

Distribution of Chromium(VI) in Various Organic Solutions during Extraction and Re-extraction

Md Monwar Hossain* and Tregan Ru

Natural Products Processing, Industrial Research Limited, P.O. Box 31-310, Lower Hutt, New Zealand

Equilibrium studies on the extraction of Cr(VI) in various solvent phases have been performed. The organic solvent phase consists of Aliquat-336 (a cationic carrier) dissolved in kerosene/Shellsol TK (as an organic solvent) and hexanol (as a phase modifier). The values of the distribution coefficient for the extraction have been obtained by varying the following experimental conditions: feed solution pH (range 9–12); initial feed phase concentration ($25 \text{ ppm} \leq \text{Cr(VI)} \leq 1000 \text{ ppm}$); and composition of the organic phase ($2 \text{ vol } \% \leq \text{Aliquat-336} \leq 50 \text{ vol } \%$). Re-extraction of Cr(VI) from the solvent phase was examined with an aqueous solution of HCl or NaCl by varying its pH (range 1–12) and concentration ($0.5\text{--}2 \text{ mol}\cdot\text{L}^{-1}$). The values of the partition coefficient for this process are also presented. The extraction and re-extraction reaction coefficients were calculated by combining the experimental data and the kinetic expressions for the interfacial reactions. These values are presented and compared with the literature values.

Introduction

The reactive extraction systems are formed by dissolving a carrier in an organic solvent and have been applied to metal removal and recovery from polluting sources.^{1–6} The efficiencies of the systems are determined by the partitioning characteristics of the “target” molecule and its ability to form a complex with the carrier and the effective diffusivity of the solute–carrier complex in the organic solvent.^{7–9} A few research groups have focused on the thermodynamic equilibrium of metals between organic and aqueous solutions, especially determination of the equilibrium partition coefficient and the extraction/re-extraction rate constant.^{10–13} Despite the increase in the number of research papers, there is a need for more published experimental data for the partitioning of metals into potentially useful extraction systems.

Hexavalent chromium, Cr(VI), is a toxic metal and has been introduced in the environment from various industrial operations, for example, leather tanning, timber processing, electroplating, and steelmaking. The concentration of this Cr(VI) in the environment can be reduced by removing it by liquid membrane-based processes which have potential advantages over the conventional ion exchange and liquid–liquid extraction processes.^{1,10,11,13} Although there are some reports claiming the superiority of the liquid membrane separations, the extraction and re-extraction behavior of Cr(VI) has not been investigated in detail. Therefore, the aim of this paper is to obtain partitioning data for Cr(VI) between an aqueous phase and various organic solutions. Special attention is given to the Aliquat 336 and Shellsol TK system because it has been demonstrated to be better than the Aliquat 336 + kerosene system that has been extensively used in the previous research studies.

The partition coefficient values obtained from the extraction and re-extraction studies will help with the design and improvement of the performance of this membrane-based

removal and recovery process. A simple mathematical model is also developed for the reaction coefficients of the extraction and re-extraction processes.

Materials and Methods

Materials: Aliquat 336 (tricaprylmethylammonium chloride, $\text{CH}_3\text{N}((\text{CH}_2)_7\text{CH}_2)_3\text{Cl}$) from Acros Organics, New Jersey; hexanol ($\text{CH}_3(\text{CH}_2)_4\text{CHOH}$) from BDH Chemicals Ltd, Poole, England; hydrochloric acid (HCl), AnalaR grade, 37%, from BDH Chemicals Ltd, Poole, England; potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) from Riedel-deHaen, Seelze, Germany; anhydrous sodium carbonate (Na_2CO_3) AnalaR grade from BDH Chemicals; sodium chloride (NaCl) and sodium hydroxide pellets (NaOH), both reagent grade from Scharlau Chemie, S.A La Jota, Ltd, Poole, England.

Solvents: Kerosene (Product Code 130013) from PJ Hobbs Industries Ltd, Papakura, Auckland; Shellsol TK (Product Code 80128) from Asia Pacific Specialty Chemicals (NZ) limited. The physical properties of these two solvents are different. Shellsol TK is an isoparaffinic hydrocarbon solvent with a characteristically low odor with boiling point 185–199 °C and flash point 60 °C. Kerosene is also a hydrocarbon solvent having higher odor with boiling point 146 °C and flash point 44 °C.

