Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Floc Foam Flotation of Nickel, Chromium, Cobalt, and Manganese. Interaction in Surface Adsorption

Joseph C. Barnes[a]; J. Michael Brown[a]; Naim A. -K. Mumallah[a]; David J. Wilson[a]
[a] DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE

To cite this Article Barnes, Joseph C. , Brown, J. Michael , Mumallah, Naim A. -K. and Wilson, David J.(1979) 'Floc Foam Flotation of Nickel, Chromium, Cobalt, and Manganese. Interaction in Surface Adsorption', Separation Science and Technology, 14: 9, 777 — 794

To link to this Article: DOI: 10.1080/01496397908060239

URL: http://dx.doi.org/10.1080/01496397908060239

SEPARATION SCIENCE AND TECHNOLOGY, 14(9), pp. 777–794, 1979

Floc Foam Flotation of Nickel, Chromium, Cobalt, and Manganese. Interaction in Surface Adsorption

JOSEPH C. BARNES, J. MICHAEL BROWN,
NAIM A-K. MUMALLAH, and DAVID J. WILSON*

DEPARTMENT OF CHEMISTRY
VANDERBILT UNIVERSITY
NASHVILLE, TENNESSEE 37235

Abstract

Adsorbing colloid flotation of nickel(II), chromium(III), cobalt(II), and manganese(II) was carried out using a variety of techniques. Satisfactory separations were developed for all but manganese; residual Mn levels could not be reduced below 0.5 mg/l, and the results were sometimes erratic. Surface potentials of flocs in the presence of adsorbable ions were calculated from a model which assumes discrete, interacting charge sites on the floc surface.

INTRODUCTION

Foam flotation techniques appear promising on the bench and pilot-plant scale for the removal of metals and some anions from wastewaters and dilute ore leachates; the literature has been recently reviewed (*1–4*). Zeitlin's group has used adsorbing colloid flotation for trace metals recovery in analytical work (*5–8*, for example); such separations of metals from seawater have also been carried out by Zhorov (*9*). Grieves and his co-workers (*10*) used precipitate flotation to remove calcium sulfite and carbonate from wet scrubber slurries, and we applied precipitate and adsorbing colloid flotation to a number of wastewaters and simulated wastewaters (*11–15*, for example).

*To whom requests for reprints should be sent.

We report here on the adsorbing colloid and precipitate flotation of nickel(II), chromium(III), cobalt(II), and manganese(II) by several procedures. The work was done on the bench scale in the batch mode.

Adsorbing colloid and precipitate flotation can be profoundly affected by the presence of interfering ions which are adsorbed by the floc. We discussed the effect previously (*15–17*), and examined the theory of the specific adsorption of ions by flocs within the frameworks of models which assumed that the intrinsic surface charge density on the floc was (a) continuous and uniform (*18*) or (b) discrete, with the sites sufficiently separated as to be noninteracting (*15*). We here consider the adsorption of ions by flocs having a discrete surface charge distribution with the sites sufficiently close together to be interacting.

EXPERIMENTAL

The apparatus used in this work was two batch columns essentially identical to those described by Chatman et al. (*13*). House air was passed through Ascarite, water (for rehumidification), and glass wool, then through a "fine" glass gas dispersion tube at the bottom of the column. Air flow rates of about 65 ml/min were used. Laboratory grade sodium lauryl sulfate (NLS) and hexadecyltrimethyl ammonium bromide (HTA) were used as collectors; all other chemicals were of reagent grade. Stock solutions (1000 mg/l of the metal ions) were mixed with the stock solution generating the carrier floc (ferric or aluminum ion, usually), and diluted to nearly 200 ml with deionized water. The pH was adjusted roughly to the desired value (usually with NaOH solution), the surfactant was added, and the pH given a final adjustment to the desired value. The solution was diluted to 200 ml and added to the column. Air flow rates were monitored with a soap film flowmeter and stopwatch. Samples for analysis were withdrawn from the bottom of the column, acidified with nitric acid, and analyzed by atomic absorption spectrophotometry.

Nickel(II)

The flotation of nickel(II) was carried out using $Fe(OH)_3$ or $Al(OH)_3$ as the carrier floc and NLS as the surfactant. One group of runs was made using Al(III) or Fe(III) at 50 mg/l, NLS at 50 mg/l, and Ni(II) at 100 mg/l. Sample volumes were roughly 200 ml, and air flow rates of 60 to 67 ml/min were used. In the pH range 5.5 to 8.0 the flocs were rapidly and completely removed, but Ni(II) removals were very poor; $Ni(OH)_2$ has a relatively large solubility product (1.6×10^{-16} mole^3/l^3). Analyses were carried out by atomic absorption spectrophotometry at 231.8 nm. The data for these runs are presented in Table 1.

