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Foam Separation of Anions: Stoichiometry

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Summary

Experimental studies have been carried out on the foam separation of I^-, $HCrO_4^-$, $S_2O_3^{2-}$, and $Ag(S_2O_3)_2^{3-}$ using a cationic surfactant as the collector-frother. The object of the work is the establishment of the stoichiometry of the foam-separated surfactant cation–anion product to gain some insight into the mode of interaction between the surfactant and the anion. The stoichiometry, S, defined as the ratio of the rate of surfactant removal to the rate of anion (colligend) removal at the gas bubble interfaces, ranges from 2.2–2.8 mole/mole (average values) for $S_2O_3^{2-}$, being a function of foaming time for the only system which does not involve the formation of particulates between the surfactant and the colligend. For $HCrO_4^-$, I^-, and $Ag(S_2O_3)_2^{3-}$, S is constant with foaming time and a particulate product is formed in the bulk solution and/or the froth. For $HCrO_4^-$, S is close to unity and is almost independent of the feed surfactant/colligend ratio, indicating minimum free surfactant. For I^-, S averages 1.3 and is a weak function of the feed ratio, indicating that free surfactant is significant. Steric effects or secondary adsorption or exchange of $Ag(S_2O_3)_2^{3-}$ onto the particulates makes S a linear function of the feed ratio.

INTRODUCTION

Inorganic and organic ions have been removed and concentrated from aqueous solution by foam separation processes, with most of the work referenced in three excellent reviews (*1–3*). An ionic surface-active agent with the long-chain ion of opposite charge to the ion (colligend) to be foam separated is added to the solution; surfactant plus colligend are accumulated at the gas–liquid interfaces associated with generated gas bubbles and are separated in a foam or froth. Before foam separation, the colligend may be complexed or precipitated. In foam separation, if an insoluble product between surfactant and colligend is not formed, the process is called foam fractionation; if an insoluble product results from interaction between the surfactant and the colligend, the process is called ion flotation; if the ion is first precipitated and then the precipitate is floated (with or without the addition of a surfactant), the process is called precipitate flotation (*4–7*).

In spite of the extensive work done on the foam separation of ions, including recent studies which include the discussion of possible mechanisms (*8–11*), very little attention has been paid to the relative rates of flotation of the surfactant and the oppositely-charged colligend. Such information is vital to the establishment of the stoichiometry of the product that is foam separated and to at least a qualitative understanding of the mode of interaction between the surfactant and the colligend. In the large majority of the studies which have been made, the concentration of the surfactant during the course of a foam separation experiment has not even been monitored. Limited consideration has been given to relative removals of surfactant and colligend (*12–15*). However, these investigators, in the development of a "relative fractionation parameter," did not use rate data, but instead relied on data at long foaming times, corresponding to no further foam formation. Such data are not ideally suited to the establishment of the stoichiometry of foam separation because they yield only the approximate rates of flotation averaged over long time periods.

In this study the instantaneous rates of foam separation of both surfactant and colligend are presented for a cationic surfactant and each of the anions I^-, $HCrO_4^-$ ($Cr_2O_7^{2-}$), $S_2O_3^{2-}$, and $Ag(S_2O_3)_2^{3-}$($Ag(S_2O_3)^-$). The stoichiometry of the foam-separated product is established in each case and the data are interpreted in terms of the mode of interaction between surfactant and colligend.

