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

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To cite this Article Okamoto, Y. and Chou, E. J.(1975) 'Foam Separation of Mercury Ion with Chelating Surfactant: The Selectivity of the Removal of Cadmium and Mercury Ions with 4-Dodecyldiethylenetriamine', Separation Science and Technology, 10: 6, 741 — 753

To link to this Article: DOI: 10.1080/00372367508058054

URL: http://dx.doi.org/10.1080/00372367508058054

SEPARATION SCIENCE, 10(6), pp. 741–753, 1975

Foam Separation of Mercury Ion with Chelating Surfactant: The Selectivity of the Removal of Cadmium and Mercury Ions with 4-Dodecyldiethylenetriamine

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Abstract

Foam separation techniques for the removal of mercury ion were studied which employed a surfactant specifically designed to chelate with the ion. The chelating surfactant was 4-dodecyldiethylenetriamine. Mercury ion was found to be removed almost quantitatively from aqueous solution using this surfactant, even in the presence of a large concentration of other metallic ions. Formation constants and surface tensions of Cd and Hg ionic complexes with the surfactant were measured. Selectivity of the removal of Cd and Hg ions is discussed.

INTRODUCTION

Mercury as a trace element highly toxic to humans and animals is well known (*1*). Fatal results of mercury poisoning are preceded by involuntary mobilization, blindness, mental and emotional deterioration, and loss of consciousness. As the requirements for clean water have become more stringent, industry has been constantly searching for techniques to produce the cleanest possible effluent at the minimum cost. Foam separations have been used for years to remove certain organic molecules and trace amounts of other dissolved materials from waste water. Recent reviews of foam separation (*2–6*) indicate the importance and varied applications of this technique. Foam separation is based on the tendency of surface-active solutes to concentrate at gas–liquid interfaces. Surface-inactive components can be removed from solution by foam separation if an appropriate surface-active material is added to unite with the surface-inactive material so that it can be adsorbed at the bubble surfaces (*7*). This can occur through the formation of a chelate, electrostatic attraction, or some other mechanism.

In spite of extensive work done on the foam separation of ions, very little attention has been paid to the chelating effect of a particular surfactant on the colligend. Ferguson et al. (*8*) have recently reported that attempts at removal of lead and cadmium ions from waste water by foam separation using commercial surfactants such as sodium lauryl sulfate become impractical when the solution contains calcium and phosphate.

Cadmium forms complexes with various alkylamines. Thus we have synthesized surfactants containing polyalkylene amines (e.g., 4-dodecyldiethylenetriamine) and have applied them to the removal of cadmium from aqueous solution by the foam separation process (*9*). It was found that cadmium ion can be removed almost quantitatively from aqueous solution using this chelating surfactant, even in the presence of a large concentration of certain other metallic ions such as calcium at pH 7 to 9.

This paper reports the removal of mercury ion from aqueous solutions using a chelating surfactant and also discusses the chelating effects of the surfactant toward both cadmium and mercury ions.

EXPERIMENTAL

The foam separation equipment used in this investigation was described in detail in a previous report (*9*). In order to determine the amount of surfactant in the foam and in the residual solution, ^{14}C-tagged 4-dodecyldiethylenetriamine was used. The synthesis and the analytical method for the determination of the amine were also reported in a previous paper (*9*). The aqueous stock solution of mercury ion was prepared from weighed amounts of mercuric chloride and a small amount of hydrochloric acid which was added to prevent hydrolysis of the mercuric chloride. The stock solution of 4-dodecyldiethylenetriamine (Eastman Kodak Co.) was dissolved in 95% alcohol. All chemicals and reagents were of analytical reagent-grade quality. An atomic adsorption spectrophotometer (Jarrell-Ash Model 82–270) with a mercury cathode was used for the measurement of mercury ion.