The effect of ionic strength on flotation of Ni(II) with $Al(OH)_3$ and NLS is shown in Table 2.

Another set of runs was made under somewhat different conditions. Initial Ni(II) concentrations were 20 mg/l, 100 mg/l of Fe(II) or Al(III), and 50 mg/l NLS, and the air flow rate was about 65 ml/min. The results are presented in Table 3.

In conclusion, we have found that residual Ni(II) concentrations below 1 mg/l are achievable at pH's of 8 to 9.5 using $Al(OH)_3$ and NLS, provided the ionic strength is not too large (< 0.1 mg/l).

TABLE 1

Effect of pH on Nickel(II) Floc Foam Flotation[a]

pH	Runs with $Al(OH)_3$, residual Ni (mg/l)	Runs with $Fe(OH)_3$, residual Ni (mg/l)
5.5	>50	>50
6.0	>50	>50
6.5	>50	>50
7.0	>50	>50
7.5	17.3	>50
8.0	10.0	38
8.5	5.5	21
9.0	3.8	1.25
9.5	0.8	1.25

[a] Residual Ni measured after 15 min of treatment.

TABLE 2

Effect of Ionic Strength on Nickel(II) Floc Foam Flotation[a]

	Added $NaNO_3$ (moles/l)			
pH	0.025	0.050	0.075	0.250
8.5	6.6	1.3	4.2	19
9.0	5.6	1.5	2.5	16
9.5	1.4	1.4	0.6	>50

[a] Residual Ni measured after 10 min of treatment.

TABLE 3

Ni(II) Flotation at Decreased Ni(II) Concentration[a]

Added $NaNO_3$ (mole/l)	pH	Residual Ni $[Al(OH)_3]$	Residual Ni $[Fe(OH)_3]$
0	6.5	6.5	7.5
	7.0	4.9	5.7
	7.5	3.2	3.4
	8.0	0.43	1.9
0.02	6.5	3.3	9.2
	7.0	3.8	6.0
	7.5	0.97	5.3
	8.0	0.68	3.2
0.05	6.5	4.5	7.3
	7.0	3.7	8.8
	7.5	2.9	4.8
	8.0	2.4	5.3
0.075	6.5	2.9	>10
	7.0	2.0	8.0
	7.5	1.5	9.3
	8.0	1.4	6.6
0.10	6.5	4.6	—
	7.0	2.2	—
	7.5	0.75	—
	8.0	0.40	—

[a] Residual Ni measured after 10 min of treatment.

Chromium

Chromium(III) itself forms a highly insoluble hydroxide floc ($K_{sp} = 7 \times 10^{-31}$ mg^4/l^4), so we carried out its flotation without the addition of Fe(III) or Al(III). Initial Cr(III) and NLS concentrations of 50 mg/l were used, and the air flow rate was about 67 ml/min. Sample volumes were about 200 ml. Samples were taken for analysis after 10 min of treatment; chromium was determined by atomic adsorption at 357.6 nm. The results are presented in Table 4, and they indicate that simple precipitate flotation of $Cr(OH)_3$ is not able to reduce Cr(III) down to the 1 mg/l range.

We therefore investigated the coprecipitation of Cr(III) with ferric hydroxide; if this provides effective removal, one would anticiptate that adsorbing colloid flotation of Cr(III) with ferric hydroxide and NLS should also be effective. Solutions were prepared containing the desired concentrations of Cr(III) and Fe(III) as nitrates, the pH's adjusted to the desired level (5, 6, or 7) with NaOH and HNO_3, the solutions slowly

TABLE 4

Precipitate Flotation of Chromic Hydroxide

	Added $NaNO_3$ (mole/l)			
pH	0	0.025	0.050	0.075
5.5	23	>40	>40	>40
6.0	18	11	15	10
6.5	8.6	5.5	4.2	12
7.0	22	16	5.4	13
7.5	>40	—	—	—
8.0	>40	—	—	—

stirred for about 5 min, the precipitates allowed to settle, and samples taken for analysis. At pH 5.0 solutions initially containing Cr (mg/l): Fe (mg/l) of 50: 50, 50: 100, 50: 150, and 25: 100 all contained more than 1 mg/l Cr(III) after precipitation; a solution of initial composition 20: 100 contained 0.5 mg/l of Cr(III) after precipitation. At pH's 6.0 and 7.0 the supernates of all the solutions contained less than 0.5 mg/l of Cr.

On the basis of these results we carried out adsorbing colloid flotation runs on solutions containing 20 mg/l of Cr(III) and 100 mg/l of Fe(III) at pH's in the range 5.5 to 7.25. The solutions were slowly stirred for 5 to 10 min after precipitation; they were then made 50 mg/l in NLS and transferred to the flotation column. Air flow rates of about 65 ml/min were used. The solutions became clear within 2 min after the initiation of flotation. The results (after 10 min of foaming) are shown in Table 5.

