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Foam Separation of Cyanide Complexed by Iron

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Summary

An experimental investigation is presented of the foam separation of cyanide, complexed with ferrous iron, using a cationic surfactant, ethylhexadecyldimethylammonium bromide (EHDA-Br). The effects of pH over the range 5.8–11.4, of iron concentration, and of surfactant and cyanide concentrations on the separation of noncomplexed and complexed cyanide are established. Prior to surfactant addition and foaming, variation of the iron-to-cyanide ratio in the initial solutions produced different species of complexed cyanide, ranging from $[Fe(CN)_6]^{4-}$ to polynucleated $[FeFe(CN)_6]^{2-}$, which, in turn, brought about markedly different solution characteristics. Initial solutions containing 0.206 and 0.351 moles of iron per mole of cyanide exhibited contrasting foam separation behavior, at pH 7 and below, but not at pH 8 and above.

The fractional residuals of complexed cyanide were approximate linear functions of the ratios of surfactant to complexed cyanide in the initial (feed) solutions, enabling the prediction of required surfactant dosages and establishing the approximate formulas $EHDA_{3.9}Fe(CN)_6$ and $EHDA_{2.1}FeFe(CN)_6$ at the two ratios. Operation at pH 7 or less and an iron-to-cyanide ratio of about 0.35 are recommended due to surfactant saving and reduction in noncomplexed cyanide.

INTRODUCTION

Ion flotation (foam separation) has been utilized by chemists and engineers for the removal and separation of inorganic and organic anions and cations from aqueous solution. The process involves the addition of a surface-active ion of opposite charge to the ion to be separated. The primary step is the electrostatic attraction between the surfactant and the ion to be separated followed by the formation of an insoluble complex. The resultant surface-active complex may be floated to the surface of the solution by means of gas bubbles to the interfaces of which it is adsorbed, and a froth may be formed. In some cases the particulate complex may be formed only in the presence of the high surfactant concentrations at the bubble interfaces.

An extensive discussion of ion-flotation processes and a review of applications have been presented by Sebba (*26*). Recently, Sebba has utilized ion flotation to remove trace amounts of strontium from aqueous solution (*5,6*), to separate aluminum from beryllium (*22*), and to concentrate the fluorozirconate ion (*23*). Other studies have been made of the recovery of uranium from carbonate leach liquors (*18,19*) and of the flotation of iron and copper (*24,25*). Grieves et al. have successfully floated dichromate ion from aqueous solution and studied both batch (*14,15*) and continuous (*12,13*) operation, including the use of a dissolved-air process (*11*).

Cyanides in simple and in complex form are found in such industrial wastes as electroplating, process steel, and coke-plant. The treatment of cyanide wastes, although mostly accomplished by alkaline chlorination, can be carried out by several methods: chlorination (*16,31*), ozonation (*1*), precipitation by ferrous sulfate and lime (*28,31*), electrolytic oxidation (*7*), ion exchange (*30*), and biological treatment (*17*). No method at present is entirely satisfactory. Investigation of the removal of complex cyanides by ion flotation is very limited. The only work reported in the literature has been by Sebba (*26,27*) in which he used an ion-flotation method to remove complexed cyanides (including ferrocyanide); however, his results were mostly qualitative.

The objective of this investigation is to establish the feasibility of foam separation for the separation of cyanides (in complex form) from aqueous solution, using a cationic surfactant which forms an insoluble product with the complexed cyanide. The simple alkali cyanide is first converted to complexed forms by reaction with iron ($FeSO_4$). The effects of the pH of the initial solutions, of iron concentration, of surfactant concentration, and of total cyanide concentration on the flotation of total cyanide are to be established.

EXPERIMENTAL

The concentration of NaCN in the initial (feed) solutions was varied from 1.54 to 3.08 m*M* (as CN). The complexed cyanide was formed by adding 1 liter of $FeSO_4 \cdot 7H_2O$ solution (with a predetermined amount of $FeSO_4 \cdot 7H_2O$) to about 1 liter of a solution of NaCN (containing from 3.08 to 6.16 mmoles of CN); then the resultant solution was mixed for 5 min in a magnetic stirrer. The pH of the solution was measured and adjusted to values in the range 5.8 to 11.4 with 0.049 *N* sodium hydroxide or with 0.049 *N* sulfuric acid. The concentration of ferrous sulfate was varied from 0.217 to 1.08 m*M* (as Fe). After the pH adjustment was completed, surfactant was added and was contacted with the solution (with mixing in a magnetic stirrer) for an additional 5 min just before the initiation of each foaming experiment. The concentration of surfactant, ethylhexadecyldimethylammonium bromide (EHDA-Br), was varied over a range of 0.265 to 1.59 m*M*.

The experimental apparatus was similar to that used in previous foam-separation studies (*9,10,14,15*). The foam column was made of Pyrex and was 82 cm in height and 9.7 cm in diameter. Nitrogen gas (high purity), saturated with water and metered with a calibrated rotameter, was dispersed through twin, sintered-glass diffusers of 50-μ porosity at a rate of 1300 ml/min (at 1 atm and 25°C). In each experiment exactly 2000 ml of initial solution (including the surfactant) was added to the column. The solution was foamed for 25 min, with foam removal from a port located 7.0 cm above the initial solution level. Temperature was maintained at 25°C throughout each experiment. After each experiment was terminated, the volume of the residual solution was measured and the residual surfactant concentration was determined by a two-phase titration technique, using sodium tetraphenylboron as the titrant and bromophenol blue as the indicator (*3*). The residual concentrations of total cyanide (*29*) and of noncomplexed (free) cyanide (*20*) were measured. This method of cyanide (total and noncomplexed) analysis was very satisfactory and gave consistently accurate results with known cyanide solutions. The precision of the technique was about 1%.