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 separation unit for foaming. Nitrogen saturated with water vapor was passed into the solution through the bubbler. When foam rose to the top of the column, timing was started. The foam collected in the beaker was collapsed by periodically stirring it with a glass rod. The foam was collected at intervals and weighed. A portion of the foam was taken for analysis. A small amount of sample (1 to 4 ml) from the residue was withdrawn for analysis after each foaming session. Mercury ion was determined by flameless atomic adsorption (*10*, *11*), using stannous chloride as a reducing agent.

The surface tension of the solution was measured with a DuNouy tensiometer, the ring of which was made from platinum–iridium wire (1.59 cm diameter). Several readings were taken and the average was computed. The instrument was calibrated over the range of scale readings involved.

RESULTS AND DISCUSSIONS

Formation of the Complex Between Surfactant (4-Dodecyldiethylenetriamine) and Mercury Ion

If a metallic ion can coordinate two or more groups in the formation of complex ions, it will do so stepwise, and an intermediate equilibrium will be present. If M represents the metallic ion and S the coordinating group, the equilibria are:

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

The formation constants (K_1 and K_2) for the 4-dodecyldiethylenetriamine complex with mercury ion were determined using a potentiometric method (*12*) and a polarographic method (*13*). In the potentiometric method, nitric acid was used instead of hydrochloric acid. The results, along with the data for cadmium ion (*9*), are summarized in Table 1.

Foam Separation of Mercury Ion

A number of factors influencing foam separation using 4-dodecyldiethylenetriamine as the chelating surfactant were investigated to find the optimum conditions. An increase in nitrogen flow led to an increase in

TABLE 1

Complex Formation Constant of Polyalkylene Amine with Cadmium and Mercury Ions

		Potentiometric method		Polarographic method
Metal ion	Complexing agent	Log K_1	Log K_2	Log K_1K_2
Mercury	Diethylenetriamine	—	—	24.8
	(at 20°C)	(21.8) (*12*)	(7.0) (*12*)	(25.1) (*14*)
	4-Dodecyldiethylenetriamine			
	(at 25°C)	7.95	5.40	14.21
Cadmium	Diethylenetriamine	8.37	5.62	13.6
	(at 20°C)	(8.45) (*12*)	(5.40) (*12*)	(14.2) (*13*)
	4-Dodecyldiethylenetriamine			
	(at 25°C)	8.06	7.00	14.01

separation, but due to increased foaming, losses of solution volume were higher, which was the limiting value for foam separation. The effect of surfactant concentration was also investigated and the results are shown in Fig. 1. The mercury–surfactant complex was found to form a good foam. The removal of mercury ion increased with an increase in the surfactant–mercury ion ratio until a particular ratio was reached above which the efficiency of removal decreased. When there was an increase in concentration of surfactant, more mercury ion–surfactant complex tended to form, i.e., there was an increase in the concentration of the complex and a decrease in the free mercury ion concentration. In this region the enrichment ratio (E_M) increased as the surfactant concentration increased. The enrichment ratio is defined as

$$E_M = (Y_{SM} + Y_M)/(X_{SM} + X_M) \quad (1)$$

where X and Y are concentrations in the residue and the foam, respectively, and the subscripts S, M, and SM denote free surfactant, free metallic ion, and metallic ion–surfactant complex, respectively. After the concentration of surfactant reached a point where all the mercury ions were complexed, any addition of surfactant competed with the complex for bubble formation. This competition would obviously decrease mercury ion removal. Similar arguments may be applied to explain the effect of mercury ion concentration. The result is shown in Fig. 2. In the region of low concentration of mercury ion, the efficiency of removal is decreased due to the large surfactant to mercury ion ratio. Removal is also found to be

