The role of some compounds on extraction of chromium(VI) by amine extractants

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Abstract

The extraction of hexavalent chromium, Cr(VI), from hydrochloric acid aqueous solution using Aliquat 336 and Alamine 336 extractants was performed under different experimental conditions. The data clarify that one molecule of amine extractants shares with approximately one molecule of HCl to extract two molecules of Cr(VI) from 1M HCl aqueous solutions. The extraction is an exothermic process and possesses enthalpy change values of -41.02 and $-28.08\,\mathrm{kJ\,mol^{-1}}$ for the extraction by Aliquat 336 and Alamine 336, respectively. The presence of potassium chloride greatly increases the extraction of Cr(VI) by amine extractants while the addition of some phenolic compounds such as phenol, dichlorophenol, *o*-nitrophenol and β-naphthol decreases this extraction under the same experimental conditions.
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1. Introduction

Chromium in aqueous solutions forms three types of ions: the chromium(II) and chromium(III) cations and the chromate and dichromate anions in which chromium has an oxidation state of +6. The chromium(II) (or chromous) ions are rather unstable and atmospheric oxygen oxidizes them readily to chromium(III) ions that are stable as well as chromium(VI). Environmentally, hexavalent chromium ions are toxic and carcinogenic and also notoriously mobile in nature because they are weakly bounded to inorganic surfaces.

Chromium compounds are produced as byproducts from different industrial activities such as leather and textile production, metal finishing, electroplating, etc. These compounds have been discharged into aquatic systems creating serious environmental problems. Extensive efforts were done in many studies using several techniques to effectively remove Cr(VI) from aqueous solutions. Among these techniques, the adsorption colloid flotation method [1]

and the reduction-coprecipitation technique [2] have been widely applied and have arising attention. Also, the removal of Cr(VI) from aqueous solutions using different carriers as metal sulfates [3], iodate [4], carbon black [5] and fly ash-wallastonite [6] was clarified by many workers.

One of the promising and effective techniques applied in removal of Cr(VI) is the liquid–liquid extraction using amines as selective extractants in the organic phase. In this technique, the use of primary amines as primene JMT [7], secondary amines as Adogen 382 and Adogen 283 [8], tertiary amines as TOA and Alamine 336 [9] and quaternary ammonium salts as Aliquat 221 and Aliquat 336 [10,11] gives a good achievement in extraction of Cr(VI). Also, these species can be extracted by tetraphenyl arsonium chloride (TPACl) [12] and the extracted species were reported to have the formula $TPA^+\cdot HCrO_4{}^-$.

Phenolic compounds were used by Katsuta et al. [13] as hydrogen bonding donors in enhancing the extraction of trivalent nuclides from radioactive wastes. In addition, they are generated, besides Cr(VI), as a byproduct in dye and textile industries producing an organic-mixed aqueous waste. Presence of such organic species would vary the treatability of

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the inorganic constituents of these mixed wastes. Therefore, the role played by these organic compounds on extraction of Cr(VI) from aquatic environment must be verified.

Hence, this work aims to study the extraction of Cr(VI) from HCl aqueous solutions under the influence of a varity of experimental factors and to clarify the effect of presence of phenol, dichlorophenol, *ortho*-nitrophenol and β-naphthol (as phenolic compounds) and KCl (as inorganic compound) on extraction of Cr(VI) by Aliquat 336 and Alamine 336.

2. Experimental

2.1. Materials

All chemicals and reagents used were of analytical grade purity and bi-distilled water was used in aqueous dissolutions. The extractants Aliquat 336 (average M.wt. = 442) and Alamine 336 (average M.wt. = 392) are products of General Mills, Kankakee, USA. ^{51}Cr isotope was prepared by irradiating potassium dichromate in the Egyptian Second Research Reactor (ERR-2) for 48 h. After a suitable cooling time, the irradiated salt was dissolved in 1 M HCl and kept for further usage.

