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Separation of Cyanide Ions by Foam Fractionation

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Abstract

The technique of adsorption of cyanide ions on foam bubbles was studied as an alternative to chemical oxidation which is practiced in cyanide waste treatment. The technique of foam fractionation was previously applied to the removal of heavy metals and proved to be successful. The free cyanide ions and complex species both responded positively to the formation of a separate foam phase. The results obtained so far show that satisfactory separation of cyanide compounds is possible if certain parameters are properly selected. There are other factors which have not been investigated before, and they seem to have a major role in the performance of this operation.

INTRODUCTION

Cyanide ions appear in the effluents of a number of industries, mainly those related to surface finishing. These species can cause severe fouling problems in biological treatment systems if the containing effluents are not treated properly.

The usual methods in practice are generally based on chemical oxidation processes, and chlorine compounds are among those most widely used for this purpose. These reactants convert the cyanide species to less harmful intermediates, such as cyanates, and finally to inert compounds in the final step. This is a two-step process which requires extensive care and chemicals of high cost.

Other chemical methods based on precipitation are less extensively practiced. These methods have not attracted much attention due to the limitations imposed by sludge handling.

Some physical methods have been proposed as alternatives. Thermal hydrolysis as explained by Tan and Teo (*1*) is an example. An activated carbon polishing step is another physical method which shows great promise as a treatment alternative, as postulated by Ku and Peters (*2*). Many adsorption principles applied in activated carbon to treat the cyanide wastes are also applicable in systems where foam bubbles are used as the adsorbent. In the technique of foam fractionation, the foam surfaces have been used extensively to separate heavy metal ions at low concentrations. The above investigators have been quite successful in the nearly total elimination of cadmium, zinc, and some other elements used in the plating industries.

One of the first reports appearing in the literature concerning the fractionation of cyanide ions belongs to Sebba (*3*). He announced the possibility of separating the complex cyanides of iron and cobalt, as well as some other ions, by a surface-active agent containing a chain at least 10 carbons long. Later, free cyanide ions were removed from aqueous solutions by complexation with ferrous sulfate and subsequently were foamed off by ethyl cetyl dimethyl ammonium bromide as the surfactant. This process took place when cyanide species were partially combined in solid particles. The residual total cyanide remaining in the treated solution was more than 40% in most cases (*4*). Almost the same type of technique was utilized to remove dichromate ions from solutions containing 25 to 100 mg/L of this ion complexed with the same type of surfactant by a molar concentration ratio of about 2 surfactant/dichromate in a dissolved air separation unit. Some nonionic polymer was also added as a coagulant. 95% of dichromate was removed under the most favorable conditons (*5*, *6*). If enzymes and proteins are considered negatively charged species, then foam separation of these materials was practiced as early as 1936 by Ostwald (*7*).

Cyanide ion, as a general rule, after being chemically reacted with a proper surface-active agent, will be adsorbed by the air–liquid bubble interface. Increasing the tendency toward cyanide adsorption improves the efficiency of separation. One approach is to decrease the tendency of the ion to remain in solution. This can be achieved by reacting the cyanide ion with a surfactant. This statement is akin to Lundelius' rule (1920) (*8*) that the least soluble materials are the most readily absorbed. Consider pH as the variable parameter. Based on the above statement, the highest tendency toward foam formation of a surfactant–cyanide compound, analogous to the highest separation of the cyanide ion, should take place at a pH near the isoelectric point of the complex.

The efficiency of free cyanide ion removal decreased when the concentration of these ions (for constant free cyanide-to-surfactant molar concentration ratios) was increased. This is the result of the lower concentration of unimolecular species of surfactant available in solution at higher concentrations. Moroi et al. (*9*) were among many others who showed that the value of the critical micelle concentration, CMC, for certain surfactants decreases according to Corrin's equation (*10*) as the concentration of the counterion species increases. That is:

$$\log \mathrm{CMC} = -a \log c_i + b \tag{1}$$

where a and b are constants for a given ionic head at a certain temperature and c_i is the total monovalent counterions in moles/liter. This effect is more pronounced for cationic and anionic surfactants. When electrolytes are added to aqueous solutions of ionic surfactants, the aggregation number is increased.

