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Relaxation Studies of the Adsorption-Desorption Equilibrium of Surfactants on the Gas-Liquid Interface. I. Theoretical Studies

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A general theory for the propagation characteristics of the capillary wave on the gas-liquid interface, where the physicochemical equilibrium exists, is proposed. The theory is developed on the basis of the two-dimensional relaxation theory and the surface thermodynamics. The relaxation parameters in the equations are closely related to the dynamic behavior of the equilibrium. As an example, the theory was applied to the surfactant solution, taking account of the adsorption-desorption and diffusion processes of the surfactant. The derived equations revealed that the adsorption-desorption process plays an important role in the surfactant transfer between the surface and the bulk phase in a concentrated surfactant solution, while the diffusion process plays such a role in a dilute solution.

The measurements of the propagation characteristics of the capillary wave, *e.g.*, the propagation velocity and the damping coefficient, are effective for the study of the dynamic properties of materials existing on the gas-liquid interface. The theoretical studies for the insoluble monolayers have been performed by Dorrestein,[1] Mayer and Eliassen,[2] and Mann and Du,[3] while those for the soluble monolayer have been performed by van den Tempel and van de Riet,[4] Hansen and Mann,[5] and Lucassen and Hansen.[6] The former has developed their theories taking account of the surface rheologies, and the latter with the assumption that the rate-determining step of surfactant transfer between the surface and the bulk phase is the diffusion process.

Provided that the physicochemical equilibrium on the interface, *e.g.*, the conformational change and the monomer-dimer reaction, is perturbed by the propagation of the wave, the relaxation effect concerned with the equilibrium may be expected. Though studies of such phenomena are valuable for the clarification of the dynamic properties of the equilibrium, theoretical studies have never been performed, while experimentally Davies and Vose[7] have observed the relaxation effect on the surfactant solution.

In the present investigation, a general theory on a surface involving the physicochemical equilibrium is developed on the basis of the relaxation theory[11] and the surface thermodynamics.[12,13]

General Equation

Let us consider a plane wave moving on a liquid surface in the x direction. Here, the motion of an incompressible liquid must satisfy the Navier-Stokes equations:[8]

$$\frac{\partial u}{\partial t} = -\frac{1}{\rho}\frac{\partial p}{\partial x} + \nu\Delta u,$$

$$\frac{\partial v}{\partial t} = -\frac{1}{\rho}\frac{\partial p}{\partial y} + \nu\Delta v - g, \tag{1}$$

with

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0,$$

where u and v are the velocity components in the x and y directions respectively; p is the hydrostatic pressure; ν, the kinematic viscosity, and g, the gravitational acceleration. u and v can be written by means of the stream function, Φ, and the potential function, Ψ:

$$u = -\frac{\partial\Phi}{\partial x} - \frac{\partial\Psi}{\partial y},$$

$$v = -\frac{\partial\Phi}{\partial y} + \frac{\partial\Psi}{\partial x}. \tag{2}$$

In order to solve Eq. 1, one must impose a boundary condition that the liquid motion becomes zero as $y \rightarrow -\infty$. Under the condition that the liquid motion satisfies the requirement of simple periodic movement, Φ and Ψ are given by the following equations:

$$\Phi = E_1 \exp(ky) \exp\{i(rt+kx)\},$$

$$\Psi = E_2 \exp(my) \exp\{i(rt+kx)\}, \tag{3}$$

with

$$m^2 = k^2 + \frac{ir}{\nu},$$

where E_1 and E_2 are the complex constants associated with the amplitudes of Φ and Ψ respectively; k is the wave number; m, the complex constant associated with the decay of liquid motion, and r, the complex angular frequency. From Eqs. 1—3, the equations for the velocities are obtained:

$$u = \{-ikE_1 \exp(ky) - mE_2 \exp(my)\} \exp\{i(rt+kx)\},$$

$$v = \{-kE_1 \exp(ky) + ikE_2 \exp(my)\} \exp\{i(rt+kx)\}. \tag{4}$$

The liquid motion at the surface is described by the elevation of the surface, ϕ:

$$\frac{\partial\phi}{\partial t} = v_s, \tag{5}$$

where the subscript s indicates the surface.

