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Chelation Effects of Surfactant in Foam Separation: Removal of Cadmium and Copper Ions from Aqueous Solution

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Abstract

Foam separation techniques for the removal of cadmium and copper ions from aqueous solution were studied by employing a surfactant which was specifically designed to chelate with these ions. Relationships between the formation constants and surface tensions of solutions of Cd- and Cu-surfactant complexes on the selectivity of the removal of these ions were discussed.

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. Foam separation can also be used as a technique for removing metallic ions that are not surface active (*1–4*). Surface-inactive compounds can be removed from solution if an appropriate surface-active material is added to unite with this material so that it can be adsorbed at the bubble surface (*5*). This can occur through the formation of a chelate, by electrostatic attraction, or through some other mechanism.

To establish the feasibility of using foam separation to effect the separation of a specified ion from one or more ions which have a similar charge, a selectivity coefficient must be determined in a similar fashion to that used in ion exchange. In spite of extensive work done on foam separation, very little attention has been paid to the chelating effect of a surfactant.

Various polyalkylenepolyamines chelate readily with metallic ions such as copper (*6*, *7*), cadmium (*8*, *9*), and mercury (*8*, *10*). Thus we have synthesized surfactants containing polyalkylene amines, i.e., 4-dodecyldiethylenetriamine, and have applied them to the removal of cadmium and mercury from aqueous solution by the foam separation process (*11*, *12*). It was found that cadmium and mercury ions can be removed almost quantitatively from aqueous solution using the chelating surfactants, even in the presence of a large concentration of certain other metallic ions such as Ca, Mg, and Na.

The purpose of this paper is to determine the effects of the concentration of surfactant and metallic ions on the selectivity of the removal of cadmium and copper ions in batch operations. The surfactant used in the present study was 4-dodecyldiethylenetriamine (*11*).

EXPERIMENTAL

A schematic diagram of the experimental apparatus is shown in Fig. 1. The foam column had an internal diameter of 4 cm and was 65 cm high. For each series of experiments, 2 liters of deionized aqueous solution containing metallic ions, surfactant, and HNO_3 or NaOH was prepared. The solution was then transferred to a flask for foaming. Nitrogen was first humidified and then passed into the flask through a rotameter and a gas dispersing device. The bubbler was a sintered glass dispersion tube of extra coarse porosity. The foam collected in the beaker was collapsed by periodically stirring it with a glass rod. The collapsed foam was collected at intervals and weighed. A small amount of residual sample (1 to 4 ml) was withdrawn for analysis after each foaming session. An atomic adsorption spectrophotometer was used to determine cadmium (*11*) and copper (*13*, *14*) ion concentrations.

The Wilhelmy method was employed to measure the surface tension of solutions used in this study. The tensiometer (Cohn RG Electro-Balance) was calibrated over the range of surface tension values under study.

RESULTS AND DISCUSSION

When a metallic ion can coordinate two or more groups in the formation of complex ions, it will do so stepwise, and an intermediate equilibria will be present. When M represents the metallic ion and S the coordination

