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Recovery and Reuse of a Surfactant in Ion Flotation

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Summary

The feasibility of virtually any commercial-scale ion flotation (foam separation) process depends on the recovery and reuse of the surfactant used as the flotation agent. For aqueous solutions of acid chromate complexed with a cationic quaternary ammonium salt, ethylhexadecyldimethylammonium bromide, a variety of paths are investigated to split the complex and to separate and recover the surfactant. These include acid chromate reduction with $NaHSO_3$ or $SnCl_2$ followed by sorption of the surfactant by and elution from a polymeric resin, Rohm and Haas Amberlite XAD-2. The most promising path is reduction of the acid chromate with $NaHSO_3$ at pH 2–3, extraction with isopropanol–chloroform in a 1:1 ratio, vacuum distillation of the solvents, and redissolution of the surfactant in aqueous solution. The minimum HSO_3/Cr ratio is established, distribution coefficients for the extraction are determined, and the recovered surfactant is tested in several ion flotation experiments, making a comparison with fresh surfactant.

INTRODUCTION

The ion flotation process involves the addition to aqueous solution of a surface-active agent of opposite charge to the ion to be separated. A reaction results in the formation of an insoluble ion-pair complex that is surface-active. The resultant particulates may be floated to the surface of the suspension by gas bubbles at the interfaces of which they are adsorbed, and a froth is formed by nonreacted surfactant acting as a frother. In some cases the ion to be separated may itself be a complex ion and may form colloidal, polynucleated species. In other cases, the insoluble ion-pair may be formed only in the presence of the high surfactant concentrations at the bubble interfaces, with the primary step being the migration of the surfactant ions to the interfaces. The formation of the insoluble complex enables the selective removal of a particular ion by a surfactant, in the presence of other, competing ions. The complex is generally stoichiometric.

Several successful applications of the ion flotation process have been reported, including a great number of most interesting feasibility studies by Sebba (*1*). Specific applications include the separation of aluminum from beryllium (*2*), the removal of trace amounts of strontium from aqueous solution (*3,4*), the flotation of acid chromate (*5–7*), and the flotation of cyanide complexed by ferrous iron (*8–10*). A very promising application is the removal and recovery of chromium from plating wastes, which has been studied using a continuous-flow, dissolved-air ion flotation unit (*11,12*). From distilled water solution at pH 5, a feed containing 48 mg/liter of hexavalent chromium can be ion floated into an effluent containing 2.3 mg/liter and a froth or scum containing 15,000 mg/liter Cr. This can be accomplished with a cationic surfactant, ethylhexadecyldimethylammonium bromide (EHDA–Br), in a molar surfactant to Cr ratio of 1.05, using a nonionic polymer, Dow N-12 at 5 mg/liter, as a flotation aid. The surfactant is separated: 29 mg/liter into the effluent and 114,000 mg/liter into the froth. From solution in ordinary tap water, the efficiency of the separation is reduced somewhat, with the effluent containing 8.2 mg/liter Cr and 34 mg/liter surfactant.

In spite of the excellent separations that can be achieved, the commercial applicability of virtually any ion flotation process depends on the recovery and reuse of the surfactant. The stoichiometry of the surfactant-ion pair complexes (e.g., EHDA–$HCrO_4$) generally necessitates large surfactant dosages that must be recovered and reused. A concomitant advantage is the recovery of the original ion of interest. In many cases, this may be the primary aim of the flotation process.

The objective of this research investigation is to determine the feasibility of the recovery and reuse of a cationic surfactant used to ion float hexavalent chromium. Several approaches are presented, including the one determined to be best, placing particular emphasis on the completeness of the recovery of the surfactant and on the elimination of any effect on the collecting and frothing ability of the surfactant that might be introduced by the initial ion flotation (including the use of a polymer as a flotation aid) and by the recovery procedures.

EXTRACTION; REDUCTION AND SORPTION STUDIES

Initial studies were carried out to determine if the cationic surfactant, EHDA–Br, could be directly extracted into organic phase, leaving the hexavalent chromium ($HCrO_4^-$) in the aqueous phase. The distilled water solutions used were about 0.026 M in surfactant and about 0.039 M in Cr, with the initial pH at 5.5. The EHDA–$HCrO_4$ complex was dissolved in alcoholic (ethanol) NaOH, elevating the pH to 13.0. Extraction of the surfactant was accomplished with chloroform. However, a very stable emulsion was formed. This problem probably could have been eliminated with other pure solvents or mixed solvent systems. However, it was felt that elevation of pH followed by extraction, solvent evaporation, dissolution of the quaternary hydroxide in water, and acidification to reform the quaternary ammonium salt was too costly in terms of quantities of acids and bases, and that reduction of the hexavalent chromium at acidic pH might be more feasible.

