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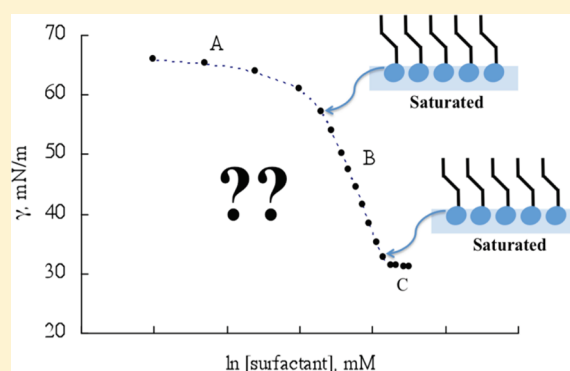
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Reply to "Should the Gibbs Analysis Be Revised?"

ABSTRACT: Plots of surface tension vs log [surfactant] show a steep linear decline until the CMC is reached. Conventional "Gibbs analysis" declares that the air/water interface is saturated with surfactant throughout this linear region, thereby enabling an area-per-molecule to be determined. We have previously provided evidence from four independent experimental methods that cast doubt on the "saturated interface" concept. In the preceding paper, Laven and de With question our results with deceptively authoritative but specious arguments devoid of any new experiments (e.g., they explain our conductance data by postulating the presence of two different coexisting micellar structures). However, consider the Gibbs analysis from strictly an intuitive standpoint. The Gibbs analysis demands that surfactant in the bulk phase (even at submillimolar concentrations) causes a dramatic decline in the surface tension of an interface that is already saturated. The Gibbs analysis also forces the conclusion that initial saturation of the interface (at the high end of the linear decline) has little effect on the surface tension. We thus maintain our position that the surface tension declines sharply because the air–water interface adsorbs more and more surfactant as surfactant is added to the bulk phase.



Plots of surface tension vs log [surfactant] display a steep linear decline (often by 30 mN/m or more) until it levels off at the CMC (region B in Figure 1). Conventional theory assumes that the air/water interface is saturated throughout this steep drop in surface tension. It is this key assumption that allows the slope of the linear decline to provide the area-per-molecule via application of the Gibbs equation (a procedure that has been commonplace in colloid chemistry for decades).¹

We have recently argued on the basis of four experimental approaches (surface tension, monolayer data, conductivity, and NMR-based diffusivity) that the steep linear decline in surface tension cannot in fact be used to obtain interfacial surface areas.^{2–4} The problem with the Gibbs method lies in the assumption that the interface is saturated throughout the linear descent so that a single discrete molecular area can be computed. If the interface were saturated throughout Region B, then why should the surface tension drop precipitously? Our answer to this "apparently odd situation"⁵ was that the interface is in fact not saturated throughout the steep decline, and that Gibbs-based calculations are, therefore, spurious. The surface tension declines, quite reasonably, because the interface is being increasingly occupied as the bulk surfactant concentration is elevated.

In the preceding paper, Laven and de With⁶ defend the classical Gibbs analysis. If one ignores their ad hominem comments (see, for example, their abstract), then what remains is a deceptively authoritative text devoid of any additional experimental data. In response, there is no need for us to repeat in detail all our experimental evidence.^{2–4} Only two experiments, based on conductivity and monolayer data, will be discussed briefly to illustrate the general tenor of the Laven and de With arguments.

We had investigated a micellar system containing dodecyltrimethylammonium bromide plus a naphthalene-trisulfonate additive (15:1). It was shown that a conductivity-based CMC (14 mM) was much higher than the break revealed by a surface

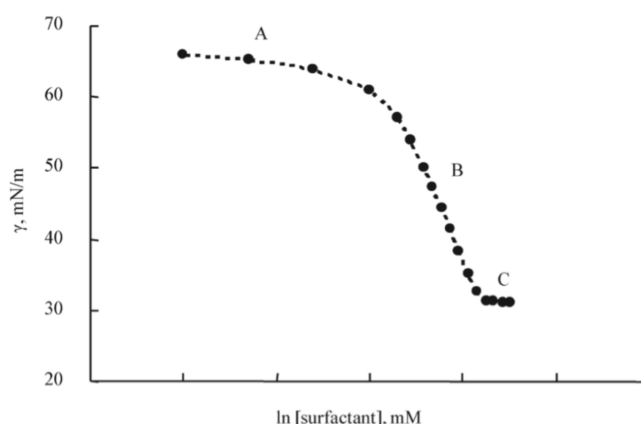


Figure 1. Three regions of a typical surface tension versus \ln [surfactant] plot. The Gibbs approach uses the linear region B to calculate molecular areas under the assumption that the interface is saturated throughout this region (otherwise a single area could not be thereby obtained).

tension-based plot (2.9 mM). We concluded that conductivity (a bulk measurement) had detected micelle formation at 14 mM, whereas the surface tension (an interfacial measurement) had detected interfacial saturation at 2.9 mM. This seems to be a rare case where saturation of the interface, unimpaired by micelle formation, has been observed.