The effect of counterion concentration on depression of CMC is not the same, however, for all ions. For the cationic dodecyl trimethyl ammonium and dodecyl pyridinium salts, the order of decreasing CMC in aqueous medium is

$$\mathrm{F^-} > \mathrm{Cl^-} > \mathrm{Br^-} > \mathrm{I^-} > \mathrm{CNS^-} \quad (11, 12) \tag{2}$$

An important point to consider when cyanide is foam separated is the effect of excess free cyanide ions on the solubility and micellization of the surfactant. It has been proven that the Krafft-point dependence of hexadecyl pyridinium salts on its related counterions is quite significant. These ions can raise not only Krafft-point temperature but they can also decrease the solubility of the surfactant in a solvent (*13*, *14*).

THE THEORY IN BRIEF

A dispersed bubble phase in a continuous liquid phase behaves as an adsorbent, and the Langmuir principle correlates in many instances. Consider a surface-active species i in the bulk. The equilibrium surface excess, or the equilibrium superficial concentration of species i on the bubble surface, is determined by Gibbs relation

$$d\sigma = -RT\Gamma_i d \ln a_i \tag{3}$$

where $d\sigma$ is the decrease in the surface tension of the solution due to addition of the species i with the activity of a_i. Γ_i is the surface concentration of species i on the bubble surface, surface excess (mol/cm^2). A concentration gradient will be established between the bulk and the bubble surface as a driving force. Species i will be attracted by the surface as long as the bubble surface concentration is below the equilibrium Γ_i. This process will take place as the bubble is rising up or falling down the column of the continuous liquid phase.

The surface tension of the solution does not change significantly if the concentration of i is below or above a certain critical concentration range, above which the molecules of the solute turn to clusters. But a plot of surface tension vs $\ln a_i$ is linear with the highest slope in the above range. Figure 1 shows this plot for sodium dodecyl sulfate, and Fig. 2 shows it for cetyl pyridinium bromide.

Now consider another component available in the solution which goes into a complex reaction with the surface-active species i. The same adsorption principles pertinent to species i will be applicable to this complex as well.

One can conclude from the Gibbs relation (Eq. 3) that for any activity of a there will be a value for surface excess Γ. The ratio of Γ/a may be used as a measure of the extent of separation, called the distribution coefficient (cm). By plotting the distribution coefficient as a function of surfactant concentration, a range may be reached in which the highest separation is possible. Somasundaram (*15*) and Karger and Miller (*16*) believe that such a plot must have a maximum. Even at this concentration the best results in separation of certain albumins was shown to be obtained if the pH was taken to be around the isoelectric point, as pointed out by Ahmad (*17*).

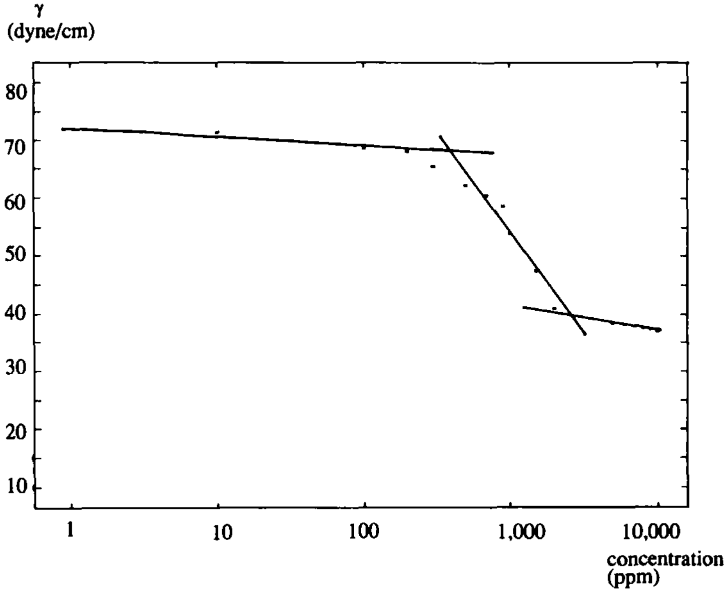

FIG. 1. Critical micelle concentration of sodium dodecyl sulfate.