Reagents: Chromium (VI) solution—a standard solution of potassium dichromate was prepared by dissolving a known mass of $\text{K}_2\text{Cr}_2\text{O}_7$ in a known mass of distilled water. This solution acted as the simulated waste water sample upon the addition of other metal ions, such as Na ions added in the form of NaOH solution. All the metal concentrations are expressed in parts per million (ppm), to be consistent with the literature.

pH Adjustment Solutions: 1 M HCl and 0.1 M NaOH. 1 M HCl was prepared by diluting 25.424 mL of HCl in a 200 mL volumetric flask. 0.1 M NaOH was prepared by dissolving 0.3981 g of NaOH pellets in a 100 mL volumetric flask.

Re-extraction was conducted with solutions of HCl/NaCl/ Na_2CO_3 ; HCl was prepared by diluting a known volume of

* To whom all correspondence should be addressed. Telephone: (64-4569000). Fax: (64-4-5690132). E-mail: m.hossain@irl.cri.nz.

HCl in distilled water. NaCl and Na₂CO₃ were prepared by dissolving known amounts of sodium chloride and sodium carbonate in distilled water, respectively. The pH of the re-extraction solution was adjusted using 0.1 M HCl and 0.1 M NaOH, respectively.

Milli-Q Water: The water used was pretreated with a reverse osmosis unit and then passed through a Milli-Q exchange cartridges system procured from Millipore.

Procedure for Equilibrium Measurements of Cr(VI).

The procedure in this section is similar to that used previously.¹⁴ All the extraction experiments were conducted at the temperature 18 °C.

Extraction into Organic Solution. The feed solution containing Cr(VI) was adjusted to the desired pH (PHM64 Research pH meter from Radiometer Copenhagen, Nicholas Victor Ltd.) using either 0.1 M HCl or 0.1 M NaOH, and it was brought into contact with an organic solution (Aliquat-336 and organic solvent and hexanol) at a volume ratio of 1:1 in the 15 mL centrifuge tubes. The initial concentration was fixed at 100 and 500 ppm (except for the experiment to study the effect of feed concentrations) and the feed pH range was within 9–12. The solution in the tubes was mixed for a period of 17 h using the rotation table (Rotating table, Parvalux motor was made by Electric Motors Ltd, Wallis down, Bournemouth, England) with a very low rotational speed (≈ 2 rpm). After mixing, the solutions were allowed to settle for 30 min to separate the two phases and obtain a clear bottom aqueous phase. There was no indication of microemulsion formation or dissolution of one phase into another. The bottom aqueous layer was removed using a Pasteur pipet and analyzed for its chromium (VI) content. The initial and final values of the pH of the aqueous phase were also measured.

Re-extraction of Cr(VI) in an Aqueous Solution.

Recovery of chromium was carried out at various concentrations of either HCl or NaCl or Na₂CO₃ solution and Milli-Q water. The recovery solution was adjusted to the desired pH, and 3 mL was then added to the organic solution enriched with Cr(VI) (retained after extraction). The pH was in the range 1–5 for acidic solutions and 7–11 for neutral/basic solutions.

This was mixed for a period of 17 h using the rotating table and then allowed to stand for 30 min to obtain a clear bottom aqueous phase. The aqueous layer was removed using a Pasteur pipet and analyzed for its chromium (VI) content. The initial and final values of pH were also measured.

Analytical Procedure for Measuring Cr(VI) Content Using a Spectrophotometric Method. The absorbance values of the initial Cr(VI) solution and the aqueous phases produced after the extraction and re-extraction experiments were measured using an atomic absorption spectrophotometer fueled by nitrous oxide (703 atomic absorption spectrophotometer from Perkin-Elmer). Some samples had to be diluted (usually 5× dilution) to have an absorbance less than the maximum absorbance. The absorbance values were taken at the wavelength 395.5 nm. They were then converted to concentration using a standard absorbance versus concentration curve. Thus, the values of the concentration for the initial solutions and the solutions after the extraction and re-extraction processes reached equilibrium were obtained. The values of the organic phase concentration were calculated differences of the initial and final aqueous phase concentrations. The distribution coefficients for extraction (DE) and stripping (DS) were calculated by using eqs 5 and 9 (defined in the next section), respectively.

