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ORIGINAL CONTRIBUTION

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Thermodynamic studies on thin liquid films. I. General formulation

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Abstract From the viewpoint that thermodynamic study is essential to elucidate the structure and properties of thin liquid films, thermodynamic equations based on a new convention and employing pressure as a thermodynamic variable are developed for adsorption at film interfaces of a plane-parallel film. The equations together with quasi-thermodynamic ones correlate the dependence of film tension on concentration, temperature, pressure, and disjoining pressure to film density, entropy and volume changes associated with adsorption, and thermodynamic film thickness, respectively. Based on the formulation adopting pressure as a variable, equations are also derived for the differences in thermodynamic quantity between the film and the bulk interfaces coexisting at equilibrium.

Keywords Thermodynamics and quasi-thermodynamics · Plane-parallel films · Pressure as a variable · Adsorption at film interface · Film and bulk interface

Introduction

Properties of thin liquid films play an important role in the stability of foams, emulsions, and suspensions [1] and are closely related to the prewetting of interfaces [2, 3] and the diffusion through a film [4]. Thin liquid films made from surfactant solutions form black films stabilized by the adsorption of surfactants at the film interfaces in the presence of inorganic salts. The black films can be a model of bilayers and the interaction between the interfaces in the film provides direct information about the surface forces and colloidal stability [1, 5, 6].

It is essential to obtain thermodynamic quantities of a thin liquid film in order to elucidate structure and physico-chemical properties of the film and interaction between interfaces in the film. Thermodynamics of thin liquid films has been developed by employing the film excess convention by Derjaguin [7, 8] and the surface excess one first by Rusanov [8, 9, 10] and subsequently by others [11, 12, 13]. These conventions eliminate the pressure in the phases separated by the film from thermodynamic variables and don't provide information about the volume conjugated with the pressure. Furthermore, from a rigorous thermodynamic viewpoint, fundamental equations based on those conventions are not applicable to experimental data because film experiments are usually conducted under constant pressure in the ambient phases.

In the previous studies on adsorption at interfaces based on the Hansen convention [14, 15, 16, 17, 18, 19, 20], pressure dependence of interfacial tension was proved to afford the volumes associated with interface formation, adsorption, and micelle formation. Therefore, thermodynamic formulation of thin liquid films employing pressure as an independent variable based on a new convention is highly required and the difference in thermodynamic quantities between film interface and bulk one is to be elucidated. This study aims to: (i) develop thermodynamics of plane-parallel films by using the convention which adopts the pressure in the phases surrounding on both sides of the film as a thermodynamic variable, (ii) clarify the physical meaning of the thermodynamic quantities of a film using quasi-thermodynamics, and (iii) compare the resultant equations with those for adsorption at the bulk interfaces coexisting in equilibrium with the film.

Fundamental equations

Let us consider a plane-parallel film formed from phase L between phases A and B and in equilibrium with the phases as shown in Fig. 1a; components a,b, and l are the solvents in the phases A, B, and L, respectively, and 1,...,c are the solutes, which are taken to be nonionic for simplicity; total number of components in the system is $c + 3$. The effects of gravity and line tension are assumed to be negligible. At equilibrium, temperature T and chemical potentials of components μ_a,μ_b,μ_l,μ_1,...,μ_c are uniform throughout the system. However, pressure p^L in the phase L is different from pressure p in the phases A and B. The Gibbs-Duhem equation for the system can be expressed by

$$-S\mathrm{d}T + V\mathrm{d}p - \sigma\mathrm{d}\gamma^f - n_a\mathrm{d}\mu_a - n_b\mathrm{d}\mu_b - n_l\mathrm{d}\mu_l - \sum_{i=1}^{c} n_i\mathrm{d}\mu_i = 0 \tag{1}$$

in the same form as the one for the corresponding system of interface [14, 21], where S denotes the entropy of the system, V the volume, σ the film area, γ^f the film tension, and n_a,n_b,n_l,n_1, ...,n_c the numbers of moles of the components. The Gibbs-Duhem equations for the phases A, B, and L per unit volume of phase are expressed by

$$-s^A\mathrm{d}T + \mathrm{d}p - c_a^A\mathrm{d}\mu_a - c_b^A\mathrm{d}\mu_b - c_l^A\mathrm{d}\mu_l - \sum_{i=1}^{c} c_i^A\mathrm{d}\mu_i = 0 \tag{2}$$

$$-s^B\mathrm{d}T + \mathrm{d}p - c_a^B\mathrm{d}\mu_a - c_b^B\mathrm{d}\mu_b - c_l^B\mathrm{d}\mu_l - \sum_{i=1}^{c} c_i^B\mathrm{d}\mu_i = 0 \tag{3}$$

and

$$-s^L\mathrm{d}T + \mathrm{d}p^L - c_a^L\mathrm{d}\mu_a - c_b^L\mathrm{d}\mu_b - c_l^L\mathrm{d}\mu_l - \sum_{i=1}^{c} c_i^L\mathrm{d}\mu_i = 0 \tag{4}$$

respectively, where s and c_i denote the entropy and the number of moles of component i per unit volume. Subtracting Eqs. (2) - (4) multiplied by the volumes V^A,V^B, and V^L of the phases A, B, and L, respectively from Eq. (1) and employing one of the conventions developed for adsorption at the interface with a floating liquid-lens [21], we have

$$\mathrm{d}\gamma^f = -s^f\mathrm{d}T + \left(v^f + v^L\right)\mathrm{d}p - v^L\mathrm{d}p^L - \sum_{i=1}^{c}\Gamma_i^f\mathrm{d}\mu_i \tag{5}$$

$$= -s^f\mathrm{d}T + v^f\mathrm{d}p + v^L\mathrm{d}\Pi - \sum_{i=1}^{c}\Gamma_i^f\mathrm{d}\mu_i \tag{6}$$

where excess quantity n_i^f of component i and the n_i^f per unit film area, Γ_i^f, which we call film density, and the corresponding thermodynamic quantities Y^f and y^f are defined by

$$\Gamma_i^f = n_i^f/\sigma = \left(n_i - V^A c_i^A - V^B c_i^B - V^L c_i^L\right)/\sigma, \qquad (i = 1, \ldots, c) \tag{7}$$

and

$$y^f = Y^f/\sigma = \left(Y - V^A y^A - V^B y^B - V^L y^L\right)/\sigma, \qquad (y = s,\ v) \tag{8}$$

and volume v^L of the phase L per unit film area is by

$$v^L = V^L/\sigma \tag{9}$$

and for an equilibrium plane film, pressure difference p–p^L is equal to the Derjaguin disjoining pressure Π [10, 11, 22],

$$\Pi = p - p^L. \tag{10}$$

Effective disjoining pressure is zero for the equilibrium film under consideration [23]. Locations of four dividing planes, which decide V^A,V^B, and V^L, were chosen so that the film densities of all the solvents are simultaneously zero:

$$\Gamma_a^f = \Gamma_b^f = \Gamma_l^f = 0. \tag{11}$$

Equation (6) shows γ^f as a function of $c+3$ independent variables T, p, Π, μ_1, ...μ_c, which is consistent with an analogue of Gibbs' phase rule for a capillary system with thin liquid films [24]. It is worth noting that the above convention is symmetric with respect to the solvent components and in conformity with the Hansen convention [14, 25, 26] for bulk interfaces when the film is thick and its core is identical with the phase L. The film excess and surface excess conventions correspond to

$$v^f = v^L = 0,\ \Gamma_i^f = 0, \qquad (i = a \text{ or } b) \tag{12}$$

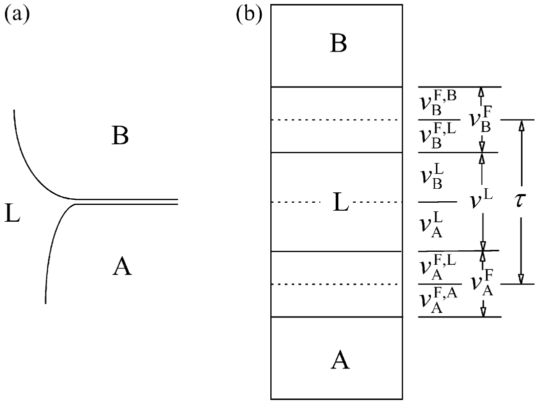

Fig. 1 Schematic illustrations of: **a** a plane-parallel film formed from the phase L between the phases A and B; **b** regions in the plane-parallel film separated by the surfaces of tension and the dividing planes. (- - -): surface of tension; (———): dividing plane

and

$$v^f = 0,\ \Gamma_i^f = \Gamma_j^f = 0, \qquad (i,\ j = a,\ b \text{ or } l;\ i \neq j) \tag{13}$$

respectively: in the former the excess quantities of a film are defined with respect to the one dividing plane ($v^f = v^L = 0$) location of which is determined by $\Gamma_i^f = 0$ and in the latter with respect to the two dividing planes ($v^f = 0$) locations of which are by $\Gamma_i^f = \Gamma_j^f = 0$. The set of variables $\{T,\mu_j,\mu_l,\mu_1,\ ...,\mu_c;\ j = a$ or b, $\neq i$ in Eq. (12)$\}$ is taken in the film excess convention and $\{T,\Pi,\mu_k,\ \mu_1,...,\mu_c;\ k = a,b$ or l, $\neq i, j$ in Eq. (13)$\}$ is by the surface excess one and p is eliminated from independent variables in both the conventions.

