# COMMENTS

## Comment on "Phase Transition in Adsorption Layers at the Water/Hexane Interface"

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Sharp inflection in the surface tension $\gamma$ vs surfactant concentration $c$ isotherms accompanied by an increase of the isotherm slope has been ascribed to a phase transition between two states at the interfaces.[1-3] However, Fainerman and Miller have recently concluded that this explanation in refs [1-3], although in agreement with the van der Waals model, contradicts with both the physical essence of the condensation phenomenon and the Gibbs equation, and discussed this contradiction in detail.[4] Their claims are summarized as follows. "The interpretation of the experimental data by using the Gibbs equation in the following form (eq 4 in ref 4)

$$\Gamma = -\frac{1}{RT}\frac{d\gamma}{d(\ln c)} \tag{1}$$

is erroneous because the $\gamma(c)$ and $\Pi(A)$ isotherms are incompatible from a thermodynamic point of view. This equation is valid only in the region that corresponds to concentrations lower than the critical concentration, whereas for concentrations higher than the critical one, the Gibbs equations *should* correctly read (eq 5 in ref 4)

$$\Gamma_\Sigma = \Gamma_1 + \Gamma_n = -\frac{1}{RT}\frac{d\gamma}{d(\ln c)} \tag{2}$$

For monolayers in a condensed state, the value of $n$ is very high so that the adsorption of aggregates $\Gamma_n$ can be neglected. Therefore, the adsorption corresponding to states below the critical concentration should be approximately the same as the adsorption of monomers immediately above the critical concentration. It then follows that the phase transition could not be identified from an inflection point in the $\gamma(c)$ isotherms because (at least, in the first approximation) in the phase transition point the condition $d\gamma/d(\ln c) = $ const holds. In refs 1-3, the existence of a condensation in the adsorption monolayer of FC12OH (1,1,2,2-tetrahydroperfluorododecanol), C18-OH (1-octadecanol), FC10OH (1,1,2,2-tetrahydroperfluorodecanol), and C20OH (1-icosanol) at the water/hexane interface was proved by the analysis of the $\gamma$ vs $c$ isotherms, based on the Gibbs eq 1. However, this analysis is not completely correct, as contradiction exists between the experimental results and their theoretical interpretation. A recent theoretical model that accounts for the aggregation of molecules in adsorption layer [5,6] predicts critical surfactant concentration for aggregation lower than those calculated in refs 1-3 from the Gibbs eq 1, whereas the observed pronounced inflection in $\gamma(c)$ isotherms does not correspond to any aggregation but rather to the saturation of the monolayer by aggregates and monomers."

That is to say, Fainerman and Miller insist that the Gibbs equation given by eq 2 should be used in the analysis of surface tension data in the presence of aggregates at the interface and the thermodynamic analysis of the surface tension data by the Gibbs equation, eq 1, does not indicate a phase transition (or onset of aggregate formation) at the interface without using an equation of state of the adsorbed film. We recognize that there are some cases in which an increase of the slope of the $\gamma$ vs $c$ is not so sharp that the discontinuous change in the adsorption of surfactant is not observed. In these cases, the aggregation number of domains may be so small that the increase in the slope does not correspond to a first-order phase transition but rather to a domain formation having a small aggregation number as pointed out by Israelachvili.[7] However, the claims of Fainermann and Miller seem to be independent of these situations.

Their claims are based on eq 2. However, eq 2 is incorrect. Here let us demonstrate by using very fundamental thermodynamic arguments that eq 1 is correct with the definition of the adsorption (p 8474 in ref 4)

$$\Gamma = \Gamma_1 + n\Gamma_n \tag{3}$$

in the presence of aggregates of $n$-mer.

Let us consider the two-phases, A and B, and three component systems, a, b, and 1. Here a and b are the solvent components of the phases A and B, and 1 is a surface-active solute. For the simplicity of discussion as is done in ref 4, we assume that solute molecules are nonionic, dissolved ideally as monomers only in the phase A, and can exist not only as monomer but also as aggregate of $n$-mer at the A/B interface. The Gibbs energy of the whole system $G$ is given by

$$dG = -S\,dT + V\,dp - \sigma\,d\gamma + \mu_a\,dn_a + \mu_b\,dn_b + \mu_1\,dn_1 + \mu_n\,dn_n \tag{4}$$

and the corresponding Gibbs−Duhem equation by

$$\sigma\,d\gamma = -S\,dT + V\,dp - n_a\,d\mu_a - n_b\,d\mu_b - n_1\,d\mu_1 - n_n\,d\mu_n \tag{5}$$

respectively, where $\mu_i$ and $n_i$ are the chemical potential and the number of moles of species $i$, and $\sigma$ is the area of the A/B interface. The Gibbs−Duhem equations per unit volume for the bulk phases A and B are, respectively, written as

