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Chromium(VI) Complexation with Triisooctylamine in Organic Solvents

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Liquid–liquid extraction of chromium(VI) from chromic acid solutions with triisooctylamine (tris(6-methylheptyl)amine, abbrev. to TIOA) dissolving in various organic solutions has been studied. The reaction between chromium(VI) and TIOA in *o*-xylene has been discussed in detail. It has been found that dichromate ion and hydrogen chromate ion coexist in the system, based on the extraction data and the IR and UV-visible spectra of the TIOA-chromium salt. The chromium extraction equilibria can be expressed as:

$$\overline{\text{TIOA}}+\text{H}^+ + \text{HCrO}_4^- \rightleftarrows \overline{(\text{TIOAH})\text{HCrO}_4}$$

$$2\overline{\text{TIOA}}+2\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightleftarrows \overline{(\text{TIOAH})_2\text{Cr}_2\text{O}_7}$$

The extraction constants are obtained.

It is well-known that chromate and dichromate ions can be extracted using TBP or an amine as an extractant. Many workers used tertiary amines to extract chromium(VI) from various acid solutions.[1–16] The extraction mechanism proposed by them is confusing. for example, Fedorov et al.[11] reported that trioctylamine extracts chromium(VI) as CrO_4^{2-} from H_2SO_4 solutions. Depula[12] reported that trioctylamine extracts chromium(VI) as $\text{Cr}_2\text{O}_7^{2-}$ from H_3PO_4 solutions and it probably involves HCr_2O_7^- from HClO_4 and concentrated HNO_3 solutions in addition to $\text{Cr}_2\text{O}_7^{2-}$. Recently Takahashi et al.[16] used 3-(4-pyridyl)-1,5-dipheylpentane (a tertiary amine) to extract chromium(VI) from sulfuric acid solutions. They reported that HCrO_4^- was extracted into organic phase. Henkel corporation[9] indicated that tertiary amines may extract chromium(VI) by solvating:

$$2\overline{\text{R}_3\text{N}}+2\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightleftarrows \overline{(\text{R}_3\text{NH})_2\text{Cr}_2\text{O}_7},$$

or by ion exchange:

$$\overline{(\text{R}_3\text{NH})_2\text{X}}+2\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightleftarrows \overline{(\text{R}_3\text{NH})_2\text{Cr}_2\text{O}_7},$$

$\text{X}=\text{SO}_4^{2-}$ or 2Cl^-.

In order to realize the behavior of chromium(VI) extracted by amines from various acid solutions, it is necessary to extract chromium(VI) from chromic acid at first. In the study, it was decided to identify amine–chromium(VI) species and determine extraction constants for triisooctylamine–chromic acid extraction system.

Experimental

Reagents: 1.92×10^{-2} M ($\text{M}=\text{mol dm}^{-3}$) stock solutions (1000 ppm chromium) were prepared by dissolving 1.923 g of chromium trioxide (99.0%) in distilled deionized water and diluting to volume in a 1 dm^3 standard flask. Appropriate amouuts of TIOA (98%) were diluted with organic solvents (E.P. grade) to obtain the desired TIOA concentrations.

Procedure: Both aguecus and organic phases were vigorously mixed in a 50 cm^3 dark centrifugal tube more than six minutes at 24±1 °C. After centrifuging, the tube was settled in a water bath at 25±0.1 °C for more than three hours. The pH value of the aqueous phase was measured by a PHM 85 precision pH meter (Radiometer & Copehagen Co.). Chromium concentrations in the aqueous phase were determined using an IL-551 type atomic absorption spectrophotometeter (Instrumentation Laboratory Inc.). The concentration of chromium in the organic phase was calculated from the difference in chromium content in the aqueous phase before and after extraction multiplied by the phase A/O ratio (volume ratio of aqueous and organic phases). The free TIOA concentration was calculated by the subtraction of chromium concentration in the organic phase from initial TIOA concentration used.