SURFACTANT–COLLIGEND INTERACTION

Consider the addition of a cationic surfactant to a neutral aqueous solution of a single electrolyte, such as NaI. The surfactant is a quaternary ammonium salt, ethylhexadecyldimethylammonium bromide (EHDA-Br), which ionizes almost completely at pH 7. The objective is the foam separation via generated gas bubbles of iodide (colligend) which has undergone some form of interaction with the EHDA cation. Three possible interactions are possible:

(a) Limited or no interaction in bulk solution. Upon gas bubble generation, the surfactant is adsorbed at the gas–liquid interfaces of the bubbles; the adsorbed surfactant layer then acts as a mobile ion exchanger:

$$(\mathrm{EHDA})\mathrm{Br}_i + \mathrm{I}^-{}_b \rightleftarrows (\mathrm{EHDA})\mathrm{I}_i + \mathrm{Br}^-{}_b$$

in which *i* and *b* stand for the interfacial and bulk solution phases, respectively. At equilibrium, a distribution or selectivity coefficient may be written for the interfacial and bulk solution phases (*10*).

(*b*) Interaction in bulk solution to form an ion pair or soluble complex which then diffuses to and is adsorbed at the bubble interfaces. At the interfaces, the concentration of EHDA^+ and I^- (or alternatively of the complex) may become great enough to precipitate (EHDA)I, resulting in an insoluble product collected in the foam.

(c) Reaction in bulk solution to form a precipitate. As the precipitate aggregates, there may be secondary adsorption or exchange of I^- or of EHDA^+ as the potential determining ion; the particles are then picked up by gas bubbles, with the reacted EHDA^+ acting as a collector; free or unreacted EHDA^+ acts as a frother and may also promote flotation by interaction at the gas bubble interfaces with the EHDA^+ on the surfaces of the precipitate particles.

These three categories are simply a convenient way of detailing surfactant–colligend interactions. However, some of the actual cases may fall in between the three categories. Considering the interaction of the monovalent EHDA^+ with a general anion, A^{q-}, and only the second and third categories, the reaction to form a complex or precipitate may be written as:

$$q\mathrm{EHDA}^+ + \mathrm{A}^{q-} \rightleftarrows (\mathrm{EHDA})_q\mathrm{A}$$

Then in the case of a precipitate, the aggregation plus secondary adsorption stages may be approximated by:

$$n(\mathrm{EHDA})_q\mathrm{A} + p\mathrm{A}^- + m\mathrm{EHDA}^+ \rightleftarrows (\mathrm{EHDA})_{nq+R}(\mathrm{A})_{n+p}$$

An increase in the bulk solution concentration of EHDA^+ may drive the first reaction to the right but may inhibit the second due to the reduction in A^{q-} whose adsorption or exchange may be vital to precipitate aggregation. The second "reaction" is likely to be relatively irreversible compared to the first.

The surfactant–colligend interaction product which is foam separated also will involve free surfactant that is adsorbed at the bubble interfaces and is balanced for electroneutrality by anions such as Br^-, OH^-, and noninteracted colligend. The most general stoichiometry of the foam separation product is

$$S = \frac{nq + m + nk}{n + p} \tag{1}$$

in which k is the moles of free surfactant per n moles of $(EHDA)_qA$. In the absence of appreciable quantities of free surfactant,

$$S = \frac{nq + m}{n + p} \tag{2}$$

and in the absence of adsorption of appreciable quantities of either A^{q-} or $EHDA^+$,

$$S = q + k \tag{3}$$

A batch foam separation process can be utilized readily to establish experimental values of S. At time equals zero, the initial solution or suspension of volume, V_i, contains $EHDA^+$ of concentration, X_i, mM and anion (colligend) A^{q-} of concentration, Z_i, mM. The gas flow is then initiated, and surfactant and colligend are foam separated. As the experiment proceeds, the total rate of removal of $EHDA^+$ is $d(X_rV_r)/dt$, while the rate of removal of $EHDA^+$ in the liquid of bulk solution concentration, X_r, which is entrained in the foam or froth, is $X_r(dV_r/dt)$. The assumption is made that most of the volume of the foam (collapsed, as liquid) consists of entrained bulk liquid. The rate of removal of $EHDA^+$ at the bubble interfaces is thus

