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A Study on Complexation and Transport of Cr(III) Through a Chromogenic Aza Crown Liquid Membrane

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A new chromogenic aza-crown-ether N-(8-hydroxyquinoline-7-methylene)-4-azadibenzo-18-crown-6-ether (HQMADCE) was synthesized through the condensation reaction of 4-azadibenzo-18-crown-6-ether, 8-hydroxy quinoline and formaldehyde. The synthesized chromogenic crown was characterized by various spectroscopic techniques and its complexation with Cr(III) was studied. The parameters like extraction constant (K_{ex}), stability constant (β), free energy change (ΔG), enthalpy change (ΔH) and change in entropy (ΔS) were calculated. Subsequently transport of Cr(III) through a bulk liquid membrane containing HQMADCE as carrier was studied. The permeation of metal was investigated as a function of various experimental variables viz. pH, carrier concentration, metal concentration and time. Furthermore, interference by other ions was also studied.

Keywords: Chromogenic azacrown ether, Cr(III) transport, liquid membrane, spectrophotometry

1 Introduction

The design and study of artificial membrane carriers have gained importance in the recent times. A study of transport through liquid membranes provides an insight into transport of metals across cell walls of living systems and their biological effects. Crown ether analogues with their ability to encapsulate metal ions have been widely explored for their transport properties. Since these model systems are much simpler than natural ionophores, they are easily analyzed (1) and many have been developed into practical molecular devices for purification, resolution of racemates (3), ion-selective electrodes (1), carriers for drug delivery (4)etc. Chromium is a naturally occurring element found in rocks, animals, plants, soils and in volcanic gases. Cr (VI) which is extensively used in ferrous and non-ferrous alloys, electroplating and leather industry, also shows marked toxicity in human beings. Transport studies of Cr (VI) have been reported by many workers (4–7). On the other hand for the trace amount of Cr (III), which is known to be a micronutrient for mammals, only few reports are available (8–9). Recent studies have shed lighton the potential role of chromium in maintaining proper carbohydrateand lipid metabolism at molecular level along with insulin (12). In some cases, symptoms of diabetes were reversed on addition of chromium (III) in the diet (13). A low chromium level has also been observed in the nails and scalp hairs of schizophrenics and alcoholics.

In the present investigation new chromogenic aza crown ether has been synthesized to study complexation, transport and spectrophotometric identification of Cr (III). The azacrown ether has a cavity formed from hydrophobic alkyl groups and hydrophilic donor atoms like oxygen and nitrogen, and it complexes with the metal cations that can pass through the lipophilic biological membranes. The binding between cations and macrocyclic ligand is highly selective as it depends on their ionic radii and electronic interactions. The latter is further enhanced by the attachment of a chromogenic 8-hydroxyquinoline moiety to the azacrown core. The newly synthesized N-(8-hydroxyquinoline-7-ylmethyl)-4-azadibenzo-18-crown-6-ether (HQMADCE) forms a neutral complex with Cr(III) which was not only partitioned into an organic phase but also estimated spectrophotometrically.

2 Experimental

2.1 Reagents and Instrumentation

All the chemicals used are of A R Grade of E-Merck, unless otherwise specified. 4-Aza dibenzo 18-crown-6 ether was prepared in the laboratory by method reported earlier (15). Buffer solutions are prepared as described elsewhere (13).

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Melting points were taken in sealed capillary tube using a Toshniwal (India) melting point apparatus and are uncorrected. Absorption spectra were recorded on Hitachi 3210 spectrophotometer with 10 mm quartz cell. Infrared spectra were recorded on FT-IR/410, JASCO Spectrometer. The ^{1}H-NMR and ^{1}C-NMR spectra were recorded on DRX 300 Spectrophotometer operating at 200 MHz in $CDCl_3$with TMS as internal standard. The FAB mass spectrum was recorded on a JEOL SX 102/DA-6000 Mass spectrometer. ICP-AES studies were carried out on Plasma scan model 710 The following experimental conditions were set for ICP-AES. Rf 27.12 MHz, incident power 200 Watts, GMK nebulizer, sample concentration 1 ng mL^{-1}, Rf power 5 Watts, Observation height 14 nm, argon coolant flow rate 10 l min^{-1}, argon carrier flow rate 1 L min^{-1}, intergap period 10 s, resolution 0.004, pump flow rate 1 mL, wavelengths 357.87 nm for Cr.