Modeling of Equilibrium

Calculation of Equilibrium Parameters. The chemical equilibrium between the chromate and the carrier can be described by the following equations⁴



The equilibrium constant (K_E) is defined as

$$K_E = \frac{C_{\text{KCl}^*(\text{aq})}^2 C_{\text{APE}^*(\text{org})}}{C_{\text{Fe}^*(\text{aq})}^2 C_{\text{ACl}^*(\text{org})}} \quad (2)$$

where $C_{\text{KCl}(\text{aq})}$, $C_{\text{APE}(\text{org})}$, $C_{\text{Fe}(\text{aq})}$, and $C_{\text{ACl}(\text{org})}$ are the concentrations of potassium chloride, the chromium–Aliquat 336 complex, Cr(VI) after extraction, and Aliquat 336, respectively. The * denotes the equilibrium values of these concentrations, and the subscripts aq and org represent the aqueous and the organic phases, respectively. The carrier concentrations refer to the total volume (carrier + solvent).

It is difficult in practice to measure accurately the concentration of chromium–carrier complex ($\text{A}_2\text{Cr}_2\text{O}_7$) in the organic phase at equilibrium. This can be calculated by knowing the initial and equilibrium concentrations of Cr(VI) in the aqueous phase (assuming negligible adsorption at the interface). Similarly, the concentration of carrier in the organic phase is also difficult to measure accurately, but given the stoichiometry that every mole of $\text{K}_2\text{Cr}_2\text{O}_7$ reacts with 2 mol of carrier, the concentration of carrier in the organic phase is therefore the initial carrier concentration minus twice the concentration of the chromium–carrier complex. This can be expressed as follows:

$$C_{\text{ACl}^*(\text{org})} = (C_{\text{ACl}(\text{org})})_i - 2(C_{\text{fi}(\text{aq})} - C_{\text{Fe}^*(\text{aq})}) \quad (3)$$

where $(C_{\text{ACl}(\text{org})})_i - C_{\text{fi}(\text{aq})}$ are the initial concentrations of the carrier in the organic phase and of Cr(VI) in the aqueous phase, respectively.

The concentration of KCl at equilibrium is determined similarly by stoichiometry, as expressed below:

$$C_{\text{Cl}^*(\text{aq})} = 2(C_{\text{fi}(\text{aq})} - C_{\text{Fe}^*(\text{aq})}) \quad (4)$$

The distribution coefficient for extraction, DE, is defined as the ratio of the concentration of Cr(VI) in the organic phase over that in the aqueous phase at equilibrium and can be described by the following expression:

$$\text{DE} = \frac{C_{\text{APE}^*(\text{org})}}{C_{\text{Fe}^*(\text{aq})}} \quad (5)$$

By combining eqs 2 and 5, a relationship between DE and K_E is obtained

$$\text{DE} = K_E \frac{C_{\text{ACl}^*(\text{org})}^2}{C_{\text{KCl}^*(\text{aq})}^2} \quad (6)$$

All the concentrations in the above equations can be measured; therefore, by determining the distribution coefficient at constant pH for various carrier concentrations, the value of K_E can be calculated using eq 6.

During re-extraction of Cr(VI) from the organic phase with an aqueous chloride solution (HCl or NaCl), the decomplexation of the chromium–carrier complex takes

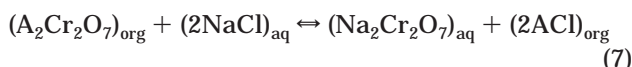
Table 1. Effect of Feed pH on Extraction of Cr(VI) with 10% Aliquat 336 in Shellsol TK

Cr(VI) conc (ppm)		%E	KE ($\times 10^3$)	DE
initial	final			
100	0.81	99.19	0.29	122.43
100	0.69	99.31	0.34	143.00
100	0.58	99.42	0.41	171.80
100	0.58	99.42	0.41	171.80

Table 2. Effect of Feed pH on Extraction of Cr(VI) with 10% Aliquat 336 in Kerosene

Cr(VI) conc (ppm)		%E	KE ($\times 10^3$)	DE	
pH	initial				final
9	100	1.16	98.84	0.20	85.41
10	100	0.81	99.19	0.29	122.43
11	100	0.69	99.31	0.34	143.00
12	100	0.69	99.31	0.34	143.00

place and the chromium is released according to the reaction



Note that, by using an aqueous chloride solution, the carrier can be replenished and then reused in the extraction process.

This reaction is characterized by a re-extraction equilibrium coefficient, K_s , which is expressed as

$$K_s = \frac{[C_{fS^*(aq)}][C_{ACl^*(org)}]^2}{[C_{APS^*(org)}][C_{NaCl^*}]^2_{aq}} \quad (8)$$

where $C_{NaCl(aq)}$, $C_{APS(org)}$, $C_{fS(aq)}$, and $C_{ACl(org)}$ are the concentrations of sodium chloride, chromium–Aliquat 336 complex, Cr(VI) after re-extraction, and Aliquat 336, respectively. The * denotes the equilibrium values of these concentrations during the re-extraction process.