$$\frac{d(X_rV_r)}{dt} - X_r\frac{dV_r}{dt} = V_r\frac{dX_r}{dt} \tag{4}$$

Similarly for the colligend, the rate of removal of A^{q-} at the bubble interfaces is,

$$\frac{d(Z_rV_r)}{dt} - Z_r\frac{dV_r}{dt} = V_r\frac{dZ_r}{dt} \tag{5}$$

Hence, S, the stoichiometry of the foam separation product collected in

TABLE 1

Summary of Experimental Conditions

Anion	pH	Reagents	Initial anion concn (*mM*)	Mixing time with surfactant (min)	Foam column diameter (cm)	Initial foam height (cm)	Air rate (liter/min)	Foaming time (min)
I^-	5.6	NaI	0.15 and 0.30	10	9.7	16.0	0.4	5–40
$HCrO_4^-$	4.2	$Na_2Cr_2O_7 \cdot 2H_2O$ HCl	0.46, 0.93, and 1.86	15	4.5	6.0	0.025	0.2–22
$Ag(S_2O_3)_2^{3-}$ $Ag(S_2O_3)^-$	4.5	$AgNO_3$ $Na_2S_2O_3 \cdot 5H_2O$[a] NaOH	1.0 and 2.0	15	9.7	7.0	0.6	0.5–90
$S_2O_3^{2-}$	4.6	$Na_2S_2O_3 \cdot 5H_2O$ HCl	0.15 and 0.30	15	9.7	7.0	0.6	5–70

[a] S_2O_3/Ag ratio of 2.0.

the surface layers at the bubble interfaces, may be determined experimentally as

$$S = dX_r/dZ_r \tag{6}$$

The ratio dX_r/dZ_r should be rather independent of experimental variations in bubble size, gas rate, foam height, column diameter, etc.

EXPERIMENTAL

The foam separation stoichiometry, $S = dX_r/dZ_r$, was determined experimentally for four systems, in each case using EHDA-Br as the surfactant. The foam separation columns were made of Pyrex, and coarse sintered glass diffusers were used to disperse filtered air. Experimental conditions are detailed in Table 1, including the anion (colligend), pH, reagents to prepare the initial bulk solution, the initial colligend concentration, column geometry, and operating conditions. For each system, except $HCrO_4^-$, the initial solution volume, V_i, was 2.0 liters. For $HCrO_4^-$, V_i = 0.40 liter. Temperature was maintained at 24°C. Concentrations of the colligends in the residual bulk solution were determined as follows: I^- by an Orion ion selective electrode, $HCrO_4^-$ by the diphenyl carbazide method (*16*), $Ag(S_2O_3)_2^{3-}$ and $Ag(S_2O_3)^-$ as Ag by atomic absorption spectroscopy after dissolution of the Ag in concentrated NH_4OH, and $S_2O_3^{2-}$ by UV absorption at 220 mμ. Surfactant concentrations in the residual solutions were determined by a two-phase titration technique, using bromphenol blue as the indicator and sodium tetraphenylboron as the titrant (*17*).

RESULTS

Relative rate data are presented for two of the four systems in Figs. 1 and 2. The residual $EHDA^+$ concentration is plotted versus the residual colligend concentration for a single initial colligend concentration, Z_i, and several initial $EHDA^+$ concentrations, X_i. Thus each line or curve represents a single series of experiments, with the foaming time as the only variable and with the points representing concentrations of $EHDA^+$ and colligend after various foaming times. All concentrations are mM ($1.0 \times 10^{-3}\,M$). The slopes of the lines or curves are S. Data for the other two systems, I^- and $Ag(S_2O_3)_2^{3-}$ ($Ag(S_2O_3)^-$), gave relations

