Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Extraction of Zinc and Chromium(III) and Its Application to Treatment of Alloy Electroplating Wastewater

Yu Keung Peter Sze[a]; Lizhen Xue[a]
[a] Department of Biology and Chemistry, City University of Hong Kong, Kowloon, Hong Kong

To cite this Article Sze, Yu Keung Peter and Xue, Lizhen(2003) 'Extraction of Zinc and Chromium(III) and Its Application to Treatment of Alloy Electroplating Wastewater', Separation Science and Technology, 38: 2, 405 — 425
To link to this Article: DOI: 10.1081/SS-120016582
URL: http://dx.doi.org/10.1081/SS-120016582

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 2, pp. 405–425, 2003

Extraction of Zinc and Chromium(III) and Its Application to Treatment of Alloy Electroplating Wastewater

Yu Keung Peter Sze* **and Lizhen Xue**

Department of Biology and Chemistry, City University of Hong Kong,
Kowloon, Hong Kong

ABSTRACT

Extraction of Zn and Cr(III) with solvents containing (1) DEHPA, di-2-ethylhexyl phosphoric acid, (2) PC-88A, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester, (3) Cyanex 272, *bis*(2,4,4-trimethylpentyl)phosphinic acid, and (4) Cyanex 302, *bis*(2,4,4-trimethylpentyl)thiophosphinic acid, was studied with a view to separately recovering the two metals from alloy electroplating wastewater. All solvents extracted Zn well. Extraction of Cr(III) required a higher pH and Cr(III) hydroxide precipitation placed an upper limit on the pH that could be used, which in turn limited the extraction percentage. Among the four extractants, DEHPA performed the best, achieving close to 100% extraction at 0.1 M. The extracted Cr(III) could not be completely stripped (back-extracted). By using ammoniated DEHPA, both the precipitation and incomplete stripping problems were

---

*Correspondence: Yu Keung Peter Sze, Department of Biology and Chemistry, City University of Hong Kong, Kowloon, Tat Chee Avenue, Kowloon, Hong Kong; Fax: 852-2788-7406; E-mail: bhpeters@cityu.edu.hk.

DOI: 10.1081/SS-120016582 0149-6395 (Print); 1520-5754 (Online)

www.dekker.com

averted. The different performances of the DEHPA and ammoniated DEHPA solvents were explained in terms of the different extracted Cr(III) species and the slow kinetics of reactions involving ligand displacement of the Cr(III) species. This explanation was supported by stoichiometric and UV–visible spectral data.

A flow sheet based on Zn extraction with DEHPA and Cr(III) extraction with ammoniated DEHPA was developed for treatment of Zn–Cr(III) alloy electroplating wastewater. The flow sheet was tested in an automated mixer–settler solvent extraction system. The treated wastewater contained $<0.1\,\mathrm{mg\,l^{-1}}$ Zn and $<1\,\mathrm{mg\,l^{-1}}$ Cr(III), and the recovered metals were in good purity.

Key Words: Zinc; Chromium(III); Extraction; Recovery; Electroplating wastewater; Waste treatment.

INTRODUCTION

The use of Cr(VI) in the electroplating industry is under pressure for replacement because of its toxicity in the wastewater[1,2] and because of the occupational safety problems associated with the release of chromic acid into the atmosphere.[1,3–5] Zn–Cr(III) alloy plating provides a superior corrosion resistance coating comparable to that of Cr(VI)[6–8] so the Zn–Cr(III) electroplating technique has been applied extensively to the manufacture of a wide range of products with excellent corrosion resistance.[9–15]

Although Cr(III) is less toxic than Cr(VI), its discharge is still regulated.[16–20] Many environmental authorities make no distinction between Cr(VI) and Cr(III).[19,20] In this case, the treatment of Cr(III) has to conform to the same stringent requirements as those of Cr(VI). The discharge of Zn is also regulated[19,20]; in addition, it is one of the strategic metals in the high priority list for recovery from waste streams, based on an overall consideration of environmental risk (toxicity) and reserve depletion rate.[21]

The conventional method for treatment of metal waste is precipitation[22] but the sludge obtained is difficult to treat to recover the metals, particularly if it is a multi-metal sludge.[23–25] The sludge is often disposed of at landfill sites, resulting in loss of useful resources and possible environmental problems at the sites. Moreover, for multi-metal wastewater, precipitation often cannot ensure total compliance with environmental regulations.[23,24,26]

Solvent extraction is well known for its ability to selectively separate and concentrate metals.[27] Recently, we used this technique to separately recover

Zn and Co in good purity from simulated rinsewater of Zn–Co alloy electroplating.[28] In this study, we extended the application to the Zn–Cr(III) system.

The major challenge of the Zn–Cr(III) system lies in the extraction of Cr(III). Although the extraction of Zn has been extensively studied,[29–31] there have been many fewer studies on Cr(III).[32] Pandey et al.[32] studied the extraction of Cr(III) using DEHPA and Cyanex 272 with a view to recovering Cr(III) from spent tanning baths. More recent studies were reported by de Juan et al.[33] and Khwaja et al.[34] using DEHPA and H_2MEHP (mono-2-ethylhexyl phosphoric acid) as extractants, respectively. In these studies, the extraction was generally successful, but difficulties were encountered in stripping the Cr(III) from the organic phase, for example, even when 8 M HCl was used, about 20% of the Cr(III) remained unstripped.[32] de Juan et al.[33] and Khwaja et al.[34] resorted to the use of redox conditions using H_2O_2 solutions to oxidize Cr(III) to the strippable, but also more toxic, Cr(VI) anions. The difficulty of stripping Cr(III) has posed an obstacle to a practical application of the solvent extraction technique for treatment of wastewater. It has not been properly examined. The objective of the present study was to perform a systematic study of the solvent extraction of Zn and Cr(III) for a better understanding of the chemistry to develop a process for selective recovery of Zn and Cr(III) from the alloy-electroplating wastewater.

