



## RECOVERY OF Cr(VI) BY QUATERNARY AMMONIUM COMPOUNDS

S. L. LO<sup>⊗</sup>\* and S. F. SHIUE

Graduate Institute of Environmental Engineering, National Taiwan University, 71 Chou-Shan Rd, Taipei, Taiwan, R.O.C.

(Received October 1996; accepted in revised form June 1997)

**Abstract**—The extraction of chromium (VI) from aqueous solutions of 0.1 M ionic strength by trioctylmethylammonium compounds (Aliquat 336) in a mixture of kerosene and xylene was investigated. The results indicate that the extraction efficiency of Cr(VI) in acidic aqueous solution is good. In these experiments, the relative affinities of different anions to Aliquat 336 were in the order of  $\text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ . Experimental results showed that hydrogen chromate ion ( $\text{HCrO}_4^-$ ) is the major extractable species of Cr(VI) at pH 3.53–3.75, expressed by the mechanism  $\text{R}_3\text{CH}_2\text{NNO}_3 + \text{HCrO}_4^- = \text{R}_3\text{CH}_2\text{NHCrO}_4 + \text{NO}_3^-$ . The equilibrium constant for the reaction is  $10^{2.078}$  (at 25°C). A computer program has been developed to simulate Cr(VI) extraction results under various conditions, the results of which fit the experimental data very well. The strippant is composed of 0.1 M sodium hydroxide and 1.0 M, sodium chloride and completely strips Cr(VI) from the loaded solvent ( $[\text{Cr}] = 0.0092 \text{ M}$ , A/O = 0.5). Thus, the recovered solution, by reducing the A/O ratio, contains a 10-times-higher concentration of Cr(VI). The stripped solvent (Aliquat 336) can then be reused for extracting Cr(VI). After five extraction cycles, the Aliquat-336/kerosene/xylene solution shows no significant loss in volume and retains the same extracting ability. © 1998 Elsevier Science Ltd. All rights reserved

**Key words**—chromium (VI), extractant, quaternary ammonium compound, solvent extraction, strippant

### INTRODUCTION

The solvent extraction method was used prevalently in early years for the uranium condensation process and, in recent years, has been adopted to hydrometallurgy. This low energy consumption technology, by means of using the appropriate extractant, selectively extracts specific metals contained in low concentrations from complicated aqueous metal solutions, allowing for higher purity and concentration after purification. The research conducted in this paper utilized a quaternary ammonium compound (Aliquat 336) as extractant to extract Cr(VI) by batch-type tests to determine the mechanism of Cr(VI) extraction. To study the effects of anions on extraction, three competitive anions were individually added to Cr(VI) solution at different concentrations and aqueous/organic solvent ratios. The extraction formula and the equilibrium constant were obtained in accordance with the experimental results. Furthermore, a computer program was developed to simulate the results of Cr(VI) extraction under various conditions. Regeneration of the extractant involved using several aqueous solutions of sodium compounds as strippants, which were analyzed for their

ability to strip and recover Cr(VI). The loss of extractant during extraction and stripping was measured by the residual volume and the effective concentration of extractant.

### MATERIALS AND METHODS

The extraction solvent was composed of the extractant and diluting agent. Aliquat 336, trioctylmethylammonium chloride (Wako, Japan, purity 86%), was used as the extractant and diluted to 0.01 M in the diluting agent (Maeck *et al.*, 1961; McDonald and Bajwa, 1977), which was a mixture of kerosene and xylene (1:1). The Cr(VI) solution was prepared by dissolving potassium chromate in deionized water.  $\text{KH}_2\text{PO}_4$  (0.001 M) was used as the buffer solution, and its ionic strength was adjusted to 0.1 M by  $\text{Na}_2\text{SO}_4$ . Sulfuric acid and sodium hydroxide were used for pH adjustment. The concentration of Cr(VI) in aqueous solution was determined by the standard addition method of atomic absorption spectrophotometry (Perkin-Elmer, U.S.A., Model 5000), which detects concentrations less than  $1 \times 10^{-4} \text{ M}$ .

