

이성분 용액의 표면장력과 표면흡착

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Surface Tension and Surface Adsorption of Binary Solutions

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초록 이성분용액의 표면을 단분자층 또는 다분자층으로 가정할 때의 표면장력식을 통계열역학적으로 유도하였다. 이 표면장력식들은 Gibbs 흡착식을 만족시켜 주며, 따라서 표면에서의 흡착을 계산할 수 있다. 또한 이때 얻은 bulk 용액의 화학포텐셜이 열역학적으로 유도된 것과 같다는 것을 보였다.

Abstract With quasi-lattice model, surface tension equations for binary solution are derived assuming both mono- and multi-layer surface models. These equations are in agreement with Gibbs adsorption isotherm, and therefore surface relative adsorption can be calculated. The chemical potentials of bulk phase components obtained are also indifferent even if the influence of surface phase is taken into account.

Introduction

Belton and Evans¹, Schuchovitzky², and Guggenheim³ assumed that the surface phase consists of unimolecular layer, and that the composition of this layer is different in general from that of the bulk phase of the solution. They also assumed that the structure of quasi-crystalline

lattice is the same on the surface as in the bulk phase. With this surface model, they calculated the mixing energy for regular solution, and then obtained following equation for the surface tension of a binary solution:

$$\sigma = \sigma_1 + \frac{kT}{\omega} \log \frac{x_1^{\omega}}{x_1} - \frac{\alpha m}{\omega} (x_2)^2 + \frac{\alpha l}{\omega} [(x_2^{\omega})^2 - (x_2)^2]$$

$$= \sigma_2 + \frac{kT}{\omega} \log \frac{x_2^{(1)}}{x_2} - \frac{\alpha m}{\omega} (x_1)^2 + \frac{\alpha l}{\omega} [(x_1^{(1)})^2 - (x_1)^2] \quad (1)$$

In deriving the above equation they supposed that a molecule in the surface layer will have lx and mz neighbours in the surface layer and in the liquid substrate, respectively; here z represents the number of the nearest neighbours of a molecule in the bulk liquid. For l and m , following relationship holds

$$l + 2m = 1$$

In equation (1), α is the characteristic constant of the interaction energy introduced by Fowler and Guggenheim; ω , representing the molecular area assuming equal for both components; x , being the mole fraction; σ with subscripts, indicating surface tension of the pure components; whereas σ without subscript, representing surface tension of liquid mixture. Subscripts 1 and 2 denote components 1 and 2, respectively; and superscripts (1) indicates the first surface monomolecular layer. The other symbols have their usual physical meanings.

Although the equation (1) has been applied successfully to many binary solutions,⁴ Defay and Prigogine⁵ showed that the equation is in contradiction with Gibbs adsorption isotherm.

Defay and Prigogine⁵ assumed a multilayer surface model, and showed that the Gibbs adsorption isotherm can be obtained from the surface tension equation obtained according to their model. The chemical potentials for the bulk phase was also derived from the partition function they proposed for two layer model;

$$\mu_1 = kT \log \frac{x_1}{f_1} + \alpha(x_2)^2 - 2\alpha m \frac{n^{(2)}}{n} (x_2 - x_2^{(2)})x_2$$

$$\mu_2 = kT \log \frac{x_2}{f_2} + \alpha(x_1)^2 + 2\alpha m \frac{n^{(2)}}{n} (x_2 - x_2^{(2)})x_1 \quad (2)$$

Here, n is the number of molecules in a layer of unit area, and superscript (2) denotes the second monomolecular layer of the surface phase. " f " is a molecular partition function. These chemical potentials differ from the ordinarily accepted one by the term comprising $n^{(2)}/n$. The extra terms, according to their interpretation, appear in the above equation because they took surface phase into consideration. However, the chemical potentials should be consistent whether or not the surface phase is taken into consideration. Introducing equation (2) into the thermodynamic relation, following equation can be obtained.