EXPERIMENTAL

Four monobasic organophosphorus acid extractants, being the most widely used to date[31,35–37]: (1) DEHPA, supplied by BDH Laboratory Supplies; (2) PC-88A, supplied by Daihachi Chemical Industry Co. Ltd.; (3) Cyanex 272, supplied by Cytec Canada Inc.; and (4) Cyanex 302, supplied by Cytec Canada Inc.; were used. Organic solvents were prepared by dissolving the extractant in the diluent, D-80, a mixture of de-aromatized petroleum hydrocarbons (Exxon Chemical International Ltd.). For ammoniated solvents, 10% v/v isodecanol ($\geq$99.5 pure, RDH) was used as a modifier. The ammoniation was performed by shaking the organic solvent with an aqueous solution of ammonia at an aqueous to organic (A/O) phase ratio of 1:1. The concentration of ammonia was twice that of the extractant (0.05 or 0.1 M). Simulated waste rinsewater was prepared by first preparing the simulated alloy plating bath containing 100 g l^{-1} (0.348 M) $ZnSO_4{\cdot}7H_2O$ ($\geq$99.5% pure, RDH), 255 g l^{-1} (0.510 M) $KCr(SO_4)_2{\cdot}12H_2O$ ($\geq$99% pure, RDH), and 30 g l^{-1} Na_2SO_4 ($\geq$99% pure, RDH),[14] which was then diluted 100-fold to produce a solution of a composition typical of that of waste rinsewater.[38,39] Aqueous solutions containing the individual metal, either Zn or Cr(III), with otherwise identical composition to that of simulated rinsewater, were similarly prepared. Solutions of NaOH (AR, RDH) or H_2SO_4 (AR, RDH) were used for pH adjustment as appropriate.

Batch extraction experiments were started within 20 min after pH adjustment. The aqueous and organic phases were shaken at an A/O ratio of 1:1 (unless otherwise specified) with a mechanical shaker at 200 cycles per min for 30 min (unless otherwise specified) in a thermostatted bath at 25 ± 0.1°C. The stripping time was also 30 min (unless otherwise specified). Mixer–settler experiments were conducted in polyvinylidene fluoride Mixer–Settler Units Model 0.3 (MSU-0.3) manufactured by Metallextraktion AB in Sweden. The active mixer volume was about 0.06 l and the settler volume was about 0.28 l.

The concentrations of Zn and Cr(III) in the aqueous and organic phases were determined with a Shimadzu Model AA-680 atomic absorption spectrophotometer and the results were checked by mass balance. For the analysis of organic solutions, methylisobutylketone (MIBK, ≥98.5% pure, Shell Chemical) was used as the carrier solvent.

RESULTS AND DISCUSSION

Extraction with DEHPA, PC-88A, Cyanex 272, and Cyanex 302

The extraction results for Zn and Cr(III) as a function of equilibrium pH are shown in Fig. 1. The "S" shape curves conform to the general extraction behavior expected for acidic extractants.[40–42] The pH_{50} (the pH at which 50% of the metal is extracted) values of the two metals, where possible, are shown in Table 1, together with the acid dissociation constants, K_a, of the extractants.[37,41,43] For the three phosphorus acids, DEHPA, PC-88A, and Cyanex 272, the pH_{50}–pK_a relationship is in accord with the behavior generally observed, that is, extraction takes place at a lower pH for extractants with higher K_a.[40–42] The extraction of Zn by Cyanex 302 is at odds with this trend and tends to infer specific interaction between Zn and this thio-substituted extractant. Significant extraction of Cr(III) by Cyanex 302 could not be achieved due to precipitate formation (see below).

The difference between the pH_{50} values of two metals, ΔpH_{50}, is a measure of the degree of separation of the two metals.[40,42] The ΔpH_{50} values reported in Table 1 suggest that Cyanex 272 provides the best separation. In practice, however, the highest Cr(III) extraction by 0.05 M Cyanex 272 was

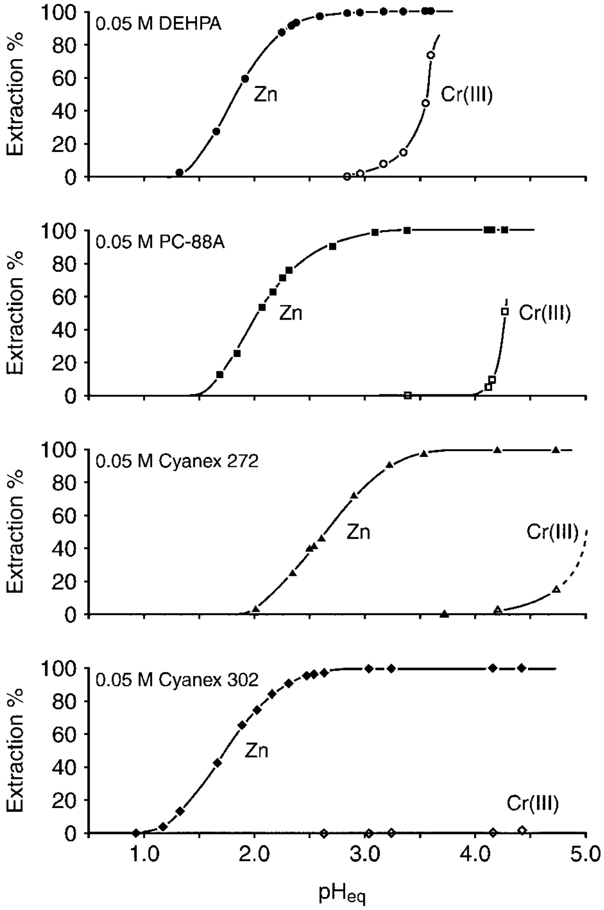

Figure 1. Extraction of Zn and Cr(III) as a function of pH$_{eq}$ (equilibrium pH) by the four extractants at 0.05 M. The aqueous solution was a simulated wastewater containing 227 mg l^{-1} Zn, 265 mg l^{-1} Cr(III), and 0.3 g l^{-1} Na_2SO_4.

only 15.2% (Fig. 1 and Table 1), further extraction by increasing pH being precluded by formation of chromium hydroxide precipitates. The precipitation problem also limited extraction by other extractants. The highest extraction achieved was with DEHPA (73.2% at 0.05 M), but even at 0.1 M DEHPA, the extraction was still incomplete (97.3%, Tables 1 and 2 and Fig. 2) and the ΔpH_{50} decreased to 1.59.

Table 1. Extraction of Zn and Cr(III) with different solvents.

