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Electrical Aspects of Adsorbing Colloid Flotation

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Abstract

The Gouy-Chapman theory of the electric double layer is applied to the calculation of the interaction energy of a charged surface film and a solid surface of opposite charge immersed in a solution of electrolyte. This model is found to account for the decrease in efficiency of precipitate flotation and adsorbing colloid flotation which is observed when ionic strength is increased. The Gouy-Chapman theory is also used to predict the existence of analogs to the phenomena of electroosmotic flow and streaming potential in foams and surface films.

INTRODUCTION

Foam separations have been of great interest in recent years, due at least in part to their ready adaptability to the separation of trace toxic impurities from industrial wastes and other effluents; the extensive literature has been reviewed by Lemlich (*1*, *2*), Somasundaran (*3*), and others. Two of the more promising of the foam separation techniques are precipitate flotation and adsorbing colloid flotation, both of which show extremely high removal ratios at the cost of relatively small quantities of surfactant.

It has been observed, however, that these two techniques do not function as efficiently in solutions of high ionic strength. A. J. Rubin and Lapp (*4*) observed that the precipitate flotation of zinc hydroxide decreases with increasing ionic strength, and Grieves and Bhattacharyya found that the precipitate flotation of cyanide complexed with Fe(II) exhibited decreasing removal ratios with increasing ionic strength (*5*). Sheiham and Pinfold observed the same effect in the precipitate flotation of $SrCO_3$, and ascribed it to a number of factors, including the effect of the ionic strength of the solution on the force between the precipitate particles and the surfactant film (*6*). Ferguson et al. observed the same effect with the adsorbing colloid flotation of Pb(II) with FeS (*7*). Mahne and Pinfold did not observe this effect with Nioxime precipitate flotation, but noted that they were carrying out precipitate flotation of the second kind in which no surfactant was used (*8*).

The Gouy-Chapman theory of the electric double layer was used many years ago to account for the stability of lyophobic colloids by Verwey and Overbeek (*9*), and Jorné and E. Rubin have used this model to analyze the effect of ionic charge and size of species present on the selectivity of foam fractionation (*10*). These works suggested to us the feasibility of using the Gouy-Chapman model to account for the effects of ionic strength on the efficiency of precipitate and adsorbing colloid foam flotation separations.

We outline below a calculation of the free energy per unit area of two plane parallel layers at positive and negative potentials, respectively, as a function of the distance between them and of the ionic strength of the solution separating them. Numerical results are presented graphically. We then briefly discuss calculations on electroosmotic flow and streaming potential phenomena which may be anticipated to occur in foams.

THE CALCULATION

We consider two plane parallel surfaces having zeta potentials ψ_1 and ψ_2, and separated by a distance l. We assume that the region between the two planes contains a solution of dielectric constant D and that it is in equilibrium with solution containing a bulk concentration c (moles/cm^3) of 1:1 electrolyte. Poisson's equation for the system is then given by (*9*)

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

where e is the electronic charge, N_0 is Avogadro's number, ψ is the electric potential, k is Boltzmann's constant, T is the absolute temperature, and ρ is the charge density. We let

$$\frac{8\pi e^2 N_0 c}{DkT} = \frac{1}{a^2}$$

and multiply Eq. (1) by $\phi = d\psi/dx$ to obtain

$$\phi \frac{d\phi}{dx} = \frac{kT}{ea^2} \sinh\left(\frac{e\psi}{kT}\right)\frac{d\psi}{dx} \tag{2}$$

which can be integrated to yield

$$\frac{d\psi}{dx} = \pm \left\{ \left(\frac{d\psi}{dx}\right)_1^2 + 2\left(\frac{kT}{ea}\right)^2 \left(\cosh\frac{e\psi}{kT} - \cosh\frac{e\psi_1}{kT}\right)\right\}^{1/2} \tag{3}$$

Here $(d\psi/dx)_1 = d\psi(x = x_1)/dx$.

