A multistate adsorption model for the adsorption of $C_{14}EO_4$ and $C_{14}EO_8$ at the solution/air interface

Valentin B. Fainerman [1], Volodymyr I. Kovalchuk [2], Eugene V. Aksenenko [3]*, Francesca Ravera [4], Libero Liggieri [4], Giuseppe Loglio [4], Alexander V. Makievski [1], Natalia O. Mishchuk[3], Emanuel Schneck [5] and Reinhard Miller [5] *

[1] SINTERFACE Technologies, Berlin D12489, Germany; fainerman@ukr.net (V.B.F.); a.makievski@sinterface.com (A.V.M.)

[2] Institute of Biocolloid Chemistry, National Academy of Sciences of Ukraine, Kyiv (Kiev) 03680, Ukraine; vladim@koval.kiev.ua

[3] Institute of Colloid Chemistry and Chemistry of Water, National Academy of Sciences of Ukraine, Kyiv (Kiev) 03680, Ukraine; Eugene_Aksenenko@ukr.net, nat_mis@ukr.net (N.O.M.)

[4] CNR-Institute of Condensed Matter Chemistry and Technologies for Energy, Unit of Genoa, 16149 Genoa, Italy; francesca.ravera@ge.icmate.cnr.it (F.R.); libero.liggieri@ge.icmate.cnr.it (L.L.); giuseppe.loglio@ge.icmate.cnr.it (G.L.)

[5] Physics Department, Technical University Darmstadt, 64289 Darmstadt, Germany; miller@fkp.tu-darmstadt.de (R.M.); schneck@fkp.tu-darmstadt.de (E.S.)

* Correspondence: miller@fkp.tu-darmstadt.de, Eugene_Aksenenko@ukr.net

S1. Assumption of multiple states

Considered here are amphiphilic molecules with a hydrophilic part presented by a flexible chain comprising of several segments, as explained in details in the main text of the article, where Model R and Model R0 are introduced. These models assume s possible adsorbed states with minimum molar area ω_1 and maximum molar area ω_s. It is assumed that molar areas in each state except the s-th depend on the coverage of the adsorbed layer θ (and therefore also on the surface pressure Π), which implies the dependence on the adsorbate concentration c. For the state with minimum molar area, this dependence takes the form shown in Equation (1) of the main text of the article. The relations between the partial molar areas. surface coverage and adsorbed amount are listed in the main text of the article, and are reproduced here for the sake of convenience:

$$\omega_1 = \left(1 - \varepsilon \Pi \theta\right) \cdot \omega_{10} \tag{S.1}$$

Here ω_{10} is the minimum molar area at infinite dilution ($\Pi = 0$), ε is the intrinsic compressibility coefficient, and the surface pressure Π is the difference between the surface tension of the pure solvent γ_0 and that of the solution γ. The molar area of the j-th state ($1 \leq j \leq s$) is related to that of the 1-st state and the s-th state as:

$$\omega_j = \frac{j-1}{s-1}\omega_s + \frac{s-j}{s-1}\omega_1 \tag{S.2}$$

It is seen that in this model the molar area increment, i.e. the difference between the areas of two neighbouring states does not depend on j:

$$\omega_0 = \omega_j - \omega_{j-1} = \frac{\omega_s - \omega_1}{s-1} \tag{S.3}$$

thus

$$\omega_j = \omega_1 + \left(j-1\right)\omega_0 \tag{S.4}$$

The assumption of constant increment simplifies the model strongly, reducing the number of the required model parameters while still preserving the most significant features of the system behaviour. The average molar area ω is determined via the total coverage θ, partial adsorption in j-th state Γ_j and total adsorption Γ:

$$\theta = \omega\Gamma = \sum_{j=1}^{s} \omega_j \Gamma_j \tag{S.5}$$

$$\Gamma = \sum_{i=1}^{n} \Gamma_j \tag{S.6}$$

S2. Multistate adsorption Model R

The equation of state of the adsorbed layer and the adsorption isotherm equation for this model are similar to those proposed in [1]:

$$-\frac{\Pi\omega_1}{RT} = \ln(1-\theta) + \theta\left(1 - \frac{\omega_1}{\omega}\right) + a\theta^2 \tag{S.7}$$

$$b_j c = \frac{\omega\Gamma_j}{(1-\theta)^{\omega_j/\omega}} \exp\left[-2a\frac{\omega_j}{\omega}\theta\right] \tag{S.8}$$

where a is the Frumkin interaction parameter, and b_j is the adsorption equilibrium coefficient (parameter) for the surfactant molecules in the j-th state, R is the gas constant, and T is absolute temperature.

