m_2 with respect to the constant n_2 value proportionally.

Despite the fact that the increases in the m_2 values from the lower to the upper concentration limit of the saturation adsorption region constitute only a small fraction of the n_2 values, they are responsible for sizable decreases in surface tension, ranging from 13 dynes/cm for polyoxyethylated dodecanol (4, 5) to 21 and 22 dynes/cm for dodecylamine hydrochloride and potassium laurate (6), respectively, and to 26 dynes/cm for dodecyl alanine (7). The decreases in interfacial tension amount to only 8–13 dynes/cm, but interfacial tensions are lower than surface tensions. Furthermore, the interfacial tension values from Ref. 3 are not available for the entire range of saturation adsorption, so the actual decreases in that range probably are larger.

Evidently, once saturation adsorption is reached, small increases in the total surface concentration of the surfactant produce large decreases in surface or interfacial tension. At that point, the monolayer of surfactant molecules adsorbed at the surface or interface of the aqueous solution is packed so densely that crowding only a few additional surfactant molecules into it substantially reduces the resistance of the surface or interface against expansion in area, *i.e.*, its surface or interfacial tension.

DISCUSSION

The large decrease in surface or interfacial tension that occurs when a small percentage of additional surfactant molecules is crowded into a monolayer in the saturation adsorption region as a result of increases in c_2 and m_2 has an analogy in monomolecular films of insoluble substances spread on water. These insoluble monolayers are characterized by plots of film pressure *versus* area per molecule. Film pressure is the lowering of surface tension caused by the monolayer, *i.e.*, the difference between the surface tension of clean water and of water plus the monolayer. It represents the expanding pressure exerted by the monolayer, which opposes the surface or contracting tension of the clean surface. When a condensed monolayer is compressed beyond the point of close packing, the film pressure–area curve rises steeply. Further small reductions in the area per adsorbed molecule, the equivalent of crowding a few additional molecules into the monolayer, cause large reductions in the surface tension of the system and, hence, large increases in its film pressure (8).

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Simultaneous GLC Analysis of Salicylamide, Phenylpropanolamine Hydrochloride, Caffeine, Chlorpheniramine Maleate, Phenylephrine Hydrochloride, and Pyrilamine Maleate in Capsule Preparations

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Received November 19, 1979, from *Adcock-Ingram Laboratories, P.O. Box 2368, Johannesburg 2000, South Africa.* Accepted for publication February 2, 1980.

Abstract □ A GLC method is described for the quantitative determination of salicylamide, phenylpropanolamine hydrochloride, caffeine, chlorpheniramine maleate, phenylephrine hydrochloride, and pyrilamine maleate. The sample was dissolved in ethanol, and an aliquot of the solution was brought to dryness and treated with 0.1 ml of 4-(dimethylamino)pyridine in pyridine–acetic anhydride (1:1). The components were isolated and measured by applying 1 μl of the reaction mixture to a chromatograph equipped with a flame-ionization detector and fitted with 8% OV-101 glass columns. The accuracy was good. Dicyclohexylphthalate was used as the internal standard.

Keyphrases □ GLC, flame ionization—simultaneous analysis of salicylamide, phenylpropanolamine, caffeine, chlorpheniramine, phenylephrine, and pyrilamine, capsule preparations □ Salicylamide—GLC analysis, capsule preparations □ Phenylpropanolamine hydrochloride—GLC analysis, capsule preparations □ Caffeine—GLC analysis, capsule preparations □ Chlorpheniramine maleate—GLC analysis, capsule preparations □ Phenylephrine hydrochloride—GLC analysis, capsule preparations □ Pyrilamine maleate—GLC analysis, capsule preparations

GLC procedures have been used extensively for the determination of salicylamide (I), phenylpropanolamine hydrochloride (II), caffeine (III), chlorpheniramine maleate (IV), phenylephrine hydrochloride (V), and pyrilamine maleate (VI) as drug substances and in certain combinations, but no single method has been developed for their simultaneous quantitation. In the preparation used in this study, phenylephrine was the only active ingredient that had to be derivatized before GLC. The other components could have been chromatographed directly using a suitable liquid phase (1, 2).

The determination of phenylephrine as the trifluoroacetate derivative (3) was not applicable to this preparation. The narrow margin allowed for temperature and reaction time was not compatible with those components that gave derivatives with the same reagent. Hista and Laubach (4) showed that a combination of phenylephrine, phenyltoloxamine, chlorpheniramine, and phenylpropanolamine could be chromatographed as trimethylsilyl derivatives using bis(trimethylsilyl)acetamide. However, following the same procedure during a preliminary analysis, the chromatogram exhibited interfering additional peaks, which made the determination of some components difficult.

In this work, the problems encountered were resolved by preparing acetyl derivatives of I, II, and V and using a mixture of 4-(dimethylamino)pyridine, pyridine, and acetic anhydride as the acetylating reagent. Connors and Albert (5) reported that 4-(dimethylamino)pyridine is an excellent catalyst for the formation of acetyl derivatives. It promoted the acetylation of various hydroxyl groups under milder conditions when compared with pyridine alone (6).

EXPERIMENTAL

Apparatus—The gas chromatograph[1] was equipped with a flame-ionization detector and an electronic integrator. The glass-coil columns, 1.8 m × 2 mm, were packed with 8% OV-101 on 80–100-mesh Chromosorb W-HP.

Reagents[2]—4-(Dimethylamino)pyridine (1.2%) in pyridine was prepared weekly. Acetic anhydride also was used.

Solution Preparation—Standard solutions[3] were prepared by weighing accurately ~58, 38, 72, and 49 mg of II, IV, V, and VI, respec-

Table I—Response Factors of I–VI with Respect to the Internal Standard [a]

Compound	Response Factor	*RSD, %*
I	0.890	1.83
II	0.995	1.11
III	0.470	1.41
IV	0.677	1.28
V	0.624	1.64
VI	0.346	2.18

[a] Five solutions were prepared and 15 measurements were made for each compound.

[1] Hewlett-Packard model 5048-A.
[2] All reagents and the internal standard were from Merck, Schuchardt, West Germany.
[3] All standard solutions were prepared from BP raw materials standardized against USP and NF reference standards.

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