Integration of Eq. (3) yields

$$\int_{\psi}^{\psi_1} \frac{d\psi}{\left\{ \left(\frac{d\psi}{dx}\right)_1^2 + 2\left(\frac{kT}{ea}\right)^2 \left(\cosh\frac{e\psi}{kT} - \cosh\frac{e\psi_1}{kT}\right)\right\}^{1/2}} = x \tag{4}$$

This integral, unlike a similar one treated by Verwey and Overbeek (9), does not reduce to convenient calculation in terms of elliptic integrals. We have here assumed that ψ_1 is negative and ψ_2 is positive. The unknown slope $(d\psi/dx)_1$ is calculated by Newton's method from

$$l = \int_{\psi_1}^{\psi} \frac{d\psi}{\left\{ \left(\frac{d\psi}{dx}\right)_1^2 + 2\left(\frac{kT}{ea}\right)^2 \left(\cosh\frac{e\psi}{kT} - \cosh\frac{e\psi_1}{kT}\right)\right\}^{1/2}} \tag{5}$$

This value is then used in Eq. (4) to generate values of x as a function of ψ over the range (ψ_1, ψ_2).

We use the method of Verwey and Overbeek (9) to calculate the free energy per unit area of the pair of double layers.

$$G(l) = \int_0^1 \frac{d\lambda}{\lambda} \int_0^l \psi'(x)\rho'(x)\, dx \tag{6}$$

$$\psi'\, d\lambda = \frac{\partial}{\partial\lambda}(\lambda\psi')\, d\lambda - \lambda \frac{\partial\psi'}{\partial\lambda}\, d\lambda \tag{7}$$

$$\rho' = \frac{-D}{4\pi}\frac{\partial^2\psi'}{\partial x^2} = -2N_0 ce\lambda \sinh\frac{\lambda e\psi'}{kT} \tag{8}$$

Substitution into Eq. (6) yields

$$G = -\int_0^1\int_0^l 2N_0 ce \sinh\left(\frac{e\lambda\psi'}{kT}\right)\frac{\partial}{\partial\lambda}(\lambda\psi')\, dx\, d\lambda + \int_0^1\int_0^l \frac{D}{4\pi}\frac{\partial^2\psi'}{\partial x^2}\frac{\partial\psi'}{\partial\lambda}\, dx\, d\lambda = I_1 + I_2 \tag{9}$$

The first integral can be rewritten as

$$I_1 = -2N_0ckT\int_0^{e\psi/kT}\int_0^l \sinh\left(\frac{\lambda e\psi'}{kT}\right)d\left(\frac{\lambda e\psi'}{kT}\right)dx$$

$$= -2N_0ckT\int_0^l\left[\cosh\frac{e\psi}{kT} - 1\right]dx \tag{10}$$

The second integral can be rewritten as

$$I_2 = \frac{D}{4\pi}\int_0^1\int_0^l\left[\frac{\partial}{\partial x}\left(\frac{\partial\psi'}{\partial x}\frac{\partial\psi'}{\partial\lambda}\right) - \left(\frac{\partial\psi'}{\partial x}\right)\frac{\partial^2\psi^1}{\partial x\partial\lambda}\right]dx\,d\lambda \tag{11}$$

$$= \frac{D}{4\pi}\int_0^1\left[\left(\frac{\partial\psi'}{\partial x}\frac{\partial\psi'}{\partial\lambda}\right)_{x=l} - \left(\frac{\partial\psi'}{\partial x}\frac{\partial\psi'}{\partial\lambda}\right)_{x=0}\right]d\lambda$$

$$- \frac{D}{4\pi}\int_0^1\int_0^l\frac{\partial\psi'}{\partial x}\frac{\partial^2\psi'}{\partial x\partial\lambda}dx\,d\lambda \tag{12}$$

Now $\partial\psi/\partial\lambda(x = 0) = \partial\psi'/\partial\lambda(x = l) = 0$, since ψ_1 and ψ_2 are kept constant during the process of charging the ionic atmosphere by increasing λ from 0 to 1. Therefore, I_2 is given by

$$I_2 = -\frac{D}{8\pi}\int_0^1\int_0^l\frac{\partial}{\partial\lambda}\left[\left(\frac{\partial\psi'}{\partial x}\right)^2\right]dx\,d\lambda$$

$$= -\frac{D}{8\pi}\int_0^l\left[\left(\frac{\partial\psi'}{\partial x}\right)^2_{\lambda=1} - \left(\frac{\partial\psi'}{\partial x}\right)^2_{\lambda=0}\right]dx \tag{13}$$