The boundary conditions for the normal and tangential stresses[4,6] are given as follows:

$$p - 2\eta\frac{\partial v}{\partial y} + \gamma\frac{\partial^2\phi}{\partial x^2} = 0,$$

$$\eta\left(\frac{\partial v_s}{\partial x} + \frac{\partial u_s}{\partial y}\right) - \frac{\partial\gamma}{\partial x} - \eta_s\frac{\partial^2 u_s}{\partial x^2} = 0. \tag{6}$$

The $\left(\frac{\partial\gamma}{\partial x}\right)$ term is expressed as

$$\frac{\partial}{\partial t}\left(\frac{\partial\gamma}{\partial x}\right) = C_s^{-1}\frac{\partial^2 u_s}{\partial x^2}, \tag{7}$$

with

$$C_s^{-1} = \left(\frac{\partial \gamma}{\partial s}\right), \tag{8}$$

where C_S is the surface compressibility, and s, the surface area per unit area. As C_S reflects the dynamic behavior of the physicochemical equilibrium on the surface, the dynamic surface compressibility has to be introduced. It is derived by applying the relaxation theory to the perturbed equilibrium system.

The following one-step equilibrium existing on a surface is considered:

$$\nu_1 R_1 + \cdots + \nu_i R_i \rightleftarrows \nu_1' P_1 + \cdots + \nu_j' P_j,$$

where ν_i and ν_j' are the stoichiometric coefficients, and R_i and P_j, the species. When the wave propagates on the surface, the accompanying liquid motion causes the periodic variation in the surface area, which acts as the external driving force for the disturbance of the equilibrium. Consenquently, the extensive variables such as the concentration or ordering parameter of species, are perturbed periodically, and so behind the external driving force. The relaxation process of the perturbed system is described by the ordering coefficient, ξ, as follows:[11]

$$\xi = LA, \tag{9}$$

with

$$\xi = \bar{\xi} + \Delta\xi \exp(i\omega' t),$$

$$\mathrm{d}\xi = \Delta\xi \exp(i\omega' t) = \frac{\mathrm{d}N_i}{\nu_i} = \frac{\mathrm{d}N_j'}{\nu_j'},$$

where A denotes the chemical affinity; L, the constant; the bar, the equilibrium state; $\omega'(=2\omega)$, the angular frequency associated with the perturbation of the surface area (see Appendix I), and N_i and N_j', the numbers of moles of the R_i and P_j species respectively. A and γ are expanded in terms of the changes in s and ξ in the vicinity of the surface:[12,13]

$$A(\xi, s, S) = \left(\frac{\partial A}{\partial \xi}\right)_{s,S} \mathrm{d}\xi + \left(\frac{\partial A}{\partial s}\right)_{\xi,S} \mathrm{d}s,$$

$$\mathrm{d}\gamma = \left(\frac{\partial \gamma}{\partial \xi}\right)_{s,S} \mathrm{d}\xi + \left(\frac{\partial \gamma}{\partial s}\right)_{\xi,S} \mathrm{d}s, \tag{10}$$

where S is the entropy. Here, the adiabatic approximation is reasonably applied (see Appendix II). If ds is zero, Eq. 10 becomes:

$$\dot{\xi} = L\left(\frac{\partial A}{\partial \xi}\right)_{s,S} \mathrm{d}\xi = -\frac{\mathrm{d}\xi}{\tau_{s,S}}. \tag{11}$$

$\tau_{s,S}$ denotes the relaxation time of the local fluctuation of equilibrium. The similarly obtained $\tau_{\gamma,S}$ is related to $\tau_{s,S}$ by the ollowing relation

$$\frac{\tau_{\gamma,S}}{\tau_{s,S}} = \frac{(C_s^{-1})_{\xi,S}}{(C_s^{-1})_{A,S}}. \tag{12}$$

The combination of Eqs. 9 and 10 gives the relationship between dγ and ds:

$$\mathrm{d}\gamma = \frac{\left(\frac{\partial \gamma}{\partial s}\right)_{A,S} + i\omega' \tau_{s,S} \left(\frac{\partial \gamma}{\partial s}\right)_{\xi,S}}{1 + i\omega' \tau_{s,S}} \mathrm{d}s. \tag{13}$$

From Eqs. 8 and 13, we obtain the dynamic surface compressibility, C_S^*:

$$(C_s^*)_S^{-1} = (C_s^{-1})_{A,S} \frac{1 + i\omega' \tau(\delta + 1)}{1 + i\omega' \tau}, \tag{14}$$

with

$$\tau_{s,S} = \tau, \quad \delta = \frac{(C_s^{-1})_{\xi,S}}{(C_s^{-1})_{A,S}} - 1,$$

were δ is the relaxation strength.