The effects of varying the initial Fe(III) concentration are shown in Table 6.

The effects of increasing the ionic strength by the addition of $NaNO_3$ are shown in Table 7.

TABLE 5

Effect of pH on Chromium(III) Floc Foam Flotation

pH	Residual Cr (mg/l)
5.5	<0.25
6.0	<0.25
6.15	<0.25
6.5	<0.25
7.0	0.5
7.25	1.3

TABLE 6

Effect of Iron(III) Concentration on Chromium(III) Floc Foam Flotation[a]

Initial Fe(III) (mg/l)	pH	Residual Cr (mg/l)
100	6.15	<0.25
80	6.1	<0.25
40	6.1	<0.25
30	6.4	<0.25
20	6.4	0.4

[a] Initial Cr(III) concentration 20 mg/l, air flow rate 65 ml/min, and run time 10 min.

TABLE 7

Effect of Inert Salt Concentration on Chromium(III) Floc Foam Flotation[a]

Added $NaNO_3$ (moles/l)	pH	Residual Cr (mg/l)
0	6.15	0.25
0.05	6.25	0.3
0.075	6.50	0.3
0.10	6.30	2.2, 3.6

[a] Initial Cr(III) concentration 20 mg/l, air flow rate 65 ml/min, and run time 10 min.

We noticed that if, in the course of adjusting the pH before flotation, one overshot and the pH got up to 9 to 10 or more (after which it was adjusted back to the desired level with 0.1 *N* HNO_3), flotation did not remove all the precipitate from the column, and the solution contained more than 1 mg/l of chromium after flotation. We explored this by carrying out four runs in which the pH was held at 10 for various periods of time, then reduced to 6.2 for another period of time before flotation was carried out. In all of these runs, 20 mg/l of Cr(III), 100 mg/l of Fe(III), and 50 mg/l of NLS were used, the air flow rate was in the range 60 to 65 ml/min, and the solution volume was 200 ml.

In the first run the pH was held at 10 for 1 min; it was then adjusted to 6.2 and flotation was immediately carried out. After 10 min of flotation the residual Cr(III) level was 0.4 mg/l, somewhat in excess of the values of $<$ 0.25 mg/l which were routinely obtained in the absence of pH overshoot. After 25 min of flotation the residual Cr(III) level was 0.2 mg/l.

The pH was held at 10 for 4 min for the second run; flotation was carried out immediately after adjustment of the pH of 6.2. After 10 min of flotation the residual Cr(III) concentration was 8.1 mg/l; after 25 min, 6.4.

The pH was held at 10 for 1 hr for the third run; the pH was then reduced to 6.2 and the solution permitted to stand for 2 hr. The pH tended to increase, and was readjusted to 6.2 several times during this period. After 10 min of flotation the residual Cr(III) concentration was 5.0 mg/l; after 25 min, 4.3.

In the fourth run the pH was kept at 10 for 8 min; the pH was then reduced to 6.2 and the solution permitted to stand overnight. The next morning the pH was again adjusted down to 6.2 and flotation carried out. After 10 min of flotation the residual Cr(III) concentration was 2.8 mg/l; after 25 min, 2.0.

We interpret these results as indicating the formation of a soluble, relatively nonlabile hydroxide complex ion of Cr(III) at pH 10. Chromium (III) complexes generally tend to be rather nonlabile. We have not observed this effect with other metals. Its occurrence with chromium dictates the careful avoidance of high pH's at all times if effective separations by floc foam flotation or by precipitation techniques are to be achieved at reasonably rapid rates.

We conclude that Cr(III) may readily be removed from aqueous solution by adsorbing colloid flotation with ferric hydroxide and NLS, provided that the pH is kept low enough to avoid the formation of soluble, relatively nonlabile chromium complexes with hydroxide.

Cobalt

The removal of Co(II) by floc foam flotation is similar to that of Ni(II). The solubility product of $Co(OH)_2$ is 2.5×10^{-15} mg^3/l^3, slightly larger than that of $Ni(OH)_2$. Samples of 200 ml were treated, air flow rates of about 67 ml/min were used, and samples were taken for analysis after 15 min of treatment. Data showing the pH dependence of the separations are shown in Table 8.

The effect of ionic strength is shown in Table 9.

We conclude that residual Co(II) levels in the range 1 to 2 mg/l can be achieved at a pH of about 8.5 provided that the ionic strength is less than 0.05 mg/l.

