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TECHNICAL NOTE

Chemistry of Cr(VI) Solvent Extraction Using Tri-*n*-octylamine

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ABSTRACT

Experiments were carried out to clarify the mechanism for the extraction of Cr(VI) from sulfate-containing aqueous solutions using tri-*n*-octylamine (TOA). The results were consistent with a two-step reaction mechanism, initially involving complexation of TOA with bisulfate followed by substitution of bisulfate with bichromate in the complex. Experimental results support the contention that the first step only occurs with bisulfate and not with sulfate, explaining why the extraction decreases rapidly for initial pH values above 2. The equilibrium coefficient for the overall extraction reaction was determined to be 10^6.

INTRODUCTION

There is increased interest in the use of liquid membrane processes for the removal and/or recovery of metal ions from aqueous waste effluents. This type of approach has the advantage of combining into a single unit operation the selective removal and concentration of the metal ion. Due to its toxic nature and common use in industry, one metal that has received considerable attention is Cr(VI). One approach is the recovery of Cr(VI) from wastewater using tertiary amines in a continuous liquid extraction procedure (1–4). A variety of mechanisms have been proposed for reactions involving tertiary amines (1–3, 5, 6). However, these mechanisms

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differ in a variety of ways, including the number of steps in the reaction mechanism, the form of chromate involved in the reactions, and the role of sulfate. To clarify the mechanism involved in a liquid–liquid extraction application for chromium, a series of batch solvent extraction experiments were conducted and the results compared with predictions made using a two-step reaction mechanism. Data are consistent with this model.

EXPERIMENTAL

Batch experiments were carried out by agitating 100 mL organic with 50 mL aqueous feed in a 250-mL separatory funnel for 90 seconds and then allowing 5 minutes for the phases to disengage. The organic phase consisted of 93 vol% Exxsol D-60 (Esso Solvents, Toronto, Ontario, Canada) as the solvent, 5 vol% tri-*n*-octylamine (TOA) (Aldrich Chemical, Milwaukee, Wisconsin, USA) as the extractant molecule, and 2 vol% 2-ethyl-1-hexanol (Aldrich) as the modifier. The aqueous feed consisted of 200 ppm Cr(VI) as $K_2Cr_2O_7$ (Aldrich) and varying levels of sulfate as K_2SO_4 (BDH, Toronto, Ontario, Canada). H_2SO_4 was used for pH adjustment. Total chromium content in the aqueous phases was measured using a Fissons Model SS-7 Direct Current Plasma (DCP) Spectrometer (ARL Canada, Unionville, Ontario, Canada). The chromium content in the organic phase was not measured directly but calculated on the basis of a mass balance on the chromium content in the aqueous phase before and after each experiment. No Cr(III) was assumed to be present since all solutions remained the yellow-orange color indicative of Cr(VI). A Dionex 2000i ion chromatograph (Sunnydale, California, USA) was used for sulfate analysis. An AS3 anion-exchange column with an AG3 guard column was used with a conductivity detector. The eluent conditions were 3.0 mM $NaHCO_3$ and 2.38 mM Na_2CO_3.

RESULTS AND DISCUSSION

The extraction of Cr(VI) has been well studied, and various loading mechanisms have been postulated. Cuer et al. (5) formulated a mechanism that involved the generation of an amine salt using sulfate to extract dichromate by substitution:

$$2R_2NH(org) + 2H^+(aq) + SO_4^{2-}(aq) \rightleftarrows (R_2NH_2)_2SO_4(org) \quad (1)$$

$$(R_2NH_2)_2SO_4(org) + 2H^+(aq) + SO_4^{2-}(aq) \rightleftarrows 2R_2NH_2HSO_4(org) \quad (2)$$

$$Cr_2O_7^{2-}(aq) + 2R_2NH_2HSO_4(org) \rightleftharpoons (R_2NH_2)_2Cr_2O_7(org) + 2HSO_4^-(aq) \quad (3)$$

$$HCr_2O_7^{2-}(aq) + R_2NH_2HSO_4(org) \rightleftharpoons R_2NH_2HCr_2O_7(org) + HSO_4^-(aq) \quad (4)$$

where R is a hydrocarbon chain.

