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A Study on the Removal of Chromium(VI) Oxanions from Acid Solutions by Using Oxonium Ion-Crown Ether Complexes as Mobile Carrier Agents

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ABSTRACT: *Crown ethers 12-crown-4 (12C4), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), nitrobenzo-18-crown-6 (NB18C6) dibenzo-18-crown-6 (DB18C6) and dicyclohexyl-18-crown-6 (DC18C6), dissolved in dichloromethane, are able to form oxonium-ion complexes in contact with aqueous sulfuric and hydrochloric acid solutions. This ability allows the transfer of Cr(VI) oxanions from the acid media, through an organic liquid membrane, into a distilled water receiving phase. Among the studied crown ethers, DC18C6 shows the highest transport efficiency. The effect of parameters influencing the process such as the crown ether concentration in the membrane, types of the organic diluent, acid concentration in the feed phase and time is investigated and discussed. Four replicate experiments show that an average of 95.6 (±1.3)% of the initial chromium in the source phase (10^{-3} M Cr(VI), 6 M H_2SO_4, 10 ml) is extracted into the distilled water(10 ml) through the membrane (DC18C6 0.05 M in CH_2Cl_2, 20 ml) after 8 h. The corresponding result, under similar conditions, in the presence of hydrochloric acid solution (4 M) was found to be 95.0 (±1.2)%. The selectivity of the process was assessed by performing the competitive transport experiments on a solution containing Cr(VI), Ni(II), Co(II), Pb(II), Mn(II), Zn(II) and Fe(III) ions. The method was used for the recovery of chromium from two real samples provided by chromium-electroplating industries.*

KEY WORDS*: Cr(VI) ions, Recovery, Electroplating waste, Liquid membrane, Crown ethers.*

INTRODUCTION

Wastewater discharged by industries is often contaminated by toxic or otherwise harmful substances which have negative effects on the environment. Thus, the decontamination of such discharges forms a basic aspect regarding the waste management strategies. The recovery and removal of such species are important not only from environment protection view point, but also for the importance as the secondary resource recycling and economical purposes [1].

Chromium and its compounds are known as strategic minerals widely used in various industrial plants such as electroplating, leather tanning, painting, pigment production and metallurgy [1,2]. Chromium oxidation states ranges from +2 to +6. Among them trivalent and

hexavalent ions are two relatively stable valance states in the natural samples [3]. Although Cr(III) is an essential component for some biological activities, Cr(VI) is categorized as one of the most toxic chemical species, being an agent for various cancers [2,4]. Thus, the removing of hexavalent chromium from industrial wastewater before discharging to the environment is a crucial concern as well as a challenging problem in industries from economical view point.

Liquid-liquid extraction [5-8], facilitated transport through liquid membrane [9-12], adsorption by activated carbon [13-16] and ion exchange [17-20] are among the thechniques frequently used for recovering of chromium ions. Nowadays, membrane technologies have gained an important role in a variety of industries such as water desalination, food processing and medical applications [12,21,22].

Depending on the chemical conditions, hexavalent chromium ions are found as chromate (CrO_4^{2-}), bichromate ($HCrO_4^-$), dichromate ($Cr_2O_7^{2-}$) and trioxochlorochromate (CrO_3Cl^-) species in aqueous solutions [3,7,23]. Therefore, the strategies regarding the separation of these ions are mainly based on the phase transfer process via the ion pair formation mechanism with a suitable counter cation. Amines, Cyanex extractants (organophosphorus compounds), Aliquat 366 and quaternary ammonium salts are among the extractant and mobile carrier agents used for such proposes [8-12]. These extractant-carriers have some drawbacks concerning the back extraction (stripping) of metal ions from organic phase. This process is important with respect to the problems encountered usually with the direct analysis of the metal ions in the organic phase on the one hand and lowering the consumption of organic solvents and recycling them in industrial process on the other.

It is noteworthy that, since the industrial waste, especially that of chromium plating plants, is normally acidic, a major part of these studies relates to the separation and removal of chromium ions from such solutions.