Several experiments were carried out to check for volatilization of hydrocyanic acid (HCN) by gas dispersion through solutions containing sodium cyanide and EHDA-Br. Gas dispersion for prolonged periods brought about foaming and surfactant removal, but no separation or loss of cyanide was observed.

SOLUTION BEHAVIOR

The addition of a ferrous salt to a solution of an alkali cyanide results in the formation of complexed cyanides (*32*). The complexed cyanides may be in the form of ferrocyanide $[Fe(CN)_6]^{4-}$ and/or other species, depending on the amount of iron used. When iron (Fe^{2+}) is added to a cyanide (CN^-) solution in stoichiometric amounts, the predominant species is $[Fe(CN)_6]^{4-}$ according to the reaction

$$Fe^{2+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$$

Complete conversion to complexed cyanide is impossible; after performing several experiments with varying amounts of ferrous sulfate, it was found that a molar iron-to-cyanide ratio of 0.206 (stoichiometric ratio to form $[Fe(CN)_6]^{4-}$ is 0.167) produced predominantly $[Fe(CN)_6]^{4-}$ and a reasonable fraction of noncomplexed cyanide of about one-fifth. The solution was clear and was yellow in color. The addition of ferric (Fe^{3+}) iron immediately produced a deep blue color (this is the standard test for $[Fe(CN)_6]^{4-}$ ion). Water will react, to a limited extent, with $[Fe(CN)_6]^{4-}$ to form ferroaquopentacyanide, $[Fe(CN)_5H_2O]^{3-}$, as suggested by Legros (*8,21*), according to the reaction

$$[Fe(CN)_6]^{4-} + H_2O \rightleftharpoons [Fe(CN)_5H_2O]^{3-} + CN^-$$

An increase in the concentration of iron to produce molar iron-to-cyanide ratios greater than 0.206 did reduce somewhat the concentration of noncomplexed cyanide; however, it brought about a most significant change in the species of complexed cyanide present, as evidenced by the formation of a blue-colored suspension which scattered light. When an iron concentration of 0.541 m*M*, corresponding to a molar iron-to-cyanide ratio of 0.351, was used, a distinct, deep blue color was observed, with the formation of what is known as soluble Prussian blue producing a suspension of polynucleated species in water. In the literature little of the constitution of Prussian blue, is reported with certainty. The Prussian blue formation may have been produced by the conversion of excess Fe^{2+} to Fe^{3+} by oxidation (O_2 from the air during stirring) and subsequent reaction with the $[Fe(CN)_6]^{4-}$ present in the solution. The composition of Prussian blue has been discussed by Davidson (*4*) and Callis (*2*). The fact that the cyanide group can coordinate by means of either its carbon or its nitrogen atom leads to supercomplex formation. The nitrogen of each cyanide group can coordinate with another heavy metal (such as Fe) and results in the formation of polynucleated species. According to Callis (*2*), ferrocyanide with ferric and/or ferrous ions gives supercomplex anions of the type $[FeFe(CN)_6]^-$ or $[FeFe(CN)_6]^{2-}$, respectively. Prussian blue may contain both of these anions and also $[Fe(CN)_6]^{3-}$ anions. On addition of EHDA-Br to the Prussian blue solution, a partial aggregation was observed. The reaction mixture produced by reacting iron and cyanide in the molar ratio of 0.351 should be considered a heterogeneous system because of the presence of polynucleated species; whereas, with an iron-to-cyanide ratio less than 0.206, a homogeneous mixture was produced.

At the lower iron-to-cyanide ratio the process conducted by surfactant addition followed by aeration would be termed ion flotation. At the higher ratio the process would be termed microflotation of the polynucleated species, although some soluble complexed cyanide species would be involved, therefore involving ion flotation. Both processes could be termed foam separation.

RESULTS AND DISCUSSION

Four series of experiments were carried out to establish the effects of hydrogen-ion concentration, of ferrous iron (complexing agent) concentration, and of surfactant (flotation agent) concentration and cyanide concentration on the foam separation of complexed and free cyanide from aqueous solution. For each batch experiment the following material balances can be written:

$$V_i = V_r + V_f \tag{1}$$

$$(Z_t)_i V_i = (Z_t)_r V_r + (Z_t)_f V_f \tag{2}$$

$$X_i V_i = X_r V_r + X_f V_f \tag{3}$$

The volumes in liters of initial solution, residual solution, and collapsed foam are represented by V_i, V_r, and V_f, respectively. V_i was always maintained at 2.0 liters. The same subscripts apply also to the cyanide and surfactant concentrations, Z and X (mM), respectively. Free (noncomplexed) cyanide is designated by Z_{nc}, complexed cyanide by Z_c, and the sum of the noncomplexed plus complexed by Z_t, all millimolar.