2.2. Extraction procedure

Aliquat 336 and Alamine 336 were firstly equilibrated for a sufficient time with equal volumes of 1 M HCl. The pre-equilibrated extractants were conducted with Cr(VI), in 1 M HCl aqueous solutions, in tightly closed glass bottles and vigorously shaken for a sufficient time at room temperature. The progress of extraction was determined by taking 2 ml of both organic and aqueous phases, after phase separation, at the selected time interval and radiometrically assayed using a pure Ge-detector connected to a 8192 multichannel analyzer. The distribution ratio ($D_{Cr(VI)}$) was calculated using the relation:

$$D_{Cr(VI)} = \frac{[activity]_{org}}{[activity]_{aq}} \tag{1}$$

The change in Cr(VI) extraction from 1 M HCl aqueous solutions using 0.018 M Aliquat 336 and 0.1 M Alamine 336 with presence of some interfering ingredients was studied by adding different initial concentrations ranged from 0.01 to 0.1 M of these additives to the working solutions and shaking the system for equilibrium time at $25 \pm 1\,^{\circ}$C. After equilibrium, the phases were separated and 2 ml of both organic and aqueous phases were withdrawn and radiometrically assayed.

3. Results and discussion

The extraction of Cr(VI) from 1 M HCl aqueous solutions was found to be affected by the following factors.
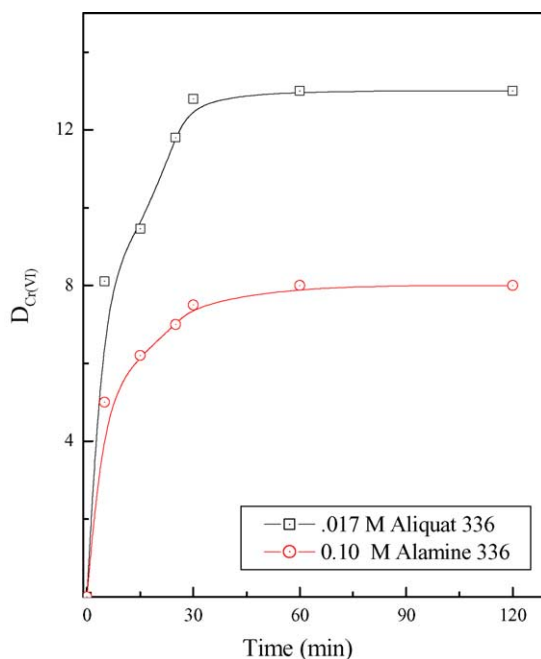

Fig. 1. Extraction of Cr(VI) by amine extractants from 1 M HCl aqueous solution at $25 \pm 1\,^{\circ}$C.

3.1. Equilibrium time

The variation in the distribution ratio of chromium(VI) ($D_{Cr(VI)}$) with elapsed time is represented in Fig. 1. The graph shows that $D_{Cr(VI)}$ increases with time till reaching equilibrium that achieved after about 30 min of contact. Also, the distribution of Cr(VI) into Aliquat 336 is higher than that into Alamine 336. This behavior may be referred to the difference in organic nature between quaternary ammonium salt in Aliquat 336 and tertiary amine in Alamine 336 where quaternary ammonium salt has a higher tendency to form chromium complexes.

3.2. Diluent type

Aliquat 336 was diluted with toluene and odorless kerosene to prepare the desired initial concentrations. 5% octanol was added to kerosene to overcome the mechanical difficulties encountered with using solutions of tertiary amines in kerosene due to third phase and gel formation. The relation between Aliquat 336 initial concentrations, in two different diluents, and $D_{Cr(VI)}$ is given in Fig. 2. The relation shows that Cr(VI) extracted into Aliquat 336/toluene was more than that into Aliquat 336/kerosene. This finding may be assigned to the complete solubility of the applied extractants in aromatic hydrocarbon [14]. Therefore, amine extractants were diluted with toluene in the rest of work.

