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Electrical Aspects of Adsorbing Colloid Flotation. X. Pretreatments, Multiple Removals, Interferences, and Specific Adsorption

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Abstract

The compatibility of the adsorbing colloid flotation of Cu(II) with $Fe(OH)_3$ and sodium lauryl sulfate with a variety of precipitation pretreatment techniques was studied. Procedures were developed which permitted precipitation pretreatment and effective foam flotation polishing. The interferences of glycerol, ClO_4^-, NO_3^-, Cl^-, CN^-, CNS^-, F^-, SO_4^{2-}, HPO_4^{2-}, $HAsO_4^{2-}$, $C_2O_4^{2-}$, $(PO_3)_6^{6-}$, and EDTA with the precipitate flotation of ferric hydroxide by sodium lauryl sulfate were studied. The simultaneous adsorbing colloid flotation of Cu(II), Pb(II), and Zn(II) with $Fe(OH)_3$ and sodium lauryl sulfate was found to be effective in the pH range 6 to 7 at ionic strengths below 0.1 mole/l. A model was analyzed for calculating surface potentials for floc surfaces having the charge distributed at discrete sites in the presence of electrolytes. Plots of surface potential versus adsorbable ion concentration were calculated for various values of the model parameters.

INTRODUCTION

Foam flotation techniques have been used at the bench and pilot-plant scales for the removal of a number of pollutants from simulated and actual industrial wastewaters; this literature has been summarized by several

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authors (*1–4*). Zeitlin and co-workers have used the adsorbing colloid flotation technique extensively for the development of trace analytical methods (*5–8* and earlier papers); their work encouraged us to apply the technique to a number of industrial wastes and simulated wastes (*9–12* and earlier papers), and to explore the theory of the adsorption of floc particles at the air–water interface (*13–15*).

Foam flotation techniques are particularly useful in dealing with quite dilute wastewaters, but may be overloaded if the concentration of material to be removed is too high. Precipitation methods, on the other hand, are quite effective in dealing with relatively concentrated wastewaters (*16*), but may not yield sufficiently low effluent concentrations of the pollutant. We were therefore interested in the compatibility of various precipitation pretreatments with adsorbing colloid flotation. The flotation procedure chosen for study was the removal of Cu(II) by adsorbing colloid flotation with ferric hydroxide and sodium lauryl sulfate (NLS).

Wastewaters generally contain several ions which require removal. Our work to date has dealt with the removal of single species, however. We present here data on the simultaneous floc foam flotation of Cu(II), Pb(II), and Zn(II) with ferric hydroxide and NLS.

The efficiency of adsorbing colloid flotation may be reduced to the vanishing point by the presence of interfering ions which are adsorbed by the floc. The theory of this effect was discussed previously (*15*, *17*), and interferences in the separation of Zn(II) were noted (*18*). We report here on the interferences of a number of anions with the flotation of ferric hydroxide with NLS.

Previously we had examined the theory of the specific adsorption of ions by flocs within the framework of a model which assumed that the intrinsic charge distribution of the solid surface was continuous and uniform (*17*). This resulted in surface potentials which looked reasonable except at low ionic strengths, where they increased rapidly in magnitude with decreasing ionic strength. We here extend our previous approach to deal approximately with a model in which the solid surface charge is located at discrete sites.

COMPATIBILITY STUDY

Foam flotation techniques are best adapted to the treatment of wastewaters which are rather dilute in the substance being removed. We also note that precipitation treatment at times does not yield an effluent of adequate quality. These facts motivated our investigation of the compatibility of several precipitation pretreatment procedures for the removal of copper(II) by adsorbing colloid flotation with $Fe(OH)_3$ as the floc and NLS as the collector. This separation was used because it had previously been shown to be a very effective one (*11*), and because the atomic absorption spectrophotometric analysis for copper at 324.8 nm is quite sensitive.

Use of Na_2CO_3 (Soda Ash) as a Precipitating Agent

Batch runs were made as follows. A solution of 500 mg/l of Cu(II) as $Cu(NO_3)_2$ was prepared, and to this was added sufficient 0.5 *M* Na_2CO_3 solution to precipitate the copper and achieve the desired pH. (Precipitation was carried out at pH's of 7.0, 8.0, and 9.0.) After the $CuCO_3$ precipitate settled out, the supernatant liquid was decanted. Foam flotation was carried out on this supernate, using 100 mg/l of Fe(III) and 100 mg/l of NLS (50 mg/l initially, 25 mg/l after 6 min, and 25 mg/l after 11 min). Flotation was carried out at pH's of 5.5, 6.0, 6.5, and 7.0. The apparatus used has been described previously (*9, 11*).