$$(Z_t) = (Z_{nc}) + (Z_c) \tag{4}$$

Effect of pH

The first series of experiments involved initial solutions of concentration 1.54 m*M* in cyanide, either 0.317 or 0.540 m*M* in iron, and 0.529 m*M* in surfactant (EHDA-Br). The effect of pH was determined over the range 5.8 to 11.4, as indicated in Fig. 1 in which the fractional residual of total cyanide, $(Z_t)_r/(Z_t)_i$, is the dependent variable. First, considering the experiments with the lower iron-to-cyanide ratio (0.206), pH had little effect. The increases in the fractional residuals (poorer flotation) with the high-pH solutions may have been produced by increased competition between $[Fe(CN)_6]^{4-}$ and OH^- for the surfactant cations. Some interconversion among the complexed cyanide species may also have occurred. No effort was made to maintain constant ionic strength in the experiments described in Fig. 1, with the ionic strength generally increasing with pH. However, two additional runs were conducted at pH 7.5 and 9.1, with sodium sulfate added to the initial solutions to achieve the same ionic strength ($\mu = 0.0025$) as was produced at

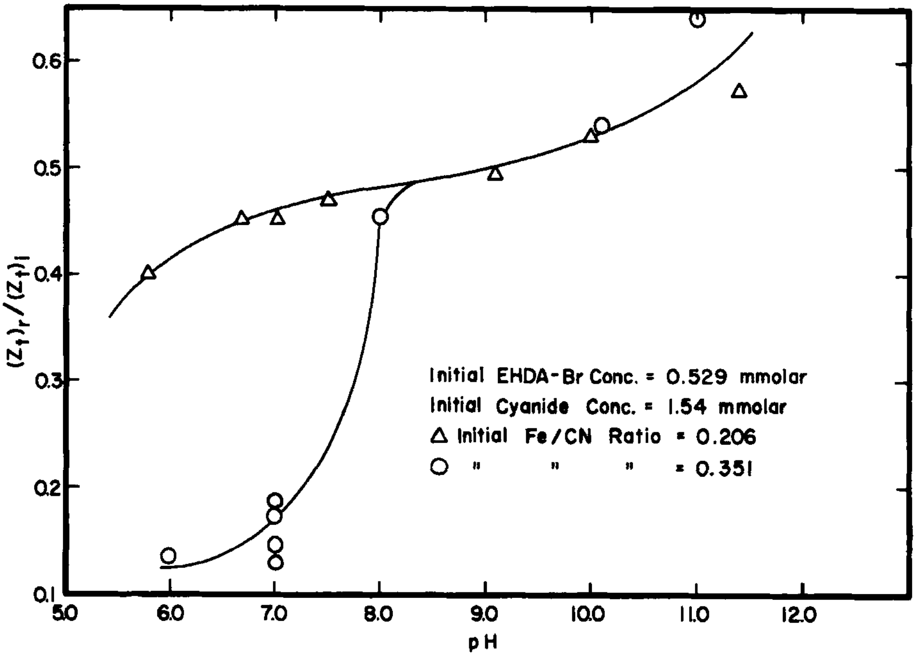

FIG. 1. Effect of pH on the fractional residual of total cyanide.

pH 10.0. These two experiments provided results identical to those shown in Fig. 1.

Second, considering the experiments with the higher iron-to-cyanide ratio (0.351), pH had a most pronounced effect over the range 6 to 7.5. In this range the initial solutions were blue, indicating the presence of the polynucleated Prussian blue species; these were floated more readily than the $[Fe(CN)_6]^{4-}$ species present at the lower iron-to-cyanide ratio. As the pH was elevated from 7 to 8, the initial solutions faded to the pale yellow color characteristic of those at the lower iron-to-cyanide ratio.

The data in Fig. 1 include both complexed and noncomplexed cyanide. For each experiment, of course, the residual solutions were also analyzed for noncomplexed cyanide alone. The fractional residuals of noncomplexed cyanide, $(Z_{nc})_r/(Z_t)_i$, were quite independent of pH; they averaged 0.20 at the lower iron-to-cyanide ratio and 0.14 at the higher iron-to-cyanide ratio. In general, there was very little flotation of the noncomplexed cyanide, as would be expected. The ratios of noncomplexed to total cyanide in the initial solutions (no flotation), $(Z_{nc})_i/(Z_t)_i$, were 0.22 and 0.17 at the lower and higher iron-to-cyanide ratios, respectively. The very limited amount of flotation that was achieved was probably produced by the conversion of some noncomplexed cyanide to complexed cyanide during the experiment, as the concentration of complexed cyanide in the residual solution was reduced by foam separation.

For these experiments the fractional quantity of the initial solution carried off as collapsed foam, V_f/V_i, varied randomly with pH at the lower iron-to-cyanide ratio: V_f/V_i increased steadily from 0.09 at pH 5.8 to 0.15 at pH 10.0 and then decreased to 0.11 at pH 11.4. At the higher iron-to-cyanide ratio, V_f/V_i decreased from 0.23 at pH 6 to 0.17 at pH 7 to 0.10 at pH 8, and then remained virtually constant over the remainder of the pH range. The decrease in foaminess with increasing pH was probably produced by the conversion of the predominantly $[FeFe(CN)_6]^{2-}$ species to the $[Fe(CN)_6]^{4-}$ species.