Now $\partial\psi'/\partial x = (\psi_2 - \psi_1)/l$ when $\lambda = 0$, so Eq. (13) can be rewritten as

$$I_2 = -\frac{D}{8\pi}\int_0^l\left(\frac{d\psi}{dx}\right)^2dx + \frac{D}{8\pi}(\psi_2 - \psi_1)^2/l \tag{14}$$

Our final expression for the free energy per unit area is therefore

$$G(l) = -2N_0ckT\int_{\psi_1}^{\psi_2}\cosh\left(\frac{e\psi}{kT} - 1\right)\frac{dx}{d\psi}d\psi$$

$$- \frac{D}{8\pi}\int_{\psi_1}^{\psi_2}\frac{d\psi}{dx}d\psi + \frac{D}{8\pi}(\psi_2 - \psi_1)^2/l \tag{15}$$

This is the free energy of the system relative to its counterpart in which the ions are not charged. We must subtract from this the work done in moving the two parallel plates infinitely far apart; this is simply $D(\psi_2 - \psi_1)^2/8\pi l$, so our final expression for the free energy is

$$G(l) = -2N_0ckT\int_{\psi_1}^{\psi_2}\left[\cosh\left(\frac{e\psi}{kT}\right) - 1\right]\frac{dx}{d\psi}d\psi - \frac{D}{8\pi}\int_{\psi_1}^{\psi_2}\frac{d\psi}{dx}d\psi \tag{16}$$

We are now able to use the table of values of x as a function of ψ obtained from Eq. (4) to evaluate $G(l)$ by means of Eq. (16); the integration is done numerically. Approximately 10 sec of computer time (XDS Sigma 7) is required to generate a typical plot of G as a function of l.

RESULTS

Plots of G vs l for concentrations of 1 : 1 electrolyte of 1, 0.1, 0.01, and 0.001 *M* are presented in Fig. 1; G is in ergs/cm^2 and l is in Angstroms. The dielectric constant of water was taken as 78.5, ψ_1 was set equal to -50 mV, and ψ_2 was set equal to $+50$ mV. A temperature of 298 °K was assumed. It is immediately evident that the range of the attractive interaction between the two planes increases drastically with decreasing ionic strength; evidently decreasing the ionic strength of the solution in effect increases the "collision cross-section" for bubble–precipitate encounters, and also increases the strength with which a captured particle of precipitate would be held.

Obviously there are other factors which contribute to the free energy of interaction between ionic surfactant-coated bubbles and precipitates—van

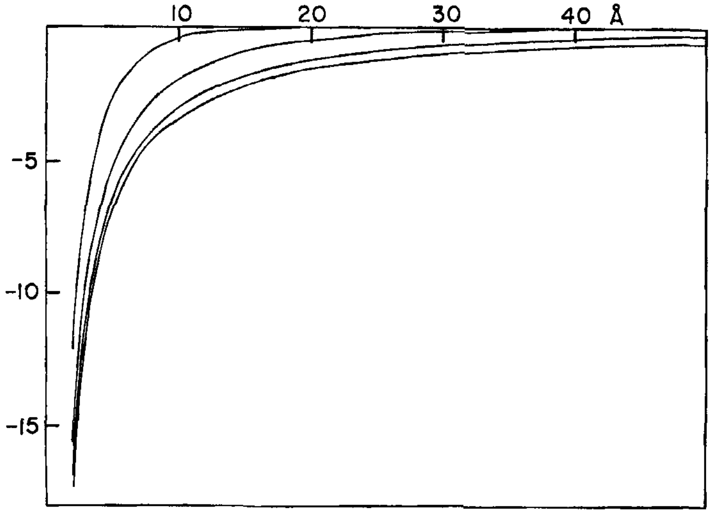

FIG. 1. Free energy (ergs/cm^2) vs distance of separation (Angstroms) for various concentrations (1, 0.1, 0.01, and 0.001 *M*) of 1:1 electrolyte. $\psi_1 = -50$ mV, $\psi_2 = +50$ mV, T = 298 °K.

