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Manuscript received November 24, 1970; revision returned July 20, 1971; paper accepted August 2, 1971.

Foam Separation of Complex Anions: Silver Thiosulfate

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An experimental study is conducted of the ion flotation of $Ag(S_2O_3)^-$ and $Ag(S_2O_3)_2^{3-}$ from an aqueous solution at *pH* 4.5 with a cationic surfactant. For initial solutions 2.0×10^{-3} to 8.0×10^{-3} M in total silver, optimum silver flotation at foam cessation is achieved at a molar thiosulfate to silver ratio (Th/Ag) of 0.75 and surfactant to silver ratio (EHDA/Ag) of 0.5, at Th/Ag = 1.0 and EHDA/Ag = 1.1, and at Th/Ag = 2.0 and EHDA/Ag = 2.2. The silver flotation is 99^+, 98^+, and 92^+ % at the three sets of ratios, respectively. At Th/Ag > 2.0, highly efficient flotation cannot be achieved due to decreased particle size, and perhaps by competition with free $S_2O_3^{2-}$ for the surfactant.

The stoichiometry of the ion flotation product is established from relative silver and surfactant flotation rates. The stoichiometry is independent of foaming time, but is a strong linear function of EHDA/Ag and Th/Ag, in contrast to the stoichiometry of flotation products of other simple and complex anions. Rate data can be fit reasonably by a first-order reversible model. The rate constant is an inverse function of EHDA/Ag, indicating the desirability of pulsed surfactant addition. Results are discussed in terms of the average ligand number of silver, particle size, and surface potential measurements.

Ion flotation is a foam separation process which involves the formation in aqueous solution of an insoluble product between an ionic surface-active agent and an ion (colligend) of charge opposite to that of the long-chain surfactant ion. The product may be formed in the bulk solution or only at higher concentrations which result from the accumulation of the surfactant at the surface layers of gas bubbles dispersed through the solution (*1* to *3*). The particulate product is collected by the bubbles and is carried into a foam or froth rising above the bulk solution. A

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considerable number of experimental foam separations has been carried out with positively charged colligends, including foam fractionations which do not involve an insoluble product (*4* to *6*), but work with anions has been limited to such species as phosphate (*7*), acid chromate (*8*, *9*), EDTA chelates of the lanthanides (*10*), ferrocyanide (*11*), fluorozirconate (*12*), aluminum oxalate (*13*), uranylchloride (*14*), and iron, mercury, and cobalt chlorides (*15*). Until one recent study (*16*), no mention had been made of the stoichiometry (surfactant/colligend molar ratio in the bubble surface layers) of the surfactant-colligend product, and little attention has been paid to the relative flotation rates of the colligend and the surfactant. A thorough ion flotation investigation has not been made that involves two ionic species (such as silver and thiosulfate) that can interact in aqueous solution to form more than one complex colligend. Silver has been foam separated only as Ag^+ in a limited study (*17*).

A possible application of the ion flotation of silver as silver thiosulfate is to the treatment of photographic wastes, particularly for the hypo solutions used in photographic fixing baths in which the thiosulfate is already present (*18*). Thiosulfate can be added to (and recovered from) other aqueous silver wastes, such as a plating waste, to recover the silver by ion flotation.

The objective of this investigation is to establish the optimum ion flotation conditions in terms of the thiosulfate/silver and surfactant/silver ratios; the maximum silver recovery and silver flotation rate for 2.0×10^{-3} to 8.0×10^{-3} M silver solutions; and the ion flotation stoichiometry in order to elucidate the nature of the surfactant-colligend product, with silver present both as $Ag(S_2O_3)^-$ and as $Ag(S_2O_3)_2^{3-}$ (and some Ag_2S).

EXPERIMENT

The major part of the experiments involved the foam separation of silver as silver-thiosulfate complex anions and/or silver sulfide colloid. The complex anions (colloids) were prepared by mixing Reagent Grade $AgNO_3$ solutions and $Na_2S_2O_3 \cdot 5H_2O$ solutions in proper molar concentration ratios. Initial solutions of thiosulfate, containing 1.0×10^{-3} M to 8.0×10^{-3} M $S_2O_3^{2-}$ were added to solutions of $AgNO_3$ containing 2.0×10^{-3} M to 8.0×10^{-3} M Ag^+. The resultant solution was allowed to mix for 10 min., and the *p*H was then adjusted to between 3.0 and 9.4 with 0.5 N NaOH. The cationic surfactant, ethylhexadecyldimethylammonium bromide (EHDA-Br) was added and was mixed with the suspension for an additional time period of 15 min. The initial EHDA-Br concentration was varied to give EHDA/Ag molar ratios between 0.25 and 3.0. It should be mentioned that the solution was never exposed to light beyond a minimal time period.