3.3. Extractant concentration

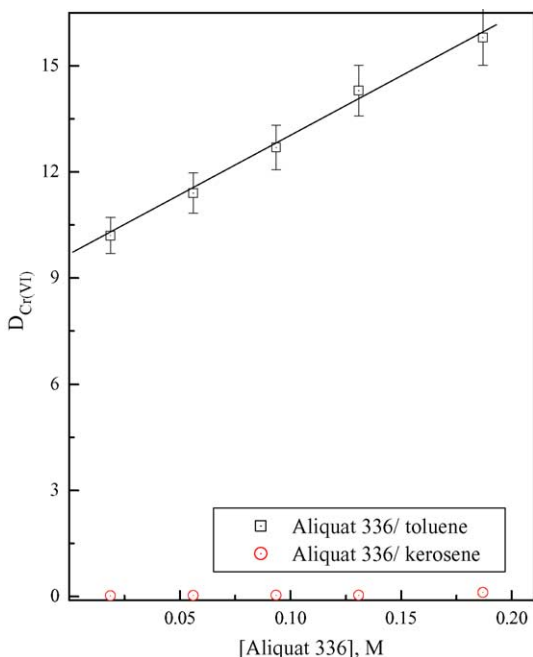Different concentrations of Aliquat 336 and Alamine 336 in toluene were used to study the extraction of Cr(VI) from

Fig. 2. Extraction of Cr(VI) by Aliquat 336 in different diluents from 1M HCl aqueous solution at $25 \pm 1\,^\circ C$.

Fig. 4. Extraction of Cr(VI) from 1M HCl aqueous solution using different Alamine 336 concentrations at different temperatures.

1 M HCl aqueous solution. The relation between $D_{Cr(VI)}$ and amine concentration is shown in Figs. 3 and 4. The figures exhibit a group of straight lines of slope ~1 implying a linear proportionality between $D_{Cr(VI)}$ and amine concentrations. This linearity indicates that one molecule of Aliquat 336 or Alamine 336 shared in extraction of the studied species.
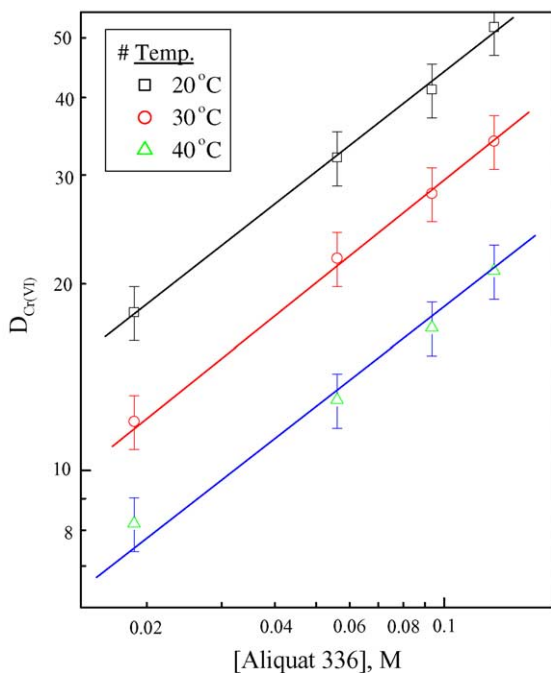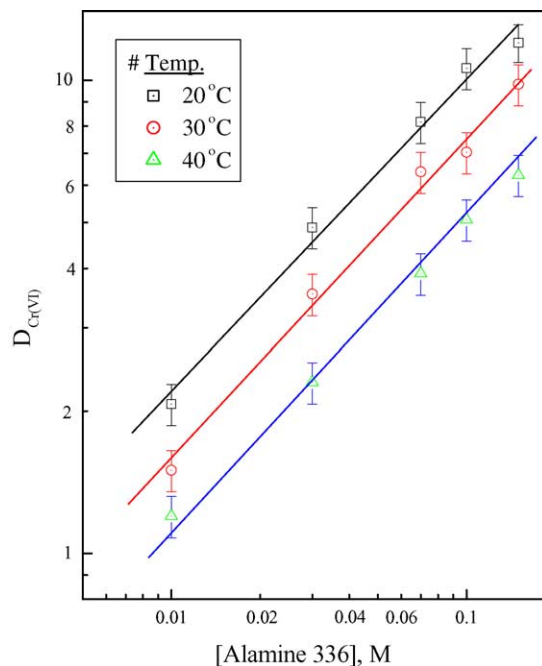
3.4. HCl concentration