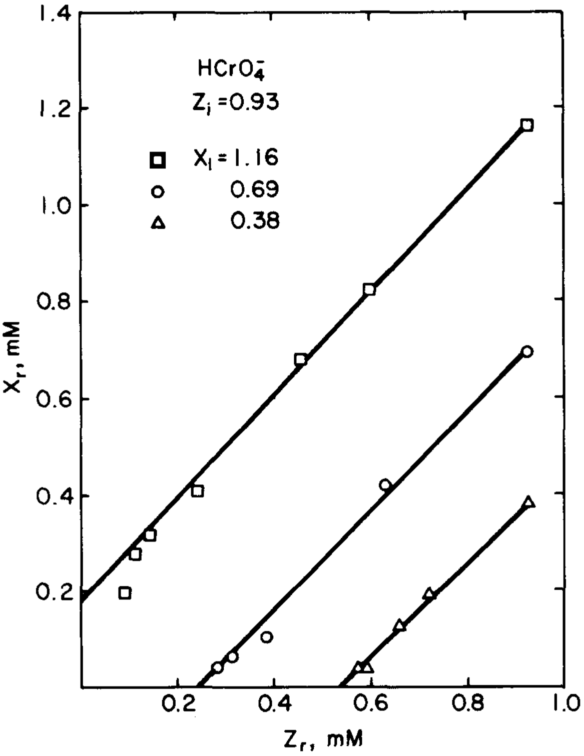

FIG. 1. Relations between the residual surfactant (EHDA$^+$) concentration and the residual acid chromate (HCrO$_4^-$) concentration at identical foaming times.

between X_r and Z_r that were clearly as linear as those for HCrO$_4^-$ in Fig. 1.

Figures 3 and 4 summarize the values of S vs. X_i/Z_i and X_r/Z_r. To clarify the mode of presentation, observe the point in Fig. 3 (top), $S = 1.33$, $X_i/Z_i = 1.0$. The point is a circle, so $Z_i = 0.15$ and therefore $X_i = 0.15$. The horizontal line shows that $S = dX_r/dZ_r = 1.33$ during the entire course of the variable foaming time series, over which the bulk solution ratio of EHDA$^+$ to I$^-$ varied from the initial value of 1.0 to the value 0.19 at the end of the series. Five series are given all together. The slanted line corresponds to $S = X_i/Z_i$. If $S < X_i/Z_i$, then X_r/Z_r must always increase during the course of a series of foaming time experiments; if $S < X_i/Z_i$, then X_r/Z_r must decrease.