In order to clarify the contribution of each film interface in a film to the thermodynamic quantities of the film and the difference in thermodynamic quantities between the film interface and bulk one, the Gibbs-Duhem equation for the system can also be expressed in terms of film interfacial tension γ_A^F and γ_B^F against the phases A and B [23, 27], respectively as

$$\begin{aligned} &-S\mathrm{d}T + V\mathrm{d}p - \sigma\tau\mathrm{d}\Pi - \sigma\Pi\mathrm{d}\tau - \sigma\mathrm{d}\left(\gamma_A^F + \gamma_B^F\right) \\ &- n_a\mathrm{d}\mu_a - n_b\mathrm{d}\mu_b - n_l\mathrm{d}\mu_l - \sum_{i=1}^{c} n_i\mathrm{d}\mu_i = 0 \end{aligned} \tag{14}$$

(Appendix I). In the same manner as that used to derive Eq. (6) and replacing Eq. (1) by Eq. (14), we have

$$\begin{aligned} &\mathrm{d}\left(\gamma_A^F + \gamma_B^F\right) \\ &\quad = \left(s_A^F + s_B^F\right)\mathrm{d}T + \left(v_A^F + v_B^F\right)\mathrm{d}p \\ &\qquad -(\tau - v^L)\mathrm{d}\Pi - \Pi\mathrm{d}\tau - \sum_{i=1}^{c}\left(\Gamma_i^{F,A} + \Gamma_i^{F,B}\right)\mathrm{d}\mu_i \end{aligned} \tag{15}$$

where τ is the distance between the surfaces of tension for the film interfaces. Excess quantity $n_i^{F,K}$ and interfacial density $\Gamma_i^{F,K}$ of component i ascribed to the film interface against the phase K and the corresponding thermodynamic quantities Y_K^F and y_K^F are defined by

$$\begin{aligned} \Gamma_i^{F,K} &= n_i^{F,K}/\sigma \\ &= \left(n_i^{K*} - V^K c_i^K - V_K^L c_i^L\right)/\sigma, \quad (i = 1, \ldots, c;\ \mathrm{K} = \mathrm{A},\ \mathrm{B}) \end{aligned} \tag{16}$$

and

$$y_K^F = Y_K^F/\sigma = \left(Y^{K*} - V^K y^K - V_K^L y^L\right)/\sigma, \qquad (y = s,\ v;\ \mathrm{K} = \mathrm{A},\ \mathrm{B}) \tag{17}$$

where n_i^{K*} and Y^{K*} are the number of moles of component i and the thermodynamic quantity of the part K* of the system separated by the surface of tension for the film, respectively. The surface of tension also divides V^L into V_A^L and V_B^L as shown in Fig. 1b. By definition,

$$\Gamma_i^f = \Gamma_i^{F,A} + \Gamma_i^{F,B} \tag{18}$$

$$\gamma^f = \gamma_A^F + \gamma_B^F. \tag{19}$$

We can also obtain Eq. (15) by substituting the equation for mechanical equilibrium of the system [27]

$$\gamma^f = \gamma_A^F + \gamma_B^F + \Pi\tau \tag{20}$$

into Eq. (6). From Eq. (15) we notice that the film interfacial tension is apparently dependent on τ other than $T,p,\ \Pi,\mu_1,\cdots,\mu_c$, and the thermodynamic quantity of each film interface like $\Gamma_i^{F,K}$ and y_K^F cannot be obtained separately.

From an experimental viewpoint, it is advantageous to take T, p, Π, and the molalities of solute components as independent variables (Appendix II). For the case of adsorption at film interfaces from the phase L which is assumed to be an ideal solution, Eqs. (6) and (15) reduce to

$$\begin{aligned} \mathrm{d}\gamma^f = &-\left(s^f - \sum_{j=1}^{c}\Gamma_j^f s_j\right)\mathrm{d}T + \left(v^f - \sum_{j=1}^{c}\Gamma_j^f v_j\right)\mathrm{d}p \\ &+ \left(v^L + \sum_{j=1}^{c}\Gamma_j^f v_j\right)\mathrm{d}\Pi - \sum_{j=1}^{c}(RT/m_i)\Gamma_i^f\mathrm{d}m_i \end{aligned} \tag{21}$$

and

$$
\begin{aligned}
&\mathrm{d}\left(\gamma_{\mathrm{A}}^{\mathrm{F}}+\gamma_{\mathrm{B}}^{\mathrm{F}}\right)\\
&=-\left[s_{\mathrm{A}}^{\mathrm{F}}+s_{\mathrm{B}}^{\mathrm{F}}-\sum_{j=1}^{c}\left(\Gamma_{j}^{\mathrm{F,A}}+\Gamma_{j}^{\mathrm{F,B}}\right)s_{j}+\Pi(\partial\tau/\partial T)_{p,\Pi,m}\right]\mathrm{d}T\\
&\quad+\left[v_{\mathrm{A}}^{\mathrm{F}}+v_{\mathrm{B}}^{\mathrm{F}}-\sum_{j=1}^{c}\left(\Gamma_{j}^{\mathrm{F,A}}+\Gamma_{j}^{\mathrm{F,B}}\right)v_{j}-\Pi(\partial\tau/\partial p)_{T,\Pi,m}\right]\mathrm{d}p\\
&\quad+\left\{v^{\mathrm{L}}+\sum_{j=1}^{c}\left(\Gamma_{j}^{\mathrm{F,A}}+\Gamma_{j}^{\mathrm{F,B}}\right)v_{j}-\left[\partial(\Pi\tau)/\partial\Pi\right]_{T,p,m}\right\}\mathrm{d}\Pi\\
&\quad-\sum_{j=1}^{c}\left[(RT/m_{i})\left(\Gamma_{i}^{\mathrm{F,A}}+\Gamma_{i}^{\mathrm{F,B}}\right)+\Pi(\partial\tau/\partial m_{i})_{T,p,\Pi,m_{i}}\right]\mathrm{d}m_{i}
\end{aligned}
\tag{22}
$$

respectively, where subscript m represents $m_1,\ldots,m_c$ are kept constant. Equations (21) and (22) show that s^{f}, v^{f}, v^{L}, $\Gamma_1^{\mathrm{f}},\ldots,\Gamma_c^{\mathrm{f}}$can be obtained from the dependence of γ^{f} or $\gamma_{\mathrm{A}}^{\mathrm{F}}$, $\gamma_{\mathrm{B}}^{\mathrm{F}}$, and τ on T, p, Π, $m_1,\ldots,m_c$. Thermodynamic equations for adsorption from the other phases can be derived as well.

Thermodynamic quantity change associated with adsorption and thermodynamic film thickness

Quasi-thermodynamics correlates the local thermodynamic quantities of inhomogeneous regions like interfaces and thin liquid films to their excess thermodynamic quantities [14, 28]. According to the rectangular coordinate system defined in Appendix I, let us make the film region be shown by $\mathrm{I_A} < z < \mathrm{I_B}$, the phase A by $z \le \mathrm{I_A}$, and the phase B by $z \ge \mathrm{I_B}$. The film density is expressed by

$$
\begin{aligned}
\Gamma_i^{\mathrm{f}} &= \int_{-\infty}^{\infty}\left[c_i(z)-c_i^{\mathrm{ABL}}(z)\right]\mathrm{d}z=\int_{\mathrm{I_A}}^{\mathrm{I_B}}\left[c_i(z)-c_i^{\mathrm{ABL}}(z)\right]\mathrm{d}z\\
&= \Gamma_i^{\mathrm{I}}-\left(\Gamma_i^{\mathrm{I,A}}+\Gamma_i^{\mathrm{I,B}}+\Gamma_i^{\mathrm{I,L}}\right),\qquad (i=a,b,l,1,\ldots,c)
\end{aligned}
\tag{23}
$$

where

$$
\begin{aligned}
c_i^{\mathrm{ABL}}(z) =&\left[1-A\left(z+v_{\mathrm{A}}^{\mathrm{F}}+v_{\mathrm{A}}^{\mathrm{L}}\right)\right]c_i^{\mathrm{A}}\\
&+\left[A\left(z+v_{\mathrm{A}}^{\mathrm{L}}\right)-A\left(z-v_{\mathrm{B}}^{\mathrm{L}}\right)\right]c_i^{\mathrm{L}}\\
&+A\left(z+v_{\mathrm{B}}^{\mathrm{F}}-v_{\mathrm{B}}^{\mathrm{L}}\right)c_i^{\mathrm{B}}
\end{aligned}
\tag{24}
$$

A(z) being the step function given by Eq. (I.3) in Appendix I. $\Gamma_i^{\mathrm{I}}$is the film density of component *i* inherent in the film, $\Gamma_i^{\mathrm{I,A}}$, $\Gamma_i^{\mathrm{I,A}}$, and $\Gamma_i^{\mathrm{I,L}}$are the ones in the portions of the film region which is separated by the dividing planes as shown in Fig. 1b and they are expressed by

$$
\Gamma_i^{\mathrm{I}}=\int_{\mathrm{I_A}}^{\mathrm{I_B}}c_i(z)\mathrm{d}z \tag{25}
$$

$$
\Gamma_i^{\mathrm{I,A}}=c_i^{\mathrm{A}}\int_{\mathrm{I_A}}^{-\left(v_{\mathrm{A}}^{\mathrm{F}}+v_{\mathrm{A}}^{\mathrm{L}}\right)}\mathrm{d}z \tag{25a}
$$

$$
\Gamma_i^{\mathrm{I,B}}=c_i^{\mathrm{B}}\int_{v_{\mathrm{B}}^{\mathrm{F}}+v_{\mathrm{B}}^{\mathrm{L}}}^{\mathrm{I_B}}\mathrm{d}z \tag{25b}
$$

$$
\Gamma_i^{\mathrm{I,L}}=c_i^{\mathrm{L}}\int_{-v_{\mathrm{A}}^{\mathrm{L}}}^{v_{\mathrm{B}}^{\mathrm{L}}}\mathrm{d}z \tag{25c}
$$

respectively. It follows from Eq. (11) that

$$
\Gamma_i^{\mathrm{I}}=\Gamma_i^{\mathrm{I,A}}+\Gamma_i^{\mathrm{I,B}}+\Gamma_i^{\mathrm{I,L}},\qquad (i=a,b,l). \tag{26}
$$

