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The Separation of Collectors Used as Coprecipitants of Trace Elements in Seawater by Adsorption Colloid Flotation*

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Abstract

Nine surfactants are screened for their ability to float six collectors, which have been used to coprecipitate trace metallic species in seawater, to the surface of seawater by adsorption colloid flotation as a function of pH.

INTRODUCTION

In the past the attention given to the determination and distribution of trace elements in natural waters was due primarily to their biogeochemical significance. More recently, there has been a mushrooming concern with their roles as environmental contaminants. Most trace elements cannot be determined directly in seawater because of lack of precise, accurate, and sensitive analytical methods and consequently require preconcentration prior to analysis. The preconcentration techniques of value include ion exchange, solvent extraction, cocrystallization, and coprecipitation. Of these, the last named is probably the favorite and most useful (*1*) because of its versatility and the wide range of elements which can be collected satisfactorily. Following filtration, the coprecipitate is determined by an appropriate method. The major disadvantages of coprecipitation are the time required for settling (several hours to overnight) and the tedious nature of the filtration. Recently, we published a series of studies (*2–6*) which described the use of conventional collectors in combination with

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an adsorbing colloid flotation process for the separation of a number of trace cationic and ionic metallic species in seawater. By employment of a collector–surfactant–air system at the optimum pH, it was possible to separate the trace metals, reproducibly and effectively, by floating them to the surface of the seawater in 2–3 min as an easily removable foam and thus eliminating the time required for settling and filtration. This work, moreover, has indicated that the technique may be of general applicability to other trace elements which can be separated from seawater by coprecipitation. The flotation method has been confined to a relatively small number of surfactants of those available and to two collectors. At the present time, we have not been able to predict in advance which surfactant–collector combination would work and consequently a trial by error procedure had to be adopted. This state of affairs has prompted a study to screen nine representative surfactants as to their ability to float, as a function of pH, six coprecipitating agents which have been employed to collect trace metals in seawater.

EXPERIMENTAL

Apparatus and Equipment

The separation was carried out in a 250-ml flotation cell of the type described previously (*2*). The pH of the seawater samples was determined with a Beckman Expandomatic pH meter.

Reagents

All chemicals used were of analytical reagent grade. Aqueous reagents were prepared in doubly distilled deionized water.

Collectors

$Fe(OH)_3$: $FeCl_3 \cdot 6H_2O$ (5.41 g/200 ml H_2O). One milliliter of reagent pipetted into 250 ml seawater sample.

$Th(OH)_4$: $Th(NO_3) \cdot 4H_2O$ (11.04 g/200 ml H_2O). One milliliter of reagent pipetted into 250 ml seawater sample.

$Al(OH)_3$: $Al_2(SO_4)_3 \cdot 18H_2O$ (13.33 g/200 ml H_2O). One milliliter of reagent pipetted into 250 ml seawater sample.

HgS: $HgCl_2$ (2.72 g/100 ml H_2O) and Na_2S (1.56 g/100 ml H_2O). Three milliliters $HgCl_2$ solution pipetted first followed by 2.5 ml Na_2S solution pipetted into 250 ml seawater sample.

CdS: $CdSO_4$ (3.85 g/100 ml H_2O) and Na_2S (1.56 g/100 ml

H_2O). Three milliliters $CdSO_4$ solution followed by 2.5 ml Na_2S solution pipetted into 250 ml seawater sample.

MnO_2: $MnSO_4 \cdot H_2O$ (4.22 g/250 ml H_2O) as stock solution, buffered $MnSO_4 \cdot H_2O$ [30 ml stock solution, 120 ml glacial acetic acid, 50 ml 4 *M* sodium acetate (27.22 g/50 ml H_2O)], and $KMnO_4$ (0.86 g/100 ml H_2O). The procedure suggested by Bachmann and Goldman (*7*) was used to precipitate the MnO_2.

(1) The seawater sample was heated to boiling.
(2) Five milliliters buffered $MnSO_4$ solution was added immediately while stirring rapidly.
(3) One-half milliliter $KMnO_4$ solution was added, also stirring constantly.
(4) The sample was allowed to stand to permit formation of the MnO_2 precipitate. Occasional stirring was employed.
(5) The sample was cooled to room temperature with the aid of an ice bath.
(6) The pH was adjusted and the surfactant injected.

Surfactants: 0.05 g/100 ml ethanol (0.05% w/v) unless otherwise noted.
Dodecyl benzene sodium sulfonate.
Lauryl pyridinium chloride.
N-Dodecylamine hydrochloride.
Sodium laurate.
Sodium lauryl sulfate.
Sodium stearate.
Stearyl amine.
Octadecyl trimethyl ammonium chloride (0.05 ml/100 ml ethanol).
Sodium octyl sulfate (0.125 ml 40% solution/100 ml ethanol).