$$0 = -s^A\,dT + dp - c_a^A\,d\mu_a - c_b^A\,d\mu_b - c_1^A\,d\mu_1 \tag{6}$$

and

$$0 = -s^B\,dT + dp - c_a^B\,d\mu_a - c_b^B\,d\mu_b \tag{7}$$

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where $s^\alpha$ and $c_i^\alpha$ are the entropy and the number of moles of species $i$ in the phase $\alpha$. Substituting eqs 6 and 7 multiplied, respectively, by undetermined multipliers $l^A$ and $l^B$ into eq 5, we have

$$d\gamma = - s^\sigma dT + v^\sigma dp - \Gamma_a^\sigma \, d\mu_a - \Gamma_b^\sigma \, d\mu_b - \Gamma_1^\sigma \, d\mu_1 - \Gamma_n^\sigma \, d\mu_n \quad (8)$$

Here introduced are the surface excess concentration of species $\Gamma_i^\sigma$ and the entropy $s^\sigma$ per unit surface area defined by

$$\Gamma_i^\sigma = n_i/\sigma - l^A c_i^A - l^B c_i^B, \quad i = a,b,1,n \quad (9)$$

and

$$s^\sigma = S/\sigma - l^A s^A - l^B s^B \quad (10)$$

Here it should be noted that the surface excess concentration of aggregates is given by putting $c_n^A = c_n^B = 0$ as

$$\Gamma_n^\sigma = n_n/\sigma \quad (11)$$

The values of $l^A$ and $l^B$ are determined by a way to choose the dividing surface(s), e.g., according to the Gibbs way ($v^\sigma = 0$ and $\Gamma_a^\sigma = 0$), the Hansen way ($\Gamma_a^\sigma = 0$ and $\Gamma_b^\sigma = 0$),[8,9] and so on. However, this is not essential with respect to the present context. By choosing the latter one,[8,9] eq 8 is written as

$$d\gamma = - s^H dT + v^H dp - \Gamma_1^H \, d\mu_1 - \Gamma_n^H \, d\mu_n \quad (12)$$

Here the surface excess concentration of monomer and that of $n$-mer are, respectively, given by

$$\Gamma_1^H = n_1/\sigma - l^{A,H} c_1^A \quad (13)$$

and

$$\Gamma_n^H = n_n/\sigma \quad (14)$$

where $l^{A,H}$ is determined by solving simultaneously the two equations:

$$\Gamma_a{}^H = n_a/\sigma - l^{A,H} c_a^A - l^{B,H} c_a^B = 0 \quad (15)$$

and

$$\Gamma_b{}^H = n_b/\sigma - l^{A,H} c_b^A - l^{B,H} c_b^B = 0 \quad (16)$$

Since the chemical potentials of the species are uniform throughout the system and also $n$-mer is in equilibrium with monomer at the interface, the chemical potential of $n$-mer at the interface $\mu_n$ is given by the chemical potential of monomer in the phase A or at the interface $\mu_1$ as

$$\mu_n = n\mu_1 \quad (17)$$

Substituting eq 17 into eq 12, we have

$$d\gamma = - s^H dT + v^H dp - (\Gamma_1^H + n\Gamma_n^H) \, d\mu_1 \quad (18)$$

Therefore the slope of the experimental surface tension $\gamma$ vs surfactant concentration $c$ curve is related to the surface excess concentration of surfactant molecules by

$$\Gamma = \Gamma_1^H + n\Gamma_n^H = - \left(\frac{\partial\gamma}{\partial\mu_1}\right)_{T,p} = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial(\ln c)}\right)_{T,p} \quad (19)$$

Equation 19 clearly shows that the slope of the $\gamma$ vs $c$ curve does not give the total surface excess concentration of the chemical species of surfactant $\Gamma_\Sigma = \Gamma_1^H + \Gamma_n^H$, but does the total surface excess concentration of surfactant molecules as monomer basis $\Gamma = \Gamma_1^H + n\Gamma_n^H$.

Therefore it is important to note that the slope of the $\gamma$ vs $c$ curve counts all the surfactant molecules at the interface whether they are in monomeric or aggregate form and whether the size of the aggregate is small or large. The slope is expected to change gradually from the onset of the aggregate formation for small $n$, but very sharply and discontinuously at the onset of it, like a first-order phase transition at the interface, for very large $n$. The recent works on the monolayers of $FC_{12}OH$ at the hexane/water interface by using synchrotron X-ray scattering[10] supports this thermodynamic view on the phase transition of $FC_{12}OH$ and therefore the analysis based on eq 19.

Fainerman and Miller have claimed, on the basis of eq 2, that the observed pronounced inflection in $\gamma(c)$ isotherms in refs 1−3 does not correspond to any aggregation. However, as described above, we believe that eq 2 is not correct and therefore their claims are also not correct.

**References and Notes**

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