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Solvent Extraction of Chromium(VI) with Tri-*n*-butyl Phosphate from Aqueous Acidic Solutions

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The solvent extraction of Cr(VI) from aqueous acidic solutions by tri-*n*-butyl phosphate (TBP) in kerosene was investigated. HCl, H_2SO_4, and H_3PO_4 were used for the pH adjustment of the aqueous phase. The results show that the distribution coefficient exhibited a maximum when HCl was used. The distribution coefficient increased with increasing TBP concentration (from (0.2 to 3.0) $mol \cdot L^{-1}$) and decreasing pH (from 2.0 to 0). The results also show that one molecule of Cr(VI) was approximately coordinated to three TBPs in the complex. The enthalpy change of $-17.4\ kJ \cdot mol^{-1}$ was determined using the van't Hoff equation, suggesting that the extraction of Cr(VI) from a HCl medium is an exothermic process. The presence of NaCl in the feed phase improved the extraction efficiency, whereas the presence of Na_2SO_4 or KH_2PO_4 has no benefit. The stripping of loaded organic and the reuse of the extractant are also discussed in this paper.

Introduction

The extensive use of chromium in electroplating, leather tanning, pulp production, and other industries has resulted in large quantities of Cr(VI) discharging into the environment. The removal of Cr(VI) from effluent is environmentally important because of its high toxicity. Several techniques have been proposed to deal with this problem, such as chemical precipitation, ion exchange, solvent extraction, adsorption, membrane separation, etc. Among them, solvent extraction is one of the most effective conventional methods to separate and recover Cr(VI) from aqueous solutions.

Despite the considerable amount of work that has been reported for the solvent extraction of Cr(VI), most of them use amine extractants, such as Aliquat-336,[1−5] Alamine-336,[2,6] TOA,[7−9] etc. Studies about the extraction equilibrium using TBP as the extractant are scanty and not systemic. TBP was one of the first organophosphorous extractants to be used industrially and commercially. Because of its low cost, excellent chemical stability, good extraction kinetics and low solubility in the aqueous phase, TBP is a good extractant of Cr(VI). It is necessary to study the extraction equilibrium of Cr(VI) for the design and optimization of solvent extraction processes.

In this work, the extraction of Cr(VI) from acidic solutions using TBP in kerosene has been investigated. The following factors have been investigated: the type of inorganic acids used to adjust the pH of the feed phase, pH value of the feed phase, the TBP concentration, and temperature. The effect of the presence of inorganic salts on the extraction efficiency was also studied. Furthermore, the stripping and reuse of the organic phase are discussed.

Experimental Section

Reagents. The following inorganic salts, acids, and organic solvent were used in the experiments without further purification: $K_2Cr_2O_4$ (> 99.8 %), NaCl (99.8 %), KCl (> 99.8 %), $CaCl_2$ (> 96.0 %), NaOH (> 96.0 %), H_2SO_4 (95 %∼98 %), HCl (36 %∼38 %), HNO_3 (65 %), H_3PO_4 (> 85 %), TBP (> 98.5 %), kerosene (density, 0.8 $kg \cdot L^{-1}$; refractivity, 1.440). Deionized water was used for preparing all the aqueous solutions.

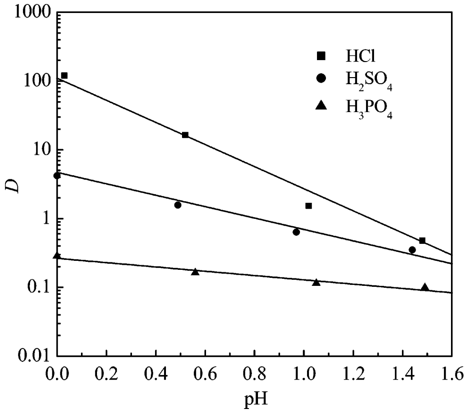

Figure 1. Extraction of Cr(VI) from different inorganic acid aqueous phases using 1.47 $mol \cdot L^{-1}$ of TBP at 298.3K; $[Cr^{6+}]_{f,ini} = 106\ mg \cdot L^{-1}$.

Extraction Experiments. The Cr(VI) solutions (feed phase) were prepared by dissolving a weighed amount of $K_2Cr_2O_7$ in a known volume of deionized water, which was used as the simulated wastewater. The pH was adjusted to the desired value by adding different inorganic acids (H_2SO_4, HCl, or H_3PO_4). The initial concentration of H^+ in the feed aqueous phase was determined by titration with standardized NaOH solution.