Size selection binding characteristics of crown ethers are the basis for many investigations concern the separation of metal ions by this class of macrocyclic receptors, where they extract the cations by a solvation mechanism [24,25]. Beside this, crown ethers have been also used for the extraction of anionic metal ion complexes

from aqueous phases [26-35]. In such applications a positively charged lipophile species is formed by complexation of a suitable cation with the crown ether. This counter cation conveys the anionic complex into the organic phase via an ion pair formation mechanism.

The phase transfer ability of crown ethers in the ion pair formation extraction systems has been evaluated by *Koshima et al.* [26-28] and the kinetic of Cr(VI) transport through bulk liquid membrane containing DC18C6 based on a two-film theory model has been studied by *Burgard et al.* [29,30].

In this report we evaluate and compare the mobile carrier properties of crown ethers- 12-crown-4 (12C4), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6) nitrobenzo-18-crown-6 (NB18C6) and dicyclohexyl-18-crown-6 (DC18C6) (Fig.1) dissolved in dichloromethane, for the extraction of chromium(VI) ions from sulfuric and hydrochloric acid solutions (feed phase), and their release into distilled water (receiving phase). The effect of parameters influencing the transport efficiencies of Cr(VI) oxanions by DC18C6 is investigated and discussed. The selectivity and reproducibility of the transport experiments are evaluated. The method is used for the removal of hexavalent chromium ions from two industrial samples.

EXPERIMENTAL
Materials

Crown ethers 12-crown-4, benzo-15-crown-5, 18-crown-6, dibenzo-18-crown-6, nitrobenzo-18-crown-6, dicyclohexyl-18-crown-6 and dicyclohexyl-18-crown-6 (mixture of isomers) were used as received (Merck or Fluka). Diluents (Merck) used were washed three times with distilled water in order to remove the diluent stabilizers and saturate them with water. CrO_3, KOH, and hydrated manganese, iron, cobalt, nickel, copper, zinc and lead nitrates (Merck) were used for preparation of the corresponding solutions. Sulfuric and hydrochloric acids (Merck) were used throughout the experiments.

Apparatus

A double beam spectrophotometer (Shimadzo, UV-240) was used for the determination of Cr(VI) concentration in the single species transport experiments by adjusting the pH of solution to 11 and measuring the absorbance at 372 nm. Analysis of the metal ions in
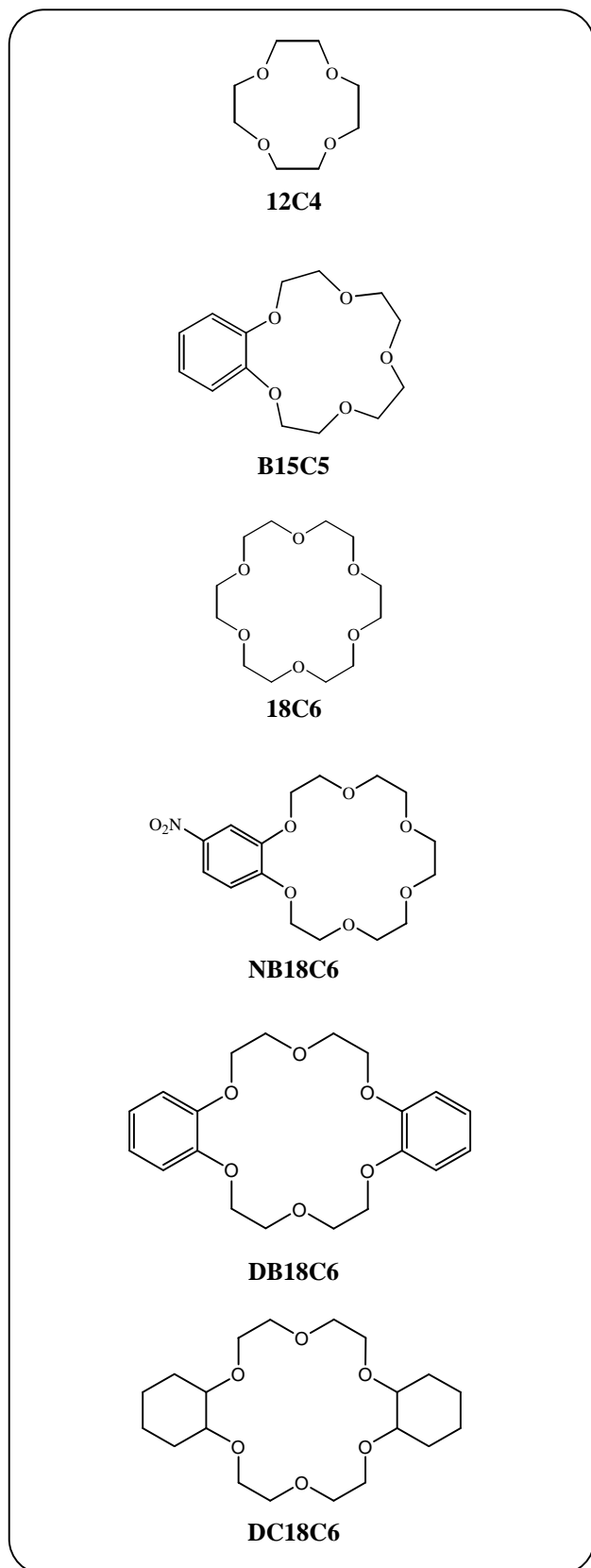
Fig. 1: Crown ethers used in this work.