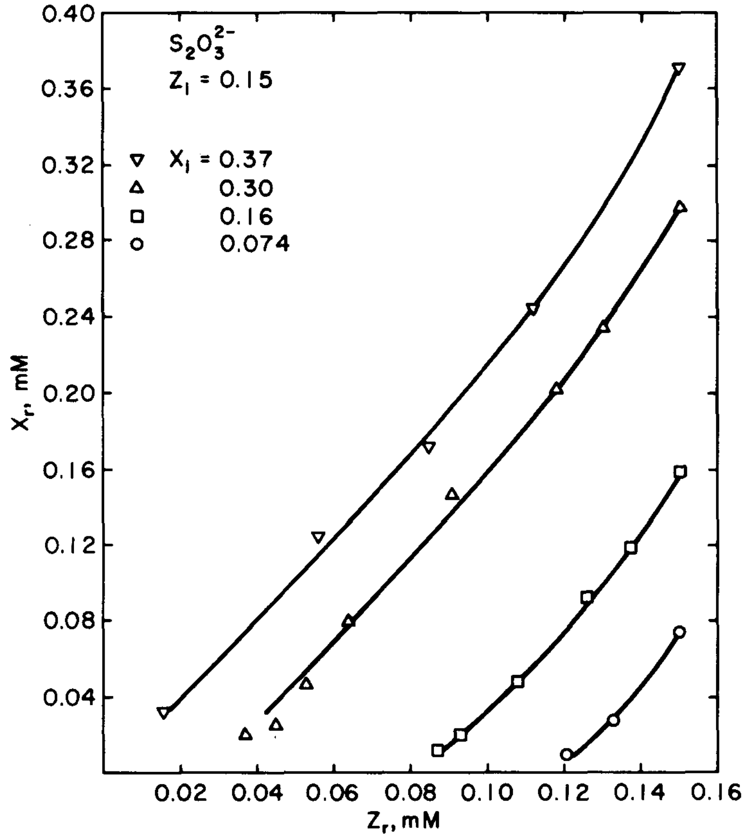

FIG. 2. Relations between the residual surfactant ($EHDA^+$) concentration and the residual thiosulfate ($S_2O_3^{2-}$) concentration at identical foaming times.

For I^-, S remained between 1.22 and 1.39 for X_i/Z_i from 0.67 to 1.33 and X_r/Z_r from 0.11 to 1.55. For $HCrO_4^-$ (Fig. 3, bottom), S remained within even tighter limits, ranging from 0.98 to 1.06 for X_i/Z_i from 0.41 to 1.25 and X_r/Z_r from 0.07 to 2.30. The system with $Ag(S_2O_3)_2^{3-}$ ($Ag(S_2O_3)^-$), indicated (Fig. 4, top) that S was a much stronger function of X_i/Z_i, although for a fixed X_i/Z_i, there was little variation in S with foaming time and thus with X_r/Z_r. The only system showing the effect of X_r/Z_r on S was $EHDA^+$-$S_2O_3^{2-}$.

For the sake of comparison, long foaming time data are given for the

$EHDA^+$–$Fe(CN)_6^{4-}$ system in Fig. 4 (bottom) (*15*). The initial solutions were prepared with NaCN and $FeSO_4 \cdot 7H_2O$ at a molar Fe/CN ratio of 0.21; the pH was adjusted to 7.0 with NaOH. Each point represents the average stoichiometry of the foam separation product during the course of an experiment, $S = (X_i - X_r)/(Z_i - Z_r)$, and does not represent the instantaneous relative removal rate, dX_r/dZ_r. Nevertheless, it is interesting to note that S only varied from 3.56 to 3.98 for X_i/Z_i from 1.29 to 3.86. Figure 4 is based on the assumption that the complexed CN was present as $Fe(CN)_6^{4-}$; if it were present as $Fe(CN)_5H_2O^{3-}$, S would vary from 2.89 to 3.31 for X_i/Z_i from 1.08 to 3.22.

A summary of results for the five systems discussed above, in addition to $EHDA^+$–$C_6H_5O^-$ (*13*) and $EHDA^+$–HPO_4^{2-} (*12*), is given in Table 2. A note is made of the presence or absence of particles formed between

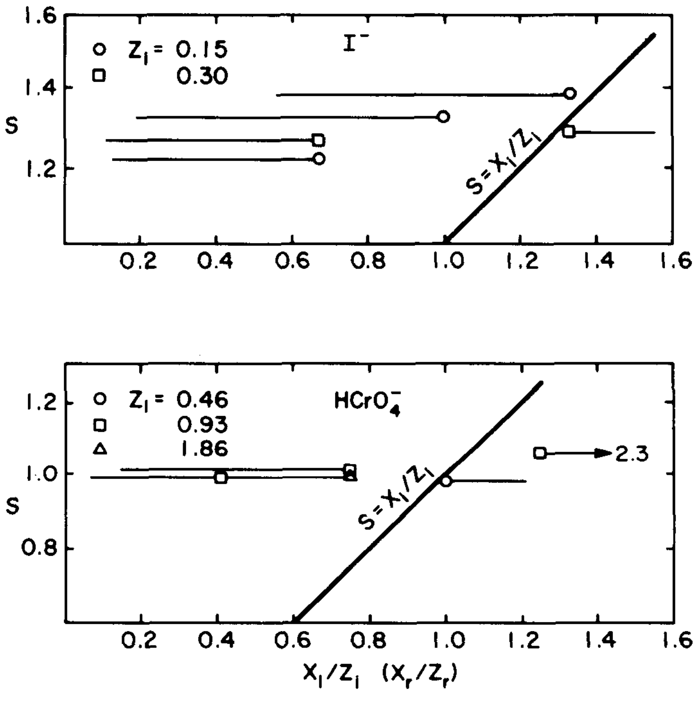

FIG. 3. Variation of the stoichiometry for the I^- and $HCrO_4^-$ systems.