Two liters of the suspension were then placed in the foam separation column. The foam separation column was made of Pyrex and was 82 cm. in height and 9.7 cm. in diameter. Air was saturated with water, metered with a calibrated rotameter, and dispersed through twin, sintered glass diffusers of 50 micron porosity at a rate of 600 ml./min. (at 1 atm. and 25°C.). The suspension was foamed for varying periods (0.5 to 90 min.), with continuous foam removal from a port located 7.0 cm. above the initial suspension level. After the start of a foaming experiment the volume of the residual suspension was noted at each selected time and residual suspension samples (5 to 10 ml.) were withdrawn with a syringe at set time intervals. Each foam run was continued until complete foam cessation occurred.

Ammonium hydroxide (0.1 to 0.3 ml. of 30% NH_3 solution) was then added to each sample to dissolve silver thiosulfate-surfactant particulates. The solution (after proper dilution) was analyzed for total silver by atomic absorption spectrophotometry. Measurement of surfactant concentrations required the separation of silver from the surfactant by a three stage extraction with chloroform. The chloroform (99.99% EHDA recovered) layer was analyzed by a two-phase titration technique, using bromphenol blue as the indicator and sodium tetraphenylboron as the titrant (*19*).

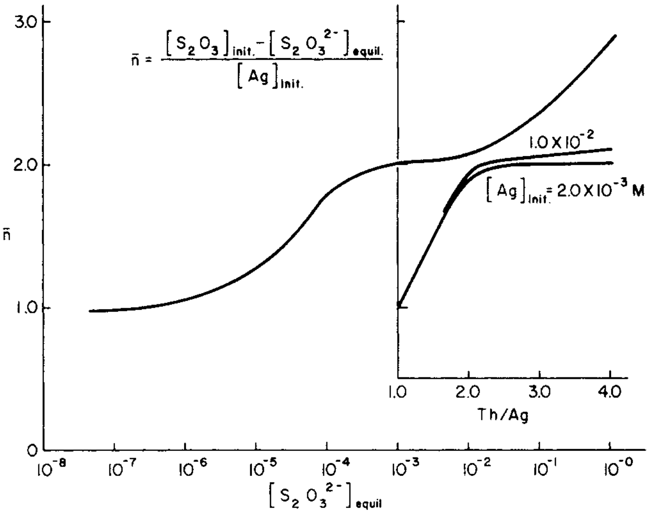

Fig. 1. Average ligand number versus equilibrium $[S_2O_3^{2-}]$ and initial thiosulfate to silver ratio.

A filtration study was carried out with several suspensions (after the addition of surfactant) to determine the molar ratio of EHDA to silver in the precipitate. The suspensions were filtered through 0.20 micron Millipore filters and the filtrate was analyzed.

An estimate of precipitate particle size (after surfactant addition) was made by observing the particles under a microscope (Bausch and Lomb, 460X). Experiments were also performed to determine the surface potential (suspension effect) on suspensions containing Th/Ag = 1.0 to 3.0 and EHDA/Ag = 0.5 to 2.25. The suspension effect (positive values indicate positive charge) was determined by the technique of Honig and Hengst (*20*).

The average bubble diameter was determined in a manner described previously (*21*) to be 600μ, yielding an average generation rate of interfacial area of 6.0 sq.m./min.

SILVER THIOSULFATE SPECIES AND INITIAL EXPERIMENTS

Silver and thiosulfate can interact in aqueous solution to form three complex anions:

$$Ag^+ + S_2O_3^{2-} \rightleftarrows Ag(S_2O_3)^- \qquad K_1 = 7.14 \times 10^8 \quad (1)$$

$$Ag(S_2O_3)^- + S_2O_3^{2-} \rightleftarrows Ag(S_2O_3)_2^{3-} \qquad K_2 = 4.01 \times 10^4 \quad (2)$$

$$Ag(S_2O_3)_2^{3-} + S_2O_3^{2-} \rightleftarrows Ag(S_2O_3)_3^{5-} \qquad K_3 = 6.47 \quad (3)$$

with the equilibrium constants (concentrations in molarity) at 25°C. (*22*). For $[S_2O_3]_{init.}/[Ag]_{init.}$ (abbreviated as Th/Ag) ratios greater than about 1.0, the system is soluble. Below Th/Ag = 1.0, Ag_2S particulates are formed, particularly for Th/Ag < 0.7 (*23*).

$$2Ag^+ + S_2O_3^{2-} + H_2O \rightleftarrows \underline{Ag_2S} + SO_4^{2-} + 2H^+ \quad (4)$$

A distribution diagram was generated using K_1, K_2, and K_3 giving the percentages of the three silver thiosulfate complex anions as a function of the equilibrium thiosulfate concentration.

