Mendeleev Commun., 2002, 12(6), 218–219

Two-dimensional equation of state for nonionic surfactant monolayers

Anatoly I. Rusanov

Mendeleev Centre, St. Petersburg State University, 199034 St. Petersburg, Russian Federation.
Fax: +7 812 428 6939; e-mail: rusanov@rus.usr.pu.ru

10.1070/MC2002v012n06ABEH001664

The derived general equation of state corrects the classical equations by van Laar and Frumkin and accounts for the effect of molecular orientation in a surfactant interfacial monolayer.

The detailed recent review[1] on the problem makes the introduction unnecessary. Note that we will exhibit here a somewhat different approach to deriving a state equation correcting the classical equations of van Laar and Frumkin and accounting for the effect of continuous molecular orientation in an interfacial surfactant monolayer. The surfactant aggregation is not regarded in this presentation.

We consider a surfactant monolayer at a flat interface. Since we are interested in the interdependence of interfacial parameters only, the surfactants are assumed to be insoluble. This allows us to perform a rigorous analysis on the basis of equilibrium thermodynamics. Soluble surfactants differ from insoluble ones in the necessity of considering the equilibrium of a monolayer with a bulk phase. However, the problem of finding the adsorption isotherm looks trivial if the interfacial state equation has already been found.

To derive a two-dimensional state equation, only two relationships are needed. The first is the Gibbs adsorption isotherm

$$d\gamma = -\sum_i \Gamma_i d\mu_i, \tag{1}$$

where γ is the surface tension, Γ_i and μ_i are the adsorption and chemical potential of the *i*th surfactant present in the monolayer. Summation in (1) is carried out over the surfactants only, although some other components of surrounding bulk phases are present in the monolayer. However, the chemical potentials of these additional substances are absent from equation (1) because they are constant at a fixed state (temperature, pressure and composition) of the surrounding bulk phases. For insoluble surfactants, adsorption Γ_i coincides with the real amount of a substance per unit monolayer area.

The second relationship required is the statistical-mechanical expression for the molecular chemical potential

$$\mu_i = \mu_i^0 + kT\ln(c_i\Lambda_i^3), \tag{2}$$

where μ_i^0 is the chemical potential of molecules of sort *i* with resting centre of mass in the test system, *k* is Boltzmann's constant, *T* is the temperature, c_i and Λ_i are the concentration and de Broglie wavelength for molecules of sort *i*, respectively (Λ_i is a function of temperature). Referring equation (2) to the monolayer, we interpret c_i as Γ_i/h, where *h* is the monolayer thickness defined correspondingly to the largest dimension of the surfactant molecules in the direction normal to the interface. By isothermal differentiating (2), we obtain

$$d\mu_i = d\mu_i^0 + kT d\ln(\Gamma_i/h). \tag{3}$$

We will derive the equation of state by integrating equation (1) under the condition that temperature, pressure and the mutual proportions of all substances are fixed (*e.g.*, on changing only the monolayer area). Under this condition, we have the thermodynamic relationship $d\mu_i = -a_i d\gamma$ (a_i is the partial molecular area) and, by analogy, for molecules at rest,

$$d\mu_i^0 = -a_i^{ex}d\gamma. \tag{4}$$

Equation (4) is substantiated by the fact that resting molecules may be regarded as a separate component to which thermodynamics is also applicable (this is often used, for example, in the thermodynamics of solids). We designate the partial molecular area of a resting molecule in (4) as an excluded area a_i^{ex}. Indeed, among moving molecules, a single resting surfactant molecule (with a fixed centre of mass) plays the role of a specific 'wall', which produces the excluded area a_i^{ex}. Substituting (3) and (4) into (1), we obtain a general two-dimensional state equation in the differential form

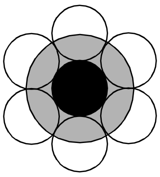

Figure 1 The excluded area (shaded) as the fourfold parking area. A resting molecule is shown as a black circle, and mobile molecules are shown as empty circles.

$$(1 - \sum_i \Gamma_i a_i^{ex})\,d\gamma = -kT\sum_i \Gamma_i d\ln(\Gamma_i/h). \tag{5}$$

Due to the presence of parameters a_i^{ex} and *h*, state equation (5) rigorously accounts for the orientation of surfactant molecules in a monolayer.

