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Ion Flotation of Chromium(VI) Species: pH, Ionic Strength, Mixing Time, and Temperature

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Abstract

Batch foam separation experiments of Cr(VI) anions with the cationic surfactant, ethylhexadecyldimethylammonium bromide, show a sharp increase in the flotation stoichiometry from 1.0 to 2.0$^+$ over pH 6–8, corresponding to the conversion of $Cr_2O_7^{2-}(HCrO_4^-)$ to CrO_4^{2-} with pH. In the acidic region for approximately 1.0×10^{-3} *M* Cr(VI) solutions, the maximum increase in the flotation stoichiometry and decrease in the fractional removal of $Cr_2O_7^{2-}$ is 12% over a fortyfold increase in ionic strength, varied with four different mono- and divalent salts; the effect is produced by a small increase in the solubility of the $(EHDA)_2Cr_2O_7$ precipitate. In the basic region, a twentyfold increase in ionic strength with NaCl produces greater than 100% changes in the same flotation parameters, indicating a foam fractionation mechanism and competition between Br^-, Cl^- and CrO_4^{2-} for surfactant exchange sites. A temperature increase from 23 to 33°C in the acidic region has no effect on the flotation, and the lack of the effect of the mixing time between the Cr(VI) and surfactant solutions over the full range of variables permits all reported data points to be the average of four replicates, within ±3%.

INTRODUCTION

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. For an ion flotation process to be commercially feasible, moderate to high gas rates must be employed in order to permit a reasonable throughput of the feed stream to be handled in the full-scale equipment. Excessive amounts of foam can be avoided by internal column reflux via foam breakers. Also, the "tieing-up" of the surfactant ions with the colligend in particles in the bulk solution substantially reduces the foam-forming tendency of the surfactant and eliminates excessive quantities of foam. If the particles are formed in the bulk solution, they must be aggregated sufficiently to be picked up by the gas bubbles, or else the bubbles will preferentially carry unreacted surfactant and competing counterions into the foam.

Several investigators have reported the occurrence of a precipitation reaction between Cr(VI) and a quaternary ammonium surfactant of the type $C_nH_{2n+1}(CH_3)_3NBr$, or the type that contains a benzyl or pyridinium group (*1–4*). In particular, Chinnick and Lincoln (*3*) have showed that the solubility of the quaternary dichromate decreased as the molecular weight of the cation increased and that the solubility was relatively unaffected by temperature over 5–15°C; Renard (*2*) found that his precipitate contained cetyltrimethylammonium ions and dichromate ions in the ratio 7: 3 rather than 2: 1; Tschoegl (*4*) reported that the precipitation technique was only useful at high concentrations and then only in the absence of appreciable quantities of inorganic salts.

Hexavalent chromium has been foam separated as a particulate product by several investigators (*5*, *6*), including Grieves et al. (*7–15*). These studies have included batch and continuous-flow operation, dispersed and dissolved (precipitated) air generation, and several surfactants. However, virtually no attention has been paid to the Cr(VI) species present, $Cr_2O_7^{2-}$, $HCrO_4^-$, and/or CrO_4^{2-}, and to the influence of pH on the species and in turn on the ion flotation response. In addition, the effects of the surfactant-Cr(VI) mixing time, ionic strength, and temperature have been largely neglected. The effects of pH and ionic strength have been investigated (*8*), but only for batch operation with pulsed surfactant addition; the excessive surfactant concentrations, which were 1.7 times the stoichiometric, may have muted any substantial variations produced by pH and ionic strength.

EXPERIMENTAL

The initial solutions were prepared by dissolving specified concentrations of Reagent Grade $Na_2Cr_2O_7 \cdot 2H_2O$ in double distilled water of conductivity 6 μmho/cm at 25 °C. The pH and/or ionic strength were adjusted to desired values with Reagent Grade HCl, NaOH, and NaCl ($CaCl_2$, Na_2SO_4, $CaSO_4$). To 1.9 liter of Cr(VI) solution was added 0.1 liter of a double distilled water solution of the cationic surfactant, ethylhexadecyldimethylammonium bromide (Technical Grade, analyzed at 97% in terms of surfactant and 97% in terms of bromide), and the solutions were mixed for time periods of 15, 45, 75, and 105 min by a magnetic mixer at 260 rpm. Each ion flotation experiment presented below represents the average of four replicate points ("replicate," except for the variation in mixing time). With the exception of points in the pH range 6–8, the pH remained constant upon Cr(VI)–surfactant contact, and no further pH adjustment was required.

