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Ion Fractionation by Foam

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Summary

Ionic charge and size of the species present govern the selectivity of surface adsorption of counterions in foam fractionation processes. A theory based on the Gouy-Chapman model of the diffuse double layer, with the restriction that the closest approach to the surface is determined by the finite size of the hydrated ions, enables one to predict the distribution factor of each species between a solution of mixed electrolytes and a surface layer, and to calculate the selective adsorption coefficient between two ions. Good agreement was found between the theoretical prediction and experimental data.

INTRODUCTION

Foam separation is a technique for separation and fractionation of surface active solutes, based on their tendency to adsorb at gas-liquid interfaces. It is a convenient and continuous way for producing and collecting large amounts of surface area. Most of the work published to date on this separation technique was reviewed (*1–3*).

Lately it has been found that foam separation can also be used as a technique for removing metallic ions that are not surface active. This application is based on the fact that the layer of the anionic surfactant adsorbed at the air-water interface must have associated with it an equivalent quantity of cations in order to neutralize the electric charge. The method was proposed mainly for purification of radioactive waste streams for nuclear fuel reprocessing (*1,4,5*). The mechanism of the counterion adsorption is either by electrostatic attraction or by formation of surface complexes between the surfactant and the counterions.

Foam Separation

The operating equation of single-stage foam column was derived by Rubin and Gaden (*1*). They introduced the distribution factor of a species, which is the ratio between the surface excess and the bulk concentration of the species in the solution, and expresses the tendency of this species to concentrate at the surface.

Using the ideal foam model, the operating equation for a single-stage foam column was derived:

$$(\Gamma/n)_i = \frac{f \times d}{6}(E_i - 1) \quad (1)$$

where $(\Gamma/n)_i$ is the distribution factor, f is the foam ratio which is the volume fraction of the liquid in the foam, and d is the average bubble diameter of the foam. E_i is the enrichment ratio defined as the ratio between the ion concentration in the collapsed foam liquid (foamate) and the residue. From this equation it is clear that the distribution factor is important for prediction of the extent of separation and the selectivity between ions in multicomponent solutions.

A few experimental studies on foam separation of metal ions have been reported. Rubin (*5*) measured the enrichment ratio of Sr^{++} and UO_2^{++} ions from solutions containing the surfactant monobutyl biphenyl sodium sulfonate (Aresket 300). A single-stage continuous circulatory-type foam system was used. The apparatus and all experimental details are described elsewhere (*5,6*). The experimental results indicated a linear relation between the enrichment ratio of the metallic ions and $1/fd$ as expected from Eq. (1). It was also found that increasing the surfactant concentration or the ion concentration reduces the distribution factor of the metallic ion and hence its enrichment ratio in a foam column under constant operation conditions (i.e., fd = constant). Experiments on foam separation of metallic ions were also reported by Walling et al. (*8*) and Wace and Banfield (*9*). They report the selectivity and selective adsorption coefficient between several mono-, di-, and trivalent metallic ions.

This paper presents a theoretical analysis, based on the model of the diffuse double layer, which enables one to predict the distribution factor of species between a solution of mixed electrolytes and a charged surface layer, and hence the selectivity and extent of separation of cations by foam separation.

THEORY

Evaluation of the Distribution Factor from the Gouy-Chapman Theory of the Diffuse Layer

Consider a solution of an anionic surfactant and several species of cations and anions. The surfactant adsorbs to the gas-liquid interface forming a negatively charged interfacial layer.

The surface excess of ions of species i of valency z_i is given by the diffuse layer theory as

$$\Gamma_i = \int_{x_0}^{\infty} n_i(v^{z_i} - 1)\, dx \tag{2}$$

where $v = \exp(-e\,\phi/kT)$, ϕ is the potential at a distance x from the interface, n_i is the bulk concentration of ions of species i, and x_0 is the distance of closest approach of ions to the surface.

