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SHORT COMMUNICATION

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Statistical thermodynamics approach for estimation of the interaction parameters in the mixed Langmuir films at the water/air interface

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Abstract The treatment of two-dimensional system of three components of molecules of different molecular sizes, adapted from statistical thermodynamics, is used to derive parameters which could be related to the interaction between molecules in the mixed Langmuir films formed at the water/air interface.

Key words Molecular interaction – Langmuir films – water/air interface

Introduction

The study of mixed monolayers has become of considerable interest both from practical and theoretical points of view. Mixed systems have advantage over those of the constituent components alone as they can be produced at a relatively lower cost than those of isomerically pure compounds and, in addition, mixtures often exhibit superior properties due to synergetic interaction between molecules.

Recently, a number of investigations has been carried out on the interaction between film forming molecules spread at the water/air interface [1–7]. The molecular interaction in the mixed Langmuir films can be studied from the point of view of miscibility between components. In this approach the mixed monolayer is considered as a two-dimensional (2D) solution and the mean molecular area of the mixed monolayer (ω_{12}) is plotted at a certain surface pressure, π, against the molar fraction of components, X_1 or X_2 [8]. The linear plot is the evidence of the additive properties of the areas: $\omega_{12} = X_1\omega_1 + X_2\omega_2$ ($\omega_1$and ω_2 are the areas of monolayer of pure components 1 and 2, respectively, for the same surface pressure as for the mixed monolayer, ω_{12}). This also indicates a kind of ideal mixing of non-interacting molecules, or complete immiscibility of the components. If the relationship is not linear, a non-ideal behavior resulting from molecular interaction at the interface exists [9].

Another approach to test the miscibility is based on the measurements of the maximum pressure which can be reached on compressing the film. On further compression the collapse occurs leading to the formation of three-dimensional (3D) structures [10–12]. This maximum pressure of the monolayer is also called the collapse pressure, π_c. At this point, film-forming molecules in the monolayer are packed in the most condensed state. From the analysis of π/A isotherm it comes out that if the components of the mixed monolayer are immiscible, two collapse states, corresponding to pure components, are observed [9]. If the components are miscible, the collapse pressure of the mixed film lies between the collapse pressures of pure components and can be expressed by the following equation [13, 14]:

$$1 = \frac{\gamma_1^s}{\gamma_1} X_{1,c}^s e^{\frac{(\pi_{c,m} - \pi_{c,1})\omega_1}{kT}} + \frac{\gamma_2^s}{\gamma_2} X_{2,c}^s e^{\frac{(\pi_{c,m} - \pi_{c,2})\omega_2}{kT}} , \qquad (1)$$

wherein: $\pi_{c,m}$ is the collapse pressure of the mixed monolayer, $X_{i,c}^s$ is the mole fraction of component "i" in the mixed monolayer at the collapse point, $\pi_{c,i}$ is the collapse pressure of the monolayer formed only by component "i", ω_i is the limiting molecular area at the collapse point of component "i". It should be mentioned here that the surface activity coefficients (γ_i^s) and the activity coefficients in the bulk phase (γ_i) in Eq. (1) correspond to mixed films and differ from those obtained for a system of one-component film. Since, in the case of Langmuir films, there is an extremely small amount of film-forming molecules in the bulk phase, it is possible to drop the bulk activity coefficients.

In this paper the above equation combined together with the expressions for the surface activity coefficients derived from statistical thermodynamics is used to calculate the parameters which can be related to the interaction between molecules in the mixed Langmuir films formed at the water/air interface.

Theory

The expression for the chemical potential of component 1 (μ_1), which has been derived using a regular solution theory extended to a system of three components of different molecular sizes, has the following form [15]:

$$\begin{aligned}\mu_1 = {} & -kT \ln q_1 - kT \ln V + kT \ln N_1 \\ & - kT(N_1 + N_2 + N_0) \\ & + \frac{1}{2} c_1 \phi_{11} + \frac{1}{2}\left(\frac{N_2^2}{V^2}\right) \Phi_{12} v_2 + \frac{1}{2}\left(\frac{N_0^2}{V^2}\right) \Phi_{10} v_0 \\ & + \frac{1}{2}\left(\frac{N_2 N_0}{V^2}\right)(\Phi_{10} v_2 + \Phi_{12} v_0 - \Phi_{20} v_1) , \end{aligned} \qquad (2)$$

wherein q_1 term includes the molecular partition function for internal motions ($q_1 = (2\pi m_1 kT)^{3/2}/h^3$), N_i is the number of molecules of the i-th kind, $v_i = V/N_i$ denotes its molecular volume, $V = N_1 v_1 + N_2 v_2 + N_0 v_0$ is the total volume of the system, ϕ_{ij} is the energy of interaction of a pair of molecules of type i and j, and Φ_{ij} is defined as $\phi_{ij}(c_i v_j + c_j v_i) - c_i \phi_{ii} v_j - c_j \phi_{jj} v_i$.

