Separation Science and Technology

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

Foam Fractionation of Negative Ions

Mohsen Moussavi[a]
[a] SHIRAZ UNIVERSITY, SHIRAZ, IRAN

To cite this Article Moussavi, Mohsen(1994) 'Foam Fractionation of Negative Ions', Separation Science and Technology, 29: 8, 1087 — 1093

To link to this Article: DOI: 10.1080/01496399408005619

URL: http://dx.doi.org/10.1080/01496399408005619

SEPARATION SCIENCE AND TECHNOLOGY, **29**(8), pp. 1087–1093, 1994

Foam Fractionation of Negative Ions

MOHSEN MOUSSAVI
SHIRAZ UNIVERSITY
SHIRAZ, IRAN

ABSTRACT

Negatively charged ions can be separated successfully by foam fractionation. Among them, free cyanide ions were removed by cetyl trimethyl ammonium bromide or a similar compound. At low concentrations (<5 mg/L), quantitative removal of free cyanide ions was observed. Further observations revealed that when the concentration was increased to 57 mg/L, a reduction in concentration equivalent to 47% could be achieved. Finally, a correlation between cyanide separation and surfactant concentration was found.

INTRODUCTION

The technique of separation by foam was known as early as the 1930s (1), but the term "foam fractionation" may have come into use with Cassidy (2). Since then, positive ions have drawn the attention of numerous investigators, and considerable achievements have resulted. Even more attention has been paid to the separation of non-ionized species by foam separation. However, only sporadic surveys have been recorded for negative ions separation by foam fractionation.

2-Naphthoic acid and 1-naphthylamine were foam fractionated with an enrichment ratio of up to 5.4 and 1.31, respectively, by using a cationic surfactant polyethoxy stearyl methyl ammonium chloride (3). Phenol was removed from aqueous solutions by using hexadecyl pyridinium chloride with an overall efficiency of separation of 73%. The phenol concentration was 1000 ppm and the surfactant concentration was 0.05 M (4). More recently, some polychloro derivatives of phenol were quantitatively removed by using hexadecyl trimethyl ammonium bromide with a surfactant molar concentration of 0.0021, almost 25 times larger than the cmc. The above derivatives were also removed quantitatively by using anionic sodium dodecyl sulfate (5). The removal of some heavy metals, such as Zn, Cd, and Co in the form of an anionic complex, proved to be feasible by using cationic cetyl trimethyl ammonium bromide as the collector, with various degrees of removal efficiency based on the presence of different ligands and acids (6).

CERTAIN ASPECTS PERTINENT TO FOAMS

The efficiency of ion removal—as well as the enrichment ratio—are sharply lowered by liquid entrainment. The liquid sheath around foam bubbles has its highest thickness as the bubbles leave the liquid pool. Most liquid with a composition identical to that of the pool but entirely different from that of the foam film will drain back into the liquid pool if the foam is allowed to rise through vertical tubing. Thus, the efficiency of ion removal and the enrichment ratio are improved. The amount of drainage depends upon the amount of time the bubbles are rising. The drained fraction of the entrained liquid is exponentially proportional to the elapsed time since the foam bubble left the liquid pool. For the lauryl sulfate–water system, the following relation was suggested:

$$V_d = 0.7t^{0.05} \tag{1}$$

where V_d is the fraction of entrained liquid which drained back after t minutes (7). It was also noticed that the rate of drainage decreased if copper sulfate was added to the pool.

Foams are drained by aging. The process of aging leads to a higher enrichment ratio and a higher recovery. However, the drained foam bubbles collapse faster, and thus fractionation is impaired.

The rate of bubble collapse can be estimated by the following treatment. As the bubbles collapse, the remaining bubbles become larger. So the increase in bubble diameter is a direct function of bubble collapse. If β is the fraction of collapsed bubbles, then the change in bubble radius, R, as it rises through a vertical foam column, Z, will be

$$dR/dZ = (R/6G)\beta \tag{2}$$

where G is the superficial gas velocity. This is based on the assumption that all bubbles have the same size, the temperature is constant, and the liquid holdup in Plateau borders is negligible (8). Rearranging the above equation yields the effect of bubble collapse on bubble size along the vertical foam path:

$$R_t = R_0 \exp(\beta Z/6G) \tag{3}$$

where R_0 and R_t represent the initial and aged bubble sizes, respectively, and the ratio can lead to an estimation of β.

The addition of electrolytes may increase or decrease the rate of drainage of entrained liquid depending on the tendency of the surfactant for hydration. It has been observed that the addition of sodium sulfate will increase drainage if the surfactant is sodium laurate and will decrease if the surfactant is sodium lauryl sulfate (9). It can be expected that an increase in bubble rise velocity will inhibit the rate of drainage drastically (10). It has also been demonstrated that electrolytes change the number of molecules in a surfactant micellar aggregate (11).