Since the general integration of equation (5) is problematic, we split further derivation into two steps. At the first step, we assume the absence of attraction forces between surfactant molecules. Integrating (5) at a given molecular orientation (when a_i^{ex} and *h* are constant) yields

$$\Pi = -\frac{kT}{a^{ex}}\ln(1 - \sum_i \Gamma_i a_i^{ex}),\ a^{ex} \equiv \frac{\sum_i \Gamma_i a_i^{ex}}{\sum_i \Gamma_i}, \tag{6}$$

where $\Pi \equiv \gamma_0 - \gamma$ is the two-dimensional pressure (γ_0 is the surface tension in the absence of the monolayer) and a^{ex} is the average value for the excluded area of molecules in the monolayer. At the second step, we add the well-known attractive term (estimated by the direct summation of pair interactions) to the right-hand side of (6):

$$\Pi = -\frac{kT}{a^{ex}}\ln(1 - \sum_i \Gamma_i a_i^{ex}) - \sum_{i,k}\alpha_{ik}\Gamma_i\Gamma_k, \tag{7}$$

where α_{ik} is the attraction constant for the interaction between molecules of sorts *i* and *k*. Note that a^{ex} in (7) should be estimated in the absence of molecular attraction. In the case of a single surfactant, equation (7) takes the form

$$\Pi = -\frac{kT}{a^{ex}}\ln(1 - \Gamma a^{ex}) - \alpha\Gamma^2. \tag{8}$$

The relation of the excluded area a^{ex} and the parking area a_0 of a molecule in general is a difficult problem of statistical mechanics. Putting $a^{ex} = a_{i0}$ converts (7) to the recent result by Fainerman *et al.*:[2]

$$\Pi = -\frac{kT}{a_0}\ln(1 - \sum_i \theta_i) - \sum_{i,k}\alpha'_{ik}\theta_i\theta_k,\ a_0 \equiv \frac{\sum_i \Gamma_i a_{i0}}{\sum_i \Gamma_i}, \tag{9}$$

where $\theta_i \equiv \Gamma a_{i0}$ is the degree of coverage of the monolayer surface by molecules of the *i*th component, and $\alpha'_{ik} \equiv a_{ik}/a_{i0}a_{k0}$ is a new value of the attraction constant. Proceeding to the case of a single surfactant, equation (8) changes to the classical Frumkin equation (written in a dimensionless form)

$$\tilde{\Pi} = -\ln(1-\theta) - \tilde{\alpha}\theta^2, \quad (10)$$

where $\tilde{\Pi} \equiv \Pi a_0/kT$ and $\tilde{\alpha} \equiv \alpha/kTa_0$ are dimensionless forms for the two-dimensional pressure and the attraction constant, respectively. In turn, the Frumkin equation changes to the known van Laar equation at $\tilde{\alpha} = 0$.

However, the statement $a_i^{\mathrm{ex}} = a_{i0}$ is wrong for non-localized adsorption. For example, assuming the parking area to be circular and equal for all the surfactant molecules, it is evident that $a_i^{\mathrm{ex}} = 4a_{i0}$ because this is just the area inaccessible to the centres of moving molecules with respect to a single resting molecule (Figure 1). Putting this value in (8) yields

$$\tilde{\Pi} = -0.25\ln(1-4\theta) - \tilde{\alpha}\theta^2 \quad (11)$$

instead of (10). The validity of equations (10) and (11) is easily verified by expanding the logarithm at small θ for the model system of hard discs. Both the Frumkin and van Laar equations yield the incorrect value $a_0/2$ for the second virial coefficient B_2, whereas equation (11) yields the correct value $B_2 = 2a_0$. However, equation (11) loses its physical sense at $\theta \geq 1/4$, whereas the maximum value of $\theta_{\max}$ is $\pi/4 \approx 0.79$ for the cubic packing or $\pi\sqrt{3}/6 \approx 0.91$ for the hexagonal packing of discs.

It is appropriate to remember that the Frumkin equation is consistent with experimental data. However, the attraction constant always acts as an empirical quantity. As being of the same functional dependence, equation (11) will also be in agreement with experimental data, but it will produce other values for the attraction constant and other constants. For example, equation (11) predicts the first-order phase transition within the range

$$0 < \tilde{\Pi} < \tilde{\Pi}_c = (\ln 2 - 0.5)/4 \approx 0.0483,\ 11.0152 > \tilde{\alpha} > \tilde{\alpha}_c = 8, \quad (12)$$

where the subscript ‘c’ refers to the critical point (in addition, $\theta_c = 1/8$). The Frumkin equation yields $\tilde{\Pi}_c$ and θ_c four times larger and $\tilde{\alpha}_c$ four times smaller.

Equations (7), (8) and (11) have been derived for a given molecular orientation but remain valid in the general case if a_i^{ex} and a_{i0} are constant (this can be secured by a dominant size of polar groups of surfactant molecules in the monolayer). In this case, the only difference is that the attraction constants depend on the orientation of surfactant molecules (usually, on the orientation of hydrocarbon chains). Turning, for simplicity, to equation (11), we assume the increment $\Delta\tilde{\alpha}$ of the attraction constant to be proportional to the increment Δh of the monolayer thickness. Regarding Δh as a result of the monolayer strain under the action of two-dimensional pressure, we write $\Delta\tilde{\alpha} \sim \Delta h \sim \Delta\tilde{\Pi}$ and

$$\tilde{\alpha} = \tilde{\alpha}_0 + \tilde{K}\Delta\tilde{\Pi}, \quad (13)$$

where $\tilde{\alpha}_0$ is the unchangeable part of the attraction constant, and $\tilde{K}$ is the proportionality factor.