For these same experiments the fractional residual of surfactant, X_r/X_i, is related to pH in Fig. 2. The residual surfactant concentration, X_r, included surfactant which had reacted with the residual complexed cyanide and "free," nonreacted surfactant. The extent and nature of this reaction undoubtedly varied with the Fe–CN ratio. X_r was affected by the quantity of surfactant floated per unit

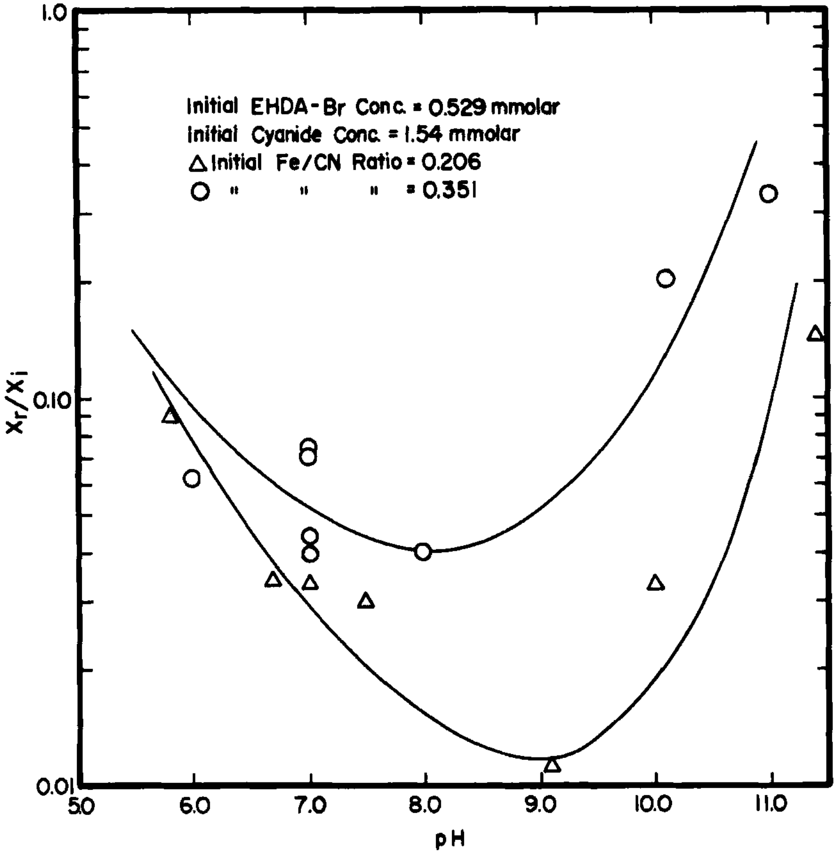

FIG. 2. Effect of pH on the fractional residual of surfactant.

quantity of complexed cyanide and therefore by the charge on the complex and its extent of polynucleation; it was also affected by the OH^- concentration and by the solution concentration of Fe^{2+}.

The pH values of the residual solutions, after foam separation, were always greater than or equal to those of the initial solutions. The only appreciable elevation of pH was over the range 6–7 for the initial solutions; for these, the pH's of the residual solutions were about 1 unit higher.

In contrast to these results, studies on the ion flotation of dichromate showed a much less pronounced effect of pH. The residual concentrations of dichromate and of surfactant were virtually independent of pH, until the pH was elevated above 10. The foam volumes were rather strong functions of pH (*15*).

Effect of Iron Concentration

The second series of experiments involved initial solutions of concentration 1.54 m*M* in cyanide, 0.529 m*M* in surfactant, and a hydroxide-ion concentration corresponding to pH 8.0. The effect of iron concentration ($FeSO_4 \cdot 7H_2O$) was established to determine the extent to which the noncomplexed cyanide could be reduced by complex formation, followed by foam separation of the complex. The pH value of 8.0 was chosen to prevent the production of different, complexed cyanide species at different iron concentrations. Figure 3 indicates data for $(Z_{nc})_r$ related to the molar iron-to-cyanide ratio in the initial solutions. It should be stressed that the noncomplexed cyanide was not removed from the initial solutions by foam separation. From Fig. 3 it can be observed that excessive quantities of iron were required to reduce the value of $(Z_{nc})_r$ substantially below 0.2 m*M* $[(Z_{nc})_r/(Z_t)_i = 0.13]$; iron-to-cyanide ratios approaching unity would be needed to reduce $(Z_{nc})_r$ below 0.1 m*M*.

For these experiments $(Z_c)_r$, V_f, and X_r did not exhibit a significant variation with respect to the initial iron-to-cyanide ratio.

Effect of Surfactant Concentration and Cyanide Concentration

A third series of experiments involved initial solutions of concentration 1.54 m*M* in cyanide and either 0.317 or 0.540 m*M* in iron, with the pH adjusted to 7.0. The effect of surfactant concentration was determined over the range 0.265 to 0.794 m*M*. The fractional residual of total cyanide is related to the initial surfactant concentration in Fig. 4. For the lower iron-to-cyanide ratio, the fractional residual of total cyanide was a decreasing linear function of the initial surfactant concentration over the entire range. The residual concentration of noncomplexed cyanide, $(Z_{nc})_r$, was practically independent of the initial surfactant concentration (it was slightly higher at the lowest values of X_i), averaging 0.31 m*M* $[(Z_{nc})_r/(Z_t)_i = 0.20]$. Thus from Fig. 4 at $X_i = 0.8$ m*M*, virtually all the complexed cyanide was floated $[(Z_c)_r/(Z_t)_i = 0]$.