The distribution diagram was used in turn to generate

Figure 1, which relates the average ligand number, $\bar{n}$ calculated from the initial and equilibrium $[S_2O_3{}^{2-}]$ and the initial [Ag], to the equilibrium $[S_2O_3{}^{2-}]$; $\bar{n}$ is thus the average moles of S_2O_3 bound per mole Ag. An additional scale and curves are given to enable the computation of $\bar{n}$ as a function of Th/Ag (and a very weak function of the initial [Ag]). For example, for $[Ag]_{init.} = 2.0 \times 10^{-3}$ M, at Th/Ag = 1.0, $\bar{n} = 1.0$ and $Ag(S_2O_3)^-$ is the predominant species; at Th/Ag = 2.0, $\bar{n} = 1.88$ and 89% of the silver is present as $Ag(S_2O_3)_2{}^{3-}$. In all cases for Th/Ag > 0.75, the equilibrium $[Ag^+]$ is negligibly small. Figure 1 also can be used to calculate the equilibrium $[S_2O_3{}^{2-}]$ for $1.0 \leq$ Th/Ag ≤ 4.0 and a range of initial [Ag].

It should be stressed that Figure 1 will apply to the silver thiosulfate solutions subjected to foam separation (and discussed below) only before the addition of surfactant. The cationic surfactant, ethylhexadecyldimethylammonium bromide (EHDA-Br), which was employed, reacted rapidly with both $Ag(S_2O_3)^-$ and $Ag(S_2O_3)_2{}^{3-}$ to form an insoluble product which was readily floatable. $EHDA^+$ also interacted with $S_2O_3{}^{2-}$ to form an ion pair or complex which remained soluble but which could also be foam separated (*16*).

Upon the addition of EHDA-Br to a system containing Ag^+, the question naturally arises about the formation (and flotation) of colloidal AgBr. However, it is readily shown that AgBr is very soluble in silver thiosulfate solutions (*24*). A few preliminary experiments were carried out in an attempt to float AgBr (in the total absence of thiosulfate) with $EHDA^+$. With a solution 5.0×10^{-4} M both in $AgNO_3$ and in EHDA-Br, zero silver flotation resulted. The addition of 2.0×10^{-3} M NaBr, before the addition of EHDA-Br in an effort to increase the negative charge on the AgBr, did not alter the silver flotation; but the addition of NaBr, then EHDA-Br, and then 2.5 mg./liter of Dow N-12, a nonionic polymer, resulted in 88% silver flotation.

Three sets of preliminary experiments with silver thiosulfate were conducted to establish the effects of the order of addition of $AgNO_3$ and $Na_2S_2O_3 \cdot 5H_2O$, the mixing times between $AgNO_3$ and $Na_2S_2O_3 \cdot 5H_2O$ and then between Ag-S_2O_3 and EHDA-Br, and *p*H. In all of the experiments discussed below, thiosulfate was added to a silver solution. The addition of silver to thiosulfate (thus forming $Ag(S_2O_3)^-$ and $Ag(S_2O_3)_2{}^{3-}$ in the presence of excess thiosulfate instead of silver) did not have a substantial effect on the flotation. For example at Th/Ag = 2.0, and initial [EHDA] and [Ag] = 2.0×10^{-3} M, the silver flotation at a foaming time of 10 min. was decreased from 65 to 62% upon reversing the order of addition. At Th/Ag = 2.0 and initial [EHDA] and [Ag] = 1.0×10^{-3} M, the silver flotation at a foaming time of 10 min. was decreased from 77 to 69% upon reversing the order of addition.

The time of mixing the $AgNO_3$-$Na_2S_2O_3 \cdot 5H_2O$ solution did not influence the flotation, with variation from 10 to 120 min. being tested. The mixing time between EHDA-Br and the $AgNO_3$-$Na_2S_2O_3 \cdot 5H_2O$ solution had virtually no effect on the percent silver flotation at long foaming times, with the mixing time varied from 15 to 120 min. At short foaming times, the longer mixing time provided some improvement to the flotation. For all experiments discussed below, 10- and 15-min. mixing times were employed, respectively, in the two contact steps.