A mechanism proposed by Frankenfeld and Li (6) involved the extraction of a dichromate by a tertiary amine under acidic conditions via amine salt formation:

$$(R_3NH)_2SO_4(org) + Cr_2O_7^{2-}(aq) \rightleftharpoons (R_3NH)_2Cr_2O_7(org) + SO_4^{2-}(aq) \quad (5)$$

No reaction was given to describe how the amine/sulfate complex forms. An extraction mechanism that does not involve sulfate was proposed by Smith et al. (2):

$$2H^+(aq) + Cr_2O_7^{2-}(aq) + 2R_3N(org) \rightleftharpoons (R_3NH)_2Cr_2O_7(org) \quad (6)$$

The differences in these mechanisms suggest that there is still considerable uncertainty concerning the role of sulfate, and whether HSO_4^- or SO_4^{2-} is involved.

The effect of initial feed pH and sulfate concentration on Cr(VI) loading is shown in Fig. 1. Loading is high for all sulfate concentrations below pH 2 and thereafter decreases with increasing pH. Since Cr(VI) remains as $HCrO_4^-$ throughout the pH range examined, the change in extraction at pH 2 is likely related to the form of sulfate present. Figure 1 illustrates that high concentrations of sulfate extend the pH range over which loading can be achieved. Sulfate is clearly involved in Cr(VI) extraction, but apparently does not compete with chromate during loading, contrary to what was suggested by Cuer et al. (5). Thermodynamic calculations show that the equilibrium concentrations of SO_4^{2-} and HSO_4^- are related by

$$\log \frac{[SO_4^{2-}]}{[HSO_4^-]} = pH - 1.91 \quad (7)$$

indicating that HSO_4^- is the dominant form of sulfate at pH less than 1.91 and SO_4^{2-} is predominant at pH greater than 1.91. On this basis, bisulfate is the expected form involved in Cr(VI) loading.

To verify that the HSO_4 and not the SO_4^{2-} form is involved in the extraction by TOA, loading experiments were conducted in K_2SO_4 solutions containing no Cr(VI) at different initial pHs. Table 1 shows the data obtained when the organic phase was contacted with 50 mL of a 4.0-mM

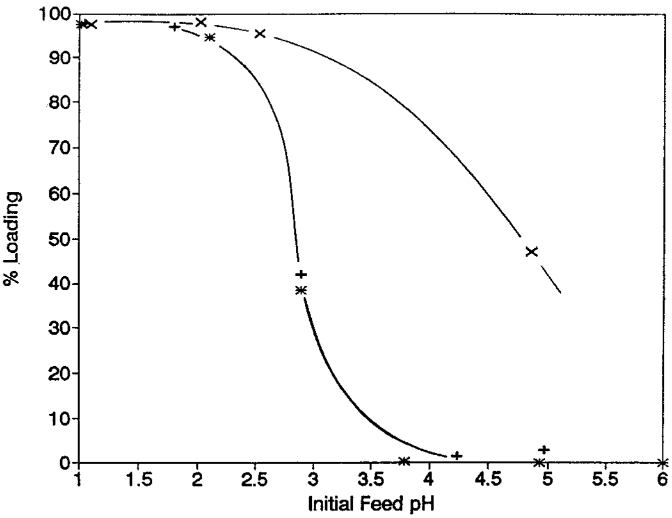

FIG. 1 Effect of initial pH and $[SO_4^{2-}]/[Cr(VI)]$ ratio on equilibrium % loading of Cr(VI). Experiments were conducted at $[SO_4^{2-}]/[Cr(VI)]$ ratios of 1 (+), 2 (*) and 100 (×).