A distribution coefficient at the organic–aqueous interface is defined by the following equation

$$DS = \frac{C_{APS^*(org)}}{C_{fS^*(aq)}} \quad (9)$$

By combining eqs 8 and 9, a relationship between DS and K_s is obtained

$$DS = \frac{1}{K_s} \frac{C_{ACl^*(org)}^2}{C_{NaCl^*(aq)}^2} \quad (10)$$

The value of K_s is calculated by using eq 10 and the experimental values of DS and C_{NaCl^*} .

The performance of the processes can be indicated by the percentage extraction and recovery of Cr(VI) as expressed in the following equations:

$$\%E = \left(1 - \frac{C_{fE^*(aq)}}{C_{fi(aq)}}\right) \times 100 \quad (11)$$

$$\%R = \frac{C_{fS^*(aq)}}{C_{fi(aq)}} \times 100 \quad (12)$$

Results and Discussion

The results are presented as percentage extracted, percentage recovered, distribution coefficients, and equilibrium constants for extraction and re-extraction proc-

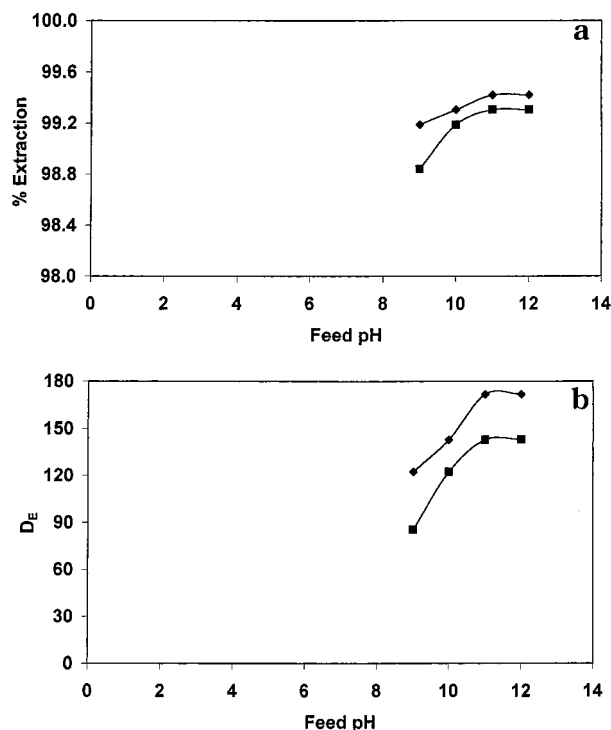


Figure 1. (a) Comparison of extraction (%) for Cr(VI) (100 ppm) between Shellsol TK (◆) and kerosene (■) with 10% Aliquat 336 and 20% hexanol. (b) Comparison of distribution coefficient for Cr(VI) (100 ppm) between Shellsol TK (◆) and kerosene (■) with 10% Aliquat 336 and 20% hexanol.

esses. These performance indicators are shown as a function of feed solution pH, composition of the organic membrane, type of the re-extracting agent and its concentration and pH, and concentration of sodium ions in the feed solution.

Effect of Feed pH on Extraction. The effects of pH on the extraction of chromium (VI) using 10–50% Aliquat-336 in Shellsol TK and kerosene are listed in Tables 1 and 2, respectively. It can be seen that the distribution coefficients (and percentage extraction) for higher carrier concentrations are generally less than those for the lower concentrations. This suggests that 10% Aliquat-336 or below in the organic solution is enough for effective removal of chromium at a basic pH. It is also observed that DE or percentage chromium extracted shows a maximum value at pH 11 for the 10% Aliquat-336 solution; thus, this indicates the best extraction pH. On the basis of this finding, graphs combining data from the two solvents, Shellsol TK and kerosene, were plotted in parts a and b of Figure 1, respectively. Both solvents seemed to perform equally well at pH 11. However, the extraction distribution coefficients provided by Shellsol TK between pH 9 and 11 are comparatively higher than those for kerosene. Therefore, it is plausible to conclude that Shellsol TK is a better solvent not only in terms of material cost (Shellsol TK costs \$3.60/L and kerosene costs \$5.90/L, price in New Zealand dollars as of March 2001) but also for offering the benefit of operating at less basic conditions in the real situation.

On the basis of the above findings, the Aliquat-336/Shellsol TK system was selected for detailed studies.