Extraction of Cr(VI) was carried out using 0.018 M Aliquat 336 and 0.1 M Alamine 336 in toluene from aqueous solutions having different concentrations of HCl. The variation of $D_{Cr(VI)}$ with HCl concentration is depicted in Fig. 5. The plot gives a straight line of slope ~1 implying that one
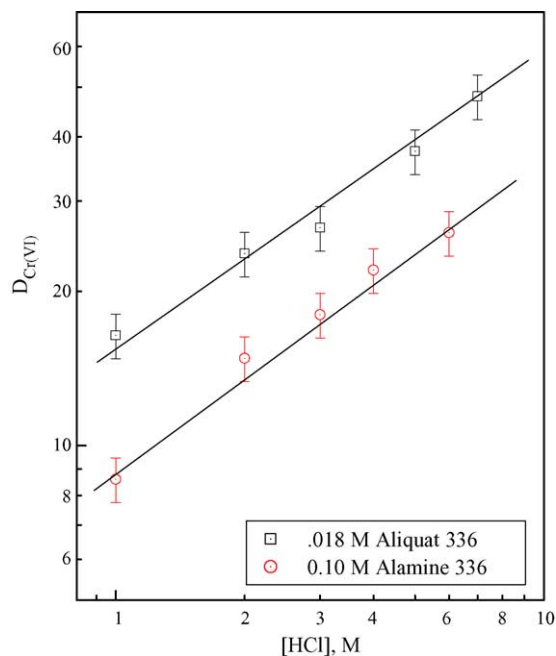

Fig. 3. Extraction of Cr(VI) from 1 M HCl aqueous solution using different Aliquat 336 concentrations at different temperatures.

Fig. 5. Extraction of Cr(VI) by amine extractants from aqueous solutions of different HCl concentrations at $25 \pm 1\,^\circ C$.

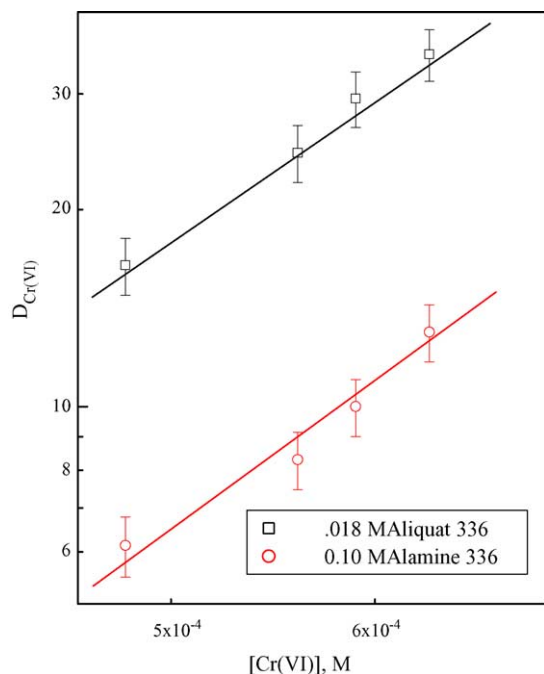Fig. 6. Effect of Cr(VI) concentration on its extraction by amin extractants from 1 M HCl aqueous solution at $25 \pm 1\,^{\circ}$C.
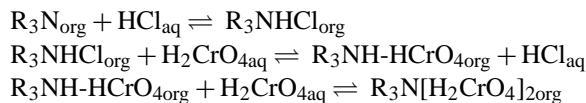
molecule of hydrochloric acid participated in the extracted species.
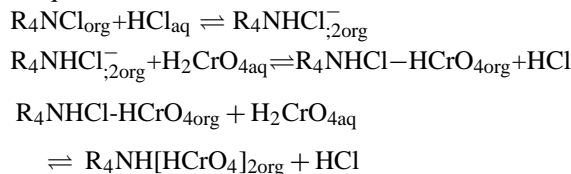
3.5. Cr(VI) concentration

Cr(VI) with different initial concentrations, in 1 M HCl aqueous solution, was extracted using 0.018 M Aliquat 336 and 0.1 M Alamine 336 in toluene. The relation between Cr(VI) initial concentrations and its distribution ratio is illustrated in Fig. 6. The revealed data clarify that two molecules of Cr(VI) are extracted using one molecule of either amine extractants.