The combination of Eqs. 2—7 and 14 gives two homogeneous equations for E_1 and E_2:

$$\{E_1(ir^2 - i\sigma^2 + 2\nu k^2 r) - E_2(\sigma^2 + 2i\nu kmr)\} \times \exp\{i(\omega t + kx)\} = 0,$$

$$\{E_1(2i\nu k^2 r + \chi^* \sigma^2) + E_2(ir^2 + 2\nu k^2 r - i\chi^* \sigma^2 mk^{-1})\} \times \exp\{i(\omega t + kx)\} = 0, \tag{15}$$

with

$$\sigma^2 = gk + \frac{\gamma k^3}{\rho}, \tag{16}$$

$$\chi^* = \frac{k^3}{\rho\sigma^2}\left\{(C_s^{-1})_{A,S} + i\eta_s r + (C_s^{-1})_{A,S} \frac{i\omega\tau\delta}{1 + i\omega'\tau}\right\}, \tag{17}$$

χ^* consisting of two terms, χ_{ela} and χ_r. The former is attributed to the surface viscoelasticity, and the latter, to the relaxation:

$$\chi_{ela} = \frac{k^3}{\rho\sigma^2}\{(C_s^{-1})_{A,S} + i\eta_s r\}, \tag{18}$$

$$\chi_r = \frac{k^3}{\rho\sigma^2}(C_s^{-1})_{A,S}\left(\frac{\omega'^2\tau^2\delta}{1 + \omega'^2\tau^2} + \frac{i\omega'\tau\delta}{1 + \omega'^2\tau^2}\right).$$

The available solution of Eq. 15 is given by the following determinant:

$$\begin{vmatrix} ir^2 - i\sigma^2 + 2\nu k^2 r & -\sigma^2 - 2i\nu kmr \\ 2i\nu k^2 r + \chi^* \sigma^2 & ir^2 + 2\nu k^2 r - i\chi^* \sigma^2 mk^{-1} \end{vmatrix} = 0. \tag{19}$$

The propagation velocity, c, and the damping coefficient, α, are defined by the following equations:

$$c = \frac{r_{re}}{k}, \tag{20}$$

$$\alpha = \frac{r_{im}}{V}, \tag{21}$$

where the re and im subscripts indicate the real and imaginary parts respectively, and where $V(=3c/2)$ is the group velocity. In the case of $\chi^* \neq 0$, the complex angular frequency, r, exhibits the frequency dispersion. Then, the dispersion terms, ε_{ela} and ε_r, are introduced as follows.

$$r = \sigma(1 + \varepsilon_{ela} + \varepsilon_r). \tag{22}$$

ε_{ela} and ε_r are concerned with the surface viscoelasticity and the relaxation respectively. From Eqs. 18, 19 and 22, ε_{ela} and ε_r are obtained as:

$$\varepsilon_{ela} = \frac{\frac{2\nu k^2}{\sigma} i + \frac{1}{2}\chi_{ela}}{1 - (1 + i)\chi_{ela}\left(\frac{2\nu k^2}{\sigma}\right)^{1/2}}. \tag{23}$$

and

$$\varepsilon_r = \frac{\chi_r}{2}.$$

Therefore, c and α are given by Eqs. 16 and 20—23:

$$c^2 = \left(\frac{g}{k} + \frac{\gamma k}{\rho}\right)(1 + 2\varepsilon_{ela,re} + 2\varepsilon_{r,re}), \tag{24}$$

$$\alpha = \frac{\sigma}{V}(\varepsilon_{ela,im} + \varepsilon_{r,im}). \tag{25}$$

These are the general equations for the propagation characteristics of the capillary wave, taking account of the relaxation process.

Propagation Characteristics of Wave on the Surface of a Surfactant Solution

The surfactant transfer between the surface and the bulk phase is expressed by the following scheme, taking account of two processes; the adsorption-desorption process between the surface and the subsurface, and the diffusion process between the subsurface and the bulk phase, as is shown schematically in Fig. 1:

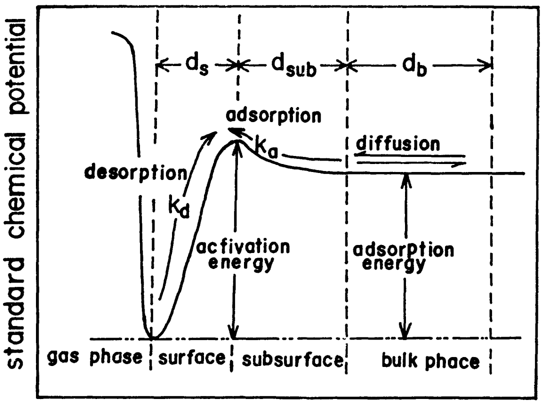

Fig. 1. Diagrammatic representation of the surfactants in the vicinity of surface. k_a and k_d are the adsorption and desorption rate constants, and d_s, d_{sub}, and d_b the thicknesses of the surface, subsurface, and bulk phase layers, respectively.

