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Adsorption of *N*-Dodecyl-*β*-alanine at the Air-Solution Interface with the Spread Monolayer of Lecithin or Dilaurin. I. Adsorption Isotherms

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The applicability of the Gibbs adsorption isotherm was examined for the adsorption of *N*-dodecyl-*β*-alanine (NDA) at the air-solution interface with the spread monolayer of lecithin (DML) or dilaurin (DIL). In order to derive adsorption isotherms, the spread monolayer was treated energetically as a part of the adsorbed monolayer. The isotherms were derived for the following cases: (a) a nonideal mixing of the spread and adsorbed molecules and (b) a nonideal adsorption associated with a conformational change due to the complex formation between monolayer molecules. The isotherm derived for case (a) coincided with the observed isotherm of NDA adsorbed into the DIL monolayer, but deviated from the observed isotherm of NDA adsorbed into the DML monolayer. The DML–NDA isotherm was regarded as to be explained by the isotherm derived for case (b). Further, the applicability of the Pethica's isotherm to the adsorption of NDA in both systems was examined.

Some adsorption isotherms of *N*-dodecyl-*β*-alanine, which adsorbs at the solution surface with the spread monolayer of lecithin or dilaurin, have been reported in the previous paper.[1] From the radiometrical determination of the adsorbed amount, the properties of both mixed monolayers have been described in detail as a function of suface composition or surface pressure. It was clear that the surfactant remarkably condensed with dilaurin or lecithin in monolayer. For such adsorption systems, however, the adsorbed amount of surfactant is expected to obey the Gibbs adsorption isotherm, such as for adsorption of surfactant at the air–solution interface.[2] Pethica[3] and McGregor and Barnes[4] have derived adsorption isotherms by assuming the accessible area for the adsorbing species in the monolayer. However, they are no unique isotherms applicable to every type of adsorption, because each set has been derived under the particular conditions of the highly condensed film of spread monolayer.

In the present study, attempts are made to elucidate the applicability of the Gibbs adsorption isotherm to the adsorption of surfactant at the air–solution interface with the insoluble film. The derivation of isotherms is achieved for the following cases: (a) a nonideal mixing of the spread and adsorbed molecules, and (b) a nonideal adsorption associated with a conformational change of the monolayer molecules. The interaction in the monolayer is introduced as the excess free energy instead of the partial molar surface area in the isotherm. The validity of the isotherms obtained are tested by comparison with the observed isotherms.

Theory

The Gibbs adsorption isotherm for the air–solution interface with spread film (1) and surfactant (2), is given at a constant temperature, assuming that the water surface is taken as the dividing surface:

$$-\mathrm{d}\gamma = \Gamma_1 \mathrm{d}\mu_1^{\mathrm{s}} + \Gamma_2 \mathrm{d}\mu_2^{\mathrm{b}}, \tag{1}$$

where γ denotes the surface tension and Γ_i and μ_i the relative surface excess per unit area and chemical potential for component i, respectively. Superscripts s and b mean the surface and bulk phases. Since the surface tension can be varied with the amount of spread film independently of the chemical potential of surfactant in the bulk phase, the adsorption of the surfactant is considered only for the solution surface which is covered with a fixed amount of spread film. When the spread and adsorbed monolayers coexist on the solution surface A_t of the surfactant of concentration C_2 at surface pressure π, the effective surface area A_2 available for the adsorption decreases by the surface area A_1 occupied by the spread monolayer. As long as the adsorbed monolayer is present in the same surface pressure, μ_2^{s} is equal to μ_2^{b}, so that the spread and adsorbed monolayers may be related by:

$$\mathrm{d}\mu_1^{\mathrm{s}} = \frac{a_1}{a_2}\mathrm{d}\mu_2^{\mathrm{b}}, \tag{2}$$

where a_i denotes the molar surface area of component i in each monolayer. Therefore, the contribution of spread film to the surface energy may be taken into account as a part of the adsorbed monolayer of the surfactant. Using Eq. 2, Eq. 1 is rewritten for the case of ideal penetration as follows:

$$-\mathrm{d}\gamma = \frac{a^{\mathrm{id}}}{a_2}(\Gamma_1+\Gamma_2)\mathrm{d}\mu_2^{\mathrm{b}}, \tag{3}$$

where $a^{\mathrm{id}}=X_1a_1+X_2a_2$, and X_i is the mole fraction of Γ_i.

If the adsorption is nonideal, the following two cases are taken into account: (a) nonideality in the simple mixing of spread and adsorbed molecules, and (b) nonideality in the case that the standard chemical potentials of the spread and/or adsorbed molecules alter due to the change in the conformation of their polar groups by complex formation, chemical reaction, or denaturation in monolayer.