In the extraction equilibrium studies, equal volumes of organic and feed aqueous phases (10 mL:10 mL) with known concentrations were shaken mechanically in a thermostatically controlled water bath for 30 min. A preliminary experiment on the effect of contact time on the Cr(VI) extraction indicated that 30 min is sufficient to achieve the extraction equilibrium. After phase separation, the Cr(VI) concentration in the aqueous phase was determined with a UV−vis spectrophotometer, and the absorption wavelength was 540 nm using 1,5-diphenylcarbazide

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as the indicator. The Cr(VI) concentration in the organic phase was calculated on the basis of a mass balance.

All the extraction equilibrium experiments were carried out in duplicate, and the analysis was carried out in triplicate for each run. The reproducibility was found to be ± 5 %.

Stripping Experiments. The loaded organic phase was obtained from the extraction experiments. All the stripping experiments were carried out using the same procedures and conditions of the extraction experiments.

The results are expressed as distribution coefficient D, extraction efficiency % E, and recovery efficiency % R defined as

$$D = \frac{[\mathrm{Cr}^{6+}]_{\mathrm{org,eq}}}{[\mathrm{Cr}^{6+}]_{\mathrm{f,eq}}} \tag{1}$$

$$\%\, E = \left(1 - \frac{[\mathrm{Cr}^{6+}]_{\mathrm{f,eq}}}{[\mathrm{Cr}^{6+}]_{\mathrm{f,ini}}}\right)\cdot 100 \tag{2}$$

$$\%\, R = \left(\frac{[\mathrm{Cr}^{6+}]_{\mathrm{s,eq}}}{[\mathrm{Cr}^{6+}]_{\mathrm{f,ini}}}\right)\cdot 100 \tag{3}$$

where the subscripts f, org, s, eq, and ini represent the feed aqueous phase, organic phase, and stripping aqueous phase at equilibrium and initial, respectively.

Results and Discussion

Effect of the Inorganic Acid. Three different types of inorganic acids, HCl, H_2SO_4, and H_3PO_4, were used for the pH adjustment of the feed aqueous phase. The operation conditions were 106 mg·L^{-1} of Cr(VI) in the feed aqueous phase and 1.47 mol·L^{-1} of TBP in kerosene at 25 °C. It has been reported that there was no difference in the extraction behavior between the sulfate and chloride ions using TBAB in dichloromethane as the organic phase.[10] Rao and Prasad[11] also found that the extraction of Cr(VI) from aqueous acidic solution was independent of the acid type using Cyanex 272. However, as shown in Figure 1, the distribution coefficient D depends strongly on the nature of the type of acid. At the same pH value, the extraction efficiency of Cr(VI) is highest when HCl is used to adjust aqueous pH. Moreover, the influence of the acid gets more and more important at lower pH. This can be attributed to the difference in the extraction mechanism between TBP and other extractants in the Cr(VI) extraction process. The distribution coefficient is improved in the following sequence: H_3PO_4 < H_2SO_4 < HCl. Thus, HCl was selected for the pH adjustment of the aqueous phase in the following experiments.

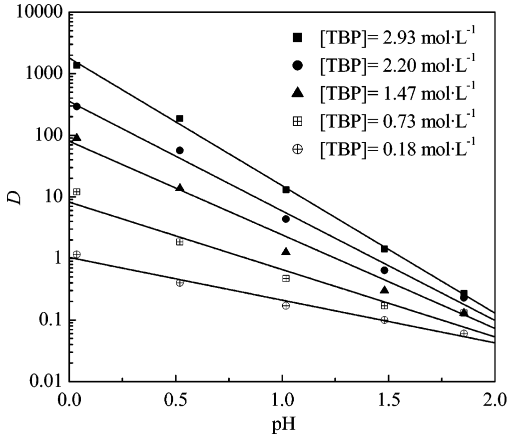

Figure 2. Effect of pH value and [TBP] on the extraction of Cr(VI) from HCl aqueous solution at 298.3 K; $[\mathrm{Cr}^{6+}]_{\mathrm{f,ini}} = 106$ mg·L^{-1}.