$$S_s \underset{\substack{k_a \\ \text{(adsorption)}}}{\overset{\substack{\text{(desorption)} \\ k_d}}{\rightleftarrows}} S_{sub} \underset{\text{(diffusion)}}{\rightleftarrows} S_b,$$

where S_b, S_{sub}, and S_s are the surfactants in the bulk phase, the subsurface, and the surface, and where k_a and k_d are the adsorption and desorption rate constants, respectively. The adsorption-desorption process is governed by the activation energy of the adsorption and desorption processes and is represented by a Langmuir-type rate equation.10,14) On the other hand, the diffusion process is expressed by the diffusion theory. Thus, the following equations are given for the adsorption-desorption mechanism:

$$\frac{\mathrm{d}c_s}{\mathrm{d}t} = k_a(1-\theta)c_{sub} - k_d c_s \quad (-d_{sub} \leq y \leq 0), \tag{26}$$

$$\frac{\mathrm{d}c_b}{\mathrm{d}t} = D\left(\frac{\partial^2 c_b}{\partial x^2} + \frac{\partial^2 c_b}{\partial y^2}\right) \quad (y < -d_{sub}), \tag{27}$$

where c_s, c_{sub}, and c_b are the molar concentrations of S_s, S_{sub}, and S_b respectively; θ is the fraction of sites occupied by S_s; d_{sub}, the thickness of the subsurface layer, and D, the diffusion coefficient. c_s and θ in Eq. 26 are related by

$$c_s = \frac{10^3 \Gamma_{max}\theta}{d_s}, \tag{28}$$

where Γ_{max} is the maximum value of the surface excess, and d_s, the thickness of the surface layer. When the equilibrium is perturbed, θ, c_{sub}, and c_b are expressed in these forms:

$$\begin{aligned} \theta &= \bar{\theta} + \Delta\theta \exp\{i(\omega' t + \kappa x)\}, \\ c_{sub} &= \bar{c}_{sub} + \Delta c_{sub} \exp\{i(\omega' t + \kappa x)\}, \\ c_b &= \bar{c}_b + \Delta c_b \exp\{i(\omega' t + \kappa x)\}, \end{aligned} \tag{29}$$

where $\kappa(=2k)$ is the wave number of perturbed variables (see Appendix I). Using Eqs. 28 and 29, Eq. 26 is rewritten as

$$i\omega'\Delta\theta = -(k_{a,\theta}\bar{c}_{sub} + k_d)\Delta\theta + k_{a,\theta}(1-\bar{\theta})\Delta c_{sub}, \tag{30}$$

with

$$k_{a,\theta} = \frac{d_s}{10^3 \Gamma_{max}} k_a.$$

The solution of Eq. 27 is

$$\Delta c_b = E_b \exp(ny), \tag{31}$$

with

$$n = d_b^{-1}, \quad n^2 = \kappa^2 + \frac{i\omega'}{D},$$

where E_b is the constant, and d_b, the thickness of the bulk phase concerned with the diffusion process. From Eq. 31, Δc_{sub} becomes (see Appendix III):

$$\Delta c_{sub} = -n d_s \Delta c_s. \tag{32}$$

c_{sub} is expressed by the theory of an electric double layer8) with the electric potential, ψ_{sub}, at $y = -d_{sub}$:

$$c_{sub} = c_0 \exp\left(-\frac{Ze\psi_{sub}}{k_B T}\right), \tag{33}$$

where c_0 is the initial concentration; Z, the valency; e, the elementary charge; k_B, the Boltzmann constant, and T, the temperature. Combining Eqs. 30, 32 and 33, the relaxation time is derived:

$$\tau^{-1} = \frac{k_{a,\theta}c_0 \exp\left(-\frac{Ze\psi_{sub}}{k_B T}\right) + k_d + k_a n_{re} d_s(1-\bar{\theta})}{1 + k_a n_{im} d_s(1-\bar{\theta})}, \tag{34}$$

with

$$n = n_{re} + i\omega' n_{im}.$$

The relaxation strength δ is derived from Eq. 10 as (see Appendix IV)

$$\delta = -\frac{\left(\frac{\partial \gamma}{\partial \xi}\right)_{s,S}\left(\frac{\partial A}{\partial s}\right)_{\xi,S}}{\left(\frac{\partial \gamma}{\partial s}\right)_{A,S}\left(\frac{\partial A}{\partial \xi}\right)_{s,S}}. \tag{35}$$