2.2 Cr (III) Solution (0.01 M)

Cr (III) stock solution was prepared by dissolving 0.666 g of $CrCl_3$. $6H_2O$ in 2 mL conc. H_2SO_4 and diluting to 250 mL with distilled water, the final concentration was determined spectrophotometrically (13).

2.3 Sample Preparation

A known weight of the biological sample (10 g each) was washed at 250°C in a crucible and then transferred to a 200 mL pyrex beaker. The residue was digested with 100 mL conc. HNO_3 for an hour and evaporated to dryness. The residue was redissolved in 0.1 M HCl and the volume rose to 100 mL.

2.4 Synthesis of N-(8-hydroxyquinoline-7-ylmethyl)-4-azadibenzo-18-crown-6Ether (HQMADCE)

To a solution of 4-aza dibenzo 18-crown-6 ether (2 g, 2.78 mmol) in 50 mL THF, 8-hydroxyquinoline (0.41 g, 2.78 mmol) and formaldehyde (0.22 g, 2.78 mmol) was added. The mixture was stirred for 75 h at room temperature. The solvent was removed *in vacuo* and the mixture obtained was purified on a silica gel column. The compound recovered on recrystallization from ethanol gave 1.8 g (63%) of a pale yellow solid. mp 183–185°C. $C_{30}H_{32}N_2O_6$ (MW. 516) Elemental analysis, Expt. C, 69.73; H, 6.25; N, 5.41% Calc: C, 69.75; H, 6.24; N, 5.42%.

IR (cm^{-1}): 3500 (O-H stretching), 1507(C=N stretching), 1340 (C-N stretching), 1254 (asymmetrical C-O-C stretching), 1057 (symmetrical C-O-C stretching).

^{1}H-NMR (ppm, $CDCl_3$): 8.86 (1H, m, quinoline ring proton), 8.18 (1H, m, quinoline ring proton), 7.3 (3H, m, aromatic protons) 6.73-6.9 (8H, m, aromatic protons), 4.19–3.86 (12H, m, O-CH_2, azacrown ring), 3.37 (2H, s, CH_2-N-), 2.46 (4H, m, N-CH_2, azacrown ring).

^{13}C-NMR (ppm, $CDCl_3$): 53.4 (C1); 72.3(C2); 146.7 (C3); 115.0 (C4); 121.0 (C5); 68.9 (C6); 45.3 (C7); 121.8 (C8); 128.4 (C9); 120.2 (C10); 127.5 (C11); 131.2 (C12); 137.9 (C13); 147.7 (C14); 145.5 (C15); 150.6 (C16).

Mass (FAB): 516(M^+), 489, 358, 328, 301, 257, 163, 121.

2.5 Procedure for Extraction of Cr(III)

An aliquot of Cr (III) solution (1×10^{-4} M to 1×10^{-2}M) was transferred into a 60 mL separation funnel and a 5 mL aliquot of 0.1% (w/v) HQMADCE reagent solution in ethanol was added. The pH of the solution was adjusted between 2.5 to 3.5 with the HCl-citrate buffer and contents were extracted into 5 mL isoamyl alcohol. The mixture was shaken gently for 5 min and allowed to stand at 25°C in a thermostat. The organic phase was separated and dried over anhydrous sodium sulphate and transferred into a 10 mL volumetric flask. The extraction was repeated with 3 mL isoamyl alcohol. Finally, the combined extracts were diluted to 10 mL with isoamyl alcohol. The absorbance of the bright yellow colored complex was measured at 410 nm against the reagent blank. The extractions were carried out in the temperature range of 298–318 K at a difference of 5 K.