Note that the Equation (S.8) is in fact the set of s equations, which should be solved simultaneously with the corresponding equation of state (S.7) to obtain the dependence of model variables on the surfactant concentration. To deal with this complication, the approach was proposed in our publication [2], which assumes the dependence between the molar areas and the adsorption equilibrium coefficients:

$$b_j = \left(\frac{\omega_j}{\omega_1}\right)^{\alpha} b_1 \tag{S.9}$$

where α is an adjustable empirical model parameter. The dependence (S.9) implies that the adsorption equilibrium parameters depend on the concentration via the dependence of ω_1, see Equation (S.1). The relation (S.9) makes it possible to express all s partial adsorption equilibrium parameters via the single one, which is chosen to be b_1, which in what follows for the sake of brevity is denoted by b. Then the Equations (S1)-(S.4) and (S.9) could be solved simultaneously with Equations (S.7), (S.8) to calculate the total adsorption value Γ as explained below.

Using expression (S.9) one can eliminate b_j (j = 2, …, s) from Equation (S.8) to obtain:

$$b_1 c = \frac{\omega\Gamma_j}{(\omega_j/\omega_1)^{\alpha}(1-\theta)^{\omega_j/\omega}} \exp\left[-2a\frac{\omega_j}{\omega}\theta\right] \tag{S.10}$$

Note that the adsorption equilibrium constant b_1 for the surfactant molecules in state 1 is on the left-hand side. Then, for j = 1 both Equation (8) and Equation (10) are:

$$b_1 c = \frac{\omega\Gamma_1}{(1-\theta)^{\omega_1/\omega}} \exp\left[-2a\frac{\omega_1}{\omega}\theta\right] \tag{S.11}$$

These equations can be combined to express the adsorption in any j-th state via the adsorption in the 1st state:

$$\Gamma_j = \Gamma_1 \left(\frac{\omega_j}{\omega_1}\right)^\alpha (1-\theta)^{(\omega_j-\omega_1)/\omega} \exp\left[2a\frac{\omega_j-\omega_1}{\omega}\theta\right]$$

$$= \Gamma_1 \left(\frac{\omega_j}{\omega_1}\right)^\alpha \exp\left\{\frac{\omega_j-\omega_1}{\omega}\left[\ln(1-\theta)+2a\theta\right]\right\} \tag{S.12}$$

The total adsorption of surfactant molecules, Equation (S.6) is:

$$\Gamma = \sum_{j=1}^{s}\Gamma_j = \Gamma_1 \sum_{j=1}^{s}\left(\frac{\omega_j}{\omega_1}\right)^\alpha \exp\left\{\frac{\omega_j-\omega_1}{\omega}\left[\ln(1-\theta)+2a\theta\right]\right\} \tag{S.13}$$

therefore

$$\Gamma_1 = \frac{\Gamma}{\displaystyle\sum_{j=1}^{s}\left(\frac{\omega_j}{\omega_1}\right)^\alpha \exp\left\{\frac{\omega_j-\omega_1}{\omega}\left[\ln(1-\theta)+2a\theta\right]\right\}} \tag{S.14}$$

and the adsorption in any j-th state of surfactant molecules, Equation (S.12) is determined by the relation:

$$\Gamma_j = \Gamma_1 \left(\frac{\omega_j}{\omega_1}\right)^\alpha \exp\left\{\frac{\omega_j-\omega_1}{\omega}\left[\ln(1-\theta)+2a\theta\right]\right\}$$

$$= \Gamma \frac{\left(\frac{\omega_j}{\omega_1}\right)^\alpha \exp\left\{\frac{\omega_j-\omega_1}{\omega}\left[\ln(1-\theta)+2a\theta\right]\right\}}{\displaystyle\sum_{j=1}^{s}\left(\frac{\omega_j}{\omega_1}\right)^\alpha \exp\left\{\frac{\omega_j-\omega_1}{\omega}\left[\ln(1-\theta)+2a\theta\right]\right\}} \tag{S.15}$$