In the equilibrium extraction test, the extraction solvent ( $V_e$ , ml) was added to the prepared Cr(VI) solution ( $V_a$ , ml) in a test-tube, and the test-tube was sealed and shaken vigorously for 30 s. The solution was allowed to settle and shaken again for another 30 s. The test-tube was then unsealed and centrifuged (Hettich EBA III, Germany, 5000 rpm max.) at 3000 rpm for 8 min. Following centrifugation, the aqueous phase at the bottom of the test-tube was drawn out with a syringe for Cr(VI) concentration analysis. The

\*Author to whom all correspondence should be addressed  
[Fax: 886-2-3928821].

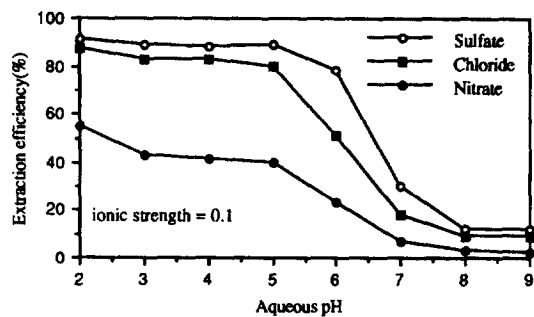


Fig. 1. Effects of competitive anions and pH on the extraction efficiency of Cr(VI).

relationship between the distribution coefficient ( $D$ ) and the percentage of extraction ( $E$ ) can be expressed by

$$D = \frac{[Cr]_{mit} \times 0.01 E \times (A/O)}{[Cr]_{mit} \times (1 - 0.01 E)} = \frac{E \times (A/O)}{100 - E} \quad (1)$$

where A/O represents the volume ratio of the aqueous to the solvent phase ( $V_a/V_o$ ). In the stripping and condensation tests, the loaded extractant ( $V_e$ , ml) and the strippant ( $V_s$ , ml) were added together into a test-tube and shaken vigorously until equilibrium was reached. After centrifugation and analysis of the Cr(VI) concentration in the aqueous strippant, the percentage of stripping ( $S$ ) can be obtained.

RESULTS AND DISCUSSION

Effects of competitive anions and pH

Three kinds of Cr(VI) solutions were prepared with different sodium salts in order to maintain a constant ionic strength of 0.1 M. The extraction results of Aliquat 336 are shown in Fig. 1 for various pH values. When the initial pH of the aqueous solution is less than 5.0, the extraction percentages for the three Cr(VI) solutions increase slightly with increasing pH. At pH higher than 5.0, however, the extraction percentage curves drop sharply. Comparing these trends with the concentrations of chrome species (Takahashi *et al.*, 1987) that were calculated from the reaction equations, equilibrium constants and activity coefficient from the Davies equation, it

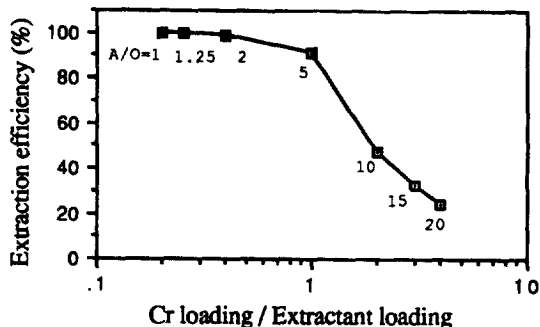
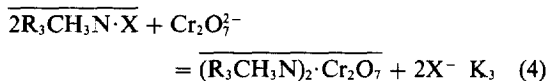
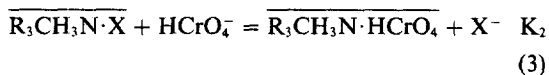
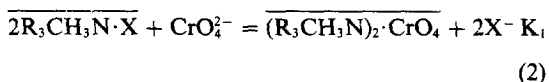