The flotation *p*H was maintained at 4.5. This value was selected as being slightly above the maximum *p*H realized upon contacting $AgNO_3$ and $Na_2S_2O_3 \cdot 5H_2O$. Variation of the flotation *p*H from 3.6 to 9.4 did not substantially modify the silver flotation: at a foaming time of 10 min. with Th/Ag = 2.0 and initial [EHDA] and [Ag] = 2.0×10^{-3} M, at *p*H 3.6, 69% flotation, at *p*H 5.0, 68% flotation, and at *p*H 9.4, 65% flotation.

FLOTATION MAXIMA

A series of ion flotation experiments was carried out at *p*H 4.5 with initial [Ag] 2.0 to 8.0×10^{-3} M, with Th/Ag from 0.5 to 4.0, and with $[EHDA]_{init.}/[Ag]_{init.}$ (EHDA/Ag) from 0.25 to 2.5. The residual concentrations of both total Ag and total EHDA were determined versus time, including points at foam cessation corresponding to maximum flotation. Results are discussed in terms of $100(1 - [Ag]_{resid}/[Ag]_{init.})$, the percent flotation, in which $[Ag]_{resid}$ is the total silver concentration in the residual suspension in the foam separation column at foam cessation.

In Figures 2 and 3, the percent flotation is related to EHDA/Ag and to Th/Ag, with each data point corresponding to the maximum flotation at that particular set of conditions. Foaming times at foam cessation ranged from 5 to 20 min. over the ranges of Th/Ag and EHDA/Ag for which 50% flotation or better was achieved. A conservative estimate of the reproducibility of $[Ag]_{resid}$ is ±10%,

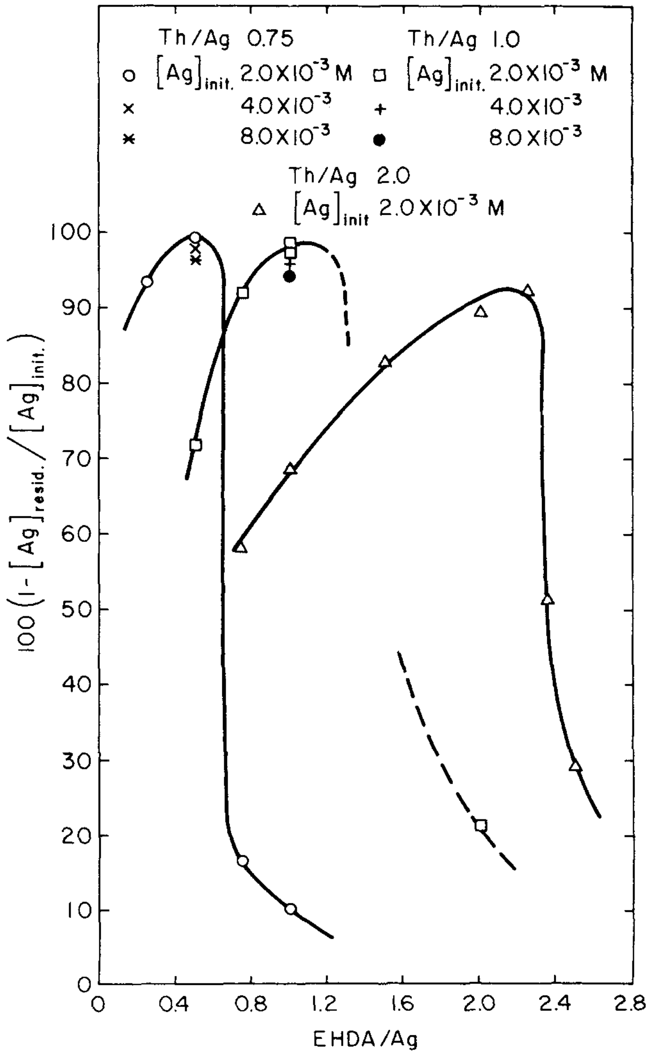

Fig. 2. Percent silver flotation at foam cessation versus initial surfactant to silver ratio.