$$\begin{aligned} \left(\frac{d\sigma}{dx_2} \right)_{P,T} &= \left(\frac{\partial\sigma}{\partial\mu_2} \right)_{P,T} \left(\frac{\partial\mu_2}{\partial x_2} \right)_{P,T} \\ &= -\frac{\Gamma_{2,1}}{x_2} \left[kT - 2\alpha x_1 x_2 \right. \\ &\quad \left. + 2\alpha m x_1 x_2 \left\{ (x_2^{(1)} - x_2) \frac{1}{x_1} \right. \right. \\ &\quad \left. \left. + \left(1 - \frac{dx_2^{(1)}}{dx_2} \right) \right\} \right] \quad (3) \end{aligned}$$

Here, $\Gamma_{2,1}$ is the relative adsorption of component 2. This formula differs from Gibbs adsorption formula by the last term in the square bracket.

Monolayer model of surface phase

In the monolayer model, although the 2nd layer (monomolecular layer adjacent to the surface layer) is assumed to take the bulk composition, its interaction energy should differ from the remaining bulk phase layer since the layer is in a different environment from the bulk phase. In Guggenheim's method, the interaction energy of the 2nd layer is taken as same

as that of the bulk liquid, and the difference of the interaction energy of the 2nd layer from that of the bulk liquid is counted into the 1st layer's interaction energy.

Since the 2nd layer has a different configuration energy from the other bulk layers, it should have a layer tension. Accordingly, it is more reasonable to distinguish the 2nd layer from the bulk phase in deriving the layer tension or surface tension equation. Calculating configuration energies of each layer according to the quasi-crystalline structure, the total mixing energy of the 1st and 2nd layers, W , is obtained as follows

$$\begin{aligned}
 W = & \frac{n_1 n_2}{n} \alpha + \frac{n_1^{(2)} n_2^{(2)}}{n^{(2)}} \alpha + \frac{n_1^{(1)} n_2^{(1)}}{n^{(1)}} \alpha (1-m) \\
 & + \frac{1}{2} n^{(1)} \alpha m (x_1^{(1)} x_2^{(2)} + x_1^{(2)} x_2^{(1)} - 2x_1^{(1)} x_2^{(1)}) \\
 & + \frac{1}{2} n^{(2)} \alpha m (x_1^{(1)} x_2^{(2)} + x_1^{(2)} x_2^{(1)} - 2x_1^{(2)} x_2^{(2)})
 \end{aligned} \tag{4}$$

The partition function in terms of independent variables, p , T , σ , μ_1 , and μ_2 is given as follows⁶

$$\begin{aligned}
 \psi = & \sum_{n_1^{(1)}, n_2^{(1)}} \sum_{n_1^{(2)}, n_2^{(2)}} \sum_{n_1, n_2} \\
 & \frac{n^{(1)}!}{n_1^{(1)}! n_2^{(1)}!} \frac{n^{(2)}!}{n_1^{(2)}! n_2^{(2)}!} \frac{n!}{n_1! n_2!} \\
 & \cdot (\lambda_1 f_1^{(1)})^{n_1^{(1)}} (\lambda_2 f_2^{(1)})^{n_2^{(1)}} (\lambda_1 f_1^{(2)})^{n_1^{(2)}} \\
 & (\lambda_2 f_2^{(2)})^{n_2^{(2)}} (\lambda_1 f_1)^{n_1} (\lambda_2 f_2)^{n_2} \cdot \exp(-W - pV \\
 & + \sigma^{(1)} Q^{(1)} + \sigma^{(2)} Q^{(2)}) / kT
 \end{aligned} \tag{5}$$

