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Electrical Aspects of Adsorbing Colloid Flotation. VIII. Specific Adsorption of Ions by Flocs

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Abstract

A Gouy-Chapman model of the solid-water interface with specific adsorption of ions is used to calculate surface and zeta potentials. The effects of sign and magnitude of ionic charge and surface charge density, ionic strength, specific binding energy, and temperature are examined. Experimental data on foam flotation of ferric hydroxide with sodium lauryl sulfate in the presence of a variety of anions support the model.

INTRODUCTION

The technique of adsorbing colloid flotation has shown considerable promise as a method for quick, efficient removal of low concentrations of heavy metals from aqueous systems; the literature has been recently reviewed by Somasundaran (*1*) and by Grieves (*2*). The work of Zeitlin and his collaborators (*3*) encouraged us to explore use of the technique for waste treatment (*4*) and to examine a number of theoretical models for the adsorption isotherms of floc particles at the air–water interface (*5*, *6*).

One of the factors which may profoundly affect the efficiency of adsorbing colloid flotation and the recovery of surfactant from the sludge in the collapsed foamate is the extent to which nonsurfactant ions are specifically adsorbed into the primary layer of the floc. In an earlier paper we examined the impact of this on the adsorption isotherms of surfactant on floc within the framework of the Fuerstenau-Somasundaran-Healy model (*7*, *8*) and on the implications for surfactant recovery (*9*). Now we examine the effect of specifically adsorbed ions in the primary layer on the zeta and surface potentials of the floc particles. We were particularly interested in some of the zeta potential data published by Riddick (*10*); he notes that for some colloids having negative zeta potentials of, say, −30 mV, the addition of small concentrations of some electrolytes causes the zeta potential to become even more negative, down to, say, −70 mV. As one goes to higher electrolyte concentrations, the zeta potential then goes through a minimum and then increases toward zero. This enhancement of the zeta potential at relatively low electrolyte concentrations should result in a marked increase in the efficiency of flotation of such colloids (silica, in this case) by cationic surfactants. Riddick reports similar behavior for kaolin and a latex preparation. We analyze Riddick's model: specific adsorption of anions at low concentrations followed by gradual reduction in magnitude of the zeta potential as the thickness of the ionic atmosphere near the surface decreases with further increase in electrolyte concentration.

We then present experimental data illustrating the effects of the adsorption of anions and glycerol on the flotation of ferric hydroxide with sodium lauryl sulfate.

ANALYSIS

We assume that our floc particle is large in comparison to the Debye length of the ionic atmosphere so that we may use planar geometry in calculating the electric potential $\psi(x)$ at a distance x from the solid–liquid interface. We let σ be the surface charge density of this interface, due to charged sites originally present and to the charges of ions adsorbed from solution into the primary layer. This surface charge density then attracts an ionic atmosphere of equal but opposite total charge. The zeta potential is the electric potential at the slip plane, one viscous drag boundary layer thickness (δ) from the solid–liquid interface.

First we need to calculate the electric potential in the vicinity of the interface; we take as our Poisson-Boltzmann equation (*11*)

$$\frac{d^2\psi}{dx^2} = \frac{-4\pi\rho}{D} = \frac{A \sinh(|z|e\psi/kT)}{1 + B\cosh(|z|e\psi/kT)} \frac{\psi_0}{|\psi_0|} \tag{1}$$

where $A = 8\pi|z|eN_0c/D(1 - 2c/c_{\max})$ (2)

$B = 2c/(c_{\max} - c)$ (3)

ρ = charge density

e = electronic charge

N_0 = Avogadro's Number

D = dielectric constant of water

c = concentration of z–z electrolyte in bulk solution, moles/cm^3

$c_{\max}$ = maximum possible concentration of z–z electrolyte in the solution

k = Boltzmann's constant

T = absolute temperature

ze = charge of ion being adsorbed

From Eq. (1) and the electrical neutrality requirement we can readily show that

$$-\frac{D}{4\pi}\frac{d\psi(0)}{dx} = \sigma \tag{4}$$

the surface charge density. We use a previously obtained first integral for Eq. (1) (*11*),

$$\frac{d\psi}{dx} = -\left[\frac{2AkT}{|z|eB}\log_e\frac{1 + B\cosh(|z|e\psi/kT)}{1 + B}\right]^{1/2}\frac{\psi_0}{|\psi_0|} \tag{5}$$

where the sign is determined by the sign of the surface charge density through Eq. (4). The surface charge density is then given by

$$\sigma = \frac{\psi_0}{|\psi_0|}\frac{D}{4\pi}\left[\frac{2AkT}{|z|eB}\log_e\frac{1 + B\cosh(|z|e\psi_0/kT)}{1 + B}\right]^{1/2} \tag{6}$$