K_2SO_4 solution at an initial pH where HSO_4^- dominates and at a pH where SO_4^{2-} is predominant. H_2SO_4 was used for pH adjustment. As is clearly shown, loading occurs only when bisulfate is present.

The results in Fig. 1 and Table 1 show that not only does HSO_4^- loading take place, but that it may be necessary in order for Cr(VI) extraction to be possible. To further confirm this, loading of sulfate/bisulfate and Cr(VI) was carried out in separate steps to isolate the effects of HSO_4^- and Cr(VI) on the overall process.

In the first step, the procedure followed to obtain the results shown in Table 1 was repeated by contacting the organic with a 70-mM K_2SO_4 solution containing no Cr(VI) at pH 2.05 and a 60-mM K_2SO_4 solution at

TABLE 1
Sulfate Remaining in Feed after Loading

Initial pH	Initial sulfate concentration (mM)	Final pH	Final sulfate concentration (mM)	Percent sulfate removed
2.13	12.32	3.27	6.96	43.48
6.94	4.13	6.91	4.10	0.51

pH 5.33. As in the previous tests, the pH of the first solution rose to 3.09, indicating that loading had taken place, whereas the second showed no pH change and consequently no evidence of any loading. In the second step of the experiment, each of the organics obtained from the first step was mixed with a solution at pH 4.92 containing 3.9 mM $HCrO_4^-$ but no sulfate. In the organic which had previously extracted HSO_4^-, loading of Cr(VI) was immediately obvious from the rapid transfer of the yellow Cr(VI) color from the aqueous to the organic phase, and the aqueous pH dropped to 2.93 due to the dissociation of HSO_4^- to SO_4^{2-} and H^+. However, in the case of the organic which had shown no evidence of HSO_4^- loading, there was no transfer of the yellow color from the aqueous to the organic and no pH change in the aqueous, indicating that no Cr(VI) extraction had occurred.

On the basis of these results, it appears that the presence of HSO_4^- is necessary for Cr(VI) loading. The fact that extraction of Cr(VI) in the second step is possible from a solution of pH 4.92 also indicates that the pH dependence of loading shown in Fig. 1 arises entirely from the requirement that HSO_4^- be predominant. Thus, pH has no effect on the second stage of the process as long as bichromate is present.

From the results of the above experiments, the following reaction scheme is proposed:

$$H^+(aq) + HSO_4^-(aq) + 2R_3N(org) \rightleftarrows (R_3NH)_2SO_4(org) \tag{8}$$

$$(R_3NH)_2SO_4(org) + HCrO_4^-(aq) \rightleftarrows (R_3NH)_2CrO_4(org) + HSO_4^-(aq) \tag{9}$$

The first step is the generation of the amine salt using bisulfate, followed by the substitution of the bisulfate with the bichromate. Once released into the aqueous, HSO_4^- ions are subject to dissociation into H^+ and SO_4^{2-} ions in the bulk solution. As mentioned previously, the data given in Fig. 1 show that sulfate loading does not compete with chromate loading. This observation is consistent with the two-step sequential reaction mechanism that is proposed rather than one involving the loading of bisulfate and bichromate in parallel reactions.

The reaction obtained by adding Eqs. (8) and (9) together, i.e.,

$$H^+(aq) + HCrO_4^-(aq) + 2R_3N(org) \rightleftarrows (R_3NH)_2CrO_4(org) \tag{10}$$

is the same as that reported by Teramoto et al. (3). However, these earlier workers did not include any role for bisulfate. Inclusion of bisulfate in the mechanism as in Eqs. (8) and (9) is important since it explains why extraction of Cr(VI) with TOA is possible only in acidic sulfate solutions (pH < 2). It should also be noted that it is likely that not all of the sulfate complex formed by Reaction (8) will exchange with bichromate via Reaction (9), with the result that the loaded organic will contain both complexes at equilibrium. This has important implications if the amount of unreacted TOA is to be determined indirectly from measurements of the total amount of complex formed.