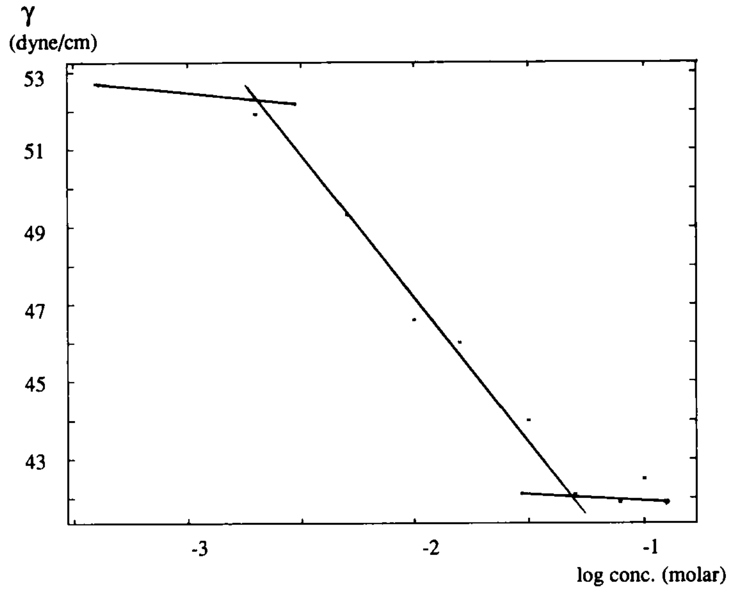

FIG. 2. Critical micelle concentration of cetyl pyridinium bromide.

EXPERIMENTAL AND METHODS

From a number of cationic surfactants, cetyl trimethyl ammonium bromide (CTAB) was selected as a collector. The experiments were conducted in a unit operating on a batch basis. A 100-mL foaming column with a liquid hold-up of about 70% of its total volume was used for treatment. The aeration was continued until no further foam was generated.

The concentration of cyanide ions was measured by a CN-selective membrane electrode (Orion Research). The reproducibility of the calibration curve was quite acceptable. The concentration of the surfactant was measured by a colorimetric method based on the reaction between the anionic surfactant and methylene blue. The colorful product of the above reaction was transferred into a chloroform phase. It was subsequently titrated with a known solution of cationic surfactant to a colorless end point.

The surface tension, and thus the critical micelle concentration and the surface excess concentration of the surfactant solution, were measured by a method based on the capillary action of the solution. In this method the rise of the liquid in a capillary tube of known diameter is a direct measure of the liquid surface tension. Further details about this section are given by Moussavi and Carleson (*18*). The product of the reaction between free

TABLE 1
Characteristics of the Gas–Liquid Chromatographic System

Column:	
Liquid phase	OV-107
Support	Chromosorb W
Carrier gas	Helium
Detector	Thermal conductivity
Solvent for sample extraction	Chloroform
Oven temperature	160°C

cyanide ions and surfactant molecules was analyzed by a gas–liquid chromatographic system (Table 1).

RESULTS AND DISCUSSION

The result of the interaction between cetyl trimethyl ammonium bromide and free cyanide ions is a complex which is in equilibrium with the reactants. The complex may be almost totally removed from the solution by foam separation. At low initial concentrations of surfactant ($C_s \ll$ CMC), it was observed that the cyanide ions could be removed from the bulk solution with an efficiency of about 70%. It was also observed that the removal efficiency was inversely proportional to the initial molar concentration ratio of cyanide of surfactant. Table 2 shows the results of the experiment.

The experiments show that the overall air volume required to remove a unit weight of the surfactant–cyanide complex is larger when the original surfactant concentration is smaller. This behavior is irrespective of the initial concentration of free cyanide ions.