Equation (2) has been derived for bulk solution, but it can be applied for the surface phase by considering the interfacial region to be a two-dimensional (2D) system. Thus, the equation for the surface phase contains instead of volume (V), molecular volume (v_i) and q_i, their 2D counterparts: surface (Ω), molecular surface (ω_i) and $q_i^s = 2\pi m_i kT/h^2$. Moreover, for the surface phase, the expression for the chemical potential is completed with the additional term ($\sigma\omega_1$) connected with the surface force field:

$$\begin{aligned}\mu_1^s = {} & -kTq_1^s - kT \ln \Omega + kT \ln N_1^s \\ & - kT(N_1^s + N_2^s + N_0^s)\frac{\omega_1}{\Omega} \\ & + \frac{1}{2} c_1 \phi_{11} + \frac{1}{2}\frac{(N_2^s)^2}{\Omega^2} \Phi_{12}\omega_2 + \frac{1}{2}\frac{(N_0^s)^2}{\Omega^2} \Phi_{10}\omega_0 \\ & + \frac{1}{2}\frac{N_2^s N_0^s}{\Omega^2}(\Phi_{10}\omega_2 + \Phi_{12}\omega_0 - \Phi_{20}\omega_1) - \sigma\omega_1 , \end{aligned} \qquad (3)$$

wherein N_i^s is the number of molecules of the i-th kind at the surface. The total surface of the system, Ω, equals $N_1^s \omega_1 + N_2^s \omega_2 + N_0^s \omega_0$ (1 and 2 denote molecules spread on water 0).

To define the standard chemical potential at the surface, $\mu_1^{0,s}$, let us assume that the activity coefficient of the component 1 at the surface, γ_1^s, approaches 1 when $X_0^s \to 1$. In these conditions, Eq. (3) has the following form:

$$\begin{aligned}\mu_1^{0,s} = {} & -kT \ln q_1^s + kT \ln n_1^s - kT\frac{\omega_1}{\omega_0} + \frac{1}{2} c_1 \phi_{11} \\ & + \frac{1}{2}\frac{\Phi_{10}}{\omega_0} - \sigma_0\omega_1 , \end{aligned} \qquad (4)$$

where $n_1^s = N_1^s/\Omega$ (or $n_1^s = X_1^s/(X_1^s\omega_1 + X_2^s\omega_2 + X_0^s\omega_0)$).

After rearrangements it becomes:

$$\begin{aligned}\mu_1^{0,s} = {} & -kT \ln q_1^s - kT\frac{\omega_1}{\omega_0} + \frac{1}{2} c_1 \phi_{11} + \frac{\Phi_{10}}{2\omega_0} \\ & - kT \ln \omega_0 - \sigma_0\omega_1 . \end{aligned} \qquad (5)$$

The chemical potential at the surface can be expressed by the following equation [16, 17]:

$$\mu_1^s = \mu_1^{0,s} + kT \ln(X_1^s \gamma_1^s) + \sigma\omega_1 . \qquad (6)$$

Introducing $\mu_1^{0,s}$ from Eq. (5) into Eq. (6) and comparing this with Eq. (3), we obtain:

$$\begin{aligned}kT \ln(X_1^s \gamma_1^s) = {} & kT \ln(n_1^s \omega_0) - kT + kTn_0^s(\omega_0 - \omega_1) \\ & + kTn_2^s(\omega_2 - \omega_1) + \frac{1}{2}(n_2^s)^2\omega_2\Phi_{12} + \frac{1}{2}(n_0^s)^2\omega_0\Phi_{10} \\ & + \frac{1}{2} n_2^s n_0^s(\Phi_{10}\omega_2 + \Phi_{12}\omega_0 - \Phi_{20}\omega_1) + kT\frac{\omega_1}{\omega_0} - \frac{\Phi_{10}}{2\omega_0} . \end{aligned} \qquad (7)$$

During compression water is squeezed out from the monolayer [13]. Although water molecules – due to the equilibrium requirements – are still present in the monolayer, just before the collapse, under these conditions n_0^s approaches zero. Therefore, all terms containing n_0^s can be neglected, so Eq. (7) can be approximated by:

$$kT\ln(X_1^s\gamma_1^s) = kT\,n_1^s\omega_0 + kT\,n_2^s(\omega_2-\omega_1) + kT\frac{\omega_1-\omega_0}{\omega_0} + \frac{1}{2}(n_2^s)^2\omega_2\Phi_{12} - \frac{\Phi_{10}}{2\omega_0}\,. \tag{8}$$

After rearrangements it is possible to express the surface activity coefficient of component 1 by the following equation:

$$\gamma_1^s = \frac{\omega_0}{X_1^s\omega_1 + X_2^s\omega_2}\, e^{\frac{X_2^s(\omega_2-\omega_1)}{X_1^s\omega_1+X_2^s\omega_2}}\, e^{\frac{(\omega_1-\omega_0)}{\omega_0}} \times e^{\left[\frac{1}{2}\mathrm{kT}\left(\frac{(X_2^s)^2\omega_2}{(X_1^s\omega_1+X_2^s\omega_2)^2}\Phi_{12}-\frac{\Phi_{10}}{\omega_0}\right)\right]}\,. \tag{9}$$