Solving this for ψ_0 yields

$$\psi_0 = \frac{\sigma}{|\sigma|}\frac{kT}{|z|e}\operatorname{argcosh}\left\{(1 + B^{-1})\exp\left[\frac{|z|eB}{2AkT}\left(\frac{4\pi\sigma}{D}\right)^2\right] - B^{-1}\right\} \tag{7}$$

We take as the charge density of the solid surface

$$\sigma = \sigma_0 + zeS\theta \tag{8}$$

where σ_0 is the intrinsic charge density of the bare surface, S is the number of occupiable sites per cm^2 of surface, and θ is the fraction of sites occupied by our specifically adsorbed ions of charge ze.

We choose as our expression for the chemical potential of an adsorbed ion

$$\mu^a = \mu_0{}^a + kT\log_e \frac{\theta}{1-\theta} + ze\psi_0(\theta) \tag{9}$$

The second term takes into account the concentration and excluded volume effect of the sorbed ions; the third describes the electrical work which must be done to bring the ion from bulk solution to the interface. This chemical potential must be equal to the chemical potential of the ion in the bulk solution,

$$\mu^s = \mu_0{}^s + kT\log_e [\gamma(c)c] \tag{10}$$

where we shall estimate the activity coefficient $\gamma(c)$ from Debye-Hückel theory,

$$\log_e \gamma(c) = \frac{-z^2e^2b}{8\pi DkT} = -gc^{1/2} \tag{11}$$

where b^{-1} is the Debye length, $[DkT/(8\pi N_0e^2z^2c)]^{1/2}$, and c is in moles/cm^3.

Equating these two chemical potentials for the ion which may be sorbed then gives us an equation relating θ and c:

$$\frac{\chi}{kT} + \log_e\frac{\theta}{1-\theta} + \frac{z}{|z|}\frac{\sigma}{|\sigma|}\operatorname{argcosh}\left\{(1+B^{-1}) \times \exp\left[\frac{|z|eB}{2AkT}\left(\frac{4\pi\sigma}{D}\right)^2\right] - B^{-1}\right\} = \log_e c - gc^{1/2} \tag{12}$$

$$\chi = \mu_0{}^a - \mu_0{}^s$$

Here we must recall that σ is a function of θ given by Eq. (8), and that A and B are functions of c given by Eqs. (2) and (3).

We calculate the surface potential, ψ_0, as follows. We choose a value of c, then solve Eq. (12) numerically for $\theta(c)$, noting that σ depends on θ through Eq. (8). We use the value of θ obtained to calculate σ from Eq. (8), and use this result to calculate $\psi_0(c)$ from Eq. (7). We then integrate Eq. (5) to obtain

$$\frac{-\sigma}{|\sigma|}\int_{\psi_0(c)}^{\zeta(c)} \frac{d\psi}{\left[\dfrac{2AkT}{|z|eB}\log_e\dfrac{1+B\cosh(|z|e\psi/kT)}{1+B}\right]^{1/2}} = \int_0^\delta dx = \delta \tag{13}$$

where δ is the distance between the solid–liquid interface and the hypothetical slip plane used to define the zeta potential, ζ.

We eliminate δ from Eq. (13) by use of a standard approximate formula relating migration velocity v to applied electric field strength E (*12*):

$$v = D\zeta E/4\pi\eta \tag{14}$$

where η is the viscosity of the solution.