After the precipitation step the Cu(II) concentration was in the range of 5 to 15 mg/l, depending on the settling pH. [Typically ~15 ml of Na_2CO_3 solution was added to 300 ml of 500 mg/l Cu(II) solution.] The carbonate ion in the supernatant solution severely hindered subsequent Cu(II) removal by foam flotation. Since carbonates form CO_2 at the lower pH's and can then be sparged from solution, the flotation runs made at acidic pH gave much better results, especially if the solution was allowed to sparge in the column for 10 min before flotation was begun. Flotation runs made at pH 7.0 gave poor Cu(II) removal; flotation runs at 6.5 caused a reduction in Cu(II) from 9.0 to 0.11 mg/l after 20 min. Similar runs in which the flotation pH was 6.0 gave a Cu(II) concentration of 0.20 to 0.40 mg/l after 25 min, depending on conditions. Similar runs in which the flotation pH was 5.5 gave somewhat poorer results; residual Cu(II) was 1.0 to 2.0 mg/l after 25 min of foaming. We also found that, if the solution is placed in the column and sparged with air at a very low pH (2.5 to 3.0) for 5 to 10 min, foam flotation at pH 6.5 readily produced residual Cu(II) concentrations in the range 0.10 to 0.20 mg/l after 10 min of foaming.

Data on the effects of settling pH and foaming pH are shown in Table 1. Data on the effects of a preliminary air sparging at low pH are shown in Table 2.

TABLE 1

Effects of Settling and Foaming pH's on Cu(II) Removal after Precipitation with Na_2CO_3

		Settling pH		
		7.0	8.0	9.0
Flotation pH	Time (min)	Cu(II) (mg/l)		
7.0	0	7.9 (10.5)[a]	7.0 (9.3)	4.3 (5.7)
	5	7.8	6.9	4.2
	10	7.8	6.7	4.3
	15	7.8	6.3	4.2
	20	8.0	6.2	4.3
	25	7.8	5.7	4.3
6.5	0	9.1 (12.1)	— (—)	6.3 (8.5)
	5	7.7	6.3	4.7
	10	5.9	5.8	4.2
	15	3.7	4.3	2.4
	20	0.85	2.29	1.67
	25	0.44	1.20	0.89
6.5[b]	0	9.0 (12.1)	4.6 (6.1)	3.9 (5.2)
	5	2.57	4.6	—
	10	1.47	2.58	—
	15	0.59	0.71	1.46
	20	0.11	0.31	0.53
	25	0.12	0.30	0.24
6.0	0	10.1 (13.5)	5.0 (6.7)	3.15 (4.2)
	5	4.5	3.6	3.3
	10	1.06	1.88	1.03
	15	0.54	0.41	0.36
	20	0.49	0.27	0.34
	25	0.47	0.24	0.31
6.0[b]	0	11.5 (15.3)	5.4 (7.1)	3.14 (4.2)
	5	1.22	1.08	0.79
	10	0.85	0.35	0.46
	15	0.68	0.37	0.34
	20	0.63	0.35	0.28
	25	0.77	0.37	—
5.5	0	10.8 (14.4)	4.6 (6.1)	3.29 (4.4)
	5	3.33	1.65	1.40
	10	2.79	1.27	1.04
	15	2.64	1.17	0.96
	20	2.42	1.09	1.00
	25	2.41	1.14	0.99
5.5[b]	0	9.5 (12.6)	7.6 (10.2)	3.4 (4.6)
	5	2.46	2.05	1.03
	10	2.11	2.09	0.99
	15	1.94	1.86	0.95
	20	1.75	1.79	0.95
	25	2.00	1.62	0.94

[a] Parenthetic values are Cu(II) concentrations in the decantate before addition of other reagent solutions.

[b] Sample sparged with air for 10 min before foaming.