The reducing agents and pH values that were employed are:

$FeSO_4$	at pH	5.5
Na_2SO_3	at pH	2.4
NaI	at pH	11.5
$SnCl_2$	at pH	5.5
$NaHSO_3$	at pH	2.4

The $FeSO_4$ was rejected because the precipitated ferric hydroxide that was formed adsorbed substantial quantities of the surfactant, and often itself settled into the organic phase when reduction was followed by solvent extraction. The Na_2SO_3 did not bring about nearly adequate reduction, even if quantities 60% in excess of the stoichiometric were utilized. The NaI produced complete reduction of the CrO_4^{2-}, but only at about 100% excess of the stoichiometric and at elevated pH. NaI was selected in an effort to provide a halide, in contrast to sulfate, counterion for the surfactant cation. The $NaHSO_3$ and $SnCl_2$ both produced complete reduction with quantities not exceeding 30% of the stoichiometric, according to the reactions

$$2HCrO_4^- + 3HSO_3^- + 5H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 5H_2O$$
$$2HCrO_4^- + 3Sn^{2+} + 14H^+ \rightarrow 3Sn^{4+} + 2Cr^{3+} + 8H_2O$$

The $SnCl_2$ has the advantage of providing a halide counterion but is approximately 40 times the cost of $NaHSO_3$, compared on a molar basis.

Reduction of the hexavalent chromium broke the complex, EHDA–$HCrO_4$. Two approaches to surfactant recovery were then attempted: the first involved sorption of the surfactant on a polymeric sorbent followed by elution with methanol; the second, which is described in the next section, involved direct extraction with a mixed solvent system. The polymeric sorbent was Amberlite XAD-2, manufactured by the Rohm and Haas Co. It consisted of hard, spherical, opaque beads, 0.30–0.45 mm in diameter. The sorbent was cross-linked polystyrene with the wet resin containing 0.40 mmoles Cl^- per gram of wet resin. The equilibrium capacity of the resin was determined to be 0.38 mole EHDA–Br/1000 grams dry resin at an equilibrium EHDA–Br concentration in solution of 0.0031 *M*. This may be compared with 0.32 (at an equilibrium concentration of 0.020 *M*) reported by Rohm and Haas for Hyamine 3500, tetradecyldimethylbenzylammonium chloride, also at 23°C. With a 15-min contact and mixing period, 97% of the EHDA–Br present in a solution was sorbed by 30% excess resin based on the equilibrium capacity.