TABLE 2

Summary of Foam Separation Results

Anion	pH	Initial anion concn. (*mM*)	Particles present in bulk solution?	Particles present in foam?	Stoichiometry range (mole EHDA/mole anion)	X_i/Z_i to give $1 - Z_r/Z_i =$ 0.90
I^-	5.6	0.15	No	Yes	1.2–1.4	1.5
$HCrO_4^-$	4.2	0.93	Yes	Yes	$1.0^- – 1.1^-$	1.1
$\left\{ Ag(S_2O_3)_2^{3-} \right.$	4.5	2.0	Yes	Yes	$\phi(X_i/Z_i)$	2.2
$\left. Ag(S_2O_3)^- \right.$						
$S_2O_3^{2-}$	4.6	0.15	No	No	2.2–2.8[a]	2.5
$\left\{ Fe(CN)_6^{4-} \right.$	7.0	0.21[b]	Yes	Yes	3.6–4.0	3.5
$Fe(CN)_5(H_2O)^{3-}$						
$C_6H_5O^-$	12.9	0.35	No	No	Varies	4.6
HPO_4^{2-}	8.0	0.26	No	No	Varies	6.2

[a] Average values; also $\phi(X_i/Z_i)$.

[b] 1.23 *mM* as CN.

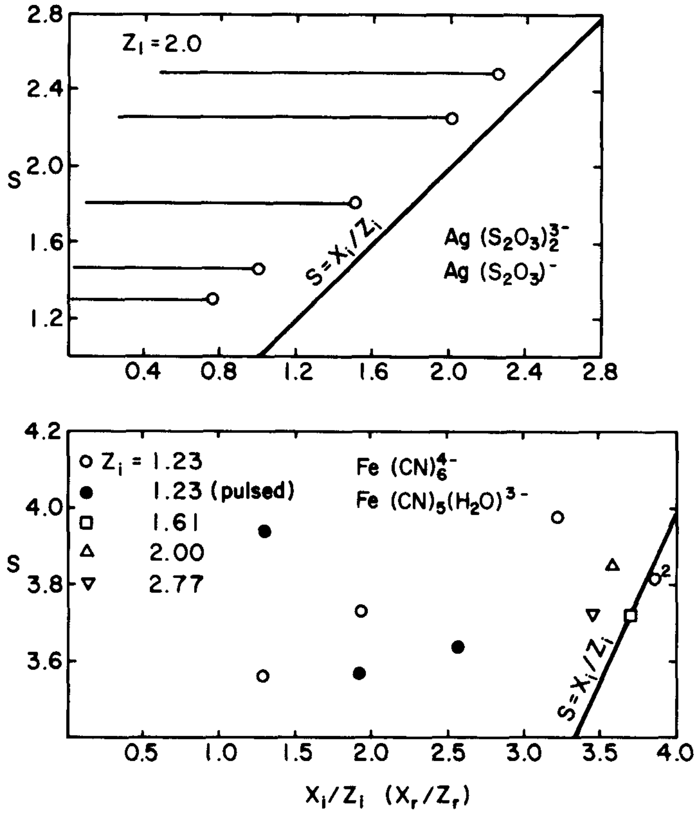

FIG. 4. Variation of the stoichiometry for the $Ag(S_2O_3)_2^{3-}$-($Ag(S_2O_3)^-$) and $Fe(CN)_6^{4-}$-($Fe(CN)_5(H_2O)^{3-}$) systems.