Results and Discussion

Extraction Equilibrium of Chromium(VI): Figure 1 shows the log–log plots of $[\overline{\text{Cr}}]$ vs. $[\overline{\text{TIOA}}](\text{H}^+)(\text{HCrO}_4^-)$ in *o*-xylene. The initial chromium concentration is varied from 2.5×10^{-4} M to 4.0×10^{-2} M. The

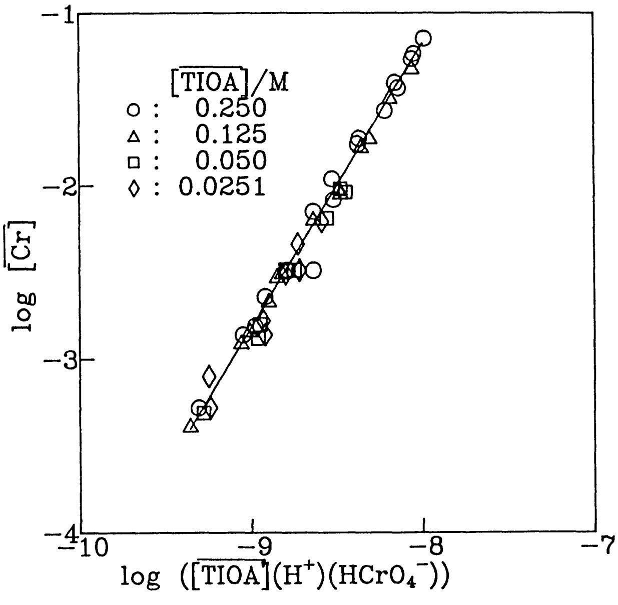

Fig. 1. Plots of $\log[\overline{\text{Cr}}]$ vs. $\log([\overline{\text{TIOA}}](\text{H}^+)(\text{HCrO}_4^-))$ for TIOA in *o*-xylene.

bar overhead in the equations denotes organic phase. It is seen from Fig. 1 that a straight line of the slope 1.6 was obtained. The result indicates that the extraction mechanism can not be described just using a single species either $HCrO_4^-$ or $Cr_2O_7^{2-}$. It is plausible that both $HCrO_4^-$ and $Cr_2O_7^{2-}$ were extracted by TIOA into the organic phase. An extraction model for the equilibria with the two components is proposed. The model involves dissociation and association of Cr(VI) species (Eqs. 1—5) in the aqueous phase, and chromium(VI) extraction equilibria (Eqs. 6 and 7) by TIOA. The values of the dissociation constants of chromic acid in Eqs. 1—5 were obtained by Neuss and Rieman,22) Davis and Prue,21) Takahashi et al.,16) Hala et al.,8) and Deptula.2)

$$H_2Cr_2O_7 \rightleftarrows H^+ + HCr_2O_7^-, \qquad (1)$$

$$K_1 = (H^+)(HCr_2O_7^-)/(H_2Cr_2O_7), \qquad K_1 = 1 \times 10^6$$

$$HCr_2O_7^- \rightleftarrows H^+ + Cr_2O_7^{2-}, \qquad (2)$$

$$K_2 = (H^+)(Cr_2O_7^{2-})/(HCr_2O_7^{2-}), \qquad K_2 = 0.85$$

$$H_2CrO_4^- \rightleftarrows H^+ + HCrO_4^-, \qquad (3)$$

$$K_3 = (H^+)(HCrO_4^-)/(H_2CrO_4), \qquad K_3 = 1.21$$

$$HCrO_4^- \rightleftarrows H^+ + CrO_4^{2-}, \qquad (4)$$

$$K_4 = (H^+)(CrO_4^{2-})/(HCrO_4^-), \qquad K_4 = 3.2 \times 10^{-7}$$

$$2HCrO_4^- \rightleftarrows Cr_2O_7^{2-} + H_2O, \qquad (5)$$

$$K_5 = (Cr_2O_7^{2-})/(HCrO_4^-)^2, \qquad K_5 = 98$$

$$2\overline{TIOA} + 2H^+ + Cr_2O_7^{2-} \rightleftarrows \overline{(TIOAH)_2Cr_2O_7}, \qquad (6)$$

$$K_6 = [\overline{(TIOAH)_2Cr_2O_7}]/[\overline{TIOA}]^2(H^+)^2(Cr_2O_7^{2-}),$$

$$\overline{TIOA} + H^+ + HCrO_4^- \rightleftarrows \overline{(TIOAH)HCrO_4}, \qquad (7)$$

$$K_7 = [\overline{(TIOAH)HCrO_4}]/[\overline{TIOA}](H^+)(HCrO_4^-).$$

The symbols [ ] and ( ) represent the molar concentration and molar activity, respectively. The activity coefficient in the organic phase is assumed to be unity for convenience. Combining the constant of Eq. 5 with that of Eq. 6 gives:

$$K_8 = [\overline{(TIOAH)_2Cr_2O_7}]/[\overline{TIOA}]^2(H^+)^2(HCrO_4^-)^2. \qquad (8)$$