Considering the higher iron-to-cyanide ratio in Fig. 4, the fractional residual was linear with respect to the initial surfactant concentration up to a value of X_i of about 0.50 m*M*; then there was a

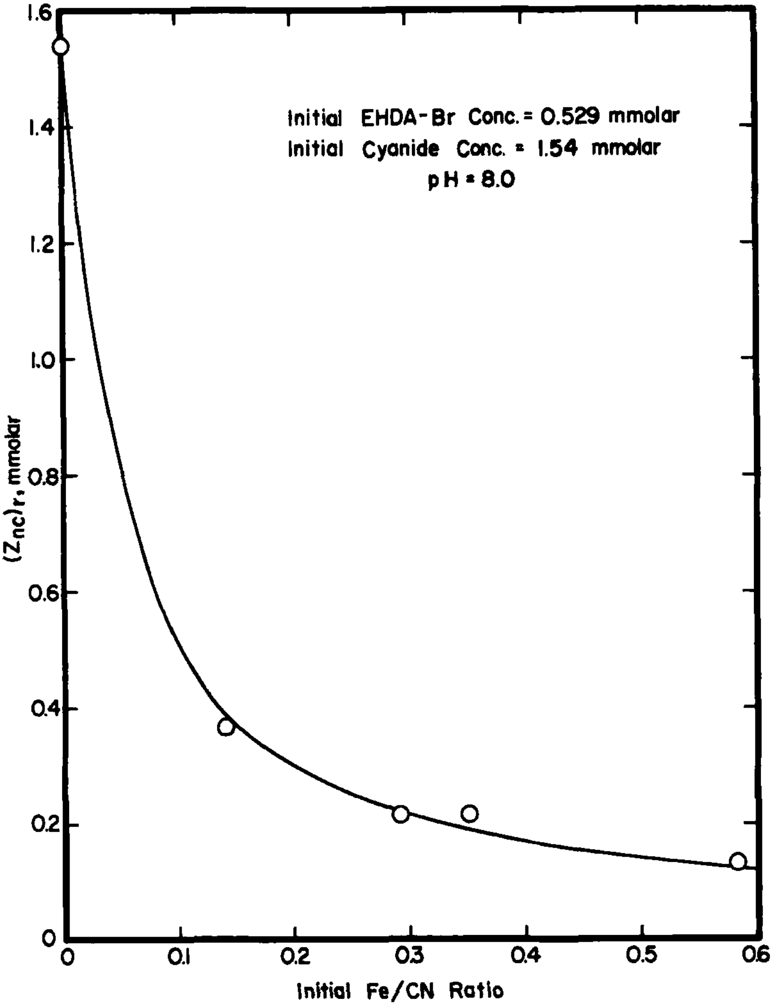

FIG. 3. Influence of the initial iron-to-cyanide ratio on the residual concentration of noncomplexed cyanide.

leveling and an ultimate increase. Again, the residual concentration of noncomplexed cyanide, $(Z_{nc})_r$, was practically independent of X_i, averaging 0.19 mM $[(Z_{nc})_r/(Z_t)_i = 0.12]$. From Fig. 4 it can be seen that the fractional residual of total cyanide approached 0.12, yielding $(Z_t)_r = 0.19$ mM, at a value of X_i slightly greater than 0.50

mM, corresponding to the flotation of all complexed cyanide. At values of X_i greater than 0.60 mM, the increase in the fractional residuals of total cyanide was brought about by excess quantities of surfactant not associated with complexed cyanide being adsorbed at the bubble surfaces and preventing the adsorption of surfactant cations which had reacted with and were associated with complexed cyanide. Similar behavior has been noted by Davis and Sebba (5). In addition, it is possible that the excess quantities of surfactant were adsorbed on the surfactant-complexed cyanide polynucleated species (by van der Waals' forces between the hydrocarbon chains), giving the species a net positive charge and preventing the further aggregation which promotes flotation.

To elaborate on the observations made from Fig. 4 at the lowest values of $(Z_t)_r/(Z_t)_i$ for both iron-to-cyanide ratios, a fourth series of experiments was conducted with initial concentrations of total cyanide from 1.92 to 3.08 mM at initial surfactant concentrations from 0.990 to 1.59 mM and Fe–CN = 0.206; and with initial concentrations of total cyanide from 1.92 to 3.08 mM at initial surfactant

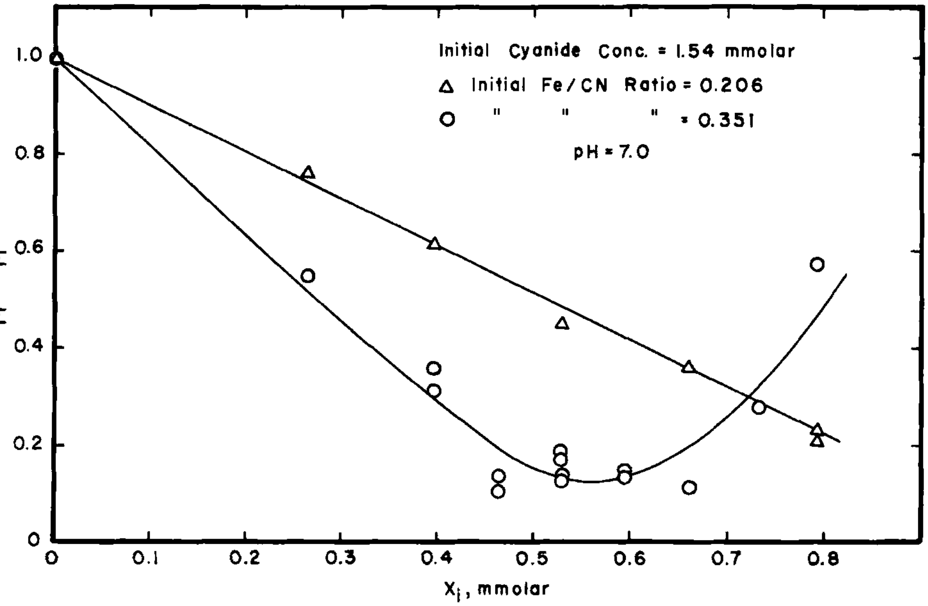

FIG. 4. Effect of the initial surfactant concentration on the fractional residual of total cyanide.