competitive experiments was performed by using a flame atomic absorption spectrometer (Varian, AA-220).

Transport Experiments

The experimental set-up used for the transport experiments was a glass apparatus described elsewhere [35]. Temperature of the solutions was kept constant (25.0±0.1 ℃) using a thermostated water circulating through the jacket of the cell. The source phase contained 10 ml of 10^{-3} M chromium ions in sulfuric or hydrochloride acid solutions. The receiving phase included 10 ml of distilled water. The aqueous phases are bridged by a dichloromethane solution (20 ml) of DC18C6 placed below the aqueous solutions. The organic layer was stirred constantly (150 rpm) by a Teflon-coated magnetic bar. It is confirmed that without DC18C6 in the organic phase, transfer of chromium ions, from both sulfuric and hydrochloric acid solutions across the membrane does not take place.

RESULTS AND DISCUSSION

Comparison of the carrier properties of the crown ethers

The ionophore nature of the cavity of crown ethers 12C4, B15C5, 18C6, NB18C6, DB18C6 and DC18C6 makes possible the complexation of hydrogen ions. The resulted oxonium ion-crown ether complexes extract the oxanions containing hexavalent chromium ions from acid aqueous phase through the liquid membrane into the receiving phase. This ability is verified by the transport experiments of Cr(VI) ions (10^{-3} M) from acid solutions (2.5 M sulfuric acid and 2 M hydrochloric acid) into a distilled water receiving phase through a bulk liquid membrane containing a crown ether (0.02 M) in dichloromethane (Fig. 2).

The results reveal the following efficiency order for the examined crown ethers; DC18C6 > DB18C6 > 18C6 > NB18C6 > B15C5 > 12C4 for the experiments from sulfuric acid solutions, and DC18C6 > NB18C6 > B15C5 > 18C6 > DB18C6 > 12C4 from hydrochloric acid solutions. The highest percentage of transported Cr(VI) from both acid media, is found by using DC18C6. The observed orders can be interpreted by considering two parameters i.e. the stability of the HCE^+ complexes (CE is the crown ether), and the distribution of the crown ethers between organic and aqueous phases. The latter parameter depends on the lipophilic nature of the ligands.

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The logarithm of the stability constant for HCE$^+$ complexes for 12C4, 18C6, DB18C6 and DC18C6 in acetonitrile determined by the potentiometric methods at 25 ºC are 2.2, 6.5, 3.7 and 8.2, respectively [36]. Such data for the other investigated crown ethers is not available. Considering these values, the efficiency of the transport from hydrochloric acid solution through the membranes containing these crown ethers i.e. DC18C6 > 18C6 > DB18C6 > 12C4, can be well described. In the presence of sulfuric acid the efficiency order presented by 18C6 and DB18C6 is inverted. This may be attributed to a lower distribution of 18C6 than DB18C6 in the presence of H$_2$SO$_4$ in comparison to that in the presence of HCl.

It is noteworthy that a complete interpretation of these data needs the information inside the stability constant of proton complexes by all studied crown ethers and the values of the distribution of the ligands between organic and aqueous phases as well.

