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Concentration Effects on Separation Selectivity in Foam Fractionation

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Abstract

Removal of cadmium, copper, and nickel ions from aqueous solution by foam fractionation has been studied using a chelating surfactant, 4-dodecyldiethylenetriamine. The rate of removal is a function of concentration of both metallic ions and surfactant. In the low concentration range for the metallic ions compared to that of the surfactant, the order of removal was found to be $Cd^{2+} > Ni^{2+} > Cu^{2+}$. However, at higher concentrations of ions, the order becomes inverse, $Cu^{2+} > Ni^{2+} > Cd^{2+}$. A selectivity coefficient for the separation of a specified ion from one or more ions using a chelating surfactant is shown to be dependent on the surface tension of the complex and the chelation constants. The relationship between separation selectivity of the removal of the metallic ions and concentration of both surfactant and metallic ions is discussed.

INTRODUCTION

In 1878, Gibbs derived the celebrated adsorption equation (*1*):

$$d\gamma = RT\sum \Gamma_i \, d\ln a_i \tag{1}$$

where γ is the surface tension, Γ_i is the surface excess of component i at the surface, and a_i is the activity of component i in the solution. For a dilute solution. Eq. (1) may be simplified to (*2*):

$$(\Gamma/C)_i = -\frac{1}{RT}(\partial\gamma/\partial C_i) \tag{2}$$

where C_i represents the concentration of component i in the solution and $(\Gamma/C)_i$ is the distribution factor of component i.

Foam fractionation is a process for separation and fractionation of of dissolved surface-active solutes based on their tendency to adsorb at gas–liquid interfaces (*3*, *4*). Surface-inactive compounds can be removed from solution if an appropriate surface-active material (surfactant) is added to unite with these compounds so that the combination can be adsorbed at the bubble surface (*5*). The efficiency of a physicochemical method of concentration and separation is determined by selectivity and other parameters. In the cases of solutions containing several surface-active species, selective adsorption at the gas–liquid interface may be expected. Several studies on selective adsorption using radiotracer techniques have been reported (*6–8*).

If a solution contains two surface-active solutes A and B, both of which tend to adsorb to the gas–liquid interface, a relative distribution coefficient (selectivity) α may be defined as the ratio of their individual distribution factors (*9*):

$$\alpha_{AB} = \frac{(\Gamma/C)_A}{(\Gamma/C)_B} \tag{3}$$

It is analogous to distribution coefficient in extraction or volatility in distillation. For Gibbs' adsorption isotherm, Eq. (3) may be modified to

$$\alpha_{AB} = \frac{(\partial\gamma/\partial C_A)}{(\partial\gamma/\partial C_B)} \tag{4}$$

For the removal of surface-inactive compounds (colligends) with a surfactant, the ion-exchange selectivity model has been applied. The surfactant adsorbed in the surface "phase" serves as a model for a soluble ion exchanger (*10*, *11*). Also, 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 smallest size of the hydrated ions, has been studied (*12*, *13*) 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.

In spite of extensive work on the selective adsorption coefficient for the foam separation of ions, very little attention has been paid to the chelating effect of a particular surfactant on the colligend. Various polyalkylenepolyamines chelate readily with metallic ions such as Cd, Cu, Hg, and Ni (*14*). Thus we have applied surfactants containing polyalkylenepolyamines, i.e., 4-dodecyldiethylenetriamine, to remove these metallic ions from aqueous solution by foam fractionation (*15*, *16*). It was found that these metallic ions can be removed almost quantitatively from aqueous solution by using this chelating surfactant, even in the presence of a large concentration of certain other metallic ions such as Ca, Mg, and Na. This paper reports the relation between separation selectivity and concentrations of both surfactant and metallic ions.

PREDICTION OF SELECTIVITY ON FOAM SEPARATION

Consider the system for the removal of the surface-inactive metallic ions x and y with a chelating surfactant. When they form 1 : 1 complexes, the equilibria are

$$\mathrm{s} + \mathrm{x} \rightleftarrows \mathrm{sx}, \qquad K_{\mathrm{x}} = \frac{C_{\mathrm{sx}}}{C_{\mathrm{s}}C_{\mathrm{x}}} \tag{5}$$

$$\mathrm{s} + \mathrm{y} \rightleftarrows \mathrm{sy}, \qquad K_{\mathrm{y}} = \frac{C_{\mathrm{sy}}}{C_{\mathrm{x}}C_{\mathrm{y}}} \tag{6}$$