	$pH_{50,Zn}$	$pH_{50,\ Cr(III)}$	ΔpH_{50} ($= pH_{50,Cr(III)} - pH_{50,Zn}$)	Highest Cr(III) extraction % achieved
0.05 M DEHPA ($pK_a = 3.8^a$)	1.86	3.59	1.73	73.2
0.05 M PC-88A ($pK_a = 4.9^a$)	2.08	4.28	2.24	50.6
0.05 M Cyanex 272 ($pK_a = 6^b$)	2.64	5.0 (extrapolated)	2.4	15.2
0.05 M Cyanex 302 ($pK_a = 5.6^c$)	1.75	—	—	1.7
0.10 M DEHPA ($pK_a = 3.8^a$)	1.60	3.19	1.59	97.3
0.10 M NH_4DEHPA	2.64	2.97	0.33	100

[a] Ref.[41].
[b] Ref.[37,41,43].
[c] Ref.[37].

Extraction with Ammoniated DEHPA, PC-88A, Cyanex 272, and Cyanex 302

To avoid the precipitation problem caused by a high initial pH that had to be used with nonammoniated solvents (see Table 2), the DEHPA, PC-88A, Cyanex 272, and Cyanex 302 solvents were pre-equilibrated with ammonia. The extraction reaction became an ion exchange reaction of the aqueous metal ion with the ammonium ion instead of with the proton of the extractant. Ammoniated Cyanex 272 and Cyanex 302 solvents showed a third phase, even with 10% isodecanol used as the modifier, and were not further tested. Ammoniated PC-88A and DEHPA, represented by NH_4PC-88A and NH_4DEHPA, respectively, were tested at 0.05 and 0.1 M. The best extraction was observed with 0.1 M NH_4DEHPA, where 100% extraction of Cr(III) could readily be achieved (Fig. 2b and Table 3). Table 3 also shows that the initial pH (pH_{init}) values were lower than those at equilibrium indicating that, in addition to the ammonium ion which exchanged with the Zn^{2+} and Cr(III) ions, some ammonia was released to the aqueous phase under the conditions of the extraction.

A comparison of Fig. 2a and Fig. 2b reveals that when the NH_4DEHPA solvent was used, the extraction curve of Zn shifted to significantly higher pH

Table 2. Extraction of Zn and Cr(III) with 0.1 M DEHPA as a function of pH_{init} (initial pH) and pH_{eq} (equilibrium pH).

pH_{init}	pH_{eq}	Zn extraction (%)	Cr(III) extraction (%)
0.84	0.95	0	0
1.02	1.10	5.4	0
1.31	1.36	20.9	0
1.61	1.62	53.7	0
1.88	1.81	74.6	0
2.20	2.00	87.5	0
2.65	2.27	95.0	0
3.11	2.37	97.1	0
3.94	2.51	98.2	0
4.80	2.91	99.7	11.7
5.18	3.11	99.8	38.5
5.90	3.40	99.9	82.5
6.68	3.67	100.0	93.7
8.10	3.87	100.0	97.3

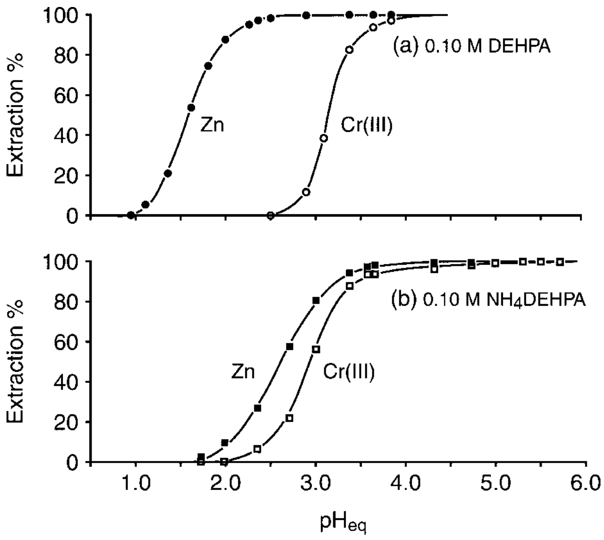

Figure 2. Extraction of Zn and Cr(III) as a function of pH_{eq} (equilibrium pH) by (a) 0.10 M DEHPA and (b) 0.10 M NH_4DEHPA. The aqueous solution was a simulated wastewater containing 227 mg l^{-1} Zn, 265 mg l^{-1} Cr(III), and 0.3 g l^{-1} Na_2SO_4.

Table 3. Extraction of Zn and Cr(III) with 0.1 M NH_4DEHPA as a function of pH_{init} (initial pH) and pH_{eq} (equilibrium pH).

pH_{init}	pH_{eq}	Zn extraction (%)	Cr(III) extraction (%)
1.04	1.72	2.4	0
1.10	1.98	9.4	0
1.15	2.35	26.7	6.5
1.20	2.71	57.6	22.0
1.26	3.00	80.7	56.3
1.29	3.38	94.3	87.9
1.31	3.58	97.6	93.4
1.34	3.66	98.3	93.8
1.36	4.32	99.9	96.3
1.42	4.74	100.0	98.2
1.47	5.00	100.0	99.3
1.58	5.31	100.0	100.0
1.67	5.50	100.0	100.0
1.80	5.72	100.0	100.0

values while the extraction curve of Cr(III) remained almost unchanged. This result can be explained by the well-documented existence of stable ammine complexes of Zn in the aqueous phase and the lack of such ammine complexes for Cr(III)[44]; The formation of the Zn–ammine complexes in the ammoniated solvent extraction system tends to retain the Zn ions in the aqueous phase and shift the extraction curve to higher pH values. The proximity of the two curves in Fig. 2b, with ΔpH_{50} for Zn and Cr(III) being 0.33 (see Table 1), suggests that selective extraction of the two metals is impractical.[40]

Stripping of Cr(III) from DEHPA Solutions

The results of stripping Cr(III) with H_2SO_4 and HCl (Fig. 3a) show that stripping levels off at about 90%. Other investigators reported that HCl at a concentration of 6 M stripped 95% Cr(III) from the Cyanex 272 impregnated resin[18] and that incomplete stripping from DEHPA or Cyanex 272 solutions occurred, leaving behind about 20% Cr(III), even when 8 M HCl was used.[32]