concentrations of 0.496 to 0.924 mM and Fe–CN = 0.351. For all the experiments the residual concentrations of noncomplexed cyanide were independent of the initial surfactant concentration and did not vary too significantly with the initial cyanide concentration. At Fe–CN = 0.206, $(Z_{nc})_r$ averaged 0.31 mM; at Fe–CN = 0.351, $(Z_{nc})_r$ averaged 0.24 mM. The residual concentrations of complexed cyanide could be correlated with the initial surfactant and cyanide concentrations according to the following equations: for Fe–CN = 0.206,

$$(Z_c)_r = (Z_t)_i - 0.31 - 1.54X_i \tag{5}$$

and for Fe–CN = 0.351,

$$(Z_c)_r = (Z_t)_i - 0.24 - 2.80X_i \tag{6}$$

The data presented in Fig. 4 were also used in developing Eqs. (5) and (6). It should be noted that $(Z_t)_i - 0.31$ and $(Z_t)_i - 0.24$, where 0.31 and 0.24 are the average values of $(Z_{nc})_r$, represent the concentrations of cyanide (complexed) that can be foam separated, assuming a rapid decrease in $(Z_{nc})_i$ to $(Z_{nc})_r$ in the initial phases of an experiment. They are actually more representative than $(Z_c)_i = (Z_t)_i - (Z_{nc})_i$, because the "equilibrium" and the concentration of noncomplexed cyanide changes somewhat during a foam-separation experiment. The average deviation of values of $(Z_c)_r$ calculated with Eq. (5) from the experimental values was 0.028 mM for the nine experiments. The average deviation of values of $(Z_c)_r$ calculated with Eq. (6) from the experimental values was 0.094 mM for the 20 experiments [points for $(Z_t)_i = 1.54$ mM and $X_i > 0.528$ mM were excluded because of the excess surfactant present]. With $(Z_t)_i = 3.08$ mM, calculated values of $(Z_c)_r$ were consistently higher than experimental values; a coefficient on X_i of 3.0 would give better results. Equations (5) and (6) can be rewritten:

$$\frac{(Z_t)_i - 0.31 - (Z_c)_r}{(Z_t)_i - 0.31} = 1.54 \frac{X_i}{(Z_t)_i - 0.31} \tag{7}$$

$$\frac{(Z_t)_i - 0.24 - (Z_c)_r}{(Z_t)_i - 0.24} = 2.80 \frac{X_i}{(Z_t)_i - 0.24} \tag{8}$$

Equations (7) and (8) indicate that the fractional removal of complexed cyanide is a linear function of the initial ratio of surfactant to complexed cyanide. The equations hold over the entire range of values of X_i and $(Z_t)_i$. The constant 1.54 in Eq. (7) shows that 1.54 moles of cyanide can be foam separated for each mole of surfactant in the initial solutions, with Fe–CN = 0.206. This indicates a possible formula for the floated species:

$$\mathrm{EHDA_{3.9}Fe(CN)_6} \quad \text{or} \quad \mathrm{EHDA_{3.8}Fe(CN)_{5.8}}$$

indicating mostly the presence of $[\mathrm{Fe(CN)_6}]^{4-}$ with some $[\mathrm{Fe(CN)_5\text{-}H_2O}]^{3-}$. The constant 2.80 in Eq. (8) shows that 2.80 moles of cyanide can be foam separated for each mole of surfactant in the initial solutions, with Fe–CN = 0.351. This indicates a possible formula for the floated species:

$$\mathrm{EHDA_{2.1}FeFe(CN)_6}$$

indicating mostly the presence of $[\mathrm{FeFe(CN)_6}]^{2-}$ with some other species, such as $[\mathrm{Fe(CN)_6}]^{3-}$, perhaps being present. These formulas assume that all the surfactant in the initial solution is foam separated; therefore the values 3.9 and 2.1 may be somewhat high.

For the third and fourth series of experiments (considered above in this subsection) involving variable initial cyanide and surfactant, concentrations of surfactant in the residual solutions did not correlate well. For the Fe–CN ratio of 0.206 and the full range of $(Z_t)_i$ and X_i, X_r/X_i varied from 0.014 to 0.084. Actually, X_r remained quite constant for all experiments and therefore X_r/X_i decreased as X_i was increased. For the Fe–CN ratio of 0.351 and the full range of $(Z_t)_i$ and X_i, X_r/X_i varied from 0.032 to 0.30 (only one value was higher than 0.20).

Considering the experiments with an initial cyanide concentration of 1.54 m*M*, the foam volume behavior is indicated in Fig. 5 as a function of the initial surfactant concentration for both values of the iron-to-cyanide ratio. Approximately linear behavior, except at very low values of V_f/V_i, is shown for both ratios. However, at the low ratio V_f/V_i increased very slightly with X_i, while at the high ratio the rate of increase was most pronounced. At the high ratio, above a value of X_i of 0.50 m*M*, excess quantities of surfactant were present which undoubtedly produced the large foam volumes. Again at the high ratio (Fe–CN = 0.351) and values of the initial cyanide concentration ranging from 1.92 to 3.08 (not plotted), variation in V_f/V_i with X_i was quite similar to that shown in Fig. 5, except there was a bit more curvature at low values of V_f/V_i. At constant X_i, V_f/V_i consistently decreased as $(Z_t)_i$ was increased.