This equation is then rewritten by means of the Maxwell relationship:11)

$$\delta = -\frac{(\Delta\gamma)^2}{(C_s^{-1})_{A,S}\left(\frac{\partial A}{\partial \xi}\right)_{s,S}}, \tag{36}$$

with

$$\Delta\gamma = \left(\frac{\partial \gamma}{\partial \xi}\right)_{s,S},$$

where $\Delta\gamma$ denotes the standard surface tension change. Meanwhile, the chemical affinity, A, is expressed by the chemical potential as follows:

$$A = -\mu_{sub} + \mu_s, \tag{37}$$

with

$$\mu_{sub} = \mu_{sub}^{\ominus} + RT \ln c_{sub},$$

$$\mu_s = \mu_s^{\ominus} + RT \ln \Gamma,$$

where μ_{sub} and μ_s are the chemical potentials of S_{sub} and S_s respectively; primsol indicates the standard state, and Γ, the surface excess. The $(\partial A/\partial\xi)_{s,S}$ term in Eq. 35 is rewritten as follows:

$$\left(\frac{\partial A}{\partial\xi}\right)_{s,S}=\left(\frac{\partial A}{\partial\mu_{\mathrm{s}}}\right)_{s,S}\left(\frac{\partial\mu_{\mathrm{s}}}{\partial\Gamma}\right)_{s,S}\left(\frac{\partial\Gamma}{\partial\xi}\right)_{s,S}+\left(\frac{\partial A}{\partial\mu_{\mathrm{sub}}}\right)_{s,S}\left(\frac{\partial\mu_{\mathrm{sub}}}{\partial c_{\mathrm{sub}}}\right)_{s,S}\left(\frac{\partial c_{\mathrm{sub}}}{\partial\xi}\right)_{s,S}, \tag{38}$$

$\mathrm{d}\xi$ being

$$\mathrm{d}\xi = \mathrm{d}n_{\mathrm{sub}} = -\mathrm{d}\Gamma, \tag{39}$$

where n_{sub} is the number of moles of S_{sub} per unit area. Meanwhile, c_{sub} and n_{sub} are related by the following relation:

$$Nn_{\mathrm{sub}} = \left(\frac{c_{\mathrm{sub}}N}{10^3}\right)^{2/3}, \tag{40}$$

The combination of Eq. 36—40 gives

$$\delta = \frac{(\Delta\gamma)^2}{RT(C_{\mathrm{s}}^{-1})_{A,S}}\left\{\frac{3}{2}\times 10^2N^{1/3}c_0^{-2/3}\exp\left(\frac{2Ze\phi_{\mathrm{sub}}}{3k_{\mathrm{B}}T}\right)+\Gamma^{-1}\right\}^{-1}. \tag{41}$$

$(C_{\mathrm{s}}^{-1})_{A,S}$ in Eqs. 18 and 41 is obtained on the assumption that the adsorption-desorption process is in equilibrium; this is the same as the assumption that the molecular transfer between the surface and the bulk phase is governed by only the diffusion process.[4–6] Thus, the following equation is obtained:

$$(C_{\mathrm{s}}^{-1})_{A,S} = \left(-\frac{\partial\gamma}{\partial\ln\Gamma}\right)\frac{1}{1-\dfrac{inD}{\omega'}\left(\dfrac{\partial c_0}{\partial\Gamma}\right)}. \tag{42}$$

According to this equation, Eq. 41 becomes

$$\delta = \frac{(\Delta\gamma)^2}{RT\left(-\dfrac{\partial\gamma}{\partial\ln\Gamma}\right)}\left\{\frac{3}{2}\times 10^2N^{1/3}c_0^{-2/3}\times\exp\left(\frac{2Ze\phi_{\mathrm{sub}}}{3k_{\mathrm{B}}T}\right)+\Gamma^{-1}\right\}^{-1}. \tag{43}$$

