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Electrostatic Binding among Equilibrating 2-D and 3-D Self-Assemblies

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We begin with an unpublished observation that originally motivated this paper: Adding a mere 7 mol % of trianion **2** (Table 1) to aqueous dodecyltrimethylammonium bromide (DTAB) substantially lowers the latter's apparent surface-tension-based critical micelle concentration (CMC). Thus, although by itself **2** is both surface-inactive and nonaggregating, **2** shifts downward the "break" in the surface tension plots (commonly taken as the CMC).[1,2] It is as if 7 mol % **2** "seeds" micelle formation by the excess DTAB.[3] As will be shown, however, the effect is in fact unrelated to micelle "seeding". Rather, it reflects a more entangled colloidal behavior than we first realized.

Studies of an ionic amphiphile in the presence of an oppositely charged additive are common enough, but generally both components self-assemble individually, e.g., a cationic and an anionic surfactant. Such combinations tend to ion-pair,[4] resulting in a reduced headgroup area that causes spontaneous formation of stable vesicles.[5−9] When the anionic/cationic ratio is precisely unity, a precipitate is possible. Long micellar lifetimes and low surface tensions also arise from anionic/cationic interactions.[10] These interactions have been further explored at the air/water interface.[11−14] But, as mentioned, our curiosity centered around low levels of nonaggregating anionic additives, bearing one to six negative charges, in the presence of a large excess of cationic amphiphile.

Figure 1A shows a surface tension vs [DTAB] plot where a DTAB/**2** ratio was maintained at 15:1 throughout. (All solutions were optically clear; pure **2** is surface-inactive as high as 15 mM.) For comparison purposes, Figure 1B shows the corresponding plot for 5:1 DTAB/NaCl. As seen, breaks are located at 2.9 and 15 mM for DTAB/**2** and DTAB/NaCl, respectively. If conventional thought is accepted at face value, then 7 mol % of **2** lowers the CMC of DTAB by a factor of 5. Only 3 mol % of the hexanion additive **1** lowers the surface tension break point by a factor of 10 (Table 1).

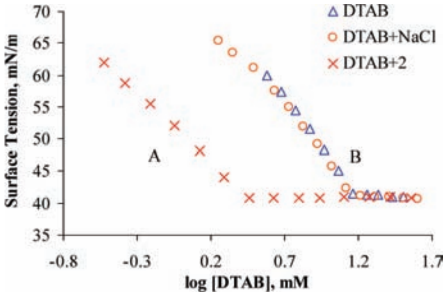
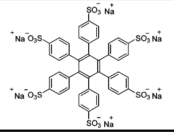
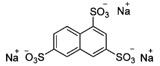
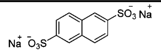
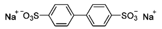
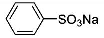
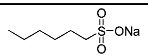


Figure 1. (A) Surface tension vs log [DTAB] in solutions with a constant DTAB/**2** ratio of 15:1. (B) Corresponding plots for DTAB and DTAB/NaCl (5:1) with no added **2**.

In Figure 2, surface tension is plotted vs log [**2**] using a constant submicellar [DTAB] of 1.8 mM. The surface tension reaches a minimum when [**2**] = 0.39 mM. Yet in the absence of **2**, a [DTAB] of 15 mM is required to lower the surface tension to a comparable value. These data suggest a profound effect of **2** upon the assembly at the air/water interface, a fact relevant to our subsequent analysis below.

Conductivity, a second major technique for measuring CMC values,[2,15] tells a different story. As seen in Figure 3, both DTAB/**2** and pure DTAB have similar plots of conductivity vs [DTAB], indicating now that **2** has a negligible effect upon the CMC. Since the surface tension and conductivity methods generally give identical CMC values, a $\mathrm{CMC}_{\text{surface tension}} = 2.9$ mM vs $\mathrm{CMC}_{\text{conductivity}} = 14$ mM constitutes a major departure from common experience.

Table 1. Properties of Anion/DTAB Self-Assemblies[a]

anion	structure	DTAB/anion[b]	"CMC" by surface tension, mM	CMC by conductivity, mM	[anion] at $\mathrm{ST}_{\min}$, mM[c]
1		30:1	1.4	15	0.016
2		15:1	2.9	14	0.39
3		10:1	3.9	14	2.5
4		10:1	3.3	14	1.2
5		5:1	10	13	31
6		5:1	8.5	12	17.4

[a] All experiments were carried out at room temperature using deionized water. DTAB and **2** were crystallized three and four times, respectively. Solutions of **1** were cloudy from 0.7−13 mM DTAB; all other solutions were optically clear. [b] Ratios were changed to keep anion/DTAB charge-ratios constant. [c] Anion concentration at minimum surface tension (with [DTAB] = 1.8 mM).