The cylindrical ion flotation column was 4.4 cm in diameter and was made of Lucite. The height above the initial solution level at which foam was removed was 5.5 cm. For each experiment, 0.4 liter of the initial Cr(VI)–surfactant solution was placed in the column and was aerated at 0.10 liter/min (at 25 °C and 1 atm) through a single, 3-cm diameter sintered glass diffuser of 50 μm nominal porosity. The average bubble diameter was 300 μm as determined by a photographic technique (*16*). The aeration or ion flotation time was 10 min, except as noted below.

At the termination of each experiment the residual solution which remained in the column was analyzed both for Cr(VI) and for surfactant. The Cr(VI) analysis was carried out by the diphenylcarbazide method (*17*) and was accurate to within ±5%. The surfactant, ethylhexadecyldimethylammonium bromide (EHDA-Br), was analyzed by a two-phase titration technique (*18*); the analysis was accurate to within ±7%.

CHROMIUM(VI) SPECIES

Chromic acid is a well-defined, dibasic acid, having dissociation equilibria as follow (*19*):

$$H_2CrO_4 \rightleftarrows H^+ + HCrO_4^- \qquad K_{25^\circ C} = 4.2 \text{ at } \mu = 1.0$$

$$HCrO_4^- \rightleftarrows H^+ + CrO_4^{2-} \qquad K_{25^\circ C} = 3.16 \times 10^{-7} \text{ at } \mu = 0$$

Chromic acid is a fairly strong acid in its first dissociation; its second dissociation is comparable to that of the first dissociation of carbonic acid. The equilibrium between $HCrO_4^-$ and CrO_4^{2-} is indicated as the solid line in Fig. 2. The parameter, S, plotted on the ordinate, which is discussed below, can represent the number of charges on the Cr(VI) anion per mole of Cr.

There is also an association among $HCrO_4^-$ to form poly-ions, the most important being the dichromate ion (*19*):

$$2HCrO_4^- \rightleftarrows Cr_2O_7^{2-} + H_2O \qquad K_{25°C} = 40.0 \text{ at } \mu = 0$$

The equilibrium, which lies far to the left for dilute solutions, is a function of the total concentration of Cr (Table 1).

TABLE 1

Equilibrium as a Function of Total Cr Concentration

Total Cr(VI) concentration (*M*)	Fraction $HCrO_4^-$ present
0.00001	0.999
0.0001	0.992
0.001	0.931
0.01	0.656
0.1	0.297

An effort was made to establish the presence of $Cr_2O_7^{2-}$ by using a Beckman DBG grating spectrophotometer and solutions of concentrations in the range used for the ion flotation experiments. At pH 4.1 the characteristic peaks for $HCrO_4^-$ at 265 and 350 millimicrometers (*20*) were observed; there was no particular indication of the $Cr_2O_7^{2-}$ peaks at 275 and 375 mμ. However, the latter may have been effectively masked by the $HCrO_4^-$ absorption behavior. Although it is probable that only about 7% of the Cr(VI) was present as $Cr_2O_7^{2-}$ in the initial solutions used in the ion flotation experiments prior to surfactant addition, the rapid reaction between Cr(VI) and the surfactant (EHDA-Br) was more likely between $Cr_2O_7^{2-}$ and $EHDA^+$ than between $HCrO_4^-$ and $EHDA^+$ (*21*). $2EHDA^+ + Cr_2O_7^{2-} \rightleftarrows (EHDA)_2Cr_2O_7$ and the $EHDA^+$ could have driven the $HCrO_4^- \rightleftarrows Cr_2O_7^{2-}$ reaction to the right. The surfactant and Cr(VI) analyses together could not distinguish between $HCrO_4^-$ and $Cr_2O_7^{2-}$, only yielding mole surfactant ion floated per mole Cr ion floated: note that the same ratio would be obtained either for $HCrO_4^-$ or $Cr_2O_7^{2-}$.

RESULTS AND DISCUSSION

Results of the ion flotation experiments are presented in terms of two parameters: the fractional removal of Cr(VI), $R = 1 - Z_r/Z_i$, in which Z_r and Z_i are the molar concentrations of Cr(VI) in the residual (after ion flotation) and initial solutions, respectively; and the flotation stoichiometry,

S (*15*), defined as the moles of surfactant (EHDA) floated per mole of Cr(VI) floated.

Throughout the experimental phase of the study, the time of mixing between the surfactant and Cr(VI) had no effect on the ion flotation results, for mixing times from 15–105 min, and over the full range of pH, ionic strength, temperature, etc. For this particular surfactant the precipitation reaction occurred instantaneously and the $(EHDA)_2Cr_2O_7$ (or EHDA-$HCrO_4$) particulates aggregated rapidly into fairly coarse flocs which were readily picked up by the dispersed air bubbles. Therefore all points reported below are averages of quadruplicates. The maximum variation within a set of four points about the average was $\pm 3\%$.