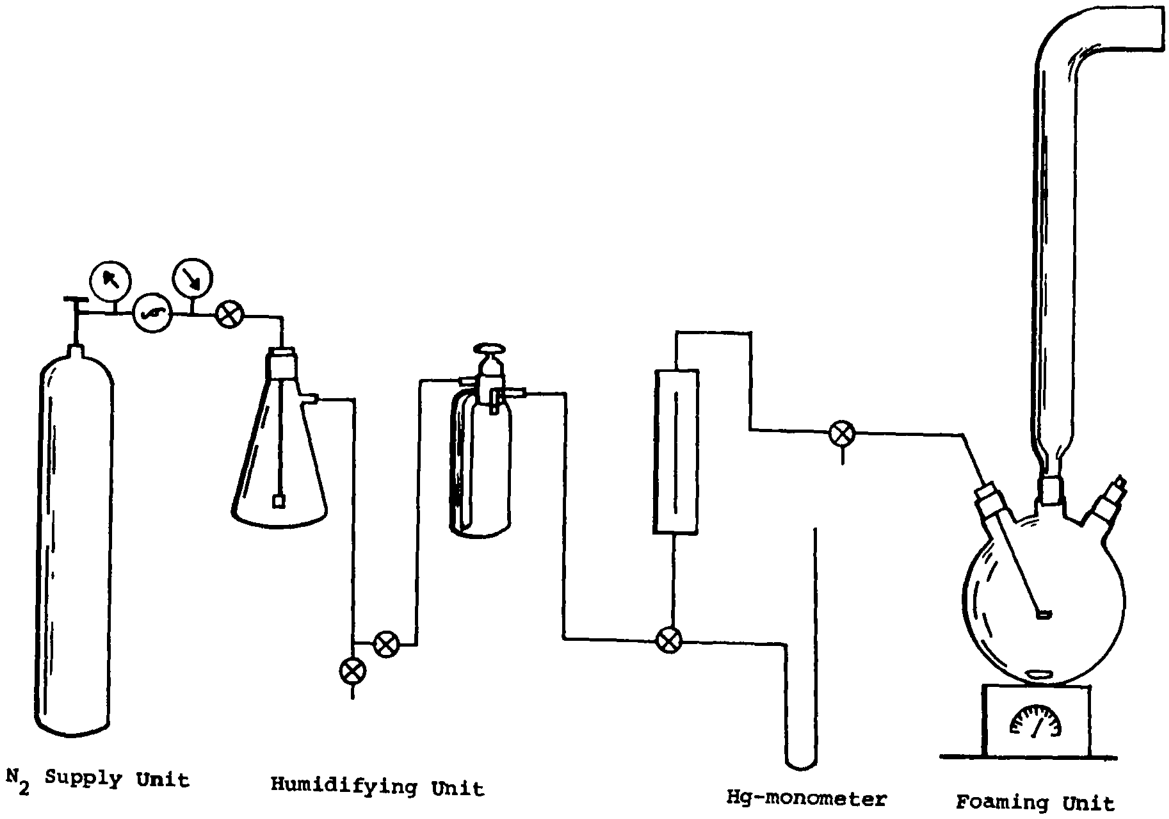

FIG. 1. Experimental setup.

group, the equilibria are

$$\begin{aligned} M + S &\rightleftarrows MS; & K_1 &= [MS]/[M]\,[S] \\ MS + S &\rightleftarrows MS_2; & K_2 &= [MS_2]/[MS]\,[S] \\ MS_2 + S &\rightleftarrows MS_3; & K_3 &= [MS_3]/[MS_2][S], \text{ etc.} \end{aligned}$$

The formation constants (K_1 and K_2) for 4-dodecyldiethylenetriamine complex with copper ion were determined using a potentiometric method (*7*) and are summerized in Table 1 along with data for cadmium (*11*).

The degree of selectivity in the removal of Cd and Cu ions with 4-dodecyldiethylenetriamine under various conditions was investigated. Typical results are shown in Table 2. Plots of the rate of removal of Cd and Cu ions vs foaming time are shown in Figs. 2 and 3. From an examination of these results it can be seen that when the concentrations of both ions are nearly equal, and the total metallic ion concentration is smaller than the surfactant concentration, cadmium is removed faster than copper. When

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

TABLE 2

Concentration Effects on Metal Ion Removal[a]

Initial concentration (× 10^{-4} mole)			% Removal	
Surfactant	Cd^{2+}	Cu^{2+}	Cd^{2+}	Cu^{2+}
6.94	6.23	6.30	12.5	35.5[b]
8.01	5.34	6.30	20.0	29.0[b]
11.6	5.34	6.30	18.5	33.5[c]
8.01	1.34	1.58	98.0	63.5[b]
10.7	1.34	1.58	91.0	66.0[c]
11.6	1.34	1.58	96.6	92.0[b]

[a] pH 9.2, room temperature after 6 hr foaming.

[b] Gas flow rate, 200 cm^3/min.

[c] Gas flow rate, 100 cm^3/min.