Effect of Carrier Concentration. Experimental results of the effect of carrier concentration for two feeds at pH 11 are plotted in parts a and b of Figure 2, respectively. For the 100 ppm feed solution, DE is fairly constant at 5% Aliquat-336 and beyond; thus, addition of further carrier is redundant for chromium removal. On the other hand, a

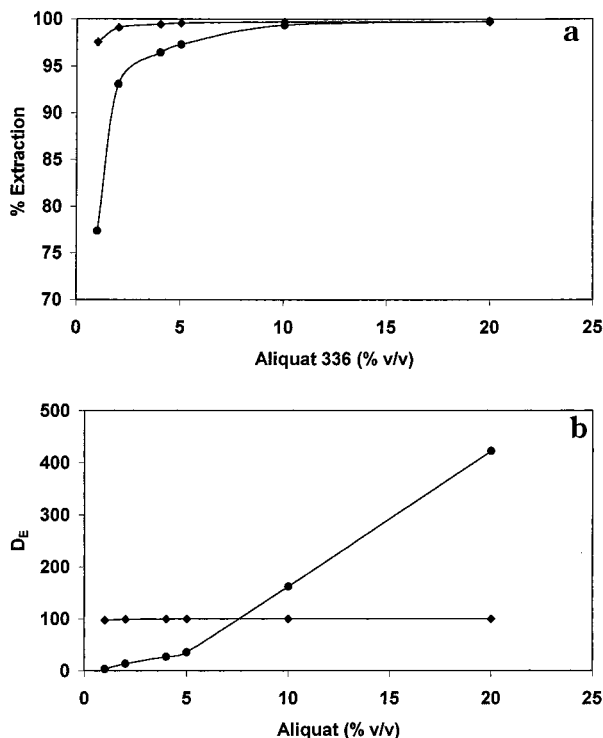


Figure 2. (a) Extraction (%) as a function of Aliquat 336 concentration in Shellsol TK with 10% hexanol and at pH 11 for two concentrations of Cr(VI): (◆) 100 ppm; (●) 500 ppm. (b) Distribution coefficient as a function of Aliquat 336 concentration in Shellsol TK with 10% hexanol and at pH 11 for two concentrations of Cr(VI): (◆) 100 ppm; (●) 500 ppm.

Table 3. Effect of Modifier (Hexanol) Concentration on Extraction of Cr(VI) Using 10% Aliquat 336 in Shellsol TK

hexanol % (v/v)	Cr(VI) conc (ppm)		%E	KE ($\times 10^3$)	DE
	initial	final			
1	100	0.35	99.65	71.27	287.00
2.5	100	0.35	99.65	11.19	287.00
5	100	0.35	99.65	2.78	287.00
10	100	0.28	99.72	0.87	359.00
20	100	0.28	99.72	0.22	359.00
1	500	4.17	99.17	837.08	119.00
2.5	500	4.03	99.19	125.66	123.14
5	500	3.75	99.25	32.73	132.33
10	500	3.95	99.21	7.62	125.32
20	500	8.26	98.35	0.89	59.50

positive linear relationship was observed between DE and carrier concentration for the 500 ppm feed solution; however, with 5% Aliquat-336, more than 99% of the chromium was successfully removed from the feed. Therefore, 5% Aliquat-336 is sufficient for >99% Cr(VI) removal for feed concentrations up to 500 ppm.

Effect of Modifier (Hexanol). The main role of the modifier in the organic membrane was to prevent the segregation of the gelatinous layer between the carrier and the solvent, and therefore to provide sound mass transfer in the extraction and re-extraction processes. Experimental results on this part of the investigation are shown in Table 3. For the 100 ppm feed solution, the highest extraction of Cr(VI) (>99%) was obtained at 10% hexanol and beyond. Meanwhile for the 500 ppm feed, addition of 10% hexanol provides better percentage extraction, and beyond 10% hexanol, extraction begins to decline due to the generation of a dilution effect of the carrier. Overall, more than 99% extraction could be achieved for 100 ppm and 500 ppm feed with a 10% hexanol addition of the modifier.