Effect of diluent

Characteristics of diluent used in liquid pertraction affect the performance of the mobile-carrier agents. In order to investigate the effect of this parameter on the efficiency of DC18C6, a series of transport experiments of Cr(VI) ions from both sulfuric and hydrochloric acid solutions has been performed. Carbon tetrachloride, chloroform, dichloromethane and 1,2- dichloroethane were the studied diluents. The results are shown Fig. 3. It is seen that the highest extraction efficiency of Cr(VI) ions from both acid media is obtained by using dichloromethane and 1,2- dichloroethane. We used dichloromethane through this study. This diluent is cheaper than 1,2-dichloroethane.

Influence of carrier concentration

In the facilitated transport processes, a carrier plays the role of a phase transfer catalyst. The carrier takes the analyte in the feed/membrane interface and release it at the membrane/receiving phase interface. Therefore, the carrier concentration can alter the rate of the transfer. This effect was assessed by carrying out five experiments with different DC18C6 concentration in the organic layer (Fig. 4). The values of transported chromium ions were enhanced with increasing the crown ether concentration.
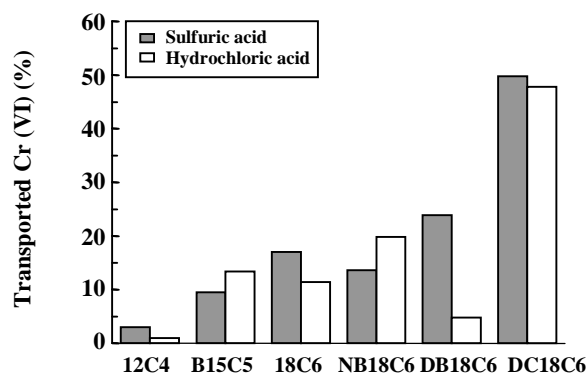