where C_{s}, C_{x} and C_{sx} are the concentrations of free surfactant s, free x, and the chelating complex of s and x, respectively. We can relate the experimentally determined distribution factor to the complex formation constant. In the experimentally measured distribution factor, the concentration is the total bulk metallic ion concentration. Thus in

$$(\Gamma/C)_{\mathrm{x}} = \frac{\Gamma_{\mathrm{sx}}}{C_{\mathrm{sx}} + C_{\mathrm{x}}} \tag{7}$$

it is assumed that no uncomplexed metallic ion will be found at the interface. Substitution from Eq. (5) for C_{x} into Eq. (7) gives

$$(\Gamma/C)_{\mathrm{x}} = \frac{\Gamma_{\mathrm{sx}}}{C_{\mathrm{sx}} + \dfrac{C_{\mathrm{sx}}}{K_{\mathrm{x}}C_{\mathrm{s}}}} \tag{8}$$

Rearrangement of Eq. (8) leads to the expression

$$(\Gamma/C)_{\mathrm{x}} = \left(\frac{\Gamma_{\mathrm{sx}}}{C_{\mathrm{sx}}}\right)\left(\frac{K_{\mathrm{x}}C_{\mathrm{s}}}{K_{\mathrm{x}}C_{\mathrm{s}} + 1}\right) \tag{9}$$

There are two parts to the right-hand side of Eq. (9), each playing a role in determining $(\Gamma/C)_{\mathrm{x}}$. The term at the extreme right is the fraction of metallic ion in the form of the chelate complex in the bulk solution.

If a Gibbs adsorption isotherm is assumed, the distribution factor of the chelate complex, Γ_{sx}/C_{sx}, can be rewritten as

$$\frac{\Gamma_{sx}}{C_{sx}} = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial C_{sx}}\right) \tag{10}$$

Equation (10) may be substituted into Eq. (9) to give

$$(\Gamma/C)_x = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial C_{sx}}\right)F_x \tag{11}$$

Let us examine the effect of F_x on $(\Gamma/C)_x$. When $K_xC_s \gg 1$ or F_x is close to 1, we observe the distribution factor depends on the surface tension of the chelate complex. As K_xC_s becomes smaller, i.e., there is less free surfactant in solution, F_x will be decreased, and as seen in Eq. (11), $(\Gamma/C)_x$ will also decrease.

Similar equations can be written for the s and y complex as

$$(\Gamma/C)_y = \left(\frac{\Gamma_{sy}}{C_{sy}}\right)F_y \tag{12}$$

and

$$(\Gamma/C)_y = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial C_{sy}}\right)F_y \tag{13}$$

where $F_y = (K_yC_s/K_yC_s + 1)$.

Substitution of Eqs. (9) and (12) or (11) and (13) for $(\Gamma/C)_x$ and $(\Gamma/C)_y$ into Eq. (3) gives

$$\alpha_{xy} = \frac{(\Gamma_{sx}/C_{sx})}{(\Gamma_{sy}/C_{sy})}\frac{F_x}{F_y} \tag{14}$$

or

$$\alpha_{xy} = \frac{(\partial\gamma/\partial C_{sx})}{(\partial\gamma/\partial C_{sy})}\frac{F_x}{F_y} \tag{15}$$

When K_x and K_y are relatively large and the concentration of surfactant is much greater than the sum of the concentrations of x and y, the values of F_x and F_y become unity and Eqs. (14) and (15) reduce to

$$\alpha_{xy} = \frac{\Gamma_{sx}/C_{sx}}{\Gamma_{sy}/C_{sy}} \tag{16}$$

and

$$\alpha_{xy} = \frac{(\partial\gamma/\partial C_{sx})}{(\partial\gamma/\partial C_{sy})} \tag{17}$$

The experimental procedures described below are designed to demonstrate the trends in the selectivity as certain parameters are varied in order to indicate the importance of the relative concentrations of surfactant and metallic ions in foam fractionation.

