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Re-evaluating the Gibbs Analysis of Surface Tension at the Air/Water Interface

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Plots of surface tension vs ln[surfactant] display three regions (Figure 1):[1] Region-A, where the surface tension hardly changes with concentration; Region-B, a steep, almost linear, decline; Region-C, an abrupt leveling at the critical micelle concentration (CMC). Conventional theory assumes that the air/water interface is saturated with surfactant throughout Region-B.[2,3] It is this key assumption that allows the calculation of the area-per-molecule via application of the Gibbs equation (eqs 1 and 2) where Γ = the surface excess; $d\gamma/d(\ln c)$ = the slope of line-B; and N = Avogadro's number. If the area-per-molecule were continuously decreasing in Region-B, instead of remaining constant owing to saturation, a unique area would obviously be unattainable. The Gibbs analysis is now accepted dogma in colloid/interface chemistry as revealed by its prevalence in the textbooks[4,5] and by the hundreds of Gibbs-based areas published in the literature.[6-16] We count ourselves among the many who have innocently applied the venerable Gibbs equation to the surface tension of air/water interfaces.[17,18] The purpose of this communication is to revise current thought on the subject.

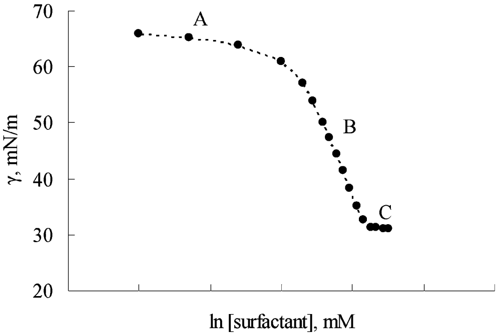

Figure 1. Three regions of a typical surface tension vs ln [surfactant] plot.

$$\Gamma = -(d\gamma/d\ln c)/(nRT) \qquad (1)$$

$$\text{Area} = 10^{16}/(N\Gamma) \qquad (2)$$

Puzzling questions emerge from the Gibbs analysis. One wonders, for example, why the surface tension remains unaltered in Region-A only to decline precipitously once saturation at the air/water interface is finally reached at the beginning of Region-B. It seems strange that the surface tension responds far more sensitively at concentrations exceeding saturation than it does while the interface is in the process of becoming saturated. The large surface tension change in Region-B is commonly explained (rather vaguely) by an "increased activity of the surfactant in the bulk phase rather than at the interface."[19] But there exists an alternative explanation that has to our knowledge not yet been explicitly considered. The adsorption might obey modified Frumkin kinetics, such as developed by Lin et al.,[20] where a plot of percent interface coverage vs concentration adopts a sigmoidal shape (Figure 2) owing to cohesive interfacial forces. The concave-upward shape of the isotherm signifies that adsorption, which is sparse at low concentrations, becomes progressively expedited as the concentration is elevated. In other words, adsorption at the air/water interface is cooperative prior to saturation when the plot finally levels off. Note that Figure 2 has an obvious mirror correspondence to the surface tension vs ln[surfactant] plot in Figure 1.

Cooperative adsorption is exactly what would be expected for a surfactant system: Initial adsorption at the air/water interface is weak, but as more and more molecules enter the interface, further adsorption becomes increasingly favorable (owing no doubt to the same attractive hydrophobic forces that cause the surfactant molecules to ultimately self-assemble into micelles). The model implies that the air/water interface is not saturated in Region-B and that, therefore, the commonplace Gibbs calculations of molecular areas (dependent upon a fortuitous linear section of the surface tension plots) are misdirected.

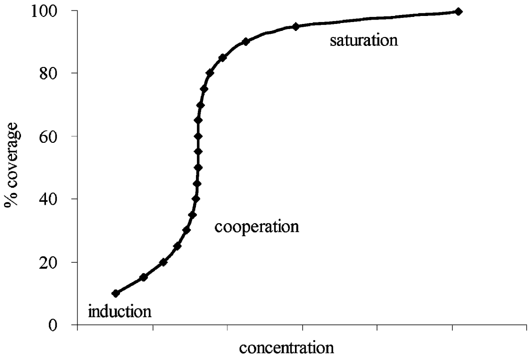

Figure 2. Example of a Frumkin adsorption isotherm (% coverage vs concn) incorporating cooperativity (see ref 20, eq 6 with a cooperativity k value of −4).

We are arguing for a continuously increasing occupancy of the interface in Region-B that corresponds smoothly to the decline in surface tension. Can one ever observe saturation of the air/water interface by surfactant? Unfortunately, micelle formation often precedes and obscures interfacial saturation. When micelles form at the CMC, additional surfactant molecules prefer to join the micelles rather than enter the interface, and the surface tension no longer decreases (Region-C in Figure 1). If the CMC lies near or below the saturation point, then the latter becomes unobservable by the surface tension method. In recent experiments, we found a rare example of a mixed surfactant system in which, according to surface tension data, the interface is saturated far below the CMC (Figure 3).[21] It is seen (arrow) that interfacial saturation lies at much lower concentrations than the CMC of the system as determined by two "bulk methods" (conductivity and NMR). The point here

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is that saturation of the interface (i.e., where the surface tension levels off unimpaired by micelle formation) is now detectable, and it appears in Region-C rather than in Region-B as assumed in the Gibbs analysis.