Here, λ is absolute activity; $\sigma^{(i)}$, the i -th layer tension, and $Q^{(i)}$, the areas of the i -th surface layer. Retaining the largest term in the partition function only, and then from the extreme conditions of the largest term,⁷

$$\left(\frac{\partial \log \psi^*}{\partial n_i} \right)_{p, T, \sigma, \lambda} = 0, \quad \left(\frac{\partial \log \psi^*}{\partial n_i^{(i)}} \right)_{p, T, \sigma, \lambda} = 0,$$

$$\left(\frac{\partial \log \psi^*}{\partial n_i^{(2)}} \right)_{p, T, \sigma, \lambda} = 0$$

with the boundary conditions,

$$\begin{aligned}
 x_1 + x_2 &= 1 \\
 x_1^{(1)} + x_2^{(1)} &= 1 \\
 x_1^{(2)} + x_2^{(2)} &= 1,
 \end{aligned}$$

the following equations can be obtained

$$\begin{aligned}
 \log \lambda_1 + \log \frac{f_1}{x_1} - \frac{\alpha}{kT} (x_2)^2 &= 0 \\
 \log \lambda_2 + \log \frac{f_2}{x_2} - \frac{\alpha}{kT} (x_1)^2 &= 0
 \end{aligned} \tag{6}$$

$$\begin{aligned}
 \frac{\sigma^{(1)} \omega^{(1)}}{kT} &= \log \lambda_1 + \log \frac{x_1^{(1)}}{f_1^{(1)}} \\
 &+ (1-m) \frac{\alpha}{kT} (x_2^{(1)})^2 + \frac{\alpha m}{2kT} [x_2 - 2(x_2^{(1)})^2] \\
 &+ \frac{\alpha m}{2kT} x_2^{(1)} (x_2 - x_1) \\
 &= -\log \lambda_2 + \log \frac{x_2^{(1)}}{f_2^{(1)}} \\
 &+ (1-m) \frac{\alpha}{kT} (x_1^{(1)})^2 \\
 &+ \frac{\alpha m}{2kT} [x_1 - 2(x_1^{(1)})^2] \\
 &+ \frac{\alpha m}{2kT} x_1^{(1)} (x_1 - x_2)
 \end{aligned} \tag{7}$$

$$\begin{aligned}
 \frac{\sigma^{(2)} \omega^{(2)}}{kT} &= -\log \lambda_1 + \log \frac{x_1}{f_1} + \frac{\alpha}{kT} (x_2)^2 \\
 &+ \frac{\alpha m}{2kT} [x_2^{(1)} - 2(x_2)^2] \\
 &+ \frac{\alpha m}{2kT} x_2 (x_2^{(1)} - x_1^{(1)}) \\
 &= -\log \lambda_2 + \log \frac{x_2}{f_2} + \frac{\alpha}{kT} (x_1)^2 \\
 &+ \frac{\alpha m}{2kT} [x_1^{(1)} - 2(x_1)^2] \\
 &+ \frac{\alpha m}{2kT} x_1 (x_1^{(1)} - x_2^{(1)})
 \end{aligned} \tag{8}$$

As it is revealed in equation (6), the extra term in equation (2) disappears even if the

surface phase is taken into account.

Combining equation (6) and (7), and also (6) and (8), and using the relation, $x_1 + x_2 = 1$, the following equations can be obtained.

$$\begin{aligned} \frac{\sigma^{(1)}\omega^{(1)}}{kT} &= \log \frac{x_1^{(1)}}{x_1} + \frac{\sigma_1\omega^{(1)}}{kT} \\ &- \frac{\alpha}{kT} [(x_2)^2 - (x_2^{(1)})^2] - \frac{\alpha m}{kT} (x_2^{(1)})^2 \\ &+ \frac{\alpha m}{2kT} [x_2 - 2(x_2^{(1)})^2] \\ &+ \frac{\alpha m}{2kT} x_2^{(1)}(x_2 - x_1) \\ &= \log \frac{x_2^{(1)}}{x_2} + \frac{\sigma_2\omega^{(1)}}{kT} \\ &- \frac{\alpha}{kT} [(x_1)^2 - (x_1^{(1)})^2] - \frac{\alpha m}{kT} (x_1^{(1)})^2 \\ &+ \frac{\alpha m}{2kT} [x_1 - 2(x_1^{(1)})^2] \\ &+ \frac{\alpha m}{2kT} x_1^{(1)}(x_1 - x_2) \end{aligned} \quad (9)$$