TABLE 2

Effects of Air Sparging at Low pH on Cu(II) Removal after Precepitation with Na_2CO_3[a]

Sparging time (min)	Time (min)	Cu(II) concentration (mg/l)
2	0	10.1 (13.5)
	5	5.3
	10	1.71
	15	0.44
	20	0.35
	25	0.26
4	0	8.7 (11.6)
	5	0.96
	10	0.26
	15	0.26
	20	—
	25	0.21
6	0	8.9 (11.8)
	5	1.30
	10	0.21
	15	0.15
	20	0.15
	25	0.15
8	0	10.6 (14.2)
	5	0.52
	10	0.15
	15	0.15
	20	0.15
	25	0.14
10	0	10.1 (13.4)
	5	0.27
	10	0.18
	15	0.10
	20	0.14
	25	0.12

[a] Solutions were sparged with air at pH 2.5 to 3.0, pH of precipitation and settling was 7.0 (Na_2CO_3), initial Cu(II) concentration was 500 mg/l. 150 ml of supernate was made 100 mg/l in Fe(III), placed in column, acidified, and sparged for the desired period. The pH was then raised to 6.5 (NaOH), 50 mg/l of NLS added initially, 25 mg/l after 6 min, and 25 mg/l after 11 min. Air flow rates were about 60 ml/min.

Use of $Ca(OH)_2$ (Lime) as a Precipitating Agent

Batch runs were as follows. Solid $Ca(OH)_2$ was added with vigorous stirring to 200 ml of a solution containing 500 mg/l of Cu(II) (as the nitrate) until a pH of ~ 12 was reached. This required approximately 1.2 g of $Ca(OH)_2$ per liter of solution. The solution was allowed to settle for 10 min and the supernatant decanted for further treatment by floc foam flotation with Fe(III) and NLS as described previously. We found that the high Ca(II) concentration prevented foaming by forming a scum with the NLS, and that foam flotation was not possible under these circumstances. The problem is solved by bubbling CO_2 through the solution until the pH drops to about 10.0; this precipitates $CaCO_3$ but does not leave excessive CO_3^{2-} or HCO_3^- in the solution to interfere with the foam flotation step. The resulting solution is readily treated by floc foam flotation [100 mg/l of Fe(II); 50, 25, and 25 mg/l of NLS initially, after 6 min, and after 11 min; air flow rate about 60 ml/min]. The results are shown in Table 3. They indicate that Cu(II) levels, already quite low after precipitation with lime, are readily reduced to extremely low values by floc foam flotation with $Fe(OH)_3$ and NLS, provided that excessive Ca(II) is removed.

Use of Al(III) or Fe(III) as Coprecipitating Agents

In these runs, solutions were prepared containing 500 mg/l of Cu(II) as the nitrate; aluminum nitrate or ferric nitrate and sodium hydroxide

TABLE 3

Effect of Foaming pH on Cu(II) Removal after Precipitation with $Ca(OH)_3$

Flotation pH time (min)	Cu(II) (mg/l) 5.5	6.0	6.5	7.0
0	0.23 (0.31)[a]	0.23 (0.31)	0.19 (0.25)	0.25 (0.35)
5	0.10	0.05	0.13	0.20
10	0.11	0.03	0.04	0.05
15	0.08	0.01	0.06	0.08
20	0.06	0.00	0.05	0.08
25	0.05	—	0.04	0.05

[a] Parenthetic values are Cu(II) concentrations in the decantate before addition of other reagent solutions.

were used to generate the coprecipitating $Al(OH)_3$ or $Fe(OH)_3$ flocs; and coprecipitation was carried out at a pH of 7.0 in all runs. After coprecipitation and settling, supernate was decanted, the pH was adjusted to the desired value with NaOH and HNO_3, Fe(III) was added (100 mg/l), and NLS was added (50 mg/l initially, 25 mg/l after 6 min, and 25 mg/l after 10 min of flotation). The air flow rate was approximately 60 ml/min.

In the first set of runs, 100 mg/l of Al(III) was used in the coprecipitation step. After coprecipitation and settling the supernate contained approximately 1.00 mg/l of Cu(II). Flotation of the supernate as described above resulted in residual Cu(II) concentrations of 0.05 mg/l (flotation pH 7.0), 0.03 mg/l (6.5), 0.03 mg/l (6.0), and 0.16 mg/l (5.5) after 25 min.

The second set of runs was made using 50 mg/l of Al(III) in the coprecipitation step; after the resulting floc had settled, the supernate contained typically 1.5 to 2.4 mg/l of Cu(II). Flotation of the supernate as described above reduced residual Cu(II) levels of 0.05 mg/l (flotation pH = 7.0), 0.03 mg/l (6.0), and 0.15 mg/l (5.5) after 25 min.