Equation (2) can be integrated using the Poisson equation:

$$\frac{d^2\phi}{dx^2} = -\frac{4\pi}{\epsilon}\rho \tag{3}$$

$$\rho = \sum_i z_i e n_i v^{z_i} \tag{4}$$

where ρ is the charge density at distance x from the interface and ϵ is the dielectric constant. By change of variables Eq. (2) can be integrated:

$$\frac{d\phi}{dx} = -\left(\frac{kT}{ev}\right)\left(\frac{dx}{dv}\right) = \pm\left(\frac{8\pi kT}{\epsilon}\right)^{1/2}\left[\sum_i n_i(v^{z_i} - 1)\right]^{1/2} \tag{5}$$

The positive sign is chosen since σ is negative and the potential gradient is positive; hence

$$(\Gamma_i/n_i) = -\left(\frac{kT\epsilon}{8\pi e^2}\right)^{1/2} \int_{v_0}^{1} \frac{(v^{z_i} - 1)\,dv}{v\left[\sum_i n_i(v^{z_i} - 1)\right]^{1/2}} \tag{6}$$

According to Gauss' theorem assuming that no specific adsorption exists and there is no oriented dipole layer at the boundary or the potential due to such a layer is negligible at $x > x_0$,

$$\sigma = -\int_{x_0}^{\infty} \rho\,dx = \frac{\epsilon}{4\pi}\int_{x_0}^{\infty}\left(\frac{d^2\phi}{dx^2}\right)dx = -\frac{\epsilon}{4\pi}\left(\frac{d\phi}{dx}\right)_{x_0} \tag{7}$$

where σ is the surface charge density at the surface expressed in (esu/cm^2).

Therefore from Eqs. (5) and (7).

$$\sigma = -2\left(\frac{kT\epsilon}{8\pi^2}\right)^{1/2}\left[\sum_i n_i({v_0}^{z_i} - 1)\right]^{1/2} \tag{8}$$

where v_0 is the value of v when $\phi = \phi_0$ at distance x_0 from the interface, or at the outer Helmholtz plane. The negative sign in Eq. (8) is chosen for the case of negatively charged surface (anionic surfactant). The surface charge density can be calculated from knowing the surface excess of the ionic surfactant, Γ_s:

$$\sigma = z_s e \Gamma_s \tag{9}$$

From Eqs. (8) and (9), v_0 (or ϕ_0) can be calculated by trial and error. Taking v_0 as the lower limit, Eq. (6) can be integrated graphically to give the distribution factor (Γ_i/n_i) of ions of species i in a multicomponent solution. It is important to note that the summation over all the ionic species includes the cations, the anions, and the surfactant ions.

The selective adsorption coefficient between two ions is defined as

$$\alpha_{AB} = \frac{(\Gamma/n)_A}{(\Gamma/n)_B} \tag{10}$$

and is given by

$$\alpha_{AB} = \frac{\displaystyle\int_{v_0}^{1} \frac{(v^{z_A} - 1)\,dv}{v\left[\sum_i n_i(v^{z_i} - 1)\right]^{1/2}}}{\displaystyle\int_{v_0}^{1} \frac{(v^{z_B} - 1)\,dv}{v\left[\sum_i n_i(v^{z_i} - 1)\right]^{1/2}}} \tag{11}$$

In the above theory it was assumed that the dielectric constant is constant over the diffuse double layer and there is not polarization of the ions. The dielectric constant should be lower in the intense electrical field near the surface. Davies (*7*, p. 79) explains the surprising agreement that was found between the predicted Gouy-Chapman theory and experimental results with surfactants by the compensation between two pairs of factors that oppose each other.

It is assumed also in the above theory that the ions are points of charge and therefore no selectivity exists between ions of the same valency. It was found experimentally that there is selectivity between different ions of the same valency (*5,8,9*). Therefore the theory needs modification that will enable one to distinguish even between different ions of the same valency.

Modification of the Simple Diffuse Layer Theory: Difference in the Distance of Closest Approach

In the simple theory described above it has been assumed that the distance of closest approach x_0 is the same for all ions in the solution. This is not true because the ionic sizes are different. The cations that are strongly solvated have larger x_0 than those that are weakly solvated. Hydrated bivalent cations are larger than univalent cations.

Suppose we have a mixture of bivalent and univalent cations and x_0' is the distance of closest approach of the univalent cation, x_0'' is that of the bivalent ions, and $x_0'' > x_0'$. (See Fig. 1.)

The diffuse layer can be divided into two regions: $x_0'' < x < \infty$, all ions are present; $x_0' < x < x_0''$, only univalent ions are present.