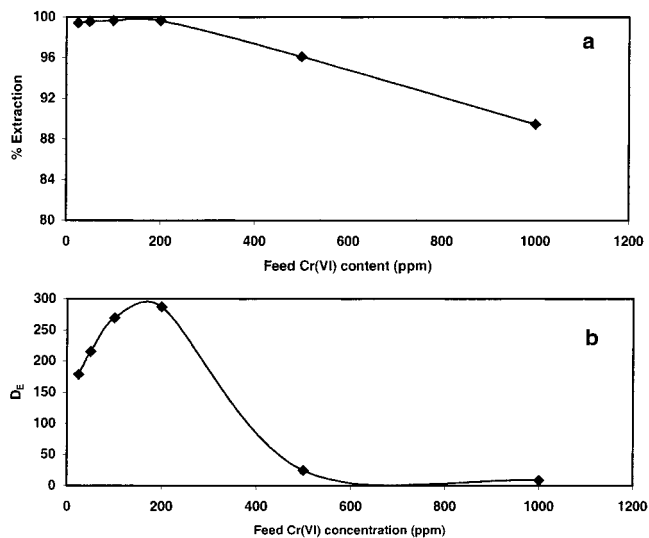


Figure 3. (a) Extraction (%) as a function of feed concentration with 10% Aliquat 336 in Shellsol TK and at pH 11. (b) Distribution coefficient as a function of feed concentration with 10% Aliquat 336 in Shellsol TK and at pH 11.

Table 4. Re-extraction of Chromium Using HCl and NaCl Solutions from Organic Solution Containing 5% Aliquat 336 in Shellsol TK with 10% Hexanol

type of agent	re-extraction solution conc (mol.L ⁻¹)	Cr(VI) conc (ppm)		%R	DS
		initial	final		
HCl	0.5	500	110.14	22.03	3.50
HCl	1	500	100.74	20.15	3.92
HCl	1.5	500	124.26	24.85	3.00
HCl	2	500	70.19	14.04	6.06
NaCl	0.1	500	180.56	36.11	1.71
NaCl	0.4	500	418.40	83.68	0.17
NaCl	0.5	500	362.27	72.45	0.37
NaCl	1	500	134.03	26.81	2.70
NaCl	1.5	500	139.24	27.85	2.56
NaCl	2	500	158.68	31.74	2.13

Effect of Initial Feed Concentration. On the basis of the above findings, an organic membrane system containing 5% Aliquat-336, 10% hexanol, and 85% Shellsol TK was selected for studying the effect of the initial feed concentration. The experimental results are presented in parts a and b of Figure 3, respectively. It is fairly obvious that the best extraction is achieved for a 200 ppm feed solution. The general trend was that the percentage extraction drops as the feed concentrations increase beyond 200 ppm, but more than 80% chromium removal can still be achieved at a feed concentration of up to 1000 ppm.

Recovery of Cr(VI) from the Organic Solution. Effect of the Type of Solute in the Re-extraction. The effect of the type of solute in the re-extraction solution and its concentration on the recovery of Cr(VI) is shown in Table 4. For a feed concentration of 500 ppm, more than 70% of the chromium could be recovered with a 0.4 M NaCl solution whereas, with HCl, the highest recovery of 27.85% was obtained at 1.5 M.

It was also found in the earlier stage of the experiment that Milli-Q water is completely ineffective in the recovery process.

Effect of pH of the Re-extraction Solution. Considering 0.4 M NaCl as the appropriate solution for the re-extraction, the effect of the pH of this solution was studied for a feed concentration of 200 ppm and the results are listed in Table 5. It is shown that 97–99% Cr(VI) was recovered at moderately acidic pH 4–5 as well as at

Table 5. Effect of pH of the Re-extraction Solution (0.4 M NaCl) on Recovery of Cr(VI) Using 5% Aliquat 336 in Shellsol TK with 10% Hexanol

pH of NaCl solution	Cr(VI) conc (ppm)		%R	DS
	initial	final		
1	200	59.26	29.63	2.35
2	200	91.67	45.83	1.17
3	200	150.93	75.46	0.31
4	200	197.22	99.35	0.01
5	200	197.00	98.50	0.01
6	200	166.90	83.45	0.19
7	200	180.09	90.05	0.10
8	200	187.96	93.98	0.06
9	200	196.30	98.15	0.01
10	200	195.83	97.92	0.01
11	200	195.37	97.69	0.02
12	200	192.59	96.30	0.03

Table 6. Effect of Na⁺ Ions (Used as NaOH) on Extraction of Cr(VI) Using 20% Aliquat 336 in Shellsol TK with 10% Hexanol