On combining Eqs. 34, 43, and 18, $\varepsilon_{\mathrm{ela}}$ and ε_{r} are obtained. Therefore, the equations for the propagation characteristics of the wave for surfactant solutions are finally given as follows:

$$c^2 = \left(\frac{g}{k}+\frac{\gamma k}{\rho}\right)(1+2\varepsilon_{\mathrm{ela,re}}+2\varepsilon_{\mathrm{r,re}}), \tag{24}$$

$$\alpha = \frac{\sigma}{V}(\varepsilon_{\mathrm{ela,im}}+\varepsilon_{\mathrm{r,im}}), \tag{25}$$

with

$$\varepsilon_{\mathrm{ela}} = \frac{\dfrac{2\nu k^2}{\rho}i+\dfrac{k^3}{2\rho\sigma^2}\left[\left(-\dfrac{\partial\gamma}{\partial\ln\Gamma}\right)\left\{1-\dfrac{inD}{\omega'}\left(\dfrac{\partial c_0}{\partial\Gamma}\right)\right\}^{-1}+i\eta_{\mathrm{s}}\sigma\right]}{1-\dfrac{k^3(1+i)}{\rho\sigma^2}\left[\left(-\dfrac{\partial\gamma}{\partial\ln\Gamma}\right)\left\{1-\dfrac{inD}{\omega'}\left(\dfrac{\partial c_0}{\partial\Gamma}\right)\right\}^{-1}+i\eta_{\mathrm{s}}\sigma\right]\left(\dfrac{2\nu k^2}{\sigma}\right)^{1/2}}, \tag{44}$$

and

$$\varepsilon_{\mathrm{r}} = \frac{k^3}{2\rho\sigma^2}\left(-\frac{\partial\gamma}{\partial\ln\Gamma}\right)\left\{1-\frac{inD}{\omega'}\left(\frac{\partial c_0}{\partial\Gamma}\right)\right\}^{-1}\left(\frac{\omega'^2\tau^2\delta}{1+\omega'^2\tau^2}+\frac{i\omega'\tau\delta}{1+\omega'^2\tau^2}\right). \tag{45}$$

The relaxation parameters in these equations are given by Eqs. 34 and 43.

Discussion

This theory is applicable to the two-dimensional relaxation phenomena on the surface of a surfactant solution and the monolayer. The derived equations can be simplified easily by evaluating the magnitudes of the parameters.

For the surfactant solutions, the two cases of approximations are given as follows.

Relaxation Effect (or χ_r) is Negligibly Small. This is satisfied at $\omega'\tau\ll 1$. Equations 24 and 25 are simplified to

$$c^2 = \left(\frac{g}{k}+\frac{\gamma k}{\rho}\right)(1+2\varepsilon_{\mathrm{ela,re}}), \tag{46}$$

$$\alpha = \frac{\sigma\varepsilon_{\mathrm{ela,im}}}{V} \equiv \alpha_{\mathrm{d}}. \tag{47}$$

$\varepsilon_{\mathrm{ela}}$ in these equations is given by Eq. 44. These equations result in those based on only the diffusion process.[4,6]

Relaxation Effect (or χ_r) is Relatively Large. In a dilute solution, c and α are given by Eqs. 24, 25, 34, 43, and 45. Since the relaxation time depends on the frequency, however, the application of the equations is troublesome. In case of the concentrated solution, the following equations are obtained (see Appendix V):

$$c^2 = \left(\frac{g}{k}+\frac{\gamma k}{\rho}\right)\left(1+2\varepsilon_{\mathrm{ela,re}}+\frac{\gamma k}{\rho c^2}\,\frac{\omega'^2\tau^2\delta'}{1+\omega'^2\tau^2}\right), \tag{48}$$

$$\alpha = \alpha_{\mathrm{d}} + \frac{\gamma k}{2V\rho c}\cdot\frac{\omega'\tau\delta'}{1+\omega'^2\tau^2}, \tag{49}$$

with

$$\tau^{-1} = k_{\mathrm{a},\theta}c_0\exp\left(-\frac{Ze\phi_{\mathrm{sub}}}{k_{\mathrm{B}}T}\right) + k_{\mathrm{d}},$$

and

$$\delta' = \frac{(C_{\mathrm{s}}^{-1})_{A,S}}{\gamma}\delta = \frac{3(\Delta\gamma)^2c_0\exp\left(-\dfrac{2Ze\phi_{\mathrm{sub}}}{3k_{\mathrm{B}}T}\right)}{2\times 10^2RT\gamma N^{1/3}},$$

where δ' is the apparent relaxation strength.

For an insoluble monolayer, the following two kinds of approximations are given.