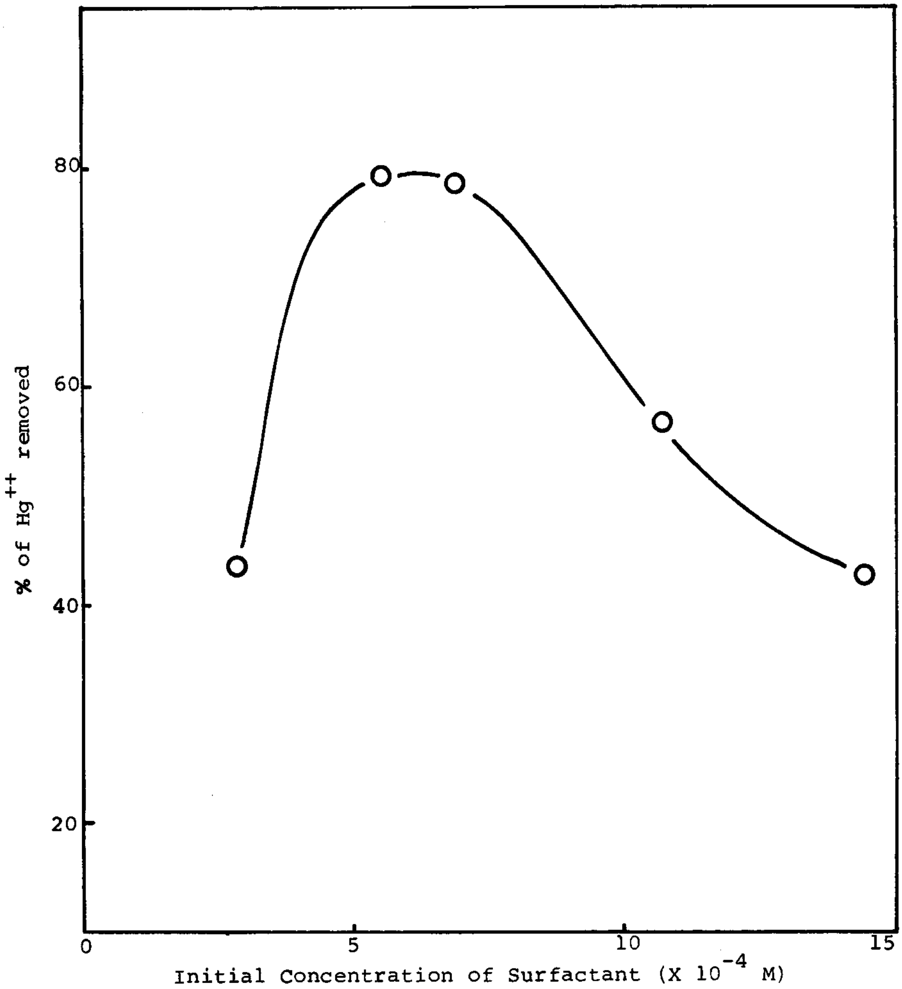

FIG. 1. The effect of surfactant concentration: initial concentration of Hg^{2+} = 10 ppm, pH = 9.2, gas flow rate = 200 cm^3/min, foaming time = 3 hr.

