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Interaction Free Energy Studies on Floc Foam Flotation

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Abstract

The Gouy-Chapman theory of the electric double layer is applied to the calculation of interaction free energy of a charged surface film and a solid surface of opposite charge immersed in a solution of electrolyte. The interaction energies calculated with a constant surface charge density model and a constant surface potential model are compared. A constant surface charge density model for floc foam flotation is found to result in less effective binding energy than the constant surface potential model. The constant surface potential model can be found to account for the decrease in efficiency of floc foam flotation which is observed experimentally when ionic strength is increased. However, studying the binding energy at various ionic strengths with the constant surface charge density model gives results that are contradictory to the experimental results. We can thus conclude that the floc foam flotation system is better analyzed with a constant surface potential model.

INTRODUCTION

A quantitative treatment of the interaction of double layers is of great interest in the understanding of many physical phenomena that are concerned with the collision of particles in an electrolyte. Verwey and Overbeek (*1*) have analyzed the interaction of identical plane double layers within the framework of the simple Gouy-Chapman model of the double layer. These theoretical studies led to the establishment of criteria for the stability of colloids. The flocculation behavior of mixed colloidal suspensions, and bubble-particle collision and binding in flotation systems may be understood through a knowledge of the interaction between dissimilar double layers. Wilson et al. have used the Gouy-Chapman picture of the electric double layer in the calculation of the adsorption isotherms of floc particles on ionic surfactant films within the frameworks of a number of physical models (*2–5*), and in the calculation of the interaction potential of two large parallel plates with opposite surface charge immersed in a solution of electrolyte (*6*, *7*). This potential was then used in investigating kinetic and equilibrium aspects of floc coagulation (*8*, *9*). Jorné and E. Rubin have used the Gouy-Chapman theory to explain the effects of ionic size and charge on the selectivity of foam fractionation (*10*). In our earlier report (*11*) we analyzed the kinetic and equilibrium factors affecting the rate of precipitation flotation by means of the Gouy-Chapman model.

The equilibrium values of surface potentials are completely determined by the compositions of the pairs of phases involved (*11*), and are not dependent on the geometric configurations of the systems involved. Consequently the interaction of double layers involving changes in configuration (distance) should be studied at constant values of the surface potentials insofar as equilibrium situations are involved. Therefore, all the work mentioned above is based on the constant surface potential model. The surface charges, on the other hand, then change with configuration.

Now it is quite conceivable that this transport of charge carriers has a sufficient high free energy of activation so that it is too slow to be equilibrated during the approach time of an encounter between the two surfaces. If so, then one might better consider the surface charge densities, rather than the surface potentials, as constant.

The same idea is applicable when the charge of the surface is not determined by an equilibrium of potential-determining ions but depends, for instance, upon the dissociation of certain groups fixed at the surface, like SO_3H groups in sulfonated coal (*12*).

In our earlier work (*7*) we discussed some aspects of the constant surface potential and the constant surface charge density models of the interaction of plane parallel interfaces. Now we present results on the interaction free energy of floc foam flotation systems treated by a constant surface charge density model, and we compare the results with those obtained by the constant surface potential model.

ANALYSIS WITH A CONSTANT SURFACE CHARGE MODEL

Consider the system having fixed surface charge density δ_1 (negative) and δ_2 (positive), separated by a distance l. Poisson's equation for the system is

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi\rho}{D} = \frac{8\pi e N_0 C_\infty}{D} \sinh\left(\frac{e\psi}{KT}\right) \tag{1}$$

where ψ = electric potential at a distance x from the surface charge density δ_1
ρ = charge density
D = dielectric constant of water
e = |electronic charge|
N_0 = Avogadro's number
C_∞ = concentration of 1–1 electrolyte, in equivalents/cm^3
K = Boltzmann's constant
T = absolute temperature

The equation can be integrated to yield (*1*, *7*)

$$\frac{d\psi}{dx} = \left\{\left(\frac{d\psi}{dx}\right)_1^2 + 2\left(\frac{KT}{ea}\right)^2\left[\cosh\frac{KT}{e\psi} - \cosh\frac{e\psi_1}{KT}\right]\right\}^{1/2} \tag{2}$$

where $\left(\frac{d\psi}{dx}\right)_1 = \left.\frac{d\psi}{dx}\right|_{x=x_1}$

$$a^2 = \frac{DKT}{8\pi e^2 N_0 C_\infty}$$

ψ_1 = surface potential (with surface charge density δ_1)

