

Interpretation of Gibbs Equation for the Case of Phase Transition in Adsorption Layers

V. B. Fainerman[†] and Reinhard Miller^{*,‡}

International Medical Physicochemical Centre,
Donetsk Medical University, Prospekt Ilischa 16,
83003 Donetsk, Ukraine, and Max-Planck-Institut für
Kolloid- und Grenzflächenforschung, Max-Planck-Campus,
D-14476 Golm, Germany

Received: February 6, 2002

It was shown by Aratono et al.¹ in a comment regarding ref 2 that, also for phase transitions in the surface layer, the form of the Gibbs' equation is the same as in the case when no phase transitions occur,

$$\Gamma = \Gamma_1 + n\Gamma_n = -\frac{1}{RT} \frac{d\gamma}{d(\ln c)} \quad (1)$$

Aratono et al.¹ argued that the equation proposed by us² for the transcritical region (in respect to bulk concentrations and adsorptions)

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

is invalid. We consider eq 1 to be rigorous enough for the choice of the dividing surface according to the models by Gibbs and Hansen. However, for another choice of the dividing surface, in particular that after Lucassen-Reynders, the Gibbs' equation does not coincide with eq 1. We want to discuss this problem here in more detail.

The position of the dividing surface according to Lucassen-Reynders is chosen by a convention which results in positive values for all adsorptions, including that of the solvent.^{3,4} For this choice^{3,5} the total adsorption of solvent (index $i = 0$) and surfactants ($i = 1/m$) is constant and equal to

$$\sum_{i=0}^m \Gamma_i = 1/\omega = \Gamma_\infty \quad (3)$$

For a saturated monolayer ($\sum_{i=1}^m \Gamma_i = 1/\omega$), the dividing surface defined by the constant-sum convention coincides with the dividing surface of the Gibbs convention, for which $\Gamma_0 = 0$.

It should be noted that the theoretical models which involve the concept of the Lucassen-Reynders' dividing surface, along with Buttler's equation,⁶ are extremely efficient in deriving equations of state of the adsorption layers and adsorption isotherms for various systems. The method was employed to derive almost all known equations which describe the solutions of individual surfactants of various nature, mixtures of ionic and nonionic surfactants (also for the case when the molar areas of the components are different), proteins, and also systems which undergo reformation, reorientation, or aggregation in the surface layer.^{7–12} Moreover, the basic equations for molecular aggregation in a surface layer, discussed in ref 2, were

derived in refs 11 and 13 for the case of the Lucassen-Reynders' dividing surface. Unfortunately, this fact was not mentioned in the criticism by Aratono et al.¹

For the solution of a single surfactant, if aggregation in the surface layer does not take place, condition (3) reads:

$$\Gamma_0 + \Gamma_1 = 1/\omega_1 = \Gamma_1^\infty \quad (4)$$

Introducing eq 4 into the Gibbs' adsorption equation for the case of $(m + 1)$ -components at constant pressure and temperature,

$$d\gamma = - \sum_{i=0}^m \Gamma_i d\mu_i \quad (5)$$

one obtains

$$d\gamma = - \Gamma_1 d\mu_1 - (\Gamma_1^\infty - \Gamma_1) d\mu_0 \quad (6)$$

As the chemical potential in the solution bulk can be approximately expressed by

$$\mu_0 = \mu_0^* + RT \ln(1 - x_1) \quad (7)$$

(where x_1 is the molar fraction of the surfactant in the solution bulk), and $d\mu_0 = -RT dx_1/(1 - x_1) \cong -RT dx_1$, it follows from eq 6 that

$$d\gamma = - \Gamma_1 RT d(\ln c) - (\Gamma_1^\infty - \Gamma_1) RT dx_1 = - (\Gamma_1 + (\Gamma_1^\infty - \Gamma_1)x_1) RT d(\ln c) \cong - \Gamma_1 RT d(\ln c) \quad (8)$$

The last equality is valid for the condition $x_1 \ll 1$. Therefore, for the solution of a single surfactant, if no interfacial aggregation occurs, the choice of the dividing surface after Lucassen-Reynders ($\Gamma_0 \neq 0$), quite expectedly, leads to the same Gibbs' adsorption equation as that obtained for the choice of the dividing surface which requires $\Gamma_0 = 0$. However, for the case of interfacial aggregate formation the situation is significantly different.