The excess thermodynamic quantity can be expressed by

$$
\begin{aligned}
y^{\mathrm{f}}&=\int_{-\infty}^{\infty}\left[y(z)-y^{\mathrm{ABL}}(z)\right]\mathrm{d}z=\int_{\mathrm{I_A}}^{\mathrm{I_B}}\left[y(z)-y^{\mathrm{ABL}}(z)\right]\mathrm{d}z\\
&=\sum_{i=a}^{c}\int_{\mathrm{I_A}}^{\mathrm{I_B}}\left[c_i(z)y_i(z)-c_i^{\mathrm{ABL}}(z)y_i^{\mathrm{ABL}}(z)\right]\mathrm{d}z
\end{aligned}
\tag{27}
$$

where

$$
\begin{aligned}
y^{\mathrm{ABL}}(z) =&\left[1-A\left(z+v_{\mathrm{A}}^{\mathrm{F}}+v_{\mathrm{A}}^{\mathrm{L}}\right)\right]y^{\mathrm{A}}\\
&+\left[A\left(z+v_{\mathrm{A}}^{\mathrm{L}}\right)-A\left(z-v_{\mathrm{B}}^{\mathrm{L}}\right)\right]y^{\mathrm{L}}\\
&+A\left(z-v_{\mathrm{B}}^{\mathrm{F}}-v_{\mathrm{B}}^{\mathrm{L}}\right)y^{\mathrm{B}}
\end{aligned}
\tag{28}
$$

and we used the relation between thermodynamic quantity y and partial molar quantity y_i for the bulk phase

$$
y=\sum_{i=a}^{c}c_iy_i \tag{29}
$$

and the corresponding one between $y(z)$ and $y_i(z)$ for the film region

$$
y(z)=\sum_{i=a}^{c}c_i(z)y_i(z) \tag{30}
$$

The integral in Eq. (27) can be reduced to

$$
\begin{aligned}
&\int_{\mathrm{I_A}}^{\mathrm{I_B}}\left[c_i(z)y_i(z)-c_i^{\mathrm{ABL}}(z)y_i^{\mathrm{ABL}}(z)\right]\mathrm{d}z=\int_{\mathrm{I_A}}^{\mathrm{I_B}}c_i(z)y_i(z)\mathrm{d}z\\
&\quad-\left[c_i^{\mathrm{A}}y_i^{\mathrm{A}}\int_{\mathrm{I_A}}^{-\left(v_{\mathrm{A}}^{\mathrm{F}}+v_{\mathrm{A}}^{\mathrm{L}}\right)}\mathrm{d}z+c_i^{\mathrm{B}}y_i^{\mathrm{B}}\int_{v_{\mathrm{B}}^{\mathrm{F}}+v_{\mathrm{B}}^{\mathrm{L}}}^{\mathrm{I_B}}\mathrm{d}z+c_i^{\mathrm{L}}y_i\int_{-v_{\mathrm{A}}^{\mathrm{L}}}^{v_{\mathrm{B}}^{\mathrm{L}}}\mathrm{d}z\right]\\
&=\Gamma_i^{\mathrm{I}}\bar{y}_i^{\mathrm{I}}-\left(\Gamma_i^{\mathrm{I,A}}y_i^{\mathrm{A}}+\Gamma_i^{\mathrm{I,B}}y_i^{\mathrm{B}}+\Gamma_i^{\mathrm{I,L}}y_i\right)
\end{aligned}
\tag{31}
$$

$$
=\Gamma_i^{\mathrm{I}}\Delta y_i,\qquad (i=a,\ b,\ l) \tag{31a}
$$

$$
=\Gamma_i^{\mathrm{f}}\bar{y}_i^{\mathrm{f}},\qquad (i=1,\ldots,\ c) \tag{31b}
$$

where mean partial molar quantities $\bar{y}_i^{\mathrm{I}}$ and $\bar{y}_i^{\mathrm{f}}$are defined by

$$
\bar{y}_i^{\mathrm{I}}=\int_{\mathrm{I_A}}^{\mathrm{I_B}}c_i(z)y_i(z)\mathrm{d}z\Big/\int_{\mathrm{I_A}}^{\mathrm{I_B}}c_i(z)\mathrm{d}z \tag{32}
$$

and

$$\bar{y}_i^{\mathrm{f}} = \int_{\mathrm{I_A}}^{\mathrm{I_B}} \left[c_i(z)y_i(z) - c_i^{\mathrm{ABL}}(z)y_i^{\mathrm{ABL}}(z)\right]\mathrm{d}z/$$

$$\int_{\mathrm{I_A}}^{\mathrm{I_B}} \left[c_i(z) - c_i^{\mathrm{ABL}}(z)\right]\mathrm{d}z \tag{33}$$

respectively and change Δy_i in the partial molar quantity of solvent *i* associated with adsorption is written by

$$\Delta y_i = \bar{y}_i^{\mathrm{I}} - \left(\Gamma_i^{\mathrm{I,A}}y_i^{\mathrm{A}} + \Gamma_i^{\mathrm{I,B}}y_i^{\mathrm{B}} + \Gamma_i^{\mathrm{I,L}}y_i\right)/\Gamma_i^{\mathrm{I}}. \tag{34}$$

The terms Γ_i^{I} and Γ_i^{f}, and $\bar{y}_i^{\mathrm{I}}$, and $\bar{y}_i^{\mathrm{f}}$ should be distinguished from each other because Γ_i^{I} and $\bar{y}_i^{\mathrm{I}}$are the quantities inherent in the film and Γ_i^{f}, and $\bar{y}_i^{\mathrm{f}}$are the excess ones defined with respect to the dividing planes. Substituting Eqs. (31a) and (31b) into Eq. (27) leads to

$$y^{\mathrm{f}} = \Gamma_a^{\mathrm{I}}\Delta y_a + \Gamma_b^{\mathrm{I}}\Delta y_b + \Gamma_l^{\mathrm{I}}\Delta y_l + \sum_{i=1}^{c}\Gamma_i^{\mathrm{f}}y_i^{\mathrm{f}} \tag{35}$$

We hence define thermodynamic quantity change Δy^{f} associated with adsorption of solutes at the film interfaces from the phase L by

$$\Delta y^{\mathrm{f}} = y^{\mathrm{f}} - \sum_{i=1}^{c}\Gamma_i^{\mathrm{f}}y_i$$

$$= \Gamma_a^{\mathrm{I}}\Delta y_a + \Gamma_b^{\mathrm{I}}\Delta y_b + \Gamma_l^{\mathrm{I}}\Delta y_l + \sum_{i=1}^{c}\Gamma_i^{\mathrm{f}}\left(\bar{y}_i^{\mathrm{f}} - y_i\right) \tag{36}$$

On the other hand, it follows from Eq. (25c) that

$$v^{\mathrm{L}} = \Gamma_l^{\mathrm{I,L}}/c_l^{\mathrm{L}} \tag{37}$$

τ^{f} can then be defined by

$$\tau^{\mathrm{f}} = v^{\mathrm{L}} + \sum_{i=1}^{c}\Gamma_i^{\mathrm{f}}v_i = \Gamma_l^{\mathrm{I,L}}/c_l^{\mathrm{L}} + \sum_{i=1}^{c}\Gamma_i^{\mathrm{f}}v_i \tag{38}$$

where the first term in the right-hand side is the thickness of film core equivalent to the phase L and the second one the total thickness of adsorbed films at the film interfaces reduced to the partial molar volumes of solutes in the phase L. We call τ^{f}thermodynamic film thickness because it is defined in terms of thermodynamic quantities. The thermodynamic thickness may correspond to the experimental thickness obtained from an interferometric thickness measurement based on the three-layer model of films [29, 30] which makes a film consist of a film core and two layers ascribed to the adsorbed films at film interfaces. The distance between two dividing planes in the surface excess convention was also termed thermodynamic thickness [8, 31], but there is no confusion of their use because the difference between the two thermodynamic thicknesses is explicit. The thermodynamic thickness τ^{f} and the mechanical one τ should also be distinguished from each other even if they give a similar value for a thick film.

Substituting Eqs. (36) and (38) into Eqs. (21) and (22), we have

$$\Delta s^{\mathrm{f}} = -\left(\partial\gamma^{\mathrm{f}}/\partial T\right)_{p,\Pi,m} \tag{39}$$

$$= -\left[\partial\left(\gamma_{\mathrm{A}}^{\mathrm{F}} + \gamma_{\mathrm{B}}^{\mathrm{F}}\right)/\partial T\right]_{p,\Pi,m} - \Pi(\partial\tau/\partial T)_{p,\Pi,m} \tag{39a}$$

$$\Delta v^{\mathrm{f}} = \left(\partial\gamma^{\mathrm{f}}/\partial p\right)_{T,\Pi,m} \tag{40}$$

$$= \left[\partial\left(\gamma_{\mathrm{A}}^{\mathrm{F}} + \gamma_{\mathrm{B}}^{\mathrm{F}}\right)/\partial p\right]_{T,\Pi,m} + \Pi(\partial\tau/\partial p)_{T,\Pi,m} \tag{40a}$$

$$\tau^{\mathrm{f}} = \left(\partial\gamma^{\mathrm{f}}/\partial\Pi\right)_{T,P,m} \tag{41}$$

$$= \left[\partial\left(\gamma_{\mathrm{A}}^{\mathrm{F}} + \gamma_{\mathrm{B}}^{\mathrm{F}}\right)/\partial\Pi\right]_{T,p,m} + \left[\partial(\Pi\tau)/\partial\Pi\right]_{T,p,m} \tag{41a}$$

$$\Gamma_i^{\mathrm{f}} = -(m_i/RT)\left(\partial\gamma^{\mathrm{f}}/\partial m_i\right)_{T,p,\Pi,m_i} \tag{42}$$

$$= -(m_i/RT)\left\{\left[\partial\left(\gamma_{\mathrm{A}}^{\mathrm{F}} + \gamma_{\mathrm{B}}^{\mathrm{F}}\right)/\partial m_i\right]_{T,p,\Pi,m_i}\right.$$

$$\left. + \Pi(\partial\tau/\partial m_i)_{T,p,\Pi,m_i}\right\}, \quad (i = 1, \cdots, c) \tag{42a}$$

We can obtain the entropy and volume changes associated with adsorption at film interfaces, the thermodynamic film thickness, and the film densities of solute components by applying the above equations to the film tension, or the film interfacial tensions and mechanical film thickness as a function of the independent variables.