When free cyanide ions are admitted to an aqueous solution containing an original amount of cetyl trimethyl ammonium bromide, a complex is formed. The concentration of this complex is linearly proportional to that of the surfactant. This proportionality continues to exist until the original surfactant concentration is less than or equal to 10 ppm. Figure 3 illustrates this for the range of molar concentration ratio of cyanide-to-surfactant <

TABLE 2
Free Cyanide Ions Removal Efficiency by Foam Fractionation (molar concentration ratio of cyanide to surfactant = 0.5–2.0)

Original surfactant concentration (ppm)	100	50
Efficiency of cyanide ions removal	0.65–0.70	0.40–0.53
a (dimensionless)	2.68	1.83
b (dL^3/mol)	0.0168	0.0168

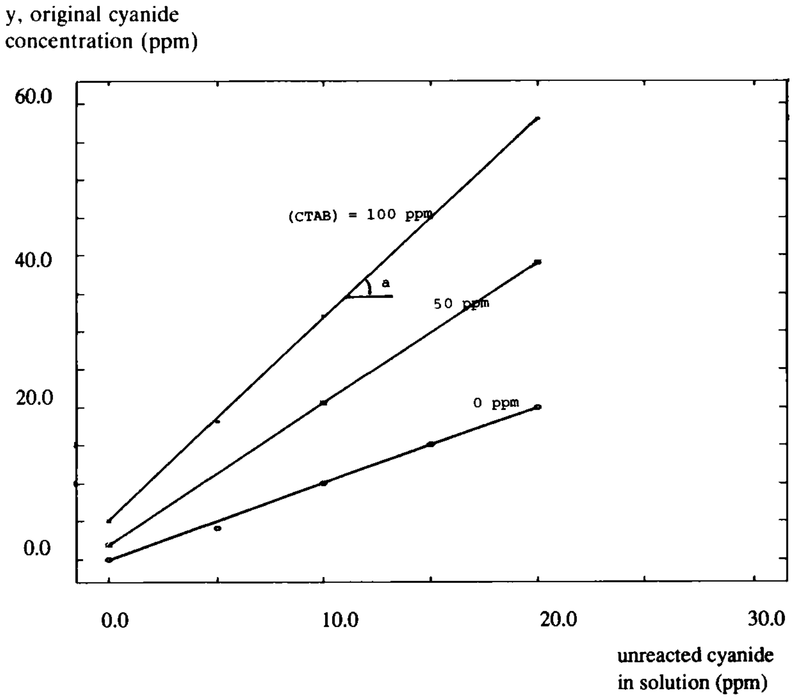

FIG. 3. Effect on free cyanide removal.

2.0. In fact, this proportionality is also a linear function of surfactant concentration, Fig. 4.

If y is taken as the original cyanide concentration and x that of free cyanide left in the solution and in equilibrium with the complex, then a straight line will be obtained in an x–y system with a slope of a:

$$a = (y - y_1)/x \quad \text{or} \quad y = ax + y_1 \qquad (4)$$

where y_1 is the y intercept for $x = 0$. Thus a family of lines will be obtained, each representing an original surfactant concentration in the solution (Fig. 3). By plotting the values of a as a function of surfactant concentration, C_s, a line is obtained:

$$a = bC_s + c \qquad (5)$$

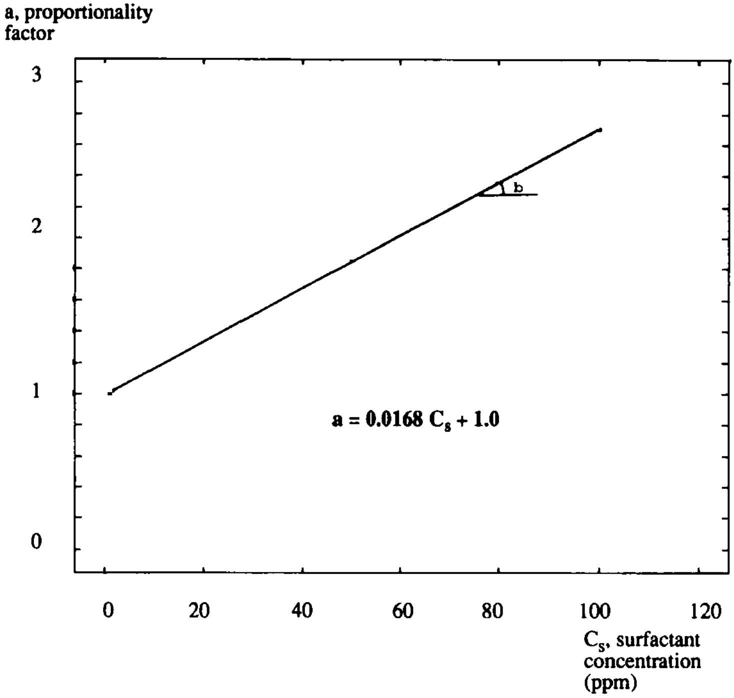

FIG. 4. Effect of surfactant concentration.

where c is a constant. When $C_s = 0$, the value of c will equal unity, that is, the original free cyanide concentration will read as x. Therefore,

$$a = bC_s + 1 \tag{6}$$

By rearranging Eq. (4), considering the case when $y \gg 10$ ppm, and neglecting y_1, the following relation will hold:

$$x = y/(bC_s + 1) \tag{7}$$

For the system with cetyl trimethyl ammonium bromide at low concentrations (< CMC), the value of b was found to be 0.0168 dL^3/mol (Table 2). The fraction of unreacted cyanide can be estimated from Eq. (7) as a function of surfactant concentration. By giving the calculated value of 0.0168 dL^3/mol to b, a plot of x/y vs C_s may be obtained. Another set of experiments was made to examine the precision of Eq. (7). It shows noticeable agreement with that equation (Fig. 5).

Based on the definition of Gibbs theorem (Eq. 3), Carleson (*19*) believes that separation by foam fractionation is made possible through the complexation reaction that takes place between a surface-active compound, so-called collector, and the compound to be separated. This is possible if the compound to be separated is not surface active. Thus the complex is rendered hydrophobic. If an electrostatic double layer exists around the small bubbles, as noticed in colloids, then there must be an attractive force for the counterions available in the bulk. This explains the adsorption and separation of cyanide ions from a solution containing a cationic surfactant with a lower concentration than the molar stoichiometric ratio. One notes that for the small bubbles the attraction of cyanide species on the bubble–liquid interface is not limited to chelation reactions with the surfactant. Other phenomena, such as Gouy or Stern electrostatic double layer charged sites, as mentioned by Stumm and Morgan (*20*), are responsible as well.

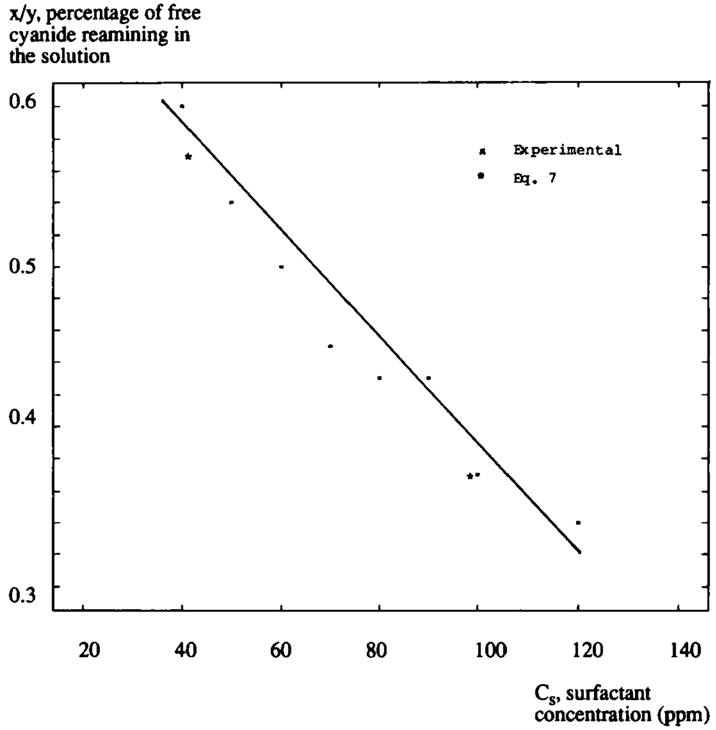

FIG. 5. Examination of Eq. (7).

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