Generally it can be asserted that, one molecule of amine extractant, either Aliquat 336 or Alamine 336, shares approximately one molecule of HCl to extract two molecules of Cr(VI) from aqueous solutions. Since the dichromate anion is mainly found as H_2CrO_4 at aqueous solutions of pH value below 1[15] and R_3N and R_4N denote to Alamine 336 and Aliquat 336 respectively, the extraction of Cr(VI) by Alamine 336 or Aliquat 336 could be represented stoichiometrically by the following equations:
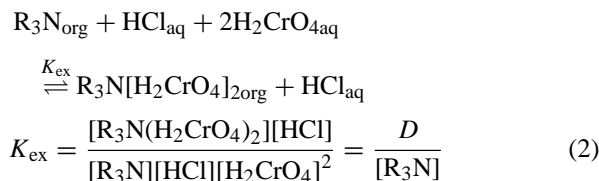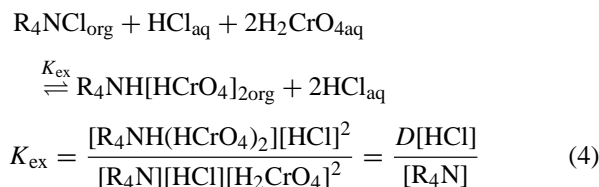
(ii) Alamine 336

$R_3N_{org} + HCl_{aq} \rightleftharpoons R_3NHCl_{org}$
$R_3NHCl_{org} + H_2CrO_{4aq} \rightleftharpoons R_3NH\text{-}HCrO_{4org} + HCl_{aq}$
$R_3NH\text{-}HCrO_{4org} + H_2CrO_{4aq} \rightleftharpoons R_3N[H_2CrO_4]_{2org}$

(ii) Aliquat 336

$R_4NCl_{org} + HCl_{aq} \rightleftharpoons R_4NHCl^-_{;2org}$
$R_4NHCl^-_{;2org} + H_2CrO_{4aq} \rightleftharpoons R_4NHCl\text{-}HCrO_{4org} + HCl$

$R_4NHCl\text{-}HCrO_{4org} + H_2CrO_{4aq}$
$\qquad \rightleftharpoons R_4NH[HCrO_4]_{2org} + HCl$

From the former equations the extraction equilibrium constant (K_{ex}) can be stated as:

(ii) Alamine 336

$R_3N_{org} + HCl_{aq} + 2H_2CrO_{4aq}$

$\overset{K_{ex}}{\rightleftharpoons} R_3N[H_2CrO_4]_{2org} + HCl_{aq}$

$$K_{ex} = \frac{[R_3N(H_2CrO_4)_2][HCl]}{[R_3N][HCl][H_2CrO_4]^2} = \frac{D}{[R_3N]} \tag{2}$$

$$\log K_{ex} = \log D - \log [R_3N] \tag{3}$$

(ii) Aliquat 336

$R_4NCl_{org} + HCl_{aq} + 2H_2CrO_{4aq}$

$\overset{K_{ex}}{\rightleftharpoons} R_4NH[HCrO_4]_{2org} + 2HCl_{aq}$

$$K_{ex} = \frac{[R_4NH(HCrO_4)_2][HCl]^2}{[R_4N][HCl][H_2CrO_4]^2} = \frac{D[HCl]}{[R_4N]} \tag{4}$$

$$\log K_{ex} = \log D - \log [R_4N] + \log [HCl] \tag{5}$$

3.6. Temperature effect

The equilibrium extraction of Cr(VI) from 1 M HCl aqueous solution at different temperatures was studied by applying a temperature covers the range 20–40 $^{\circ}$C on the extraction system. The variation in $D_{Cr(VI)}$ with the extractants concentrations at different temperatures is displayed in Figs. 3 and 4. The plots exhibit a decrease in the distribution of Cr(VI) with rising temperature revealing an exothermic nature of the extraction process. Using Eqs. (1), (3) and (5), the values of log K_{ex} were calculated and plotted against $1/T$, Fig. 7. The figure shows linear relationships from their slopes the thermodynamic parameters for the proposed reaction were calculated and given in Table 1.