The corresponding energy change Δu^{f} and enthalpy change Δh^{f} can also be evaluated; combination of Eq. (36) and the following equations

$$H = U + pV - \gamma^{\mathrm{f}}\sigma \tag{43}$$

$$G = H - TS \tag{44}$$

U, *H*, and *G* being the energy, enthalpy, and Gibbs free energy of the system, respectively, leads to

$$\Delta g^{\mathrm{f}} = \Delta h^{\mathrm{f}} - T\Delta s^{\mathrm{f}} \tag{45}$$

and

$$\Delta u^{\mathrm{f}} = \Delta h^{\mathrm{f}} - p\Delta v^{\mathrm{f}} - \Pi\tau^{\mathrm{f}} + \gamma^{\mathrm{f}} \tag{46}$$

Since $\Delta g^{\mathrm{f}} = 0$ by definition,

$$\Delta u^{\mathrm{f}} = T\Delta s^{\mathrm{f}} - p\Delta v^{\mathrm{f}} - \Pi\tau^{\mathrm{f}} + \gamma^{\mathrm{f}} \tag{47}$$

and

$$\Delta h^{\mathrm{f}} = T\Delta s^{\mathrm{f}} \tag{48}$$

Difference in thermodynamic quantity between film interface and bulk one

When a film is thin, structure and properties of the film interfaces are different from those of the corresponding thick film because interaction takes place between the interfaces in the film. It is useful to see the difference in thermodynamic properties between the film interfaces and the adjacent meniscuses coexisting at equilibrium because they are identical with each other when the film is thick.

The interfacial tension γ_{K} of the phase L against the phase K can be expressed by

$$\begin{aligned}\mathrm{d}\gamma_{\mathrm{K}} &= -s_{\mathrm{K}}^{\mathrm{H}}\mathrm{d}T + v_{\mathrm{K}}^{\mathrm{H,K}}\mathrm{d}p + v_{\mathrm{K}}^{\mathrm{H,L}}\mathrm{d}p^{\mathrm{L}} - \sum_{i=1}^{c}\Gamma_i^{\mathrm{H,K}}\mathrm{d}\mu_i \\ &= -\Delta s_{\mathrm{K}}\mathrm{d}T + \Delta v_{\mathrm{K}}\mathrm{d}p + \left(\sum_{j=1}^{c}\Gamma_j^{\mathrm{H,K}}v_j - v_{\mathrm{K}}^{\mathrm{H,L}}\mathrm{d}\Pi\right. \\ &\quad -\sum_{i=1}^{c}(RT/m_i)\Gamma_i^{\mathrm{H,K}}\mathrm{d}m_i, \qquad (\mathrm{K}=\mathrm{A},\ \mathrm{B})\end{aligned} \tag{49}$$

employing the Hansen convention and assuming the interfaces to be spherical [32] and the phase L to be an ideal solution. Here $\Gamma_i^{\mathrm{H,K}}$, $s_{\mathrm{K}}^{\mathrm{H}}$, and $v_{\mathrm{K}}^{\mathrm{H}}$ are the interfacial density of component i and the corresponding entropy and volume, respectively, and $v_{\mathrm{K}}^{\mathrm{H,K}}$ and $v_{\mathrm{K}}^{\mathrm{H,L}}$ are the parts of the $_{\mathrm{K}}^{\mathrm{H}}$ separated by the surface of tension for the interface. Entropy change Δs_{K} and volume change Δv_{K} associated with adsorption are defined by

$$\Delta y_{\mathrm{K}} = y_{\mathrm{K}}^{\mathrm{H}} - \sum_{i=1}^{c}\Gamma_i^{\mathrm{H,K}}y_i, \qquad (y = s,\ v) \tag{50}$$

Combination of Eq. (49) with Eqs. (21) and (22) leads to

$$\Delta s^{\mathrm{fH}} = -\left[\partial\left(\gamma^{\mathrm{f}} - \gamma_{\mathrm{A}} - \gamma_{\mathrm{B}}\right)/\partial T\right]_{p,\Pi,m} \tag{51}$$

$$= -\left[\partial\left(\gamma_{\mathrm{A}}^{\mathrm{F}} - \gamma_{\mathrm{A}} + \gamma_{\mathrm{b}}^{\mathrm{F}} - \gamma_{\mathrm{B}}\right)/\partial T\right]_{p,\Pi,m} - \Pi(\partial\tau/\partial T)_{p,\Pi,m} \tag{51a}$$

$$\Delta v^{\mathrm{fH}} = \left[\partial\left(\gamma^{\mathrm{f}} - \gamma_{\mathrm{A}} - \gamma_{\mathrm{B}}\right)/\partial p\right]_{T,\Pi,m} \tag{52}$$

$$= \left[\partial\left(\gamma_{\mathrm{A}}^{\mathrm{F}} - \gamma_{\mathrm{A}} + \gamma_{\mathrm{B}}^{\mathrm{F}} - \gamma_{\mathrm{B}}\right)/\partial p\right]_{T,\Pi,m} + \Pi(\partial\tau/\partial p)_{T,\Pi,m} \tag{52a}$$

$$\sum_{j=1}^{c}\Gamma_j^{\mathrm{fH}}v_j - v^{\mathrm{fH,L}} + \tau = \left[\partial\left(\gamma^{\mathrm{f}} - \gamma_{\mathrm{A}} - \gamma_{\mathrm{B}}\right)/\partial\Pi\right]_{T,p,m} \tag{53}$$

$$= \left[\partial\left(\gamma_{\mathrm{A}}^{\mathrm{F}} - \gamma_{\mathrm{A}} + \gamma_{\mathrm{B}}^{\mathrm{F}} - \gamma_{\mathrm{B}}\right)/\partial\Pi\right]_{T,p,m} + \left[\partial(\Pi\tau)/\partial\Pi\right]_{T,p,m} \tag{53a}$$

$$\Gamma_i^{\mathrm{fH}} = -(m_i/RT)\left[\partial\left(\gamma^{\mathrm{f}} - \gamma_{\mathrm{A}} - \gamma_{\mathrm{B}}\right)/\partial m_i\right]_{T,p,\Pi,m_i} \tag{54}$$

$$\begin{aligned}&= -(m_i/RT)\Big\{\left[\partial\left(\gamma_{\mathrm{A}}^{\mathrm{F}} - \gamma_{\mathrm{A}} + \gamma_{\mathrm{B}}^{\mathrm{F}} - \gamma_{\mathrm{B}}\right)/\partial m_i\right]_{T,p,\Pi,m_i} \\ &\quad + \Pi(\partial\tau/\partial_i)_{T,p,\Pi,m_i}\Big\}, \qquad (i = 1,\ldots,c)\end{aligned} \tag{54a}$$

where difference Γ_j^{fH} between the film density and interfacial densities and the corresponding thermodynamic quantities Δy^{fH} are defined by

$$\Gamma_j^{\mathrm{fH}} = \Gamma_j^{\mathrm{f}} - \left(\Gamma_j^{\mathrm{H,A}} + \Gamma_j^{\mathrm{H,B}}\right) = \Gamma_j^{\mathrm{FH,A}} + \Gamma_j^{\mathrm{FH,B}} \tag{55}$$

and

$$\begin{aligned}\Delta y^{\mathrm{fH}} &= \Delta y^{\mathrm{f}} - (\Delta y_{\mathrm{A}} + \Delta y_{\mathrm{B}}) \\ &= \Delta y_{\mathrm{A}}^{\mathrm{FH}} + \Delta y_{\mathrm{B}}^{\mathrm{FH}}, \qquad (y = s,\ v)\end{aligned} \tag{56}$$

respectively, $\Gamma_j^{\mathrm{FH,K}}$ and $\Delta y_{\mathrm{K}}^{\mathrm{FH}}$being the differences in interfacial density and thermodynamic quantity change between the film interface and adjacent meniscus,

$$\Gamma_j^{\mathrm{FH,K}} = \Gamma_j^{\mathrm{F,K}} - \Gamma_j^{\mathrm{H,K}}, \qquad (\mathrm{K} = \mathrm{A},\ \mathrm{B}) \tag{57}$$

$$\Delta y_{\mathrm{K}}^{\mathrm{FH}} = \Delta y_{\mathrm{K}}^{\mathrm{F}} - \Delta y_{\mathrm{K}} \tag{58}$$

$$\Delta y_{\mathrm{K}}^{\mathrm{F}} = y_{\mathrm{K}}^{\mathrm{F}} - \sum_{i=1}^{c}\Gamma_i^{\mathrm{F,K}}y_i \tag{59}$$

Here we used the relation

$$\tau^{\mathrm{f}} = \sum_{j=1}^{c}\Gamma_j^{\mathrm{f}}v_j - \left(v_{\mathrm{A}}^{\mathrm{F,L}} + v_{\mathrm{B}}^{\mathrm{F,L}}\right) + \tau \tag{60}$$

and the $v^{\mathrm{fH,L}}$ defined by

$$v^{\mathrm{fH.L}} = v_{\mathrm{A}}^{\mathrm{FH,L}} + v_{\mathrm{B}}^{\mathrm{FH,L}} = v_{\mathrm{A}}^{\mathrm{F,L}} - v_{\mathrm{A}}^{\mathrm{H,L}} + v_{\mathrm{B}}^{\mathrm{F,L}} - v_{\mathrm{B}}^{\mathrm{H,L}} \tag{61}$$

where $v_{\mathrm{A}}^{\mathrm{F,L}}$ and $v_{\mathrm{B}}^{\mathrm{F,L}}$ are the parts of the $v_{\mathrm{A}}^{\mathrm{F}} + v_{\mathrm{B}}^{\mathrm{F}}$ divided by the surfaces of tension for the film interfaces, respectively, as shown in Fig. 1b.