Manganese

The relatively high solubility product of $Mn(OH)_2$, about 10^{-19}, suggests that the floc flotation of $Mn(OH)_2$ with ferric or aluminum hydroxides should not yield very high efficiencies of removal. In preliminary runs this was found to be the case. It was evidently necessary to

TABLE 8

Floc Foam Flotation of Cobalt(II) with $Al(OH)_3$ or $Fe(OH)_3$ and NLS

pH	$Al(OH)_3$ runs,[a] Residual Co(II) (mg/l)	pH	$Fe(OH)_3$ runs,[b] Residual Co(II) (mg/l)
6.5	>8	6.0	>8
7.2	7.6	6.5	>8
7.4	5.4	7.0	7.2
7.8	3.5	7.5	3.0
8.3	1.2	8.0	2.4
8.8	1.4	8.5	1.9
		9.0	6

[a] Initial Al(III) concentration = 100 mg/l.

[b] Initial Fe(III) concentration = 20 mg/l. Initial Co^{2+} concentration = 50 mg/l.

TABLE 9

Effect of Ionic Strength on Flotation of Co(II) with $Al(OH)_3$ and NLS

	Added $NaNO_3$			
pH	0	0.025	0.050	0.075
7.2	7.6	5.3	2.7	6.3
7.8	3.5	2.4	2.4	2.5
8.3	1.2	1.5	2.2	2.7
8.8	1.4	3.6	8.2	—
9.3	6.	8.1	—	—

either convert the manganese to a higher oxidation state (MnO_2) or to carry out the flotation of other less soluble manganese(II) compounds. Both of these options were explored.

We first report on the floc foam flotation of MnO_2–$Mn(OH)_3$ with $Fe(OH)_3$ and NLS. Solutions of Mn(II) as nitrate were adjusted with NaOH to a pH of 9.0 and aerated with vigorous stirring with a magnetic stirrer for 1 hr. The pH dropped during the course of the aeration because of the consumption of OH^- by the reaction

$$2Mn^{2+} + 4OH^- + O_2 \rightarrow 2MnO_2 + 2H_2O$$

and was readjusted as needed. After aeration, 50 mg/l of NLS and 100 mg/l of Fe(III) were added and the pH was adjusted to the values given in Table 10. The suspension was then foamed in the batch apparatus for 10 min, and then a sample was taken for analysis. The progress of the

TABLE 10

Flotation of MnO_2 with NLS and $Fe(OH)_3$ after 1-hr Alkaline Aeration

Initial Mn (mg/l)	Fe(III) (mg/l)	NLS (mg/l)	Flotation pH	Visual results	Final Mn (mg/l)
22	100	50	6.0	Incomplete removal	—
0	100	50	6.0	″	—
10	100	50	6.0	″	—
10	100	50	6.0	″	—
10	100	75	6.0	″	—
5	100	50	5.5	Good removal	2
7	100	50	5.5	″	1.8
10	100	50	5.5	″	2.5
15	100	50	5.5	″	6
20	100	50	5.5	″	6
30	100	50	5.5	″	8
50	100	50	5.5	″	>10
50	0	50	5.5	″	>10
100	100	50	5.5	″	>10
50	100	50	5.5	″	>10

flotation of the floc was also followed visually. The results are shown in Table 10.

These results indicated incomplete conversion of Mn^{2+} to highly insoluble MnO_2, so solutions were aerated at a pH of 10.0 for 24 hr and then treated by adsorbing colloid flotation as before. The results indicated some improvement in the separation, as shown in Table 11. Evidently little oxidation of Mn(II) occurs after the first 24-hr period.

TABLE 11

Flotation of MnO_2 with NLS and $Fe(OH)_3$ after Extended Alkaline Aeration

Initial Mn (mg/l)	Fe (mg/l)	NLS (mg/l)	pH	Final Mn (mg/l)	Aeration period (hr)
30	100	50	5.5	1.8	24
15	100	50	5.5	0.5	24
30[a]	100	50	5.5	1.8	24
15[a]	100	50	5.5	0.5	24
15	100	50	5.0	1	48
30	100	50	5.5	2	48
30	100	50	5.0	3	48
50	100	50	5.5	2	48
50	100	50	5.0	5	48

[a] These solutions were heated to incipient boiling for 2 hr after aeration.