We take the electric drag force, F_E, on the particle as

$$F_E = 4\pi r_0^2 \sigma_1(\delta) E \tag{15}$$

where $\sigma_1(\delta)$ is the net surface charge density at the slip plane, given by

$$\sigma_1(\delta) = \frac{-D}{4\pi}\frac{d\psi(\delta)}{dx} \tag{16}$$

$$= \frac{\psi_0}{|\psi_0|}\frac{\sigma}{|\sigma|}\frac{D}{4\pi}\left[\frac{2AkT}{|z|eB}\log_e\frac{1 + B\cosh(|z|e\zeta/kT)}{1 + B}\right]^{1/2} \tag{17}$$

(We assume here that $r_0 \gg \delta$.) The viscous drag force, F_v, we estimate as

$$F_v = 4\pi r_0^2 \eta v/\delta \tag{18}$$

On using Eq. (14) we obtain from this

$$F_v = r_0^2 DE\zeta/\delta \tag{19}$$

Equating the electric and viscous forces then yields

$$\delta = \frac{|\zeta|}{\left[\frac{2AkT}{|z|eB}\log_e\frac{1 + B\cosh(|z|e\zeta/kT)}{1 + B}\right]^{1/2}} \tag{20}$$

We recall that δ is also given by Eq. (13); equating the two expressions for δ yields

$$\frac{-\zeta}{\left[\log_e\frac{1 + B\cosh(|z|e\zeta/kT)}{1 + B}\right]^{1/2}} = \int_{\psi_0}^{\zeta}\frac{d\psi}{\left[\log_e\frac{1 + B\cosh(|z|e\psi/kT)}{1 + B}\right]^{1/2}} \tag{21}$$

This equation we then solve numerically for ζ.

One might be tempted to estimate δ by use of Stoke's Law. This yields

$$6\pi\eta r_0 v = 4\pi r_0^2 \eta \frac{v}{\delta} \tag{22}$$

The boundary layer thickness obtained thusly is

$$\delta = 2r_0/3 \tag{23}$$

which is far too large in that this simple calculation ignores completely the tendency of the ions in the ionic atmosphere to migrate in the direction opposite to that of the particle. The net result of this is a very substantial decrease in the boundary layer thickness.

RESULTS

Surface potentials ψ_0 and zeta potentials were calculated as functions of $\log_{10}$ salt concentration for a variety of values of the different parameters of the theory. Approximately 1 min of XDS Sigma 7 time was required per curve.

The effect of varying the charge of the adsorbed anions is shown in Fig. 1. As one goes to extremely low salt concentrations, the magnitude of the surface potential increases without limit due to the finite limiting surface charge density, σ_0; this is an unrealistic aspect of the model, as counterions would be held by electrostatic attraction at the discrete ionic sites on the surface even as the salt concentration approaches zero. At higher salt concentrations we find the trivalent anions ($z = 3$) less readily adsorbed on the negatively charged surface than are univalent anions, as one would expect. And at still higher salt concentrations the magnitude of the surface potential is diminished by the ionic atmosphere. Here the curves all approach the same limiting behavior. The humps we see in the curves at $\log_{10} c \simeq -2.5$ to -3 are caused by the specific adsorption of the anions on the solid surface, which increases the magnitude of the surface charge density and, thereby, the magnitude of ψ_0.

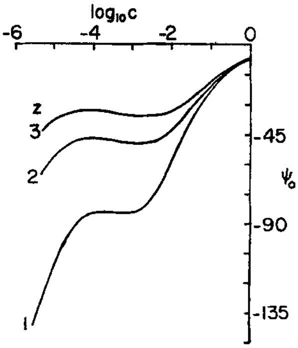

FIG. 1. Dependence of surface potential–log concentration plots on charge of adsorbed ion. $T = 298$, $\sigma_0 = -480.3$ esu/cm^2, $\chi = -0.70 \times 10^{-12}$ erg, $S = 10^{13}$ sites/cm^2, $c_{\max} = 0.01$ mole/cm^3, z = charge of adsorbed ion $(-1, -2, -3)$.

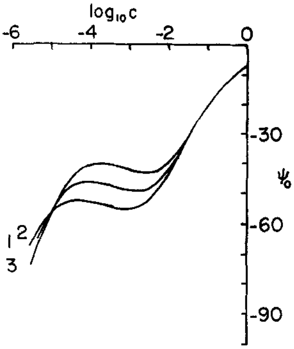

FIG. 2. Dependence of surface potential–log concentration plots on temperature. $T(1) = 273$, $T(2) = 298$, $T(3) = 323$°K; $z = -2$; other parameters as in Fig. 1.