Fig. 3. Cr(VI) extraction results for different A/O ratios ( $Cr_{mit} = 0.002$  M, phosphate = 0.001 M, ionic strength = 0.1, pH = 3.5, Aliquat 336 = 0.01 M).

is found that the lower extraction percentage is related to the decrease in fractions of  $HCrO_4^-$  and  $Cr_2O_7^{2-}$  with the increasing pH. Therefore, two extraction equations (3 and 4) are proposed besides the existing extraction mechanism (equation 2) (Sato *et al.*, 1984; Molinari *et al.*, 1989):



where  $X^-$  is the competitive anion and  $R_3CH_3N \cdot X$  is Aliquat 336 dissolved in the organic phase. Figure 1 shows significant differences between the extraction efficiencies of the three sodium salts that were used for ionic strength adjustment. The aqueous solution containing  $NO_3^-$  had the lowest extraction efficiency, while the solution containing  $SO_4^{2-}$  had the highest. Thus, the relative affinities of these three anions to Aliquat 336 are in the order of  $NO_3^- > Cl^- > SO_4^{2-}$ , which corresponds to the order of complexing ability given by Ritcey and Ashbrook (1984).

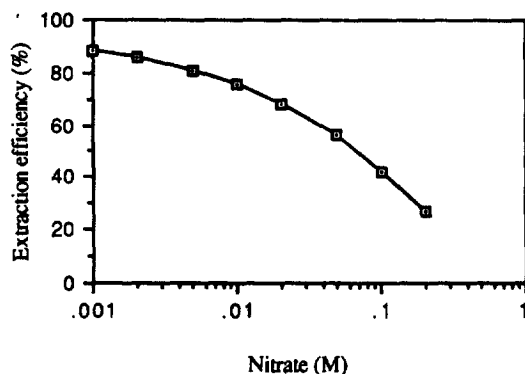


Fig. 2. Effect of  $NO_3^-$  on the extraction efficiency of Cr(VI) ( $Cr_{mit} = 0.001$  M, phosphate = 0.001 M, ionic strength = 0.1, pH = 3.5, Aliquat 336 = 0.01 M, A/O = 10).

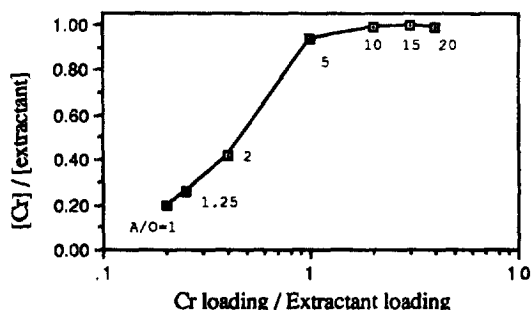


Fig. 4. Ratio of Cr(VI) in extractant and Aliquat 336 ( $Cr_{mit} = 0.002$  M, phosphate = 0.001 M, ionic strength = 0.1, pH = 3.5, Aliquat 336 = 0.01 M).

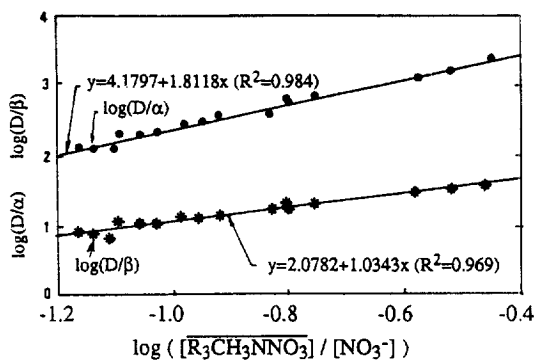


Fig. 5. Data analysis for extraction mechanism tests.