2.6 Procedure for the Transportation of Cr (III)

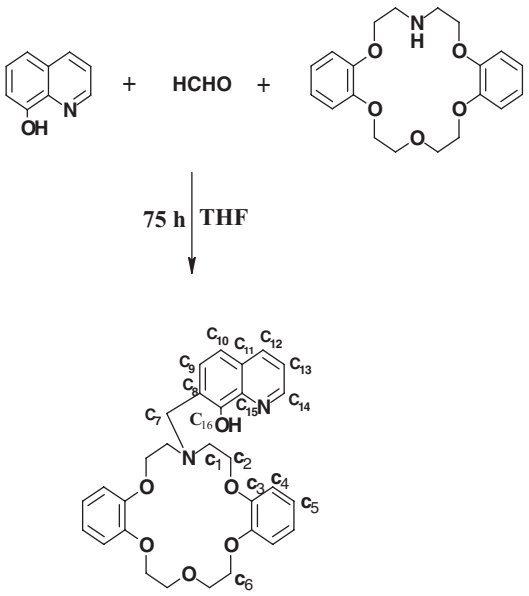
A 0.1% (w/v) solution of HQMADCE in chloroform was used as a liquid membrane, and transferred to specially designed glass apparatus, which was maintained at 25±1°C.A 30 ml aliquot of solution containing Cr(III) (5–25 mg) at pH 2.5 to 3.5 was taken as source phase. 30 mL 2M H_2SO_4 was used as receiving phase. The membrane phase was stirred with a Teflon stirrer. 0.2 mL aliquots of samples were taken at intervals of 5 min from the source and the receiving phase and chromium (III) was determined spectrophotometrically and by ICP-AES. The procedure was continued until the receiving phase showed a constant concentration of chromium ions. Transport of chromium was negligible in the absence of carrier.

3 Results and Discussion:

The new chromogenic azacrown ether (HQMADCE) was synthesized according to Scheme 1. The 8-hydroxyquinoline moiety was attached to azacrown moiety using methylene group as a spacer (14). The product was characterized by elemental analysis, IR, NMR and Mass spectroscopy.

3.1 Spectral Characteristics of Cr (III)-HQMADCE

The yellow colored Cr (III)-HQMADCE complex extracted into iso-amyl alcohol at pH range 2.5–3.5, showed



Sch. 1. Synthesis of HQMADCE.

maximum absorbance (λ_{max}) at 410 nm. The reagent blank does not show any absorbance at this wavelength. The system obeys Beer's law in the range of 9.6×10^{-4}–1.15×10^{-2} M of Cr (III) and the molar absorptivity was 1.38×10^4 l mol^{-1} cm^{-1}. The Sandell's sensitivity (15) is 0.0038 μg/mL and Ringbom range was 0.07–5.6 μg/mL of Cr (III). The regression analysis represents concentration (ppm) = 1.880 × absorbance +0.025 with correlation coefficient 0.9998 for Cr (III)-HQMADCE complex. The method is more sensitive and selective than the method for the direct determination of the Cr (III) by 8- hydroxyquinoline having molar absorptivity less than 1×10^4l mol^{-1} cm^{-1}. The stability constant calculated according to Harvey and Manning (16) method for Cr(III)-HQMADCE complex was found to be 4238.06.

3.2 Optimization of Various Extraction Parameters

Maximum extraction of Cr (III) with HQMADCE is obtained in the pH range 2.5–3.5, but as the pH increases or decreases, the extraction also decreases. It was observed that 4 min of shaking time was sufficient for quantitative extraction and color of the extracted complexes was stable up to 20 h. The effect of pH on the extraction of Cr (III) is shown in Figure 1.