Na ⁺ conc (ppm)	Cr(VI) conc (ppm)		%E	KE ($\times 10^3$)	DE	final Na ⁺ conc (ppm)	%E (Na ⁺)
	initial	final					
0	200	0.24	99.89	2.05	845.67	0.00	0.00
50	200	0.54	99.73	0.90	372.53	49.00	2.00
100	200	0.84	99.58	0.57	237.13	95.00	5.00
200	200	1.05	99.48	0.46	189.50	180.00	10.00
400	200	1.42	99.29	0.34	140.11	390.00	2.50
800	200	2.36	98.82	0.20	83.67	790.00	1.20
1000	200	2.99	98.50	0.16	65.84	975.00	2.50
1600	200	4.97	97.51	0.09	39.11	1580.00	1.20
0	1000	1.44	99.86	42.36	691.73	0.00	0.00
50	1000	2.36	99.76	25.84	422.33	49.00	2.00
100	1000	4.46	99.55	13.62	223.18	95.00	5.00
200	1000	6.30	99.37	9.61	157.75	190.00	5.00
400	1000	24.15	97.59	2.42	40.41	391.00	2.20
800	1000	66.35	93.36	0.81	14.07	785.00	1.90
1000	1000	73.49	92.65	0.72	12.61	993.00	0.70
1600	1000	80.00	92.00	0.65	11.50	1575.00	1.60

alkaline pH 9–10. Therefore, 0.4 M NaCl can be recommended as the best re-extraction solution at those pH values.

Effect of Other Sodium Ion on Cr(VI) Recovery. In a real life situation, it is likely that other metal ions such as Na⁺, K⁺, and Li⁺ will be present in effluent streams. This experiment was designed purely to investigate the organic carrier's affinity for Cr(VI) in the presence of other metal ions during the extraction phase. Only results of sodium ions are presented in Table 6. It is clearly indicated by the results that Na⁺ ions at concentrations greater than 500 ppm cause a quick drop in extraction. However, for all samples, 90% extraction of Cr(VI) could still be achieved; meanwhile, more than 90% of the sodium ions remained unextracted. Therefore, it is possible to separate chromium in the presence of sodium with a little loss in extraction performance.

Correlations for the Distribution Coefficients. The effect of feed pH (in the range 9–12) on the distribution coefficient (D_E) of the solutes in Aliquat-336 can be correlated by the empirical formula given below

$$\log_{10}(D_E) = a + b(\text{pH}) \quad (13)$$

The values of the parameters a and b for the extraction of Cr(VI) are listed in Table 7. The plots of the left-hand side of eq 13 are shown in Figure 4. The data show a good correlation that is a positive logarithm relationship with increasing pH.

Comparison of Equilibrium Constants. The K_E values for chromium extraction with various concentrations

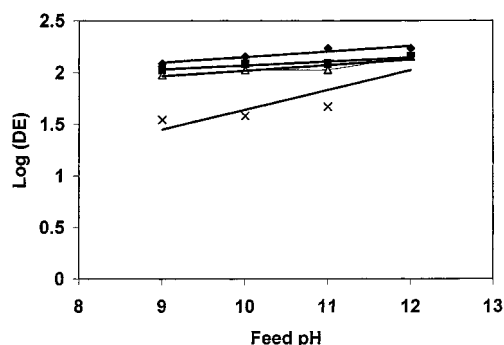
Table 7. Parameter Values for the Correlation of the Distribution Coefficient for Chromium Extraction

membrane composition/ % v/v Aliquat 336	parameter	value
10	a	1.63
	b	0.05
20	a	1.69
	b	0.04
40	a	1.49
	b	0.05
50	a	0.28
	b	0.19

Table 8. Comparison of Equilibrium Constants for Cr(VI) Extraction

membrane composition/ % v/v Aliquat 336	initial conc of Cr(VI) (ppm)	KE ($\times 10^3$)	pH
10	150	0.81 ^a	not mentioned
	100	0.65 ^a	not mentioned
	50	0.15 ^a	not mentioned
5	50	0.60 ^a	not mentioned
1	25	0.70 ^a	not mentioned
1	10	0.69 ^a	not mentioned
5	50	2.31 ^b	11
10	100	0.87 ^b	11

^a Reference 4. It is believed that the K_E values obtained from ref 4 are for pH 11, despite it not being mentioned in the article.
^b From this research.

**Figure 4.** Plot of log(DE) versus feed pH at various Aliquat 336 concentrations: (◆) 10%; (■) 20%; (△) 40%; (×) 50%.

of Aliquat 336 in Shellsol TK are compared in Table 8. It is observed that all the K_E values obtained for the Aliquat 336–Shellsol TK system are considerably higher than those reported by Alonso et al.⁴ This could be due to the different modifier and solvent being used in our experiments; Alonso et al.⁴ used 3,7-dimethyl-3-octanol and kerosene as the modifier and solvent, respectively.