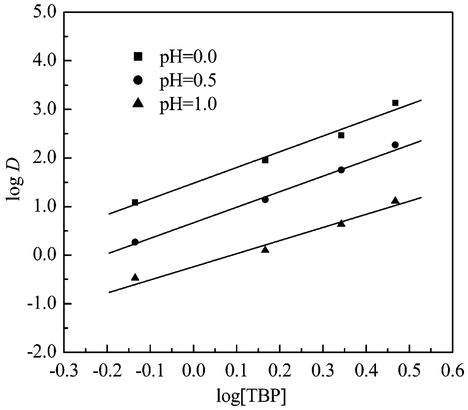

Figure 3. Plot of log D versus log [TBP] at various pH values of the aqueous phase at 298.3 K; $[\mathrm{Cr}^{6+}]_{\mathrm{f,ini}} = 106$ mg·L^{-1}.

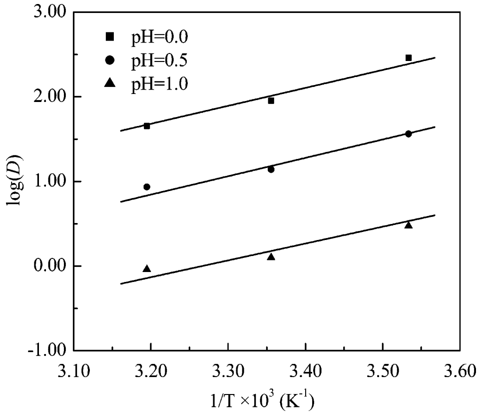

Figure 4. Plot of log D versus 1/T for extraction of Cr(VI) by 1.47 mol·L^{-1} of TBP from HCl aqueous solution at various pH values; $[\mathrm{Cr}^{6+}]_{\mathrm{f,ini}} = 106$ mg·L^{-1}.

Table 1. Effect of pH Value and [TBP] on the Extraction of Cr(VI) from HCl Aqueous Solution at 298.3 K[a]

[TBP] mol·L^{-1}	pH	$[\mathrm{Cr}^{6+}]_{\mathrm{f,eq}}$ mg·L^{-1}	% E	D
0.18	0.0	49.09	53.7	1.2
0.18	0.5	75.90	28.4	0.4
0.18	1.0	90.36	14.8	0.2
0.18	1.5	96.12	9.3	0.1
0.18	2.0	99.83	5.8	0.1
0.73	0.0	8.12	92.3	12.0
0.73	0.5	37.18	64.9	1.8
0.73	1.0	72.24	31.8	0.5
0.73	1.5	90.25	14.9	0.2
0.73	2.0	94.18	11.2	0.1
1.47	0.0	1.16	98.9	90.0
1.47	0.5	7.17	93.2	13.8
1.47	1.0	46.92	55.7	1.3
1.47	1.5	81.55	23.1	0.3
1.47	2.0	93.40	11.9	0.1
2.20	0.0	0.36	99.7	292.1
2.20	0.5	1.85	98.2	56.2
2.20	1.0	19.87	81.3	4.3
2.20	1.5	64.77	38.9	0.6
2.20	2.0	86.09	18.8	0.2
2.93	0.0	0.08	99.9	1358.7
2.93	0.5	0.57	99.5	186.1
2.93	1.0	7.54	92.9	13.1
2.93	1.5	43.88	58.6	1.4
2.93	2.0	83.21	21.5	0.3

[a] $[\mathrm{Cr}^{6+}]_{\mathrm{f,ini}} = 106$ mg·L^{-1}.

Table 2. Effect of Inorganic Salts on the Extraction of Cr(VI) from HCl Aqueous Solution at 298.3 K[a]

