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 Rubin, Alan J. and Lapp, Wilbert L.(1971) 'Foam Fractionation and Precipitate Flotation of Zinc(II)', Separation Science and Technology, 6: 3, 357 — 363

To link to this Article: DOI: 10.1080/00372367108055561

URL: http://dx.doi.org/10.1080/00372367108055561

SEPARATION SCIENCE, 6(3), pp. 357–363, June, 1971

Foam Fractionation and Precipitate Flotation of Zinc(II)

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Summary

The hydrolytic behavior of a metal can be related to its removal by foaming. In this study the effect of pH and ionic strength on the foam separation of 0.1 m*M* zinc(II) was investigated using different concentrations of sodium lauryl sulfate as the collector. At low pH Zn^{2+} ion was removed by foam fractionation while above pH 8 $Zn(OH)_2(s)$ was removed by precipitate flotation. The results demonstrate that precipitate flotation is a more efficient removal process than the foam separation of soluble metal species.

INTRODUCTION

Metals in solution as ions or in suspension as precipitate may be removed from a liquid phase by a number of separation processes. The nature of the transport to the foam phase depends primarily on the state of dispersion of the metal salt. Flotation results whenever the metal and its reaction product with the collector surfactant are insoluble. When the system is completely homogeneous a partition mechanism operates and the process is called foam fractionation (*1*). With hydrolyzable metals, then, the mechanistic regime is determined by the pH of the solution (*2*, *3*).

Recently the authors described a study in which the removal of lead(II) was examined as a function of pH at different collector concentrations and ionic strength (*4*). Precipitate flotation was not observed at any pH since lead is completely soluble at 1.0×10^{-4} *M*, the concentration examined. In contrast, zinc(II) forms the insoluble hydroxide in the ca. $10^{-4} M$ concentration range; hence, precipitate flotation would be expected.

EXPERIMENTAL

All runs were conducted in batch using an experimental volume of 400 ml. A 600-ml glass Büchner funnel with a fine sintered-glass frit served as the foam column. The experimental apparatus as shown schematically in Fig. 1 consisted essentially of a nitrogen cylinder in series with a gas humidifier, glass-wool filter, and low-flow-rate controller. A fine needle valve was used to adjust the gas flow rate. Line pressure and gas rate were measured with an open mercury U-tube manometer and rotameter, respectively. This apparatus and the experimental procedures have been described in detail elsewhere (*2–4*).

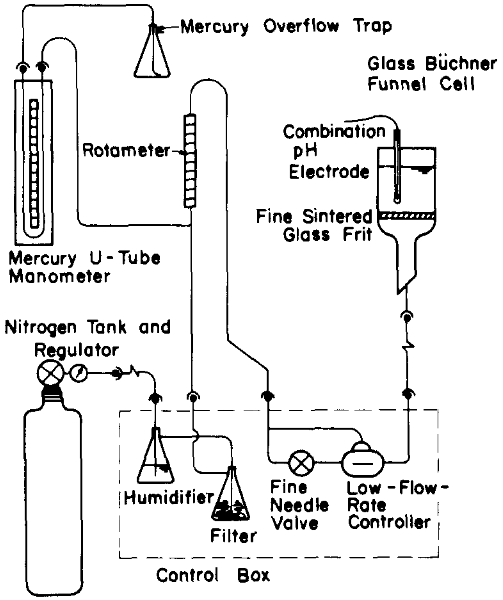

FIG. 1. Schematic of experimental apparatus.

Stock solutions of the metal were prepared from reagent grade zinc nitrate using deionized distilled water. Solutions of reagent grade sodium hydroxide, sodium perchlorate, and nitric acid were used to adjust the ionic strength and/or pH. The collector was sodium lauryl sulfate and absolute alcohol was used as the frother. Zinc concentrations were determined by a modified dithiozone procedure. A single extraction in chloroform was carried out at pH 11 using an ammonia–citric acid buffer. The collector did not interfere with this analysis and was itself determined using the methylene blue method for anionic surfactants (*5*). Transmittances were measured using a Bausch and Lomb Spectronic 20, and a Sargent model LS pH meter and large combination electrode were used to monitor pH during each experimental run.

RESULTS AND DISCUSSION

Typical results with 0.1 m*M* zinc nitrate at different pH, ionic strength, and molar ratio, *S*, of collector to metal are shown in Fig. 2.