TABLE 12

Flotation of MnS with HTA and CuS

Initial Mn (mg/l)	Cu (mg/l)	Initial sulfide (mg/l)	Ageing time	pH	Final Mn (mg/l)
50	100	300	20 min	6.5	>10
50	50	400	20 min	7.8	1.5
50	50	400	20 min	7.0	4
30	50	400	20 min	9.0	>10
30	50	400	2 days	9.0	0.5
50	75	550	1 day	9.0	1.5
50	75	550	1 day	8.0	>10
30	50	400	1 day	9.0	< 0.5
35	50	550	2 days	10.0	>10
35	50	550	2 days	10.5	>10
35	50	550	2 days	9.0	>10
35	0	400	2 days	9.5	>10
35	5	400	2 days	9.5	>10
35	0	400	2 days	8.0	>10
50	50	550	2 days	10.0	2
50	50	550	2 days	10.0	0.5
50	50	550	2 days	10.0	3
50	50	550	2 days	10.5	1.5
50	50	550	2 days	11.0	3
50	50	550	2 days	9.5	3

We had hoped to achieve somewhat more complete separation than resulted from this technique. We therefore tried the floc foam flotation of $MnCO_3$ with ferric hydroxide and NLS at pH 5 to 6 and also the precipitate flotation of $MnCO_3$ with HTA at a pH of 9. These efforts were not promising, so we turned to the floc foam floatation of MnS with CuS or FeS and HTA. The experiments with FeS did not appear promising and were dropped. The data on Mn removal with CuS and HTA are given in Table 12. Precipitation and flotation were carried out at the same pH. Extended flotation ($\sim$45 min) with HTA in the pH range 9.0 to 10.0 seems to give the best results; residual Mn levels of about 0.5 mg/l could consistently be achieved.

ADSORPTION OF IONS ON DISCRETE INTERACTING SITES

The long range of the electrical forces involved in the surface adsorption of ions on discrete sites raises some doubts about our earlier assumption that these adsorption sites act independently of each other. We here extend our previous treatment (*15*) to include interactions between adjacent sites. The intrinsic charge on the surface we assume to be distributed at discrete, regularly spaced hemispherical sites of radius a; we chose this geometry to permit the use of spherical coordinates. Our notation is as follows.

$\psi(r)$ = electric potential at a distance r from the center of the charged site of interest
ρ = charge density
D = dielectric constant of water
T = temperature, °K
k = Boltzmann's constant
x = number of sites neighboring a given site, taken to be six
ze = charge of adsorbed ion
$z'e$ = |charge| of 1–1 inert electrolyte ions
$z''e$ = charge of vacant site
e = |electron charge|
l = distance between adjacent sites
a = radius of an adsorption site
b = radius of an adsorbed ion
$\beta' = z'e/kT$
$A = \dfrac{8\pi z' e c'_\infty}{(1 - 2c'_\infty/c'_{\max})D}$
$B = 2c'_\infty/(c'_{\max} - 2c'_\infty)$
c'_∞ = concentration in the bulk solution of the 1–1 inert electrolyte establishing the ionic atmosphere, cations (or anions)/cm^3.
$c'_{\max}$ = maximum possible concentration of this electrolyte, ions/cm^3
$\psi_v(r)$ = electric potential at a distance r from the (vacant) site of interest due to the site and its ionic atmosphere
$\psi_0(r)$ = electric potential at a distance r from the (occupied) site of interest due to the site, the adsorbed ion, and the associated ionic atmosphere

We first solve the Poisson-Boltzmann equation for vacant and for occupied sites; we use a form of this equation which takes into account the finite volumes of the ions (*19*):

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

Then we calculate the electrostatic binding energy of an adsorbed ion on a site surrounded by vacant sites, and the change in this binding energy when an adjacent site is also occupied. We neglect interactions other than between nearest neighbors. The adsorption isotherm of the adsorbed ion is then calculated by a method described by Fowler and Guggenheim which permits one to take such interactions into account (*20*). Then the mean charge density and mean surface potential are calculated.

The calculations of $\psi_v(r)$, the electric potential due to a vacant site, and $\psi_0(r)$, the electric potential due to an occupied site, are done by numerical integration of

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

The boundary conditions that

$$\psi(\infty) = 0 \tag{3}$$

and

$$\frac{d\psi}{dr}(a) = -\frac{2Q}{a^2 D} \tag{4}$$

(the second comes from the requirement of electrical neutrality) are replaced by

$$\psi_N = 0 \tag{5}$$

and

$$\frac{\psi_2 - \psi_1}{\Delta r} = -\frac{2Q}{a^2 D} \tag{6}$$

Here

$$\psi_n = \psi(r_n)$$

$$r_n = a + (n - 1)\Delta r$$

$$Q = \text{charge of central site, } z'e \text{ or } (z' + z)e$$

and

$$r_N = \text{about five Debye lengths}$$

We solve Eq. (2) and satisfy the boundary conditions, Eqs. (5) and (6), by the iterative procedure described earlier (*15*); this gives us the electric potentials in the vicinity of an occupied [$Q = (z'' + z)e$, $\psi = \psi_0$] and a vacant [$Q = z''e$, $\psi = \psi_v$] site isolated from the adjacent sites.