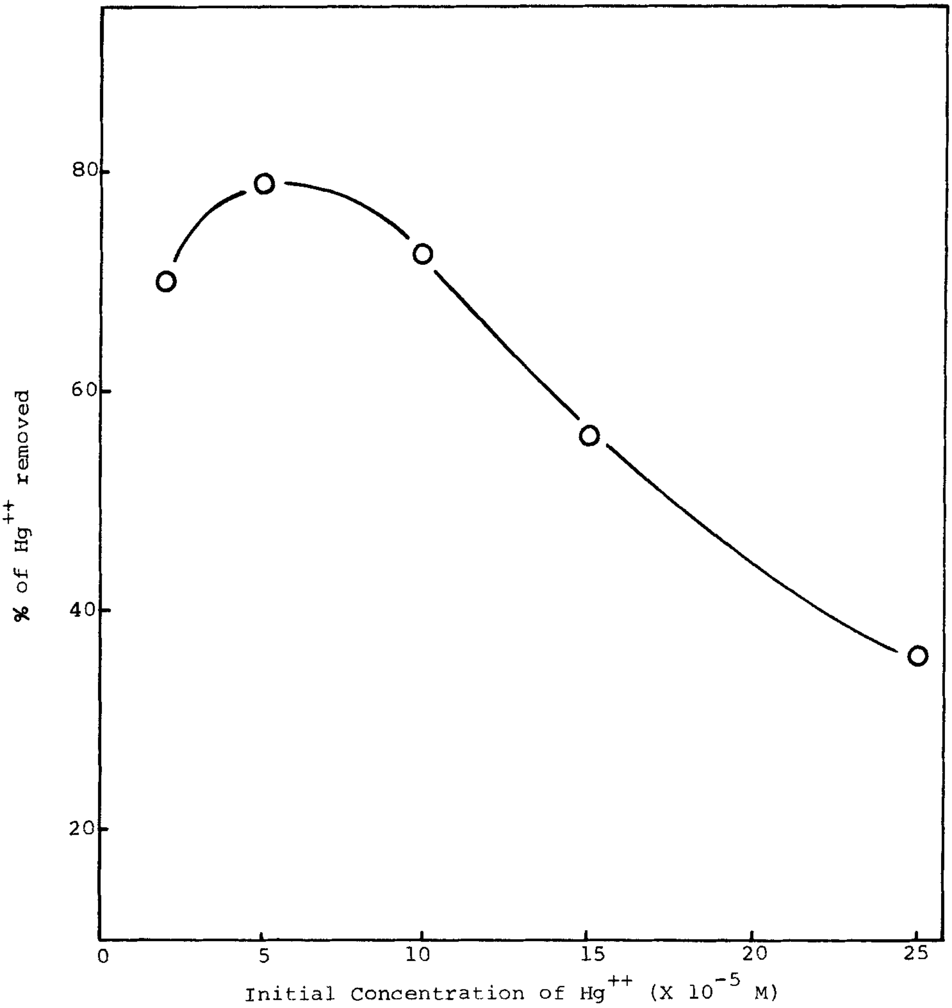

FIG. 2. The effect of mercury ion concentration: initial concentration of surfactant = 5.35×10^{-4} *M*, pH = 9.2, gas flow rate = 200 cm^3/min, foaming time = 3 hr.

decreased at high mercury ion concentration, which may be due to exceeding the critical collector concentration as was mentioned by Rubin and Gaden (*4*).

The effect of pH on the removal of mercury ion is shown in Fig. 3. At low pH the surfactant formed a salt, and the concentration of free surfactant available for complex formation was decreased. At high pH, mercury ion was hydrolyzed to form a hydroxy compound which apparently did not form a strong complex with the surfactant.

Foam Separation of Mercury Ion with Chelating Surfactant in the Presence of Other Ions

A number of experiments were conducted to determine the effects of other metallic ions present on mercury ion removal. Typical results are summarized in Table 2. Mercury ion can be removed effectively even when a large concentration of various other metallic ions is present. This may be due to the fact that these foreign ions do not form a complex with the surfactant.

Selectivity of the Removal of Cadmium and Mercury Ions

Rubin and Gaden (*4*) reported that in foam separation of metallic ions with a foaming agent the distribution factor for the metallic ion, $(\Gamma/X)_M$,

TABLE 2

Removal of Mercury Ion by 4-Dodecyldiethylenetriamine[a]

Time (hr)	From pure aq $Hg(NO_3)_2$	From NaCl containing $Hg(NO_3)_2$ solution[b]	From $MgSO_4$ containing $Hg(NO_3)_2$ solution[c]	From $Ca(NO_3)_2$ containing $Hg(NO_3)_2$ solution[d]
0	0	0	0	0
1	18.8	14.9	11.5	10.5
2	44.7	26.4	24.8	21.7
3	62.4	44.6	39.6	34.8
∞[e]	96.2	—	—	—

[a] Gas flow rate 150 cm^3/min and pH 9.0. Initial concentration of Hg^{2+} and surfactant were 5 and 290 ppm, respectively.

[b] 17,000 ppm NaCl.

[c] 1272 ppm magnesium.