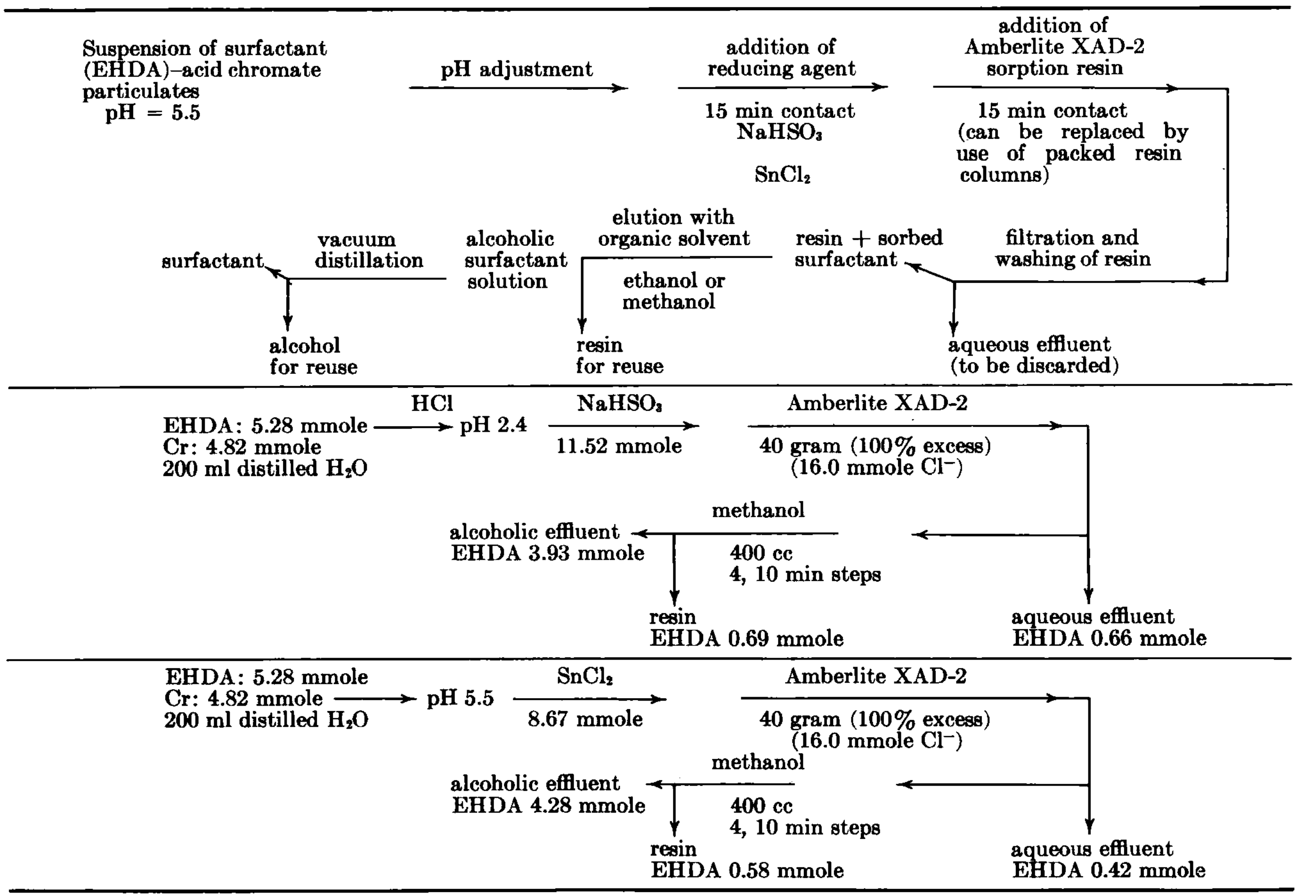
Two series of experiments were carried out, as indicated by the general schematic diagram shown in Table 1. Results for each series are indicated in the lower diagrams in Table 1. The first involved reduction with $NaHSO_3$ at pH 2.4, followed by sorption and elution with methanol. The second involved reduction with $SnCl_2$ at pH 5.5, followed by sorption and elution with methanol. The surfactant recoveries were 74% and 81%, respectively.

The sorption-elution process holds some promise for the recovery of a surfactant. However, it is a somewhat involved process, compared to direct extraction. The surfactant's collecting and frothing ability were not affected too significantly by complexing with acid chromate, reduction of the hexavalent chromium, sorption on XAD-2, elution with methanol, vacuum distillation of the methanol, and redissolution of the surfactant in aqueous solution. Experiments with fresh surfactant and recovered surfactant as the ion flotation agent gave about the same flotation of acid chromate and of surfactant, with both being somewhat decreased (poorer flotation) in the case of the recovered surfactant.

REDUCTION AND EXTRACTION STUDIES

An alternate recovery technique, particularly appropriate with highly concentrated surfactant–acid chromate solutions, was investi-

TABLE 1


Suspension of surfactant (EHDA)–acid chromate particulates pH = 5.5
pH adjustment
addition of reducing agent
15 min contact
NaHSO₃
SnCl₂
addition of Amberlite XAD-2 sorption resin
15 min contact (can be replaced by use of packed resin columns)
filtration and washing of resin
resin + sorbed surfactant
aqueous effluent (to be discarded)
elution with organic solvent
ethanol or methanol
resin for reuse
alcoholic surfactant solution
vacuum distillation
surfactant
alcohol for reuse
EHDA: 5.28 mmole
Cr: 4.82 mmole
200 ml distilled H₂O
HCl
pH 2.4
NaHSO₃
11.52 mmole
Amberlite XAD-2
40 gram (100% excess)
(16.0 mmole Cl⁻)
methanol
400 cc
4, 10 min steps
alcoholic effluent
EHDA 3.93 mmole
resin
EHDA 0.69 mmole
aqueous effluent
EHDA 0.66 mmole
EHDA: 5.28 mmole
Cr: 4.82 mmole
200 ml distilled H₂O
pH 5.5
SnCl₂
8.67 mmole
Amberlite XAD-2
40 gram (100% excess)
(16.0 mmole Cl⁻)
methanol
400 cc
4, 10 min steps
alcoholic effluent
EHDA 4.28 mmole
resin
EHDA 0.58 mmole
aqueous effluent
EHDA 0.42 mmole

gated next. The process involved reduction with $NaHSO_3$ at pH 2.4, followed by extraction of the surfactant by a mixed solvent system. The feed solution used throughout this series of experiments (unless indicated otherwise) consisted of the following:

EHDA–Br	0.145 *M*
Cr($Na_2Cr_2O_7 \cdot 2H_2O$)	0.144 *M*
Dow N-12, nonionic polymer	0.47 gram/liter
pH reduced from about 5.5 to 2.4 with HCl	
Distilled water solution	

The concentrations in the solution were in the order of the concentrations in the foam or froth that might be collected from a dissolved-air, ion flotation process, with the nonionic polymer added as a flotation aid (*11,12*).

Studies on the reduction of hexavalent chromium in the above solution showed that complete reduction could be achieved in 15–30 min with a molar ratio of HSO_3/Cr of 1.80. The trivalent chromium was partly in the form of a precipitate, with precipitation promoted by EHDA–Br. A stoichiometric ratio of 1.5 did not provide complete reduction within a reasonable time period and the remaining hexavalent chromium interfered with the extraction process. Belevtsev et al. (*13*) reported previously that complete reduction occurred in 5 min at a ratio of 1.75 or greater.

Numerous studies have been made on the extraction of anionic species into organic phase, utilizing a cationic surfactant dissolved in the organic phase (*14,15*). However, little is reported on the extraction of a cationic surfactant from acid aqueous solution into organic phase to separate it from a precipitate. A series of single and mixed solvent systems was studied, using commerically available and easily handled solvents. The three systems that yielded the best result were methanol–chloroform, isopropanol–chloroform, and isopropanol–carbon tetrachloride. The first was discarded because of the loss of methanol into the aqueous phase and the last did not give as complete extraction as the isopropanol–chloroform system.

The optimum volume ratio of isopropanol to chloroform was established to be about unity. The procedure was to take a 50-ml sample of the 0.145 *M* feed solution and to contact it with 50 to 150 ml of isopropanol and chloroform in a 500-ml separatory funnel. The funnel was shaken vigorously for 5 min and then allowed to equilibrate for an additional 55 min. The aqueous phase was then removed and analyzed for EHDA, using a two-phase titration technique *(16)*. Actually, the distribution coefficients did not vary substantially over the range of isopropanol to chloroform volume ratios from 0.83 to 1.25, averaging 55 (mole EHDA/liter organic phase)/(mole EHDA/liter aqueous phase) for 11 experiments. Values of the ratio greater than 1.25 gave lower distribution coefficients. The lowest recovery of the solvents was 97%, indicating a maximum loss into the aqueous phase of 3%. However, if the ratio of the volume of the total organic phase to the volume of the aqueous phase was reduced to less than 0.6, a stable emulsion was formed and an effective separation could not be made.

A distribution diagram was determined for EHDA–Br with acid chromate reduced by bisulfite solutions at pH 2.4, extracted by isopropanol–chloroform at a volume ratio of unity. The concentration of EHDA–Br in the aqueous feed solutions was 0.00173, 0.0143, 0.0964, or 0.145 *M* (with proportional concentrations of acid chromate, bisulfite, and Dow N-12), the volume of the feed solutions was 50, 100, or 150 ml, and the volume of the mixed solvents was 60, 100, 120, 200, or 300 ml. The ratio of the volume of the total organic phase to the aqueous phase was 0.6 or greater. The two phases were equilibrated for 20 hours (note that the data described in the previous paragraph were for an extraction time of one hour), and results are given in Fig. 1. The approximate linear relationship yields a distribution coefficient of 65 (mole EHDA/liter organic phase)/(mole EHDA/liter aqueous phase). Some of the scatter may have been produced by the presence of a third phase, the trivalent chromium precipitate.

Equilibrium was approached very rapidly: with an EHDA–Br concentration of 0.145 *M* and with a ratio of the volume of the organic phase to the volume of the aqueous phase of 1.2, 1.4% of the EHDA was not extracted after 5 min, 0.82% after 20 hours; with a ratio of 4.0, 0.77% was not extracted after 5 min, 0.51% after 20 hours.