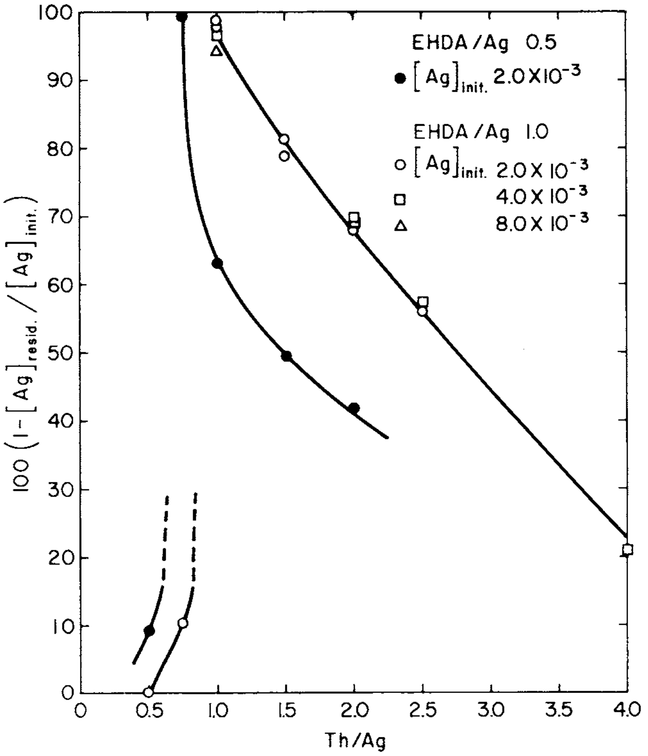

Fig. 3. Percent silver flotation at foam cessation versus initial thiosulfate to silver ratio.

TABLE 1. AVERAGE PARTICLE SIZE AND RELATIVE SURFACE POTENTIAL OF EHDA-Ag-S_2O_3 PRECIPITATES

	EHDA/Ag	Average particle size, μm	Suspension effect (surface potential), mv
Th/Ag = 1.0			
	0.5	40	+0.3
	1.0	25	+0.7
Th/Ag = 2.0			
	0.5	65	−0.2
	1.0	40	−0.6
	2.0	20	−0.3
	2.25	20	+1.5
	2.5	5	—
	2.7	<1	—
	3.0	0.013*	—
EHDA/Ag = 1.0			
	Th/Ag		
	1.0	25	+0.7
	2.0	40	−0.5
	2.5	15	−0.8
	2.8	15	−1.1
	3.0	15	−1.3
	3.5	8	—
	4.0	<1	—

* From electron micrograph.

with the variation among replicate experiments always being well within this bound. This would result in $100(1 - [Ag]_{resid}/[Ag]_{init}) = 50 \pm 5$; $= 90 \pm 1$; and $= 95 \pm 0.5$, etc.

Figure 2 indicates that $99^+\%$ flotation was achieved at Th/Ag = 0.75 and EHDA/Ag = 0.5, that $98^+\%$ flotation was achieved at Th/Ag = 1.0 and EHDA/Ag = 1.1, and that $92^+\%$ was obtained at Th/Ag = 2.0 and EHDA/Ag = 2.2. The increase in EHDA/Ag with Th/Ag was related of course to the silver thiosulfate species that were present, as discussed below in greater detail. Obviously, if Th/Ag could be controlled (in contrast to a photographic waste in which Th/Ag was already determined), a value of 0.75 would be the choice, giving the maximum flotation and the minimum required EHDA/Ag. At a constant value of Th/Ag, an increase in EHDA/Ag improved the flotation until a certain value was reached, and then the flotation fell off most abruptly. This was produced by the adsorption of excess $EHDA^+$ on the precipitate (perhaps with the charged head group pointing outwards and the hydrocarbon chain toward the particle (*25*)), preventing the aggregation of the particles that was necessary for effective flotation. This can be validated, at least qualitatively, from particle size and surface potential [suspension effect (*20*)] measurements given in Table 1 at Th/Ag = 1.0 and 2.0.

Figure 3 includes a few points from Figure 2 but extends the range of Th/Ag from 0.5 to 4.0. At Th/Ag = 0.5, the positively-charged Ag_2S particulates which were present could not be floated by the cationic surfactant. The positive charge was validated by successful silver flotation with an anionic surfactant, sodium dodecylsulfate. At Th/Ag = 0.75, particulates were also present before EHDA-Br was added, but they were floatable due probably to charge reversal by $S_2O_3{}^{2-}$ or $Ag(S_2O_3)^-$. Erkut (*23*) has reported maximum stability of Ag_2S sols (formed from Ag^+ and $S_2O_3{}^{2-}$ according to Equation (4) at Th/Ag = 0.63. At Th/Ag = 0.75, excellent flotation was achieved at EHDA/Ag = 0.5, but EHDA/Ag = 1.0 was an overdosage of surfactant.