The tabulated data clarify that the extraction is an exothermic process indicating a bond formation between Cr(VI) and amine molecules. The values of ΔG are negative and small suggesting a spontaneous reaction with high preference of Cr(VI) for amine extractants. ΔS has negative value specifying a decreased randomness during the extraction process where the extracted species lose their transtionallity allowing such randomness depression.

3.7. Potassium chloride addition

Different concentrations of KCl from 0.05 M up to 1 M was added to the aqueous solution of Cr(VI) to specify the

Table 1
The thermodynamic parameters for extraction of Cr(VI)

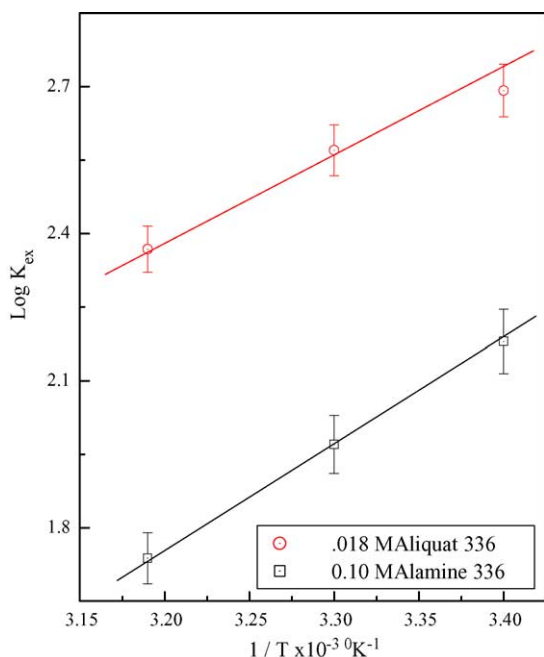| Amine	$-\Delta H$ (kJ mol^{-1})	$-\Delta G$ (kJ mol^{-1})	$-\Delta S$ (J degree^{-1} mol^{-1})
Aliquat 336	41.02	12.35	96.20
Alamine 336	28.08	11.06	57.10

Fig. 7. A plot of Log K_{ex} against $1/T$ for extraction of Cr(VI) by amine extractants from 1 M HCl aqueous solution.

Table 2
Dissociation of KCl at 18 °C [14]

Concentration (mol liter^{-1})	Degree of dissociation	Dissociation constant
2.0	0.712	3.52
1.0	0.756	2.34
0.5	0.788	1.46
0.1	0.862	0.54
0.01	0.942	0.15

layers surrounding chromate anions and so facilitates their interaction with amine extractant molecules. Also, increasing the initial concentrations of KCl increases the distribution ratio of Cr(VI). This behavior may arise from the increase in KCl dissociation constant with its initial molar concentration and this causes more contraction to the solvated layers around chromate molecules. The relation between the dissociation constant of KCl and its concentrations is given in Table 2.

3.8. Phenolic compounds addition

The change in extraction of Cr(VI) from aqueous solution with presence of some interfering phenolic compounds was performed using different compounds with various substituted groups. In this concern, Different initial concentrations of the compounds: phenol, dichlorophenol, *ortho*-nitrophenol and β-naphthol were added to different working solutions with 0.018 M Aliquat 336 or 0.1 M Alamine 336 to extract Cr(VI) from 1M HCl aqueous solution. The relation between $D_{Cr(VI)}$ and the initial concentrations of these phenolic compounds is illustrated in Figs. 9–12. The plots clarify that $D_{Cr(VI)}$ into Aliquat 336 and Alamine 336