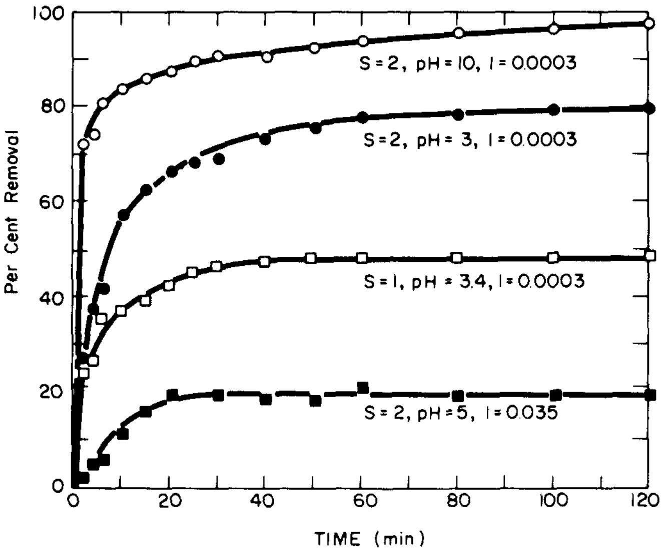

FIG. 2. Foam separation of 0.1 m*M* zinc(II) with varying amounts of sodium lauryl sulfate at different pH and ionic strength.

At a gas flow rate of 24.8 ml/min the maximum or steady-state removals were reached in about 20 to 40 min. Steady-state removals as estimated by 100-minute removal data at several collector concentrations are summarized in Fig. 3 as a function of pH and in Fig. 4 as

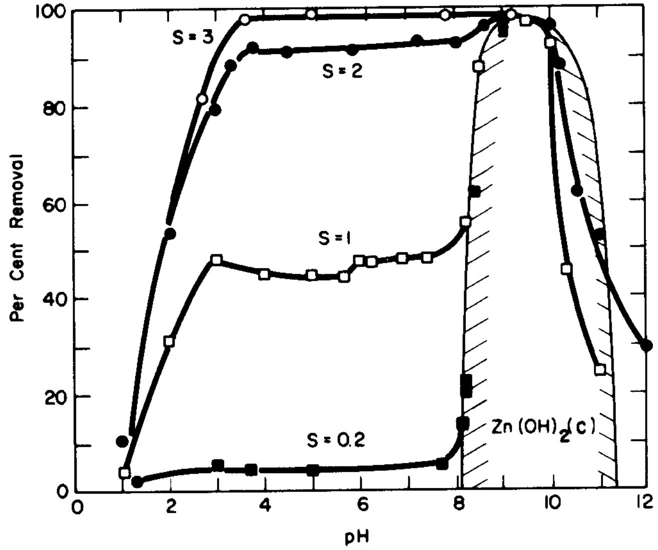

FIG. 3. Effect of pH on the foam separation of zinc(II) at different collector ratios.

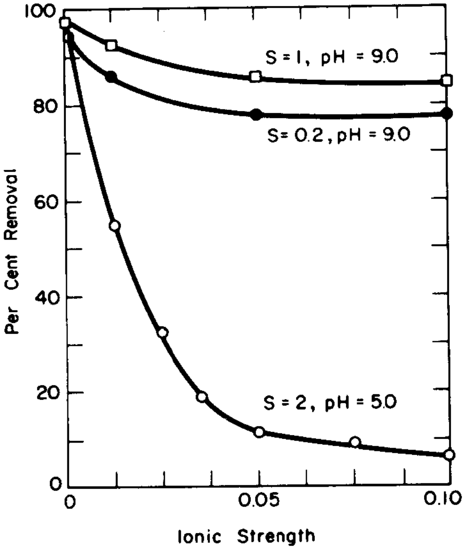

FIG. 4. Effect of ionic strength on the foam separation of zinc(II) at pH 5 and 9.

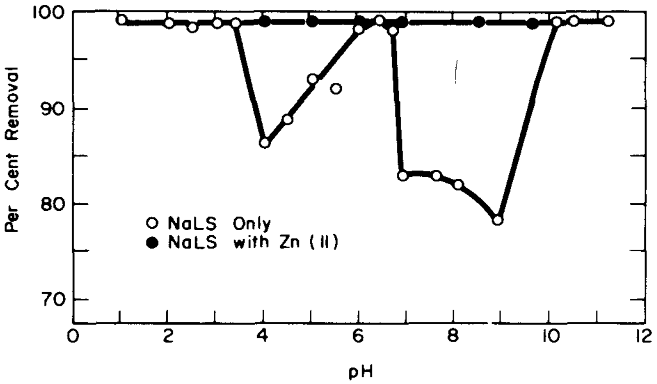

FIG. 5. Foam fractionation of sodium lauryl sulfate with and without zinc(II).

a function of ionic strength. The effect of zinc on the removal of sodium lauryl sulfate is shown in Fig. 5.