For a mixture of surfactants with different molar areas, the value of ω in eq 3 is determined as the weighted average over the adsorptions,^{11,13–15}

$$\omega = (\sum_{i \geq 1} \Gamma_i \omega_i) / (\sum_{i \geq 1} \Gamma_i) \quad (9)$$

When both monomers and aggregates (n -mers) are present in the surface layer, one obtains

$$\omega = \frac{\omega_{11} + n\omega_1 \Gamma_n}{\Gamma_1 + \Gamma_n} \quad (10)$$

Introducing eq 10 into eq 3 one obtains the expression for the adsorption of the solvent,

$$\Gamma_0 = \frac{1}{\omega} - \Gamma_1 - \Gamma_n = \frac{\Gamma_1 + \Gamma_n}{\omega_1 \Gamma_1 + n\omega_1 \Gamma_n} - \Gamma_1 - \Gamma_n = (\Gamma_1 + \Gamma_n) \frac{1 - \theta}{\theta} \quad (11)$$

Here $\theta = (\Gamma_1 + n\Gamma_n)\omega_1$ is the total coverage of the surface

* Corresponding author.

[†] International Medical Physicochemical Centre, Donetsk Medical University.

[‡] Max-Planck-Institut für Kolloid- und Grenzflächenforschung.

layer by monomers and aggregates. Assuming equilibrium between monomers and aggregates ($\mu_n = n\mu_1$), and using eqs 7 and 10, one can represent the generalized Gibbs' eq 5 in the form

$$d\gamma = -\Gamma_1 d\mu_1 - n\Gamma_n d\mu_n - (\Gamma_1 + \Gamma_n) \frac{1-\theta}{\theta} d\mu_0 = -\left(\Gamma_1 + n\Gamma_n - (\Gamma_1 + \Gamma_n) \frac{1-\theta}{\theta} x_1\right) RT d(\ln c) \quad (12)$$

In contrast to eq 8, the last term on the right-hand side of eq 12 cannot be neglected, because θ in the denominator approaches zero at small adsorption values. As the sign of this term is opposite to the sign of the other terms on the right-hand side, the slope of the γ vs $\ln c$ isotherm for the case of aggregation is lower than that calculated from the first two terms in eq 12, i.e., from eq 1.

Equation 12 can be presented in more detail, noting that under equilibrium conditions the chemical potentials in the solution bulk are equal to those in the surface layer, i.e., $\mu_i = \mu_i^s$. Using condition (3) one can express the molar fractions of the monolayer components via the surface fractions.^{3-5,7-13}

$$\sum_{i=0}^m x_i^s = \sum_{i=0}^m \omega_i \Gamma_i = \sum_{i=0}^m \theta_i = 1 \quad (13)$$

Therefore, one can obtain approximate expressions for the chemical potentials of the solvent and surfactant in the surface layer,

$$\mu_0^s = \mu_0^{s*} + RT \ln(1 - \theta); \mu_1^s = \mu_1^{s*} + RT \ln \theta \quad (14)$$

where $\theta = (\Gamma_1 + n\Gamma_n)\omega_1$. Differentiation of eq 14 with respect to θ yields the expression for the derivative $d\mu_0/d\mu_1$,

$$\frac{d\mu_0^s}{d\mu_1^s} = \frac{d\mu_0}{d\mu_1} = -\frac{\theta}{1-\theta} \quad (15)$$

Introducing the derivative (15) into eq 12 we obtain:

$$d\gamma = -\Gamma_1 d\mu_1 - n\Gamma_n d\mu_n - (\Gamma_1 + \Gamma_n) \frac{1-\theta}{\theta} d\mu_0 = -\Gamma_n(n-1)RT d(\ln c) \quad (16)$$

It is seen from this equation that, for bulk concentrations in the transcritical region near the critical aggregation (cluster formation) concentration c_c , the derivative $d\gamma/d(\ln c)$ is approximately zero, because in this region $\Gamma_n(n-1) \cong \Gamma - \Gamma_1 \cong 0$. This shows that the slope of the γ vs c isotherm in the transcritical region is essentially lower than the value predicted earlier from our eq 2. This result is quite consistent with our previous calculations using an equation of state and adsorption isotherm for the formation of large clusters, see Figures 3 and 4 in ref 16.