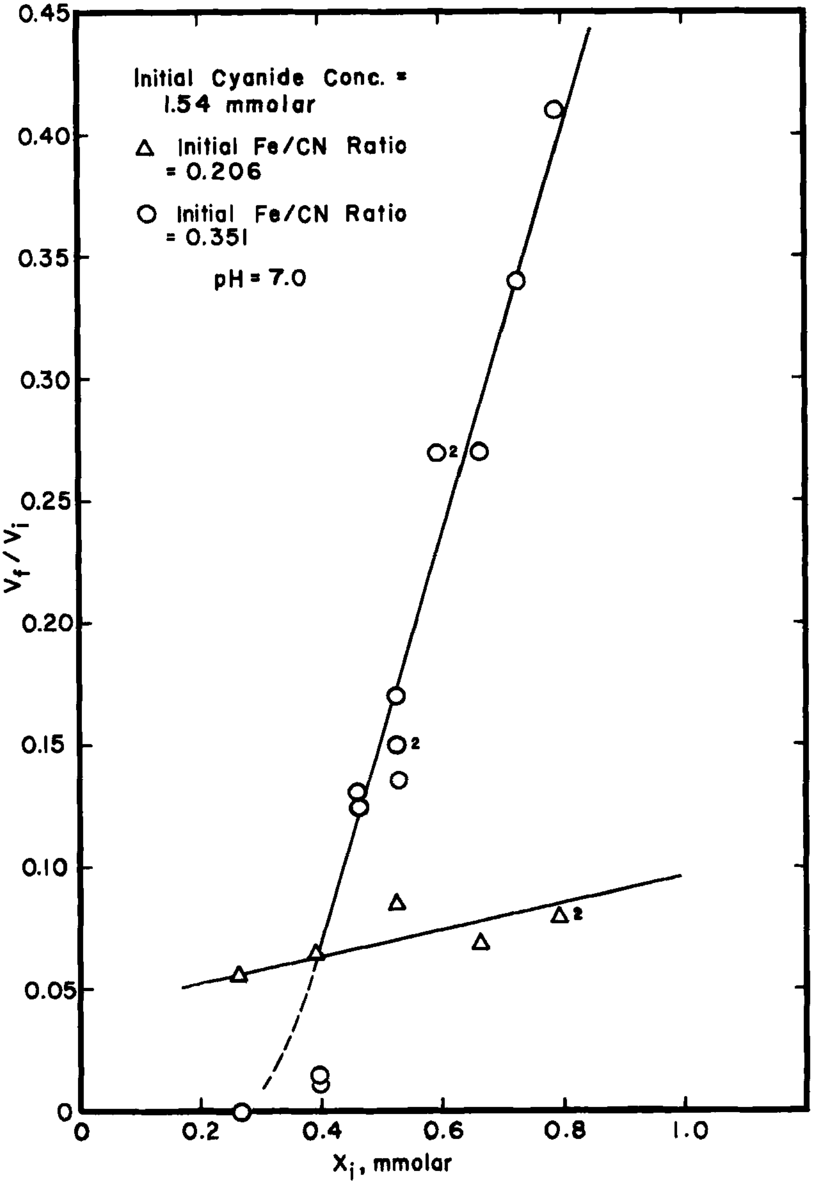

FIG. 5. Effect of the initial surfactant concentration on the fraction of the initial solution carried off as foam (collapsed).