role played by such electrolytes on Cr(VI) extraction using 0.018 M Aliquat 336 and 0.1 M Alamine 336. The relation between $D_{Cr(VI)}$ and concentration of KCl is represented in Fig. 8. The graph shows that the distribution of Cr(VI) is greatly enhanced with presence of increased concentrations of KCl. This enhancement may be referred to the salting out effect of potassium chloride since the addition of such strong electrolyte to aqueous solution causes attraction to the solvate
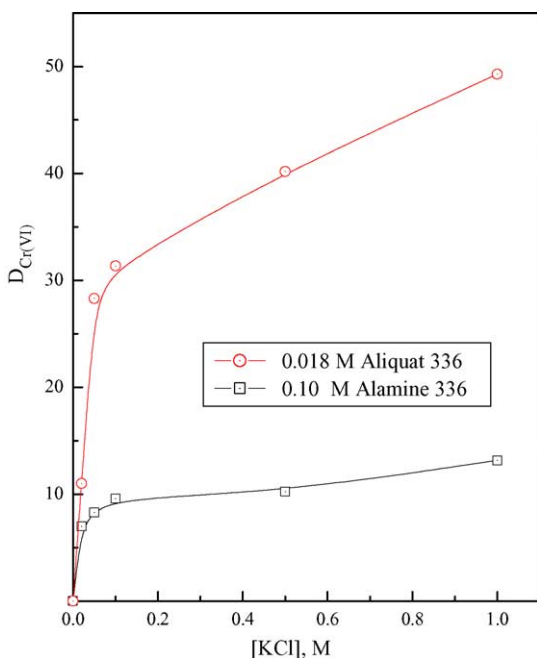

Fig. 8. Extraction of Cr(VI) by amine extractants from aqueous solution of different KCl concentrations at 25 ± 1 °C.
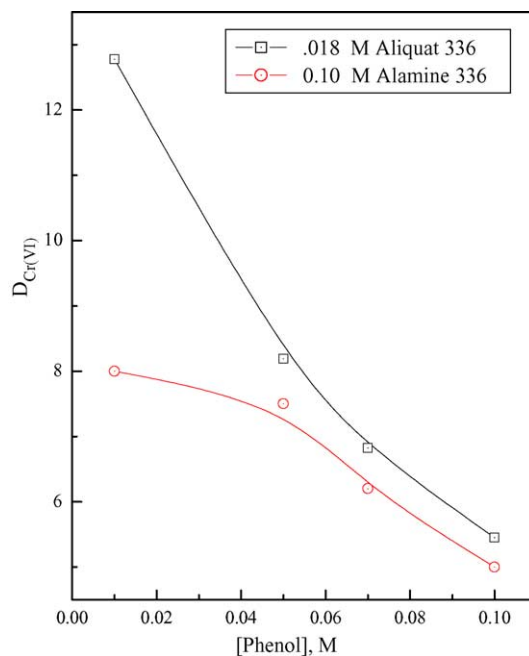

Fig. 9. Extraction of Cr(VI) by amine extractants from 1 M HCl aqueous solution with presence of different phenol concentrations at 25 ± 1 °C.
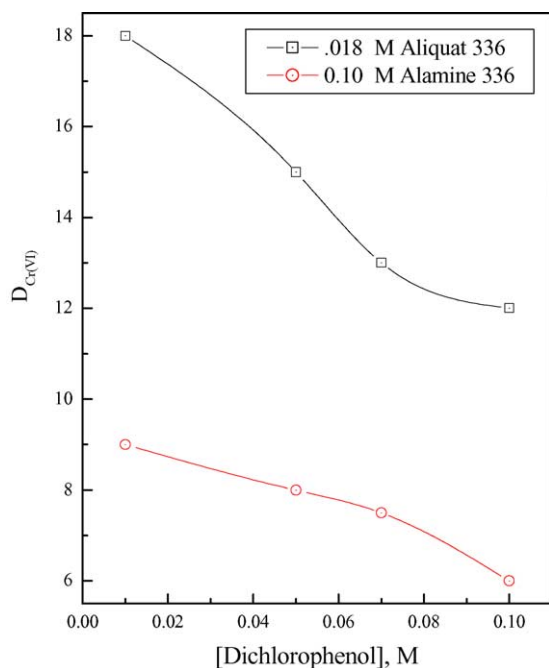
Fig. 10. Extraction of Cr(VI) by amine extractants from 1 M HCl aqueous solution with presence of different dichlorophenol concentrations at $25 \pm 1\,^\circ$C.