[d] 400 ppm calcium.

[e] After foaming ceased.

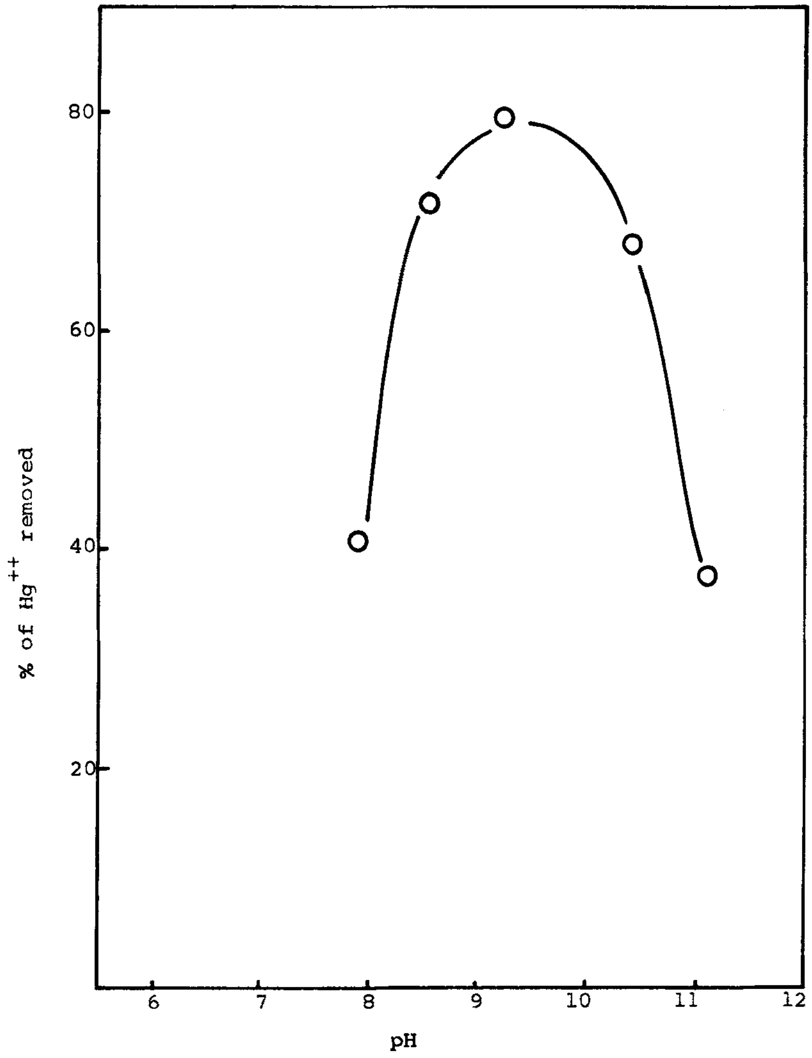

FIG. 3. The effect of pH in the solution: initial concentration of Hg^{2+} = 100, initial concentration of surfactant = 5.35×10^{-4} *M*, gas flow rate = 200 cm^3/min, foaming time = 3 hr.

is defined as

$$(\Gamma/X)_M = (E_M - 1)(lD/6) \tag{2}$$

where E_M is the enrichment ratio of metallic ion, l is the foam ratio in ml liquid/ml foam, and D is the bubble diameter. The distribution factor can be measured by a static method (*15*) or a dynamic method (*14*). The selective adsorption coefficient (α) between ions A and B is given by:

$$\alpha_{AB} = (\Gamma/X)_A/(\Gamma/X)_B = \frac{(E_A - 1)}{(E_B - 1)} \tag{3}$$

In order to obtain the distribution factor, a study was made of the relationship between the surface tension and the concentration of 4-dodecyldiethylenetriamine with metallic ions. Data from this study are shown in Fig. 4. Figure 5 shows the relation of the distribution factors to the concentration of metallic ion when either cadmium or mercury ion was present in the solution. The distribution factors obtained were calculated from Gibb's equation (static method) and from Eq. (2) (dynamic method). The bubble diameter was measured by a photographic technique. The distribution factors obtained by the dynamic method agreed well with those obtained by the static method.