In Case (a). The surface tension change is defined as follows:

$$\mathrm{d}\gamma = \mathrm{d}\gamma^{\mathrm{id}} + \mathrm{d}\gamma^{\mathrm{v}}, \tag{4}$$

where $\mathrm{d}\gamma^{\mathrm{id}}$ is given by Eq. 3. The $\mathrm{d}\gamma^{\mathrm{v}}$ term is the change of surface tension caused by the nonideal mixing of the spread and the adsorbed molecules. From Goodrich's convention for estimating the excess free energy of mixing,[5] we obtain:

$$\mathrm{d}\gamma^{\mathrm{v}} = \frac{\Delta a}{a}\mathrm{d}\gamma, \tag{5}$$

where $\Delta a=a-a^{\mathrm{id}}$, and a is real molar surface area measured by experiment. Substituting Eq. 5 into 4, we obtain

$$\begin{aligned} \mathrm{d}\gamma &= \left(1-\frac{\Delta a}{a}\right)^{-1}\mathrm{d}\gamma^{\mathrm{id}} \\ &\simeq \left(1+\frac{\Delta a}{a}\right)\mathrm{d}\gamma^{\mathrm{id}} \end{aligned} \tag{6}$$

by neglecting higher terms in the expansion with respect to $\Delta a/a$. For the nonideal adsorption, from Eqs. 3 and 6 we obtain:

$$-\mathrm{d}\gamma = \frac{a^{\mathrm{id}}}{a_2}(\Gamma_1+\Gamma_2)(\mathrm{d}\mu_2^{\mathrm{b}}+\mathrm{d}\Delta\xi^{\mathrm{v}}), \tag{7}$$

where $\mathrm{d}\Delta\xi^{\mathrm{v}}=(\Delta a/a)\mathrm{d}\mu_2^{\mathrm{b}}$. Hence, $\Delta\xi^{\mathrm{v}}$ means the excess free energy arising from the nonideal adsorption of a surfactant. Then $\mathrm{d}\Delta\xi^{\mathrm{v}}$ may be equated with $(a_2/a^{\mathrm{id}})RT\mathrm{d}\ln f^{\mathrm{v}}$ thermodynamically; here f^{v} is the surface activity coefficient at mixing. When $\Delta a=0$ or $f^{\mathrm{v}}=1$, Eq. 7 is reduced to Eq. 3.

Consequently, when the activity coefficient of surfactant in the bulk phase is assumed to be unity,[6] from Eq. 7 Γ_2 is given by:

$$\Gamma_2 = \frac{\left[\dfrac{-\partial\gamma}{RT\partial\ln C_2}\right]_{\Gamma_1}}{\left[\dfrac{a^{\mathrm{id}}}{a_2}\right]_{\Gamma_1}+\left[\dfrac{\partial\ln f^{\mathrm{v}}}{\partial\ln C_2}\right]_{\Gamma_1}} - \Gamma_1. \tag{8}$$

In Case (b). We define an equation similar to Eq. 4 as follows:

$$\mathrm{d}\gamma = \mathrm{d}\gamma^{\mathrm{id}} + \mathrm{d}\gamma^{\mathrm{v}} + \mathrm{d}\gamma^{\mathrm{c}}, \tag{9}$$

where $\mathrm{d}\gamma^{\mathrm{c}}$ denotes the surface tension change caused by an alteration in the molecular structure owing to the complex formation or chemical reaction in the monolayer. The $\mathrm{d}\gamma^{\mathrm{c}}$ term can not be experimentally separated from the $\mathrm{d}\gamma^{\mathrm{v}}$ term, because both are functions of surface compositions of the film. We assume, in this case, that $\mathrm{d}\gamma^{\mathrm{v}}$ defined by Eq. 5 refers only to the nonideal mixing of film-forming molecules, after the complex formation or chemical reaction has been completed. Eventually, we have the following equation, analogous to Eq. 7:

$$-\mathrm{d}\gamma = \frac{a^{\mathrm{id}}}{a_2}(\Gamma_1+\Gamma_2)(\mathrm{d}\mu_2^{\mathrm{b}}+\mathrm{d}\Delta\xi^{\mathrm{v}}+\mathrm{d}\Delta\xi^{\mathrm{c}}), \tag{10}$$

where $\mathrm{d}\Delta\xi^{\mathrm{c}}(=(a_2/a^{\mathrm{id}})RT\mathrm{d}\ln f^{\mathrm{c}})$ denotes the change of excess free energy resulting from the alteration in the molecular structure due to complex formation. Finally, the adsorbed amount is estimated by:

$$\Gamma_2 = \frac{\left[\dfrac{-\partial\gamma}{RT\partial\ln C_2}\right]_{\Gamma_1}}{\left[\dfrac{a^{\mathrm{id}}}{a_2}\right]_{\Gamma_1}+\left[\dfrac{\partial\ln f^{\mathrm{v}}}{\partial\ln C_2}\right]_{\Gamma_1}+\left[\dfrac{\partial\ln f^{\mathrm{c}}}{\partial\ln C_2}\right]_{\Gamma_1}} - \Gamma_1. \tag{11}$$