Fig. 2: Percentage of transported Cr(VI) ions from sulfuric (2.5 M) and hydrochloric acid (2 M) feed phases (initial Cr(VI) concentration 10^{-3} M, 10 ml) through the membrane (DC18C6 in dichloromethane, 0.02 M, 20 ml) into the receiving phase (distilled water, 10 ml) after 4 h under stirring of the organic phase (150 rpm) at 25 ºC.
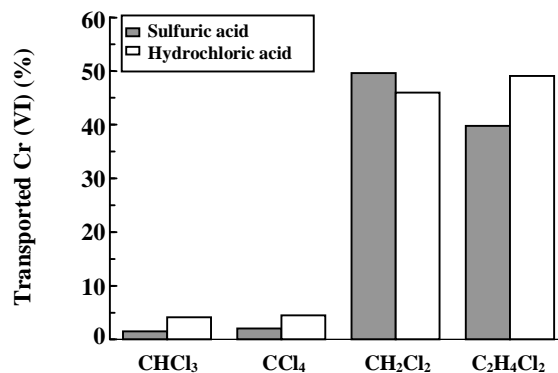
Fig. 3: Percentage of transported Cr(VI) ions from sulfuric and hydrochloric acid solutions through the membranes containing crown ethers in different diluents. Experimental conditions: see Fig. 2.
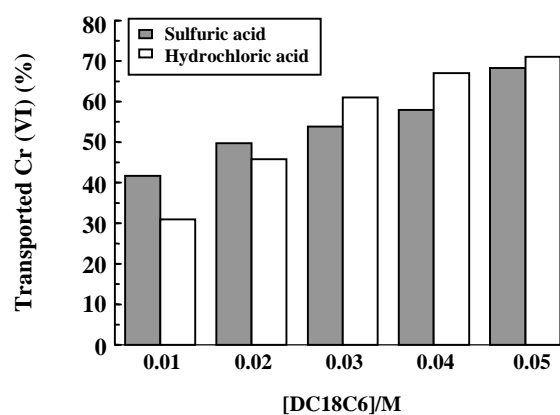
Fig. 4: Percentage of transported Cr(VI) ions from sulfuric and hydrochloric acid solutions through the membranes containing different concentration of crown ethers. Experimental conditions: see Fig. 2.
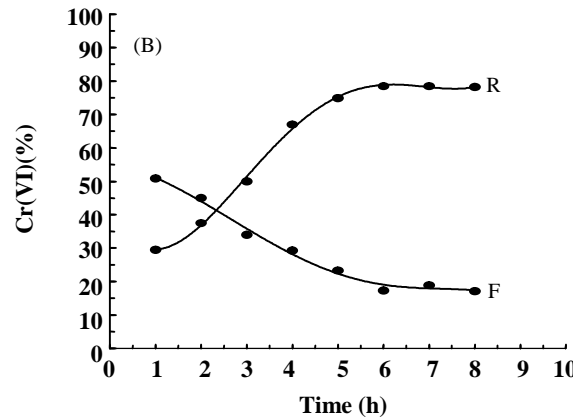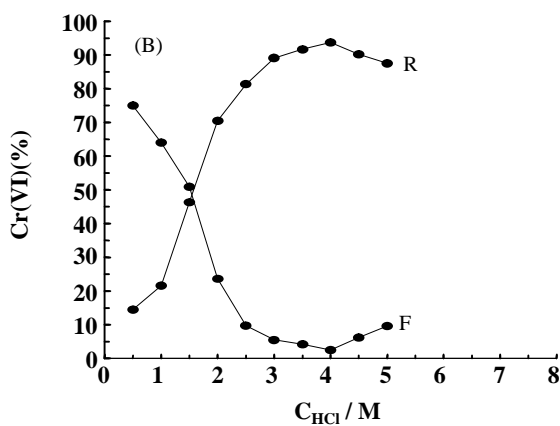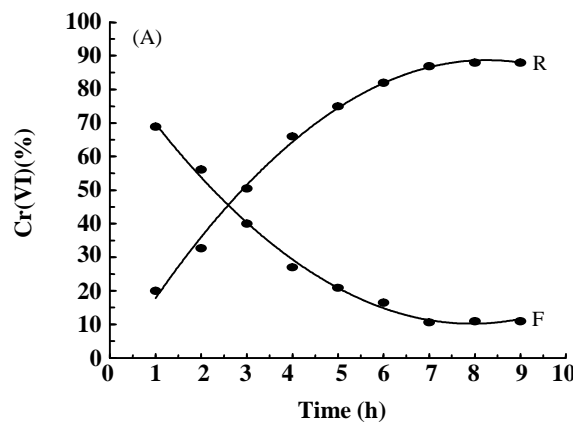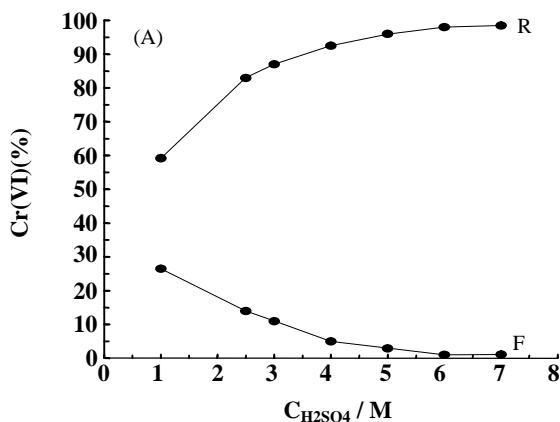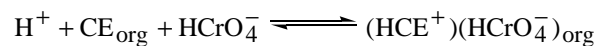
Fig. 5: Variation of the Cr(VI) concentration in the feed (F) and receiving (R) phases as a function of sulfuric (A) and hydrochloric (B) acid concentration in the feed phase. Experimental conditions: see Fig. 2 except for the carrier concentration that is 0.05 M.
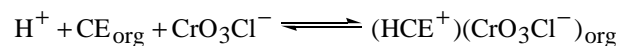
Fig. 6: Variation of the Cr(VI) concentration in the feed (F) and receiving (R) phases as a function of time in the presence of 2.5 M sulfuric (A) and 2 M hydrochloric (B) acid solutions. Other experimental conditions: see Fig. 5.