[TBP]		salt conc.	NaCl			Na_2SO_4			KH_2PO_4		
$mol \cdot L^{-1}$	pH	$g \cdot L^{-1}$	$[Cr^{6+}]_{f,eq}$ ($mg \cdot L^{-1}$)	% *E*	*D*	$[Cr^{6+}]_{f,eq}$ ($mg \cdot L^{-1}$)	% *E*	*D*	$[Cr^{6+}]_{f,eq}$ ($mg \cdot L^{-1}$)	% *E*	*D*
0.73	0.5	0	37.18	64.9	1.8	37.18	64.9	1.8	37.18	64.9	1.8
0.73	0.5	10	23.78	77.6	3.5	64.82	38.8	0.6	68.09	35.76	0.6
0.73	0.5	30	21.18	80.0	4.0	81.55	23.1	0.3	91.24	13.92	0.2
0.73	0.5	50	17.96	83.0	4.9	91.85	13.4	0.2	96.62	8.85	0.1
0.73	0.5	70	16.19	84.7	5.6	96.39	9.1	0.1	98.39	7.18	0.1
0.73	0.5	100	12.37	88.3	7.6	99.27	6.3	0.1	99.27	6.34	0.1
1.47	0.5	0	7.17	93.2	13.8	7.17	93.2	13.8	7.17	93.2	13.8
1.47	0.5	10	5.49	94.8	18.3	10.78	89.8	8.8	17.63	83.4	5.0
1.47	0.5	30	4.31	95.9	23.6	23.61	77.7	3.5	51.92	51.0	1.0
1.47	0.5	50	3.23	97.0	31.9	39.34	62.9	1.7	81.22	23.4	0.3
1.47	0.5	70	2.61	97.5	39.6	50.31	52.5	1.1	90.41	14.7	0.2
1.47	0.5	100	1.96	98.2	53.0	59.21	44.2	0.8	93.46	11.8	0.1
1.47	1.0	0	46.92	55.7	1.3	46.92	55.7	1.3	46.92	55.7	1.3
1.47	1.0	10	38.35	63.8	1.8	79.67	24.8	0.3	91.80	13.4	0.2
1.47	1.0	30	27.71	73.9	2.8	95.18	10.2	0.1	97.89	7.6	0.1
1.47	1.0	50	21.90	79.3	3.8	96.23	9.2	0.1	99.00	6.6	0.1
1.47	1.0	70	17.76	83.2	5.0	96.50	9.0	0.1	99.11	6.5	0.1
1.47	1.0	100	12.33	88.4	7.6	98.39	7.2	0.1	99.11	6.5	0.1

[a] $[Cr^{6+}]_{f,ini} = 106\ mg \cdot L^{-1}$.

Table 3. Effect of NaOH Concentration on Stripping of Cr(VI) from Loaded Organic at 298.3 K[a]

[NaOH]	$[Cr^{6+}]_{f,ini}$	$[Cr^{6+}]_{s,eq}$	
$mol \cdot L^{-1}$	$mg \cdot L^{-1}$	$mg \cdot L^{-1}$	% *R*
0.1	106	70.25	66.3
0.3	106	75.46	71.2
0.5	106	75.79	71.5
1.0	106	75.29	71.0

[a] $[TBP] = 1.47\ mol \cdot L^{-1}$.

Effects of pH Value and the TBP Concentration. To investigate the effect of pH value and TBP concentration on the extraction of Cr(VI), the experiments were carried out with pH value and TBP concentration variation in the range of (0 to 2.0) $mol \cdot L^{-1}$ and (0.2 to 3.0) $mol \cdot L^{-1}$, respectively. The results are shown in Table 1 and Figure 2. It is clear that the relationship between log *D* and pH is a straight line, and the distribution coefficient increases with decreasing pH at each TBP concentration. When the hydrochloric acid concentration increases, more Cr(VI)−chloro-oxo complex ($HCrO_3Cl$) exists in the feed phase, which is the species extracted by TBP from the HCl medium.[12] At the lowest pH of 0.0, with increasing TBP concentration from (0.18 to 2.93) $mol \cdot L^{-1}$, the distribution coefficient increases from 0.16 to a maximum value of 1359. Figure 3 shows the relationship between the log of the TBP concentration in the organic phase and the distribution coefficient *D*. The slopes of the straight line are 3, independent of the pH value of the aqueous phase. This indicates that one molecule of Cr(VI) is approximately coordinated to three TBPs in the complex.

In addition, experiments were performed in which no acids were used for pH adjustment in the aqueous phase or the solvent contained no TBP. No detectable extraction of Cr(VI) was found in the experiment, suggesting that in the Cr(VI) extraction process the participation of both TBP and H^+ is necessary.

Effect of Temperature. The effect of temperature on the extraction of Cr(VI) was studied from (283.3 to 313.3) K. Figure 4 shows the results for the extraction of Cr(VI) with 1.47 $mol \cdot L^{-1}$ of TBP from an HCl medium as a plot of the log *D* versus the reciprocal of temperature, $1/T$, depending on the pH value of the aqueous phase. The linear relation between log *D* and $1/T$ is found as described in the van't Hoff equation, and the slopes of the three straight lines are $2.1 \cdot 10^3$ (pH = 0), $2.2 \cdot 10^3$ (pH = 0.5), and $2.0 \cdot 10^3$ (pH = 1.0), respectively. The slope remains almost constant, indicating that the pH value has no influence on the enthalpy change under the experimental conditions. The enthalpy change of $-17.4\ kJ \cdot mol^{-1}$ was determined using the van't Hoff equation, suggesting that the extraction of Cr(VI) from HCl medium using TBP is an exothermic process. This conclusion agrees with the study of the Cr(VI) extraction by amine extractants (Aliquat 336, Alamine 336) from 1 $mol \cdot L^{-1}$ of HCl aqueous solution.[2]