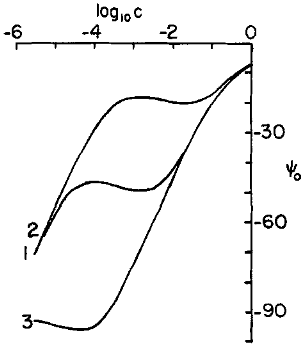

FIG. 3. Dependence of surface potential–log concentration plots on specific adsorption energy χ. $\chi(1) = -0.50 \times 10^{-12}$ erg, $\chi(2) = -0.70 \times 10^{-12}$ erg, $\chi(3) = -1.00 \times 10^{-12}$ erg; $z = -2$; other parameters as in Fig. 1.

The effect of temperature is shown in Fig. 2; as one would anticipate, the specific adsorption of anions is impeded by increasing the temperature. When the diffuse double layer becomes thinner and more dense (as $\log_{10} c$ increases), the effects of temperature on specific adsorption and on the double layer appear to cancel out for this choice of parameters. Figure 3 exhibits the effect of the χ, the free energy of specific adsorption in the absence of an electric potential. The results are very much as one would anticipate; the stronger the binding, the lower the salt concentration at which specific adsorption occurs. In these plots as well as the plots shown in Figs. 1 and 2, the intrinsic surface charge density, σ_0, is assumed to be

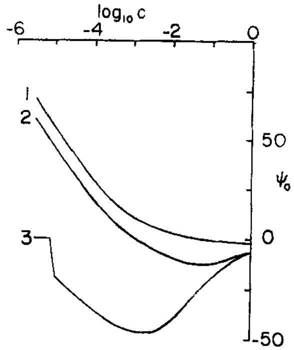

FIG. 4. Dependence of surface potential–log concentration plots on specific adsorption energy χ. $\sigma_0 = +480.3$ esu/cm^2; $\chi(1) = -0.30 \times 10^{-12}$, $\chi(2) = -0.45 \times 10^{-12}$; $\chi(3) = -0.70 \times 10^{-12}$ erg; $z = -2$; other parameters as in Fig. 1.

negative. In the plots shown in Fig. 4, σ_0 is taken as positive, and it is again assumed that anions are specifically adsorbed. Increasing the magnitude of χ again results in increased adsorption, and we see that the surface potential changes sign for two of the three curves. The irregularity in the third curve is an artifact of the numerical analysis.

The effect of varying the number of adsorption sites per cm^2 on the solid surface is shown in Figs. 5 and 6. In Fig. 5 σ_0 is negative; in Fig. 6, positive. The interplay of the electrical interactions, the forces involved in specific adsorption, and the damping effects of the diffuse double layer

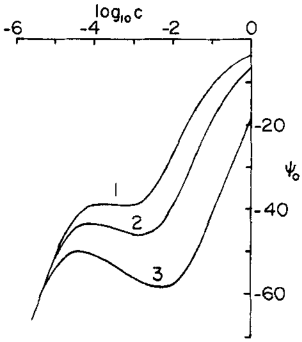

FIG. 5. Dependence of surface potential–log concentration plots on density of adsorption sites S. $S(1) = 0.5 \times 10^{13}$, $S(2) = 1.0 \times 10^{13}$, $S(3) = 3.0 \times 10^{13}$ sites/cm^2; $z = 2$; other parameters as in Fig. 1.

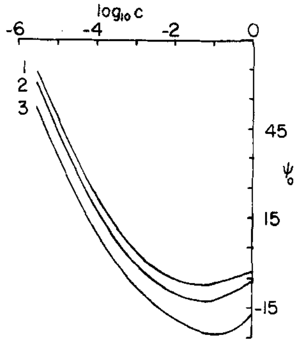

FIG. 6. Dependence of surface potential–log concentration plots on density of adsorption sites S. $\sigma_0 = +480.3$ esu/cm^2; other parameters as in Fig. 5.

