

《Original》

## Adsorptive Bubble Separation of Zinc (II) Using Capric Acid as Collector

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추출제로 카프르산을 사용한 아연(II)의 흡착 기포 분리

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### Abstract

The removal of zinc (II) from aqueous solutions has been studied by the adsorptive bubble separation processes such as solvent sublation and foam fractionation processes using capric acid as collector. The efficiency of the removal process has been studied by changing the ionic strength and pH and the bubble separation method has been compared with the solvent extraction process using the capric acid dissolved in benzene as extractant.

### 요 약

흡착 기포 분리에 의하여 수용액으로 부터 아연(II)을 회수하는 방법에 관하여 연구하였다. 그리고 흡착 기포 분리에서 용매부선 과정과 거품 분별 과정이 채용되었고 이들 분리 과정에서 카프르산을 아연의 회수 물질로 사용하였다. 이온 강도 및 수소이온의 농도가 분리 과정의 효율에 어떤 영향을 미치는지를 기술하였으며, 추출제로 벤젠에 녹은 카프르산을 이용한 용매 추출과정과도 상호 비교하였다.

### Introduction

Recently, the use of adsorptive bubble separation techniques is taking its place among the array of processes commonly used for the treatments of municipal and/or radioactive waste waters.

A considerable number of studies have been made on the use of long-chain carboxylic acids

and their salts as extractants of metal ions,<sup>1-4</sup> but the studies on their uses in adsorptive bubble separation have been limited.<sup>5-6</sup>

Jones and Robinson made comparisons between solvent extraction and adsorptive bubble separation of nickel,<sup>6</sup> and the latter was restricted mainly to solvent sublation, using versatic acid (and/or its salts) and octan-1-ol as collector and immiscible organic solvent, respectively. Solvent sublation is defined here as a nonfoaming

adsorptive bubble separation in which enriched materials on bubble surfaces are collected into immiscible organic phases.<sup>5</sup> However, octan-1-ol which had been used as an organic solvent was found to behave as an extractant as well and this fact could give possible difficulties in comparisons between the two processes.<sup>6</sup>

In the present work, the study of solvent sublation of zinc ion from aqueous solution has been carried out to compare adsorptive bubble separation with solvent extraction processes, using capric acid and/or its sodium salt as a collector in the adsorptive bubble separation as well as an extractant for solvent extraction. In addition to solvent sublation, studies of foam fractionation of zinc ion from aqueous solution have been carried out. The term "foam fractionation" is used here as the process of foaming-off dissolved material from a solution via an adsorption at the bubble surfaces. In the present work, benzene has been chosen as an immiscible organic solvent, so as to eliminate the difficulties when using less volatile polar solvents such as octan-1-ol<sup>6</sup> or to compare more easily the separation data obtained here with those published by other workers.<sup>1,2,6</sup>

## Experimental

### material

Capric acid (AR grade, Aldrich Chemical Co.) was used without further purification. Sodium caprate was prepared by neutralizing the free acid. An appropriate amount of the acid was dissolved in benzene and diluted to an appropriate concentration with benzene as the organic phase in solvent extraction. A stock solution of zinc perchlorate was prepared by eliminating chloride ions from zinc chloride (AR grade, Wako Pure Chem. Ind.) in a hot perchloric acid solution. Sodium perchlorate (AR grade, Hayashi Chem. Co.) was used to

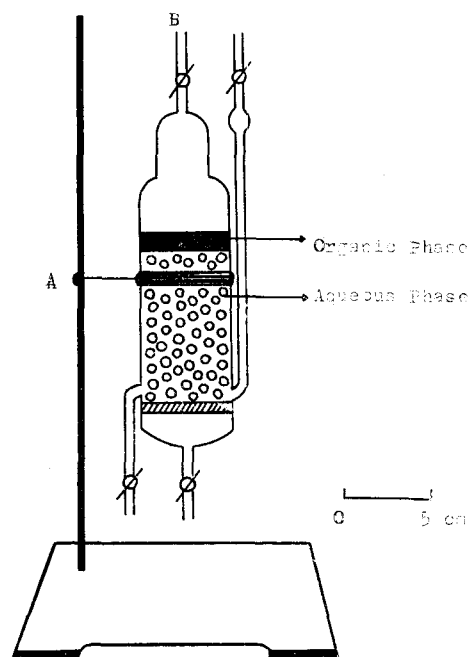


Fig. 1. Experimental Apparatus for Adsorptive Bubble Separation.

adjust the ionic strength of various aqueous solutions. Disodium EDTA (AR grade, Wako Chem. Co.), EBT (AR grade, Junsei Chem. Co.) and others were used as received.

### Adsorptive Bubble Separation Process

The apparatus for these studies was made as suggested by previous workers as follows.<sup>6,7</sup>

A glass cell of 8 cm internal diameter and 1 L capacity was used in the study as shown in Fig. 1. A glass frit (Pyrex porosity No. 4) of diameter 7 cm was fused into one end of the cell and two sockets were included in the lower port of the cell. One of these was fitted with a two-way tap to enable samples to be taken from the cell and other socket was used for feeding samples. The bottom of the cell was fitted with an inlet tube of nitrogen, which was used as the source of gas bubbles. The gas was passed through a bubbler containing water to saturate the gas and through an empty bubbler before being admitted into the

cell. Gas flow rates of the order of 60 cm<sup>3</sup> per min were adjusted when 40 mL benzene and 500 mL of sodium caprate solution of appropriate ionic strength and pH were used in the cell. Similar flow rates were also used for foam fractionation studies. Initial zinc concentration and the content ratio of sodium caprate to zinc in the both processes of foam fractionation and solvent sublation are  $1.0 \times 10^{-3}$  M and 2, respectively. A run time of 60 min was applied for the attainment of the steady state condition in both the solvent sublation and foam fractionation. The top of the cell was fitted with an outlet tube B to enable any excess foam produced during the runs to be collected. This outlet tube was also used for the separation between two phases by reversing the cell through the axis A shown in Fig. 1 after solvent sublation was completed.

pH measurements were made with a Fisher Accumet pH meter(model 140) and a combination electrode for the aqueous solutions.