The total concentration of chromium in the organic phase can be expressed as:

$$[\overline{Cr}] = [\overline{(TIOAH)HCrO_4}] + 2[\overline{(TIOAH)_2Cr_2O_7}]. \qquad (9)$$

Substituting Eqs. 7 and 8 into Eq. 9 and rearranging gives:

$$[\overline{Cr}]/\{[\overline{TIOA}](H^+)(HCrO_4^-)\} = K_7 + 2K_8[\overline{TIOA}](H^+)(HCrO_4^-). \qquad (10)$$

Equation 10 indicates that the plot of $[\overline{Cr}]/\{[\overline{TIOA}](H^+)(HCrO_4^-)\}$ vs. $[\overline{TIOA}](H^+)(HCrO_4^-)$ will give a linear line. The slope of it is $2K_8$ and the intercept is K_7.

Figure 2 shows the plots of $[\overline{Cr}]/\{[\overline{TIOA}](H^+)(HCrO_4^-)\}$ vs. $\{[\overline{TIOA}](H^+)(HCrO_4^-)\}$. The activity coefficient of chromium in the aqueous phase was calculated by Guntelberg expression.19) The total activity of chromium in aqueous phase ($(Cr)_{aq,total}$) is as follows:

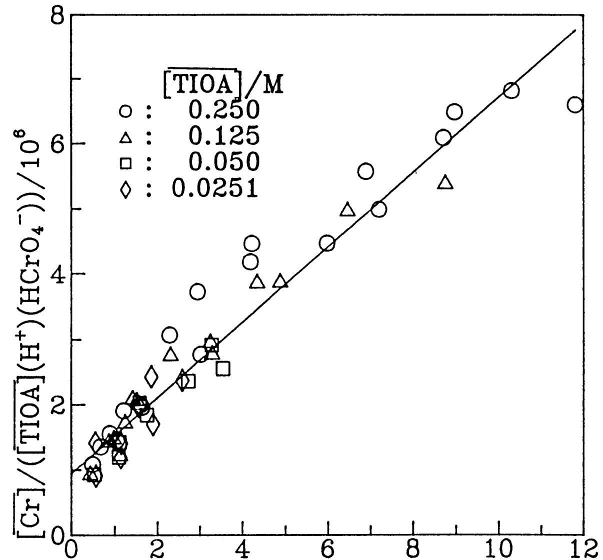

Fig. 2. Plots of $[\overline{Cr}]/([\overline{TIOA}](H^+)(HCrO_4^-))$ vs. $[\overline{TIOA}](H^+)(HCrO_4^-)$ for TIOA in *o*-xylene.

$$(Cr)_{aq,total} = 2(H_2Cr_2O_7) + 2(HCr_2O_7^-) + 2(Cr_2O_7^{2-}) + (H_2CrO_4) + (HCrO_4^-) + (CrO_4^{2-}). \qquad (11)$$

Then, from Eqs. 1—5, $(Cr)_{aq,total}$ can be expressed in terms of $(HCrO_4^-)$ as well as the appropriate equilibrium constants involved.

$$\begin{aligned}(Cr)_{aq,total} &= 2\{(H^+)^2/K_1K_2 + (H^+)/K_2 + 1\}(Cr_2O_7^{2-}) \\ &\quad + \{(H^+)/K_3 + 1 + K_4/(H^+)\}(HCrO_4^-) \\ &= \{2K_5/K_1K_2\}\{(H^+)^2 + K_1(H^+) + K_1K_2\}(HCrO_4^-)^2 \\ &\quad + \{1/K_3(H^+)\}\{(H^+)^2 + K_3(H^+) + K_3K_4\}(HCrO_4^-). \qquad (12)\end{aligned}$$

The activity of $HCrO_4^-$ in the aqueous phase was calculated from Eq. 12. As shown in Fig. 2, a linear line confirms the extraction model suggested. The values of $\log K_7 = 6.01$ and $\log K_8 = 14.5$ were obtained in *o*-xylene, and those in other solvents are shown in Table 1.

Table 1. Extraction Constants of Triisooctylamine–Chromium System in Various Organic Diluents

Diluent	$\log K_7$ a)	$\log K_8$ b)	ε c)	δ d)
Chloroform	7.73	17.1	4.90	9.3
Benzene	6.62	15.6	2.28	9.15
Toluene	6.49	14.7	2.24	8.9
o-Xylene	6.01	14.5	2.56	9.0
Carbon tetrachloride	5.62	13.7	2.21	8.6
Hexadecane	5.35	12.9	2.10	—
Hexane	4.59	12.7	1.89	7.3

a) $K_7 = [\overline{(TIOAH)HCrO_4}]/[\overline{TIOA}](H^+)(HCrO_4^-)$. b) $K_8 = [\overline{(TIOAH)_2Cr_2O_7}]/[\overline{TIOA}]^2(H^+)^2(HCrO_4^-)^2$. c) From Ref. 23. d) From Ref. 24.