Effect of Inorganic Salts. To explore the effect of the presence of inorganic salts on the extraction of Cr(VI) from the HCl medium, NaCl, Na_2SO_4, and K_2PO_4 were added to the aqueous phase with the salt's initial concentration variation in the range (10 to 100) $g \cdot L^{-1}$. It is found that the presence of salts has a significant influence on the extraction process, as shown in Table 2. At different TBP concentrations and pH values, the addition of NaCl improved Cr(VI) extraction efficiency from the HCl medium and the distribution coefficient increased with increasing NaCl concentration. This improvement mainly results from the increasing amount of $HCrO_3Cl$ in the aqueous phase. The influence of $HCrO_3Cl$ on the extraction has been discussed above. In contrast, the distribution coefficient decreases sharply with increasing concentration of Na_2SO_4 and KH_2PO_4, which may be due to competitive extraction between Cr(VI) and SO_4^{2-}, PO_4^{2-} with TBP as extractant. For example, the distribution coefficient decreases from 13.8 to 0.79 and to 0.13 with increasing Na_2SO_4 and KH_2PO_4 concentration [(0 to 100) $g \cdot L^{-1}$, $[TBP] = 1.47\ mol \cdot L^{-1}$, pH = 0.5], respectively.

Stripping of Loaded Organic and Reuse of the Extractant. For any commercial operation, it is necessary to reuse the organic phase without significant loss of extraction ability. Sodium hydroxide was used as the stripping reagent in this work. The effect of its concentration on the recovery of Cr(VI) is shown in Table 3. For a feed concentration of 106 $mg \cdot L^{-1}$, more than 70 % of the Cr(VI) could be recovered with a 0.3 $mol \cdot L^{-1}$ NaOH solution. Further increases in NaOH concentration had no significant improvement on the recovery efficiency.

For assessment of the recycling behavior of TBP, successive extraction and stripping cycles of Cr(VI) were carried out. The feed aqueous phase was equilibrated with the organic phase at a 1:1 phase ratio. The raffinate was separated, and the loaded organic phase was stripped with 0.5 $mol \cdot L^{-1}$ of NaOH solution. After separation of the strip solution, the regenerated extractant was used for further cycles of extraction and stripping tests.

Table 4. Effect of Regeneration Steps on the Extraction Efficiency, % *E*, of Cr(VI) from HCl Aqueous Solution at 298.3 K[a]

[TBP]	regeneration steps								
mol·L^{-1}	1	2	3	4	5	6	7	8	9
1.47	91.4	89.4	919	90.2	90.0	90.5	93.3	92.4	93.7
2.20	98.4	97.9	99.0	98.3	98.4	98.1	98.6	98.4	98.7

[a] [TBP] = 1.47 mol·L^{-1}.

No appreciable decrease in the extraction efficiency, % *E*, was observed during nine regeneration steps (Table 4).

Conclusion

Solvent extraction of Cr(VI) from aqueous acidic solutions was carried out using TBP as extractant. The extraction efficiency of Cr(VI) from different inorganic acid solutions follows the order: HCl > H_2SO_4 > H_3PO_4. At the lowest pH value 0 and highest TBP concentration, the maximum distribution coefficient 1359 and an extraction efficiency of 99.9 % were achieved. The log *D* vs log [TBP] plots were straight lines with slope values of 3 indicating 3 mol of the extractant was involved with 1 mol of the extracted metal species. On the basis of the results in this paper, the extraction of Cr(VI) by TBP from hydrochloric acid solutions is exothermic, and thus the extraction proceeds better at low temperatures. The presence of chloride improves the extraction efficiency of Cr(VI) from the HCl medium by TBP, while the addition of sulfate and phosphate greatly decreases the extraction. More than 70 % of the Cr(VI) could be recovered with 0.3 mol·L^{-1} of NaOH solution, and TBP has a good recycling capacity. This study can be considered as an initial step toward further studies examining Cr(VI) recovery from industrial wastewater.

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