EXPERIMENTAL

Apparatus

A unit based on continuous operation was utilized in this study. A Pyrex column of about 150 mL effective volume and 5 cm (i.d.) was employed for separation. The bottom of the column was terminated with a fritted glass-type sparger (ASTM 40-60 type C). The top of the column was tapered to a ground glass joint to which vertical neck of glass tubing (1.0 cm i.d.) was fixed. The vertical neck was utilized to facilitate the drainage of the entrained liquid back into the liquid pool. Finally, the open end of the neck was directed to a foam receiver by a horizontal and a downward-directed vertical piece of tubing.

Pressurized air was passed first through a bed of glass fibers and then through a bed of molecular sieve type 5A for removal of solid fine particles and oily droplets. Subsequently, its flow rate was measured and then it was saturated with moisture and eventually admitted into the liquid pool inside the glass column through the fritted glass sparger at a constant rate of 20 mL/min.

The feed was entered at the top of the column and the reclaimed water (raffinate) was removed from the bottom, thus the column behaved overall as a stripper.

The drained foam, after leaving the liquid pool, was collapsed at 70°C by an electric thermal blanket wrapped around the horizontal part of the glass tubing.

TABLE 1
Characteristics of the Surfactant Cetyl Trimethyl Ammonium Bromide (CTAB)

Formula	$C_{19}H_{42}NBr$
Molecular weight	364.5
CMC (at 25°C)	8.0×10^{-4} mol/L (12)

Distilled water for preparation of the solutions was taken from a unit which distilled tap water by evaporation–condensation. The product of this unit was boiled off from a solution containing 1% potassium permanganate and 0.49% sulfuric acid. The condensate of this unit was used for the preparation of surfactant and feed solutions.

The surfactant selected was cetyl trimethyl ammonium bromide (CTAB) with the characteristics appearing in Table 1.

Analytical

The concentration of the surfactant was measured by a method based on the capillary action of the solution. Further details are given by Moussavi and Carleson (7).

The concentration of the removing compound was generally measured by a gas chromatographic technique. The complex product of the removing compound and the surfactant was transferred into a chloroform phase, and samples were injected into a column with a packing of Chromosorb W coated with OV-107, OV-17, or DC200 based on the best response received from the detector.

The detector was a thermal conductivity bridge, and the chosen carrier gas was helium. The concentration of unreacted removing compound, such as CN^-, was measured by ion-selective membrane electrodes.

RESULTS AND DISCUSSION

The formation of the complex resulting from the reaction of CN^- and CTAB is concentration dependent and is in equilibrium with the reactants. At low concentrations of cyanide (<5 ppm) and a molar concentration ratio of $CTAB/CN^- = 1.8$, a total separation of cyanide is possible.

As the concentration of CN^- increases, the removal efficiency decreases, however, the amount of cyanide removed per unit weight of CTAB will increase (Fig. 1).

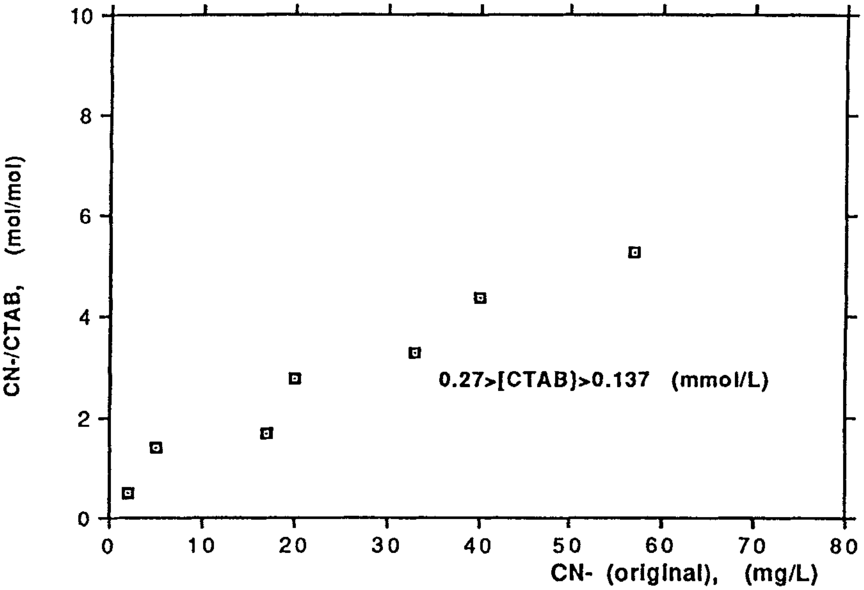

FIG. 1 Effect of [CN$^-$] on CTAB efficiency of removal.