Next let us approximate that the electric potential in the vicinity of the site of interest can be written as the sum of the potential of the site of interest and the potentials of the adjacent sites. This approximation is exact if one uses the linearized Poisson-Boltzmann equation; it is exact only through quadratic terms in the potential if the nonlinear Poisson-Boltzmann Eq. (1) is used.

With this approximation we calculate the electrostatic binding energy of an adsorbed ion as

$$E_{\text{elec}} = [\psi_v(a + b) + (x - n)\psi_v(l) + n\psi_0(l)]ze \tag{7}$$

where n is the number of sites adjacent to the site of interest which are occupied. Rearranging yields

$$E_{\text{elec}} = [\psi_v(a + b) + x\psi_v(l)]ze + n[\psi_0(l) - \psi_v(l)]ze \tag{8}$$

Evidently the interaction energy associated with an occupied pair of sites is

$$[\psi_0(l) - \psi_v(l)]ze \equiv 2w/x \tag{9}$$

which defines w. This interaction energy is always positive because it is due to the screened Coulombic repulsion of the two adsorbed ions (which have the same charge), so no condensation phenomenon occurs. We define

$$\chi_0 = -[\psi_v(a + b) + x\psi_v(l)]ze + \Delta\mu_0 \tag{10}$$

where

$$\Delta\mu_0 = \mu_0^{\text{soln}} - \mu_0^{\text{adsorbed}} \tag{11}$$

is the difference between the chemical potential of an adsorbed ion and that of the ion in solution. This term takes into account any coordinate bond formation which takes place between the adsorption site and the adsorbed ion.

The adsorption isotherm is then calculated by the method of Fowler and Guggenheim (*20*):

$$c(\theta) = c' \exp(-\chi_0/kT)\frac{\theta}{1 - \theta}\left(\frac{2 - 2\theta}{\beta + 1 - 2\theta}\right)^x \tag{12}$$

where

$$\beta = \left\{1 - 4\theta(1 - \theta)\left[1 - \exp\left(-\frac{2w}{xkT}\right)\right]\right\}^{1/2} \tag{13}$$

and c' is independent of θ and depends only slightly on the temperature. $c(\theta)$ is the concentration of the adsorbable ion in solution when the fraction of sites occupied is θ.

The mean surface charge density is then given by

$$\sigma(\theta) = [(z'' + \theta z)e]\frac{2}{\sqrt{3}l^2} \tag{14}$$

if $x = 6$. The term in brackets is the average charge per site; $\sqrt{3}l^2/2$ is the area per site if we assume $x = 6$ and a hexagonal array of sites.

To calculate the mean surface potential of the charged interface, we use an equation derived previously (*18*),

$$\psi_0 = \frac{\sigma}{|\sigma|}\frac{kT}{z'e}\operatorname{argcosh}\left\{(1 + B^{-1})\exp\left[\frac{z'eB}{2AkT}\left(\frac{4\pi\sigma}{D}\right)^2\right] - B^{-1}\right\} \tag{15}$$

We next examine plots of surface potential versus $\log_{10} C$, where C is a reduced concentration obtained by setting $c' = 1$ in Eq. (12). Figure 1 shows the effect of increasing temperature. This effect is rather complex. Increasing temperature strengthens the Coulombic attraction between the adsorbed ion and the charged site by making the ionic atmospheres of both more diffuse and less effective at screening these charges from each other, tending to shift the curves to the left. On the other hand, increasing temperature increases the thermal energies which tend to dissociate adsorbed ions from the adsorption sites to which they are bound. One cannot predict by qualitative, intuitive arguments which effect will predominate, and the plots show that in fact either one may be predominant. One does

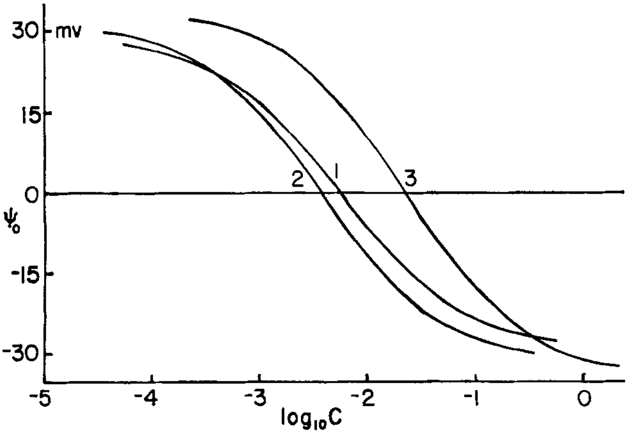

FIG. 1. Plot of ψ_0 vs $\log_{10} C$. Effect of temperature. $a = 2.0, b = 3.0, l = 50$ Å; $c' = 6.0 \times 10^{18}$, $c'_{\max} = 6.0 \times 10^{20}$ ions/cm^3; $\Delta\mu^\circ = 1.0 \times 10^{-13}$ erg; $z = -2, z' = 1, z'' = 1$; $T = 278$ (1), 298 (2), 318°K (3).

observe an increase in $|\psi_0|$ with increasing T for surfaces which are free of adsorbed ions (the left ends of the curves) and for surfaces which are saturated with adsorbed ions (the right ends of the curves), as expected.