The surface coverage by surfactant molecules, Eq. (S.5) becomes:

$$\theta = \omega\Gamma = \sum_{j=1}^{s}\omega_j\Gamma_j = \Gamma \frac{\displaystyle\sum_{j=1}^{s}\omega_j\left(\frac{\omega_j}{\omega_1}\right)^\alpha \exp\left\{\frac{\omega_j-\omega_1}{\omega}\left[\ln(1-\theta)+2a\theta\right]\right\}}{\displaystyle\sum_{j=1}^{s}\left(\frac{\omega_j}{\omega_1}\right)^\alpha \exp\left\{\frac{\omega_j-\omega_1}{\omega}\left[\ln(1-\theta)+2a\theta\right]\right\}} \tag{S.16}$$

where ω is the average molar area of the surfactant molecule, or

$$\omega = \frac{\displaystyle\sum_{j=1}^{s}\omega_j\left(\frac{\omega_j}{\omega_1}\right)^\alpha \exp\left\{\frac{\omega_j-\omega_1}{\omega}\left[\ln(1-\theta)+2a\theta\right]\right\}}{\displaystyle\sum_{j=1}^{s}\left(\frac{\omega_j}{\omega_1}\right)^\alpha \exp\left\{\frac{\omega_j-\omega_1}{\omega}\left[\ln(1-\theta)+2a\theta\right]\right\}} \tag{S.17}$$

It is convenient to introduce the dimensionless variables Ω and Ω_0:

$$\Omega = \frac{\omega}{\omega_1}, \qquad \Omega_0 = \frac{\omega_0}{\omega_1} \tag{S.18}$$

Note that the quantities Ω and Ω_0 defined by this relation are relevant only for Model R, i.e. are related to Section S2 only. It follows from expression (S.4) that:

$$\frac{\omega_j}{\omega_1} = 1+(j-1)\Omega_0, \qquad \frac{\omega_j-\omega_1}{\omega} = (j-1)\frac{\Omega_0}{\Omega} \tag{S.19}$$

In this notation Equation (S.17) becomes:

$$\Omega = \frac{\sum_{j=1}^{n}\left[1+(j-1)\Omega_0\right]\left[1+(j-1)\Omega_0\right]^{\alpha}\exp\left\{(j-1)\frac{\Omega_0}{\Omega}\left[\ln(1-\theta)+2a\theta\right]\right\}}{\sum_{j=1}^{n}\left[1+(j-1)\Omega_0\right]^{\alpha}\exp\left\{(j-1)\frac{\Omega_0}{\Omega}\left[\ln(1-\theta)+2a\theta\right]\right\}}$$

$$= 1+\Omega_0\frac{\sum_{j=1}^{n}(j-1)\left[1+(j-1)\Omega_0\right]^{\alpha}\exp\left\{(j-1)\frac{\Omega_0}{\Omega}\left[\ln(1-\theta)+2a\theta\right]\right\}}{\sum_{j=1}^{n}\left[1+(j-1)\Omega_0\right]^{\alpha}\exp\left\{(j-1)\frac{\Omega_0}{\Omega}\left[\ln(1-\theta)+2a\theta\right]\right\}}$$

(S.20)

Introducing new auxiliary function $\Xi = \Xi(\Omega,\theta)$ which is the denominator of (S.20), and noting that the term with $j = 1$ is equal to 1 one obtains:

$$\Xi = \sum_{i=1}^{n}\left[1+(i-1)\Omega_0\right]^{\alpha}\exp\left\{(i-1)\frac{\Omega_0}{\Omega}\left[\ln(1-\theta)+2a\theta\right]\right\}$$

$$= 1+\sum_{i=2}^{n}\left[1+(i-1)\Omega_0\right]^{\alpha}\exp\left[(i-1)X(\Omega,\theta)\right]$$