A relationship developed in another study (11) relates to a good approximation the concentration ratio of cyanide ions in the treated solution (x_r) to that of the original solution (x_0):

$$x_r/x_0 = 1/(0.0168C_s + 1) \tag{4}$$

where C_s is the CTAB concentration (mg/L). This relationship may be used to predict the residual cyanide in the treated solution. Based on the observed data, a correlation may be derived to relate the residual concentration of cyanide species as a function of surfactant concentration in the solution. For any original cyanide concentration x_0, the residual concentration in the solution at equilibrium, x_r, can be calculated by

$$x_r = Sx_0 - a(C_s)^{0.5} \tag{5}$$

where S = slope of the relative curve and a = 0.2. It is clear that based on the critical micelle concentration of CTAB (291.6 mg/L), the maximum allowable cyanide concentration in the feed solution must be less than or equal to 16 mg/L if total removal is desired (Fig. 2).

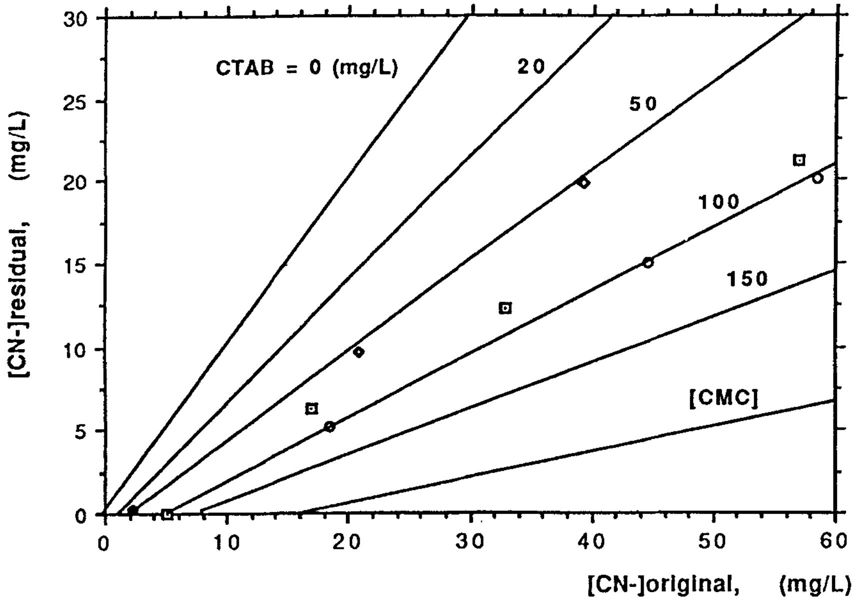

FIG. 2 Effect of [CN⁻] original on [CN⁻] residual.

CONCLUSIONS

A literature survey reveals that in spite of a promising potential for the separation of negative ions by foam separation, few investigators have contributed to this field compared to that of positive ions.

This study shows that quantitative removal of free cyanide ions is possible at concentrations less than or equal to 5 mg/L. As the cyanide concentration is increased to 57 mg/L, the removal efficiency is reduced to 47%.

Other results of this study show that separation does not only take place through chemical complexation. It is obvious (Fig. 1) that the process of separation is also influenced by electrical attractive forces of charged counterions on the solution–air bubble interface.

ACKNOWLEDGMENT

This work was financially supported by a grant through the Shiraz University Research Council (Grant 69-EN-627-331).

REFERENCES

1. R. Dubrisay, *Chim. Ind.*, *1045* (June 1933).
2. H. G. Cassidy, "Adsorption and Chromatography," in *Technique of Organic Chemistry* (A. Weissberger, Ed.), Interscience, New York, 1951, pp. 260–262.
3. B. L. Karger and L. B. Rogers, *Anal. Chem.*, *33*, 1165–1168 (1961).
4. S. D. Christian et al., *Langmuir*, *1*, 564–567 (1985).
5. E. Pramauro, *Ann. Chim.* (*Rome*), *80*, 101 (1990).
6. K. Jurkiewicz, *J. Colloid Interface Sci.*, *139*, 117–127 (1990).
7. M. Moussavi and T. E. Carleson, "The Effect of Drainage on Metal Ions Removal and Reclamation Efficiency from Contaminated Waters by Foam Separation," *Iran. J. Sci. Technol.*, *16*(2,3), 187–195 (1993).
8. L. Brown et al., *Biotechnol. Bioeng.*, *36*, 947–959 (1990).
9. K. Jurkiewicz, *Int. J. Miner. Process.*, *28*, 173–187 (1990).
10. C. Walling et al., *J. Phys. Chem.*, *56*, 989–993 (1952).
11. M. Moussavi, *Sep. Sci. Technol.*, *27*, 783–792 (1992).
12. M. Schick, *J. Am. Oil Chem. Soc.*, *43*, 681 (1966).

Received by editor January 20, 1993
Revised August 16, 1993