Fe(III) at 50 mg/l was used as the coprecipitating agent in the third set of runs. After settling, the supernate contained 3.0 to 4.0 mg/l of Cu(II). Flotation of this solution as described above produced Cu(II) levels of 0.01 mg/l (flotation pH = 7.0), 0.05 mg/l (6.5), 0.03 mg/l (6.0), and 0.23 mg/l (5.5). It was found that the Cu(II) concentrations after coprecipitation with 100 mg/l of Fe(III) were approximately the same as those resulting when 50 mg/l of Fe(III) was used. See Table 4.

We conclude that coprecipitation with $Al(OH)_3$ or $Fe(OH)_3$ is quite compatible with adsorbing colloid flotation.

INTERFERENCES

One of the factors which can very markedly affect the efficiency of adsorbing colloid flotation and surfactant recovery from flotation sludges is the extent to which other ions are adsorbed into the primary layer of the floc. The theory of this effect is discussed in Refs. *15* and *17*. The very large changes in surface potential and in surface concentration of surfactant result (in the model analyzed) from varying the salt concentration and identity of added salts. Earlier we demonstrated very marked differences in the ability of different anions to interfere with the flotation of zinc(II) with $Al(OH)_3$ and NLS; in order of increasing interference we found $NO_3^- < SO_4^{2-} \ll HPO_4^{2-} \approx HAsO_4^{2-}$ (*18*). Here we examine the effects of various added salts on the batch flotation of ferric hydroxide flocs with NLS at pH 5.0. We chose this system and these conditions

TABLE 4

Effect of Foaming pH on Cu(II) Removal after Coprecipitation with $Al(OH)_3$ or $Fe(OH)_3$

Flotation pH	Time (min)	Precipitating agent and concentration		
		100 mg/l Al(III)	50 mg/l Al(III)	50 mg/l Fe(III)
7.0	0	0.95 (1.27)[a]	2.40 (3.20)	4.5 (5.9)
	5	0.21	0.25	0.15
	10	0.07	0.13	0.01
	15	0.07	0.07	0.01
	20	0.07	0.07	0.01
	25	0.05	0.07	0.01
6.5	0	0.89 (1.19)	2.26 (3.01)	4.0 (5.3)
	5	0.20	0.13	0.30
	10	0.03	0.04	0.06
	15	0.03	0.03	0.06
	20	0.03	0.03	0.05
	25	0.03	0.03	0.05
6.0	0	1.05 (1.40)	1.80 (2.40)	2.70 (3.60)
	5	0.16	0.07	0.08
	10	0.03	0.03	0.05
	15	0.03	0.03	0.03
	20	0.03	0.03	0.03
	25	0.03	0.03	0.03
5.5	0	1.13 (1.51)	1.37 (1.83)	2.82 (3.76)
	5	0.20	0.17	0.34
	10	0.19	0.15	0.26
	15	0.17	0.15	0.24
	20	0.17	0.15	0.23
	25	0.16	0.15	0.23

[a] Parenthetic values are Cu(II) concentrations in the supernate before addition of other reagent solutions.

[100 mg/l of Fe(III), 50 mg/l of NLS] because (1) flotation is very rapid in the absence of added salts, (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.

Batch runs of about 200 ml were made in an apparatus of the sort previously described (*9*, *11*). 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). Glycerol, which coordinates readily with Fe(III), was also investigated. The results are shown in Table 5.

We found 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 a 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 wastewater 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.

SIMULTANEOUS FLOTATION

Most metal-containing industrial wastes contain several different metal ions, motivating our work on the simultaneous removal of copper, lead, and zinc from solutions containing these metals. The concentration of each of the metal ions was 20 mg/l, 100 mg/l of NLS was used as the collector, sample volumes were about 200 ml, air flow rates were about 67 ml/min, and flotation was carried out for 20 min. Copper, lead, and zinc analyses were carried out by atomic adsorption. Ionic strength was varied by the addition of sodium nitrate.

The results of this work are shown in Table 6, and they indicate that simultaneous removal of several metals by floc foam flotation is possible.

SURFACE POTENTIALS

We are here concerned with the calculation of surface potentials in the vicinity of an infinite plane solid surface in contact with an electrolyte solution. We assume that the charge on the surface is distributed at

TABLE 5

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

	Concentration (moles/l)[a]					
Substance	0.0025		0.01	0.03	0.05	
$NaClO_4$			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.