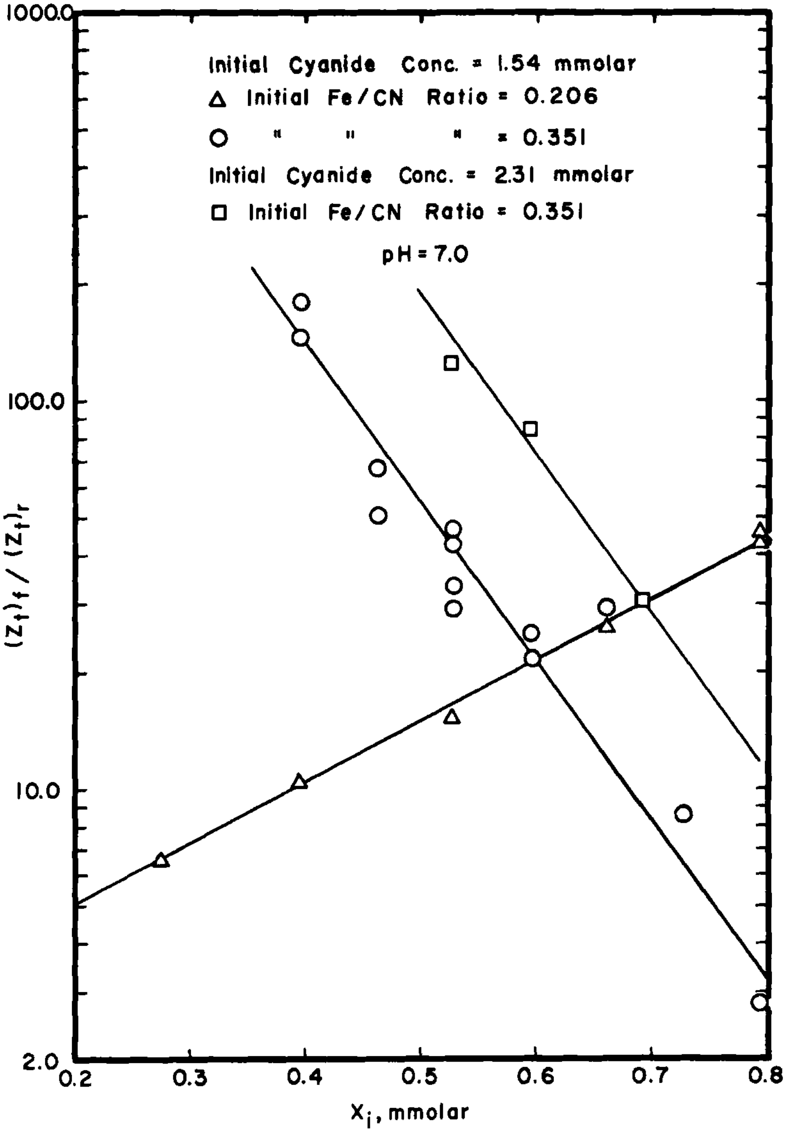

FIG. 6. Effect of the initial surfactant concentration on the enrichment ratio of total cyanide.

From experiment to experiment, V_f/V_i reproduced quite well, virtually always within an absolute error of 0.007.

A final contrast may be made between the initial solutions containing the iron-to-cyanide ratio of 0.206 and the ratio of 0.351. The concentration of total cyanide in the accumulated, collapsed foam [$(Z_t)_f$ divided by the concentration in the residual solution, $(Z_t)_r$, defined as the enrichment ratio] has been of value in other foam-separation studies (*11,12,14,15*). Enrichment ratios are plotted versus the initial surfactant concentrations in Fig. 6 on semilogarithmic coordinates. At the lower iron-to-cyanide ratio, the foam volume was rather independent of X_i; as X_i was increased, $(Z_t)_r$ was decreased and $(Z_t)_f$ was increased, producing increases in the enrichment ratio. At the higher iron-to-cyanide ratio and the two values of the initial cyanide concentration shown, the foam volume increased appreciably with X_i; thus as X_i was increased and $(Z_t)_r$ was decreased, the large quantities of entrained bulk liquid diluted the foam and the decrease in $(Z_t)_f$ was greater than the decrease in $(Z_t)_r$, producing a decreasing enrichment ratio. A similar trend was noted at other values of the initial cyanide concentration.

Discussion

At pH 7 the foam-separation behavior of the initial solutions containing an Fe–CN ratio of 0.206 is clearly quite different from those containing an Fe–CN ratio of 0.351. This probably was produced by the presence of polynucleated species before surfactant addition in the solutions with the 0.351 ratio. However, the behavior of those with the low ratio is quite dissimilar to that of dichromate solutions (*14,15*) which were also clear, true solutions before surfactant addition. The chief contrast with the low iron-to-cyanide ratio is the ability to foam separate the complexed cyanide at surfactant concentrations well below the so-called "stoichiometric" concentration, that is, at the concentration determined by the formula $EHDA_{3.9}Fe(CN)_6$. For example, at $(Z_t)_i = 1.54$ mM [$(Z_t)_i - (Z_{nc})_r = 1.23$ mM], a separation could be achieved at $X_i = 0.3$ mM, more than 62% lower than the "stoichiometric" value of $1.23\ (3.9)/6 = 0.8$ mM. At the Fe–CN ratio of 0.351, operation at a value of X_i less than 35% lower than the stoichiometric would not be recommended due to the lack of foam production. In general, at the low ratio it appeared that the foam-stabilizing properties of the surfactant were altered to a different extent than in the case of the high ratio or in the case of dichromate. In the latter cases, free, noncomplexed surfactant was necessary to provide the foam which was the carrying medium for the surfactant–anion particulates. In the former the surfactant associated with the $[Fe(CN)_6]^{4-}$ anions appeared still to affect foam stability. The behavior trends were similar to the solutions with the high iron-to-cyanide ratio and with dichromate; however, specific differences could be noted here also. It is evident that different modes and extents of interaction between surfactant and anion were involved in the three cases under discussion. In addition, no case is similar to that observed with ferric oxide colloidal particulates (*9,10*).

Operation at a pH of 7 or less and at the Fe–CN ratio of about 0.35 would be recommended clearly, because the saving in surfactant, 2.1:3.9, exceeded the expenditure of the iron salt, 0.35:0.21. The iron salt is considerably less expensive per unit weight than the surfactant. In addition, the residual concentration of noncomplexed cyanide was 22% (on the average) lower than with the lower iron-to-cyanide ratio. It is conceivable that operation at pH 7 and a higher Fe–CN ratio might yield some additional improvement.

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List of Symbols

V	volume of solution (suspension), liter
X	concentration of cationic surfactant, EHDA-Br, mM
(Z_c)	concentration of complexed cyanide, mM
(Z_{nc})	concentration of noncomplexed cyanide, mM
(Z_t)	concentration of total cyanide, mM
f	subscript referring to the collapsed foam solution (suspension)
i	subscript referring to the initial solution (suspension), before foam separation
r	subscript referring to the residual solution (suspension)

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