From Fig. 5, we can predict that cadmium ion will be removed faster than mercury ion. A plot of the rate of removal of cadmium and mercury ions vs foaming time is shown in Fig. 6. The initial concentrations of surfactant and metallic ions were 5.35×10^{-4} *M* and 5×10^{-5} *M*, respectively. Since the all-metallic ions form complexes with the surfactant at this concentration, the selective adsorption coefficient can be predicted by the distribution factor as shown in Eq. (3). This predicts that cadmium should be removed faster than mercury. If the concentration of surfactant is less than the total concentration of metallic ion, then the selective adsorption coefficient should depend on the complex formation constant, and high values for formation constants may give higher selective adsorption coefficients. The relation of the selective adsorption coefficient to the complex formation constant is currently under investigation.

Recovery of Surfactant

The feasibility of virtually any commercial-scale foam separation process depends on the recovery and recycling of the surfactant used as the foaming agent. Thus, in view of economic and environmental considerations, it is important to recover and recycle the surfactant. The

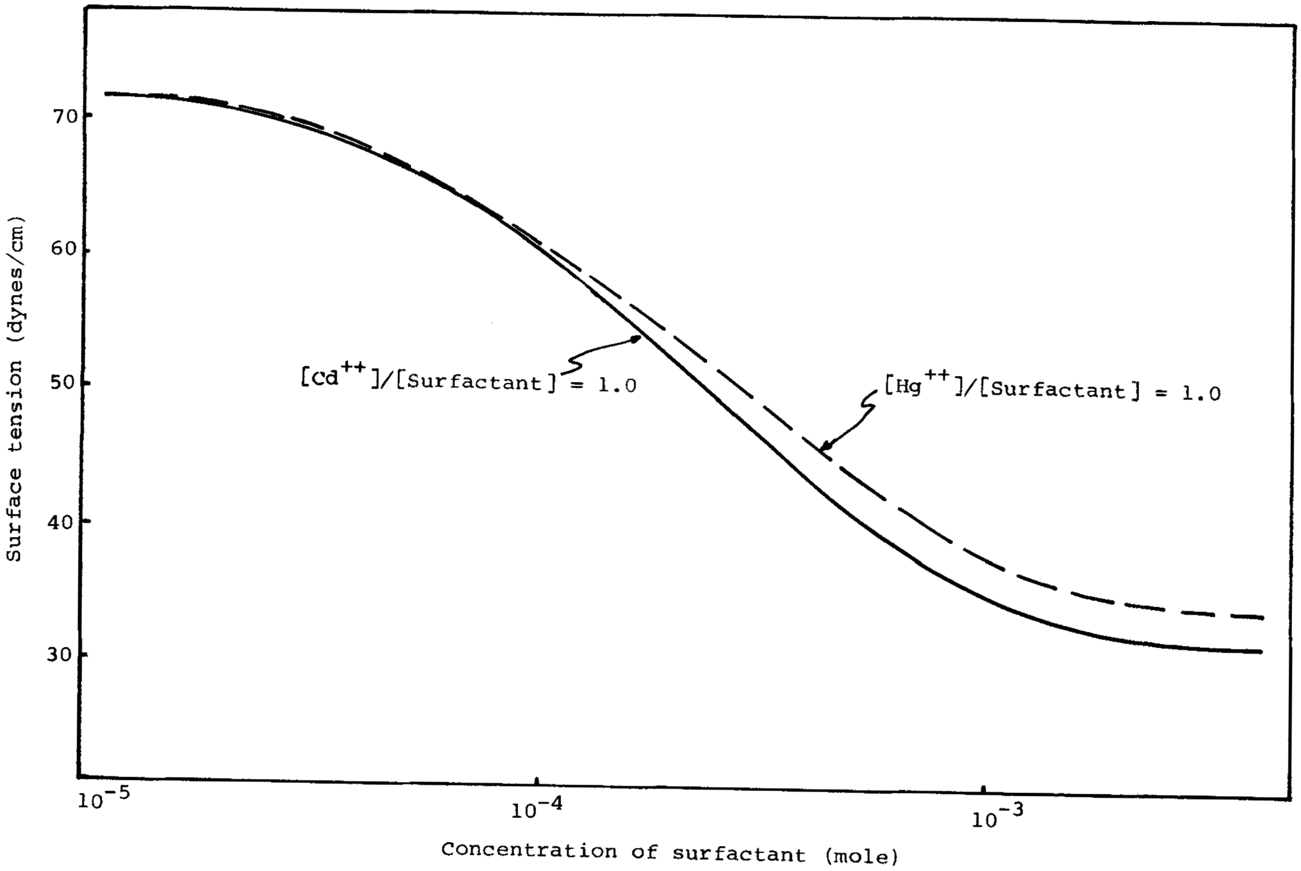

FIG. 4. Surface tension vs concentration of 4-dodecyldiethylenetriamine.