The suggested *recovery process* is:

1. Depression of pH to between 2 and 3 with HCl.

2. Reduction with $NaHSO_3$ at a molar HSO_3/Cr ratio of 1.85 for 15 min.

3. Extraction with isopropanol–choloroform in a volume ratio of about unity with an organic phase to aqueous phase volume ratio of 1.0 or greater, yielding an equilibrium distribution coefficient of 65 and 99% recovery in 15 min.

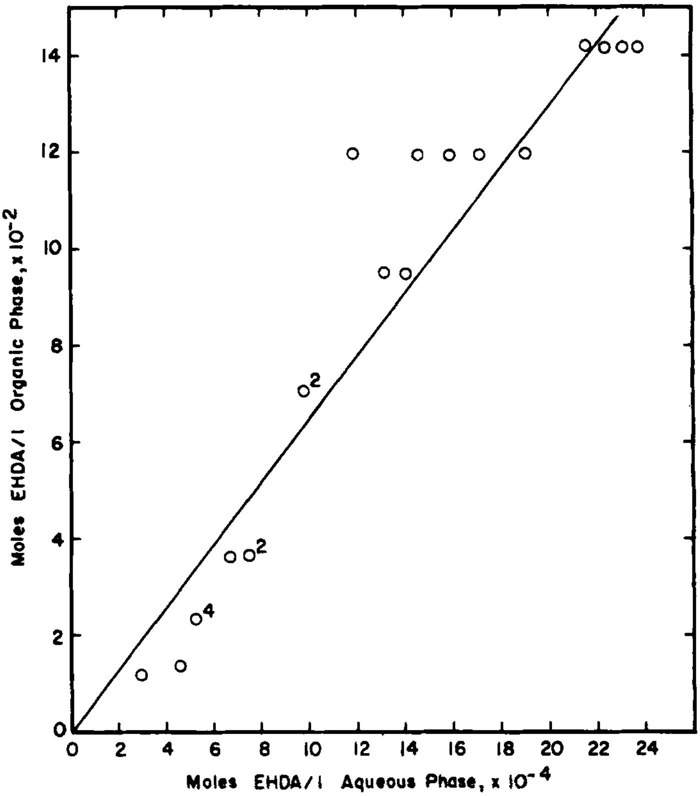


FIG. 1. Equilibrium extraction diagram for surfactant by isopropanol–chloroform in a 1:1 volume ratio.

4. Vacuum distillation to dryness at a temperature less than 85°C, condensing and recovering the isopropanol and chloroform.

5. Redissolution of the cationic surfactant in aqueous solution and reuse of the surfactant in ion flotation.

ION FLOTATION EXPERIMENTS

Two series of experiments were carried out to test the collecting and frothing ability of the recovered surfactant. Each series was identical except that in one, fresh EHDA–Br was used, and in the other, recovered EHDA–Br was used. The apparatus and procedure are the same as those employed in previous ion flotation studies (7). Each feed solution in tap water (conductivity: 400 μmho/cm at 23°C) was $1.06 \times 10^{-3} M$ (400 mg/liter) in surfactant, $0.93 \times 10^{-3} M$ (48.3 mg/liter) in hexavalent chromium, and contained 5 mg/liter of Dow N-12. The pH was adjusted to 4.2. The mixing time of acid chromate with surfactant was 15 min, that of Dow N-12 with the mixture was 15 min, and the ion flotation time was 15 min at an air rate of 1440 ml/min @ 20°C and one atmosphere.

For 13 identical experiments with *fresh surfactant,* the averaged results were as follows:

Residual Cr concentration:	$7.8 \times 10^{-5} M$
Range of variation:	5.8×10^{-5} to $11.4 \times 10^{-5} M$
Residual surfactant concentration:	$1.3 \times 10^{-4} M$
Percent of feed solution volume remaining:	82%

For 6 identical experiments with *recovered surfactant,* the averaged results were as follows:

Residual Cr concentration:	$7.5 \times 10^{-5} M$
Range of variation:	3.8×10^{-5} to $12.9 \times 10^{-5} M$
Residual surfactant concentration:	$0.90 \times 10^{-4} M$
Percent of feed solution volume remaining:	68%

A comparison of the two series indicates that the removal of hexavalent chromium by the recovered surfactant was virtually identical to that by the fresh surfactant. The recovered surfactant acted as a better frother, providing a greater collapsed foam volume (smaller volume remaining) and lower residual surfactant concentration. This may have been produced by the presence of small amounts of isopropanol with the recovered surfactant. The recovery and reuse of a cationic surfactant for the ion flotation of acid chromate appears to be a feasible and promising process.

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