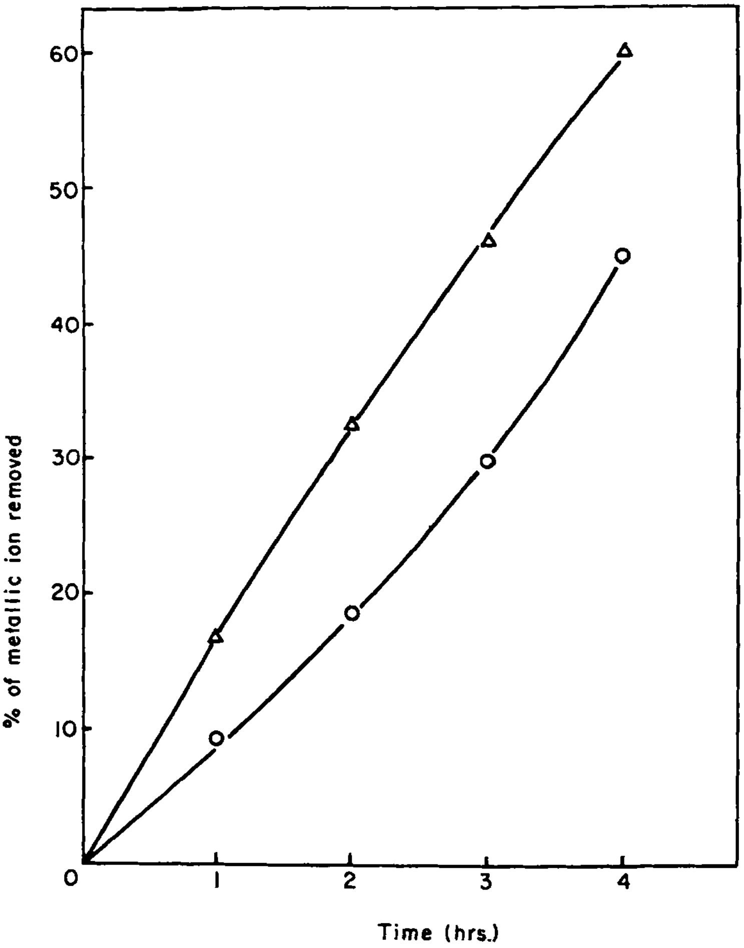

FIG. 2. Selectivity of the removal of Cd^{2+} and Cu^{2+}. The initial concentrations of surfactant, Cd^{2+} (△), and Cu^{2+} (○) are 8.01×10^{-4} *M*, 1.34×10^{-4} *M*, and 1.58×10^{-4} *M*, respectively. Gas flow rate, 100 cm^3/min; pH, 9.2.

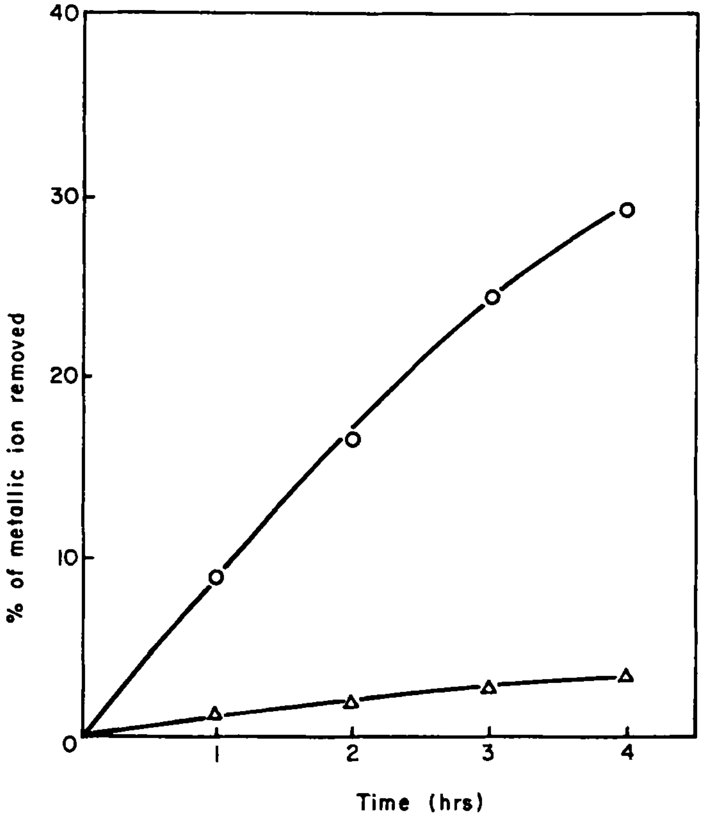

FIG. 3. Selectivity of the removal of Cd^{2+} and Cu^{2+}. The initial concentrations of surfactant, Cd^{2+} (△), and Cd^{2+} (○) are 6.94×10^{-4} *M*, 6.23×10^{-4} *M*, and 6.30×10^{-4} *M*, respectively. Gas flow rate, 200 cm^3/min; pH, 9.2.

the total metallic ion concentration is larger than the surfactant concentration, however, it is found that copper ion can be removed faster than cadmium.

The surface tensions of various concentrations of 1:1 Cd and Cu ion–surfactant mixtures were determined, and the results are shown in Fig. 4. Over a wide range of concentrations the surface tensions of the Cd–surfactant mixtures were found to be lower than those of the Cu–surfactant mixtures.