General Procedure

The basic working procedure utilized clear, uncontaminated 250 ml seawater samples. The collector was added, the pH adjusted with HCl and NH_3 to cover a range of 3 through 9 where possible, and 2 ml of surfactant injected. The air flow for the flotation unit (*2*) was set at 7.5 psi at a rate of 2–4 ml/min. The air was turned on just prior to the injection of the surfactant and turned off after separation occurred. At times the air flow was terminated, the coprecipitate allowed to rise, and the air gently

returned in order to float, if necessary, any remaining precipitate. Only a relatively gentle air flow is necessary in order to effect a separation. A visual evaluation was made as to the ability of each surfactant to float a collector to the surface at a given pH and a rating made according to the following scale:

+++	stable foam or froth, cell cleared rapidly.
++	cell cleared, less rapidly.
+	cell cleared, color tint.
−	cell nearly cleared.
−−	cell cloudy.
−−−	no froth or foam, no clearance of cell.

RESULTS AND DISCUSSION

The results of the evaluation are compiled in Tables 1–6. The ability of a given surfactant to float a collector fluctuated widely and in most cases was dependent upon pH. The characteristics of the foam or froth formed also varied considerably. Noteworthy observations are provided in order to acquaint the reader with typical visual phenomena encountered.

$Fe(OH)_3$: Sodium lauryl sulfate worked very well at pH 3.0–6.0. A

TABLE 1

Collector: $Fe(OH)_3$

	pH						
Surfactant	3.00	4.00	5.00	6.00	7.00	8.00	9.00
Sodium stearate	−	−	+	+	+	−−	
Sodium laurate	+++	+++	+++	+++	+++	−	
Dodecylbenzene sodium sulfonate	+++	+++	+++	+++	++	−−	
Sodium octylsulfate	−	−	++	++	−−	−−	
Sodium lauryl sulfate	+++	+++	+++	+++	−−	−−−	
Octadecyltrimethyl ammonium chloride	−−−	−−−	−−−	−−	−−	−−	
N-Dodecylamine HCl	+	−−	−	−	−−	−−	
Stearylamine	−	−−	−−	+++	+++	−−	
Laurylpyridinium chloride	−−	−	+++	+++	+++	++	

TABLE 2

Collector: $Th(OH)_4$

Surfactant	pH 3.00	4.00	5.00	6.00	7.00	8.00	9.00
Sodium stearate		++	++	+++	+++	−	−−−
Sodium laurate		+++	+++	+++	+++	−	−−
Dodecylbenzene sodium sulfonate		−−	−−	−−	−−	−−	−−−
Sodium octylsulfate		−−−	−−	−−	−−−	−−−	−−−
Sodium lauryl sulfate		+++	+++	−−	−−	−	−−−
Octadecyltrimethyl ammonium chloride		+	−−−	−−−	−−−	−−−	−−−
N-Dodecylamine HCl		+++	+++	+++	+++	−	−−−
Stearylamine		−	+	+	+++	−−	−−−
Laurylpyridinium chloride		+	++	−	−−	−−−	−−−

TABLE 3

Collector: $Al(OH)_3$

Surfactant	pH 3.00	4.00	5.00	6.00	7.00	8.00	9.00
Sodium stearate		−	−	−	−−	−−−	+++
Sodium laurate		+	+	++	++	++	++
Dodecylbenzene sodium sulfonate			−−	−−	−−	−−	+++
Sodium octylsulfate			−−−	−−−	−−−	−−−	−−−
Sodium lauryl sulfate		+++	−	−−	−−	−−	+++
Octadecyltrimethyl ammonium chloride			−−	−−	−−	−	−−
N-Dodecylamine HCl		−−−	−−−	−−−	−−−	−−−	−−−
Stearylamine			−−−	−−−	−−−	−−−	−−
Laurylpyridinium chloride		−	−−	−−	−−−	−−−	−−

TABLE 4

Collector: HgS

Surfactant	pH						
	3.00	4.00	5.00	6.00	7.00	8.00	9.00
Sodium stearate	+++	++	++	−	−−−	−−−	
Sodium laurate	+++	+++	+++	+++	+++	+++	
Dodecylbenzene sodium sulfonate	−−−	−−−	−−−	−−−	−−−	−−−	
Sodium octylsulfate	+++	+++	+++	+++	+++	+++	
Sodium lauryl sulfate	−−−	−−−	−−−	−−−	−−−	−−−	
Octadecyltrimethyl ammonium chloride	+++	+++	+++	+++	+++	+++	
N-Dodecylamine HCl	+++	+++	+++	+++	+++	+++	
Stearylamine	+++	+++	+++	+++	+++	+++	
Laurylpyridinium chloride	+++	+++	+++	+++	+++	+++	