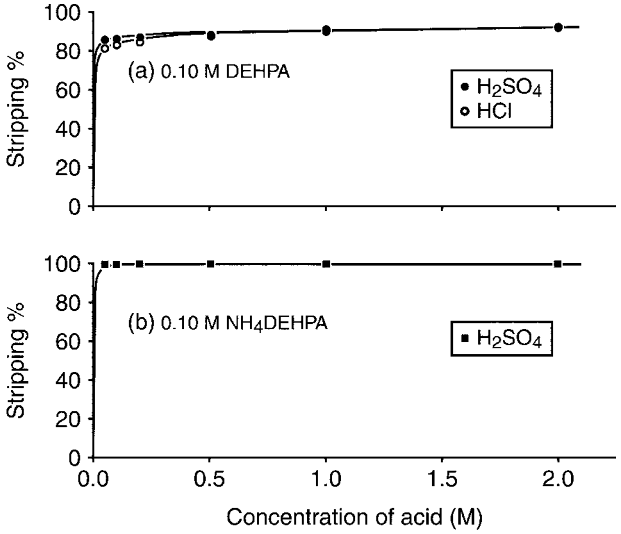

Figure 3. Stripping of Cr(III) from (a) 0.10 M DEHPA with H_2SO_4 and HCl and (b) 0.10 M NH_4DEHPA with H_2SO_4, at an aqueous/organic volume ratio of 1:1. The organic solutions were preloaded with Cr(III) by shaking an aqueous solution containing 265 $mg\,l^{-1}$ Cr(III) and 0.3 $g\,l^{-1}$ Na_2SO_4 with DEHPA at initial and equilibrium pH values of 7.2 and 4.1, respectively; and with NH_4DEHPA at 1.6 and 5.4, respectively.

Stripping of Zn from DEHPA Solutions

Zn could be readily stripped from DEHPA solutions. The stripping efficiencies with 0.20 and 0.50 M H_2SO_4 from a 0.1 M DEHPA solution loaded with 450 $mg\,l^{-1}$ Zn were 98.9 and 99.8%, respectively.

Stripping of Cr(III) from NH_4DEHPA

Figure 3b shows the results of stripping from a 0.1 M NH_4DEHPA solution preloaded with Cr(III). Cr(III) could readily be stripped; for example, 0.1 M H_2SO_4 could strip virtually all the Cr(III). This is in direct contrast to the results observed for nonammoniated DEHPA (Fig. 3a), where the stripping percentage levels off at about 90%.

Difference in the Cr(III) Stripping Behaviors from Ammoniated and Nonammoniated DEHPA Solutions

Cr(III) exists in aqueous solutions as the hydrated $Cr(H_2O)_6{}^{3+}$ cation,[45] and monomeric $Cr(OH)(H_2O)_5{}^{2+}$,[45] dimeric $Cr_2(OH)_2(H_2O)_8{}^{4+}$,[46] trimeric $Cr_3(OH)_4(H_2O)_9{}^{5+}$,[47] and tetrameric $Cr_4(OH)_6(H_2O)_{11}{}^{6+}$[48] hydroxo cations. The species are octahedrally coordinated and in the dimer, trimer, and tetramer, the OH^- is a bridge between two Cr(III). The relative concentrations of the species depend on the pH and the total concentration of Cr(III).[18,49,50] To extract a substantial amount of Cr(III) with DEHPA, a pH_{init} of >5 is required (see Table 2). At these pH values, Cr(III) exists as the hydrated $Cr(H_2O)_6{}^{3+}$ cation together with the monomeric, dimeric, and trimeric hydroxo cations, according to the "species concentration-pH" relationship for Cr(III).[18,49,50]

Cr(III) complexes are well known for their exceedingly slow kinetics in reactions involving ligand displacement.[50,51] On the other hand, extraction of Cr(III) proceeds very rapidly. Figure 4a shows that the extraction percentage plotted as a function of equilibration time, levels off within a minute, in line with other workers' results.[33,52] This characteristic, together with the exceedingly slow ligand displacement kinetics, suggests that the Cr(III) cations in the aqueous phase are extracted into the organic phase without change in the first coordination sphere. In other words, outer-sphere complexes (ion-pairs) of the types, $Cr(H_2O)_6{}^{3+}\cdot(DEHPA^-)_3$, $Cr(OH)(H_2O)_5{}^{2+}\cdot(DEHPA^-)_2$, $Cr_2(OH)_2(H_2O)_8{}^{4+}\cdot(DEHPA^-)_4$, and $Cr_3(OH)_4(H_2O)_9{}^{5+}\cdot(DEHPA^-)_5$, are formed in the extraction, where $DEPHA^-$ represents deprotonated DEHPA. This is in accord with published observations[53,54] that Cr(III) retaining an intact hydration sphere was rapidly extracted from perchlorate and trichloroacetate solutions with trioctylphosphine oxide (TOPO). On the contrary, extraction involving displacement of hydration water to form the extracted 2-thenoyltrifluoroacetonato Cr(III) complex was slow.[55]

In the simplest case, extraction of a metal ion by an acidic extractant can be represented by

$$M^{n+}_{(aq)} + n\,HA_{(org)} \rightleftharpoons MA_{n(org)} + nH^{+}_{(aq)}$$

where M^{n+} represents a metal ion of valance n and HA represents a molecule of an acidic extractant.[40] In stripping, an acid in aqueous phase is used to shift the equilibrium of the above equation to the left to drive the metal into the aqueous phase. The situation is more complicated for the Cr(III)–DEHPA system, because in addition to the simple hydrated Cr^{3+} cation,

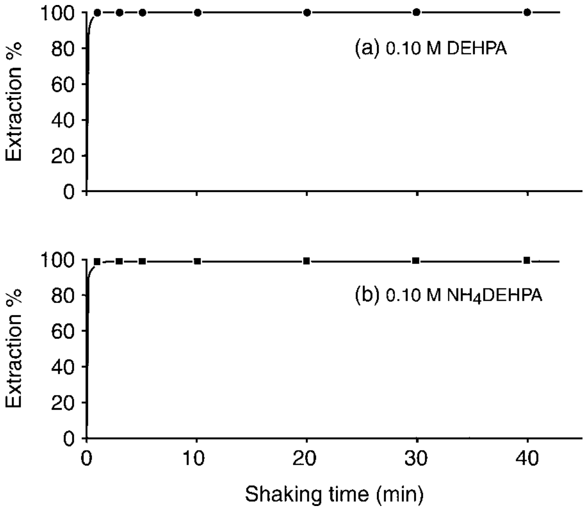

Figure 4. Extraction of Cr(III) as a function of shaking time by (a) 0.10 M DEHPA and (b) 0.10 M NH_4DEHPA. The initial and equilibrium pH values for extraction with DEHPA were 6.9 and 3.9, respectively; and with NH_4DEHPA were 1.6 and 5.4, respectively.

the monomeric, dimeric, and trimeric cation species were also extracted, as per earlier discussion.