*Effects of NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup>*

To understand the influence of NO<sub>3</sub><sup>-</sup> concentration on chrome extraction, Cr(VI) solutions with different NaNO<sub>3</sub> concentrations (0.001–0.2 M) were prepared and tested at pH 3.5. The results (Fig. 2) indicated that, when the NaNO<sub>3</sub> concentration was less than 0.001 M, the extraction percentage was equivalent to that of Cr(VI) solution containing 0.033 M Na<sub>2</sub>SO<sub>4</sub> (as shown in Fig. 1). The extraction efficiency gradually decreased with increasing NO<sub>3</sub><sup>-</sup> concentration. Since the aqueous phase pH slightly changed before and after extraction, phosphate buffer was utilized to maintain pH. Two aqueous Cr(VI) solutions (control = 0.001 M Cr, 0.033 M Na<sub>2</sub>SO<sub>4</sub>; experimental = 0.001 M Cr, 0.033 M Na<sub>2</sub>SO<sub>4</sub>, 0.001 M KH<sub>2</sub>PO<sub>4</sub>), were tested to determine whether PO<sub>4</sub><sup>3-</sup> ions from the buffer affected the system. No difference was evident between both extraction efficiencies, verifying that the added 0.001 M KH<sub>2</sub>PO<sub>4</sub> did not affect Cr(VI) extraction. Because SO<sub>4</sub><sup>2-</sup>, also present in the solution, has the least affinity to Aliquat 336, its effect on extraction was considered negligible.

*Effect of A/O*

The Cr(VI) extraction results for different A/O values are shown in Fig. 3. The x coordinate is expressed by the ratio of Cr loading (mole) and extractant loading (mole). When the ratio is less than 1, meaning that the extractant loading is higher than Cr(VI) loading in the extracting system, the

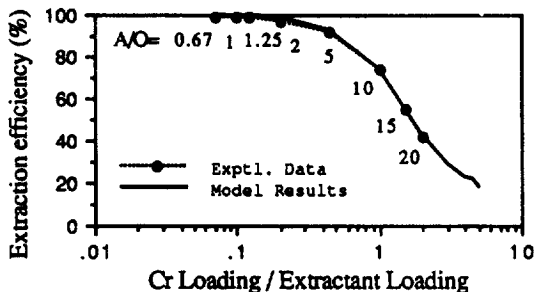


Fig. 6. Comparison of simulation and test results.

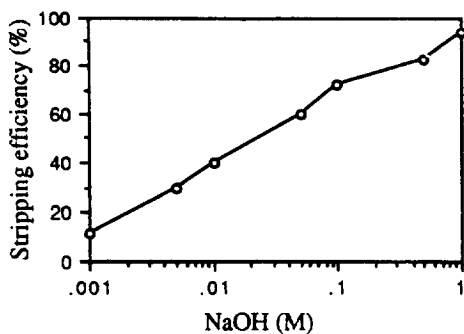


Fig. 7. Stripping efficiency for different concentrations of NaOH solutions.

extraction efficiencies are excellent. When the ratio is higher than 1, almost all of the extractant is combined with Cr(VI), leading to maximum utilization of the extractant. The ratio of Cr(VI) in the extractant to the dosage of Aliquat 336 is nearly 1:1 under these circumstances (Fig. 4). Thus, it can be assumed that 1 mole of Aliquat 336 extracts 1 mole of Cr(VI). Both equations (3) and (4) satisfy this conclusion.

*Extraction mechanism tests*

From equation (3) and the definition of distribution coefficient, one obtains

$$D = [Cr]/[Cr]_{eq} = \beta \times K_2 \times \frac{[R_3CH_3N \cdot X]}{[X^-]} \quad (5)$$

where  $\beta$  is the concentration fraction of HCrO<sub>4</sub><sup>-</sup>. The equilibrium constant ( $K_2$ ) in equation (5) can be obtained by plotting  $\log(D/\beta)$  versus  $\log([R_3CH_3N \cdot X]/[X^-])$  on log-log paper. The straight-line form of the equation is

$$\log(D/\beta) = \log K_2 + \log([R_3CH_3 \cdot X]/[X^-]) \quad (6)$$

Similarly, from equation (4) and the distribution coefficient, one obtains

$$\log(D/\alpha) = \log(2K_3) + 2 \log([R_3CH_3N \cdot X]/[X^-]) \quad (7)$$

where  $\alpha$  is the concentration fraction of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>. The correct extraction mechanism can be found from the slopes of both straight lines. During these tests, NO<sub>3</sub><sup>-</sup> was used as the competitive ion of HCrO<sub>4</sub><sup>-</sup> or Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>. It is known that the affinity of NO<sub>3</sub><sup>-</sup> to Aliquat 336 is stronger than that of Cl<sup>-</sup>. If Aliquat 336 comes into