der Waals forces and modified Debye–Hückel interactions of the ions in the regions of modified concentrations, for instance. The geometry of the model is also rather oversimplified. Still, the magnitude of the interaction (roughly in the range of 1–15 ergs/cm^2) is substantial (for comparison, the surface tension of water is 72.8 ergs/cm^2 at 20°C). And at 25°C, if we assume an interaction energy of 1 erg/cm^2, an area of interacting surface of only $20 \times 20\text{Å}^2$ would provide kT of binding energy. The fact that even at 1 *M* concentrations of electrolyte the free energy is quite substantially less than -1 erg/cm^2 at physically attainable distances accounts for the fact that precipitate and adsorbing colloid flotation separations do take place even in media of high ionic strength. The fact that the attractive force extends out to much greater distances at lower ionic strength accounts for the greater efficiency of the technique in media of low ionic strength.

ELECTROOSMOSIS AND STREAMING POTENTIAL ANALOGS

The Gouy-Chapman model also leads one to anticipate that foams made with ionic surfactants might well be expected to exhibit phenomena similar to electroosmotic flow and streaming potential (*11*). Under circumstances where the bulk of the foam drainage (of entrained liquid, recycled foamate, etc.) takes place along the Plateau borders of the films, the analogy with conventional electroosmotic flow and streaming potential is immediately evident when we recall that the surfaces of the films whose junctures form the Plateau borders are charged. Movement of these surfaces is impeded by surface viscosity and by the bound Plateau borders.

In the case where flow occurs primarily through the film itself, one can work out exact treatments. We do so first for the electroosmotic analog.

We let E be the electric field strength tangent to the film, l the half-thickness of the film, x the distance measured from the center of the film, and other variables as above. Our starting point is again Eq. (1), which yields a first integral

$$\frac{d\psi}{dx} = \pm\sqrt{2}\,\frac{kT}{ea}\left[\cosh\frac{e\psi}{kT} - \cosh\frac{e\psi_0}{kT}\right]^{1/2} \qquad (17)$$

where we have made use of the fact that $d\psi/dx\ (x = 0) = 0$ from the symmetry of the problem $[\psi(-l) = \psi(l)]$, and have set $\psi(0) = \psi_0$.

Equation (17) integrates to yield

$$\int_{\psi_0}^{\psi(x)} \frac{d\psi}{\left[\cosh\frac{e\psi}{kT} - \cosh\frac{e\psi_0}{kT}\right]^{1/2}} = \sqrt{2}\frac{kT}{ea}x \tag{18}$$

assuming $\psi(x) \geqq \psi_0$, $x \geqq 0$. This integral can be recast in the form of a combination of elliptic integrals of the first kind:

$$x = 2a\exp\left(\frac{-e\psi_0}{kT}\right)\int_{\phi}^{\pi/2} \frac{d\phi'}{[1 - \sin^2\alpha\sin^2\phi']^{1/2}} \tag{19}$$

$$\sin^2\alpha = \exp(-2e\psi_0/kT)$$

$$\phi = \arcsin\left[\exp\left\{\frac{e(\psi_0 - \psi)}{2kT}\right\}\right]$$

as shown by Verwey and Overbeek (*9*). The unknown potential ψ_0 is calculated from

$$l = 2a\exp\left(\frac{-e\psi_0}{kT}\right)\int_{\phi(l)}^{\pi/2} \frac{d\phi'}{\left[1 - \exp\left(\frac{-2e\psi_0}{kT}\right)\sin^2\phi'\right]^{1/2}} \tag{20}$$

by use of Newton's method. Here

$$\phi(l) = \arcsin\left\{\exp\left[\frac{-e(\psi(l) - \psi_0)}{2kT}\right]\right\} \tag{21}$$