Hence the integration can be carried out as described above but the region between x_0' and x_0'' contains only univalent ions; therefore we have a correction term $\Delta\Gamma_B$ in addition to the excess of the smaller ion between the limits $x_0' < x < x_0''$. For *Z-Z* electrolyte

$$\Delta\Gamma_B = \int_{x_0'}^{x_0''} n_B \left[\exp\left(-\frac{ze\phi}{kT}\right) - 1\right] dx \tag{12}$$

This integral can be evaluated analytically because this region contains approximately only a single symmetrical electrolyte (*10*).

$$\Delta\Gamma_B \cong \frac{1}{ze}\left(\frac{kT\epsilon n_B}{2\pi}\right)^{1/2} [(v_0')^{1/2} - (v_0'')^{1/2}] \tag{13}$$

The approximation that the anions are distributed according to a

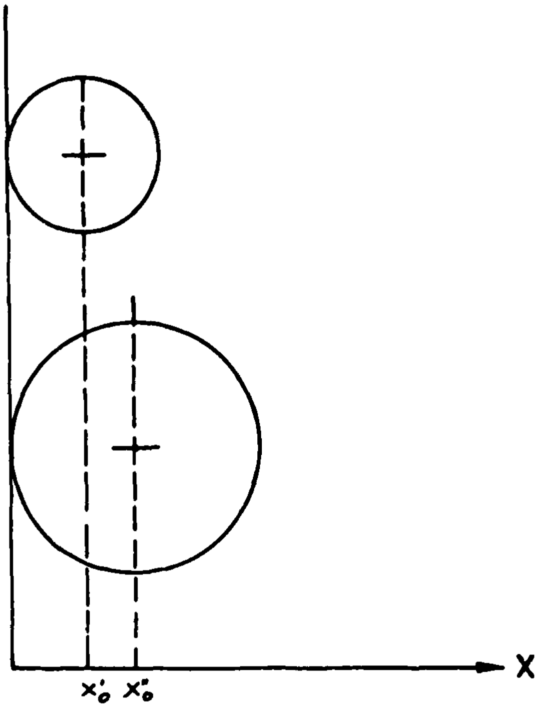

FIG. 1. Distance of closest approach to surface of two different cations.

single symmetrical electrolyte does not introduce a significant error because there is a strong repulsion of anions from this close region and the contribution of the anions to the total charge density is almost negligible. In order to evaluate $\Delta\Gamma_B$ it is necessary to find that relation between ϕ_0' and ϕ_0'' (or equivalently v_0' and v_0'').

$$4\pi\sigma = -\epsilon\left(\frac{d\phi}{dx}\right)_{x_0} \tag{14}$$

for Z-Z single electrolyte (*10*),

$$\sigma = \left(\frac{2kT\epsilon n}{\pi}\right)^{1/2} \sinh\left(\frac{ze\phi}{2kT}\right) \tag{15}$$

$$\left(\frac{d\phi}{dx}\right) = -\left(\frac{2kT}{ze}\right) K \sinh\left(\frac{ze\phi}{2kT}\right) \tag{16}$$

where $K^2 = 8\pi z^2e^2n/\epsilon kT$. By integration with the boundary conditions $x = x_0'$, $\phi = \phi_0'$; $x = x_0''$, $\phi = \phi_0''$; we get the desired relation:

$$\tanh(ze\phi_0'/4kT) = \exp[K(x_0'' - x_0')]\tanh(ze\phi_0''/4kT) \tag{17}$$

where $(x_0' - x_0'')$ is the difference in closest approach to the surface, and K is the Debye-Hückel characteristic reciprocal length.

The distribution coefficients of the two cationic species are:

$$(\Gamma/n)_A = \left(\frac{kT\epsilon}{8\pi e^2}\right)^{1/2} \int_{v_0''}^{1} \frac{(v^{z_A} - 1)\,dv}{v\left[\sum_i n_i(v^{z_i} - 1)\right]^{1/2}} \tag{18}$$

$$(\Gamma/n)_B = \left(\frac{kT\epsilon}{8\pi e^2}\right)^{1/2} \left\{ \int_{v_0''}^{1} \frac{(v^{z_B} - 1)\,dv}{v\left[\sum_i n_i(v^{z_i} - 1)\right]^{1/2}} + 2(1/n_B)^{1/2}[(v_0')^{1/2} - (v_0'')^{1/2}] \right\} \tag{19}$$

where A is the larger ion (e.g., bivalent) and B is the smaller ion (e.g., univalent).

