A NEW PROGRESS IN THE THEORY ON ADSORPTION OF SURFACTANT AT SOLID/LIQUID INTERFACE

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Keywords: Adsorption theory, Surfactant, Solid-Liquid interface Isotherm equation

In our previous work^[1] an adsorption theory was proposed, which is particularly applicable to the adsorption of surfactant from solution onto solid surface, but might also be useful in other cases^[1]. Based on the two-step adsorption model the general adsorption isotherm equation was derived by the mass action treatment^[1] and the statistical approach^[2]. The general isotherm equation is written as

$$\Gamma = \frac{\Gamma_{\infty} \left(\frac{1}{n} k_1 c + k_1 k_2 c^n \right)}{1 + k_1 c + k_1 k_2 c^n} \quad (1)$$

where Γ is the amount of surfactant adsorbed at concentration c and Γ_{∞} the limiting adsorption at high concentrations, both of them can be measured from adsorption experiment. k_1 and k_2 are the equilibrium constants of the first step and second step, respectively; n is the equivalent aggregation number of hemimicelle. The equation has been applied successfully to various types of surfactant adsorption isotherms from both aqueous and nonpolar solvents (including Langmuir (L-), S- and LS-types)^[1]. It has not only represented the various adsorption results but also provided further information on adsorption and adsorption film^[3]. The equation shows that the adsorption isotherm, hence the various properties of the interfacial film would be determined by the three parameters: k_1 , k_2 and n . The number of parameters involved in this equation is much less than those in the equations suggested by others^[4-7] and make it the unique one which is able to apply to the various practical systems of surfactants adsorbed onto solid-liquid interfaces and to interpret the experimental adsorption data for all the three types of isotherms. However, it is not convenient enough for evaluating the three parameters from the experimental adsorption data, particularly for the adsorption system showing LS-type isotherms, and has not shown any ability for prediction.

Now, based on the same adsorption model, relations between the three parameters have been found and new isotherm equations with two parameters and even with only

one parameter have been provided.

1 Isotherm Equation with Two Parameters

According to the two-step adsorption model, product of the two equilibrium constants ($k_1 k_2$) can be given as

$$k_1 k_2 = \Gamma_{hm} / (\Gamma_s c^n) \quad (2)$$

where Γ_{hm} and Γ_s are the amount of hemimicelles and empty sites on unit area of the adsorbent, respectively. For the adsorption systems showing LS-type isotherms, at hmc , $\Gamma_{hm} = \Gamma_s$, thus

$$k_1 k_2 = hmc^{-n} \quad (3)$$

Since [1]

$$hmc = \left(\frac{n-2}{n} \right)^{\frac{n}{n-1}} k_2^{\frac{1}{1-n}} \quad (4)$$

Combining eqns. (1) to (4) the two parameters isotherm equation is obtained

$$\Gamma = \frac{\Gamma_s \left(\frac{k_1 c}{n} + \left(\frac{n-2}{n} \right)^{\frac{n^2}{n-1}} (k_1 c)^n \right)}{1 + k_1 c + \left(\frac{n-2}{n} \right)^{\frac{n^2}{n-1}} (k_1 c)^n} \quad (5)$$

This equation has been applied to many practical systems successfully. It is easier to be applied than the original one and provides all the same information.

For the case of the system showing S-shape isotherm we have had an equation with two parameters which can be obtained by reducing the general isotherm equation (1) or by derivation based on the one step adsorption model [1].

2 Isotherm Equation with One Parameter

According to the chemical thermodynamics the change of standard free energy for the second step of adsorption of surfactant at solid-liquid interface (ΔG_2^0) can be given as

$$\Delta G_2^0 = -RT \ln k_2 = (n-1) \Delta G_{hm}^0 + \Delta G_b^0 \quad (6)$$

Where ΔG_{hm}^0 is the standard free energy change for one mole of surfactant from aqueous solution to the surface micelles, being equal to that for micellization in bulk solution ($\Delta G_m^0 = RT \ln cmc$). ΔG_b^0 is that for one mole adsorbed monomers changing to surface micelles which is much less than ΔG_{hm}^0 in the case of LS-type isotherm. Therefore, we have

$$-RT \ln k_2 = (n-1) RT \ln cmc$$

and

$$k_2 = cmc^{1-n} \quad (7)$$

Combining eqns. (1), (3), (4) and (7) we have

$$k_1 = cmc^{-1} \left(\frac{n-2}{n} \right)^{\frac{n^2}{n-1}} \quad (8)$$

and

$$\Gamma = \frac{\Gamma_{\infty} \left[\frac{1}{n} \frac{c}{\text{cmc}} + \left(\frac{c}{\text{cmc}} \right)^n \right]}{\left(\frac{n}{n-2} \right) \frac{n^2}{1-n} + \frac{c}{\text{cmc}} + \left(\frac{c}{\text{cmc}} \right)^n} \quad (9)$$

It is seen that there is only one parameter, n , in this equation, except the cmc which is the basic parameter for describing the characteristics of the surfactant, always available in literature or obtainable by experiments other than the measurement of adsorption at solid-liquid interface. Thus, if the limiting adsorption amount in the high concentration area (Γ_{∞}) and the adsorption amount at the first plateau (Γ_1) are known, the whole adsorption isotherm curve of LS-type can be given, since $n = \Gamma_{\infty}/\Gamma_1$. Obviously, the procedures for investigation of the surfactant adsorption at solid-liquid interface are simplified significantly. Furthermore, equation (8) has shown the relation of k_1 to cmc and n . From the view points of both experience and theoretical, it is reasonable that the k_1 and Γ_1 values for the homologs of an ionic surfactant adsorbed on a solid of opposite charge would be the same. Therefore, we may calculate k_1 from the cmc, Γ_1 and Γ_{∞} of anyone in the homologous series, then calculate the n values using this k_1 and various cmc values for various homologs. All the adsorption isotherms for various homologous compounds except one on the solid can be predicted without the need of any measurement on adsorption of these compounds at the solid-liquid interface. This procedures have been applied to calculate the adsorption isotherms of alkylpyridinium chlorides on aerosil 200. The calculated curves correspond with the experimental points very well.

References

- 1 Zhu B Y, Gu T. *Adv. Colloid & Interface Sci.*, 1991, 1, 37 (Nos 1/2)
- 2 Zhu B Y. *J. Chem. Soc. Faraday Trans.*, 1992, 38 (in press)
- 3 Zhu B Y, Gu T. *J. Chem. Soc. Faraday Trans.*, 1991, 87, 2745
- 4 Klimenko N A. *Kolloidn Zh.*, 1978, 40, 1105; 1979, 41, 781
- 5 Koganovski A M, Klimenko N A, Chobanu M M. *Kolloidn Zh.*, 1977, 39, 358
- 6 Rudzinski W, Dominko A, Partyka S, *et al. Adsorption Sci. & Techn.*, 1985, 2, 207
- 7 Kronberg B. *J. Colloid Interface Sci.*, 1983, 96, 55

表面活性剂在固/液界面吸附理论的新进展

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摘 要 根据两阶段吸附模型^[1], 导出了两常数及一常数吸附等温线公式。不仅可以方便地应用于各种类型的表面活性剂在固/液界面上的吸附数据, 而且具有预示能力。对于显示LS型等温线的体系只需测定第一平台处和饱和的吸附量即可给出整个的吸附等温线。对于离子型表面活性剂在反电性固体上的吸附, 可自一个化合物的吸附预示出一系列同系物在同一吸附剂上的吸附等温线。

关键词: 吸附理论 表面活性剂 固/液界面 等温线公式