10.1021/ja902174g CCC: $40.75

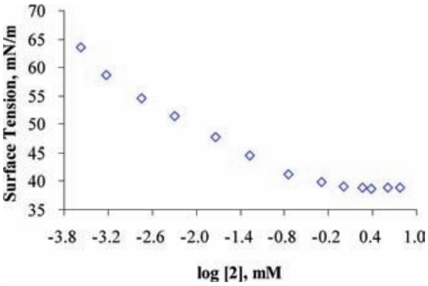


Figure 2. Surface tension vs log [**2**] at a constant submicellar [DTAB] of 1.8 mM.

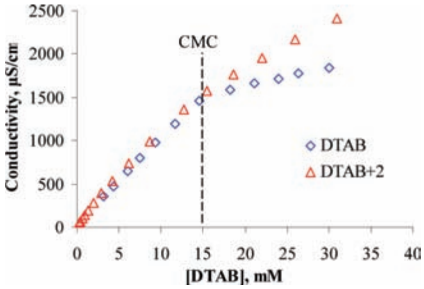


Figure 3. Conductivity vs [DTAB] and vs DTAB/**2** = 15:1 showing no alteration in the CMC by **2**.

Note that all anionic additives listed in Table 1 likewise display method-based inequalities with magnitudes directly dependent upon the charge content of the anions.

Classical theory has it that sharp breaks in surface tension plots, such as in Figure 1, stem from the following:[16] Surface tension declines as added surfactant adsorbs to the air/water interface. At some point (i.e., the CMC) micelles begin to assemble. Since additional surfactant molecules then prefer to join the micelles rather than bind further to the air/water interface, the surface tension plot levels off abruptly. But our data support an entirely different mechanism: According to Figure 1A, when a mixed monolayer of absorbed DTAB/**2** reaches a surface tension minimum at 41 mN/m, the interface becomes saturated. Consequently, the plot levels off at 2.9 mM DTAB, prior to any micelle formation. Since at saturation the surface tension has already reached its minimum, micelles that form at 15 mM DTAB are never detected by surface tension. Normal micelle formation at 15 mM is, however, revealed by a "bulk" property such as conductivity (Figure 2). A schematic of binding to the 2-D air/water interface is given in Figure 4.

Pulse gradient spin echo NMR ("diffusion NMR") confirms the preceding model. PGSE-NMR provides diffusion coefficients which, when plotted vs the reciprocal DTAB concentration (not shown), give lines intersecting at a CMC of ~14 mM with or without added **2**. Thus, both PGSE-NMR and our other "bulk" method, conductivity, affirm that Figure 1 represents solely an interfacial effect. NMR studies also show that the diffusion coefficient of **2** decreases from 4.5×10^{-10} m^2/s in water to 0.80×10^{-10} m^2/s in 15:1 DTAB/**2** at 32 mM DTAB. Thus, **2** binds to the 3-D micelles, following saturation of the 2-D air/water interface, but the CMC is hardly affected.

In summary, rather than reflecting the early "seeding" of DTAB micelles, Figure 1A reveals entry of trianions into the air/water interface. Micellization at higher DTAB concentrations is unaffected by the trianions, as seen from Figure 3, although diffusion NMR shows that the trianions do indeed bind to the micelles. Lack of a CMC effect on the micelles can ostensibly be attributed in part to the small number (3−4) of trianions per micelle. Geometric considerations may also play a role. As shown in Figure 4, large, flat multianionic species can readily insert into a gaseous 2-D monolayer. But they probably bind loosely and tangentially to a spherical micelle surface so as to avoid penetration deep into the Stern layer and, thereby, cause an unfavorable chain spreading. In any event, the mechanism serves as a cautionary note: The sharp "leveling off" routinely seen in surface tension-based "CMC plots" need not in fact attest to micelle formation. It is hardly the first time that a time-honored notion falls victim to the malleability of science.

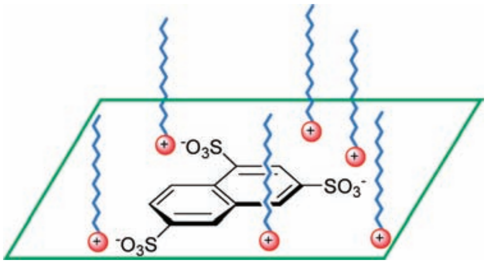


Figure 4. Schematic showing a trianion absorbed at the air/water interface in which DTAB molecules are present.

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Supporting Information Available: Synthetic procedures, characterizations of new compounds, and detailed descriptions of experimental methods. This material is free of charge via the Internet at http://pubs.acs.org.

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