The validity of Eqs. 8 and 11 is experimentally tested later.

Experimental

The monolayer of L-α,β-dimyristoyllecithin (DML) or α,α′-dilaurin (DIL) was formed by spreading on the aqueous solution surface of *N*-dodecyl-β-alanine (NDA), *i.e.* 3-(dodecylammonio)propionate. The adsorbed amount was determined by the radiotracer method, using tritiated NDA. Surface tension was registered by the Wilhelmy plate method. The experiments and procedures to measure the surface excess and surface tension have been reported in the preceding paper.[1] All measurements were made at 30±0.2 °C.

Results and Discussion

Figure 1 shows the plots of surface pressure *vs.* bulk concentration of the surfactant solution at various spread amounts of DIL or DML. Figure 2 exhibits the adsorption isotherms of NDA measured by the

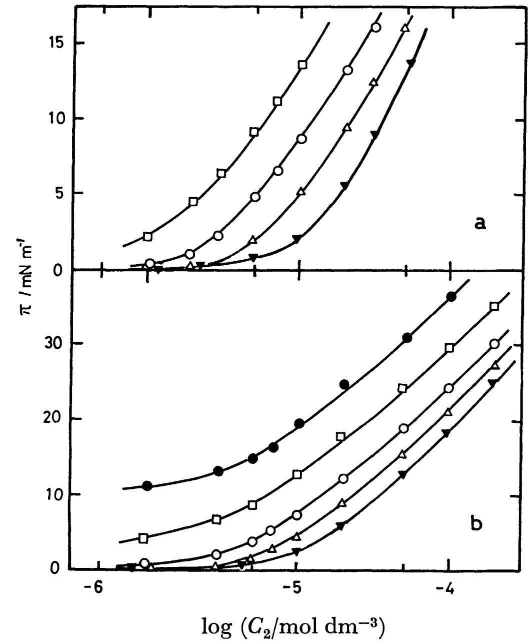

Fig. 1. π *vs.* C_2 curves for DIL–NDA (a) and DML–NDA (b) at various spread amounts (Γ_1/μmol m⁻²). ▼: 0, △: 0.5, ○: 1.0, □: 1.5, ●: 2.0.

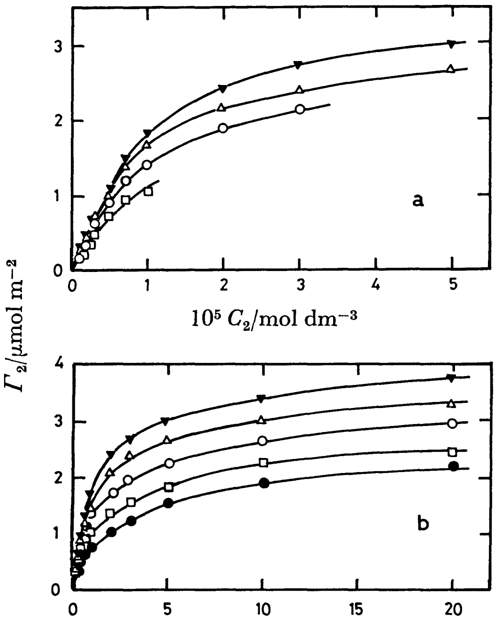

Fig. 2. Adsorption isotherms of NDA measured by the radiometry at various spread amounts (Γ_1/μmol m⁻²) of DIL(a) or DML(b). ▼: 0, △: 0.5, ○: 1.0, □: 1.5, ●: 2.0.

radiometry at various spread amounts of DIL or DML. Figure 3 shows the π *vs.* Γ curves for each spread film of DIL and DML and for the adsorbed film of NDA. The validity of derived theoretical isotherms for the adsorption systems of DIL–NDA and DML–NDA is tested with using the experimental data shown in Figs. 1, 2, and 3.