These results can be explained by examining the hydrolytic reactions of zinc (*6*):

$$Zn^{2+} + H_2O = ZnOH^+ + H^+;\ pK_1 = 9.85 \quad (1)$$

$$ZnOH^+ + H_2O = Zn(OH)_2(aq) + H^+;\ pK_2 = 8.0 \quad (2)$$

$$Zn(OH)_2(aq) + H_2O = Zn(OH)_3^- + H^+;\ pK_3 = 9.9 \quad (3)$$

$$Zn(OH)_3^- + H_2O = Zn(OH)_4^{2-} + H^+;\ pK_4 = 12.7 \quad (4)$$

$$Zn(OH)_2(s) = Zn(OH)_2(aq);\ pK_d = 5.59 \quad (5)$$

For simplicity the waters of hydration are not shown. At the concentration examined there was no evidence of soluble polynuclear species and thus the above are adequate to completely describe the distribution of zinc(II) with pH. These equilibria reveal that the free unhydrolyzed Zn^{2+} ion is the species in greatest concentration up to a pH of about 8; the concentration of $ZnOH^+$ being almost completely negligible. Above pH 8.5 and below pH 11 the insoluble hydroxide is predominant with the soluble $Zn(OH)_2$ species making up less than 3% of the total.

As shown in Fig. 3 the removals are greatest, even at very low collector concentrations, in the pH region corresponding to the formation of $Zn(OH)_2(s)$. Agreement with the lower pH limit of hydroxide formation is excellent. Removal above pH 10 decreases upon the formation of negatively charged zinc species; however, this occurs at lower pH than predicted by the solubility limits of the precipitate on its basic side. There is the possibility that the precipitate has acquired a negative charge at the higher pH due to adsorption of hydroxide ions and thus has a lowered affinity for the collector.

Although the removals are relatively insensitive to collector concentration above pH 8, at lower pH the removal of Zn^{2+} is quite dependent upon this parameter. At a stoichiometric collector ratio ($S = 2$) the removals averaged about 92% between pH 3 to 8, forming a plateau in the removal curve. This plateau is indicative of a single predominant ionic species. The difference between the observed removal and the theoretical of 100% is due to the instability of the zinc–lauryl sulfate complex. Removals drop off sharply below pH 3, most likely due to protonation of the collector.

This latter effect, competition between zinc and other cations in solution for the collector (the "ionic strength" effect), is demonstrated in Fig. 4. Experiments were conducted at pH 5 where the Zn^{2+} ion predominates and at pH 9 where essentially all of the metal is present as the precipitate. Removals at the lower pH are significantly reduced with increasing salt concentration, the results resembling those found earlier for copper and lead (*4*). The figure also shows a fundamental difference between precipitate flotation and the foam separation of soluble species—presumably the foam fractionation of Zn^{2+} in this case. Precipitate flotation is significantly less affected by the presence of high concentrations of competing cations even at very low collector concentrations ($S = 0.2$ in Fig. 4). However, the effect of cations in reducing removals is greater with zinc hydroxide than observed earlier with copper hydroxide (*3*).

The foam separation of sodium lauryl sulfate was also examined as a function of pH. Removals approached 100% over most of the pH range except pH 4 where they dropped to 87% and between pH 7 and 9 where the removals were reduced to between 78 and 83%. In the presence of zinc as shown in Fig. 5 or upon increasing the ionic strength removals were complete over the entire pH range. It was observed that collector removal was more rapid at high salt concentrations and the foams were drier. Sengupta and Pipes (*7*) also observed that the foams due to ABS were wetter at lower salt concentrations. In general the zinc–lauryl sulfate foam was much less stable than that produced when foaming lead, rapidly being redissolved into the bulk after ceasing the gas flow. No scum was produced and as with the foam separation of soluble copper the removal mechanism was most likely a foam fractionation (see Ref. *2* for further discussion).

CONCLUSION

The foam separation of zinc(II) was investigated as a function of pH, collector concentration, and ionic strength. The results have been related to the hydrolytic behavior of the metal. Zn^{2+} is the predominant form of the metal below pH 8 and is apparently removed by a foam fractionation mechanism. The per cent removals of soluble zinc increased with increasing concentration of sodium lauryl sulfate, an anionic collector. The addition of salts adversely affected the removals. Above pH 8 zinc was present as the insoluble hydroxide and was removed by precipitate flotation. This process was much less sensitive to ionic strength and collector concentration. From the results it can be concluded that pH 9.2 is the optimum for zinc removal.

Sodium lauryl sulfate was completely removed over the entire pH range investigated only in the presence of zinc or at high salt concentrations.

Acknowledgment

This work was supported in part by a grant from the Office of Water Resources Research, U. S. Department of the Interior.

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Received by editor July 23, 1970