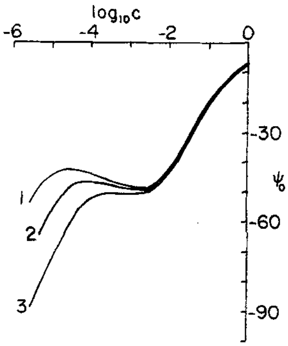

FIG. 7. Dependence of surface potential–log concentration plots on intrinsic surface charge density σ_0. $\sigma_0(1) = -240.15$, $\sigma_0(2) = -480.3$, $\sigma_0(3) = -960.6$ esu/cm^2; $z = 2$; other parameters as in Fig. 1.

lead to plots of ψ_0 vs $\log_{10} c$ with a good deal of structure—changes of sign, or maxima and minima.

Figures 7 and 8 illustrate the effect of varying the intrinsic surface charge density, σ_0. At high salt concentrations the surface charge density is determined primarily by the surface concentration of adsorbed anions, and the effect of σ_0, seen at lower concentrations, is masked. As with the other plots, these show an increase without limit in the magnitude of the surface potential as the salt concentration approaches zero, the result of approximating the intrinsic surface charge by a uniform charge density.

The calculation of zeta potentials from Eq. (21) is fraught with some

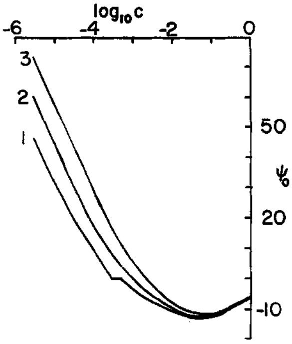

FIG. 8. Dependence of surface potential–log concentration plots on intrinsic surface charge density σ_0. $\sigma_0(1) = +240.15$, $\sigma_0(2) = +480.3$, $\sigma_0(3) = +960.6$ esu/cm^2; $\chi = 0.45 \times 10^{-12}$ erg; other parameters as in Fig. 7.

peril because of the use of Eq. (14), an approximate relationship of somewhat uncertain validity. In any case, for the flotation of flocs and precipitates the surface potential is the more important quantity. Nevertheless, the zeta potential has the advantage of being directly accessible experimentally, and one may anticipate extensive use of zeta potential measurements in the optimization of precipitate and adsorbing colloid flotation methods. Figure 9 shows the effect on zeta potential of varying the charge on the ions; all the parameters are as in Fig. 1. Note the change in scale of the ordinate. At quite low salt concentrations the numerical solution of Eq. (21) is not very accurate; this is troublesome principally in that concentration range in which $|\psi_0|$ is increasing rapidly as c approaches 0,

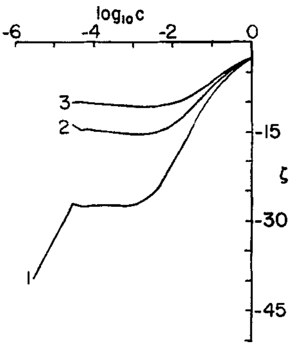

FIG. 9. Dependence of zeta potential–log concentration plots on charge of adsorbed ion. All parameters as in Fig. 1.

TABLE 1

Boundary Layer Thickness and Debye Length as Functions of Salt Concentration. $z = 2$, $T = 298\,°\mathrm{K}$, $c_{\max} = 10$ mole/l, $\chi = -7.0 \times 10^{-13}$ erg, $S = 1.0 \times 10^{13}$ sites/cm², $\sigma_0 = -480.3$ esu/cm². See Figs. 1 and 9

$\log_{10} c$ (m/l)	σ (Å)	Debye length (Å)
−4.52	305	277
−4.30	212	214
−4.15	177	181
−4.00	145	152
−3.52	83.1	87.7
−3.30	64.3	67.9
−3.15	54.2	57.4
−3.00	45.4	48.0
−2.52	26.2	27.7
−2.30	20.3	21.5
−2.15	17.2	18.2
−2.00	14.5	15.2
−1.52	8.50	8.77

previously noted as an artifact of the model. In general, the plots of zeta potential roughly parallel the plots of surface potential, but are scaled down. The boundary layer thickness calculated from Eq. (20) tends to be roughly equal to the Debye length, a result which is hardly surprising. Table 1 shows a comparison for one of the runs ($z = 2$) shown in Fig. 9.