In case of isomegetic molecules $\omega_1 = \omega_2 = \omega_0$ and Eq. (9) simplifies to the expression:

$$\gamma_1^s = e^{\left[\frac{(X_2^s)^2\Phi_{12}-\Phi_{10}}{2\mathrm{kT}\omega}\right]}\,. \tag{10}$$

Analogically, for the second component at the surface, the activity coefficient can be expressed by:

$$\gamma_2^s = e^{\left[\frac{(X_2^s)^2\Phi_{12}-\Phi_{20}}{2\mathrm{kT}\omega}\right]}\,. \tag{11}$$

Equation (1), completed with expressions for surface activity coefficients (Eq. (9) for molecules of different sizes or Eq. (10) in the case of isomegetic molecules), allows us to calculate the parameter of interaction between film-forming molecules (Φ_{12}) as well as between molecules in the surface film and water (Φ_{10} and Φ_{20}).

Verification of the theory

Surface pressure/area (π/A) isotherms (at 15 °C) of the three mixed systems involving 1-heptadecanonitrile, 1-heptadecanoic acid and 1-hexadecanol, published in ref. [18], were used to calculate the parameters Φ_{ij} which can be related to the total interaction between molecules in the mixed spread films at the most condensed state of the monolayer.

Numerical calculations

Numerical fitting of Φ_{ij} (calculated from Eqs. (1) and (9)) was performed using Monte Carlo and Simplex methods [19].

Results and discussion

The obtained results are compiled in Table 1.

The parameter of interaction between molecules of 1-heptadecanonitrile and water (Φ_{10}) is almost the same for both systems studied. In mixtures of 1-heptadecanonitrile with 1-heptadecanoic acid and 1-hexadecanol, the parameter of interaction between molecules of 1-heptadecanoic acid (or 1-hexadecanol) and water (Φ_{20} or $\Phi_{2'0}$) is about the same order of magnitude as Φ_{10}, however, the sign is opposite. Since the mixtures of 1-heptadecanonitrile with 1-heptadecanoic acid and 1-hexadecanol can be considered as miscible systems, the parameters of interaction (Φ_{12}, $\Phi_{12'}$, $\Phi_{22'}$) can be related to the enthalpy of mixing. According to ref. [15] (Eq. (8)), the expression for the increase in potential energy, ΔU, when a solution containing N_1 molecules of the first kind and N_2 molecules of the second kind is formed from components in their pure state, has the following form:

$$\Delta U = U - U^0 = N_1\left(\frac{1}{2}c_1\phi_{11}\right) + N_2\left(\frac{1}{2}c_2\phi_{22}\right) + \left(\frac{N_1N_2}{2V}\right)\Phi_{12} - \left[N_1\left(\frac{1}{2}c_1\phi_{11}\right) + N_2\left(\frac{1}{2}c_2\phi_{22}\right)\right] = \frac{N_1N_2}{2V}\Phi_{12}\,. \tag{12}$$

For the surface mixture (2D solution), $\Delta U^s = [(N_1^sN_2^s)/(2\Omega)]\Phi_{12}$. For the static system considered, this quantity

Table 1 Molecular parameters of interaction, Φ_{ij} (in J · m^2), for mixed films of 1-heptadecanonitrile (1) with 1-heptadecanoic acid (2) and 1-hexadecanol (2′)

System	Φ_{12}, $\Phi_{12'}$ or $\Phi_{22'}$	Φ_{10}	Φ_{20} ($\Phi_{2'0}$)
1 + 2	$-4.2\cdot10^{-39} \pm 0.17$*	$-8.5\cdot10^{-40} \pm 0.55$	$1.2\cdot10^{-39} \pm 0.05$
1 + 2′	$-1.3\cdot10^{-39} \pm 0.05$	$-7.8\cdot10^{-40} \pm 0.51$	$1.4\cdot10^{-39} \pm 0.06$
2 + 2′	$-1.8\cdot10^{-39} \pm 0.07$	–	$-2.5\cdot10^{-40} \pm 0.11$ $(2.1\cdot10^{-40} \pm 0.10)$

* Estimated SD.

Table 2 Values of ΔU^s (expressed in J/molecule) for the mixtures of 1-heptadecanonitrile (1) with 1-heptadecanoic acid (2) and 1-hexadecanol (2′)

System	ΔU^s
$1 + 2$	$-5.18 \cdot 10^{-21} \pm 0.20$*
$1 + 2'$	$-1.57 \cdot 10^{-21} \pm 0.06$
$2 + 2'$	$-2.32 \cdot 10^{-21} \pm 0.09$

* Estimated SD.

represents the energy during the mixing of the pure components (enthalpy of mixing under isobaric conditions) and is proportional to the parameter Φ_{12}. Thus, the negative sign of Φ_{ij} can suggest that the mixing process is exotermic while the positive sign suggests the endotermic process. The values of ΔU^s for the investigated systems are compiled in Table 2.

It would be interesting to verify the theory by comparing the enthalpy of mixing calculated from the values of Φ_{ij} with the enthalpy of mixing obtained from calorimetric experiments.

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