Effect of acid concentration in the feed phase

Under the experimental conditions (low chromium and high acid concentrations in the feed phase), it is suggested that the major chromium species are found as $HCrO_4^-$ and CrO_3Cl^- [3] in the presence of sulfuric and hydrochloric acid solutions, respectively. Therefore, the uptake of Cr(VI) ions can be described by the following equations:

$$H^+ + CE_{org} + HCrO_4^- \rightleftharpoons (HCE^+)(HCrO_4^-)_{org}$$

and

$$H^+ + CE_{org} + CrO_3Cl^- \rightleftharpoons (HCE^+)(CrO_3Cl^-)_{org}$$

Here, the subscript "org" denotes the species present in the membrane. Therefore, the formation of oxonium ion-DC18C6 complex (HCE^+) depends on the acid concentration in the aqueous phase. This reveals that the acid concentration may influence the efficiency of the process. In order to investigate the effect of this parameter, the transport experiments of chromium(VI) ions from sulfuric and hydrochloric acid solutions by DC18C6 in dichloromethane as a function of acid concentration in the aqueous phases have been performed (Fig. 5). It is seen that the extraction value of Cr(VI) ions increases with increasing the acid concentration. Under specified conditions (see the figure caption) a quantitative transport is achieved beyond 6 and 4 M acid concentration from H_2SO_4 and HCl solutions, respectively.

The Cr(VI) fluxes in the presence of hydrochloric acid decrease above 4 M acid concentration. This can be explained in terms of competition between CrO_3Cl^- and Cl^- ions.

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Table 1: Percentage of transported metal ions (T%) and the ratio of the chromium to the other metal ions fluxes (J_{Cr}/J_{M}), from H₂SO₄ and HCl solutions of the mixture of seven metal ions by DC18C6 in dichloromethane into receiving phase [a].

| Ion	T%		J_{Cr}/J_{M}	
	H_2SO_4	HCl	H_2SO_4	HCl
Cr (VI)	89	94.6	1	1
Ni(II)	0.2	1.7	445	55.6
Co(II)	[b]	0.6	-	157.7
Pb(II)	[b]	0.14	-	657.7
Mn(II)	[b]	[b]	-	-
Zn(II)	1.1	13.7	81	6.9
Fe(III)	0.9	11.0	98.9	8.6

a) Feed phase (10 ml): initial concentration of each metal ion, 10^{-3}M; acid concentration, H₂SO₄ (HCl), 6M (4M). Receiving phase (10 ml): distilled water. Membrane (20 ml): DC18C6 (0.05 M) in dichloromethane. Time: 8h. Stirring rate: 150 rpm. Temperature: 25 °C. b) Less than detection limit.

Variation of Cr(VI) concentration in the feed and receiving phases as a function of time

The transport efficiency is a time dependent process. A sufficient time allows achieving a quantitative extraction of analyte from the feed phase into the receiving phase in a uphill transport. Variations of Cr(VI) concentration in the feed and srtripping phase as a function of time in receiving phase are shown in Fig 6. It is observed that a relatively quantitative transport of chromium ions can take place after 7 hours for the extraction from sulfuric acid (2.5 M). However, the equilibrium is achieved after 8 hours for the transport from hydrochloric acid (2 M) solution.

Selected conditions of the transport process

Four replicate transport experiments of Cr(VI) ions (initial concentration 10^{-3} M) from sulfuric acid (6 M) through a dichloromethane solution of DC18C6 (0.05 M) show an average of 95.6 (±1.3)% of chromium ions are transported into the receiving phase (distilled water) after 8 h. However, in the similar conditions except for the concentration of acid which was 4 M, the amount of initial chromium concentration was determined to be 95.0 (±1.2)%.
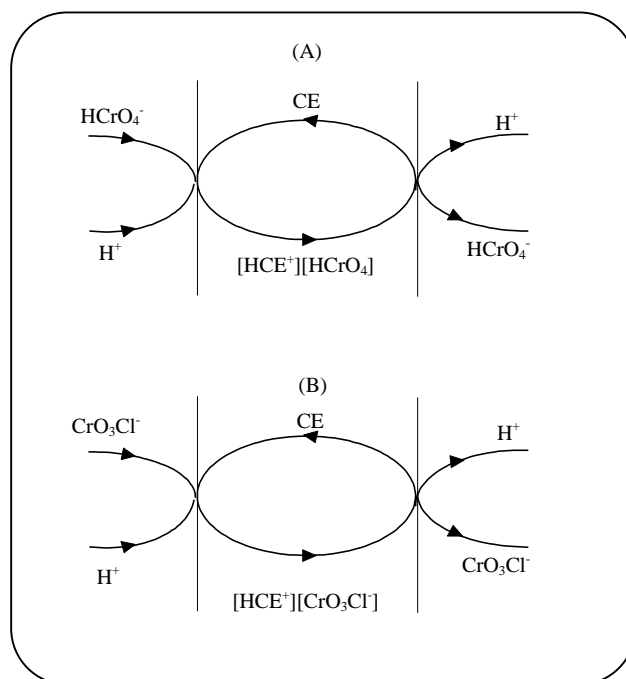
Fig. 7: Schematic representation of the transport of Cr(VI) ions from sulfuric (A) and hydrochloric (B) acid solutions by DC18C6 (CE).