EXPERIMENTAL SECTION

The foam fractionation technique used in this investigation was described in detail in previous reports (*15*, *16*). 4-Dodecyldiethylenetriamine was used as the chelating surfactant and was obtained from Eastman Kodak Co. The aqueous stock solutions of Cd, Cu, and Ni ions were prepared from weighed amounts of their nitrate salts, and the ionic concentrations were determined by atomic adsorption spectrometry (Perkin-Elmer Model 303) with standard solutions. For each of a series of experiments, 2 liters of deionized aqueous solution containing metallic ions, surfactant, and HNO_3 or NaOH for adjusting the pH was prepared. The solution was then transferred to a separation unit for foaming. Compressed air saturated with water was passed into the solution through the bubbler. When foam rose to the top of the column, timing was started. The foam collected in a beaker was collapsed by stirring. The foamate was collected at intervals and weighed. The metallic ions in both the foamate and residue were determined with an atomic adsorption spectrophotometer. The surface tensions of the solutions were measured by a tensiometer (Cohn RG Electro-Balance) using the Wilhelmy method.

RESULTS AND DISCUSSION

The surface tension of various concentrations of 1:1 metallic ion surfactant mixtures were determined and the results are shown in Fig. 1. The surface tensions of the systems were found to be in the order of Cu^{2+}–surfactant > Ni^{2+}–surfactant > Cd^{2+}–surfactant throughout the concentration range of 10^{-1} to 10^{-6} *M*. Two molecules of 4-dodecyldiethylenetriamine chelated strongly with each ion, and the chelating constants are summarized in Table 1 (*15*, *16*). The order was found to be $Cu^{2+} > Ni^{2+} > Cd^{2+}$.

The degree of selectivity in the removal of Cu and Ni ions with the surfactant was investigated. Typical results are shown in Table 2. Plots of the rate of removal of those ions vs foaming time are shown in Figs. 2 and 3. From an examination of these data, it can be seen that when the total concentration of both ions is much smaller than the concentration

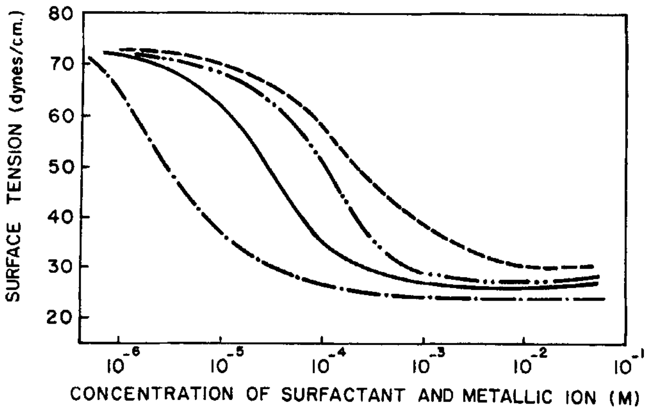

FIG. 1. Surface tension vs concentration of 4-dodecyldiethylenetriamin: (——) with Cd^{2+}, (----) with Cu^{2+}, (—··—) with Ni^{2+}, and (—·—) surfactant.

TABLE 1

Complex Formation Constants of 4-Dodecyldiethylenetriamine with Metallic Ions

Metallic ion	Log K_1	Log K_2
Cadmium	8.06	7.00
Copper	13.91	6.45
Nickel	11.1	8.08

TABLE 2

Concentration Effects on Selectivity between Cu^{2+} and Ni^{2+a}

Run no.	Metallic ion	Initial conc (× 10^{-4} *M*)	% of metallic ion removed 1 hr	2 hr	3 hr	4 hr
D-1	Cu^{2+}	0.79	—	20.95	36.76	55.14^b
	Ni^{2+}	0.85	9.15	28.02	49.10	65.33^b
D-2	Cu^{2+}	1.57	3.04	5.13	10.26	25.67^c
	Ni^{2+}	1.70	4.21	14.95	17.29	27.37^c
D-3	Cu^{2+}	3.15	7.74	10.17	25.42	—^{c}
	Ni^{2+}	3.41	3.29	8.68	9.78	13.47^c
D-4	Cu^{2+}	6.30	6.86	12.43	17.02	22.60^c
	Ni^{2+}	6.81	0.87	2.61	3.48	6.59^c

[a] Initial concentration of surfactant is 13.81 × 10^{-4} *M*.
[b] Gas flow rate: 200 cm^3/min.
[c] Gas flow rate: 100 cm^3/min.