Initial series of experiments were carried out to determine the best aeration time (ion flotation time) and initial surfactant and Cr(VI) concentrations at which to carry out the pH, ionic strength, and temperature studies. The effect of the initial surfactant to Cr(VI) ratio, X_i/Z_i (X_i = initial surfactant concentration, mM), on S and R, for the three initial Cr(VI) concentrations of 0.46 mM (0.46×10^{-3} M), 0.93 mM, and 1.85 mM, is indicated in Fig. 1. The pH was maintained at 4.2, the ionic strength at 0.001 M, and the temperature at 23 °C. The data include several points reported previously, including those obtained in a larger ion flotation column at a considerably larger air rate (*11*, *15*, *22*). For the stoichiometry, S, a few points obtained by filtering and washing the precipitate and analyzing the filtrate are included. S remained relatively invariant with X_i/Z_i until X_i/Z_i became greater than unity [the "stoichiometric ratio" for $(EHDA)_2Cr_2O_7$ or EHDA-$HCrO_4$ particulates]. The reaction thus went close to completion, and almost complete flotation of the precipitate was achieved (the dotted straight line on the R vs X_i/Z_i graph); this was evidenced by the presence of a small amount of fine particles at the termination of each flotation experiment. Above $X_i/Z_i = 1.0$, S increased and R decreased due to the competition of unreacted (and thus excess) EHDA-Br for the bubble surface sites and due to the formation of an adsorbed surfactant layer on the particle surfaces, peptizing the precipitate and making it less suited for bubble attachment (*23*). The optimum ion flotation conditions, both in terms of R and S, appeared to be $0.9 < X_i/Z_i < 1.0$.

Another initial series of experiments at variable aeration (ion flotation) time indicated the optimum time, at the air rate of 0.025 liter/min, to be $\simeq$ 10 min: the maximum flotation of Cr(VI) was achieved although foam formation had not completely ceased. In all experiments detailed below, $Z_i = 0.93$ mM, $X_i/Z_i = 0.92$, and aeration time = 10 min.

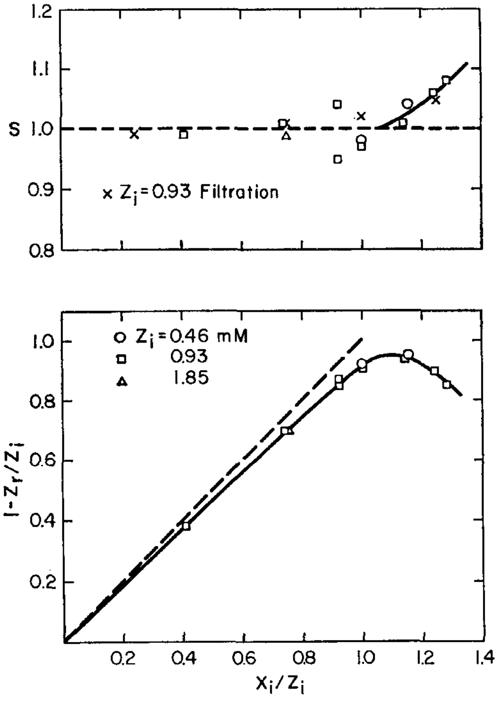

FIG. 1. Effects of the initial surfactant/Cr(VI) ratio on the stoichiometry and fractional removal at pH 4.2.

Figure 2 indicates the effect of pH on the flotation stoichiometry, *S*, at a constant temperature of 23 °C and ionic strength of ≃ 0.001 *M*. Each point is the average of four experiments. The curve is plotted from the $HCrO_4^- \rightleftarrows CrO_4^{2-}$ equilibrium. It was virtually impossible to obtain an accurate point around pH 7 due to the constant variation in pH obtained upon mixing the surfactant solution with the Cr(VI) solution. Below pH 6.3, bright orange particles were evident in the bulk solution and in the foam.

Above pH 7.6, no particles were present in the greenish bulk solution. The lack of particle formation during the foaming process, together with a value of *S* up to 20% in excess of the stoichiometric value of 2.0, indicates a foam fractionation mechanism (*15*, *24*). The CrO_4^{2-} evidently was in competition with Br^- for ion pair or soluble complex formation with the $EHDA^+$. For these experiments in the basic region, excessive foam forma-