DIL–NDA System. In the mixed monolayer composed of DIL and NDA, a contraction of surface area has been reported in Ref. 1 as a function of the surface pressure. The contribution of such a contraction to the surface energy is expressed by $(\partial \ln f^{v}/\partial \ln C_2)_{\Gamma_1}$ in Eqs. 8 and 11, which may be estimated from the concentration dependence of the Goodrich's convention. The comparison of Γ_2 calculated by Eq. 8 with the experimental values is shown in Fig. 4. It was found that the calculated values (solid lines) were in good agreement with the observed ones. Since DIL and NDA molecules have been known to form a simple mixed monolayer without forming any complex,[1] the result in Fig. 4 gives an experimental confirmation of the validity of Eq. 8 or Eq. 11 where $f^{c}=1$. However, these equations are not valid for a mixed film in which the surface pressure of single NDA solutions, π_2°, is lower than that of DIL film alone, π_1°: for instance, in the case where Γ_{DIL} is 1.5 μmol m^{-2} π_1° is 1.0 mN m^{-1} and is equal to that of π_2° at NDA concentration of about 8 μmol dm^{-3}, as may be found from Figs. 1 and 3. Hence, below this concentration (corresponding to the arrow in Fig. 6-a) the calculated value from Eq. 8 or 11 gradually deviates from the observed values, because π_1° in this region is higher than π_2°.

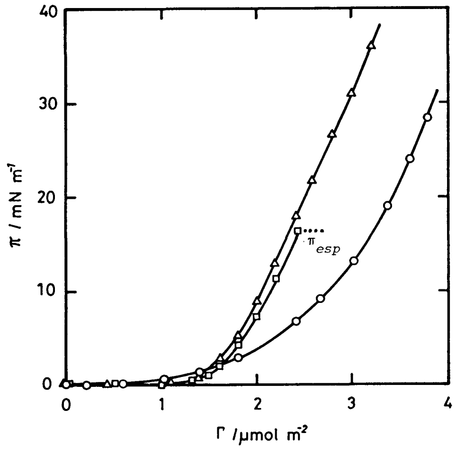

Fig. 3. π *vs.* Γ curves for each spread film of DIL(□) and DML(△) and for the adsorbed film of NDA(○). The curve for the NDA film is calculated from the data in Figs. 1 and 2. π_{esp}: the equilibrium spreading pressure of DIL film (16.6 mN m^{-1}).

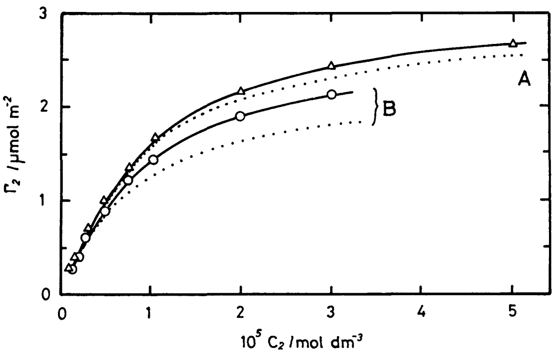

Fig. 4. Test of Eqs. 8 (solid lines) and 12 (dotted lines) at various amounts (Γ_1/μmol m^{-2}) of DIL. Curve A=0.5, curve B=1.0. Observed values are marked by signs.

Consequently, Eq. 8 or 11 is valid only in mixed films where π_1° is lower than π_2°, according to the requirement of Eq. 2.

DML–NDA System. Figure 5 shows the comparison of the observed and the calculated values for NDA which adsorbs at the solution surface with various amounts of spread DML. Here, the calculation was made according to Eq. 8, using $(\partial \ln f^{v}/\partial \ln C_2)_{\Gamma_1}$ values obtained for DML system. The predicted isotherm of Eq. 8 does not coincide with the observed one, unlike the findings for DIL system. The reason for this deviation seems to be the following. When NDA molecules adsorb at the solution surface with presence of DML molecules, the DML–NDA ion pair is formed in monolayer,[1] so that the standard chemical potentials of these molecules shift because of the structural changes in their polar groups. Therefore, the adsorption of NDA in the present system is considered to obey Eq. 11, according to the arguments described above. Thus the difference between the observed (signs) and the calculated (solid lines) isotherms in Fig. 5 corresponds to the values of the $(\partial \ln f^{c}/\partial \ln C_2)_{\Gamma_1}$ term in Eq. 11. From this reasoning, we can obtain thermodynamic information about the ion pair formed between the ampholytic moieties of DML and