We can obtain γ^{f}–γ_{A}–γ_{B} directly from the contact angles between the film and the meniscuses or $\gamma_{\mathrm{A}}^{\mathrm{F}} - \gamma_{\mathrm{A}} + \gamma_{\mathrm{B}}^{\mathrm{F}} - \gamma_{\mathrm{B}}$ from the ones between the film interfaces and the meniscuses [8, 33] if γ_{A} and γ_{B} are known, and then evaluate the differences in thermodynamic quantities by applying Eqs. (51) - (54a) to the experimental results of the tension differences. The corresponding differences Δu^{fH} and Δh^{fH} in energy and enthalpy changes can be derived from Eqs. (47), (48), (56) and the analogues of Eqs. (47) and (48) for meniscuses:

$$\Delta u^{\mathrm{fH}} = T\Delta s^{\mathrm{fH}} - p\Delta v^{\mathrm{fH}} - \Pi\left(\sum_{j=1}^{c}\Gamma_j^{\mathrm{fH}}v_j - v^{\mathrm{fH,L}} + \tau\right) + \gamma^{\mathrm{f}} - \gamma_{\mathrm{A}} - \gamma_{\mathrm{B}} \tag{62}$$

$$\Delta h^{\mathrm{fH}} = T\Delta s^{\mathrm{fH}} \tag{63}$$

Application to a symmetric film and the case in which solvents are immiscible

Symmetric film

Studies of symmetric films like foam and emulsion films are more fundamental than those of asymmetric films because the two film interfaces in a symmetric film are identical with each other and hence the thermodynamic quantities of single film interface and the interaction between the same interfaces can be obtained, unlike the cases of asymmetric films.

For a symmetric film, let γ^{F}, γ, Γ_i^{F}, and Δy^{F}be the film interfacial tension, the interfacial tension of the adjacent meniscus, the interfacial density of component i at film interface, and the thermodynamic quantity change associated with adsorption at film interface, respectively. Equations (20), (18), and (36) then reduce to

$$\gamma^{\mathrm{f}} = 2\gamma^{\mathrm{F}} + \Pi\tau \tag{64}$$

$$\Gamma_i^{\mathrm{f}} = 2\Gamma_i^{\mathrm{F}}, \quad (i = 1, \ldots, c) \tag{65}$$

$$\Delta y^{\mathrm{f}} = 2\Delta y^{\mathrm{F}}, \quad (y = s,\ v,\ u,\ h) \tag{66}$$

respectively. Substitution of Eqs. (64) - (66) into Eqs. (39) - (40a), (41a) - (42a), (47), and (48) gives

$$\Delta s^{\mathrm{F}} = -(1/2)\left(\partial\gamma^{\mathrm{f}}/\partial T\right)_{p,\Pi,m} \tag{67}$$

$$= -\left(\partial\gamma^{\mathrm{F}}/\partial T\right)_{p,\Pi,m} - (1/2)\Pi(\partial\tau/\partial T)_{p,\Pi,m} \tag{67a}$$

$$\Delta v^{\mathrm{F}} = (1/2)\left(\partial\gamma^{\mathrm{f}}/\partial p\right)_{T,\Pi,m} \tag{68}$$

$$= \left(\partial\gamma^{\mathrm{F}}/\partial p\right)_{T,\Pi,m} + (1/2)\Pi(\partial\tau/\partial p)_{T,\Pi,m} \tag{68a}$$

$$\tau^{\mathrm{f}} = \left(\partial\gamma^{\mathrm{F}}/\partial\Pi\right)_{T,p,m} + [\partial(\Pi\tau)/\partial\Pi]_{T,p,m} \tag{69}$$

$$\Gamma_i^{\mathrm{F}} = -(1/2)(m_i/RT)\left(\partial\gamma^{\mathrm{f}}/\partial m_i\right)_{T,p,\Pi,m_i} \tag{70}$$

$$= -(m_i/RT)\left[\left(\partial\gamma^{\mathrm{F}}/\partial m_i\right)_{T,p,\Pi,m_i} + (1/2)\Pi(\partial\tau/\partial m_i)_{T,p,\Pi,m_i}\right], \quad (i = 1, \ldots, c) \tag{70a}$$

$$\Delta u^{\mathrm{F}} = T\Delta s^{\mathrm{F}} - p\Delta v^{\mathrm{F}} - (1/2)\Pi\left(\tau^{\mathrm{f}} - \tau\right) + \gamma^{\mathrm{F}} \tag{71}$$

$$\Delta h^{\mathrm{F}} = T\Delta s^{\mathrm{F}} \tag{72}$$

Equations. (55), (56), and (61) similarly reduce to

$$\Gamma_i^{\mathrm{fH}} = 2\Gamma_i^{\mathrm{FH}} \tag{73}$$

$$\Delta y^{\mathrm{fH}} = 2\Delta y^{\mathrm{FH}} \tag{74}$$

and

$$v^{\mathrm{fH,L}} = 2v^{\mathrm{FH,L}} \tag{75}$$

respectively, where $\Gamma_i^{\mathrm{FH}}$is the difference in interfacial density of component i between the film interface and the meniscus and $\Delta y^{\mathrm{FH}}$is the corresponding difference in thermodynamic quantity change associated with adsorption. Substituting Eqs. (73) - (75) into Eqs. (51) - (54a), (62), and (63) we have

$$\Delta s^{\mathrm{FH}} = -(1/2)\left[\partial\left(\gamma^{\mathrm{f}} - 2\gamma\right)/\partial T\right]_{p,\Pi,m} \tag{76}$$

$$= -\left[\partial\left(\gamma^{\mathrm{F}} - \gamma\right)/\partial T\right]_{p,\Pi,m} - (1/2)\Pi(\partial\tau/\partial T)_{p,\Pi,m} \tag{76a}$$

$$\Delta v^{\mathrm{FH}} = (1/2)\left[\partial\left(\gamma^{\mathrm{f}} - 2\gamma\right)/\partial p\right]_{T,\Pi,m} \tag{77}$$

$$= \left[\partial\left(\gamma^{\mathrm{F}} - \gamma\right)/\partial p\right]_{T,\Pi,m} + (1/2)\Pi(\partial\tau/\partial p)_{T,\Pi,m} \tag{77a}$$

$$\sum_{j=1}^{c}\Gamma_j^{\mathrm{FH}}v_{j-}v^{\mathrm{FH,L}} + (1/2)\tau = (1/2)\left[\partial\left(\gamma^{\mathrm{f}} - 2\gamma\right)/\partial\Pi\right]_{T,p,m} \tag{78}$$

$$= \left[\partial\left(\gamma^{\mathrm{F}} - \gamma\right)/\partial\Pi\right]_{T,p,m} + (1/2)[\partial(\Pi\tau)/\partial\Pi]_{T,p,m} \tag{78a}$$

$$\Gamma_i^{\mathrm{FH}} = -(1/2)(m_i/RT)\left[\partial\left(\gamma^{\mathrm{f}} - 2\gamma\right)/\partial m_i\right]_{T,p,\Pi,m_i} \tag{79}$$

$$= -(m_i/RT)\left\{\left[\partial\left(\gamma^{\mathrm{F}} - \gamma\right)/\partial m_i\right]_{T,p,\Pi,m_i} + (1/2)\Pi(\partial\tau/\partial m_i)_{T,p,\Pi,m_i}\right\}, \quad (i = 1, \ldots, c) \tag{79a}$$

$$\Delta u^{\mathrm{FH}} = T\Delta s^{\mathrm{FH}} - p\Delta v^{\mathrm{FH}} - \Pi\left(\sum_{j=1}^{c}\Gamma_j^{\mathrm{FH}}v_j - v^{\mathrm{FH,L}}\right) + \gamma^{\mathrm{F}} - \gamma \tag{80}$$

$$\Delta u^{\mathrm{FH}} = T\Delta s^{\mathrm{FH}} \tag{81}$$

Case in which solvents are immiscible

When the solvents are practically immiscible among one another and the phase L is not necessarily an ideal solution, the concentrations of solvents in the phases A, B, and L are assumed to be zero except c_a^{A}, c_b^{B}, and c_l^{L}, and Eq. (II.17) in Appendix II then reduces to

$$\mathrm{d}\mu_i = s_i \mathrm{d}T + v_i \mathrm{d}p - v_i \mathrm{d}\Pi + \sum_{j=1}^{c} \mu_{ij} \mathrm{d}m_j \tag{82}$$

Substituting Eq. (82) into Eqs. (6) and (15), we obtain the same equations as Eqs. (39) - (41a) and

$$\sum_{j=1}^{c} \Gamma_j^{\mathrm{f}} \mu_{ji} = -\left(\partial\gamma^{\mathrm{f}}/\partial m_i\right)_{T,p,\Pi,m_i} \tag{83}$$

$$=-\left[\partial\left(\gamma_{\mathrm{A}}^{\mathrm{F}} + \gamma_{\mathrm{B}}^{\mathrm{F}}\right)/\partial m_i\right]_{T,p,\Pi,m_i} - \Pi(\partial\tau/\partial m_i)_{T,p,\Pi,m_i}, \quad (i = 1, \ldots, c) \tag{83a}$$

Since

$$\Gamma_a^{\mathrm{I,A}} = \Gamma_a^{\mathrm{I}}, \;\; \Gamma_b^{\mathrm{I,B}} = \Gamma_b^{\mathrm{I}}, \;\; \Gamma_l^{\mathrm{I,L}} = \Gamma_l^{\mathrm{I}} \tag{84}$$

and thereby from Eq. (34)

$$\Delta y_a = \bar{y}_a^{\mathrm{I}} - y_a^{\mathrm{A}}, \;\; \Delta y_b = \bar{y}_b^{\mathrm{I}} - y_b^{\mathrm{B}}, \;\; \Delta y_l = \bar{y}_l^{\mathrm{I}} - y_l \tag{85}$$

Eqs. (36) and (38) reduce to

$$\Delta y^{\mathrm{f}} = \Gamma_a^{\mathrm{I}}\left(\bar{y}_a^{\mathrm{I}} - y_a^{\mathrm{A}}\right) + \Gamma_b^{\mathrm{I}}\left(\bar{y}_b^{\mathrm{I}} - y_b^{\mathrm{B}}\right) + \Gamma_l^{\mathrm{I}}\left(\bar{y}_l^{\mathrm{I}} - y_l\right) + \sum_{i=1}^{\mathrm{c}} \Gamma_i^{\mathrm{f}}\left(\bar{y}_i^{\mathrm{f}} - y_i\right) \tag{86}$$

and

$$\tau^{\mathrm{f}} = \Gamma_l^{\mathrm{I}}/c_l^{\mathrm{L}} + \sum_{i=1}^{c} \Gamma_i^{\mathrm{f}} v_i \tag{87}$$

respectively. The right-hand side of Eq. (86) is the change in thermodynamic quantity upon the formation of film interfaces from the given phases, hence we call Δy^{f} the thermodynamic quantity of film-interface formation. The first term in the right-hand side of Eq. (87) just corresponds to the film core thickness in the three-layer model of films. Δu^{f} and Δh^{f} are given by the same equations as Eqs. (47) and (48), respectively.