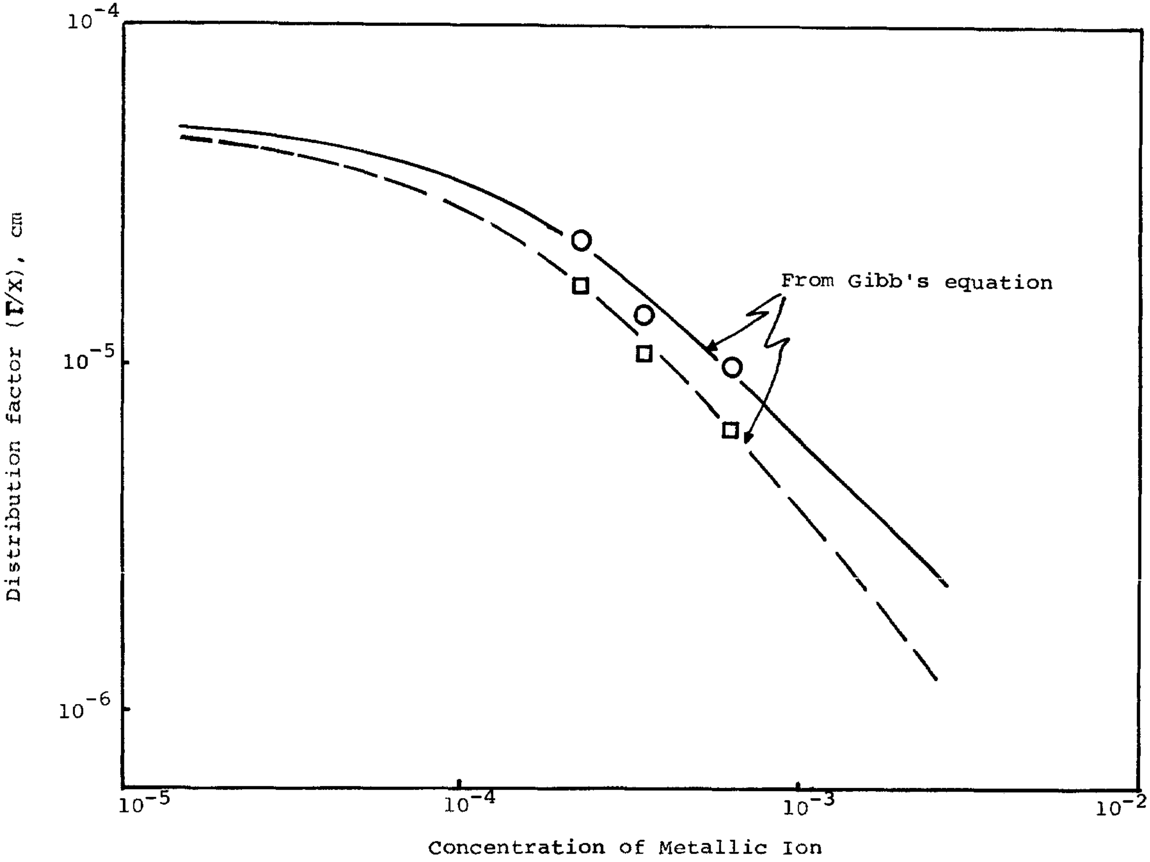

FIG. 5. Distribution factor vs concentration of metallic ion: (○) Cd^{2+} and (□) Hg^{2+} calculated from Eq. (2).

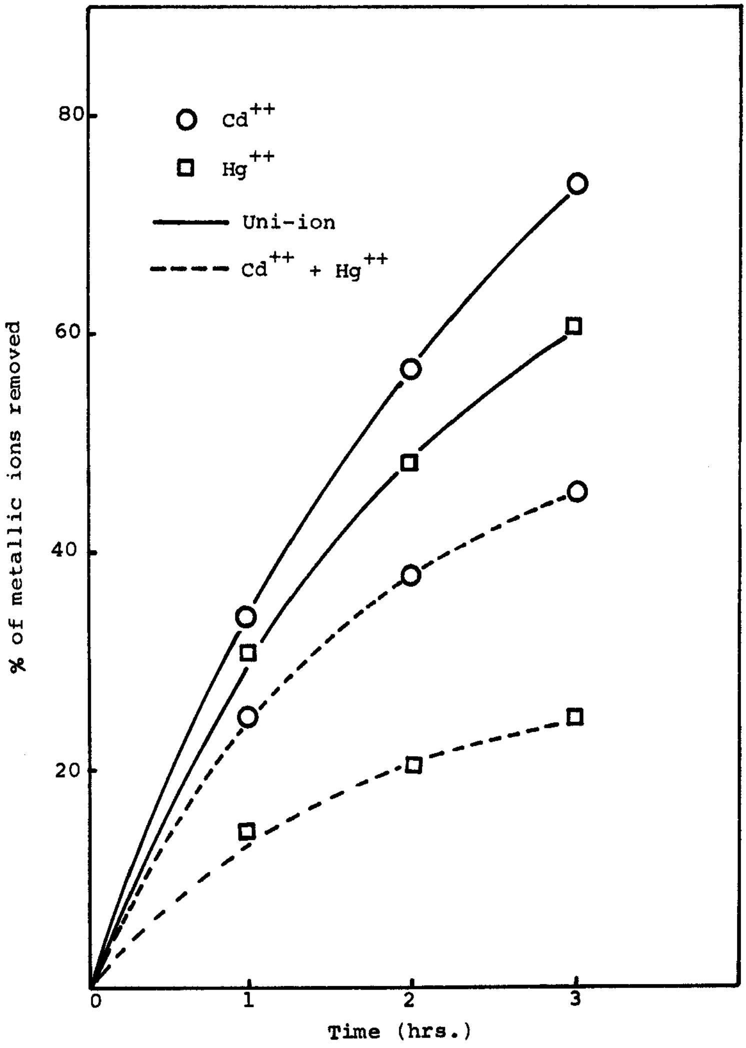

Fig. 6. Selectivity of the removal of Cd^{2+} and Hg^{2+}. Initial concentration of surfactant = 5.35×10^{-4} *M*, initial concentration of each metallic ion:(——) 1×10^{-4} *M* and (- -) 5×10^{-5} *M*.

method of recovery used was to employ H_2S for sulfidization and then to remove the precipitated H_2S by filtration. The mercury concentration in the filtrate was reduced to 0.1 ppm, and the regenerated surfactant was recycled.

Acknowledgments

The authors wish to thank Drs. W. H. McCoy and M. S. Brook for their helpful discussion. This project has been financed in part with federal funds from the Office of Saline Water, Department of the Interior, under Grant No. 14–30–3150.

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Received by editor February 5, 1975