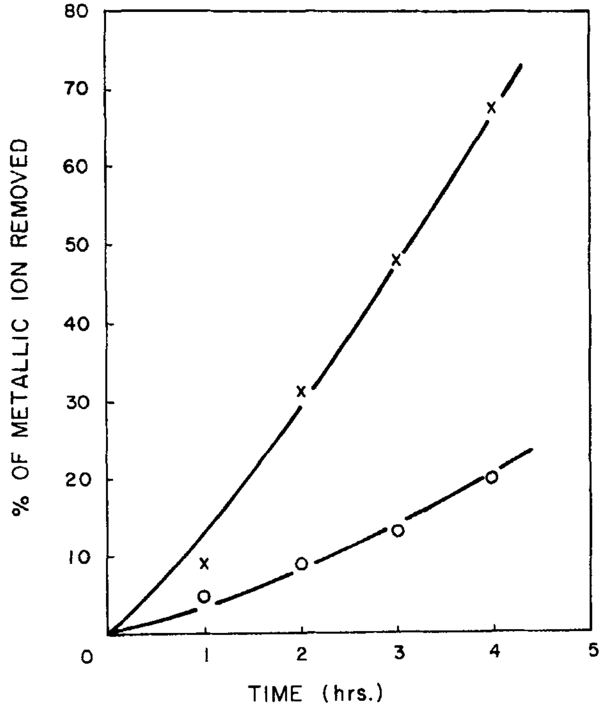

FIG. 2. Selectivity of the removal of Cu^{2+} and Ni^{2+}. The initial concentrations of surfactant, Cu^{2+} (○), and Ni^{2+} (×) are 13.81×10^{-4} *M*, 2.36×10^{-4} *M*, and 2.55×10^{-4} *M*, respectively. Gas flow rate, $200\ cm^3/min$; pH = 9.1.

of surfactant, Ni^{2+} is removed faster than Cu^{2+}. However, when the concentration of the ions is increased, Cu^{2+} can be removed faster than Ni^{2+}. As described in Eq. (15), when the sum of the concentrations of these metallic ions is smaller than that of the surfactant, all metallic ions in particular are complexed with the surfactant and thus there is no competition for surfactant complex formation. Then the bubble formation is controlled by the respective surface tensions of the complexes, and the selectivity for the removal of these ions can be calculated by Eq. (17). Because the surface tension of the solution of Ni^{2+}–surfactant was lower than that of Cu^{2+}–surfactant, it could be predicted that bubble formation should favor species containing Ni^{2+} and that ion should be removed faster. This was found to be the case as illustrated in Fig. 2. Conversely, when the concentrations of those metallic ions were increased, there was

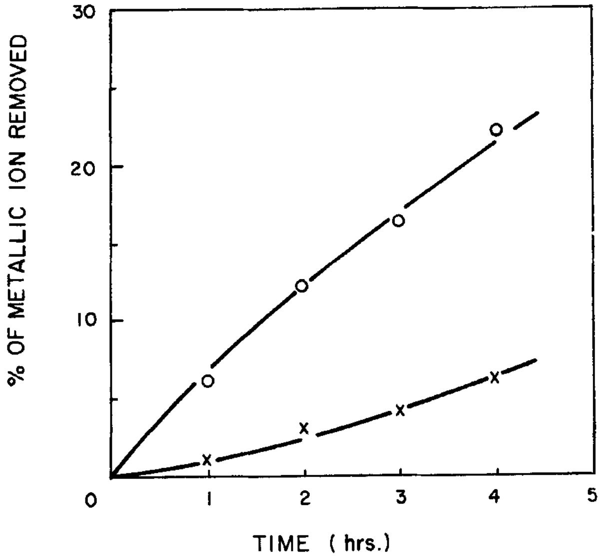

FIG. 3. Selectivity of the removal of Cu^{2+} and Ni^{2+}. The initial concentrations of surfactant, Cu^{2+} (○), and Ni^{2+} (×) are 13.81 × 10^{-4} *M*, 6.30 × 10^{-4} *M*, and 6.81 × 10^{-4} *M*, respectively. Gas flow rate, 100 cm^3/min; pH = 9.1.