The selective adsorption coefficient between ion A and ion B is given by:

$$\alpha_{AB} = \frac{(\Gamma/n)_A}{(\Gamma/n)_B} = \frac{\displaystyle\int_{v_0''}^{1} \frac{(v^{z_A} - 1)\,dv}{v\left[\sum_i n_i(v^{z_i} - 1)\right]^{1/2}}}{\displaystyle\int_{v_0''}^{1} \frac{(v^{z_B} - 1)\,dv}{v\left[\sum_i n_i(v^{z_i} - 1)\right]^{1/2}} + 2(1/n_B)^{1/2}[(v_0')^{1/2} - (v_0'')^{1/2}]} \tag{20}$$

DISCUSSION

The distribution coefficients for different solutions containing Sr^{++} or UO_2^{++} in the presence of monobutyl biphenyl sodium sulfonate were calculated as a function of the surfactant's concentration and ionic strength, and were compared to the experimental results (*5*). The surface excess of the surfactant was taken as 2.4×10^{-10} moles/cm^2 from adsorption isotherm of the surfactant (*5*).

In Figs. 2 and 3 the enrichment ratio of Sr^{++} and UO_2^{++} were plotted versus $(1/fd)$. The theoretical lines that were calculated according to the modified diffuse layer theory and Eq. (1) are in very good agreement with experimental results. The difference in closest approach be-

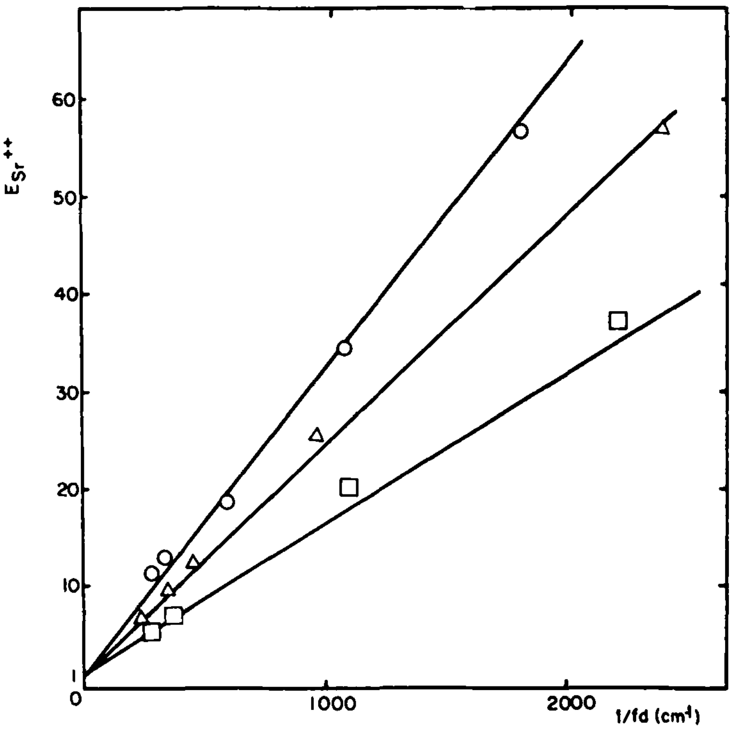

FIG. 2. Effect of $1/fd$ on enrichment ratio of Sr^{++} ions. Sr^{++} concentration: 1.6×10^{-6} *M*; surfactant concentrations: ○, 1.6×10^{-3} *M*; △, 2.24×10^{-3} *M*; □, 3.2×10^{-3} *M*; lines—theoretical, points—experimental (*5*).

tween Sr^{++} and Na^+ was calculated as 2.5 Å from the molar volumes and the hydration numbers of the hydrated ions under the assumption that the hydrated ions are spheres (*10*). The difference in closest approach between UO_2^{++} and Na^+ was assumed to be 2.8 Å because of the absence of data on the hydration number or molar volume of uranyl ion. The hydration number is an experimental number that depends on the experimental technique (see Table 1), and this fact introduces some uncertainty in the calculation of the radius of the hydrated ion.