The distribution factor for the metal–surfactant complex $(\Gamma/X)_{SM}$ is related to the surface tension, and this relationship can be shown by Gibbs' adsorption equation (*15*, *16*):

$$(\Gamma/X)_{SM} = \frac{-1}{RT}\left(\frac{d\gamma}{dX_{SM}}\right)$$

where Γ is the surface excess, X is the concentration of the metal–surfactant complex (SM) in the residue, and γ is the surface tension. Therefore, when the total concentration of Cd and Cu ions is smaller than that of the surfactant, practically all metallic ions are complexed with the surfactant and thus there is no competition for surfactant complex formation. The bubble formation in this instance is controlled by the respective surface tensions of the complexes, and since the solutions of Cd complex were found to have consistently lower surface tensions than those containing the Cu complex, it could be predicted that bubble formation should favor species containing Cd, and thus Cd should be removed faster. This was found to be the case as is illustrated in Fig. 2. Conversely, when the total concentration of Cd and Cu ions is larger than the surfactant concentration, there is competition for complex formation. From an examination of the complex formation constants, the K_1 value for the Cu complex is found to almost 1 million times larger than the K_1 value for the Cd complex, i.e., $\log K_1 = 13.9$ for Cu and 8.00 for Cd. Therefore the Cu competes more favorably for complex formation, and it may be predicted that any bubble formed would preferentially contain Cu ion. This can be seen to be so from the data compiled in Fig. 3, and the Cu ion is removed faster than Cd.

Acknowledgment

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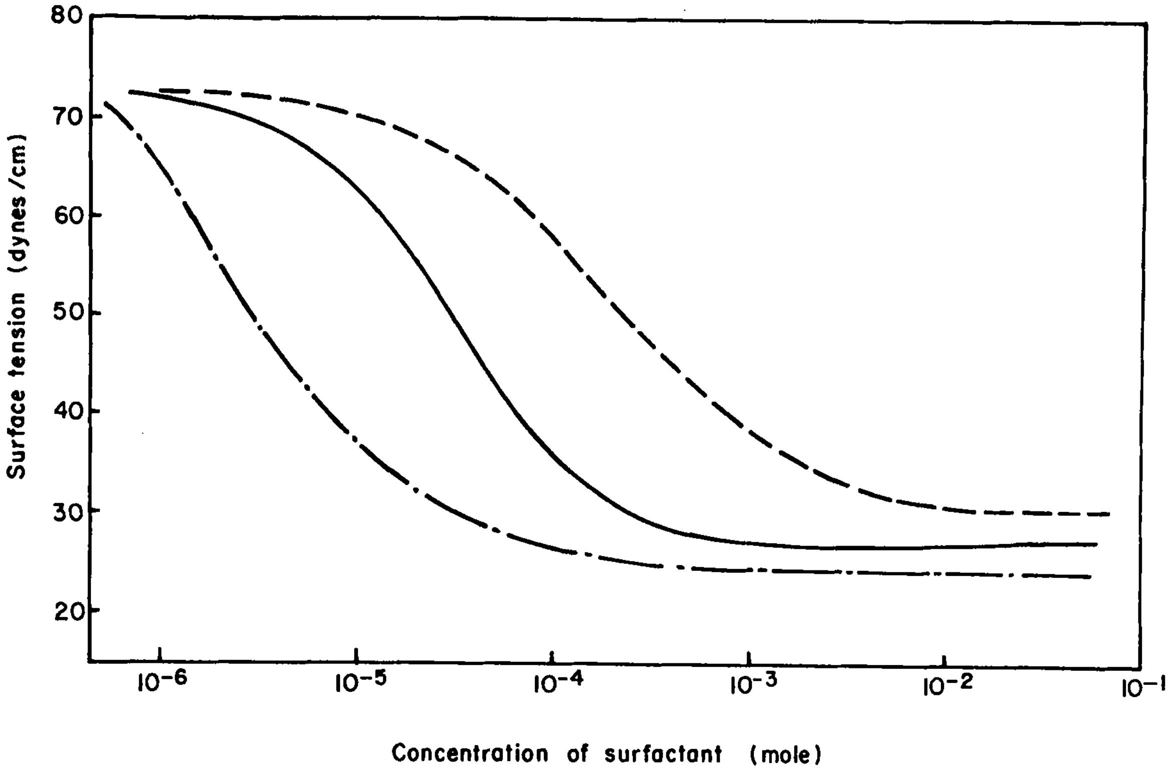

FIG. 4. Surface tension vs concentration of 4-dodecyldiethylenetriamine: (—) with Cd^{2+}, (- -) with Cu^{2+}, and (- ·) surfactant.

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