TABLE 6

Results of the Floc Foam Flotation of Cu(II), Pb(II), and Zn(II) with $Fe(OH)_3$ and NLS

Added $NaNO_3$ (moles/l)	pH	Fe(III) (moles/l)	Residual		
			Cu(II) (mg/l)	Pb(II) (mg/l)	Zn(II) (mg/l)
0.02	6.1	100	0.30	0.20	3.2
0.02	6.5	100	0.25	0.15	2.1
0.02	7.02	100	0.20	0.20	1.8
0.05	6.05	100	0.27	0.15	2.9
0.05	6.55	100	0.26	0.15	2.9
0.05	7.05	100	0.30	0.30	2.2
0.10	6.05	100	0.35	0.4	3.2
0.10	6.56	100	0.26	0.30	2.8
0.10	7.02	100	1.25	1.2	2.9
0.075	8.05	100	7.75	>10	3.3
0.075	8.05	150	>8.0	>10	3.5
0.075	8.05	200	>8.0	>10	3.5

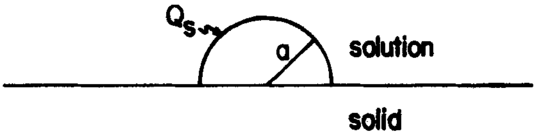

FIG. 1. The model.

discrete sites sparsely distributed on the surface so that the interaction between sites can be neglected. The sites we assume to be hemispherical of radius a; this geometry is chosen to permit the use of spherical coordinates. We let Q_s be the total charge of a site. See Fig. 1.

Poisson's equation is given by

$$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) = \frac{-4\pi\rho}{D} \tag{1}$$

where $\psi(r)$ = electric potential at a distance r from the center of the charged site

ρ = charge density

D = dielectric constant of water, given by $78.54 + 0.361187(T - 298) + 0.689621 + 10^{-3}(T - 298)^2$ (a least squares fit to data given in Ref. *19*)

T = temperature, degrees Kelvin

We obtain a boundary condition for Poisson's equation by integrating it over the volume of the solution and making use of the electrical neutrality requirement:

$$\int_a^\infty \int_0^{\pi/2} \int_0^{2\pi} \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= 2\pi \int_a^\infty \frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) dr = -2\pi a^2 \frac{\partial \psi(a)}{\partial r}$$

$$= \frac{-4\pi}{D} \int_a^\infty \int_0^{\pi/2} \int_0^{2\pi} \cdot \rho r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= \frac{+4\pi}{D} Q_s \tag{2}$$

from which we have

$$\frac{\partial \psi(a)}{\partial r} = \frac{-2Q_s}{a^2 D} \tag{3}$$

From previous work (*20*) we take for our Poisson-Boltzmann equation

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) = \frac{A \sinh \beta' \psi}{1 + B \cosh \beta' \psi} \tag{4}$$

where $\beta' = z'e/kT$

$A = \dfrac{8\pi z' e c'_\infty}{(1 - 2c'_\infty / c'_{\max})D}$

$B = 2c'_\infty / (c'_{\max} - c'_\infty)$

z' = |charge| on the ions of 1–1 electrolyte present to establish the ionic atmosphere, in units of e

e = electronic charge

c'_∞ = concentration of the electrolyte establishing the ionic atmosphere in the bulk solution, cations (or anions) per cm^3

$c'_{\max}$ = maximum possible concentration of this electrolyte

k = Boltzmann's constant

This Poisson-Boltzmann equation is intractable to analytical solution, so we rewrite it as

$$\frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r}\frac{\partial \psi}{\partial r} = \frac{A \sinh \beta' \psi}{1 + B \cosh \beta' \psi} \tag{5}$$

and then use the following discrete representation for this equation:

$$\frac{\psi_{n-1} - 2\psi_n + \psi_{n+1}}{\Delta r^2} + \frac{\psi_{n+1} - \psi_{n-1}}{r_n \Delta r} = \frac{A \sinh \beta' \psi_n}{1 + B \cosh \beta' \psi_n} \tag{6}$$

where $r_n = a + (n - 1)\Delta r, \quad 1 \leq n \leq N$
$\psi_n = \psi(r_n)$

This yields

$$\psi_{n-1} = \psi_n \frac{2r_n}{r_{n-1}} - \psi_{n+1}\frac{r_{n+1}}{r_{n-1}} + \frac{r_n}{r_{n-1}}(\Delta r)^2 \frac{A \sinh \beta' \psi_n}{1 + B \cosh \beta' \psi_n} \tag{7}$$