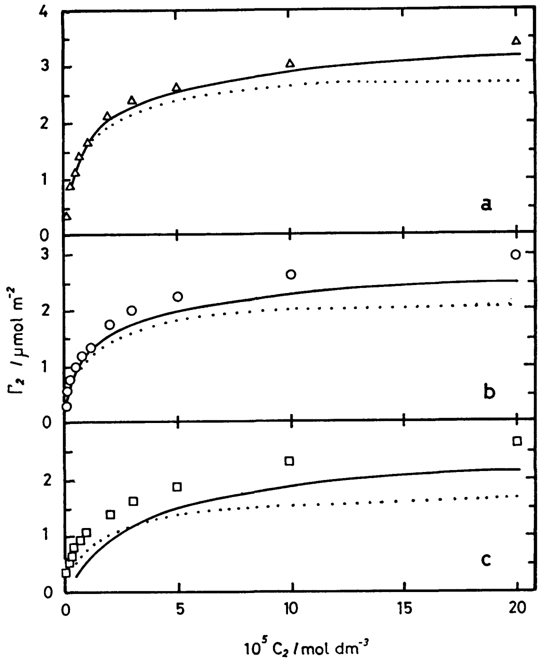

Fig. 5. Test of Eqs. 8 (soild lines) and 12 (dotted lines) at various amounts (Γ_1/μmol m^{-2}) of DML. a: 0.5, b: 1.0, c: 1.5. Observed values are marked by signs.

NDA in monolayer. Further discussion about this will be made elsewhere.

Pethica's Isotherm. Pethica has derived Eq. 12 for the penetration of sodium dodecyl sulfate at the air–solution interface with a fixed amount of cholesterol:[3)]

$$d\pi = \Phi RT\Gamma_2 d\ln C_2 \qquad (12)$$

where $\Phi = a_1/(a_1 - \bar{a}_1)$, and $\bar{a}_1$ is the partial molar surface area of the monolayer. The Γ_2 values, which have been calculated by Eq. 12 for the DIL–NDA and DML–NDA systems, are shown by the respective lines in Figs. 4 and 5, and compared with the observed values. These dotted lines deviate greatly from the observed isotherms, except for the low concentrations of the surfactant. Since Eq. 12 should be applied to the adsorption of a surfactant into highly condensed monolayer, the adsorption isotherms in such a case are shown in Fig. 6. It is clear that for DIL–NDA system (Fig. 6-a) the predicted isotherm by Eq. 12 follows the observed one at C_2 less than 3 μmol dm^{-3}, whereas the isotherm given by Eq. 8 coincides above 8 μmol dm^{-3}, as indicated by the arrow in Fig. 6-a: *i.e.*, below this concentration the requirement for Eq. 2 is not satisfied. Therefore, Eq. 12 seems to allow the calculation in the adsorption region unsuitable for Eq. 8. On the other hand, in the DML–NDA system the observed values deviate from the isotherm calculated by Eq. 12 as well as by Eq. 8, even though the solution surface is covered with DML film of 2.0 μmol m^{-2}. Hence, Eq. 12 appears not to be useful for the DML–NDA system.

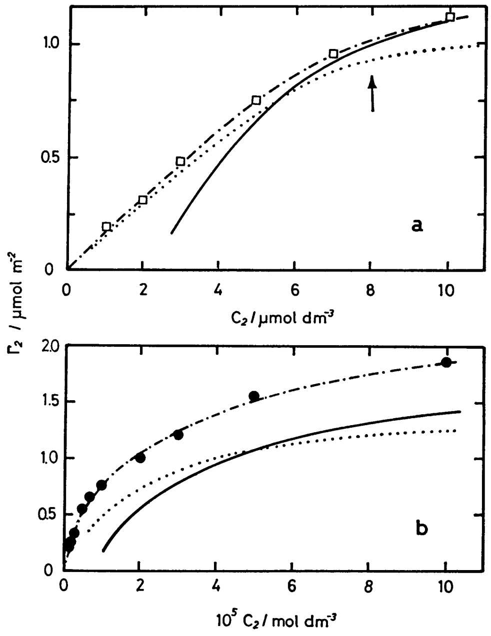

Fig. 6. Comparison of calculated isotherm by Eqs. 8 (solid lines) and 12 (dotted lines) with experimental values (—·□·, —·●—) at spread amount of DIL= 1.5 μmol m^{-2} (a) or of DML=2.0 μmol m^{-2} (b).

In conclusion, Eq. 8, derived for the simple non-ideal adsorption system, could sufficiently explain the observed isotherm for the DIL–NDA system, but could not be applied to the DML–NDA system. Thus, Eq. 11, derived for the complex formation system, was the best one to use for predicting the adsorption of NDA in the DML–NDA system.

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