Using these two equilibrium values, we can obtain the concentrations of (TIOAH)$HCrO_4$ and $(TIOAH)_2Cr_2O_7$ in the organic phase. The molar ratio of (TIOAH)$HCrO_4$ to $(TIOAH)_2Cr_2O_7$ in the organic phase can be expressed as:

$$[\overline{(TIOAH)HCrO_4}]/[\overline{(TIOAH)_2Cr_2O_7}] = K_7/\{K_8[\overline{TIOA}](H^+)(HCrO_4^-)\}, \quad (13)$$

which indicates that increasing value of $[\overline{TIOA}](H^+)(HCrO_4^-)$ will increase the molar fraction of $(TIOAH)_2Cr_2O_7$ in the organic phase.

IR and UV-visible Absorption Spectra Studies: It has been reported that the UV absorption spectra of $HCrO_4^-$ and $Cr_2O_7^{2-}$ anions show the maximum at 350 and 370 nm, respectively.[8,17)] Figure 3 shows absorption spectra of TIOA–chromium salt solutions in *o*-xylene. As shown in Fig. 3, the absorption maxima of solutions 1 to 4 appear at 352.0, 353.5, 364.5, and 366.0 nm, respectively, suggesting the presence of $HCrO_4^-$ ion in solutions 1 and 2, and $Cr_2O_7^{2-}$ ion in solutions 3 and 4 as main species. Indeed, the values of $[\overline{TIOA}](H^+)(HCrO_4^-)$ in solutions 1 to 4 are estimated as $10^{-9.52}$, $10^{-9.25}$, $10^{-8.16}$ to $10^{-7.93}$, respectively, and by substituting these values into Eq. 13, we obtained the molar ratios of (TIOAH)$HCrO_4$ to $(TIOAH)_2Cr_2O_7$ to be 10.7, 5.6, 0.46, and 0.27, respectively. Consequently, the coexistence of both $HCrO_4^-$ and $Cr_2O_7^{2-}$ in the organic phase may be concluded.

The vibration spectrum of the dichromate ion had been studied. According to Stammreich et al.,[18)] a weak symmetric stretching Cr–O–Cr vibration appears at 567 cm⁻¹ and antisymmetric Cr–O–Cr vibrations appears at 762 cm⁻¹ (strong) and 795 cm⁻¹ (weak). Figure 4 shows the IR spectrum for solution 4 in Fig. 3. For comparison, the IR spectrum of pure TIOA was also shown in Fig. 4. The peaks appearing at 562, 762, and 800 cm⁻¹ make sure that $(TIOAH)_2Cr_2O_7$ exits in the organic phase.

Solvent Effect: The extraction of chromium by TIOA was examined in various diluents, toluene, benzene, chloroform, carbon tetrachloride, hexane, and hexadecane. For the former four extraction systems, linear lines are obtained in the plots of $[\overline{Cr}]/$

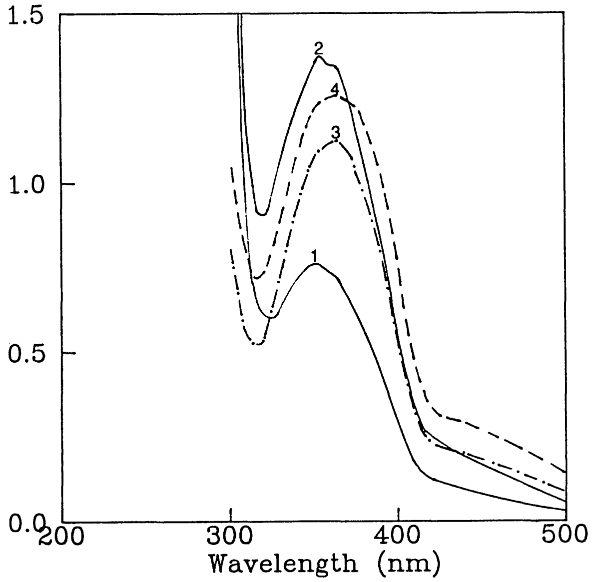

Fig. 3. UV/vis absorption spectra of Cr(VI) in the organic phase.
1 and 2: $[Cr]_i$=0.00192 M; [TIOA]=0.025 M; V_A/V_O=0.25 and 0.5 respectively.
3 and 4: $[Cr]_i$=0.0192 M; [TIOA]=0.25 M; V_A/V_O=2 and 4, respectively.