(S.21)

where

$$X(\Omega,\theta) = \frac{\Omega_0}{\Omega}\left[\ln(1-\theta)+2a\theta\right]$$

(S.22)

Noting that the term with $j = 1$ in the numerator of the second term in (S.19) vanishes, one expresses this numerator as:

$$\sum_{j=1}^{n}(j-1)\left[1+(j-1)\Omega_0\right]^{\alpha}\exp\left\{(j-1)\frac{\Omega_0}{\Omega}\left[\ln(1-\theta)+2a\theta\right]\right\}$$

$$= \sum_{j=2}^{n}(j-1)\left[1+(j-1)\Omega_0\right]^{\alpha}\exp\left[(j-1)X(\Omega,\theta)\right]$$

(S.23)

to express Equation (S.20) as:

$$\Omega = 1+\Omega_0\frac{\sum_{j=2}^{n}(j-1)\left[1+(j-1)\Omega_0\right]^{\alpha}\exp\left[(j-1)X(\Omega,\theta)\right]}{1+\sum_{j=2}^{n}\left[1+(j-1)\Omega_0\right]^{\alpha}\exp\left[(j-1)X(\Omega,\theta)\right]}$$

(S.24)

This equation provides one relation between the variables Ω and θ. Next, the surfactant adsorption isotherm equation follows from Equation (S.8) with $j = 1$:

$$b_1 c = \frac{\omega\Gamma_1}{(1-\theta)^{1/\Omega}}\exp\left[-2a\frac{\omega_1}{\omega}\theta\right] = \frac{\omega\Gamma_1}{(1-\theta)^{1/\Omega}}\exp\left[-2a\frac{\theta}{\Omega}\right]$$

(S.25)

It follows from Eqs. (13) and (20) that:

$$\Gamma_1 = \frac{\Gamma}{\Xi(\Omega,\theta)}$$

(S.26)

then, as $\omega\cdot\Gamma = \theta$, the adsorption isotherm equation for the surfactant is:

$$b_1 c = \frac{\theta}{\Xi(\Omega,\theta)}\frac{\exp\left[-2a\frac{\theta}{\Omega}\right]}{(1-\theta)^{1/\Omega}}$$

(S.27)

For known model parameter values, the simultaneous solution of Equations (S.24) and (S.27) yields the Ω and θ values for any c. However, the complete solution of the model equations requires to determine the surface pressure Π, which is involved in the concentration dependence of ω_1, Equation (S.1). The equation of state (S.7) in the dimensionless quantities becomes:

$$p = -\left[\ln(1-\theta) + \theta\left(1 - \frac{1}{\Omega}\right) + a\theta^2 \right]$$

(S.28)

where the dimensionless surface pressure $p = \Pi\omega_1/RT$ is introduced. Note the dependence of ω_1 on Π (hence on p), Equation (S.1), while the value of p is in turn dependent on ω_1 via Eq. (S.28). Therefore, this set of model equations involves additional non-linear equation:

$$\omega_1 = \left(1 - \varepsilon\frac{RT}{\omega_1}p\theta\right)\omega_{10}$$

(S.30)

Introducing new dimensionless constant $\kappa = \varepsilon RT/\omega_{10}$ and dimensionless variable $\psi = \left(\omega_{10} - \omega_1\right)/\omega_{10}$ one obtains the final equation necessary to obtain the solution:

$$\psi = \kappa\frac{p\theta}{\left(1-\psi\right)}$$

(S.31)

The set of equations above allows to calculate the dependencies of the total surface coverage θ, the total adsorbed amount Γ, the average molar area ω, and the surface tension γ as functions of the surfactant concentration in the bulk, if the model parameters b = b_1, ω_{10}, ω_s, ε, a, α and s are known.