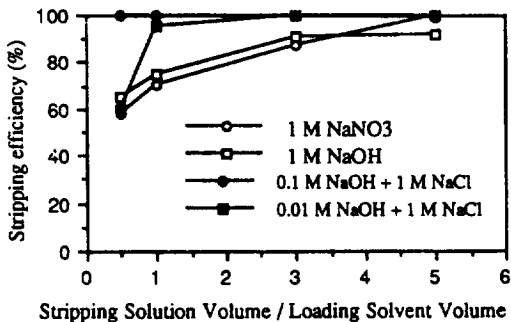
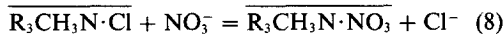


Fig. 8. Effects of strippants and A/O ratio on stripping.

Table 1. Recovery concentration of Cr(VI) at different A/O ratios

| Strippant                | A/O = 5   | A/O = 3   | A/O = 1   | A/O = 0.5 |
|--------------------------|-----------|-----------|-----------|-----------|
| 1.0 M NaNO <sub>3</sub>  | 0.00187 M | 0.00266 M | 0.00645 M | 0.0105 M  |
| 1.0 M NaOH               | 0.00168 M | 0.00277 M | 0.00689 M | 0.0119 M  |
| 0.1 M NaOH + 1.0 M NaCl  | 0.00182 M | 0.00308 M | 0.00954 M | 0.0192 M  |
| 0.01 M NaOH + 1.0 M NaCl | 0.00184 M | 0.00322 M | 0.00873 M | 0.0108 M  |

contact with aqueous solution containing NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> will be replaced by NO<sub>3</sub><sup>-</sup> and cause the extractant to become a quaternary ammonium nitrate:



Since the concentration of released Cl<sup>-</sup> is very low, Cl<sup>-</sup> competition is ignored. Cr(VI) in the chrome solutions (pH 3.5, 0.001 M Cr(VI)) was extracted by 0.01 M Aliquat 336 at various NaNO<sub>3</sub> concentrations and at A/O = 4, 5 and 6. Through data analysis of experimental results, Fig. 5 shows that the log(D/β) versus log([R<sub>3</sub>CH<sub>3</sub>N·NO<sub>3</sub>]/[NO<sub>3</sub><sup>-</sup>]) linear-plotted slope is 1.034, which is consistent with equation (6) and that the equilibrium constant is K<sub>2</sub> = 10<sup>2.078</sup> (at 25°C, ionic strength = 0.1). The log(D/α) slope, 1.811, is also quite close to its theoretical value of 2 (equation 7). However, because the log(D/β) slope is closer to its theoretical value, it is thought more accurate to conclude that HCrO<sub>4</sub><sup>-</sup> is the major species extracted at pH 3.5.

#### Simulation and verification of Cr(VI) extraction

Combining equations (5) and (1), one obtains

$$D = \{E \times (A/O)/(100 - E)\} \\ = \beta \times K_2 \times [\overline{R_3CH_3N \cdot NO_3}]/[NO_3^-] \quad (9)$$

Equation (9) can be used to simulate the results of Cr(VI) extraction at 0.1 ionic strength at 25°C. The concentration of the free extractant that is not reacting with HCrO<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> in aqueous solution at equilibrium can be calculated by

$$[\overline{R_3CH_3N \cdot NO_3}] = [\overline{R_3CH_3N \cdot Cl}]_0 \\ - [Cr]_0 \times 0.01 E \times (A/O) \quad (10)$$

$$[NO_3^-] = [NO_3^-]_0 - \{[\overline{R_3CH_3N \cdot Cl}]_0 \\ - [Cr]_0 \times 0.01 E \times (A/O)\}/(A/O) \quad (11)$$