Stability of the membrane

The stability of the membrane was assessed by measuring the transported amount of chromium ions in repeated experiments which were carried out by renewal the feed and receiving phases.

An average of 96.1 (±0.7) % and 95.8 (±0.9) % of chromium ions for four replicate experiments in the presence of sulfuric acid (6 M) and hydrochloric acid (4 M) in the feed phase, respectively, reveals a good stability of the membrane.

Selectivity of the process

The selectivity of the method toward Cr(VI) ions was tested by performing the removal of these ions from the mixtures containing Ni(II), Co(II), Pb(II), Mn(II), Zn(II) and Fe(III) ions in the presence of sulfuric and hydrochloric acid solutions. The experimental conditions together with the results are given in table 1.

The results show higher transport efficiency from hydrochloric acid solutions. However, if one compares the relative fluxes of the chromium ions to that of the other ions it is seen that this advantage is not accompanied with a better selectivity, with respect to that from the sulfuric acid solutions. This can be attributed to the possibility of

Table 2: Application of the method for the separation of Cr(VI) ions from real samples in the presence of H_2SO_4 (6 M), using a dichloromethane membrane containing DC18C6 (0.05M).[a]

	Ion	$[M^{n+}]_0$[b]	$[M^{n+}]_R$[c]	T%[d]	$[Cr]_0/[M]_0$[e]	$[Cr]_R/[M]_R$[f]
Sample 1	Cr(VI)	2.78×10^{-3} M	2.20×10^{-3} M	79.1	1	1
	Ni(II)	2.11×10^{-4} M	-	-	13	-
	Co(II)	2.88×10^{-4} M	-	-	9.7	-
	Pb(II)	1.39×10^{-4} M	-	-	20	-
	Mn(II)	8.08×10^{-5} M	-	-	34.4	-
	Zn(II)	4.38×10^{-4} M	5.31×10^{-5} M	12.1	6.4	41.4
	Fe(III)	3.55×10^{-4} M	3.97×10^{-5} M	11.2	7.8	55.4
Sample 2	Cr(VI)	3.44×10^{-3} M	2.16×10^{-3} M	62.8	1	1
	Ni(II)	2.17×10^{-3} M	1.27×10^{-6} M	0.06	1.6	1700
	Co(II)	1.27×10^{-3} M	5.01×10^{-4} M	39.4	2.7	4.3
	Pb(II)	1.53×10^{-3} M	5.32×10^{-7} M	0.03	2.2	4060
	Mn(II)	7.53×10^{-4} M	7.08×10^{-6} M	0.9	4.6	305
	Zn(II)	3.38×10^{-3} M	7.87×10^{-4} M	23.3	1	2.7
	Fe(III)	2.51×10^{-3} M	1.29×10^{-5} M	0.5	1.4	167

a) "Sample 1" is obtained by dilution of an electroplating bath solution before use and "Sample 2" is a diluted electroplating waste solution. b) Initial concentration of the metal ions. c) concentration of the ions in the receiving phase after 8 h. d) Transported value of the ions in percent. e) [Cr]/[M] ratio in the samples before performing the transport experiment. f) [Cr]/[M] ratio in the receiving phase at the end of the experiment.

Table 3: Application of the method for the separation of Cr(VI) ions from real samples in the presence of HCl (4 M), using a dichloromethane membrane containing DC18C6 (0.05M).