Although we had provided a well-behaved, ordinary plot of conductivity vs [surfactant] (Figure 2, left),⁴ Laven and de With recast our data in the form of molar conductance vs log [surfactant] (Figure 2, right). Laven and de With then used their plot, with its

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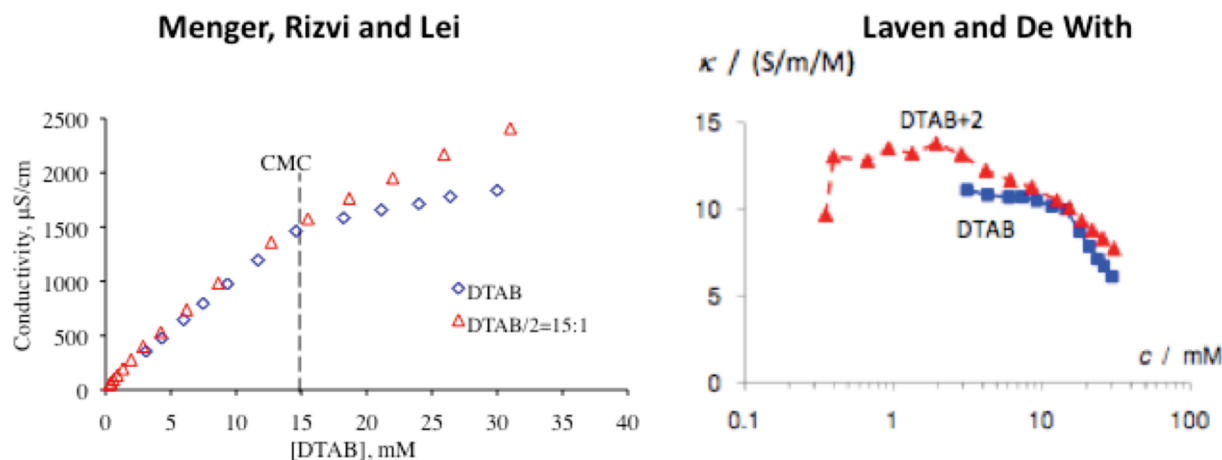


Figure 2. Left: Conductivity of DTAB and DTAB + naphthalene-trisulfonate vs [DTAB] (where DTAB = dodecyltrimethylammonium bromide) as published by us.⁴ Right: Our data refashioned by Laven and de With as molar conductance vs log [DTAB] from which they deduced the presence of two different micelles coexisting in solution. Tortured data confess to anything.

highly compressed conductance scale, to claim the presence of two CMCs. The structures of the two coexistent micellar assemblies were not specified. Yet their two-micelle theory, despite its problems with entropic considerations (not to mention Occam's razor), was cited as key evidence against our conclusions.

We also addressed the problem by directly measuring the surface tension vs area/molecule of insoluble monolayers at the air/water interface of a Langmuir surface balance. As stated in our paper,² it was assumed that the morphologies of soluble and insoluble monolayers are comparable. Thus, an insoluble monolayer of hexadecanol will have its hydroxyl in the water and its hydrocarbon tail projecting into the air—the identical situation found with a soluble monolayer of octanol. In brief, we found that by assuming total saturation throughout the linear decline in a Gibbs analysis, the true area-per-molecule is greatly overestimated.

How did Laven and de With counter this conclusion? Their main criticism is embodied in the following quote of theirs: "The Gibbs adsorption isotherm supposes equilibrium between the surfactant activities and the bulk. With the extremely small solubility of such surfactants it is doubtful whether equilibrium will ever be established between the bulk and surface within accessible time frames." Ironically, we deliberately selected amphiphiles with low water solubilities (equilibrium being an irrelevancy). As anyone who actually has worked with insoluble monolayers knows, diffusion of surfactant into the bulk aqueous subphase upon compression actually destroys the experiment. As long as one accepts a morphological relationship between soluble and insoluble monolayers, the Langmuir surface balance data support our model.

In comparing surface areas from surface tension with other methods, two scholarly papers by R. K. Thomas et al. are particularly noteworthy.^{7,8} One of the papers has the following quote: "Radio-tracer measurements generally obtain a higher coverage concentration below the critical micelle concentration (cmc) than surface tension measurements and the Gibbs equation."⁷ Although there has also been substantial disagreement between surface excesses obtained by neutron reflectivity and surface tension, disparities can be reduced by adjusting (without a rigorous justification) the prefactor in the Gibbs equation.⁷ The presence of divalent-ion contamination at the air/water interface has also been invoked to dismiss inconsistent Gibbs equation data. R. K. Thomas writes in

this regard: "In any case, even if there is an unresolvable disagreement between the two types of measurement [neutron scattering and surface tension], the neutron measurement is a direct measure of the surface excess and is the appropriate quantity to use in any discussion."⁸ We agree with this sentiment (difficult as it is, obviously, to abandon time-honored ideas).

One final point is perhaps the most incisive. The Gibbs analysis demands that surfactant in the bulk phase (even at submillimolar concentrations) causes a dramatic decline in the surface tension of a surfactant-saturated air/water interface. Equally perplexing, the Gibbs analysis demands that at the high end of Region B in Figure 1, where the interface is ostensibly saturated, the surface tension is reduced only slightly. In other words, the Gibbs analysis forces the conclusion that initial saturation of the interface has little effect upon its surface tension. In contrast, we propose that the surface tension declines sharply because the air/water interface adsorbs more and more surfactant as surfactant is added to the bulk phase. The latter model seems, apart from our experimental support, intuitively more acceptable.

Laven and de With protest loudly with the following (in order of appearance):⁶ "misunderstanding; inaccurate treatment; if properly treated; incorrect arguments; misdirected; too weak scientific basis; confusion; misunderstanding; obvious inconsistency; has no ground; misunderstanding; misinterpretation; if properly interpreted." We hope that readers will pay more attention to reason than to invective.

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