EXPERIMENTAL

The very large changes in surface potential which result in this model from varying the salt concentration and identity suggested that it would be interesting to investigate the effectiveness of floc foam flotation as a function of the concentration and identity of added salts. Previous work has already demonstrated very marked differences in the ability of salts to interfere with the floc foam flotation of zinc with $Al(OH)_3$ and sodium lauryl sulfate; in order of increasing interference we found $NO_3^- < SO_4^{2-} \ll HPO_4^{2-} \approx HAsO_4^{2-}$ (*13*). In the present work we examine the effects of various added salts on the batch flotation of ferric hydroxide flocs with sodium lauryl sulfate at pH 5.0. We choose this system and these conditions [100 mg/l of Fe(III), 50 mg/l of sodium lauryl sulfate] because (1) in the absence of added salts flotation is very rapid, (2) the system is quite effective for a number of separations, and (3) the flotation of the strongly colored $Fe(OH)_3$ is readily observed visually.

TABLE 2

Effect of Various Added Salts and Glycerol on the Flotation of Ferric Hydroxide

	Concentration (moles/l)[a]					
Substance	0.0025	0.005	0.01	0.03	0.05	0.01
$NaClO_4$			R	S	S	N
$NaNO_3$			R	R	R	R
NaCl			R	R	R	R
KCN			S-R	S	S	N
KCNS		R	S	S	S	S
NaF	R	S	N			
Glycerol			S	S	S	S
Na_2SO_4	R	S	S	N		
Na_2HPO_4	N	N	N			
Na_2HAsO_4	N	N	N			
Concentration	0.0005	0.005				
Na_2EDTA	N	N				
Concentration	2.5×10^{-5}	6.25×10^{-5}	1.25×10^{-4}	3.13×10^{-4}	6.25×10^{-4}	1.25×10^{-3}
$Na_2C_2O_4$	R	S	S	S	N	N
Concentration	4.2×10^{-4}	8.3×10^{-4}	1.67×10^{-3}	5×10^{-3}	8.3×10^{-3}	
$(NaPO_3)_6$	N	N	N	N	N	

[a] R = rapid removal; S = slow and/or incomplete removal after 5 min; N = no visible removal. Operating conditions: pH = 5.0 ± 0.1; 100 ppm Fe(III); 50 ppm NLS; air flow 85 ml/min.

Batch runs of about 200 ml were made in an apparatus of the sort previously described (*14*). Removal rates were graded as rapid [removal of $Fe(OH)_3$ visually complete in 5 min], slow [visual evidence of $Fe(OH)_3$ in the foam, but removal not complete in 5 min], or none [no visual evidence of $Fe(OH)_3$ in the foam]. A variety of anions was chosen having different charges and coordination affinities for Fe(III) (*15*); glycerol, which coordinates readily with Fe(III), was also investigated. The results are shown in Table 2.

We find that phosphate, hexaphosphate, arsenate, EDTA, and oxalate are extremely effective in suppressing the flotation of ferric hydroxide under conditions at which, in the absence of these ions, it floats rapidly and completely. In all the runs the possibly interfering substance was added to the solution after the ferric hydroxide was precipitated to avoid possible loss of the interfering ion by coprecipitation in the bulk of the solid where it would presumably be ineffective. It was somewhat surprising to us that cyanide and thiocyanate, both of which complex readily with Fe(III) in solution, were nowhere nearly as effective in blocking flotation as the ions mentioned above. Neither did we anticipate that ClO_4^- would be somewhat more effective than NO_3^- and Cl^- in blocking flotation, since it is one of the weakest-binding ligands known.

These results suggest a number of potential applications. Addition of interfering anions might be used to make precipitate flotation more selective and could also facilitate the recovery of surfactant from foam flotation sludges. Our findings also introduce a complication into the use of foam flotation techniques for the removal of metals from wastewaters which may contain interfering ions. The behavior of the flocs in the presence of interfering ions suggests that these ions may interfere severely with precipitation separations also.

Acknowledgments

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