Equation 2 was derived using an "indirect" method: via the analysis of equations of state and adsorption isotherms presented in refs 2 and 16. Let us first illustrate the adequacy of this approach for solutions of single surfactants, using the following equations of the Szyszkowski-Langmuir model:

$$\Pi = \gamma_0 - \gamma = -\frac{RT}{\omega_1} \ln(1 + \theta_1) \equiv \frac{RT}{\omega_1} \ln(1 + bc) \quad (17)$$

$$\theta_1 = \frac{1}{\omega_1} \frac{bc}{1+bc}; bc = \frac{\theta_1}{1-\theta_1} \quad (18)$$

where $\theta_1 = \Gamma_1\omega_1$. Calculating the derivatives of $d\gamma/dc$ from eq 17 and $d\theta_1/dc$ from eq 18, respective algebraic transformations yield the ordinary Gibbs' equation for the solution of a single surfactant:

$$d\gamma = -\Gamma_1 RT d(\ln c) \quad (19)$$

For the formation of infinitely large clusters (two-dimensional condensation in the surface layer), the equations of state and adsorption isotherm were derived in ref 16:

$$\Pi = -\frac{RT\theta_c}{\omega_1\theta} \ln(1 - \theta) \quad (20)$$

$$bc = \frac{\theta}{(1-\theta)^{\theta_c/\theta}} \quad (21)$$

where $\theta = (\Gamma_1 + n\Gamma_n)\omega_1$ is the total surface layer coverage and $\theta_c = \Gamma_1\omega_1$ the coverage with monomers to the onset of the two-dimensional condensation. An exact solution for the derivative $d\gamma/d(\ln c)$ from eqs 20 and 21 can be obtained only for relatively small θ values. Retaining only the two leading terms in the series expansion of the logarithmic factor in eq 20 and the denominator of eq 21, one obtains the approximate relations

$$\Pi = -\frac{RT\theta_c(1 + \theta/2)}{\omega_1} \quad (22)$$

$$bc = \theta(1 + \theta_c) \quad (23)$$

The derivative $d\gamma/dc$ from eq 22, and $d\theta/dc$ from eq 23, together with some algebraic transformations, gives

$$d\gamma = \frac{\Gamma_c bc}{(1 + \theta_c)} = -\frac{\theta_c}{2} \Gamma RT d(\ln c) \quad (24)$$

Equation 24 differs from eq 1 in the factor of $\theta_c/2$. If the value $\theta_c/2$ is close to zero, the dependence of γ vs $\ln c$ immediately above the critical point ($c > c_c$) is almost parallel to the abscissa. It was shown above that a similar behavior is predicted also by eq 16. In this respect, eq 2 resembles eq 1 more closely, because it does not predict a zero slope above the critical point. This equation was derived in best agreement with eqs 20 and 21 in the region of medium and high values of θ and θ_c . It is seen from the detailed analysis presented here, that eq 2, similarly to eq 1, overestimates the slope of the isotherm γ vs $\ln c$ in the region of small θ and θ_c values.