Relaxation Effect (or χ_r) is Negligibly Small. Since the solubility of molecules is negligibly small, Eq. 44 is simplified:

$$\varepsilon_{\mathrm{ela}} = \frac{\dfrac{2\nu k^2}{\sigma}i+\dfrac{k^3}{2\rho\sigma^2}\{(C_{\mathrm{s}}^{-1})_{\mathrm{mo}}+i\eta_{\mathrm{s}}\sigma\}}{1-\dfrac{k^3(1+i)}{\rho\sigma^2}\{(C_{\mathrm{s}}^{-1})_{\mathrm{mo}}+i\eta_{\mathrm{s}}\sigma\}\left(\dfrac{2\nu k^2}{\sigma}\right)^{1/2}}, \tag{50}$$

where $(C_{\mathrm{s}}^{-1})_{\mathrm{mo}}$ is obtained from the (surface pressure)-(molecular surface area) curve. Inserting Eq. 50 into Eqs. 46 and 47, Dorrestein's equations[1] can be obtained.

Relaxation Effect (or χ_r) is Relatively Large. The relaxation time in χ_{r} is derived by solving the rate equation related to the equilibrium on monolayer. The relaxation strength is also derived in the same manner as in the treatment for a surfactant solution. Then, ε_{r} is expressed by the concentration of species and the kinetic parameters connected with the equilibrium. Consequently, from Eq. 50 and the equation for ε_{r}, Eqs. 24 and 25 are represented in a concrete form.

In conclusion, the derived equations can be extensively applied, particularly to concentrated surfactant solutions, and can be expected to give kinetic parameters associated with the adsorption-desorption process of the surfactant. The experimental results of the propagation characteristics of the wave on the surface of various surfactant solutions and the applicability of the equations obtained in the present study will be reported in a subsequent paper.

Appendix

I. The relative change in the surface area, β, is expressed by the following equation, in which the wave is represented by $a=a_0\sin(\omega t+kx)$:

$$\beta = \left(\frac{a_0k}{2}\right)^2[1+\cos\{2(\omega t+kx)\}]$$
$$= \left(\frac{a_0k}{2}\right)^2\{1+\cos(\omega' t+\kappa x)\},$$

where a_0 is the amplitude, and ω, the frequency of the wave. As is seen from this equation, the surface tends to expand at the nodes.

II. The thermal diffusion coefficient, D_T, in water is 1.4×10^{-3} cm^2 s^{-1}, while that in gas is of the order of 10^{-4} cm^2 s^{-1}. Under the present experimental conditions, the wavelength is about 9.8 mm at the lowest frequency (25 Hz) and 0.4 mm at the highest frequency (2 kHz).[9] Therefore, the $2\pi/kD_T \gg k/\omega$ condition is always satisfied; *i. e.*, the adiabatic approximation can be applied.

III. The thickness of the subsurface layer, d_{sub}, is much thinner than $d_b(=n^{-1})$. From Eq, 29, therefore, Δc_{sub} is approximated as

$$\Delta c_{sub} = E_b \exp(-nd_{sub}) \simeq E_b.$$

Moreover, the law of mass conservation is given as

$$d_s\Delta c_s = \int_{-d_{sub}}^{-\infty} E_b \exp(ny)\,\mathrm{d}y \simeq -\frac{E_b}{n}.$$

The above equations lead to the relation between Δc_{sub} and Δc_s:

$$\Delta c_{sub} = -nd_s\Delta c_s.$$

IV. By eliminating $\mathrm{d}\xi$ from Eqs. 9 and 10, $\mathrm{d}\gamma$ becomes:

$$\mathrm{d}\gamma = \left\{\left(\frac{\partial\gamma}{\partial s}\right)_{\xi,S} - \left(\frac{\partial\gamma}{\partial\xi}\right)_{s,S}\left(\frac{\partial A}{\partial s}\right)_{\xi,S}\left(\frac{\partial A}{\partial\xi}\right)_{s,S}^{-1}\right\}\mathrm{d}s + \left(\frac{\partial\gamma}{\partial\xi}\right)_{s,S}\left(\frac{\partial A}{\partial\xi}\right)_{s,S}\mathrm{d}A.$$

Therefore

$$\left(\frac{\partial\gamma}{\partial s}\right)_{A,S} = \left(\frac{\partial\gamma}{\partial s}\right)_{\xi,S} - \left(\frac{\partial\gamma}{\partial\xi}\right)_{s,S}\left(\frac{\partial A}{\partial s}\right)_{\xi,S}\left(\frac{\partial A}{\partial\xi}\right)_{s,S}^{-1}.$$

δ is obtained from the above equation and Eq. 14:

$$\delta = -\frac{\left(\frac{\partial\gamma}{\partial\xi}\right)_{s,S}\left(\frac{\partial A}{\partial s}\right)_{\xi,S}}{\left(\frac{\partial\gamma}{\partial s}\right)_{A,S}\left(\frac{\partial A}{\partial s}\right)_{s,S}}.$$