We choose $N\Delta r$ to be about five Debye lengths, set $\psi_N = 0$, ψ_{N-1} finite (of the order of 10^{-7} statvolts), and use Eq. (7) to continue the solution to $r_1 = a$. We then compare $\partial\psi(a)/\partial r = -2Q_s/a^2D$ with $(\psi_2 - \psi_1)/\Delta r$, multiply the initial value of ψ_{N-1} by $2Q_s\Delta r/a^2D(\psi_1 - \psi_2)$, and repeat the numerical integration of Eq. (7) with this new value of ψ_{N-1}. We repeat this process until successive solutions are essentially identical and

$$\frac{\psi_2 - \psi_1}{\Delta r} = -\frac{2Q_s}{a^2D} \tag{8}$$

to the desired level of accuracy. An accuracy of 0.02% typically requires about eight iterations.

We next calculate the adsorption isotherm of a specifically adsorbed ion on these charged sites. We assume here that the sites are independent. New symbols are as follows:

c_∞ = bulk concentration of specifically adsorbed ion, assumed $\ll c'_\infty$
μ^a = chemical potential of specifically adsorbed ion in the surface phase
μ^s = chemical potential of specifically adsorbed ion in the bulk solution
θ = fraction of surface sites occupied by the specifically adsorbed ion
$\psi_e = \psi(a + b)$
b = effective radius of specifically adsorbed ion
z = charge of the specifically adsorbed ion in units of e
γ = activity coefficient of specifically adsorbed ion

We take Eq. (9) for the chemical potential of the adsorbed ion in the surface phase,

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

and Eq. (10) for that of this ion in the bulk solution,

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

At equilibrium these chemical potentials must be equal, which yields

$$\frac{\mu_0{}^s - \mu_0{}^a}{kT} + \log_e[\gamma c_\infty] - \frac{ze\psi_e}{kT} = \log_e\frac{\theta}{1-\theta} \tag{11}$$

Solving this for θ yields

$$\theta = \frac{\exp\left[\dfrac{-ze\psi_e}{kT} + \dfrac{\Delta\mu^\circ}{kT}\right]\gamma c_\infty}{1 + \exp\left[\dfrac{-ze\psi + \Delta\mu^\circ}{kT}\right]\gamma c_\infty} \tag{12}$$

$$\Delta\mu^\circ = \mu_0{}^s - \mu_0{}^a$$

$$\log_e\gamma = -0.5 \times \frac{2.303z^2\sqrt{I}}{1+\sqrt{I}} \tag{13}$$

$$I = (z^2c_\infty + z'^2c'_\infty)(1000/N_0) \tag{14}$$

where N_0 = Avogadro's number.

So, for given values of c_∞ and c'_∞ we can calculate the fraction of sites occupied by the specifically adsorbed ion by use of Eq. (12).

We next wish to calculate the mean surface potential of the surface. We do so as follows. The mean charge density is given by

$$\bar{\sigma} = SQ_s + zeS\theta \tag{15}$$

where S = number of adsorption sites per cm^2.

Then, from Ref. *17*, we have

$$\psi_0 = \frac{\bar{\sigma}}{|\bar{\sigma}|}\frac{kT}{z'e}\operatorname{argcosh}\left\{(1+B^{-1})\exp\left[\frac{z'eB}{2AkT}\left(\frac{4\pi\bar{\sigma}}{D}\right)^2\right] - B^{-1}\right\} \tag{16}$$

as the mean surface potential.

We next examine some of the results obtained by this procedure. First we examine the dependence of the surface potential ψ_0 on the concentration of the adsorbable ion (present in low concentrations) when the concentration of the inert electrolyte is held constant. In Fig. 2 we see the effect on plots of ψ_0 versus adsorbable ion concentration (log scale) of changes in $\Delta\mu^\circ$, a concentration of inert electrolyte of 10^{-2} mole/l. Univalent cations are being adsorbed on univalent anion sites, and we see $|\psi_0|$ decrease with increasing concentration of adsorbed ions. We also observe