Above Th/Ag = 0.75 (for EHDA/Ag = 0.5) and Th/Ag = 1.0 (for EHDA/Ag = 1.0), the flotation fell off, principally due to the conversion of $Ag(S_2O_3)^-$ to $Ag(S_2O_3)_2{}^{3-}$ (see Figure 1) as Th/Ag was increased, giving rise to a larger demand for $EHDA^+$. Above Th/Ag = 2.0, where the free $S_2O_3{}^{2-}$ became appreciable (Figure 1), some surfactant probably became associated with the free $S_2O_3{}^{2-}$, reducing the amount of $EHDA^+$ available to float the $Ag(S_2O_3)_2{}^{3-}$. Flotation experiments at $[S_2O_3]_{init.} = 1.5 \times 10^{-4}$ M and $[EHDA]_{init.} = 3.7 \times 10^{-4}$ M, with no silver present, yielded 89% flotation of the $S_2O_3{}^{2-}$ (*16*), although no particulate product was formed between the $EHDA^+$ and $S_2O_3{}^{2-}$. The interaction of $EHDA^+$ with either $Ag(S_2O_3)^-$ or $Ag(S_2O_3)_2{}^{3-}$ was considerably greater than with $S_2O_3{}^{2-}$, but with high concentrations of $S_2O_3{}^{2-}$, the interference of free $S_2O_3{}^{2-}$ could become appreciable. From Table 1, above Th/Ag = 2.0, the particle size decreased, with the particles virtually dissolving at Th/Ag $\geqq$ 4.0, and the negative surface potential increased, due to adsorption of free $S_2O_3{}^{2-}$ on the particulates.

Referring to the experiments indicated in Figures 2 and 3 for which the flotation was 50% or greater, the volume of foam (collapsed, as liquid) in which the silver thiosulfate and surfactant were concentrated, ranged from 0.03 to 0.28 liter at Th/Ag = 0.75, increasing of course with EHDA/Ag; at Th/Ag = 1.0, from 0.03 to 0.28; and at Th/Ag = 2.0, from 0.05 to 0.82. The volume of the initial solution was always maintained at 2.0 liters. At EHDA/Ag = 0.5, the foam volume was almost independent of Th/Ag, ranging from 0.01 to 0.04 liter. At EHDA/Ag = 1.0, the range was 0.10 to 0.15.

For the foam cessation experiments, the concentrations of total EHDA in the residual solutions were generally low, and the range was 1.0×10^{-5}M to 3.0×10^{-5} M, increasing with EHDA/Ag but being rather independent of Th/Ag.

ION FLOTATION RATES AND STOICHIOMETRY

In a batch ion flotation experiment, the stoichiometry of the surfactant-colligend interaction product in the surface layers of the gas bubbles can be established directly from the slope of a graph of residual surfactant concentration versus residual colligend concentration, with each point corresponding to a different foaming time (*16*). The stoichiometry S is defined as $\frac{d\,[\mathrm{EHDA}]_\theta}{d\,[\mathrm{Ag}]_\theta}$, in which $[\mathrm{EHDA}]_\theta$ and $[\mathrm{Ag}]_\theta$ are total surfactant and total silver concentrations after a foaming time $= \theta$, min.

For the silver thiosulfate system, with $[\mathrm{Ag}]_{\mathrm{init.}} = 2.0 \times 10^{-3}$ M, Th/Ag from 0.75 to 2.5, and EHDA/Ag from 0.25 to 2.25, S was independent of foaming time, and graphs of $[\mathrm{EHDA}]_\theta$ versus $[\mathrm{Ag}]_\theta$ were invariably linear. This behavior can be contrasted to that with EHDA^+ and $\mathrm{S_2O_3}^{2-}$ (no silver) in which S varied with foaming time (*16*).

For the silver thiosulfate system, S was a strong linear function of EHDA/Ag (at constant Th/Ag) as indicated at the left side of Figure 4. Each point corresponds to the slope of a linear relation between $[\mathrm{EHDA}]_\theta$ and $[\mathrm{Ag}]_\theta$. This behavior is in contrast to that with EHDA^+ and $\mathrm{HCrO_4}^-$, EHDA^+ and I^-, and EHDA^+ and $\mathrm{Fe(CN)_6}^{4-}$, in which S was independent of the initial surfactant to colligend ratio (*16*). Variation of S with EHDA/Ag indicates that the relative molar quantities of EHDA and Ag (as silver thiosulfate) that entered the precipitate particles, as they formed, grew, and agglomerated, were a function of the solution concentration ratio and that the particulates were nonstoichiometric.

This hypothesis, made from ion flotation results, was tested further by filtering suspensions of surfactant and silver thiosulfate, analyzing the filtrate, and using a material balance to generate the precipitate analysis. The filtration results invariably agreed with the ion flotation results, as noted from Figure 4.