$$\begin{aligned} \frac{\sigma^{(2)}\omega^{(2)}}{kT} &= \frac{\alpha m}{2kT} [x_2^{(1)} - 2(x_2)^2] \\ &+ \frac{\alpha m}{2kT} x_2(x_2^{(1)} - x_1^{(1)}) \\ &= \frac{\alpha m}{2kT} [x_1^{(1)} - 2(x_1)^2] \\ &+ \frac{\alpha m}{2kT} x_1(x_1^{(1)} - x_2^{(1)}) \end{aligned} \quad (10)$$

Assuming $\omega^{(1)} = \omega^{(2)} = \omega$, equation (9) and (10) can be combined to give

$$\begin{aligned} \frac{\sigma\omega}{kT} &= \log \frac{x_1^{(1)}}{x_1} + \frac{\sigma_1\omega}{kT} \\ &- \frac{\alpha}{kT} [(x_2)^2 - (x_2^{(1)})^2] - \frac{\alpha m}{kT} (x_1^{(1)})^2 \\ &- \frac{\alpha m}{kT} (x_2 - x_2^{(1)})^2 \\ &= \log \frac{x_2^{(1)}}{x_2} + \frac{\sigma_2\omega}{kT} \\ &- \frac{\alpha}{kT} [(x_1)^2 - (x_1^{(1)})^2] - \frac{\alpha m}{kT} (x_1^{(1)})^2 \\ &- \frac{\alpha m}{kT} (x_1 - x_1^{(1)})^2 \end{aligned} \quad (11)$$

Here, σ is the surface tension of the solution, that is the sum of the layer tensions, $\sigma^{(1)} + \sigma^{(2)}$. Equation (11) is the desired expression with which surface tension and surface concentration can be calculated.

To assure the calculated surface tension and concentration be acceptable, it should be shown that the equation (11) is consistent with Gibbs adsorption formula. Differentiating equation (9) and (10) with respect to x_2 , following equations can be obtained, respectively.

$$\begin{aligned} \frac{\omega}{kT} \frac{d\sigma^{(1)}}{dx_2} &= \left(\frac{x_1^{(1)}}{x_1} - \frac{x_2^{(1)}}{x_2} \right) \\ &- \frac{2\alpha}{kT} (x_1^{(1)}x_2 - x_1x_2^{(1)}) \\ &+ \frac{\alpha m}{2kT} (x_1^{(1)} - x_2^{(1)}) \\ &+ \frac{\alpha m}{2kT} (x_2 - x_1) \frac{dx_2^{(1)}}{dx_2} \end{aligned} \quad (12)$$

$$\begin{aligned} \frac{\omega}{kT} \frac{d\sigma^{(2)}}{dx_2} &= \frac{\alpha m}{2kT} (x_2^{(1)} - x_1^{(1)}) \\ &+ \frac{\alpha m}{2kT} (x_1 - x_2) \frac{dx_2^{(1)}}{dx_2} \end{aligned} \quad (13)$$

Summing equations (12) and (13), it can be obtained

$$\begin{aligned} \frac{\omega}{kT} \frac{d\sigma}{dx_2} &= \left(\frac{x_1^{(1)}}{x_1} - \frac{x_2^{(1)}}{x_2} \right) \\ &- \frac{2\alpha}{kT} (x_2x_1^{(1)} - x_1x_2^{(1)}) \end{aligned} \quad (14)$$

Neglecting the concentrations in the vapor phase in comparison with those in the liquid phase, the relative adsorption of component 2 can be expressed, by definition, as follows

$$\Gamma_{2,1} = \frac{1}{\omega} \left(x_2^{(1)} - x_1^{(1)} \frac{x_2}{x_1} \right) \quad (15)$$

Introducing equation (15) into (14), Gibbs adsorption formula can be obtained;

$$\frac{d\sigma}{dx_2} = -\frac{\Gamma_{21}}{x_2}(kT - 2\alpha x_1 x_2) \quad (16)$$

Multilayer model of surface phase

Two-layer surface model is used at first, and then the results are extended to a general multi-layer model. As in the case of monolayer model, it is considered that the 3rd layer will contribute to the surface tension to some extent in the two-layer model.