According to the “species concentration–pH” relationship,[18,49,50] under a strongly acidic condition such as the one used in stripping (pH < 2), the predominant species in the aqueous phase is almost 100% $Cr(H_2O)_6{}^{3+}$, with less than 1% $Cr(OH)(H_2O)_5{}^{2+}$. The dimeric and trimeric cations etc. are virtually nonexistent as they are the thermodynamically unfavored species in the aqueous phase.

For a species in the organic phase to be favorably stripped into the aqueous phase, the species must be compatible with the aqueous environment or be able to be converted into a species compatible with the aqueous environment in the time scale of stripping. Consequently, the $Cr(H_2O)_6{}^{3+}$ cation is strippable. The $Cr(OH)(H_2O)_5{}^{2+}$ cation, which combines rapidly with a proton to form $Cr(H_2O)_6{}^{3+}$,[50] is also strippable. On the other hand, the dimeric and trimeric cations react with the stripping acid to form $Cr(H_2O)_6{}^{3+}$ very slowly, because the reactions involve ligand displacement; and they are virtually nonstrippable and are responsible for the incomplete stripping observed in Fig. 3a.

Similar to DEHPA, the extraction with NH_4DEHPA also proceeded very rapidly (Fig. 4b). In contrast to the DEHPA extraction, the pH_{init} for 100% extraction of Cr(III) was only about 1.6 (see Table 3). At this pH, Cr(III) exists exclusively as $Cr(H_2O)_6^{3+}$[18,49,50] and it is extracted without change in its first coordination sphere due to the rapid extraction.

We further studied the stoichiometry of the extracted species by the saturation loading method[40,56] and the results are shown in Fig. 5. The saturation concentrations of Cr(III) in the organic phase containing 0.051 M and 0.102 M NH_4DEHPA were 1.70×10^{-2} M and 3.40×10^{-2} M, respectively, both corresponding to a molar ratio of NH_4DEHPA to Cr(III) of 3.00, consistent with $Cr(H_2O)_6^{3+} \cdot (DEHPA^-)_3$ being the only major extracted species. We also obtained the UV–visible absorption spectrum of the organic solution obtained by extracting Cr(III) into 0.1 M NH_4DEHPA from an aqueous solution of Cr(III) at pH_{init} 1.6, where $Cr(H_2O)_6^{3+}$ was the predominating species.[18,49,50] The similarity between this spectrum and the spectrum of the aqueous solution (Fig. 6) suggests that $Cr(H_2O)_6^{3+}$ is the only major species in the organic phase. Since $Cr(H_2O)_6^{3+}$ is strippable, 100% stripping can be expected, which was indeed observed (Fig. 3a).

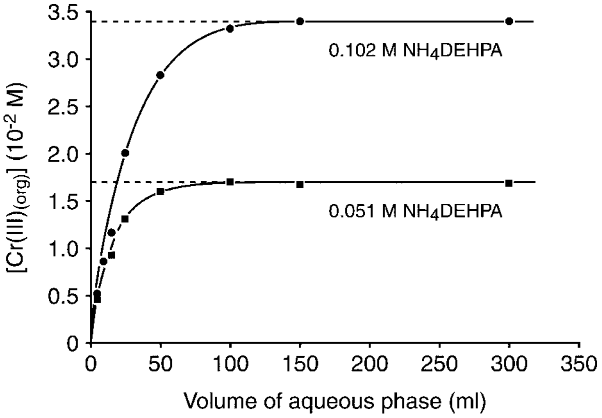

Figure 5. Saturation loading of the organic phase by Cr(III). The aqueous solution contained 265 mg l^{-1} Cr(III) and 0.3 g l^{-1} Na_2SO_4. The volume of the organic phase was fixed at 5 mL while different volumes of the aqueous solution were used. The equilibrium pH was 5.

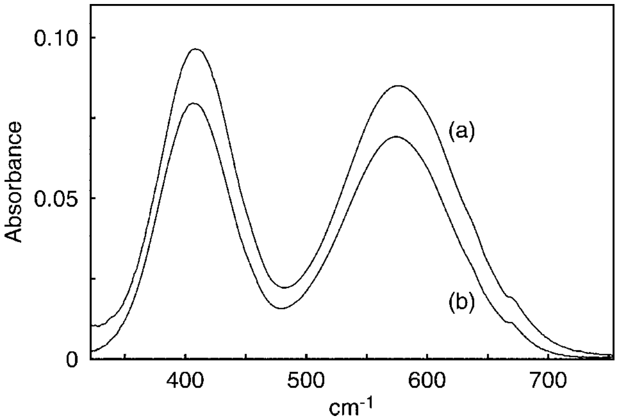

Figure 6. Spectra of (a) a 0.10 M NH_4DEHPA solution loaded with 264.8 mg l^{-1} Cr(III) and (b) an aqueous solution containing 265.0 mg l^{-1} Cr(III) and 0.3 g l^{-1} Na_2SO_4 at pH 1.6. Solution (a) was obtained by shaking a 0.10 M NH_4DEHPA solvent with solution (b).

Stripping of Zn–Cr(III) from NH_4DEHPA

The proximity of the two extraction curves of Zn and Cr(III) in Fig. 2a suggests that the two metals cannot be separately stripped,[40] which is confirmed by the results in Table 4. In view of this and the lack of complete stripping of Cr(III) from loaded DEHPA solutions (see Fig. 3a), a flow sheet that can individually recover Zn and Cr(III) requires two separate extractions. In the first, a DEHPA solvent is used to extract Zn. In the second, a NH_4DEHPA solvent is used to extract Cr(III). This forms the basis of our flow sheet development strategy.

Flow Sheet for Individual Recovery of Zn and Cr(III), and Contactor Runs

Standard procedures were followed to construct the appropriate McCabe–Thiele diagrams.[40] The McCabe–Thiele diagram for extraction of Zn by DEHPA is shown in Fig. 7a, which indicates that two or three stages are required for Zn extraction, while for Zn stripping, two stages are required (Fig. 7b). Extraction of Cr(III) by NH_4DEHPA and stripping of Cr(III) from

Table 4. Stripping of Zn and Cr(III) with mineral acids from 0.1 M NH_4DEHPA solutions preloaded with 227 mg l^{-1} Zn and 265 mg l^{-1} Cr(III).