V. If $c_0>10^{-3}$ mol dm^{-3}, $k_a<10^6$ s^{-1}, $\theta>0.95$, and $\phi_{sub}\approx 0$, Eq. 34 is simplified, with $\omega'\approx 10^3$ s^{-1}, $D\approx 10^{-6}$ cm^2 s^{-1}, $d{\approx}_s 10^{-7}$ cm and $\Gamma_{max}\approx 5\times 10^{-10}$ mol cm^{-2}:

$$\tau^{-1} = k_{a,\theta}c_0\exp\left(-\frac{Ze\phi_{sub}}{k_BT}\right) + k_d.$$

The second term in the bracket in Eq. 43 is neglected compared with the first term:

$$\delta = \frac{3(\Delta\gamma)^2c_0\exp\left(-\frac{2Ze\phi_{sub}}{3k_BT}\right)}{2\times 10^2RT(C_s^{-1})_{A,S}N^{1/3}}.$$

Notations

A;	chemical affinity.
a, a_0;	displacement and amplitude of wave respectively.
C_s;	surface compressibility (10^{-5} N/cm).
$C_s{}^*$;	dynamic surface compressibility.
$(C_s{}^{-1})_{mo}$;	reciprocal surface compressibility for an insoluble monolayer.
c;	propagation velocity of the capillary wave.
c_b;	concentration of the surfactant solution in the bulk phase.
c_0;	initial concentration.
c_s, c_{sub};	concentrations of S_s and S_{sub} respectively.
D;	diffusion coefficient.
D_T;	thermal diffusion coefficient.
d_b;	thickness of the bulk phase concerned with the diffusion process.
d_s, d_{sub};	thicknesses of the surface and the subsurface layers respectively.
E_1, E_2;	complex constants associated with the amplitudes of Φ and Ψ respectively.
E_b;	amplitude of perturbed concentration in the bulk phase.
e;	elementary charge.
g;	gravitational acceleration.
k;	wave number.
k_a, k_d;	adsorption rate constant (s^{-1}) and desorption rate constant (s^{-1}) respectively.
$k_{a,\theta}$;	converted adsorption rate constant (mol^{-1} dm^3·s^{-1}).
k_B;	Boltzmann constant.
L;	proportional constant in the relaxation equation.
m;	complex constant.
N;	Avogadro number.
N_i, N_j';	numbers of moles of R_i and P_j species respectively.
n;	reciprocal of the thickness of the bulk phase concerned with the diffusion process.
n_{sub};	number of moles of S_{sub} per unit surface area.
p;	hydrostatic pressure.
P_j, R_i;	species in equilibrium.
R;	gas constant.
r;	complex angular frequency.
S;	surface entropy.
S_s, S_{sub}, S_b;	surfactants on surface, subsurface, and bulk phase respectively.
s;	surface area per unit area.
T;	temperature.
t;	time.
u, v;	horizontal and vertical components of liquid velocity respectively.
V;	$(3/2)c$, group velocity.
x,y;	Cartesian coordinate.
Z;	valency of surfactant.
α;	damping coefficient (cm^{-1}).
β;	relative change in the surface area.
Γ;	surface excess.
γ;	sulface tension (10^{-5} N cm^{-1}).
$\Delta\gamma$;	standard surface tension change.
δ;	relaxation strength.
ε_{ela}, ε_r;	dispersion terms of the angular frequency.
η;	viscosity (10^{-5} N s cm^{-2}).
η_s;	surface viscosity (10^{-5} N s cm^{-1}).
θ;	fraction of sites occupied by S_s.
κ;	$2k$, wave number.

μ_s, μ_{sub};	chemical potentials of S_s and S_{sub} respectively.
ν;	$\eta/,\rho$ kinematic viscosity.
ν_i, ν_j'	stoichiometric coefficients of R_i and R_j respectively.
ξ;	ordering coefficient.
ρ;	density.
σ;	$(g/k+\gamma k^3/\rho)^{1/2}$, angular frequency of the wave.
$\tau_{s,S}$, $\tau_{r,S}$;	relaxation times.
Φ, Ψ;	stream and potential functions respectively.
ϕ;	elevation of the surface.
χ^*;	dimensionless parameter associated with the dynamic surface compressibility and the surface viscosity.
ψ_{sub};	electric potential at $y=-d_{sub}$.
ω, $\omega'(=2\omega)$;	angular frequencies of the wave and the external driving force respectively.

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