TABLE 3

Average Values of S for $EHDA^+$-$S_2O_3^{2-}$ System

$Z_i(mM)$	X_i/Z_i	S_{avg}
0.15	2.47	2.66
0.15	1.99	2.53
0.15	1.06	2.29
0.15	0.50	2.21
0.30	1.99	2.81
0.30	1.06	2.49

$EHDA^+$ and the individual colligend, both in the bulk solution and in the foam. The range of values of S is given for each system: for $Ag(S_2O_3)_2^{3-}$($Ag(S_2O_3)^-$), the values are strong functions of X_i/Z_i and can be obtained in Fig. 4; for $S_2O_3^{2-}$ the average relative rates (average slopes of the curves in Fig. 2) for the range of X_i/Z_i are given in Table 3. For $C_6H_5O^-$ and HPO_4^{2-}, relative rate data were not available.

The final column of Table 2 gives the required value of X_i/Z_i to yield 90% flotation ($1 - Z_r/Z_i = 0.90$) of each of the colligends.

DISCUSSION

Some interpretation of the values of S and of their dependency on X_i/Z_i and time (X_r/Z_r) may be given utilizing Eqs. (1), (2), and (3) and a few additional experimental observations. For $EHDA^+$–$HCrO_4^-$, S averaged close to 1.0 and was almost independent of X_i/Z_i, indicating that m, p, and k were relatively small (Eq. 1) and that $S = q = 1.0$, according to the primary reaction

$$EHDA^+ + HCrO_4^- \rightleftarrows (EHDA)HCrO_4$$

A series of filtration experiments was carried out, filtering suspensions 0.93 mM in $HCrO_4^-$, with $X_i/Z_i = 0.25$, 0.75, and 1.0, and analyzing the filtrate for both $EHDA^+$ and $HCrO_4^-$. The values of S for the particles caught by the 0.2 μ membrane filter were 0.99, 1.01, and 1.02, and in each experiment approximately 10% of the $EHDA^+$ passed through the filter, indicating that 90% or greater of the total surfactant present had reacted with the $HCrO_4^-$. A final filtration experiment with $X_i/Z_i = 1.25$ yielded $S = 1.05$ and 20% of the initial surfactant passing through the filter. The product of the residual $EHDA^+$ and $HCrO_4^-$ concentrations in the filtrate was 1.5, 1.9, 1.1, and 0.9×10^{-8} M for the four experiments, giving an average value of the solubility product for $(EHDA)(HCrO_4)$ of 1.35×10^{-8}. In summary for $HCrO_4^-$, a rapid precipitation reaction occurred, but there was little evidence of appreciable adsorption of $HCrO_4^-$ or $EHDA^+$ on the particulates. Values of S from foam separation were identical to filtration values; filtration values indicated 10% free $EHDA^+$, but foam separation values yielded about 1%.

In the case of I^-, no particulates were observed in the bulk solution, but fine crystals were observed in the foam. Thus the reaction

$$EHDA^+ + I^- \rightleftarrows (EHDA)I$$

may have occurred in the bulk solution to form an ion pair or complex; however, the aggregation "reaction" only occurred at the gas–liquid interfaces of the bubbles. S was not a strong function of X_i/Z_i, indicating that p was small in Eq. (1) (little secondary adsorption of I^- on the particles). However, in contrast to $HCrO_4^-$, S was appreciably greater than 1.0, indicating that the free surfactant was significant and Eq. (3) applied. Also, S did increase as a weak function of X_i/Z_i; this could be predicted from the equilibrium of

$$\mathrm{EHDA^+ + I^- \rightleftharpoons (EHDA)I}$$

which gives an increase in the ratio of free to reacted $EHDA^+$, with an increase in X_i/Z_i. However, because S was independent of X_r/Z_r and foaming time, the free surfactant and the reacted surfactant were removed at rates proportional to their concentrations in bulk solution, with approximately equal rate constants.