Extraction with varying concentrations of HQMADCE showed that 5 mL of 0.1% (w/v) reagent was adequate for the quantitative extraction of Cr(III). The extraction of Cr (III)-HQMADCE complex was also carried out with various solvents viz. isoamyl alcohol, carbon tetrachloride, dichloromethane, benzene, chloroform and toluene. Quantitative extraction was obtained in isoamyl alcohol and was selected for further studies.

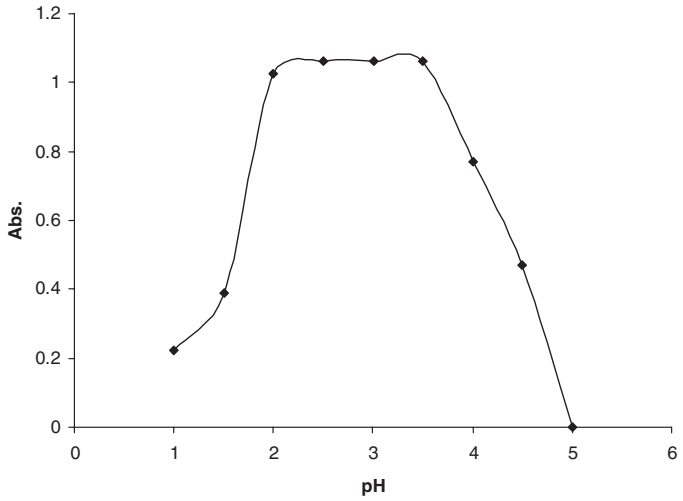


Fig. 1. Effect of pH on Cr(III) extraction.

3.3 Stoichiometry of the Complex

The composition of Cr (III)-HQMADCE complex had been studied by the slope ratio method (17). The plot of (log Dm) against –log (HQMADCE) gave a straight line of slope 1.08 indicating that the stoichiometry of the extracted species Cr (III):HQMADCE is 1:1 (Fig. 2).

The organic phase containing Cr (III)-HQMADCE complex was evaporated to dryness, washed with a few milliliters of cold isoamyl alcohol and dried under vacuum. A known weight of the dried complex was digested in an acid mixture and the Cr (III) content determined by ICP-AES was 8.12%. This corresponds to the calculated value of 8.14% for Cr(III)-HQMADCE complex ($C_{30}H_{31}Cl_2CrN_2O_6$).

3.4 Determination of Physical Constants

In order to test the stability of the chromium complex, the physical parameters like extraction constant (K_{ex}),

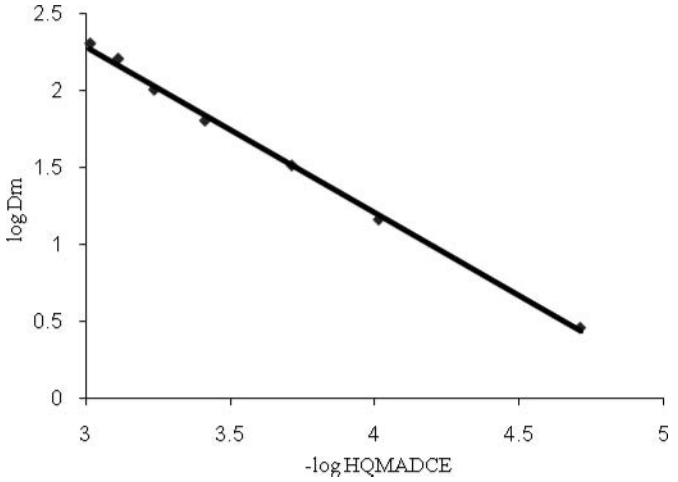


Fig. 2. Plot of (log Dm) against (-log HQMADCE) for Cr (III)-HQMADCE complex.

stability constant (β), free energy change (ΔG), enthalpy change (ΔH) and change in entropy (ΔS) were obtained. The extraction of the metal ions was performed at various temperatures in the range of 298–318 K and the mathematical calculations were as follows:

$$Cr^{3+} + HL \rightarrow Cr(L)^{2+} + H^{+}$$

$$K_{ex} = \frac{[Cr(L)^{2+}]_{org}[H^{+}]_{aq}}{[Cr^{3+}]_{aq}[HL]_{org}}$$

$$\log K_{ex} = \log D - pH - \log[HL]_{org}$$

where D is the ratio of distribution of Chromium in organic and aqueous phase.