Integration of Eq (2) yields

$$\int_{\psi_1}^{\psi(x)} \frac{d\psi}{\left\{\left(\frac{d\psi}{dx}\right)_1^2 + 2\left(\frac{KT}{ea}\right)^2\left[\cosh\frac{e\psi}{KT} - \cosh\frac{e\psi_1}{KT}\right]\right\}^{1/2}} = x \tag{3}$$

The relation between surface charge density δ_n and surface potential ψ_n is given by

$$\delta_n = (-1)^n \frac{D}{4\pi}\left(\frac{d\psi}{dx}\right)_n, \qquad n = 1, 2 \tag{4}$$

Evaluating Eq. (2) at $x = x_2$ yields

$$\left(\frac{d\psi}{dx}\right)_2 = \left\{\left(\frac{d\psi}{dx}\right)_1^2 + 2\left(\frac{KT}{ea}\right)^2\left[\cosh\frac{e\psi_2}{KT} - \cosh\frac{e\psi_1}{KT}\right]\right\}^{1/2} \tag{5}$$

We rearrange Eq. (5) to obtain

$$\left\{\left[\left(\frac{d\psi}{dx}\right)_2^2 - \left(\frac{d\psi}{dx}\right)_1^2\right]\Big/2\left(\frac{KT}{ea}\right)^2\right\} + \cosh\frac{e\psi_1}{KT} = \cosh\frac{e\psi_2}{KT} = W \tag{6}$$

$$\psi_2 = \frac{KT}{e}\operatorname{argcosh} W \tag{7}$$

Thus ψ_2 is expressed in terms of knowns δ_1 and δ_2, and unknown ψ_1, from Eqs. (4), (6), and (7). The unknown ψ_1 is then calculated by Newton's method from Eq. (8), which is obtained by setting $x = l$, $\psi(x) = \psi_2$ in Eq. (3).

$$l = \int_{\psi_1}^{\psi_2} \frac{d\psi}{\left\{\left(\frac{d\psi}{dx}\right)_1^2 + 2\left(\frac{KT}{ea}\right)^2\left[\cosh\frac{e\psi}{KT} - \cosh\frac{e\psi_1}{KT}\right]\right\}^{1/2}} \tag{8}$$

The resulting value of ψ_1 is then used in Eq. (3) to generate x as a function of ψ over the range (ψ_1, ψ_2).

We now examine the problem of calculating the free energy of the system.

During the interaction, no charge is transfered from one phase to the other, so the contribution to the chemical part of the free energy of the potential-determining ions is a constant and need not be considered. The important part of the free energy is then the work necessary to charge the double layers in a reversible way starting from zero charge. The charge of the potential-determining ions is imagined to be transported gradually from the solution to the surfaces. After each small increase of the surface charge, the ions in the solution are allowed to rearrange themselves according to a new equilibrium, during which no work is done, so the electric part of the free energy of the double layers per cm^2 can be written

$$G_{\text{elec}}(l) = \int_0^{\delta_1}\left(\psi_1' + \frac{\delta_2}{\delta_1}\psi_2'\right)d\delta_1' \tag{9}$$

where ψ_1' and ψ_2' are the surface potentials at x_1 and x_2 when the two surfaces are separated by a distance l with charge densities δ_1' and $\delta_2' = \delta_2\delta_1'/\delta_1$, respectively. For given values of δ_1' and δ_2' the corresponding values of ψ_1' and ψ_2' are calculated from Eqs. (4) through (8), permitting (rather laborious) numerical evaluation of the integral in Eq. (9).

The electrical part of the free energy at infinite separation is also given by Eq. (9), except that ψ_1' and ψ_2' are evaluated when $l = \infty$. The total free energy of the system G_∞ when $l = \infty$ is (*1*, *6*)

$$G_\infty = -8N_0C_\infty KTa\left(\cosh\frac{e\psi_{1a}}{2KT} + \cosh\frac{e\psi_{2a}}{2KT} - 2\right) \tag{10}$$

where ψ_{1a} and ψ_{2a} are the surface potentials evaluated at $l = \infty$. The chemical part of the free energy is $-\delta_1\psi_{1a} - \delta_2\psi_{2a}$, so the electric free energy at infinite separation can also be calculated as

$$G_{\text{elec}}(\infty) = G_\infty + \delta_1\psi_{1a} + \delta_2\psi_{2a} \tag{11}$$

where G_∞ is evaluated from Eq. (10).