Equations for the difference in thermodynamic quantity between film and meniscuses are identical with those in the case of an ideal solution and those for the difference between film density and interfacial densities are expressed by

$$\sum_{j=1}^{c} \Gamma_j^{\mathrm{fH}} \mu_{ji} = -\left[\partial\left(\gamma^{\mathrm{f}} - \gamma_{\mathrm{A}} - \gamma_{\mathrm{B}}\right)/\partial m_i\right]_{T,p,\Pi,m_i} \tag{88}$$

$$= -\left[\partial\left(\gamma_{\mathrm{A}}^{\mathrm{F}} - \gamma_{\mathrm{A}} + \gamma_{\mathrm{B}}^{\mathrm{F}} - \gamma_{\mathrm{B}}\right)/\partial m_i\right]_{T,p,\Pi,m_i} - \Pi(\partial\tau/\partial m_i)_{T,p,\Pi,m_i} \quad (i = 1, \ldots, c). \tag{88a}$$

Appendix I

Let us consider the hypothetical system mechanically equivalent to the actual system, which consists of three phases A, B, and L and two surfaces of tension for the film interfaces at which film interfacial tension is defined as shown in Fig. 1b. We define a rectangular coordinate system (x, y, z) with the z axis normal to the plane-parallel film and directed from the phase A to the phase B and with the (x, y) plane at the surface of tension for the film; positions of the surfaces of tension for the film interfaces are at $\mathrm{z} = -\left(v_{\mathrm{A}}^{\mathrm{L}} + v_{\mathrm{A}}^{\mathrm{F,L}}\right)$ and $\mathrm{z} = v_{\mathrm{B}}^{\mathrm{L}} + v_{\mathrm{B}}^{\mathrm{F,L}}$. Then the work $\delta\mathrm{W}$ done on the system by a small strain is given by

$$\begin{aligned}
\delta\mathrm{W} =& -\int\int\int_{-\infty}^{\infty} \left(p_{\mathrm{T}} e_{xx} + p_{\mathrm{T}} e_{yy} + p_{\mathrm{N}} e_{zz}\right)\mathrm{d}x\mathrm{d}y\mathrm{d}z \\
=& -\int\int\int p^{\mathrm{ABL}}\left(e_{xx} + e_{yy} + e_{zz}\right)\mathrm{d}x\mathrm{d}y\mathrm{d}z \\
& + \int \left(p^{\mathrm{ABL}} - p_{\mathrm{T}}\right)\mathrm{d}z \int\int \left(e_{xx} + e_{yy}\right)\mathrm{d}x\mathrm{d}y \\
=& -\Bigg[p\int\int\int \left(e_{xx} + e_{yy} + e_{zz}\right)\mathrm{d}x\mathrm{d}y\mathrm{d}z \\
& + \left(p^{\mathrm{L}} - p\right)\int_{-\left(v_{\mathrm{A}}^{\mathrm{L}} + v_{\mathrm{A}}^{\mathrm{F,L}}\right)}^{v_{\mathrm{B}}^{\mathrm{L}} + v_{\mathrm{B}}^{\mathrm{F,L}}} \mathrm{d}z \int\int \left(e_{xx} + e_{yy}\right)\mathrm{d}x\mathrm{d}y\Bigg] \\
& + \left[\int_{-\infty}^{0} \left(p^{\mathrm{ABL}} - p_{\mathrm{T}}\right)\mathrm{d}z + \int_{0}^{\infty} \left(p^{\mathrm{ABL}} - p_{\mathrm{T}}\right)\mathrm{d}z\right] \\
& \int\int \left(e_{xx} + e_{yy}\right)\mathrm{d}x\mathrm{d}y \\
=& -p\delta\mathrm{V} + \Pi\tau\delta\sigma + \left(\gamma_{\mathrm{A}}^{\mathrm{F}} + \gamma_{\mathrm{B}}^{\mathrm{F}}\right)\delta\sigma
\end{aligned} \tag{I.1}$$

where p_{T} is the tangential component of the pressure tensor at z, directed along the film, p_{N} is that normal to the film, and e_{xx},e_{yy}, and e_{zz} are the diagonal components in the matrix of strain tensor. From the condition of mechanical equilibrium, p_{N} can be expressed by

$$\begin{aligned}
p_{\mathrm{N}}(z) =& p^{\mathrm{ABL}}(z) \\
=& \left[1 - A\left(z + v_{\mathrm{A}}^{\mathrm{L}} + v_{\mathrm{A}}^{\mathrm{F,L}}\right)p\right] \\
& + \left[A\left(z + v_{\mathrm{A}}^{\mathrm{L}} + v_{\mathrm{A}}^{\mathrm{F,L}}\right) - A\left(z - v_{\mathrm{B}}^{\mathrm{L}} - v_{\mathrm{B}}^{\mathrm{F,L}}\right)p^{\mathrm{L}}\right] \\
& + A\left(z - v_{\mathrm{B}}^{\mathrm{L}} - v_{\mathrm{B}}^{\mathrm{F,L}}\right)p
\end{aligned} \tag{I.2}$$

A(z) being the step function

$$\begin{aligned}
A(z) =& 1, (z \geqslant 0) \\
=& 0, (z < 0).
\end{aligned} \tag{I.3}$$

Here we used the relations

$$\gamma_{\mathrm{A}}^{\mathrm{F}} = \int_{-\infty}^{0} (p_{\mathrm{N}} - p_{\mathrm{T}})\mathrm{d}z, \qquad \gamma_{\mathrm{B}}^{\mathrm{F}} = \int_{0}^{\infty} (p_{\mathrm{N}} - p_{\mathrm{T}})\mathrm{d}z \tag{I.4}$$

and

$$\begin{aligned} \delta \mathrm{V} &= \int\int\int \left(e_{xx} + e_{yy} + e_{zz}\right)\mathrm{d}x\mathrm{d}y\mathrm{d}z, \\ \delta\sigma &= \int\int \left(e_{xx} + e_{yy}\right)\mathrm{d}x\mathrm{d}y, \end{aligned} \tag{I.5}$$

[34].

For the internal energy U of the system, we have from Eq. [I.1]

$$\begin{aligned} \mathrm{d}U =& T\mathrm{d}S - p\mathrm{d}V + \Pi\tau\mathrm{d}\sigma + \left(\gamma_{\mathrm{A}}^{\mathrm{F}} + \gamma_{\mathrm{B}}^{\mathrm{F}}\right)\mathrm{d}\sigma \\ & + \mu_a\mathrm{d}n_a + \mu_b\mathrm{d}n_b + \mu_l\mathrm{d}n_l + \sum_{i=1}^{c}\mu_i\mathrm{d}n_i. \end{aligned} \tag{I.6}$$

The enthalpy H and Gibbs free energy G are defined by

$$H = U + pV - \Pi\tau\sigma - \left(\gamma_{\mathrm{A}}^{\mathrm{F}} + \gamma_{\mathrm{B}}^{\mathrm{F}}\right)\sigma \tag{I.7}$$

and

$$G = H - TS. \tag{I.8}$$

Hence

$$\begin{aligned} \mathrm{d}G =& -S\mathrm{d}T + V\mathrm{d}p - \sigma\tau\mathrm{d}\Pi - \sigma\Pi\mathrm{d}\tau - \sigma\mathrm{d}\left(\gamma_{\mathrm{A}}^{\mathrm{F}} + \gamma_{\mathrm{B}}^{\mathrm{F}}\right) \\ & + \mu_a\mathrm{d}n_a + \mu_b\mathrm{d}n_b + \mu_l\mathrm{d}n_l + \sum_{i=1}^{c}\mu_i\mathrm{d}n_i. \end{aligned} \tag{I.9}$$

It follows by Euler's theorem that

$$G = n_a\mu_a + n_b\mu_b + n_l\mu_l + \sum_{i=1}^{c} n_i\mu_i \tag{I.10}$$

Combination of Eqs. (I.9) and (I.10) yields Eq. (14).