	Ion	$[M^{n+}]_0$[b]	$[M^{n+}]_R$[c]	T%[d]	$[Cr]_0/[M]_0$	$[Cr]_R/[M]_R$[f]
Sample 1	Cr(VI)	2.78×10^{-3} M	1.97×10^{-3} M	70.8	1	1
	Ni(II)	2.11×10^{-4} M	2.70×10^{-6} M	1.2	13	730
	Co(II)	2.88×10^{-4} M	5.65×10^{-7} M	0.2	9.7	3490
	Pb(II)	1.39×10^{-4} M	1.00×10^{-6} M	0.7	20	1970
	Mn(II)	8.08×10^{-5} M	-	-	34.4	-
	Zn(II)	4.38×10^{-4} M	7.38×10^{-5} M	16.8	6.4	26.7
	Fe(III)	3.55×10^{-4} M	4.65×10^{-5} M	13.0	7.8	42.4
Sample 2	Cr(VI)	3.44×10^{-3} M	2.03×10^{-3} M	59	1	1
	Ni(II)	2.17×10^{-3} M	5.45×10^{-6} M	0.25	1.6	372.5
	Co(II)	1.27×10^{-3} M	1.25×10^{-6} M	0.1	2.7	1624
	Pb(II)	1.53×10^{-3} M	9.75×10^{-6} M	0.6	2.2	208.2
	Mn(II)	7.53×10^{-4} M	-	-	4.6	-
	Zn(II)	3.38×10^{-3} M	5.01×10^{-4} M	14.8	1	4.1
	Fe(III)	2.51×10^{-3} M	3.75×10^{-4} M	14.9	1.4	5.4

a-e) See the footnotes of table 2.

the formation of the anionic chloride complexes of the other metal ions in hydrochloric acid solution.

It is noteworthy that, the presence of other metal ions in the mixture decreases the percentage of chromium transported in comparison with those in the single species transport experiments. This probably being due to a multi-ion competition or crowding effect [12,37].

Suggested Mechanism of the processes

The transport mechanism of Cr(VI) ions from sulfuric and hydrochloric acid solutions are presented in Fig. 7. The oxonium ion-crown ether complexes ([HCE$^+$]) are formed at the first interface. The ion pair formation of anionic chromium species with these complexes formed a lipophilic species diffusing in the organic layer. At the second interface because of low H$^+$ concentration in the receiving phase the ion-pair is dissociated and thus the chromium species released in this phase.

Application of the method

The applicability of the processes was checked by the separation of Cr(VI) ions from two real samples provided by two different electroplating industries (tables 2 and 3). "Sample 1" is a diluted solution of a chromium plating bath industry before use, and "Sample 2" is a diluted solution of a used chromoplating bath obtained from another factory. The results demonstrate that the method is able to extract efficiently the chromium ions in the samples from sulfuric as well as hydrochloric acid solutions.

These results show an enhancement of the ratio of Cr(VI) ions with respect to the other metal ions. For the transport from both sulfuric and hydrochloric acid the efficient separation is observed with respect to Ni, Co, Pb and Mn ions. The enhancement factor is better for the separation from sulfuric acid in comparison with those obtained for the separation from hydrochloric acid solutions. As mentioned earlier this can be a consequence of the formation of anionic chloro-complexes of the metal ions in chloride ion media.

CONCLUSIONS

The removal of Cr(VI) ions from sulfuric and hydrochloric acid solutions can be performed by using crown ethers 12-crown-4, benzo-15-crown-5, 18-crown-6, nirobenzo-18-crown-6, dibenzo-18-crown-6 and dicyclohexyl-18-crown-6 in dichloromethane via an ion

pair formation mechanism. Among the studied crown ethers, DC18C6 has shown the highest mobile carrier efficiency.

Competitive transport experiments of Cr(VI) ions show a significant selectivity towards these ions especially from sulfuric acid solutions. Although the selectivity of the method is better for the extraction of chromium ions from sulfuric acid, the efficiency of the method is higher for the separation of these ions from hydrochloric acid media. The lower separation efficiency in hydrochloric acid solutions is attributed to the formation of extractable anionic chloro-complexes of other metal ions. The method is successfully used for lowering the chromium concentration in synthetic and real samples.

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