At Th/Ag = 2.0, from Figure 1 it is apparent that 89% of $[\mathrm{Ag}]_{\mathrm{init.}}$ was present as $\mathrm{Ag(S_2O_3)_2}^{3-}$, before surfactant addition, giving a theoretical stoichiometry of $0.89(3) + 0.11(1) = 2.78$. The actual stoichiometry varied from 1.3 to 2.5. It is evident that $\mathrm{Ag(S_2O_3)_2}^{3-}$ entered in the precipitate structure together with Na^+ (instead of EHDA^+) and that the amount of Na^+ versus EHDA^+ was a function of EHDA/Ag. It is likely that steric effects prevented three EHDA cations from interacting with each $\mathrm{Ag(S_2O_3)_2}^{3-}$. It could also be argued that interaction between EHDA^+ and $\mathrm{Ag(S_2O_3)}^-$ shifted the equilibrium from the trivalent $\mathrm{Ag(S_2O_3)_2}^{3-}$, reversing Equation (2); however, for S to increase as EHDA/Ag were increased, the steric effect would have to override the shift in equilibrium. It is also possible that the stoichiometry behavior was due to secondary adsorption or exchange of $\mathrm{Ag(S_2O_3)_2}^{3-}$ on the surfaces of the precipitate particles as they grew and aggregated. This could be validated in part from Table 1, showing a decreasingly negative surface potential as EHDA/Ag was increased. (The suspension effect measurement at EHDA/Ag = 0.5 is questionable because so little precipitate was present.) From particle size measurements, it appears that $\mathrm{Ag(S_2O_3)_2}^{3-}$ adsorption promoted aggregation.

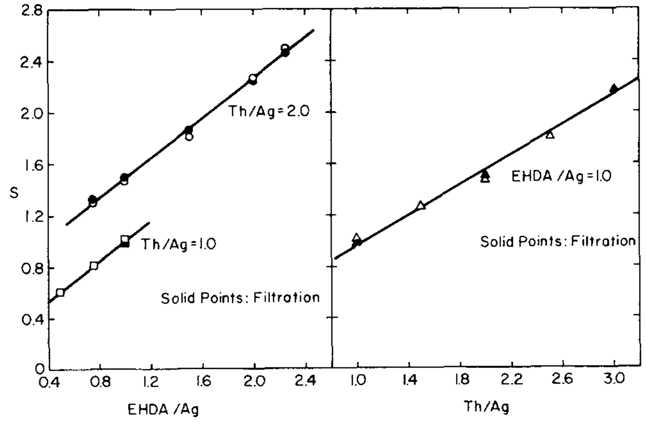

Fig. 4. Stoichiometry of ion flotation product versus initial surfactant to silver and thiosulfate to silver ratios.

Similar behavior was observed at Th/Ag = 1.0 (Figure 4). At Th/Ag = 0.75, $S = 0.26$ at EHDA/Ag = 0.25 and $S = 0.52$ at EHDA/Ag = 0.50. For the flotation of particles present before surfactant addition, it would be expected that $S = \phi(\mathrm{EHDA/Ag})$ would depend on particle surface character.

At constant EHDA/Ag, S also varied linearly with Th/Ag, from Figure 4 (right). In this case, the silver thiosulfate species changed (Figure 1), with the percentage $\mathrm{Ag(S_2O_3)_2}^{3-}$ present increasing linearly with Th/Ag up to Th/Ag = 2.0. However, for Th/Ag > 1.0, S remained substantially less than the theoretical value. Also from Th/Ag = 2.0 to Th/Ag = 3.0, S continued to increase. This could occur only if EHDA^+ influenced the silver thiosulfate equilibria, producing a decrease in $\bar{n}$ at a given Th/Ag, compared to the theoretical value obtained from Figure 1.

In addition to maximum silver flotation and the stoichiometry of the ion flotation product, the feasibility of a foam separation process depends on the rate of flotation. Rate data were taken over the full range of Th/Ag and EHDA/Ag at $[\mathrm{Ag}]_{\mathrm{init.}} = 2.0 \times 10^{-3}$ M. A reasonable fit was obtained with a simple first order-reversible model

$$\frac{d\,[\mathrm{Ag}]_\theta}{d\theta} = -k([\mathrm{Ag}]_\theta - [\mathrm{Ag}]_{\mathrm{resid.}}) \qquad (5)$$

in which $[\mathrm{Ag}]_{\mathrm{resid.}}$ corresponds to foam cessation. The model was generally quite good over the first few minutes of foaming, during which most of the silver thiosulfate was being floated. Results are indicated in Figure 5 for Th/Ag