The mixing energies for each layer is calculated quite similiary as in the monolayer model, and the results are summed up to give a total mixing energy as shown below.

$$\begin{aligned} W = & \frac{n_1 n_2}{n} \alpha + \frac{n_1^{(1)} n_2^{(1)}}{n^{(1)}} \alpha (1-m) \\ & + \frac{n_1^{(2)} n_2^{(2)}}{n^{(2)}} \alpha + \frac{n_1^{(3)} n_2^{(3)}}{n^{(3)}} \alpha \\ & + \frac{1}{2} n^{(1)} \alpha m (x_1^{(1)} x_2^{(2)} + x_2^{(1)} x_1^{(2)} - 2x_1^{(1)} x_2^{(1)}) \\ & + \frac{1}{2} n^{(2)} \alpha m (x_1^{(2)} x_2^{(1)} + x_2^{(2)} x_1^{(1)} - 2x_1^{(2)} x_2^{(2)}) \\ & + \frac{1}{2} n^{(3)} \alpha m (x_1^{(2)} x_2^{(3)} + x_1^{(3)} x_2^{(2)} - 2x_1^{(2)} x_2^{(2)}) \\ & + \frac{1}{2} n^{(3)} \alpha m (x_1^{(3)} x_2^{(2)} + x_1^{(2)} x_2^{(3)} - 2x_1^{(3)} x_2^{(3)}) \end{aligned}$$

The partition function can also be given quite similiary as equation (5), except the terms arising from the consideration of one more surface layer. Using Stirlings formula and taking the largest terms only with similar extreme conditions, the following equations can be obtained.

$$\begin{aligned} \frac{\sigma^{(1)} \omega^{(1)}}{kT} = & \log \frac{x_1^{(1)}}{x_1} + \frac{\sigma_1^{(1)} \omega_1^{(1)}}{kT} \\ & - \frac{\alpha}{kT} [(x_2)^2 - (x_2^{(1)})^2] - \frac{\alpha m}{kT} (x_2^{(1)})^2 \\ & + \frac{\alpha m}{2kT} [x_2^{(2)} - 2(x_2^{(1)})^2] \\ & + \frac{\alpha m}{2kT} x_2^{(1)} (x_2^{(2)} - x_1^{(2)}) \end{aligned}$$

$$\begin{aligned} = & \log \frac{x_2^{(1)}}{x_2} + \frac{\sigma_2^{(1)} \omega_1^{(1)}}{kT} \\ & - \frac{\alpha}{kT} [(x_1)^2 - (x_1^{(1)})^2] - \frac{\alpha m}{kT} (x_1^{(1)})^2 \\ & + \frac{\alpha m}{2kT} [x_1^{(2)} - 2(x_1^{(1)})^2] \\ & + \frac{\alpha m}{2kT} x_1^{(1)} (x_1^{(2)} - x_2^{(2)}) \end{aligned} \quad (17)$$

$$\begin{aligned} \frac{\sigma^{(2)} \omega^{(2)}}{kT} = & \log \frac{x_1^{(2)}}{x_1} + \frac{\sigma_1^{(2)} \omega^{(2)}}{kT} \\ & - \frac{\alpha}{kT} [(x_2)^2 - (x_2^{(2)})^2] + \frac{\alpha m}{2kT} \{ [x_2^{(1)} \\ & - 2(x_2^{(2)})^2] + [x_2 - 2(x_2^{(2)})^2] \} \\ & + \frac{\alpha m}{2kT} x_2^{(2)} \{ (x_2^{(1)} - x_1^{(2)}) + (x_2 - x_1) \} \\ = & \log \frac{x_2^{(2)}}{x_2} + \frac{\sigma_2^{(2)} \omega^{(2)}}{kT} - \frac{\alpha}{kT} [(x_1)^2 \\ & - (x_1^{(2)})^2] + \frac{\alpha m}{2kT} \{ [x_1^{(1)} - 2(x_1^{(2)})^2] \\ & + [x_1 - 2(x_1^{(2)})^2] \} + \frac{\alpha m}{2kT} x_1^{(2)} \{ (x_1^{(1)} \\ & - x_2^{(1)}) + (x_1 - x_2) \} \end{aligned} \quad (18)$$