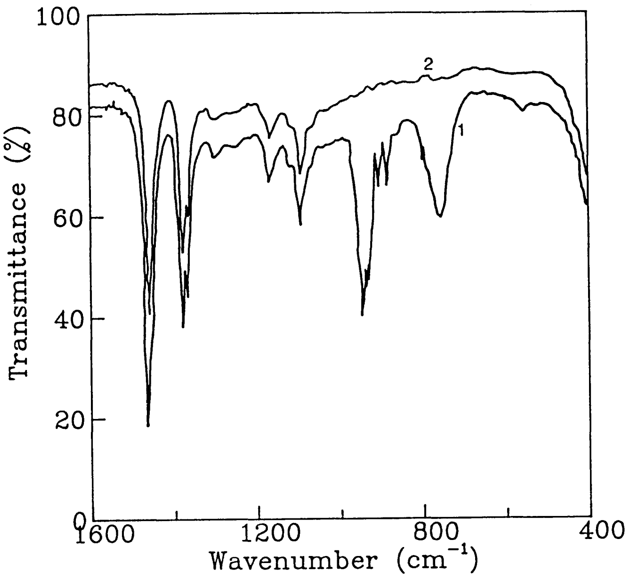

Fig. 4. IR absorption spectra of Cr(VI) in the organic phase.
Curve 1: TIOA-chromate salt. Curve 2: pure TIOA.

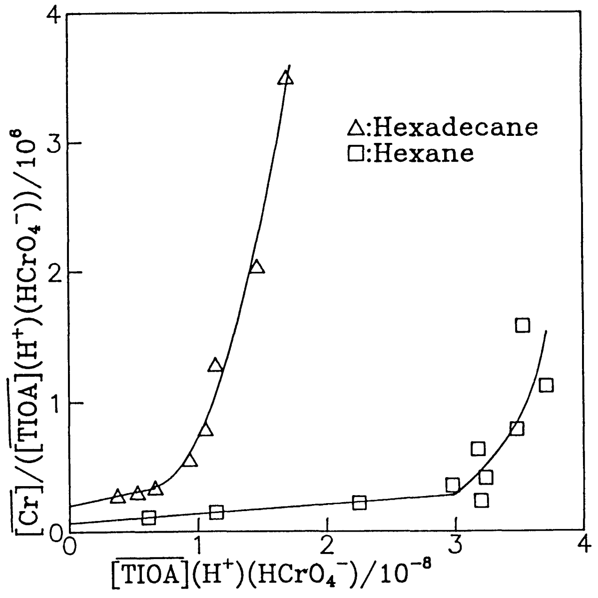

Fig. 5. Plots of $[\overline{Cr}]/([\overline{TIOA}](H^+)(HCrO_4^-))$ vs. $[\overline{TIOA}](H^+)(HCrO_4^-)$ for 0.25 M TIOA in hexane and hexadecane.

$\{[\overline{\mathrm{TIOA}}](\mathrm{H}^+)(\mathrm{HCrO}_4^-)\}$ vs. $\{[\overline{\mathrm{TIOA}}](\mathrm{H}^+)(\mathrm{HCrO}_4^-)\}$. However, for the latter two diluents, as shown in Fig. 5, the linear line only suits for a limited range. Beyond the linear range the slope of the lines tremendously increases. The phenomenon may be attributed to the aggregation of TIOA–chromium salt in the high chromium concentration in the organic phase. The aggregation may be caused from the low dielectric constant or low solubility parameter of hexane and hexadecane. The values of log K_7 and log K_8 for the reaction between chromium(VI) and TIOA in the diluents studied are shown in Table 1. Diamond[20] used trilaurylamine to extract HBr from aqueous phase. He found that in general, the higher the dielectric constant of the organic solvent, the better the extraction. For comparison, the dielectric constants of the solvents are also shown in Table 1. It is seen that except for the *o*-xylene system, the values of K_7 and K_8 obtained decrease with the decrease of the dielectric constant of the solvent, i.e.: chloroform>benzene>toluene>carbon tetrachloride>hexadecane>hexane. This tendency is in good agreement with that indicated by Diamond.[20] In this work, we also attempt to correlate extraction constant with the solubility parameter of solvent. As shown in the last column of Table 1, obviously a similar result as the dielectric constant was obtained.

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