Fig. 12. Extraction of Cr(VI) by amine extractants from 1 M HCl aqueous solution with presence of different β-naphthol concentrations at $25 \pm 1\,^\circ$C.

decreases with increasing concentration of these compounds. This behavior indicates that presence of phenolic compounds depresses Cr(VI) distribution into amine extractants to a varied extent depending upon the nature of each compound. This depression may arise from a side organic–organic interaction between amine molecules and phenolic compounds.
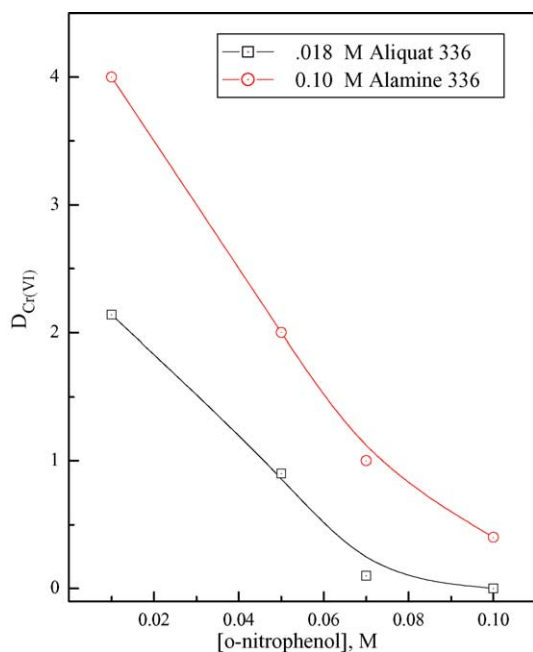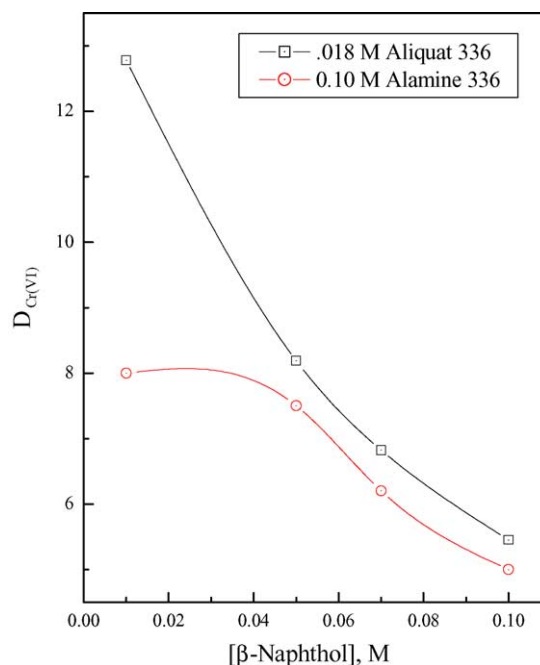

Fig. 11. Extraction of Cr(VI) by amine extractants from 1 M HCl aqueous solution with presence of different *o*-nitrophenol concentrations at $25 \pm 1\,^\circ$C.

The highest depression achieved with *ortho*-nitrophenol may be referred from the increase in its organic nature, comparing with the other compounds, due to the intramolecular hydrogen bonding between –OH and –NO$_2$ groups within the single molecule. This nature increases the interaction between *ortho*-nitrophenol and amine molecules and thus decreases the available extractant molecules for Cr(VI) extraction.

Generally, this extraction depression leads us to firstly remove the organic solutes from aqueous wastes before extraction of its inorganic constituents. In this concern, a cheap adsorbent prepared from a natural product was applied to remove such organic ingredients from aqueous solutions [16]. The prepared adsorbent effectively and quantitatively removed the solutes phenol, *o*-nitrophenol, naphthalene, β-naphthol, benzoic acid and EDTA from aqueous solution. The maximum sorption capacity of this adsorbent for the former organic solutes were 13.23, 15.54, 16.60, 15.66, 15.95 and 36.64 mg g^{-1}, respectively.

4. Conclusion

It is recommended to eliminate phenolic compounds from waste solutions before any Cr(VI) separation process. The presence of these compounds highly decreases the extraction of Cr(VI) by Aliquat 336 or Alamine 336. The extraction of Cr(VI) is an exothermic process preferred to be carried out at low temperatures through participation of one molecule of amine extractant with one molecule of HCl to extract two molecules of Cr(VI). The presence of KCl in aqueous solution increases the extraction of Cr(VI).

Acknowledgement

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