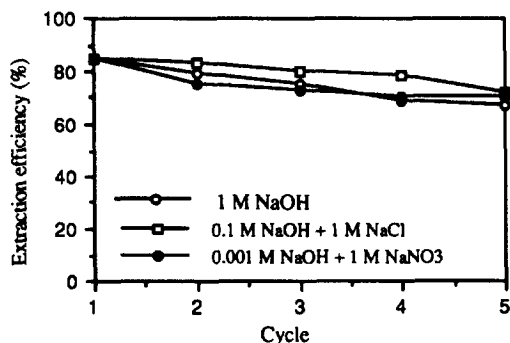
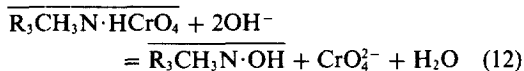


Fig. 9. Extraction efficiency after different cycles.

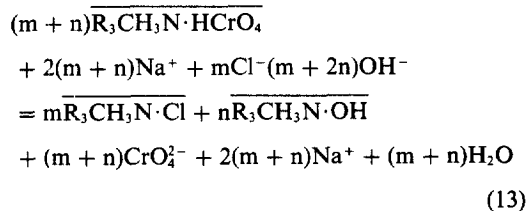
where  $[\overline{R_3CH_3N \cdot Cl}]_0$  is the total concentration of extractant (M) and  $[NO_3^-]_0$  is the initial concentration of NO<sub>3</sub><sup>-</sup> in aqueous solution (M). Substituting equations (10) and (11) into equation (9), a quadratic equation of *E* is obtained. The value of *E* can be calculated by trial and error. Figure 6 shows the simulation results of Cr(VI) extraction for different A/O ratios. The simulation results fit the experimental data very well.

#### Selection of strippant

Five strippants (1 M NaCl, 4 M NaCl, 1 M NaOH, 0.33 M Na<sub>2</sub>SO<sub>4</sub>, 1 M NaNO<sub>3</sub> solutions) were tested preliminarily for Cr(VI) stripping. As expected, NO<sub>3</sub><sup>-</sup>, which has a strong affinity to Aliquat 336, had a stripping efficiency as high as 87%, while Cl<sup>-</sup>, even at 4 M, had an efficiency of only 41.8%. For 0.33 M Na<sub>2</sub>SO<sub>4</sub> solution, the stripping efficiency was 10.4%. NaOH solution (1 M) stripped the most Cr(VI) (91%). In strong alkaline solutions, CrO<sub>4</sub><sup>2-</sup> is the major species of chrome. An alkaline solution will not only reduce the concentration of HCrO<sub>4</sub><sup>-</sup> but also cause OH<sup>-</sup> to combine with Aliquat 336:



Furthermore, the results indicated that the stripping percentage decreased with decreasing NaOH concentration (Fig. 7) when different concentrations of NaOH solutions were used for stripping. At higher NaOH concentrations, however, the solubility of Aliquat 336 increased, i.e. the loss of extractant increased. As for using NaNO<sub>3</sub> as strippant, although it showed good results, the nitrate form of the extractant hinders the Cr(VI) extraction efficiency with repeated use of the extractant. If NaOH is added into the NaCl solution to increase its pH, it will help to reduce the HCrO<sub>4</sub><sup>-</sup> concentration and achieve a more complete stripping process:



The results of the stripping tests for different A/O ratios and strippants are shown in Fig. 8 and Table 1. A mixture of 0.1 M NaOH and 1.0 M NaCl completely stripped Cr(VI) from the loaded solvent. A higher recovery of Cr(VI) was obtained from lowering the

volume of all strippants. However, all of the strippants, except for the mixture of 0.1 M NaOH and 1.0 M NaCl, had lower stripping efficiencies at lower A/O ratios, which meant that the extractant could not be regenerated for reuse. Thus, the 0.1 M NaOH and 1.0 M NaCl solution, with a condensation ratio (9.6) close to the ideal value (10), is the best strippant.