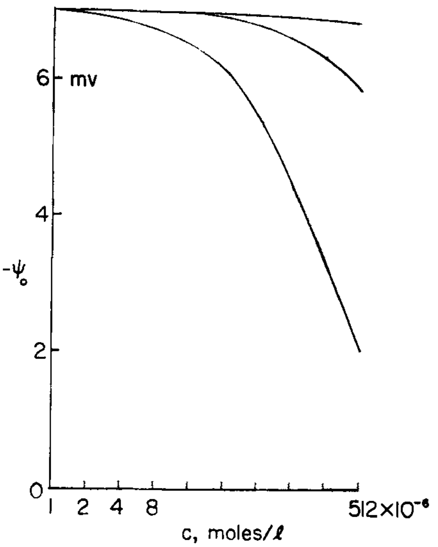

FIG. 2. Plots of ψ_0 versus c (logarithmic scale). $S = 10^{12}\ \mathrm{cm}^{-2}$; $Q_s = -1\cdot e$; $a = 2 \times 10^{-8}$, $b = 2.5 \times 10^{-8}$ cm; $T = 298\,°\mathrm{K}$; $c' = 10^{-2}$, $c'_{\mathrm{max}} = 10$ moles/l; $z = 1$, $z' = 1$; $\Delta\mu^\circ = -2.0$, -1.9, and -1.8×10^{-12} erg, top to bottom.

that decreasing $\Delta\mu^\circ$ merely shifts the curves to the right on the concentration scale.

Figure 3 shows a similar set of plots made at a concentration of inert electrolyte of 10^{-3} mole/l. At the lower concentration of inert electrolyte the anionic sites are less shielded by their ionic atmospheres, and adsorption of the adsorbable ions takes place at lower concentrations. The decreased shielding also increases the range over which ψ_0 varies. In one of the plots the surface sites are essentially 100% occupied at the higher concentrations of adsorbable ions; since we are adsorbing univalent cations on univalent anionic sites, this results in zero surface charge, and ψ_0 vanishes. Figure 4 shows plots for an identical system except that the density of surface adsorption sites has been doubled to $2 \times 10^{12}/\mathrm{cm}^{-2}$. The surface potentials are essentially doubled in value at any given concentration of the adsorbable ion, an intuitively reasonable result.

In Figs. 5 and 6 we have univalent anionic sites which are adsorbing divalent cations. This results in ψ_0 versus log c' plots in which ψ_0 changes sign; ψ_0 vanishes when the surface sites are 50% occupied, and becomes positive at higher concentrations of adsorbable cations. In Fig. 5 the

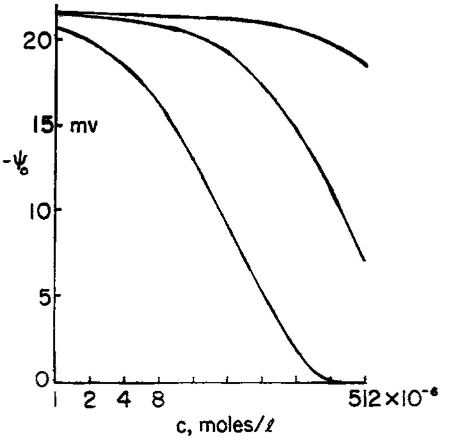

FIG. 3. Plots of ψ_0 versus c. All parameters are as in Fig. 2 except that $c' = 10^{-3}$ mole/l.

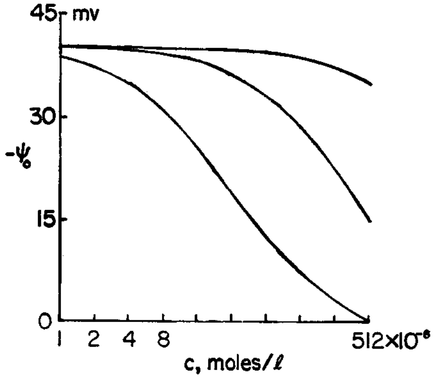

FIG. 4. Plots of ψ_0 versus c. All parameters are as in Fig. 2 except that $c' = 10^{-3}$ mole/l and $S = 2 \times 10^{12}$ cm^{-2}.

concentration of inert electrolyte is 10^{-2} mole/l; in Fig. 6 this concentration is 10^{-3} mole/l, resulting in a shift of the curves to the left and an increase in the range over which ψ_0 varies.