Conclusion

Experimental results are reported for the partitioning of chromium using two different organic solvents, Shellsol TK and kerosene, with detailed data on Shellsol TK, as this system gives excellent values. It is shown that the value of DE is much higher for Shellsol TK than that for kerosene. The experimental conditions that gave the highest value of DE were 5% Aliquat-336 in Shellsol TK with 10% hexanol as modifier, 200 ppm feed at pH 11, and less than 500 ppm of other metal ions (i.e. Na⁺).

Sodium chloride solution at a concentration of 0.4–0.5 M and at pH 4–5 was found to be an excellent agent for recovering Cr(VI). Its performance far exceeds those of all the other aqueous solutions (i.e., Milli Q water, Na₂CO₃, and HCl) considered in this study. Thus, it is possible to extract and recover chromium from aqueous solutions.

Literature Cited

- (1) Teramoto, M.; Tohno, N.; Ohnishi, N.; Matsuyama, H. Development of a spiral-type flowing liquid membrane module with high stability and its application to the recovery of chromium and zinc. *Sep. Sci. Technol.* **1989**, *24*, 981–999.
- (2) Fraser, B. G.; Pritzker, M. D.; Legge, R. L. Development of liquid membrane pertraction for the removal and recovery of chromium from aqueous effluents. *Sep. Sci. Technol.* **1994**, *29*, 2097–2111.
- (3) Hochhauser, A. M.; Cussler, E. L. Concentrating chromium with liquid surfactant membranes. *AIChE Symp. Ser.* **1975**, *71*, 136–142.
- (4) Alonso, A. I.; Irabien, A.; Ortiz, M. I. Nondispersive extraction of Cr (VI) with Aliquat 336: Influence of carrier concentration. *Sep. Sci. Technol.* **1996**, *31*, 271–282.
- (5) Chaudry, M. A.; Ahmad, S.; Malik, M. T. Supported liquid membrane technique applicability for removal of chromium from tannery wastes. *Waste Manage.* **1997**, *17*, 211–218.
- (6) Oritz, I.; Galan, B.; Irabien, A. Membrane mass transport coefficient for the recovery of Cr(VI) in hollow fibre extraction and back-extraction modules. *J. Membr. Sci.* **1996**, *118*, 213–221.
- (7) Alonso, A. I.; Urriaga, A. M.; Irabien, A.; Ortiz, M. I. Extraction of Cr(VI) with Aliquat 336 in hollow fibre contactors: Mass transfer analysis and modelling. *Chem. Eng. Sci.* **1994**, *49*, 901–909.
- (8) Oritz, I.; Galan, B.; Irabien, A. Kinetic analysis of the simultaneous nondispersive extraction and back-extraction of chromium (VI). *Ind. Eng. Chem. Res.* **1996**, *35*, 1369–1377.
- (9) Huang, T.-C.; Huang, C.-C.; Chen, D.-H. Transport of chromium(VI) through a supported liquid membrane containing Tri-*n*-octylphosphine oxide. *Sep. Sci. Technol.* **1998**, *33*, 1919–1935.
- (10) Alonso, A. I.; Galan, B.; Irabien, A.; Ortiz, I. Separation of Cr(VI) with Aliquat: Chemical equilibrium modelling. *Sep. Sci. Technol.* **1997**, *32*, 1543–1555.
- (11) Huang, T.-C.; Huang, C.-C.; Chen, D.-H. Thermodynamic equilibria of the extraction of chromium(VI) with tri-*n*-octylphosphine oxide from aqueous solutions. *Solvent Extr. Ion Exch.* **1997**, *15*, 837–862.
- (12) Huang, Y.-H.; Chen, C.-Y.; Kuo, J.-F. Extraction of chromium(VI) from acid solutions by tri-iso-octylamine. *J. Chem. Eng. Jpn.* **1991**, *24*, 149–154.
- (13) Monlinari, R.; Drioli, E.; Pantano, G. Stability and effect of diluents in supported liquid membranes for Cr(III), Cr(VI) and Cd(II) recovery. *Sep. Sci. Technol.* **1989**, *24*, 1015–1032.
- (14) Hossain, M.; Fenton, G. Extraction equilibria of amino acids and dipeptides in various organic solutions. *J. Chem. Eng. Data* **1999**, *44*, 1279–1285.

Received for review May 30, 2001. Accepted November 20, 2001. The financial assistance of the Foundation for Research, Science and Technology (FoRST), New Zealand, in the Industrial Mass Transfer Operations Program C08X0005-3, is gratefully acknowledged.

JE010164A