	% stripped with H_2SO_4		% stripped with HCl		% stripped with HNO_3	
Concentration of acid (M)	Zn	Cr(III)	Zn	Cr(III)	Zn	Cr(III)
0.02	93.8	97.2	29.1	31.1	—	—
0.05	99.6	98.2	74.8	88.9	—	—
0.10	99.8	99.2	99.7	97.6	99.7	97.6

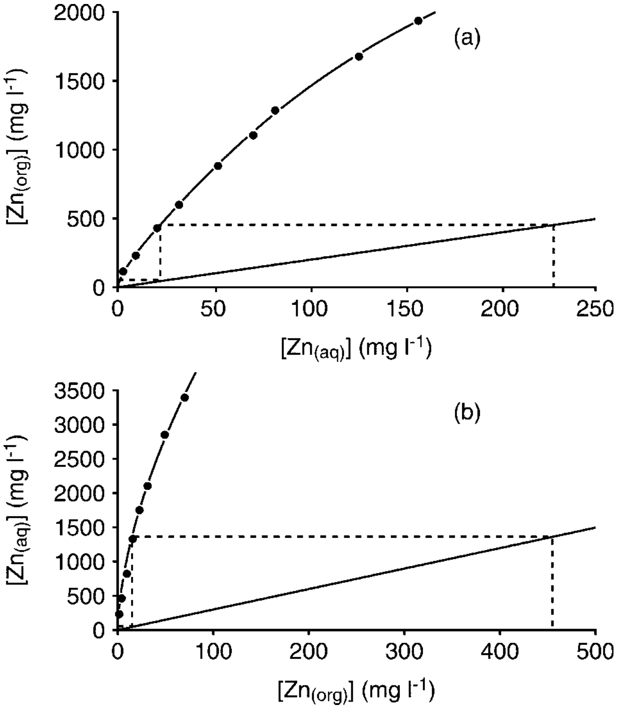

Figure 7. (a) McCabe–Thiele diagram for extraction of Zn with 0.1 M DEHPA. The distribution data were obtained at different phase ratios and at an equilibrium pH of 2.3. The operating line represents an aqueous/organic flow ratio of 2:1. (b) McCabe–Thiele diagram for stripping of Zn. 0.2 M H_2SO_4 was used for stripping at different phase ratios. The organic solution containing about 450 mg l^{-1} Zn was prepared by shaking the solvent with a simulated wastewater at an aqueous/organic phase ratio of 2:1 and at an equilibrium pH of 2.3. The operating line represents an aqueous/organic flow ratio of 1:3.

NH_4DEHPA are effective and requires only one stage for the respective operation according to the McCabe–Thiele diagrams (not shown).

Based on the previous discussion, we considered two flow sheets (flow sheets A and B), which are almost identical, except that flow sheet A has two stages for Zn extraction (Fig. 8) while flow sheet B has three stages. The pH of the Cr(III) wastewater reservoir was maintained at 1.8 with H_2SO_4. The flow sheets were tested with mixer–settler units for a total of 780 min for flow sheet A (Run No. 1) and 720 min for flow sheet B (Run No. 2). Both runs were successful without operational problems and steady state was achieved within 120 min. A comparison of the salient features of the two runs in terms of steady-state concentrations is shown in Table 5.

In both runs, the treatment rendered both Zn and Cr(III) to very low concentrations, fulfilling stringent environmental discharge requirements.[20] The recovered Zn and Cr(III) products were in good purity. The incorporation

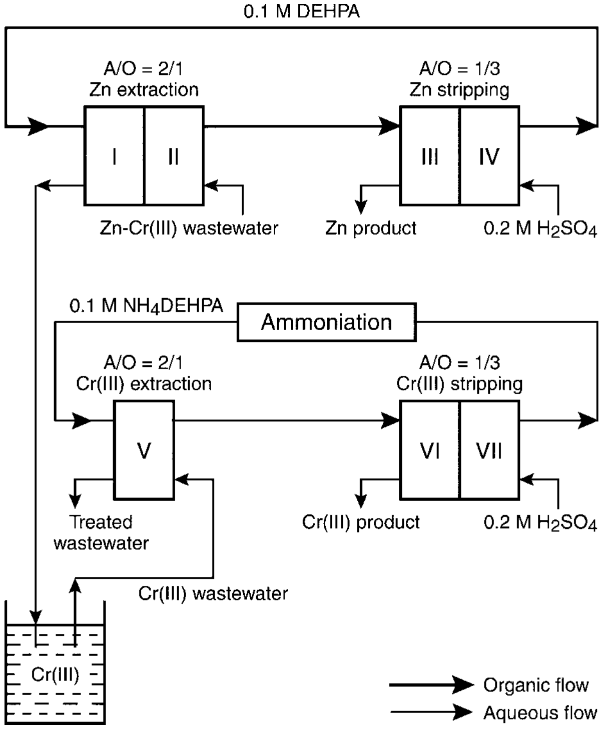

Figure 8. Flow sheet A for separative recovery of Zn and Cr(III).

Table 5. A comparison of the results of the two mixer–settler runs for treatment of a simulated wastewater containing 227 mg l^{-1} Zn, 265 mg l^{-1} Cr(III), and 0.3 g l^{-1} Na_2SO_4.

	Run no. 1	Run no. 2
In treated wastewater:		
Conc. of Zn (mg l^{-1})	0.037 ± 0.009	0.046 ± 0.008
Conc. of Cr(III) (mg l^{-1})	0.62 ± 0.06	0.52 ± 0.03
In Zn product:		
Conc. of Zn (mg l^{-1})	1223 ± 7	1231 ± 5
Conc. of Cr(III) (mg l^{-1})	1.99 ± 0.09	2.24 ± 0.08
In Cr(III) product:		
Conc. of Cr(III) (mg l^{-1})	1296 ± 9	1302 ± 8
Conc. of Zn (mg l^{-1})	5.18 ± 0.18	2.82 ± 0.12

Conc. = Concentration.

of one more extraction stage for Zn in Run No. 2 reduced the Zn concentration in the Cr(III) product to 2.82 mg l^{-1} from 5.18 mg l^{-1}.

CONCLUSION

DEHPA provides satisfactory selective extraction of Zn from Cr(III). For Cr(III), NH_4DEHPA is recommended for its much better performance in extraction without the precipitation problem and also in complete stripping with dilute acids. Complete stripping allowed recycling of the solvent without progressively increasing concentration of residual Cr(III). This property is due to $Cr(H_2O)_6^{3+}\cdot(DEHPA^-)_3$ being the only important species in the organic phase.