$$\begin{aligned} \frac{\sigma^{(3)} \omega^{(3)}}{kT} = & \frac{\alpha m}{2kT} [x_2^{(2)} - 2(x_2)^2] \\ & + \frac{\alpha m}{2kT} x_2 (x_2^{(2)} - x_1^{(2)}) \\ = & \frac{\alpha m}{2kT} [x_1^{(2)} - 2(x_1)^2] \\ & + \frac{\alpha m}{2kT} x_1 (x_1^{(2)} - x_2^{(2)}) \end{aligned} \quad (19)$$

The layer tensions and layer concentrations can be obtained with the above three equations by iteration method. By differentiating the equations with respect to x_2 and adding the results, an equation analogous to equation (14) can be obtained as follows.

$$\begin{aligned} \frac{\omega}{kT} \frac{d\sigma}{dx_2} = & \left(\frac{x_1^{(1)} + x_1^{(2)}}{x_1} - \frac{x_2^{(1)} + x_2^{(2)}}{x_2} \right) \\ & - \frac{2\alpha}{kT} \{ x_2 (x_1^{(1)} - x_1^{(2)}) \\ & - x_1 (x_2^{(1)} - x_2^{(2)}) \} \end{aligned} \quad (20)$$

Taking relative adsorption of component 2 as

$$r_{2,1} = \frac{1}{\omega} \left\{ (x_2^{(1)} + x_2^{(2)}) - (x_1^{(1)} + x_1^{(2)}) \frac{x_2}{x_1} \right\} \quad (21)$$

Gibbs adsorption formula of equation (16) can be obtained.

For a surface model of more than two layers, the equation (18) with appropriate superscripts holds for through 2nd to i -th layers, i being the number of the layers of the surface phase. From equation (17), (19) with superscript ($i+1$), and analogous equations of (18), the following expression which is analogous to equation (20) can be derived;

$$\begin{aligned} \frac{\omega}{kT} \frac{d\sigma}{dx_2} = & \sum_{i=1} \left(\frac{x_1^{(i)}}{x_1} - \frac{x_2^{(i)}}{x_2} \right) \\ & - \frac{2\alpha}{kT} \left\{ (x_2 x_1^{(1)} - x_1 x_2^{(1)}) - \sum_{i=1} (x_2 x_1^{(i+1)} \right. \\ & \left. - x_1 x_2^{(i+1)}) \right\} \quad (22) \end{aligned}$$

Gibbs adsorption isotherm of equation (16) can be obtained from equation (22), taking the relative adsorption of component 2 as

$$r_{2,1} = \frac{1}{\omega} \sum_{i=1} \left(x_2^{(i)} - x_1^{(i)} \frac{x_2}{x_1} \right) \quad (23)$$

Conclusion

For regular solutions, it can be concluded that the surface tension equations for both monolayer

and multi-layer model lead to the Gibbs adsorption formula, if the ($i+1$)-th layer contribution to the surface tension is considered. Accordingly, it is possible to calculate relative adsorption and surface tension using the expressions obtained in this work. Moreover, chemical potentials of bulk phase components are indifferent, even if the influence of the surface phase is taken into account.

This result is in accordance with the surface model in which the boundary layer of the surface phase have the same composition as that of the adjacent bulk phase. Therefore, it can be concluded that the monolayer model assumed in this work is nothing else but a two-layer model, and two-layer model is a three-layer model, and so on.

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