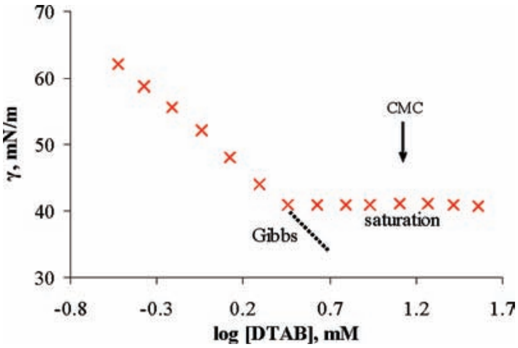

Figure 3. Plot of surface tension vs log[dodecyltrimethylammonium bromide] mixed-micellar system described in ref 21. The arrow points to the CMC of that same system as determined by conductivity and NMR. Dotted line represents predicted Gibbs behavior.

Incredulousness (however legitimate) over a saturated Region-B in the Gibbs analysis does not constitute a disproof. To obtain evidence for or against the saturation assumption, we turned to the behavior of insoluble monolayers at the air/water interface. Insoluble monolayers differ from the soluble monolayers formed from most surfactants in two ways: (a) Insoluble monolayers have the adsorbent delivered from the air phase, while soluble monolayers have the adsorbent delivered from the aqueous phase. (b) A soluble monolayer cannot be compressed because molecules under compression will simply depart from the air/water interface and enter the bulk water phase. But otherwise the morphologies of the two monolayers are similar. Thus, an insoluble monolayer of hexadecanol will have its hydroxyl in the water and its hydrocarbon tail projecting in the air, the identical situation found with a soluble monolayer of octanol.

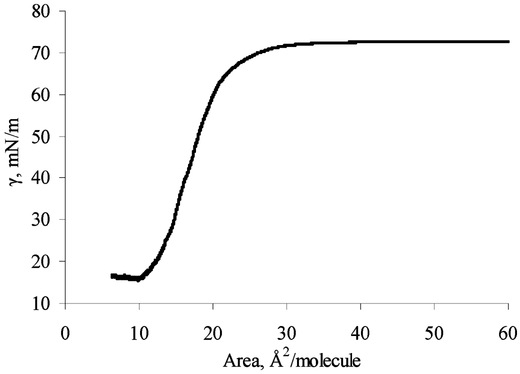

Figure 4. Plot of surface tension vs area/molecule for an insoluble monolayer of hexadecanol.

A plot of surface tension vs area-per-molecule for hexadecanol, obtained from a Langmuir surface balance, is given in Figure 4. It is seen that the surface tension has a constant "water value" of 72 mN/M between 60 and 40 Å^2 per hexadecanol molecule. But Gibbs-determined areas for single-chained surfactants fall into this range (e.g., $C_{12}H_{25}SO_3^-$ Na$^+$, 65 Å^2/mol; $C_{18}H_{37}N(CH_3)_3^+$ Br$^-$, 64 Å^2/mol; $C_{12}H_{25}Pyr^+$ Cl$^-$, 62 Å^2/mol; $C_{12}H_{25}(OC_2H_4)_4OH$, 46 Å^2/mol).[16] This means that when the Gibbs method is applied to steeply declining surface tension plots (Region-B), the resulting areas correspond, according to Figure 4, to zero surface tension change. This contradiction can be avoided by assuming cooperative binding at the air/water interface, leading to only minor adsorption at low concentrations followed by an abrupt increase in adsorption (and precipitous decline in surface activity) as the interface becomes saturated. Implied by this model is an air/water interface in Region-B that is merely filling up with adsorbent on its way toward saturation. By assuming total saturation throughout Region-B, the Gibbs analysis greatly overestimates the true areas-per-molecule at saturation.

In summary, we have shown that molecular areas calculated by applying the Gibbs equation to Region-B are based on an incorrect assumption, namely that the interface is already saturated when the surface tension first begins its precipitous decline. An alternative model, in which the adsorbent progressively and cooperatively fills the interface in Region-B, explains three observations (aside from avoiding the need to postulate the surface tension drop as occurring under saturation conditions): (a) the initial "induction" (Region-A), typical of cooperative processes; (b) why the surface tension plots are consistent with a classical adsorption isotherm (Figure 2) after correction for cooperativity effects; (c) most decisively, (when the Gibbs approach does not) why in Figure 3 the surface tension levels off at higher concentrations. Normally, the phenomenon is ascribed to micelle formation, but in this case the leveling effect occurs far below the CMC, which can be explained only by saturation subsequent to the Gibbs Region-B.

The substantial literature in this area should be reconsidered accordingly.

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