Appendix II

The chemical potential of component i can be expressed by

$$\mathrm{d}\mu_i = s_i^{\mathrm{A}}\mathrm{d}T + v_i^{\mathrm{A}}\mathrm{d}p + \mu_{ib}^{\mathrm{A}}\mathrm{d}m_b^{\mathrm{A}} + \mu_{il}^{\mathrm{A}}\mathrm{d}m_l^{\mathrm{A}} + \sum_{j=1}^{c}\mu_{ij}^{\mathrm{A}}\mathrm{d}m_j^{\mathrm{A}} \tag{II.1}$$

$$= -s_i^{\mathrm{B}}\mathrm{d}T + v_i^{\mathrm{B}}\mathrm{d}p + \mu_{ia}^{\mathrm{B}}\mathrm{d}m_a^{\mathrm{B}} + \mu_{il}^{\mathrm{B}}\mathrm{d}m_l^{\mathrm{B}} + \sum_{j=1}^{c}\mu_{ij}^{\mathrm{B}}\mathrm{d}m_j^{\mathrm{B}} \tag{II.2}$$

$$= -s_i\mathrm{d}T + v_i\mathrm{d}p^{\mathrm{L}} + \mu_{ia}\mathrm{d}m_a + \mu_{ib}\mathrm{d}m_b + \sum_{j=1}^{c}\mu_{ij}\mathrm{d}m_j, \quad (i = a,\ b,\ l,\ 1, \ldots,\ c) \tag{II.3}$$

where m_i^{A}, m_i^{B}, and m_i denote the molalities of component i in the phases A, B, and L, respectively, y_i^{A}, y_i^{B}, and y_i the corresponding partial molar quantities, and μ_{ij}^{A}, μ_{ij}^{B}, and μ_{ij} the corresponding partial derivatives of the chemical potential of component i with respect to the molality of component j at constant temperature and pressure defined by

$$\mu_{ij} = \left(\partial\mu_i/\partial m_j\right)_{m_j} \tag{II.4}$$

subscript m_j denoting all the molalities except m_j being kept constant. Let us consider the adsorption at film interfaces from the phase L and take T, p, Π, m_1,...,m_c as experimental variables of the system. Combinations of Eq. (II.3) with Eqs. (II.1) and (II.2) yield

$$\begin{aligned} &\mu_{ia}\mathrm{d}m_a + \mu_{ib}\mathrm{d}m_b - \mu_{ib}^{\mathrm{A}}\mathrm{d}m_b^{\mathrm{A}} - \mu_{il}^{\mathrm{A}}\mathrm{d}m_l^{\mathrm{A}} - \sum_{j=1}^{c}\mu_{ij}^{\mathrm{A}}\mathrm{d}m_j^{\mathrm{A}} \\ &= -\left(s_i^{\mathrm{A}} - s_i\right)\mathrm{d}T + \left(v_i^{\mathrm{A}} - v_i\right)\mathrm{d}p + v_i\mathrm{d}\Pi - \sum_{j=1}^{c}\mu_{ij}\mathrm{d}m_j \end{aligned} \tag{II.5}$$

and

$$\begin{aligned} &\mu_{ia}\mathrm{d}m_a + \mu_{ib}\mathrm{d}m_b - \mu_{ia}^{\mathrm{B}}\mathrm{d}m_a^{\mathrm{B}} - \mu_{il}^{\mathrm{B}}\mathrm{d}m_l^{\mathrm{B}} - \sum_{j=1}^{c}\mu_{ij}^{\mathrm{B}}\mathrm{d}m_j^{\mathrm{B}} \\ &= -\left(s_i^{\mathrm{B}} - s_i\right)\mathrm{d}T + \left(v_i^{\mathrm{B}} - v_i\right)\mathrm{d}p + v_i\mathrm{d}\Pi - \sum_{j=1}^{c}\mu_{ij}\mathrm{d}m_j \end{aligned} \tag{II.6}$$

Adding the sum of Eq. (II.5) multiplied by $m_i^{\mathrm{A}}$and the one of Eq. (II.6) by m_i^{B}yields

$$\begin{aligned} &\left(\sum_{i=a}^{c} m_{\mathrm{i}}^{\mathrm{K}}\mu_{ia}\right)\mathrm{d}m_a + \left(\sum_{i=a}^{c} m_{\mathrm{i}}^{\mathrm{K}}\mu_{ib}\right)\mathrm{d}m_b \\ &= \sum_{i=a}^{c} m_{\mathrm{i}}^{\mathrm{K}}\left[-\left(s_i^{\mathrm{K}} - s_i\right)\mathrm{d}T + \left(v_i^{\mathrm{K}} - v_i\right)\mathrm{d}p + v_i\mathrm{d}\Pi - \sum_{j=1}^{c}\mu_{ij}\mathrm{d}m_j\right], \\ &(\mathrm{K} = \mathrm{A},\ \mathrm{B}) \end{aligned} \tag{II.7}$$

where we used the Gibbs-Duhem equations for the phases A and B at constant $T$and p,

$$\sum_{i=a}^{c} m_i^{\mathrm{K}}\mu_{ij}^{\mathrm{K}} = 0, \qquad (j = a,\ b,\ l,\ 1, \ldots,\ c;\ \mathrm{K} = \mathrm{A},\ \mathrm{B}) \tag{II.8}$$

Equation (II.7) can be rewritten as

$$\begin{aligned} D_a^{\mathrm{K}}\mathrm{d}m_a + D_b^{\mathrm{K}}\mathrm{d}m_b =& -D_s^{\mathrm{K}}\mathrm{d}T + D_v^{\mathrm{K}}\mathrm{d}p + D_{\mathrm{L}}^{\mathrm{K}}\mathrm{d}\Pi \\ & - \sum_{j=1}^{c} D_j^{\mathrm{K}}\mathrm{d}m_j. (\mathrm{K} = \mathrm{A},\ \mathrm{B}) \end{aligned} \tag{II.9}$$

where D_j^{K}, D_y^{K}, and $D_{\mathrm{L}}^{\mathrm{K}}$ denote

$$\begin{aligned} D_j^{\mathrm{K}} &= m_a^{\mathrm{K}}\mu_{aj} + m_b^{\mathrm{K}}\mu_{bj} + m_l^{\mathrm{K}}\mu_{lj} \\ &\quad + \sum_{i=1}^{c} m_i^{\mathrm{K}}\mu_{ij} (j = a,\ b,\ 1,\ldots,c;\ \mathrm{K} = \mathrm{A},\ \mathrm{B}) \end{aligned} \tag{II.10}$$

$$\begin{aligned} D_y^{\mathrm{K}} &= m_a^{\mathrm{K}}\left(y_a^{\mathrm{K}} - y_a\right) + m_b^{\mathrm{K}}\left(y_b^{\mathrm{K}} - y_b\right) + m_l^{\mathrm{K}}\left(y_l^{\mathrm{K}} - y_l\right) \\ &\quad + \sum_{i=1}^{c} m_i^{\mathrm{K}}\left(y_i^{\mathrm{K}} - y_i\right) \quad (y = s,\ v;\ \mathrm{K} = \mathrm{A},\ \mathrm{B}) \end{aligned} \tag{II.11}$$

$$D_{\mathrm{L}}^{\mathrm{K}} = m_a^{\mathrm{K}} v_a + m_b^{\mathrm{K}} v_b + m_l^{\mathrm{K}} v_l + \sum_{i=1}^{c} m_i^{\mathrm{K}} v_i, \qquad (\mathrm{K} = \mathrm{A},\ \mathrm{B}) \tag{II.12}$$

respectively, or in the matrix form

$$\begin{pmatrix} D_a^{\mathrm{A}} & D_b^{\mathrm{A}} \\ D_a^{\mathrm{B}} & D_b^{\mathrm{B}} \end{pmatrix} \begin{pmatrix} \mathrm{d}m_a \\ \mathrm{d}m_b \end{pmatrix} = \begin{pmatrix} D_s^{\mathrm{A}} & D_v^{\mathrm{A}} & D_{\mathrm{L}}^{\mathrm{A}} & D_1^{\mathrm{A}} & \cdots & D_c^{\mathrm{A}} \\ D_s^{\mathrm{B}} & D_v^{\mathrm{B}} & D_{\mathrm{L}}^{\mathrm{B}} & D_1^{\mathrm{B}} & \cdots & D_c^{\mathrm{B}} \end{pmatrix} \times \begin{pmatrix} -\ \mathrm{d}T \\ \mathrm{d}p \\ \mathrm{d}\Pi \\ -\ \mathrm{d}m_1 \\ \vdots \\ -\ \mathrm{d}m_c \end{pmatrix} \tag{II.13}$$

Hence we have the dependence of m_a and m_b on T, p, Π, $m_1,\ldots,m_c$

$$\mathrm{d}m_a = D^{-1}\left(-D_s^a \mathrm{d}T + D_v^a \mathrm{d}p + D_{\mathrm{L}}^a \mathrm{d}\Pi - \sum_{j=1}^{c} D_j^a \mathrm{d}m_j\right) \tag{II.14}$$

$$\mathrm{d}m_b = D^{-1}\left(-D_s^b \mathrm{d}T + D_v^b \mathrm{d}p + D_{\mathrm{L}}^b \mathrm{d}\Pi - \sum_{j=1}^{c} D_j^b \mathrm{d}m_j\right) \tag{II.15}$$

where D, D_s^k, D_v^k, D_{L}^k, and D_j^k, $(k = a,\ b)$ are the determinants:

$$D = \begin{vmatrix} D_a^{\mathrm{A}} & D_b^{\mathrm{A}} \\ D_a^{\mathrm{B}} & D_b^{\mathrm{B}} \end{vmatrix},\ D_x^a = \begin{vmatrix} D_x^{\mathrm{A}} & D_b^{\mathrm{A}} \\ D_x^{\mathrm{B}} & D_b^{\mathrm{B}} \end{vmatrix},$$

$$D_x^b = \begin{vmatrix} D_a^{\mathrm{A}} & D_x^{\mathrm{A}} \\ D_a^{\mathrm{B}} & D_x^{\mathrm{B}} \end{vmatrix}, (x = s,\ v,\ \mathrm{L},\ 1,\ldots,c) \tag{II.16}$$