The free energy of interaction of the two surfaces is then given by

$$V(l) = G_{\text{elec}}(l) - G_{\text{elec}}(\infty) \tag{12}$$

Constant Surface Potential Model

The free energy per unit area of a system composed of two large parallel surfaces separated by a distance l and immersed in an electrolyte solution is (*1*, *6*)

$$G(l) = -2N_0C_\infty KT\int_0^l\left[\cosh\frac{e\psi}{KT} - 1\right]dx - \frac{D}{8\pi}\int_0^l\left(\frac{d\psi}{dx}\right)^2 dx \tag{13}$$

The free energy of interaction per cm^2 of the two surfaces is then given by

$$V(l) = G(l) - G_\infty \tag{14}$$

where G_∞ is given by Eq. (10), as before.

RESULTS AND DISCUSSION

The free energy of interaction V between two parallel surfaces is calculated with a constant surface charge model for very small l ($l = 2$ Å), and is plotted as a function of the surface charge density in Fig. 1. The negative of the electrical part of the free energy at infinite separation of the two surfaces is also plotted in the same figure as a function of surface charge density. Here we have set the charge densities of the two surfaces equal in magnitude but of opposite sign. Our earlier report (*7*) showed that G_{elec} approaches zero since ψ_0 approaches zero when l approaches zero. Therefore, $|V|$ approaches the value $-G_{\text{elec}}(\infty)$, shown in Fig. 1, as expected from Eq. (12).

Plots of V vs l (with the constant surface charge model) at various

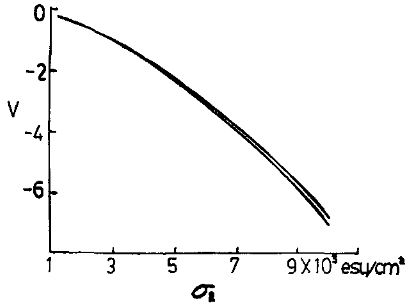

FIG. 1. Dependence of V (upper curve) and $-E_{elec}$ (infinity) (lower curve) on surface charge density, constant surface charge model. $T = 298\,^\circ\mathrm{K}$ (in all figures), $D = 78.5$ (in all figures), $C = 10^{-6}\ M$, $L = 2 \times 10^{-8}$ cm, $-\sigma_1 = \sigma_2$.

surface charge densities are shown in Fig. 2. The absolute value of the free energy of interaction $|V|$ is greater for larger surface charge densities, as expected. Plots of V vs l at various concentrations of a 1–1 electrolyte with the surface charge fixed at a certain value are shown in Fig. 3. The free energy of interaction is greater in magnitude at lower electrolyte concentrations.

Figures 4 and 5 show the comparison of V's calculated by the constant surface potential model and by the constant surface charge model as functions of l. The constant surface charge model results in a smaller binding energy $|V|$ than would be obtained with the constant surface potential model, as we predicted earlier (7).

The surface potential of an isolated plane surface in an electrolyte is dependent on the concentration of the potential-determining ions and independent of the bulk electrolyte concentration. In other words, the surface potential remains constant while the surface charge density varies with variation of the electrolyte concentration. In order to compare the effect of electrolyte concentration on binding energy, we should therefore change the surface charge density with changing electrolyte concentration in such a manner as to maintain the surface potential at infinite separation at a constant value. Then we evaluate V as a function of l at various concentrations of electrolyte and the corresponding surface charge densities with the constant surface charge model. The results are shown in Fig. 6. Somewhat surprisingly, the binding energy $|V|$ at small separation is greater for higher ionic strengths. The reason for this result can be explained as follows: When surfaces with the same surface potential are

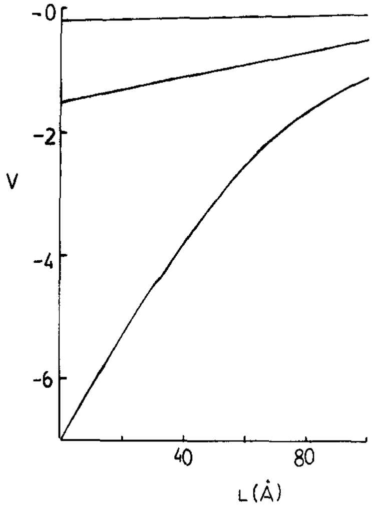

FIG. 2. Dependence of V on distance of separation and surface charge density, constant surface charge model. $C = 10^{-6}\ M$, $-\sigma_1 = \sigma_2 = 0.125 \times 10^4$, 0.376×10^4, and 0.101×10^5 esu/cm^2 from top to bottom.