Having identified the loading reactions, it is also possible to determine the equilibrium constant for Cr(VI) extraction. Assuming ideal solutions in both phases, the equilibrium constant K_e for Reaction (10) can be written as

$$K_e = \frac{[(R_3NH)_2CrO_4]_{org}}{[R_3N]^2_{org}[HCrO_4^-]_{aq}[H^+]_{aq}} \tag{11}$$

This expression can be rearranged to yield

$$\log E - 2\log[R_3N]_{org} = -pH + \log K_e \tag{12}$$

where E represents the ratio of Cr(VI) complexed in the organic to the amount remaining in the aqueous phase. To further confirm the proposed reaction and to obtain a value for K_e, batch loading from aqueous solutions of known Cr(VI) concentrations was carried out at various organic/aqueous volume ratios. From the measurement of the chromate left in the aqueous phase at equilibrium, the left-hand side of Eq. (12) could be determined and plotted versus the observed equilibrium pH. The results given

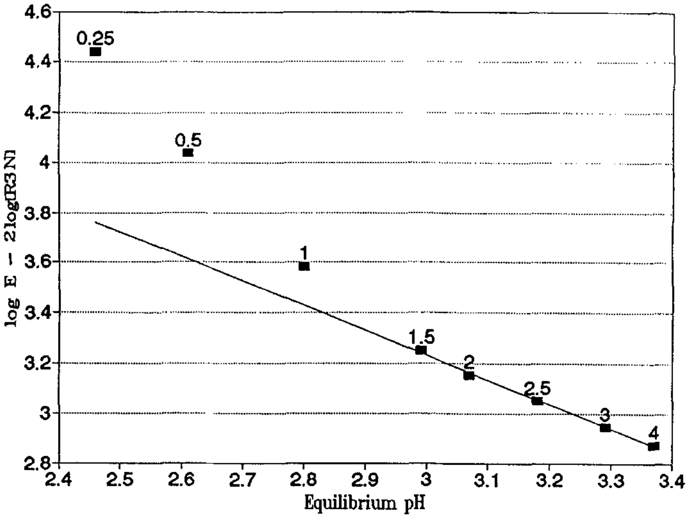

FIG. 2 Determination of equilibrium constant from Eq. (12) in the text. The number next to each point denotes the organic/aqueous volume ratio.

in Fig. 2 show that for volume ratios greater than 1.5 the data fall along a straight line with slope -0.98 ($r^2 = 0.9983$) and an intercept yielding a value of K_e of 10^6. The observed slope is in excellent agreement with the value of -1 expected from Eq. (12), providing further support for the proposed mechanism.

The deviation from this behavior at volume ratios below 1.5 is likely due to the very small volumes involved and the change in the complex formed at the very high Cr(VI) concentrations generated in the organic phase. The loaded organics obtained at these volume ratios appeared orange in color rather than the yellow normally observed with the loading of $HCrO_4^-$. The orange color is more characteristic of the loading of $Cr_2O_7^{2-}$, which is the predominant form of Cr(VI) at high concentrations. A similar result has been reported by Sengupta et al. (7). For the loading of the dichromate form, a plot of $\log E - 2\log[R_3N]$ versus pH is predicted to have a slope of -2, which is consistent with the rise in the slope observed in Fig. 2 at volume ratios below 1.5.

CONCLUSION

A series of solvent extraction experiments were performed to verify the loading mechanism proposed in this paper. Experimental results confirm that the extraction of chromium from an aqueous stream using a tertiary amine proceeds via a sequential two-step process. The first step involves the formation of an amine salt with bisulfate. Experiments confirmed that bisulfate and not sulfate participates in the first step, thus requiring a low pH. The second step is the substitution of bisulfate with bichromate. This step can occur at higher pH once the first step has been completed. For organic/aqueous volume ratios greater than 1.5, the equilibrium data were found to closely follow the behavior expected for the proposed mechanism and yielded an equilibrium constant of 10^6 for the overall loading reaction.

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