[HL] is conc. of ligand in organic phase.

$$\log \beta = \log D + pKa - pH - \log [HL]_{org}$$

The acid dissociation constant of HQMADCE obtained by spectrophotometric method is 8.30 (18). From the values of β at different temperatures, the other thermodynamic constants were determined by the following equations:

$$\log \frac{\beta 2}{\beta 1} = -\frac{\Delta H}{2.303 R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

$$\Delta G = -2.303\, RT \log K_{ex}$$

$$\Delta G = \Delta H - T\Delta S$$

It was observed that with the increase in temperature, the stability of the complex increases as is shown by the decreasing free energy in Table 1. The value of log K_{ex} increases with an increase in temperature, indicating that the selectivity of ligand for the chromium ion increases.

3.5 Effect of Diverse Ions

The effect of diverse ions associated with Cr (III) is given in Table 2. The interference studies were made by measuring the absorbance of the extracted organic phase. The tolerance limit was set as the amount of foreign ions causing a change of ± 0.02 in absorbance. Most of the ions did not interfere under the above mentioned conditions.

Table 2. Effect of diverse ions

Ion	*Added as*	*Tolerance limit (mg)*
Ag^{+}	$AgNO_3$	35
As^{3+}	As_2O_3	35
Be^{2+}	$BeCl_2$	35
Mg^{2+}	$MgCl_2$	35
Ca^{2+}	$Ca(NO_3)_2$	30
Ba^{2+}	$BaCl_2$	30
Sn^{2+}	$Sn(NO_3)_2$	35
Pb^{2+}	$Pb(NO_3)_2$	40
Cd^{2+}	$CdCl_2$	40
Co^{2+}	$CoCl_2$	35
Cu^{2+}	$CuCl_2$	30
Al^{3+}	$AlCl_3$	40
Hg^{2+}	$HgCl_2$	35
Ni^{2+}	$NiCl_2$	40
Fe^{2+}	$FeSO_4$	40
Fe^{3+}	$FeCl_3$	35
Mn^{2+}	$MnCl_2$	35
Zn^{2+}	$ZnCl_2$	30
Ti^{4+}	TiO_2	30
Mo6+	$(NH_4)_6Mo_7O_{24}$	30
Zr^{4+}	$Zr(NO_3)_4$	30
Nb^{5+}	Nb_2O_5	30
Ta^{5+}	Ta_2O_5	35
W^{6+}	Na_2WO_4	30
PO_4^{3-}	Na_3PO_4	40
SO_4^{2-}	$Na_2\,SO_4$	40

3.6 Sample Analysis

In order to test the accuracy and applicability of the proposed method to the analysis of real samples, some reference materials were analyzed. Matrix interference is verified by comparison of the slopes of the calibration graphs with those using standard addition methods. The results of the analysis of biological samples are given in Table 3. In the case of industrial effluents, Cr (VI) was reduced to Cr (III) by adding 2 mL 0.2% hydroxylamine hydrochloride.

3.7 Transportation of Chromium Through Liquid Membrane

The transportation of Cr (III) was studied because of its increasing importance to biological systems. Hence, in the

Table 1. Determination of physical constants

Temperature K	*log D*	K_{ex}	*log* β	ΔH *KJ/mol*	ΔG *KJ/mol*	ΔS *J/mol K*
298	1.61	1.69×10^{4}	9.87	–	−57.0	−214.0
303	1.94	6.60×10^{5}	10.20	−122.5	−58.5	−211.0
308	2.28	2.75×10^{6}	10.54	−122.5	−60.0	−203.0
313	2.32	1.12×10^{7}	10.87	−122.3	−61.2	−196.0
318	2.65	3.55×10^{7}	11.20	−123.3	−62.3	−189.0