S3. Multistate adsorption Model R0

For this model the equation of state and adsorption isotherm equation are similar to those considered in [3]:

$$-\frac{\Pi\omega_{10}}{RT} = \ln(1-\theta) + \theta\left(1 - \frac{\omega_{10}}{\omega}\right) + a\theta^2$$

(S.32)

$$b_jc = \frac{\omega_{10}\Gamma_j}{\left(1-\theta\right)^{\omega_j/\omega_{10}}}\exp\left[-2a\frac{\omega_j}{\omega_{10}}\theta\right]$$

(S.33)

Assuming the same dependence between the molar areas and the adsorption equilibrium coefficients as in Eq. (S.9) one obtains the expression for the adsorbed amount in any j-th state:

$$\begin{aligned}\Gamma_j &= \Gamma_1\left(\frac{\omega_j}{\omega_1}\right)^{\alpha}\left(1-\theta\right)^{(\omega_j - \omega_1)/\omega_{10}}\exp\left[2a\frac{\omega_j - \omega_1}{\omega_{10}}\theta\right]\\ &= \Gamma_1\left(\frac{\omega_j}{\omega_1}\right)^{\alpha}\exp\left\{\frac{\omega_j - \omega_1}{\omega_{10}}\left[\ln(1-\theta) + 2a\theta\right]\right\}\end{aligned}$$

(S.34)

which is different from Equation (S.12) because the adsorption isotherm equations for this model is different from that for the Model R. Then the dimensionless values are introduced:

$$\Omega = \frac{\omega}{\omega_{10}}, \quad \Omega_0 = \frac{\omega_0}{\omega_{10}}, \quad \Omega_1 = \frac{\omega_1}{\omega_{10}} = 1 - \varepsilon\Pi\theta$$

(S.35)

Note that the quantities Ω and Ω_0 defined by this relation are different from those defined by Equation (S.18), and are relevant only for Model R0, i.e. are related to Section S3 only. Then, much in the same way as Equation (S.24) was derived, one obtains the relation between Ω and θ valid for this model:

$$\Omega = \Omega_1 \frac{1 + \sum_{j=2}^{n} \left[1 + (j-1)\Omega_{01} \right]^{\alpha+1} \exp\left[(j-1)\Upsilon(\theta) \right]}{1 + \sum_{j=2}^{n} \left[1 + (j-1)\Omega_{01} \right]^{\alpha} \exp\left[(j-1)\Upsilon(\theta) \right]} \tag{S.36}$$

where

$$\Upsilon(\theta) = \Omega_0 \left[\ln(1-\theta) + 2a\theta \right] \tag{S.37}$$

And, in the same way as Equation (S.27) was derived, one obtains the adsorption isotherm equation for this model:

$$b_1 c = \frac{1}{Z(\Omega, \theta)} \frac{\theta}{\Omega(1-\theta)^{\Omega_1}} \exp(-2a\theta\Omega_1) \tag{S.38}$$

where

$$Z(\Omega, \theta) = \sum_{j=1}^{s} \left[1 + (j-1)\Omega_{01} \right]^{\alpha} \exp\left[(j-1)\Upsilon(\theta) \right] \tag{S.39}$$

The equation of state (S.32) in dimensionless values becomes:

$$q = -\left[\ln(1-\theta) + \theta\left(1 - \frac{1}{\Omega}\right) + a\theta^2 \right] \tag{S.40}$$

where the dimensionless surface pressure $q = \Pi\omega_{10}/RT$ is introduced different from those defined in Section 2. The set of equations (S.6), (S.38) and (S.40) is sufficient to calculate the model values Π, Γ, θ and Ω for any relevant concentration c and the set of model parameters.

4. Computation

To solve the sets of equations described above, the Newton-Raphson algorithm as described in [4] was applied. For the chosen set of model parameters, the isotherm was tabulated along the concentration axis with nodes distributed in the logarithmic scale, starting from the c values sufficiently small for the initial approximations to be valid; at each subsequent step the initial approximation was calculated via suitable extrapolation formulae.

The model was implemented as a module integrated into the computer program IsoPlotM, employed also for calculations described earlier. The program possesses the graphic interface, and is capable to perform the calculations of tensiometric and rheological quantities which are displayed on the screen and stored in files compatible for treating by common matrix processing packages (e. g. Excel or Origin). The software is under development for routine application by many external users.

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