One has to distinguish between two cases in the theory of monolayers. (*a*) The case of sequential processes. The first-order phase transition proceeds at a fixed initial (as in a two-dimensional gas) molecular orientation with the formation of an expanded liquid phase. Then, on attaining a certain two-dimensional pressure, the transition to orientation occurs as an order/disorder second-order phase transition (to be noticed as a breakpoint in the two-dimensional pressure isotherm). The region of this transition ends (a second breakpoint) with the reverse disorder/order second-order phase transition with formation of a condensed phase (at the normal orientation of all molecules). (*b*) The case of parallel processes. Molecular orientation occurs already in the course of the first-order phase transition, which leads to the formation of a condensed phase at once.

Let us consider the second case and assume orientation to occur at sufficiently low pressures, so that one may set $\Delta\tilde{\Pi} \approx \Pi$. Then putting (13) in (11) results in the state equation

$$\tilde{\Pi} = -\frac{\ln(1-4\theta) - \tilde{\alpha}_0\theta^2}{4(1+\tilde{K}\theta^2)}. \quad (14)$$

According to equation (14), the sign of the derivative $\mathrm{d}\tilde{\Pi}/\mathrm{d}\theta$ changes twice as θ increases, irrespective of the coefficient $\tilde{K}$. This means that equation (14) predicts a first-order phase transition within a certain range of state parameters. Thus, the case of parallel processes (which was experimentally discovered previously[3]) also acquires theoretical foundation.

We return to equation (5) to describe the general case of varying orientation. For simplicity, we consider a monolayer with a single surfactant and, passing to the two-dimensional pressure with accounting for attractive forces, write (5) as

$$(1 - \Gamma a^{\mathrm{ex}})\mathrm{d}(\Pi + \alpha\Gamma^2) = kT\Gamma\,\mathrm{d}\ln(\Gamma/h). \quad (15)$$

Using the same reasoning as when deriving (13), we have

$$\alpha = \alpha_0 + K\Delta\Pi,\ h = h_0 + L\Delta\Pi, \quad (16)$$

where K and L are proportionality factors. In the course of orientation, a^{ex} decreases with increasing two-dimensional pressure. If one sets $a^{\mathrm{ex}}h \equiv v^{\mathrm{ex}}$ = a constant (as for molecules of a cylindrical shape), the dependence of a^{ex} on Π is given by the relationship

$$a^{\mathrm{ex}} = \frac{v^{\mathrm{ex}}}{h} = \frac{v^{\mathrm{ex}}}{h_0 + L\Delta\Pi}. \quad (17)$$

Putting (16) and (17) in (15) leads to the state equation ($\Delta\Pi$ is the two-dimensional pressure counted off from the transition point)

$$\frac{\mathrm{d}\Delta\Pi}{\mathrm{d}\Gamma} = \frac{kT - 2(\alpha_0 + K\Delta\Pi)\Gamma(1 - \dfrac{\Gamma v^{\mathrm{ex}}}{h_0 + L\Delta\Pi})}{(1 - \dfrac{\Gamma v^{\mathrm{ex}}}{h_0 + L\Delta\Pi})(1 + K\Gamma^2) + \dfrac{kT\Gamma L}{h_0 + L\Delta\Pi}} \quad (19a)$$

or, in the most compact notation,

$$\frac{\mathrm{d}\Pi}{\mathrm{d}\Gamma} = \frac{kT - 2\alpha\Gamma(1 - \Gamma a^{\mathrm{ex}})}{(1 - \Gamma a^{\mathrm{ex}})(1 + K\Gamma^2) + LkTc}. \quad (19b)$$

The constants K and L can be regarded as parameters of inclusion of orientation. It can be seen in (18) that, at a given Γ, the appearance of these parameters leads to a decrease in the value of the derivative $\mathrm{d}\Pi/\mathrm{d}\Gamma$. This means that the point of the second-order phase transition related to the beginning of orientation is marked with a decrease of the positive slope in the two-dimensional pressure isotherm and of the negative slope in the surface tension isotherm.

As a concluding remark, note that the above approach differs by using the excluded area as the main quantity for the analysis. Further progress in this direction will depend on accounting for surface molecular aggregation and its influence on the excluded area.

This work was supported by the Russian Foundation for Basic Research (grant nos. 00-15-97357 and 01-03-32334).

References

1 V. B. Fainerman, R. Miller and E. V. Aksenenko, *Adv. Colloid Interface Sci.*, 2002, **96**, 339.

2 V. B. Fainerman, E. H. Lucassen-Reynders and R. Miller, *Colloids Surf.*, 1998, **A143**, 141.

3 Y. Hayami, A. Uemura, N. Ikeda, M. Aratono and K. Motomura, *J. Colloid Interface Sci.*, 1995, **172**, 142.

Received: 16th September 2002; Com. 02/1991