Contactor runs demonstrated the feasibility of the treatment process, which recovered Zn and Cr(III) with good separation from each other. The treated wastewater contained Zn and Cr(III) at levels meeting stringent environmental standards.

ACKNOWLEDGMENTS

This work was supported by a grant from the Research Grants Council of Hong Kong (Project No. 9040539), which is appreciated. Thanks are due to Cytec Canada Inc. for supplies of Cyanex 272 and Cyanex 302.

REFERENCES

1. Wynn, P.C.; Bishop, C.V. Replacing hexavalent chromium. Plat. Surf. Finish **2001**, *88* (2), 12–14.
2. Shahin, G.E. Alloys are promising as chromium or cadmium substitutes. Plat. Surf. Finish **1998**, *85* (8), 8–14.
3. Klingenberg, M.L.; Pavlik, M.A.B.; Brooman, E.W. Alloy deposition of alternatives to chromium and cadmium. *Proc. AESF Surf/Finish Annu. Int. Tech. Conf.* 1999, 771–779.
4. El-Sharif, M.R. Replacing hexavalent chromium in electroplating. Trans. Inst. Metal Finish **1997**, *75* (6), B143–B146.
5. Murphy, M. Focus on chromium. Metal Finish **1995**, *93* (8), 34–39.
6. El-Sharif, G.E.; Su, Y.J.; Watson, A.; Chisholm, C.U. Factors influencing the codeposition of zinc–chromium alloys. *Proc. AESF Surf/Finish Annu. Int. Tech. Conf.* 1993, 1083–1089.
7. Su, Y.L.; Watson, A.; El-Sharif, M.R.; Chisholm, C.U. The electrodeposition and corrosion properties of zinc–chromium alloys. Surf. Eng. **1993**, *1*, 79–92.
8. Watson, A.; Su, Y.J.; El-Sharif, M.R.; Chisholm, C.U. The electrodeposition of zinc–chromium alloys and the formation of conversion coatings without use of chromate solutions. Trans. Inst. Metal Finish **1993**, *71*, 15–20.
9. Ohgai, T.; Ki, J.S.; Akiyama, T.; Fukushima, H. Electrodeposition process of Zn–Cr alloys from sulfate baths. *Value-Addition Metallurgy*; The Minerals, Metals and Materials Society: Warrendale, 1998; 225–234.
10. Shouson, K.; Suzuki, S.; Kousaka, A.; Kanamaru, T. Manufacture of Steel Sheet Electroplated with Chromium–Zinc Alloy. Japanese Patent 09316686, 1997.
11. Yamazaki, F.; Saito, K.; Tejima, S. Manufacture of Corrosion-Resistant Steel Sheets by Electroplating with Zinc–Chromium Alloy. Japanese Patent 07300694, 1995.
12. Nakamaru, H.; Katagiri, T.; Hasegawa, K.; Kurokawa, S.; Mochizuki, K. Zinc–Chromium Alloy Multiplayer Electroplated Rustproofing Steel Sheet with Excellent Corrosion Resistance. Japanese Patent 06235087, 1994.
13. Hasegawa, K.; Nakamaru, H.; Mochizuki, K.; Katagiri, T.; Morito, N.; Kurokawa, S. Method of Producing Zinc–Chromium Alloy Plated Steel Sheet with Excellent Plating Adhesiveness. US Patent 05,273,643, 1993.

14. Ando, S.; Abe, M.; Sagyama, M. Manufacture of Chromium–Zinc Base Alloy-Electroplated Steel Sheets Having Excellent Corrosion Resistance. Japanese Patent 05345996, 1993.
15. Berezin, N.B.; Gudin, N.N.; Filippova, A.G.; Matulenis, E.A.; Borisov, Yu.V. Role of complex formation during the cathodic deposition of zinc–chromium electroplates from acidic glycine-containing bath. Zashch. Met. **1992**, *28*, 961–966.
16. Groshart, E. The hazards of chromium compounds. Metal Finish **1988**, *86* (9), 63–65.
17. Schugerl, K.; Segelken, G.; Gudorf, M. Extractive recovery of chromium(III) from effluents of fur finishing industry. *Value Adding Through Solvent Extraction*; University of Melbourne: Parkville, Australia, 1996; Vol. 2, 1531–1536.
18. Mendoza, N.R.; Medina, S.T.I.; Vera, A.; Rodriguez, A.M.A. Study of the sorption of Cr(III) with XAD-2 resin impregnated with di-(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272). Solvent Extr. Ion Exch. **2000**, *18*, 319–343.
19. *Effluent Limitations Guidelines, Pretreatment Standards, and New Source Performance Standards for the Centralized Waste Treatment Point Source Category. Final Rule*, Federal Register, Vol. 65, No. 247; US Environment Protection Agency, 2000; 81242–81313.
20. *Technical Memorandum—Standards for Effluents Discharged into Drainage and Sewerage Systems, Inland and Coastal Waters*; Hong Kong Government: Hong Kong, 1994; 1–14.
21. Patterson, J.W. Metals separation and recovery. *Metals Speciation, Separation and Recovery*; Lewis Publishers: Chelsea MI, 1987; 63–93.
22. Grosse, D.W. Review of treatment for hazardous waste streams. In *Encyclopedia of Environmental Control Technology*; Gulf Publishing: Houston, Texas, 1990; Vol. 4, 541–611.
23. Sauer, N.N.; Smith, B.F. *Metal-ion Recycle Technology for Metal Electroplating Waste Waters*, Los Alamos National Laboratory Report, LA 12532 MS; Los Alamos National Laboratory: Los Alamos, New Mexico, 1993; 1–14
24. Brooks, C.S. Waste metal recovery case histories. Proc. Ind. Waste Conf. **1986**, 647–651.
25. Cerna, M. Use of solvent extraction for the removal of heavy metals from liquid wastes. Environ. Mon. Assess. **1995**, *34*, 151–162.
26. Walton, P.H. Methods of metal capture from effluent. *Chemistry of Waste Minimization*; Blackie Academic and Professional: London, 1995; 473–474.