Table 3. Estimation of chromium in various samples

	Chromium found ($\mu g/g$)	
Samples	*ICP-AES*	*Spectrophotometry**
Scalp hair	4.9 ± 0.1	4.6 ± 0.1
Finger nails	7.2 ± 0.1	7.1 ± 0.1
Mango	3.8 ± 0.1	3.8 ± 0.1
Grapes	2.5 ± 0.2	2.5 ± 0.2
Effluent (Vatva)	8.0 ± 0.2	7.8 ± 0.2
Effluent (Narol)	7.8 ± 0.2	7.8 ± 0.2
Effluent (Naroda)	9.1 ± 0.2	9.0 ± 0.2

* = Average of six determinations

present investigation, focus is on the transportation of Cr (III) at the temperature condition of biological systems. The study may help in understanding the transportation in biological systems.

The conditions for transport such as pH of source and receiving phase, concentration of ligand in the membrane, solvent etc. were optimized.

3.8 Kinetics of Transportation

The overall transport process consists of a series of complexation, decomplexation and diffusion steps at the two independent interfaces. The equipment designed to study membrane transport is shown in Figure 3 and the mechanism of transport is shown in Figure 4. Cr (III) ion concentrations, with respect to time, were determined in both donor (C_d) and acceptor (C_a) phases spectrometrically. For practical reasons, the dimensionless reduced concentrations (R) were used:

$$R_d = \frac{C_d}{C_{d0}} \quad R_m = \frac{C_m}{C_{d0}} \quad R_a = \frac{C_a}{C_{d0}} \tag{1}$$

Where C_{d0} is the initial Cr (III) concentration in the donor phase while C_d, C_m and C_a represent the Cr (III)

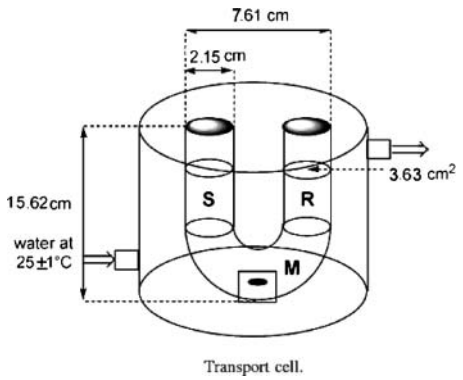


Fig. 3. Design of the transport cell used for the liquid membrane studies.

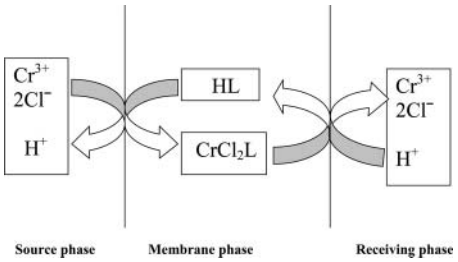


Fig. 4. Mechanism of transportation of Cr(III) through liquid membrane.

concentration in donor, membrane and acceptor phases, respectively. The material balance can be established as $R_d + R_m + R_a = 1$. When R_d, R_m and R_a values are inspected, the results suggest that the Cr (III) ion transport obeys the kinetic laws of two consecutive irreversible first-order reactions according to the kinetic scheme.

$$C_d \xrightarrow{k1} C_m \xrightarrow{k2} C_a \tag{2}$$

Where k_1 is the rate constants of the extraction of Cr (III) from aqueous donor phase to organic membrane phase and k_2 is the rate constant of the stripping of Cr (III) from organic membrane phase to aqueous acceptor phase. Equation 2, for consecutive irreversible reactions, can be described by considering the reduced concentrations as follows:

$$\frac{dR_d}{dt} = -k_1 R_d \equiv J_d \tag{3}$$

$$\frac{dR_m}{dt} = k_1 R_d - k_2 R_m \tag{4}$$

$$\frac{dR_a}{dt} = k_2 R_m = J_a \tag{5}$$

Where J represents the flux. When $k_1 \neq k_2$, integrating Equations 3–5 gives the following expressions:

$$R_d = \exp(-k_1 t) \tag{6}$$

$$R_m = \frac{k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \tag{7}$$

$$R_a = 1 - \frac{k_1}{k_2 - k_1}[k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \tag{8}$$