For $Ag(S_2O_3)_2^{3-}(Ag(S_2O_3)^-)$, the value of q could be calculated from the various equilibria involving Ag^+ and $S_2O_3^{2-}$ (*18*); at a molar S_2O_3/Ag ratio of 2.0, $q = 2.8$. All values of S were significantly smaller than 2.8, and S was a strong function of X_i/Z_i, indicating that secondary adsorption or exchange of $Ag(S_2O_3)_2^{3-}$ on the particles was significant during the aggregation process. Also, it is quite possible that $Ag(S_2O_3)_2^{3-}$ was incorporated in the precipitate structure with Na^+ (instead of $EHDA^+$) due to steric effects (*18*). In addition, the presence of $EHDA^+$ may have shifted the equilibrium toward $Ag(S_2O_3)^-$ and the stoichiometry toward 1.0. Filtration experiments were carried out, filtering suspensions 2.0 *mM* in Ag and with $X_i/Z_i = 0.5$, 1.0, and 2.0. The values of S were 1.22, 1.49, and 2.25, consistent with values plotted in Fig. 4, indicating minimal free surfactant in foam separation (less than 1.0%) and that $k = 0$ and Eq. (2) applied. In each experiment, 20% of the $EHDA^+$ passed through the filter, with most of it, evidently, as very fine particles. From values of S in Fig. 4,

$$S = \frac{nq + m}{n + p} = 0.77\ (X_i/Z_i) + 0.72 \tag{7}$$

Equation (7) fits the five experimental points to within 1.4% accuracy. The linear relation of S with X_i/Z_i may be contrasted to the slight dependence of S on X_i/Z_i for $HCrO_4^-$ and I^-.

In the case of $S_2O_3^{2-}$, there was no evidence of the formation of particulates, either in the bulk solution or in the foam. From Fig. 2, S was clearly a function of X_r/Z_r, but was also a function of X_i/Z_i from

Table 3. With the surfactant acting as a mobile ion exchanger, S would decrease during the course of an experiment as the ratio of Br^- to $S_2O_3^{2-}$ built up, because S is analogous to the moles of "ion exchange resin" per mole of $S_2O_3^{2-}$ carried with the resin (but is not analogous to an ion exchange selectivity coefficient). The stoichiometry, S, would also be, by necessity, an increasing function of X_i/Z_i, because the molar Br^- (the surfactant counterion) to $S_2O_3^{2-}$ ratio in the initial solution increased with X_i/Z_i. This effect was also quite clear in the case of HPO_4^{2-} (*12*).

CONCLUSIONS

Each of the four systems $EHDA^+$ with $HCrO_4^-$ ($Cr_2O_7^{2-}$), I^-, $Ag(S_2O_3)_2^{3-}$($Ag(S_2O_3)^-$), and $S_2O_3^{2-}$ yielded somewhat different behavior with respect to surfactant–colligend interaction and the stoichiometry of the foam separation product. Free surfactant was of significance with I^-, and steric effects or secondary adsorption of $Ag(S_2O_3)_2^{3-}$ made S a strong function of X_i/Z_i. Neither free surfactant nor secondary adsorption was important with $HCrO_4^-$, giving a constant value of S close to unity. No surfactant–colligend particles were evident for $S_2O_3^{2-}$ for which an ion exchange mechanism was likely, and they were only present in the foam for I^-. The stoichiometry ranged from 1.2–1.4 for I^-, 2.2–2.8 for $S_2O_3^{2-}$ (S varied with foaming time for the entirely soluble system), and from 1.3–2.5 for $Ag(S_2O_3)_2^{3-}$($Ag(S_2O_3)^-$). Previous data showed $Fe(CN)_6^{4-}$ to be similar to $HCrO_4^-$, and HPO_4^- and $C_6H_5O^-$ to be somewhat similar to $S_2O_3^{2-}$.

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