27. Deorkar, N.V.; Tavlarides, L.L. Zinc, cadmium, and lead separation from aqueous streams using solid-phase extractants. Ind. Eng. Chem. Res. **1997**, *36*, 399–406.
28. Sze, Y.K.P.; Xue, L.Z.; Lee, M.Y. Treatment of alloy-electroplating wastewater by an automated solvent extraction technique. Environ. Technol. **2001**, *22*, 979–991.
29. Wassink, B.; Dreisinger, D.; Howard, J. Solvent extraction separation of zinc and cadmium from nickel and cobalt using aliquat 336, a strong base anion exchanger, in the chloride and thiocyanate forms. Hydrometallurgy **2000**, *57*, 235–252.
30. Sainz-Daiz, C.I.; Klocker, H.; Marr, R.; Bart, H.J. New approach in the modeling of the extraction equilibrium of zinc with *bis*-(2-ethylhexyl) phosphoric acid. Hydrometallurgy **1996**, *42*, 1–11.
31. Amer, S.; Figueiredo, J.M.; Luis, A. The recovery of zinc from the leach liquors of the CENIM-LNETI process by solvent extraction with di(-2-ethylhexyl) phosphoric acid. Hydrometallurgy **1995**, *37*, 323–337.
32. Pandey, B.D.; Cote, G.; Bauer, D. Extraction of chromium(III) from spent tanning baths. Hydrometallurgy **1996**, *40*, 343–357.
33. de Juan, D.; Meseguer, V.; Lozano, L.J. Chromium extraction with organic solvents. Part I, extraction with DEHPA. Revista de Metalurgia **1998**, *34*, 253–260.
34. Khwaja, A.R.; Singh, R.; Tandon, S.N. Mono(2-ethylhexyl) phosphoric acid as an extractant for Cr(III) and its application to industrial waste. Sep. Sci. Technol. **2000**, *35*, 447–455.
35. Reddy, B.R.; Parija, C.; Sarma, P.V.R.B. Processing of solutions containing nickel and ammonium sulphate through solvent extraction using PC-88A. Hydrometallurgy **1999**, *53*, 11–17.
36. Zhou, N.; Wu, J.; Sarathy, P.K.; Liu, F.; Neuman, R.D. Comparison of aggregates formed by acidic organophosphorus extractants and metals (Ni–Co) in solvent extraction. *Solvent Extraction 1990*; Elsevier: New York, 1992; 165–170.
37. Rickelton, W.A. Novel uses for thiophsophinic acids in solvent extraction. J. Miner. Meter. Mat. Soc. **1992**, (5), 52–54.
38. Eilbeck, W.J.; Mattock, G. *Chemical Processes in Waste Water Treatment*; Ellis Horwood: Chichester, England, 1987; 81.
39. Cushnie, G.C., Jr. *Electroplating Wastewater Pollution Control Technology*; Noyes Publications: Park Ridge, NJ, 1985; 11.
40. Ritcey, G.M.; Ashbrook, A.W. *Solvent Extraction Principles and Applications to Process Metallurgy*, Parts I and II; Elsevier: Amsterdam, 1984; 37.

41. Yuen, C.; Xu, Q.; Yuan, S. Quantitative structure-reactivity study of mono-basic organophosphorus acids in cobalt and nickel extraction. Solvent Extr. Ion Exch. **1988**, *6*, 393–416.
42. Yao, B.; Nagaosa, Y.; Satake, Y.M.; Nomura, A.; Horita, K. Solvent extraction of metal ions and separation of nickel(II) from other metal ions by organophosphorus acids. Solvent Extr. Ion Exch. **1996**, *14*, 849–870.
43. Danesi, P.R.; Reichley-Yinger, L.; Mason, G.; Kaplan, L.; Horwitz, E.P.; Diamond, H. Selectivity-structure trends in the extraction of Co(II) and Ni(II) by dialkyl phosphoric, alkyl alkylphosphonic, and dialkylphosphinic acids. Solvent Extr. Ion Exch. **1985**, *3*, 435–452.
44. Sillen, L.G. *Stability Constants of Metal-Ion Complexes.* Special Publication No. 17; Chemical Society: London, 1964; 154–155.
45. Emerson, K.; Graven, W.M. Equilibria in acidic solutions of chromium(III) perchlorate. J. Inorg. Nucl. Chem. **1959**, 309–313.
46. Kolaczkowski, R.W.; Plane, R.A. The characterization of $[Cr(H_2O)_4OH]_2{}^{4+}$, and its formation by oxygen oxidation of chromous solutions. Inorg. Chem. **1964**, *3*, 322–324.
47. Finholt, J.E.; Thompson, M.E.; Connick, R.E. Hydrolysis polymerization of chromium(III) species. Inorg. Chem. **1981**, *20*, 4151–4155.
48. Stunzi, H.; Werner, M. Early stages of hydrolysis of chromium(III) in aqueous solutions. 1. characterization of a tetramer species. Inorg. Chem. **1983**, *22*, 2145–2150.
49. Stunzi, H.; Spiccia, L.; Rotzinger, F.P.; Marty, W. Earlier stages of the hydrolysis of chromium(III) in aqueous solution. 4. stability constants of the hydrolytic dimer, trimer, and tetramer at 25°C and $I = 1.0\,M$. Inorg. Chem. **1989**, *28*, 66–71.
50. Baes, C.F.; Mesmer, R.E. *The Hydrolysis of Cation*; Krieger Publishing: Malabar, Florida, 1988; 211–221.
51. Cotton, F.A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th Ed.; John Wiley: New York, 1988; 686–687.
52. Islam, F.; Biswas, R.K. The solvent extraction of chromium(III) with *bis*-(2-ethyl hexyl) phosphoric acid in benzene and other solvents. J. Inorg. Nucl. Chem. **1979**, *41*, 229–233.
53. Yamada, M.; Kusakabe, S.; Prekopova, J.; Sekine, T. Solvent extraction of seven trivalent metal ions in aqueous perchlorate solutions with trioctylphosphine oxide in hexane and rapid extraction of chromium(III). Anal. Sci. **1996**, *12*, 405–410.
54. Imura, H.; Kiba, T.; Honjo, T. The extraction of the chromium(III) ion from trichlroacetate solutions to inert solvents containing trioctylphosphine oxide. Bull. Chem. Soc. Jpn. **1979**, *52*, 2563–2568.

55. Yamada, M.; Honda, N.; Takasugi, R.; Sekine, T. Rate of solvent extraction of chromium(III) in aqueous solutions with 2-thenoyltrifluoroacetone into chloroform. Solvent Extr. Res. Dev. Jpn **1999**, *6*, 41–50.
56. Aguilar, M. Graphical treatment of liquid–liquid equilibrium data. *Developments in Solvent Extraction*; Ellis Horwood: Chichester, England, 1988; 87–118.

Received December 2001
Accepted December 2001