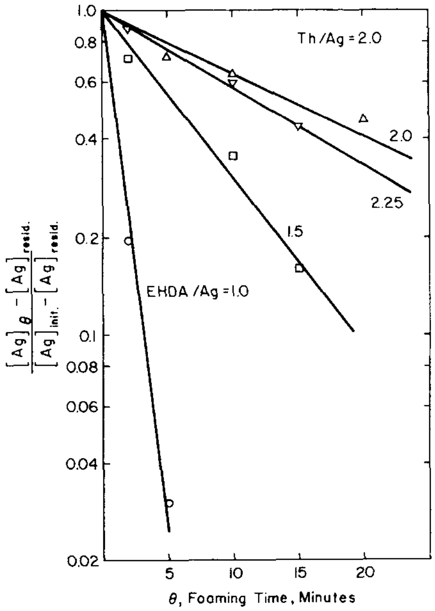

Fig. 5. Test of fit of integrated form of Equation (5) for initial thiosulfate to silver ratio of 2.0.

TABLE 2. VALUES OF RATE CONSTANTS IN EQUATION (5)

	EHDA/Ag	k, 1/min.
Th/Ag = 0.75		
	0.25	2.1
	0.50	0.097
Th/Ag = 1.0		
	0.50	1.4
	0.75	1.3
	1.0	1.1
Th/Ag = 2.0		
	1.0	0.74
	1.5	0.12
	2.0	0.045
	2.25	0.055
EHDA/Ag = 1.0		
	Th/Ag	
	1.0	1.1
	1.5	1.1
	2.0	0.86
	2.5	0.14

= 2.0 and EHDA/Ag = 1.0, 1.5, 2.0, and 2.25. Values of the rate constant k are given in Table 2. At constant Th/Ag = 2.0 and 0.75, k decreased substantially as EHDA/Ag was increased, and decreased slightly with EHDA/Ag at Th/Ag = 1.0. At constant EHDA/Ag, the rate fell off only at high Th/Ag. The decrease in k with an increase in EHDA/Ag could have been produced by competition between nonreacted EHDA$^+$ and that reacted with the silver thiosulfate for the bubble interfaces. Also the formation of the precipitate in the presence of excess silver thiosulfate (low EHDA/Ag) tended to promote aggregation which in turn enhanced the flotation rate.

CONCLUSIONS

From foam cessation experiments, optimum flotation is achieved at Th/Ag = 0.75 and EHDA/Ag = 0.5, Th/Ag = 1.0 and EHDA/Ag = 1.1, or Th/Ag = 2.0 and EHDA/Ag = 2.2. Above Th/Ag = 2.0, the flotation is not complete as particle size decreases and negative surface potential increases. At each of the optima, the rate of ion flotation is slower, by as much as an order of magnitude or more, than the rate at one-half the desired EHDA/Ag ratio. Pulsed surfactant dosage (*26*, *27*) might be the answer, adding the surfactant in several smaller dosages with aeration between each dose. The continuous-flow analogue would be columns-in-series operation, with additional surfactant added to the feed to each ion flotation column. The stoichiometry of the ion flotation product that is obtained is independent of foaming time, but is a strong linear function of Th/Ag and EHDA/Ag, indicating some steric effects and the possible influence of EHDA$^+$ on the silver thiosulfate equilibrium. The surfactant could be separated readily from the product by dissolution in NH_4OH, followed by extraction into chloroform. This would also enable the recovery of silver as ammonia complexes.

NOTATION

$[\mathrm{Ag}]_{\mathrm{init.}}$ = concentration of total silver, molar, in initial suspension before foam separation
$[\mathrm{Ag}]_{\theta}$ = concentration of total silver, molar, in suspension after θ minutes of foaming
$[\mathrm{Ag}]_{\mathrm{resid.}}$ = concentration of total silver, molar, in residual suspension at foam cessation
[EHDA] = concentration of surfactant, molar, in suspension with subscript references same as to Ag
EHDA/Ag = molar surfactant to total silver ratio in initial suspension
$[S_2O_3^{2-}]_{\mathrm{equil.}}$ = concentration of free $S_2O_3^{2-}$, molar, in suspension at equilibrium
$[S_2O_3]_{\mathrm{init.}}$ = concentration of total thiosulfate, molar, in initial suspension
Th/Ag = molar total thiosulfate to total silver ratio in initial suspension
k = first-order rate constant, 1/min.
$\bar{n}$ = average ligand number (Figure 1)
S = stoichiometry: moles of surfactant in surface layers per mole of total silver
θ = foam separation time, min.

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Manuscript received July 6, 1971; revision received August 24, 1971; paper accepted August 25, 1971.