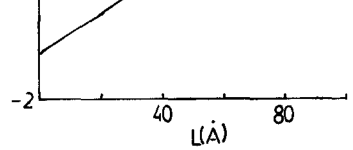

FIG. 3. Dependence of V on distance of separation and salt concentraction, constant surface charge model. $-\sigma_1 = \sigma_2 = 0.4 \times 10^4$ esu/cm^2, $C = 10^{-4}$, 10^{-5}, and $10^{-6}\ M$ from top to bottom.

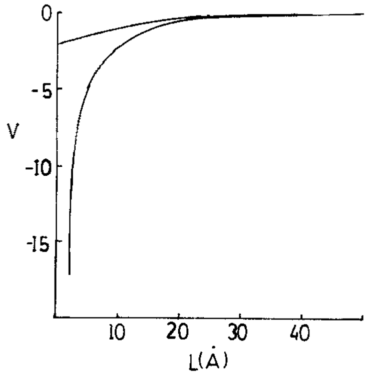

FIG. 4. Dependence of V on distance of separation with constant surface charge model (upper curve) and constant surface potential model (lower curve). $C = 10^{-4}$ M, σ(infinity) = $\pm 0.125 \times 10^5$ esu/cm^2 (constant surface charge model), ψ(infinity) = ± 50 mV (constant surface potential model).

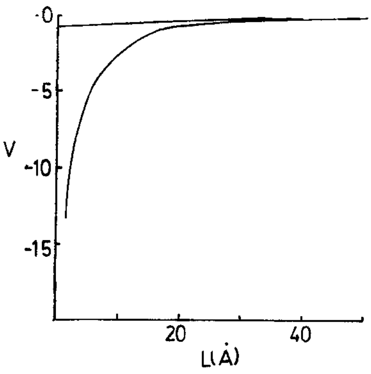

FIG. 5. Dependence of V on distance of separation with constant surface charge model (upper curve) and constant surface potential model (lower curve). $C = 10^{-5}$ M, other parameters as in Fig. 4.

immersed in solutions at various ionic strengths, the surface charge density is greater in magnitude at higher ionic strengths (7), and therefore $-G_{\text{elec}}(\infty)$ is found to be greater in magnitude at higher ionic strengths by inspection of Eq. (9). The binding energy $|V|$ at small l approaches the value $-G_{\text{elec}}(\infty)$ (shown in Fig. 1), and therefore it is greater for systems at higher ionic strengths if the surface charge densities remain constant during the approach time of two surfaces with opposite charge signs.

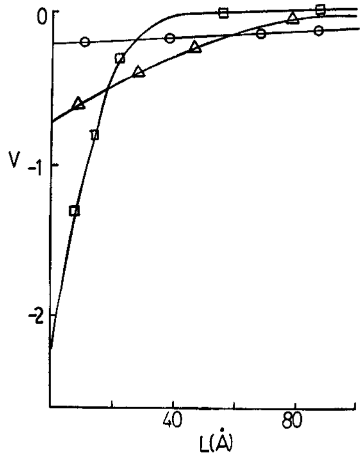

FIG. 6. Dependence of V on distance of separation and ionic strength, constant surface charge model. Ψ(infinity) = ±50 mV; (□) $C = 10^{-4}\ M$, $\sigma = \pm 0.125 \times 10^5$ esu/cm^2; (△) $C = 10^{-5}\ M$, $\sigma = \pm 0.400 \times 10^4$ esu/cm^2; (○) $C = 10^{-6}\ M$, $\sigma = \pm 0.125 \times 10^4$ esu/cm^2.

However, this result, obtained by the constant surface charge model, contradicts actual experimental observation. Our earlier experimental work on floc foam flotation (*7*, *13*) and work of others (*14–18*) have shown that the efficiency of floc foam flotation, and thus of binding energy, decreases with increasing ionic strength. This contradiction indicates that the constant surface charge model is not suitable for calculating the binding energy in the floc foam flotation system under the influence of the attractive force between the charged particle surface and the charged surfactant film surface. The surface charge apparently does have enough time to reach its equilibrium value as the surfaces approach each other. We thus conclude that the floc foam flotation system should be analyzed with a constant surface potential model.

On the other hand, the constant surface charge model may still be feasible for analyzing the stability of colloidal systems where the force among colloidal particles is repulsive and the approach time for colloidal particles is fairly limited.

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