In summary, it was shown that different models for the surface layer (i.e., for a different choice of the dividing surface) can result in different forms of the Gibbs' equation for the case of aggregation in the surface layer. The final decision about the correct choice can be done on the basis of accurate experimental data only. We strongly believe that the majority of the experimental data (in addition to the results presented in refs 2 and 16, the results for dodecanol solutions reported in¹⁷ also should be mentioned) indicate that at the onset of the phase transition in the surface layer the γ vs $\ln c$ dependence get a much smaller slope, and in some cases this curve is parallel to the abscissa axis. These facts could be regarded as evidence for the deficiency of approaches based on the Gibbs equation using the choice of the dividing surface according to the condition $\Gamma_0 = 0$. It was mentioned yet by Rusanov¹⁴ that the interpretation of results obtained by this method is quite ambiguous in cases of transitions in the bulk/surface (including

aggregation). It is also well-known that the Gibbs equation is not able to adequately describe macromolecular systems, in particular, proteins. More precisely, results from this equation cannot be used for a correct data interpretation. Note that aggregates in the surface layer are essential for macromolecules. For example, when the Π vs $\ln c$ isotherm for BSA (a globular protein, which is almost unable to change the conformation in the surface layer), according to the data first reported in ref 18 and confirmed in a number of subsequent publications, are interpreted in the isoelectric point, are processed via the Gibbs equation,¹⁹ the BSA adsorption value amounts to about 300 mg/m². At the same time, the directly measured adsorption is 100 times lower. Moreover, the two-dimensional solution theory based on the approach proposed in refs 3–5 provides a satisfactory description of the steep shape of Π vs $\ln c$ isotherm with ordinary values of the protein adsorption.¹⁰

Finally, we thank M. Aratono and co-workers for their interest in our work and the criticism, which was useful in view of a clearer understanding of some details of this complicated and still not completely solved problem.

References and Notes

- (1) Aratono, M.; Hayami, Y.; Takiue, T. Comments on "Phase Transitions in Adsorption Layers at the Water/Hexane Interface" *J. Phys. Chem. B* **2002**, *106*, 4560.
- (2) Fainerman, V. B.; Miller, R. *J. Phys. Chem. B* **2000**, *104*, 8471.
- (3) Lucassen-Reynders, E. H.; van den Tempel, M. Proceedings of the IVth International Congress on Surface Active Substances, Brussels, 1964.
- (4) Joos, P. *Bull. Soc. Chim. Belg.* **1967**, *76*, 591.
- (5) Lucassen-Reynders, E. H. *J. Phys. Chem.* **1966**, *70*, 1777.
- (6) Butler, J. A. V. *Proc. R. Soc., Ser. A* **1932**, *138*, 348.
- (7) Lucassen-Reynders, E. H. In *Anionic Surfactants (Physical Chemistry of Surfactant Action)*; Lucassen-Reynders, E. H., Ed.; Marcel Dekker Inc.: New York-Basel, 1981; p 1.
- (8) Lucassen-Reynders, E. H. *Prog. Surf. Membr. Sci.* **1976**, *10*, 253.
- (9) Lucassen-Reynders, E. H.; Lucassen, J.; Giles, D. *J. Colloid Interface Sci.* **1981**, *81*, 150.
- (10) Lucassen-Reynders, E. H. *Colloids Surf., A* **1994**, *91*, 79.
- (11) Fainerman, V. B.; Lucassen-Reynders, E. H.; Miller, R. *Colloids Surf., A* **1998**, *143*, 141.
- (12) Lucassen-Reynders, E. H.; Cagna, A.; Lucassen, J. *Colloids Surf., A* **2001**, *186*, 63.
- (13) Fainerman, V. B.; Miller, R. *Langmuir* **1996**, *12*, 6011.
- (14) Rusanov, A. I. *Fazovye Ravnovesija i Poverchnostnye Javlenija*; Khimija: Leningrad, 1967.
- (15) Joos, P. *Dynamic Surface Phenomena*; VSP: Utrecht, The Netherlands, 1999.
- (16) Fainerman, V. B.; Aksenenko, E. V.; Miller, R. *J. Phys. Chem. B* **2000**, *104*, 5744.
- (17) Vollhardt, D.; Fainerman, V. B.; Emrich, G. *J. Phys. Chem. B* **2000**, *104*, 8536.
- (18) Graham, D. E.; Phillips, M. C. *J. Colloid Interface Sci.* **1979**, *70*, 415.