The extraction percentages after different extraction/stripping cycles are shown in Fig. 9. When the stripped solvent was reused for Cr(VI) extraction, the extraction efficiency decreased with increasing number of times the extractant was recycled. After five extraction cycles, the Aliquat-336-kerosene-xylene solution showed little loss in volume and retained quite a high extracting ability.

The more common method of removing Cr(VI) from water is ion exchange with synthetic resins. Ion exchange and the process studied in this paper, solvent extraction using ion association systems, differ only in that ion exchange uses a solid anion exchanger and solvent extraction uses a liquid. Cr(VI) removal efficiency is actually higher using ion exchange because the synthetic resins most prefer Cr(VI) to other common anionic species (Clifford, 1990). Further information on Cr(VI) removal by ion exchange can be found in the literature.

#### CONCLUSION

The efficiency of Cr(VI) extraction by Aliquat 336 is better in acidic aqueous solution. The relative affinity of three anions to Aliquat 336 are in the order of  $\text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ . Using nitrate ion as the competitive anion, the experimental results showed that  $\text{HCrO}_4^-$  is the major extractable species of Cr(VI) from pH 3.53 to 3.75 and can be expressed by the mechanism  $\text{R}_3\text{CH}_3\text{NNO}_3 + \text{HCrO}_4^- = \text{R}_3\text{CH}_3\text{NHCrO}_4 + \text{NO}_3^-$ . The equilibrium constant

for the reaction is  $10^{2.078}$  (at 25°C). A computer program was developed to simulate Cr(VI) extraction results, which fit the experimental data very well under various conditions. A mixture of 0.1 M NaOH and 1.0 M NaCl as strippant can completely strip Cr(VI) from the loaded extractant, and recovered solutions containing very high concentrations of Cr(VI) can be obtained by reducing the A/O ratio. After five extraction/stripping cycles, the Aliquat-336/kerosene/xylene solution shows little loss in volume and retains its high extracting ability.

*Acknowledgements*—This study was supported by the National Science Council, Taiwan, under Contract NSC81-0410-E002-34.

#### REFERENCES

- Clifford D. A. (1990) Ion exchange and inorganic adsorption. In *Water Quality and Treatment: A Handbook of Community Water Supplies*, AWWA, 4th edn., pp. 561–640. McGraw-Hill, New York.
- Maeck W. J., Booman G. L., Kussy M. E. and Rein J. E. (1961) Extraction of the elements as quaternary (propyl, butyl, and hexyl) amine complexes. *Anal. Chem.* **33**, 1775–1780.
- McDonald C. W. and Bajwa R. S. (1977) Removal of toxic metal ions from metal-finishing wastewater by solvent extraction. *Sep. Sci. Technol.* **12**, 435–445.
- Molinari R., Drioli E. and Pantano G. (1989) Stability and effect of diluents in supported liquid membranes for Cr(III), Cr(VI) and Cd(II) recovery. *Sep. Sci. Technol.* **24**, 1015–1032.
- Ritcey G. M. and Ashbrook A. W. (1984) *Solvent Extraction: Principles and Applications to Process Metallurgy—Part 1*. Elsevier Science, New York.
- Sato T., Nakamura T. N. and Takeuchi Y. (1984) The extraction of chromium (VI) from alkaline solution by long-chain alkyl quaternary ammonium compound. *Solv. Extract. Ion Exch.* **2**, 1033–1045.
- Takahashi K., Hirayama K. and Takeuchi H. (1987) Solvent extraction of chromium (VI) by 3-(4-pyridyl)-1,5-diphenyl pentane. *Solv. Extract. Ion Exch.* **5**, 393–418.