TABLE 5

Collector: CdS

Surfactant	pH						
	3.00	4.00	5.00	6.00	7.00	8.00	9.00
Sodium stearate	−−	++	++	++	++	++	+++
Sodium laurate	−	+++	+++	+++	+++	+++	+++
Dodecylbenzene sodium sulfonate	−−−	−	+	+++	+++	+++	+
Sodium octylsulfate	−−	−−	+	++	++	+++	+++
Sodium lauryl sulfate	−−−	−−	−	+++	+++	+++	+++
Octadecyltrimethyl ammonium chloride	+++	+++	+++	+++	+++	+++	+++
N-Dodecylamine HCl	++	++	+++	+++	+++	+++	+++
Stearylamine	+	+	+	++	++	++	+++
Laurylpyridinium chloride	++	++	++	+++	+++	+++	++

TABLE 6

Collector: MnO_2

	pH						
Surfactant	3.00	4.00	5.00	6.00	7.00	8.00	9.00
Sodium stearate	+++	+++	+++	+++	+++	+++	−−−
Sodium laurate	+++	+++	+++	+++	+++	+++	+++
Dodecylbenzene sodium sulfonate	+++	+++	+++	+++	+++	+++	−−−
Sodium octylsulfate	+++	+++	+++	+++	+++	−	−−−
Sodium lauryl sulfate	−−−	−−	−−	+	+	+++	−−−
Octadecyltrimethyl ammonium chloride	+++	+++	+++	−	−	−	−−−
N-Dodecylamine HCl	+++	+++	+++	+++	+++	+++	+++
Stearylamine	+++	+++	+++	+++	+++	+++	++
Laurylpyridinium chloride	+++	+++	+++	+++	−	−	−−−

striking stable soapy white foam was formed with a yellow brown precipitate of $Fe(OH)_3$ on top. Similar results were observed with dodecyl benzene sodium sulfonate. This collector, probably the most widely used, has proved to be extremely effective in conjunction with several surfactants in picking up, by flotation, model trace elements studied (*4*). The foams with sodium laurate and lauryl pyridinium chloride were gel-like rather than foamy.

$Th(OH)_4$: At pH 3.0 very little coprecipitate was obtained. The froth formed was gel-like. None of the surfactants tested were outstanding.

$Al(OH)_3$: This agent did not precipitate well at pH 3.0–4.0. The use of sodium laurate produced a gel-like white froth. A pH of 9.0 worked well occasionally but in most cases negative results were obtained.

HgS: Na_2S should not be added to the seawater first since a very light precipitate of HgS was formed. When $HgCl_2$ was added followed by Na_2S, a good precipitate of HgS formed immediately. The use of *N*-dodecyl amine hydrochloride, lauryl pyridinium chloride, and stearyl amine is recommended since they were effective and worked rapidly.

CdS: The collector worked well with many of the surfactants tested. Unfortunately, according to the literature (*1*), very few trace elements are collected by this agent, the notable exception being mercury.

MnO_2: A relatively complicated and time-consuming procedure has to be followed in order to produce this light fluffy dark brown coprecipitate. It works well with many of the surfactants over a wide pH range (Table 6). pH 7.0 and 8.0 worked most effectively with sodium stearate. A foamy froth was formed with dodecylbenzene sodium sulfonate which floated to the surface at pH 7.0 in 15–20 sec. A similar phenomenon was observed with *N*-dodecylamine hydrochloride although a brownish tinge was observed in the underlying water in some instances. Sodium laurate worked well at pH 5–9 although the cell appeared to clear up more rapidly on the acid side. Stearylamine worked rapidly in the entire pH range tested. Lauryl pyridinium chloride was most effective on the acid side.

In conclusion, this study is intended to be of assistance to a worker interested in the separation of a trace element from seawater by flotation. It was not considered necessary to include directly the trace elements in the screening procedures. Riley and Skirrow (*1*) have provided comprehensive tables which include information on the coprecipitation of trace metallic consituents, radio-elements and radio-nuclides. Armed with the knowledge of the trace element that is picked up by a given collector, one may select the surfactant which will float the collector and the pH at which the separation is effective. The separation works best when flotation is commenced immediately after introduction of the collectors and adjustment of the pH. It is emphasized that it is necessary to verify the separation by standard addition techniques; optimize the parameters of pH, volume, and concentration of surfactant; and finally evaluate recovery data through analysis for the trace element. The majority of collectors which are known to pick up trace elements have been included in this study. The nine surfactants, on the other hand, are representative of many others which are available and remain as yet untested.

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