In Figs. 7 and 8 no inert electrolyte is present; the ionic strength is determined by the adsorbable ion. Univalent cations are being adsorbed on univalent anionic sites. Figure 7 shows the expected increase in $|\psi_0|$ as

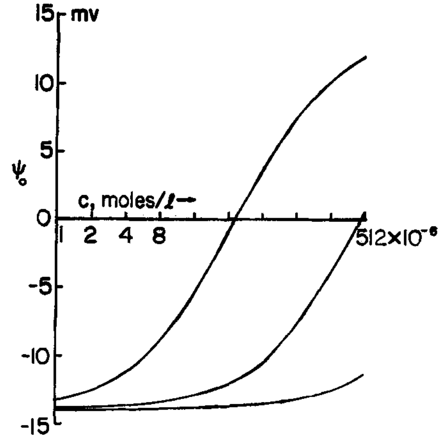

Fig. 5. Plots of ψ_0 versus c. All parameters are as in Fig. 2 except that $S = 2 \times 10^{12}$ cm^{-2} and $z = 2$ (the adsorbable ion is doubly charged).

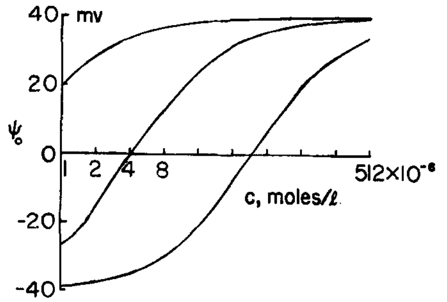

Fig. 6. Plots of ψ_0 versus c. All parameters are as in Fig. 2 except that $S = 2 \times 10^{12}$ cm^{-2}, $z = 2$, and $c' = 10^{-3}$ mole/l.

one goes to progressively lower concentrations, as we had seen in our earlier model. If, however, we go to still lower concentrations, as shown in Fig. 8, we find that there is a concentration below which the surface potential rapidly drops to zero. As the concentration decreases, the shielding of the adsorption sites becomes weaker and more diffuse, resulting in quite large potentials in the immediate vicinity of the charged site. This, in turn, results in greatly increased binding energies of the adsorbed ions, so that they are strongly adsorbed even though the solution is quite dilute. This is in very marked contrast to our previous result for a

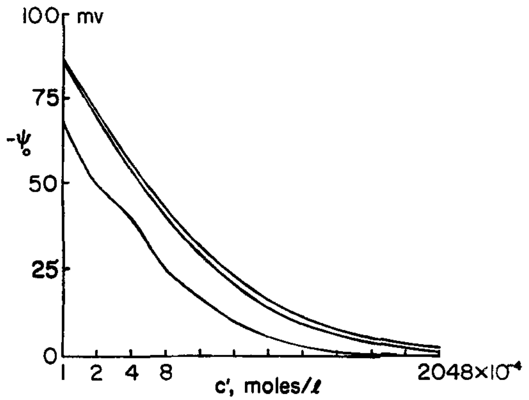

FIG. 7. Plots of ψ_0 versus c. No supporting electrolyte is present. $S = 2 \times 10^{-12}\,\mathrm{cm}^{-2}$; $Q_s = -1 \cdot e$; $a = 2 \times 10^{-8}$, $b = 2.5 \times 10^{-8}$ cm; $T = 298\,°\mathrm{K}$; $c_{\max} = 10$ moles/l; $z = 1$; $\Delta\mu° = -2.2, -2.0, -1.9$, and -1.8×10^{-12} erg, top to bottom. (The -2.2 and -2.0 curves are indistinguishable.)

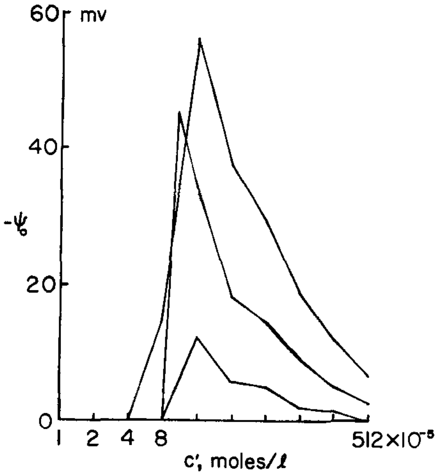

FIG. 8. Plots of ψ_0 versus c. No supporting electrolyte is present. Parameters are as in Fig. 7 except that $\Delta\mu° = -1.80, -1.75$, and -1.70×10^{-12} erg, top to bottom, and the concentration range is lower.

surface having a uniform charge density; for that model $|\psi_0| \rightarrow \infty$ as $c' \rightarrow 0$. Zeta potential measurements at very low electrolyte concentrations should permit discrimination between the two models.

This model should permit the construction of an improved theory of the interference of adsorbable nonhydrophobic ions with precipitate and adsorbing colloid flotation. It can also be used to model the scavenging of adsorbable ions by flocs.

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