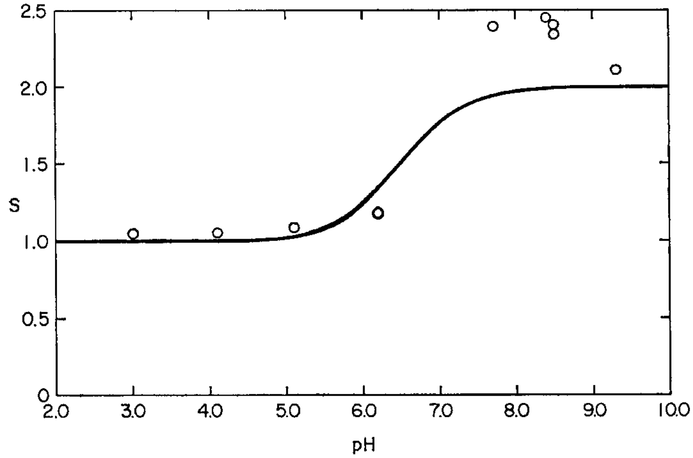

FIG. 2. Variation of the theoretical and experimental flotation stoichiometry at $X_i/Z_i = 0.92$, $Z_i = 0.93$ mM, and $\mu = 0.001$ M.

tion occurred at the 0.10 liter/min air rate; therefore to obtain the data, the air rate was reduced to 0.025 liter/min and the residual solution concentrations were measured at foam cease. The sharp acid–base transition had not been reported previously (*8*): pulsed surfactant dosage had been employed and $X_i/Z_i = 1.7$ (instead of 0.92); also the flotation results had been reported only in terms of Z_r at foam cease conditions.

The effects of ionic strength (varied with NaCl) and temperature throughout the acidic pH region are given in Table 2. At a constant temperature and pH, both *R* and S were only slightly variant over a twentyfold increase in ionic strength. *R* consistently decreased with ionic strength and *S* consistently increased, probably due to the increased solubility of the $(EHDA)_2Cr_2O_7$ particulates; however, the maximum changes in both *R* and *S*, at pH 6.2, were about 12%.

Making the comparison at an ionic strength of 0.021 *M*, an elevation in temperature from 23 to 33°C (Table 2) had virtually no influence on the ion flotation of $(EHDA)_2Cr_2O_7$.

Table 3 shows the effect at pH 4.1 and 23°C of greater increases in ionic strength and of varying the ionic strength with different salts. The ratio X_i/Z_i was raised slightly to 1.0. Clearly, the valency of the cation or anion could be taken into account by ionic strength and, in particular, there was no evidence of a specific interaction between SO_4^{2-} and $EHDA^+$. Similar effects had been reported previously (*8*), but only at pH 5.0, with

TABLE 2

Effects of Ionic Strength and Temperature in the Acidic Region

pH	Ionic Strength (*M*)	*S*	*R*
	Temperature = 23 °C		
2.0	0.011	1.05	0.85
	0.021	1.04	0.83
3.0	0.002	1.03	0.86
	0.012	1.07	0.84
	0.022	1.09	0.82
4.1	0.001	1.04	0.86
	0.011	1.08	0.83
	0.021	1.11	0.80
5.1	0.001	1.08	0.83
	0.011	1.11	0.80
	0.021	1.13	0.79
6.2	0.001	1.17	0.72
	0.011	1.31	0.65
	0.021	1.32	0.64
	Temperature = 33 °C		
4.1	0.021	1.12	0.80
5.1	0.021	1.17	0.77
6.2	0.021	1.45	0.62

TABLE 3

Effect of Salt Variation and Ionic Strength at pH 4.1

Ionic strength (*M*)	Salt	*S*	*R*
0.011	NaCl	1.06	0.89
	$CaCl_2$	1.05	0.90
	Na_2SO_4	1.14	0.86
	$CaSO_4$	1.01	0.87
0.021	NaCl	1.09	0.85
	$CaCl_2$	1.04	0.87
	Na_2SO_4	1.00	0.84
	$CaSO_4$	1.13	0.82
0.031	Na_2SO_4	1.11	0.83
0.041	NaCl	1.09	0.80
	$CaCl_2$	1.02	0.84
	Na_2SO_4	1.09	0.82
	$CaSO_4$	1.05	0.83

TABLE 4

Effect of Ionic Strength in the Basic Region

pH	Ionic strength (M)	S	R
7.2–7.7	0.001	2.38	0.37
	0.011	3.60	0.25
	0.021	5.29	0.17
8.9–9.3	0.001	2.10	0.41
	0.011	4.89	0.18
	0.021	5.40	0.16

the excessive $X_i/Z_i = 1.7$ ($Z_i = 0.46$ mM) and only in terms of the normalities of the individual anions.

The effect of ionic strength (varied with NaCl) was severe in the basic region at 23°C and $X_i/Z_i = 0.92$, as shown in Table 4, producing increases in S and decreases in R of over 100% for a twenty fold variation in ionic strength. Here a foam fractionation mechanism was apparent with the Cl^- (and the Br^- counterion of the surfactant) evidently competing with CrO_4^{2-} for the $EHDA^+$. This effect was also partly shown at pH 6.2 (at which some CrO_4^{2-} was present): ionic strength had a considerably stronger influence on the flotation than at pH ≤ 5.1.

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