In Fig. 2 we see the expected decrease in the magnitude of ψ_0 as the ionic strength of the solution increases and the mean surface charge density is screened by a thinner, more compact atmosphere. The curves are also shifted to the right with increasing ionic strength, since the decrease in the free energy of adsorption of the ions due to the increased screening of the charges must be counterbalanced by an increase in this free energy which can only come from an increased concentration of adsorbable ions in the bulk solution.

The effects of varying the distance l between the charged sites in the surface are shown in Fig. 3. We expect that the mean surface charge density should be at least roughly proportional to $1/l^2$, and so ψ_0 should increase roughly like $1/l^2$. The quantities $1/l^2$ stand in the ratio 1:1.56:3.06; at the lowest concentrations the quantities ψ_0 stand in the ratio 1:1.90:2.84, in approximate agreement. The curves pass through $\psi_0 = 0$ at a common value of the concentration of adsorbable ions. The most interesting effect is the increase in the range of the transition region between the low concentration and high concentration limits of ψ_0 as the distance between the charged sites in the surface decreases. At low values of $\log_{10} C$ the sites are sparsely occupied, so most of them are positively charged. Sites

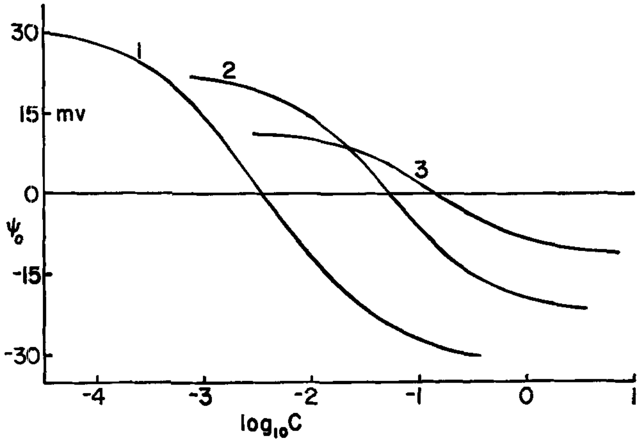

FIG. 2. Plot of ψ_0 vs $\log_{10} C$. Effect of inert electrolyte concentration. $T = 298\,°K$; $c' = 0.6$ (1), 1.2 (2), 4.8×10^{19} ions/cm³ (3); other parameters as in Fig. 1.

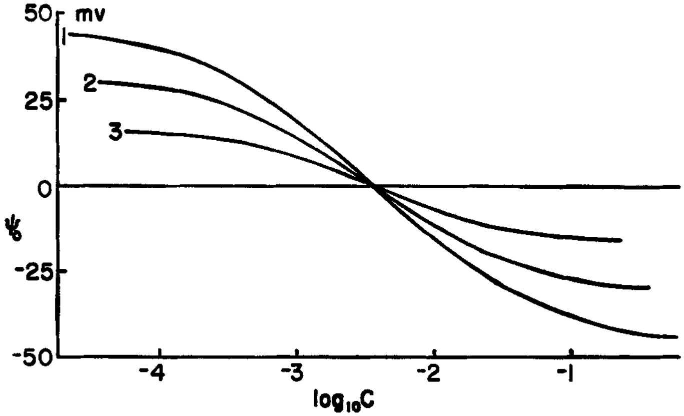

FIG. 3. Plot of ψ_0 vs $\log_{10} C$. Effect of adsorption site spacing. $T = 298°\text{K}$; $l = 40$ (1), 50 (2), 60 Å (3); other parameters as in Fig. 1.

adjacent to the site of interest therefore tend to increase the binding energy of an adsorbed negative ion ($z = -2$) to the site of interest, permitting adsorption to take place at lower values of C than would be possible if interaction with neighboring sites did not occur. At high values of $\log_{10} C$ most of the sites are occupied and therefore (in our example) have a net charge of $+1 - 2 = -1$. Sites adjacent to the site of interest therefore tend to decrease the binding energy of an adsorbed negative ion to the site of interest, forcing adsorption to take place at higher values of C than would be possible if interaction between neighboring sites did not occur. These effects certainly increase as the sites are moved closer together, resulting in the extension of the transition region with decreasing l which we observe.