Eliminating d m_a and d m_b in Eq. (II.3) by use of Eqs. (II.14) and (II.15), we have

$$\begin{aligned} \mathrm{d}\mu_i = &-\left[s_i + D^{-1}\left(D_s^a\mu_{ia} + D_s^b\mu_{ib}\right)\right]\mathrm{d}T \\ &+\left[v_i + D^{-1}\left(D_v^a\mu_{ia} + D_v^b\mu_{ib}\right)\right]\mathrm{d}p \\ &-\left[v_i - D^{-1}\left(D_{\mathrm{L}}^a\mu_{ia} + D_{\mathrm{L}}^b\mu_{ib}\right)\right]\mathrm{d}\Pi \\ &+\sum_{j=1}^{c}\left[\mu_{ij} - D^{-1}\left(D_j^a\mu_{ia} + D_j^b\mu_{ib}\right)\right]\mathrm{d}m_j. \end{aligned} \tag{II.17}$$

Substitution of Eq. (II.17) into Eqs. (6) and (15) leads to

$$\begin{aligned} \mathrm{d}\gamma^{\mathrm{f}} = &-\left\{s^{\mathrm{f}} - \sum_{j=1}^{c}\Gamma_j^{\mathrm{f}}\left[s_j + D^{-1}\left(D_s^a\mu_{ja} + D_s^b\mu_{jb}\right)\right]\right\}\mathrm{d}T \\ &+\left\{v^{\mathrm{f}} - \sum_{j=1}^{c}\Gamma_j^{\mathrm{f}}\left[v_j + D^{-1}\left(D_v^a\mu_{ja} + D_v^b\mu_{jb}\right)\right]\right\}\mathrm{d}p \\ &+\left\{v^{\mathrm{L}} + \sum_{j=1}^{c}\Gamma_j^{\mathrm{f}}\left[v_j - D^{-1}\left(D_{\mathrm{L}}^a\mu_{ja} + D_{\mathrm{L}}^b\mu_{jb}\right)\right]\right\}\mathrm{d}\Pi \\ &-\sum_{i=1}^{c}\left\{\sum_{j=1}^{c}\Gamma_j^{\mathrm{f}}\left[\mu_{ji} - D^{-1}\left(D_i^a\mu_{ja} + D_i^b\mu_{jb}\right)\right]\right\}\mathrm{d}m_i \end{aligned} \tag{II.18}$$

and

$$\begin{aligned} \mathrm{d}\left(\gamma_{\mathrm{A}}^{\mathrm{F}} + \gamma_{\mathrm{B}}^{\mathrm{F}}\right) = &-\Bigg\{\left(s_{\mathrm{A}}^{\mathrm{F}} + s_{\mathrm{B}}^{\mathrm{F}}\right) - \sum_{j=1}^{c}\left(\Gamma_j^{\mathrm{F,A}} + \Gamma_j^{\mathrm{F,B}}\right) \\ &\left[s_j + D^{-1}\left(D_s^a\mu_{ja} + D_s^b\mu_{jb}\right)\right] \\ &+\Pi(\partial\tau/\partial T)_{p,\Pi,m}\Bigg\}\mathrm{d}T \\ &+\Bigg\{\left(v_{\mathrm{A}}^{\mathrm{F}} + v_{\mathrm{B}}^{\mathrm{F}}\right) - \sum_{j=1}^{c}\left(\Gamma_j^{\mathrm{F,A}} + \Gamma_j^{\mathrm{F,B}}\right) \\ &\left[v_j + D^{-1}\left(D_v^a\mu_{ja} + D_v^b\mu_{jb}\right)\right] \\ &-\Pi(\partial\tau/\partial p)_{T,\Pi,m}\Bigg\}\mathrm{d}p \\ &+\Bigg\{v^{\mathrm{L}} + \sum_{j=1}^{c}\left(\Gamma_j^{\mathrm{F,A}} + \Gamma_j^{\mathrm{F,B}}\right) \\ &\left[v_j - D^{-1}\left(D_{\mathrm{L}}^a\mu_{ja} + D_{\mathrm{L}}^b\mu_{jb}\right)\right] \\ &-[\partial(\Pi\tau)/\partial\Pi]_{T,p,m}\Bigg\}\mathrm{d}\Pi \\ &-\sum_{i=1}^{c}\Bigg\{\sum_{j=1}^{c}\left(\Gamma_j^{\mathrm{F,A}} + \Gamma_j^{\mathrm{F,B}}\right) \\ &\left[\mu_{ji} - D^{-1}\left(D_i^a\mu_{ja} + D_i^b\mu_{jb}\right)\right] \\ &+\Pi(\partial\tau/\partial m_i)_{T,p,\Pi,m_i}\Bigg\}\mathrm{d}m_i. \end{aligned} \tag{II.19}$$

If the phase L is assumed to be an ideal dilute solution, then we have

$$\mu_i = \mu_i^{\mathrm{o}}\left(T, p^{\mathrm{L}}\right) + RT\ln m_{i,} \qquad (i = 1,\ldots,c) \tag{II.20}$$

and

$$\begin{aligned} \mu_{ij} &= RT/m_i, \quad (i = j) \\ &= 0, \quad\quad\;\; (i \neq j) \end{aligned} \tag{II.21}$$

where $\mu_i^o$is the standard chemical potential of component i in the phase L.Substituting Eq. (II.21) into Eqs. (II.18) and (II.19) yields Eqs. (21) and (22).

Appendix III: Nomenclature

c_i^{K}	number of moles of component i per unit volume in phase K (K = A, B, L)
$c_i(z)$	number of moles of component i per unit volume at point z
G	Gibbs free energy
Δg^{f}	Gibbs free energy change associated with adsorption at film interfaces
H	enthalpy
Δh^{f}, Δh^{F}	enthalpy change associated with adsorption at film interfaces and the one at film interface of symmetric film
Δh^{fH}, Δh^{FH}	difference in enthalpy change between film interfaces and bulk ones and the one between film interface and bulk one for symmetric film
m_i	molality of component i
n_i	number of moles of component i
$n_i^{\mathrm{K}*}$	number of moles of component i in part K* divided by surface of tension for film
n_i^{f}	excess quantity of component i
$n_i^{\mathrm{F,K}}$	excess quantity of component i ascribed to film interface against phase K (K = A, B)
p	pressure
p^{L}	pressure in phase L
S	entropy
s_i	partial molar entropy of component i
s^{K}	entropy per unit volume in phase K (K = A, B, L)
s^{f}	excess entropy per unit film area
$s_{\mathrm{K}}^{\mathrm{F}}$, $s_{\mathrm{K}}^{\mathrm{H}}$	excess entropies per unit area ascribed to film interface and bulk one against phase K (K = A, B)
Δs^{f}, Δs^{F}	entropy change associated with adsorption at film interfaces and the one at film interface of symmetric film
Δs_{K}	entropy change associated with adsorption at bulk interface against phase K (K = A, B)
Δs^{fH}, Δs^{FH}	difference in entropy change between film interfaces and bulk ones and the one between film interface and bulk one for symmetric film
T	temperature
U	energy
Δu^{f}, Δu^{F}	energy change associated with adsorption at film interfaces and the one at film interface of symmetric film
Δu^{fH}, Δu^{FH}	difference in energy change between film interfaces and bulk ones and the one between film interface and bulk one for symmetric film
V	volume
V^{K}	volume of phase K (K = A, B, L)
v_i	partial molar volume of component i
v^{f}	excess volume per unit film area
$v_{\mathrm{K}}^{\mathrm{F}}$, $v_{\mathrm{K}}^{\mathrm{H}}$	excess volumes per unit area ascribed to film interface and bulk one against phase K (K = A, B)
$v_{\mathrm{K}}^{\mathrm{F,K}}$, $v_{\mathrm{K}}^{\mathrm{F,L}}$	parts of $v_{\mathrm{K}}^{\mathrm{F}}$ divided by surface of tension
$v_{\mathrm{K}}^{\mathrm{H,K}}$, $v_{\mathrm{K}}^{\mathrm{H,L}}$	parts of $v_{\mathrm{K}}^{\mathrm{H}}$ divided by surface of tension
v^{L}	volume of phase L per unit film area
$v_{\mathrm{K}}^{\mathrm{L}}$	part of v^{L} divided by surface of tension for film
Δv^{f}, Δv^{F}	volume changes associated with adsorption at film interfaces and the one at film interface of symmetric film
Δv_{K}	volume change associated with adsorption at bulk interface against phase K (K = A, B)
Δv^{fH}, Δv^{FH}	difference in volume change between film interfaces and bulk ones and the one between film interface and bulk one for symmetric film
$v^{\mathrm{fH,L}}$, $v^{\mathrm{FH,L}}$	difference in part of excess volume per unit area between film interfaces and bulk ones and the one between film interface and bulk one for symmetric film
$\bar{y}_i^{\mathrm{f}}$, $\bar{y}_i^{\mathrm{I}}$	mean partial molar quantity of component i in film and the one inherent in film
γ^{f}	film tension
$\gamma_{\mathrm{K}}^{\mathrm{f}}$, γ^{F}	film interfacial tension against phase K and the one of symmetric film (K = A, B)
γ_{K},γ	interfacial tension against phase K and the one in symmetric film system (K = A, B)
Γ_i^{f}	film density of component i
$\Gamma_i^{\mathrm{F,K}}$, $\Gamma_i^{\mathrm{H,K}}$	interfacial densities of component i ascribed to film interface and bulk one against phase K (K = A, B)
Γ_i^{F}	interfacial density of component i in film interface of symmetric film
Γ_i^{I}, $\Gamma_i^{\mathrm{I,K}}$	film densities of component i inherent in film and portions of film region (K = A, B, L)
Γ_i^{fH}	difference between film density and interfacial densities of component i
$\Gamma_i^{\mathrm{FH,K}}$, Γ_i^{FH}	difference in interfacial density of component i between film interface and bulk one against phase K and the one in symmetric film system (K = A, B)

μ_i	chemical potential of component *i*
μ_{ij}	partial derivative of chemical potential of component *i* with respect to molality of component *j*
Π	disjoining pressure
σ	film area
τ	distance between surfaces of tension for film interfaces
τ^f	thermodynamic film thickness

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