Now the electric force on an element of volume at (x, y, z) is given by $E\rho\, dx\, dy\, dz$; at steady state this is cancelled by the viscous drag on this element, $\eta(d^2v\, dx\, dy\, dz/dx^2)$. We thus have

$$E\rho(x) = \eta\frac{d^2v}{dx^2} \quad \text{or} \quad \frac{-ED}{4\pi\eta}\frac{d^2\psi}{dx^2} = \frac{d^2v}{dx^2} \tag{22}$$

Integrating twice, and noting that $dv/dx(0) = v(\pm l) = 0$, yields (*11*)

$$v(x) = \frac{ED}{4\pi\eta}[\psi(l - \psi(x)] \tag{23}$$

The flow rate per unit width of film, dV/dt, is then given by

$$\frac{dV}{dt} = \frac{ED}{2\pi\eta}\int_0^l [\psi(l) - \psi(x)]\, dx \tag{24}$$

If the film is thick compared to the thickness of the ionic atmosphere, we can approximate $\psi(x)$ by zero over most of the range of integration to obtain

$$\frac{dV}{dt} \cong \frac{ED}{2\pi\eta}\psi(l)l \tag{25}$$

Let us next examine the streaming potential analog. We let P be the pressure difference causing streaming, b the length of the film in the direction of flow and other notations as before. We again assume that the surfaces of the film are stationary. At steady state the charge transported by the moving double layer per unit time will be

$$i = 2\int_0^l \rho(x)v(x)\,dx \tag{26}$$

The usual treatment of viscosity yields

$$v = P(l^2 - x^2)/2\eta b \tag{27}$$

Setting $\rho = -D(d^2\psi/dx^2)/4\pi$ in Eq. (26) yields

$$i = \frac{-D}{2\pi}\int_0^l v(x)\frac{d^2\psi}{dx^2}\,dx \tag{28}$$

Two integrations by parts and use of the boundary conditions that $d\psi/dx|_{x=0} = 0$, $v(l) = 0$, and $dv(l)/dx = -Pl/\eta b$ gives the result that

$$i = \frac{DP}{2\pi\eta b}\int_0^l [\psi(x) - \psi(l)]\,dx \tag{29}$$

At steady state this current will be counterbalanced by an equal and opposite current due to the streaming potential V_s:

$$i = 2\int_0^l \frac{\lambda(x)}{b}V_s\,dx \tag{30}$$

Here $\lambda = \lambda_0^+c^+ + \lambda_0^+c^-$ is the specific conductivity which, on use of $c^+ = c\exp(-e\psi/kT)$, $c^- = c\exp(e\psi/kT)$, yields, on equating Eq. (29) to Eq. (30).

$$\frac{DP}{2\pi\eta b}\int_0^l [\psi(x) - \psi(l)]\,dx = \frac{2cV_s}{b}\int_0^l \left[\lambda_0^+\exp\left(\frac{-e\psi}{kT}\right) + \lambda_0^-\exp\left(\frac{e\psi}{kT}\right)\right]dx \tag{31}$$

The streaming potential is then given by

$$V_s = \frac{DP}{4\pi\eta c} \frac{\int_0^l [\psi(x) - \psi(l)]\, dx}{\int_0^l \left[\lambda_0^+ \exp\left(\frac{-e\psi}{kT}\right) + \lambda_0^- \exp\left(\frac{e\psi}{kT}\right)\right] dx} \tag{32}$$

We obtain an approximate formula by assuming that $|\psi(x)| \ll |\psi(l)|$ over most of the range $0 \leqq x \leqq l$, and that $e\psi/kT \ll 1$. This gives

$$V_s \cong \frac{DP\psi(l)}{4\pi\eta c(\lambda_0^+ + \lambda_0^-)} \tag{33}$$

Usually P will be due to a difference in hydrostatic head,

$$P = \rho_{\text{sol}} g b \cos\theta \tag{34}$$

where b is the length of the film, θ is the angle it makes with the vertical, ρ_{sol} is the density of the film solution, and g is the gravitational constant.

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