TABLE 3

Concentration Effects on Metallic Ion Removal[a]

Run no.	Metallic ion	Initial conc (× 10^{-4} *M*)	% of metallic ion removed				
			1 hr	2 hr	3 hr	4 hr	∞[b]
T-1	Cd^{2+}	0.89	14.38	31.51	45.55	57.88	68.50
	Cu^{2+}	0.79	2.49	—	5.25	9.12	34.81
	Ni^{2+}	0.85	5.42	—	22.62	33.32	—
T-2	Cd^{2+}	2.22	0	0	1.32	—	2.56
	Cu^{2+}	2.36	4.22	6.96	10.26	—	24.52
	Ni^{2+}	2.56	4.13	6.79	10.69	—	27.15
T-3	Cd^{2+}	3.11	0	0	0	—	0
	Cu^{2+}	3.15	3.72	10.53	17.72	—	37.40
	Ni^{2+}	2.98	2.04	4.17	6.98	—	27.36

[a] Initial concentration of surfactant is 13.81 × 10^{-4} *M* and gas flow rate is 200 cm^3/min.

[b] The sample was taken after no more foam formed.

competition for the complex formation. Since Eqs. (14) and (15) were derived by assuming that the surfactant forms 1:1 complexes with the metallic ions, the selectivity cannot be obtained directly by using these equations. However, qualitatively, the second terms of Eqs. (14) and (15) become the important factors for the selectivity. The complex formation constant K_1 for Cu^{2+} was found to be about 100 times larger than the K_1 for Ni^{2+}. Thus Cu^{2+} competes more favorably for complex formation, and it is predicted that any bubble formed would preferentially contain Cu^{2+}. This can be seen to be so from the data compiled in Fig. 3 for Cu^{2+} and Ni^{2+}. Similar results for the removal of cadmium and copper ions were reported (*16*).

The degree of selectivity in the removal of metallic ions from the solution containing three similar ions (Cd^{2+}, Cu^{2+}, and Ni^{2+}) with 4-dodecyldiethylenetriamine was investigated under various conditions, and typical data are summerized in Table 3. In the low concentration

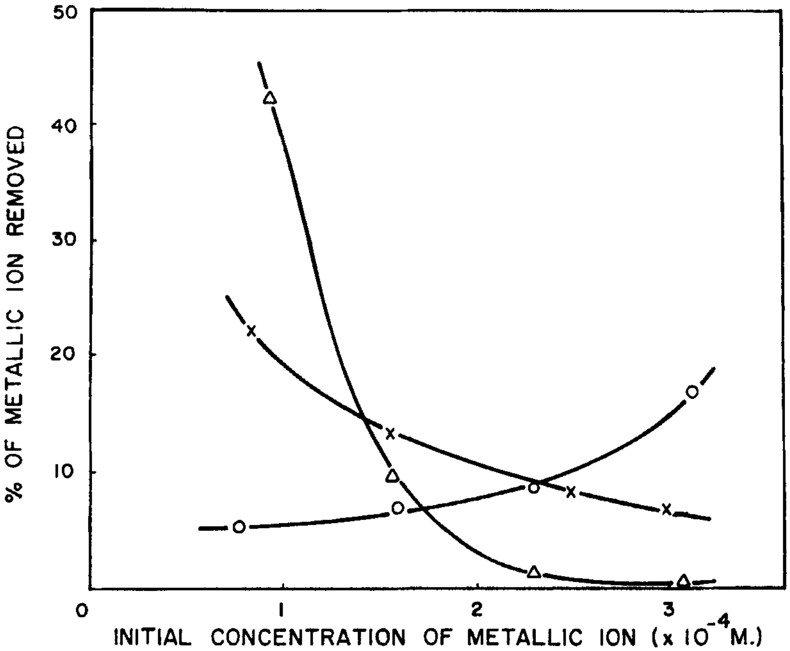

FIG. 4. Concentration effects on removal of metallic ions: Cd (△), Cu (○), and Ni (×). Initial concentration of surfactant, 13.81 × 10^{-4} M; gas flow rate, 200 cm^3/min; foaming time, 3 hr.

range for these ions compared to that of the surfactant, the order of removal was found to be $Cd^{2+} > Ni^{2+} > Cu^{2+}$. This result could be predicted from the surface tensions of the systems. At higher concentrations of these ions, however, the order becomes inverted ($Cu^{2+} > Ni^{2+} > Cd^{2+}$), which also could be predicted from their chelate formation constants. This can be seen to be so from the data compiled in Fig. 4. This result strongly indicates that there are two major factors that control the selectivity of removal of similar metallic ions with chelating surfactants by foam separation. One is complex formation and the other is the surface tension of the complex.

We are presently carrying out experiments designed to extend this separation concept to other metallic ions by using various chelating surfactant.

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