#### Solvent Extraction Process

Appropriate aqueous solutions of zinc perchlorate (ca. 0.01M) were adjusted to the appropriate values of ionic strength (ca. 0.1M), using an sodium perchlorate. The pH of aqueous solutions was adjusted with sodium hydroxide and perchloric acid. Organic phases of 0.5M capric acid in benzene were prepared. A 15 mL volume of each aqueous solution was then equilibrated with an equal volume of the organic phase in a glass-stoppered tube of 50 mL capacity. In order to ensure that equilibrium was attained, the tube was rotated head-over-tail for 1 hr. The phases were allowed to settle for one hour before being separated.

#### Analysis of Zinc Content

The zinc content in the aqueous solution was determined compleximetrically by use of EBT

as an indicator<sup>8</sup>. The zinc content in the organic phase was determined similarly after back extraction of zinc ions into 0.5 M hydrochloric acid.

### Results and Discussion

As indicated in Fig. 2 the caprate ion acts as a collector for zinc on both foam fractionation and solvent sublation processes. For the foam fractionation, an increase in the ionic strength of the aqueous solution resulted in a reduction on the removal of zinc ions at any given pH. In addition, the amount of foam produced in the system is decreased as the ionic strength increases, and the results are similar to the removal of nickel ions by the versatate anion collector<sup>6</sup>. Nakasuka et al. have indicated the possibility of coextraction of zinc along with sodium by caprate ions. They have demonstrated further the extractability of sodium ions by caprate ions even in the absence of zinc ions<sup>1</sup>. The reduction in the efficiency of foam frac-

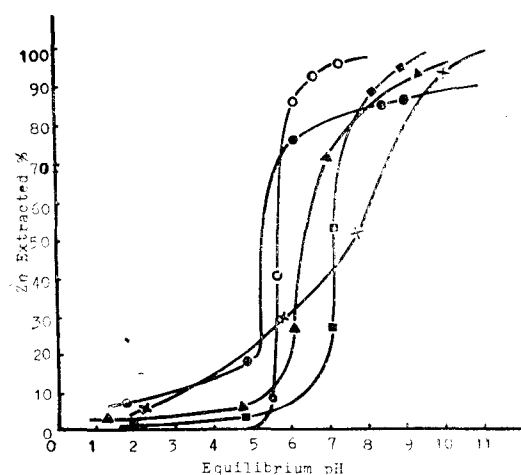


Fig. 2, Zinc Extracted vs. Equilibrium pH at Various Ionic Strength by Foam Fractionation (●: No NaClO<sub>4</sub>, ▲:  $1.0 \times 10^{-2}$  M, ■:  $1.0 \times 10^{-1}$  M), by Solvent Sublation (×:  $1.0 \times 10^{-2}$  M) and by Solvent Extraction (○:  $1.0 \times 10^{-1}$  M)

tionation of zinc with increasing ionic strength probably arises from competition for the caprate collector between zinc and sodium counter ions but not from coextraction of both ions by the collector. In addition, the presence of electrolyte will affect the stability of the foam and will change the extent of ionization of the collector, affecting the equilibria between soluble and insoluble zinc species in the system as well, as described by previous workers.<sup>6</sup>

Solvent sublation was found to give a greater removal of zinc at low pH but a lower removal at high pH compared to the corresponding foam fractionation as shown in Fig. 2. The difference in the removal of colligend could be attributable to the difference in the phase number between two processes as described by others<sup>6</sup>. In addition, the redispersal of the colligend complex may be aided by the presence of the benzene phases. These low recoveries, particularly at high pH, can be contrasted with the corresponding high values of solvent extraction as shown in Fig. 2.

The removal of the colligend by adsorptive bubble separation methods was dependent on pH values as shown in Fig. 2. The low recoveries on the solvent sublation compared to the solvent extraction, particularly at high pH, could be attributable to the decrease of capric acid concentration in the organic with increasing pH due to dissociation of the acid into the aqueous phase, considering that the concentration of the collector (0.002M) in the solvent sublation is lower than the concentration (0.5M) in solvent extraction.

The pH values have a marked effect on the nature and charge of the colligend as well. A consideration on the species distribution plot obtained from published stability constant data<sup>9</sup>, assuming the solution is ideal, show that the hydrated zinc cation is the main species up to about pH 8.0. At pH 8.2 about 10 per cent

of zinc is present as a sparingly-soluble hydroxy species and at pH 9.5 this increases to a maximum value of 50%, but in case of nickel<sup>6</sup> the corresponding maximum value is 95%. However, the difference between these values could not affect the efficiency of the metal removals because of rapid equilibrium between the species at higher pH. When the ionic strength increases the zinc removal curve is shifted to a slightly higher pH. The fact could be attributable to a shifting of the zinc species distribution as the ionic strength increases.

On the removal of metals by adsorptive bubble separation, an ion flotation mechanism will be applied at lower pH, whereas precipitate flotation mechanism will be applied at higher pH. In the pH range suitable for hydroxide formation, a combination of these two mechanisms may be applicable. The maximum removal of zinc by solvent extraction as well as adsorptive bubble separation were obtained around at the pH corresponding to the metal hydroxide, and the facts are generally in agreement with the formation of the metal hydroxide<sup>6</sup> on the nickel removal by versatic acid.

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