The effect of the surfactant concentration on $(\Gamma/n)_{Sr^{++}}$ is shown in Fig. 4. There is a good agreement between the theoretical curve and the experimental results below the critical micelles concentration (C.M.C.), above which the character of the solution is changed and the experimental results are higher than the calculated curve, as can be expected.

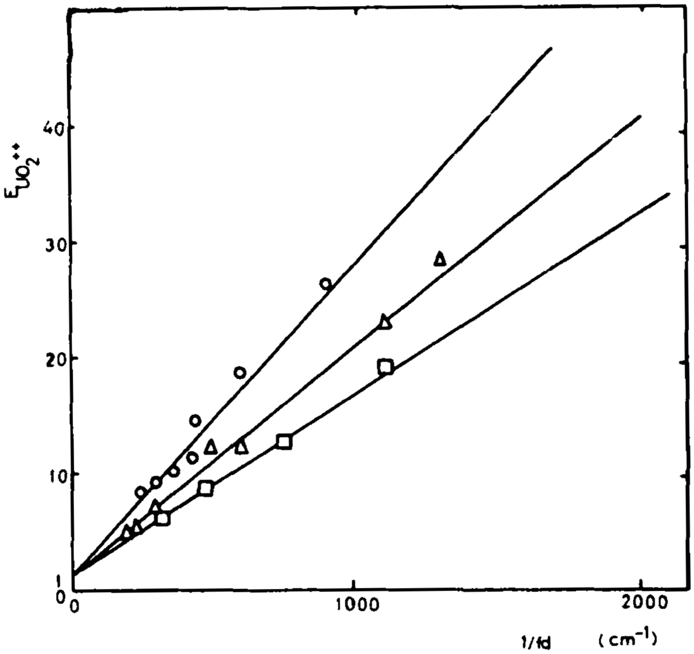

FIG. 3. Effects of $1/fd$ on enrichment ratio UO_2^{++} ions. UO_2^{++} concentration: 1.5 to 2.7×10^{-6} *M*; surfactant concentrations: ○, 1.6×10^{-3} *M*; △, 2.4×10^{-3} *M*; □, 3.2×10^{-3} *M*; lines—theoretical, points—experimental (*5*).

TABLE 1

Hydration Numbers of Several Cations in Aqueous Solution

Ion	From mobility measurements (*10*)	From entropy of hydration (*10*)	From ion exchanger at infinite swelling (*11*)
Cs^+			0
NH_4^+			0.4
K^+		3	0.6
Na^+	2	4	1.5
Li^+	3.5	5	3.3
H^+		5	3.9
Ba^{++}	5	8	
Sr^{++}			4.7
Ca^{++}	7.5	10	5.2
Mg^{++}	10.5	13	7.0
Cu^{++}	10.5	12	
Al^{+++}		21	

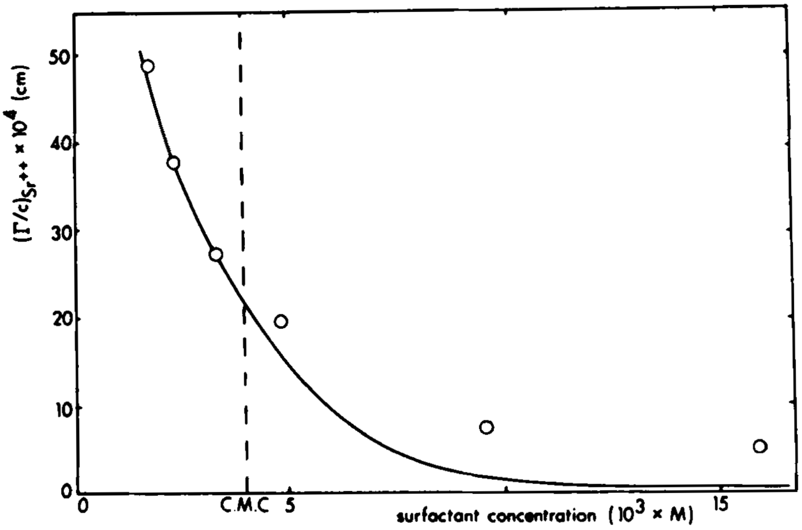

FIG. 4. Effect of surfactant concentration on distribution factor of Sr^{++} Sr^{++} concentration: 4.5 to 10.3×10^{-7} *M*; solid line—theoretical, points—experimental (*5*).