The effects of the charge of the adsorbed ions are shown in Fig. 4, and are what one would intuitively expect. For $z = -2$, $z' = 1$ the Coulombic stabilization energy is largest, and the curve lies shifted to quite low concentrations. For $z = 1$, $z' = 1$ the Coulombic energy is actually repulsive, and the curve lies shifted far to the right, as expected. The total changes in ψ over the entire range of C are exactly of the sort one would expect for ($z = -2$, $z' = 1$), ($z = -1$, $z' = 1$), and ($z = 1$, $z' = 1$).

We conclude that our results are consistent with the earlier model in which a discrete surface charge distribution was analyzed, but that interactions between surface sites tend to increase the range of adsorbable ion concentrations over which the surface potential is varying. We note again

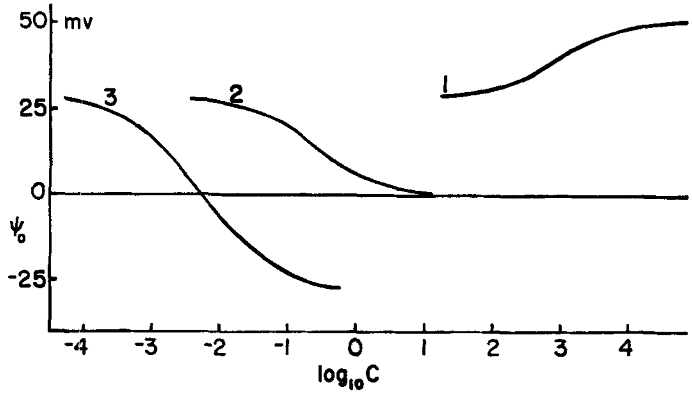

FIG. 4. Plot of ψ_0 vs $\log_{10} C$. Effect of charge of adsorbed ion. $T = 278\,°K$; $z = 1$ (1), -1 (2), -2 (3); other parameters as in Fig. 1.

that our calculation presupposes that the adsorbable ions constitute a negligible fraction of the ions responsible for the ionic strength of the solution.

Acknowledgments

This work was supported by grants from the U.S. Environmental Protection Agency and the Vanderbilt University Research Council.

REFERENCES

1. R. Lemlich (ed.), *Adsorptive Bubble Separation Techniques*, Academic, New York, 1972.
2. P. Somasundaran, *Sep. Sci.*, *10*, 93 (1975).
3. R. B. Grieves, *Chem. Eng. J.*, *9*, 93 (1975).
4. A. N. Clarke and D. J. Wilson, *Sep. Purif. Methods*, *7*, 55 (1978).
5. D. Voyce and H. Zeitlin, *Anal. Chim. Acta*, *69*, 27 (1974).
6. F. Chaine and H. Zeitlin, *Sep. Sci.*, *9*, 1 (1974).
7. N. Rothstein and H. Zeitlin, *Anal. Lett.*, *9*, 461 (1976).
8. M. Hagadone and H. Zeitlin, *Anal. Chim. Acta*, *86*, 289 (1976).
9. V. A. Zhorov, V. P. Barannik, S. V. Lyashenko, A. I. Kirchanova, and A. G. Kobylyanskaya, *Izv. Vyzzh. Uchebn. Zaved., Tsvetn. Metall.*, *6*, 12 (1976); *Chem. Abstr.*, *86*, 143432d (1976).
10. R. B. Grieves, R. M. Schwartz, and D. Bhattacharyya, *Sep. Sci.*, *10*, 777 (1975).
11. D. J. Wilson, *Foam Flotation Treatment of Heavy Metals and Fluoride-Bearing Industrial Wastewaters*, Environmental Protection Technology Series, EPA-600/2-77-072, April 1977.

12. D. J. Wilson and E. L. Thackston, *Foam Flotation Treatment of Industrial Wastewaters. Laboratory and Pilot Scale*, Environmental Protection Technology Series, to be published by EPA.
13. T. E. Chatman, S.-D. Huang, and D. J. Wilson, *Sep. Sci.*, *12*, 461 (1977).
14. A. N. Clarke, B. L. Currin, and D. J. Wilson, *Sep. Sci. Technol.*, *14*, 141 (1979).
15. B. L. Currin, R. M. Kennedy, A. N. Clarke, and D. J. Wilson, *Ibid.*, *14*, 669 (1979).
16. B. L. Currin, F. J. Potter, D. J. Wilson, and R. H. French, *Ibid.*, *13*, 285 (1978).
17. R. P. Robertson, D. J. Wilson, and C. S. Wilson, *Sep. Sci.*, *11*, 569 (1976).
18. A. N. Clarke, D. J. Wilson, and J. H. Clarke, *Sep. Sci. Technol.*, *13*, 573 (1976).
19. D. J. Wilson, *Sep. Sci.*, *11*, 391 (1976).
20. R. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge University Press, Cambridge, England, 1952, pp. 429–443.

Received by editor May 1, 1979