Surfactant Adsorption Parameters from Surface Tension Measurements

An interesting laboratory project "Surfactant Adsorption: A Revised Physical Chemistry Lab" was recently presented by Bresler and Hagen in this *Journal (1)*. These authors describe the determination of the critical micelle concentration (CMC) and of the molecular cross-sectional area and equilibrium constant for adsorption of the surfactant molecule at the air–water interface from surface tension measurements. The surfactant studied was Igepal CO-630, $C_9H_{19}C_6H_4(OC_2H_4)_nOH$, with $n = 9$ (average value due to polydispersity). An important aspect of this project, as stated by the authors, is the introduction of the students to nonlinear curve fitting techniques, by means of Excel's Solver package. The same experimental project has been used regularly and successfully in our physical chemistry laboratory for about two decades *(2)*, the only difference being that another closely related nonionic surfactant is studied: Triton X-100, $C_8H_{17}C_6H_4(OC_2H_4)_nOH$, with $n = 9.5$ (average value).

Based on my experience, I would like to comment on two aspects of Bresler and Hagen's project. First, as stated in ref *1*, the surface tension of the solutions with concentrations lower than the CMC is well described by the Szyskowski equation

$$\gamma = \gamma_0 - \frac{RT}{\omega}\ln\left(1 + K_{\text{ad}}\,C\right)$$

where γ is the surface tension, γ_0 is the surface tension of pure water, ω is the molar cross-sectional area, K_{ad} is the equilibrium constant for adsorption of the surfactant molecule at the air–water interface, and C is the molar concentration. However, even for fairly low surfactant concentrations and owing to the large value of the adsorption equilibrium constant, this equation reduces to

$$\begin{aligned}\gamma &= \left(\gamma_0 - \frac{RT}{\omega}\ln K_{\text{ad}}\right) - \frac{RT}{\omega}\ln C \\ &= \left(\gamma_0 + \frac{\Delta_{\text{ad}}G^\circ}{\omega}\right) - \frac{RT}{\omega}\ln C\end{aligned}$$

Hence from a linear plot of γ versus $\ln C$ both $\Delta_{\text{ad}}G^\circ$ and ω can be determined, as γ_0 is known. Indeed, from the fit given in the caption of Figure 2 in ref *1*,

$$\gamma\Big/\left(\text{mN m}^{-1}\right) = 60.5 - 7.72\ln\left(C/\mu\text{M}\right)$$

or alternatively rewritten as

$$\gamma\Big/\left(\text{N m}^{-1}\right) = -46.2\times10^{-3} - 7.72\times10^{-3}\ln\left(C/\text{M}\right)$$

Using $\gamma_0 = 72 \times 10^{-3}$ N/m (298 K), one obtains $\omega = 3.2 \times 10^5$ m^2/mol and $\Delta_{\text{ad}}G^\circ = -38$ kJ/mol, well within the experimental errors reported. In this way, even for the lowest concentration used, $K_{\text{ad}}C >> 1$ and the error due to the linearization procedure is much smaller than the experimental error, as can be seen from the residuals in Figures 2 and 3 in ref *1*. The message for the students is that *nonlinear fitting is preferable in general, but may not be mandatory*. Furthermore, even if nonlinear fitting is the final step, linearization as a preliminary procedure is an easy way to obtain good initial estimates for the parameters *(3)*, a problem faced by the students in Bresler and Hagen's project *(1)*.

Second, above the CMC, the surface tension should be nearly constant, as the monomer concentration stabilizes and added detergent only increases the micellar concentration, a fact that does not significantly affect the monomer adsorption equilibrium *(4)*. A continuous decrease of the surface tension is however observed in Figure 2 in ref *1*, although less marked than for the concentrations below the estimated CMC (39 μM). The published CMC range for Igepal CO-630, not reported in ref *1*, is 50–80 μM *(5)*, in agreement with the value given by the manufacturer, 5×10^{-3}% (80 μM) *(6)*.

Literature Cited

1. Bresler, M. R.; Hagen, J. P. *J. Chem. Educ.* **2008,** *85,* 269–271.
2. Physical Chemistry Laboratory Guide (in Portuguese), IST: Lisbon, 2008 (latest edition); PDF version available upon request.
3. Sarova, G.; Berberan-Santos, M. N. *J. Phys. Chem. B* **2004,** *108,* 17261–17268.
4. Rosen, M. *Surfactants and Interfacial Phenomena,* 3rd ed.; Wiley-Interscience: Hoboken, NJ, 2004; pp 62–64.
5. Guerrero-Martínez, A.; González-Gaitano, G.; Murciano E. M.; Tardajos, G. *J. Incl. Phenom. Macrocycl. Chem.* **2007,** *57,* 251–256.
6. Rhodia, Igepal CO-630 Product Data Sheet.

Supporting JCE Online Material

http://www.jce.divched.org/Journal/Issues/2009/Apr/abs433_1.html

Keywords; Full text (HTML and PDF) with link to cited *JCE* article

Mário N. Berberan-Santos
Centro de Química-Física Molecular
Instituto Superior Técnico
Universidade Técnica de Lisboa
1049-001 Lisboa, Portugal; *berberan@ist.utl.pt*