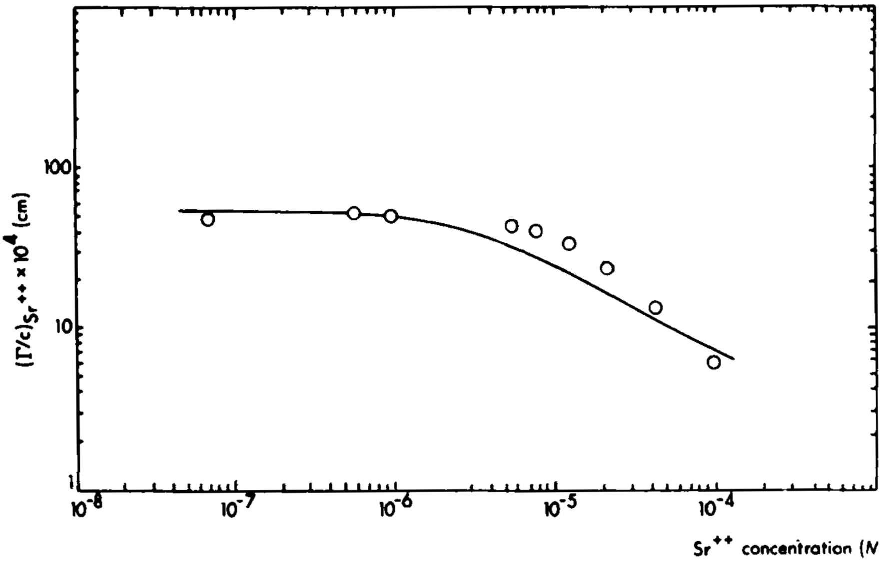

FIG. 5. Effect of Sr^{++} concentration on its distribution factor. Surfactant concentration: 1.6×10^{-3} *M*; line—theoretical; points—experimental (*5*).

The effect of Sr^{++} concentration on its distribution factor is shown in Fig. 5. A good agreement was found between the predicted theoretical curve and the experimental results. The same general behavior was found for the separation of UO_2^{++} from Na^+ solution.

Other evidence that the size of the hydrated ion determines the selectivity in foam separation can be found in other works. Walling et al. (*8*) found that the order of increased selectivity is: $H^+ < Na^+ < K^+ < NH_4^+$, which is the order of decreased hydration number (Table 1). Wace and Banfield (*9*) found values of the selective adsorption coefficient in foam separation,

$$\alpha_{Sr^{++},Cs^+} = 58, \quad \alpha_{Ca^{++},Cs^+} = 38.5, \quad \alpha_{Ce^{+++},Cs_+} = 3.3$$

in agreement with the corresponding values of the hydration numbers. The low value of $\alpha_{Ce^{+++},\ Cs^+}$ can be explained by the possibility of hydrolized Ce^{+3} ions, or by the possibility of high hydration number which reduces the effect of the high valency.

CONCLUSIONS

Experimental data on the separation of Sr^{++} and UO_2^{++} ions and other qualitative data were compared with the proposed theory based on the diffuse layer theory with the restriction of different closest approach to the surface for each ion. From the good agreement between the theoretical lines and the experimental data it is concluded that the charge and the size of the hydrated ion govern the selectivity in foam fractionation of metallic ions.

List of Symbols

d	average bubble diameter
e	electron charge
E_i	enrichment ratio, y_i/n_i
f	volume fraction of liquid in the foam
k	Boltzmann constant
K	Debye-Hückel characteristic reciprocal length
n_i	concentration of solute i in bulk liquid
T	absolute temperature
x	distance from interface
x_0	distance of closest approach
y_i	concentration of solute i in collapsed foam liquid
Γ	surface excess, moles/area

ϵ dielectric constant
ρ charge density at distance x from interface
σ surface charge density
ϕ potential at distance x from interface

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