The maximum values of R_m and t_{max} when $dR_m/dt = 0$, can be written as follows:

$$R_m^{\max} = \left(\frac{k_1}{k_2}\right)^{-k_2/(k_1 - k_2)} \tag{9}$$

$$t_{\max} = \left(\frac{1}{k_1 - k_2}\right) \ln \frac{k_1}{k_2} \tag{10}$$

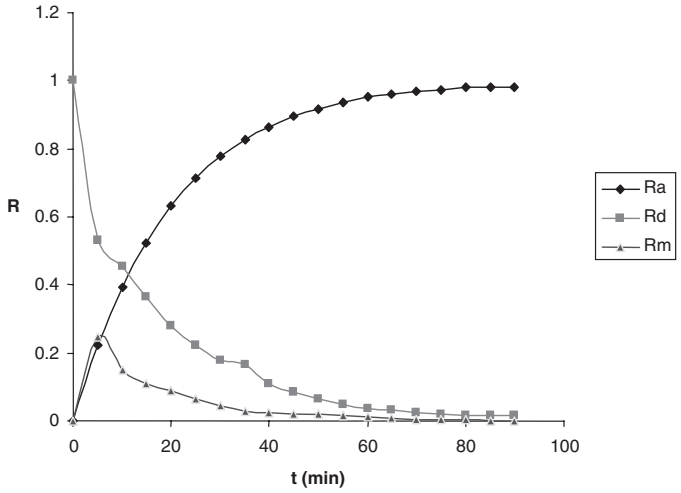


Fig. 5. Time dependence conc. of R_d, R_m and R_a of Cr (III) through liquid membrane.

Where by considering the first-order time differentiation of Equations 6–8 leads to the following forms:

$$\left(\frac{dR_d}{dt}\right)_{\max} = -k_1\left(\frac{k_1}{k_2}\right)^{-k_1/(k_1-k_2)} \equiv J_d^{\max} \tag{11}$$

$$\left(\frac{dR_a}{dt}\right)_{\max} = k_2\left(\frac{k_1}{k_2}\right)^{-k2/(k_1-k_2)} \equiv J_a^{\max} \tag{12}$$

$$\left(\frac{dR_m}{dt}\right)_{\max} = 0 \tag{13}$$

$$\left(\frac{dR_d}{dt}\right)_{\max} = \left(\frac{dR_a}{dt}\right)_{\max} \tag{14}$$

It should be noted that the system is assumed to be in a steady state at $t = t_{max}$, since the concentration of Cr (III) ions in the membrane does not vary with time Equation 13. Consequently, the entrance and exit fluxes are equal having opposite signs.

$$-J_d^{\max} = J_a^{\max} \tag{15}$$

Considering the biological importance of Cr(III), all measurements were carried out at 293 K. The extraction rate constant, k_1, was obtained from Equation 6 by using donor phase concentration , while the rate constant, k_2, was determined from the acceptor phase concentration by using Equation 8 or indirectly from the membrane phase data calculated (k_2) on the basis of Equation 7. Rate constants like k_1, k_2, were respectively 4.7×10^{-2} min^{-1} and 1.7×10^{-1} min^{-1}, respectively. Flux values $J_a^{\max}$ and $J_d^{\max}$ were 2.9×10^{-2} min^{-1} and -2.9×10^{-2} min^{-1}. Calculation shows that maximum time required for equilibrium was found to be 10.15 min and $R_m^{\max}$ equal to 0.16. The time dependence R_d, R_m and R_a concentractions of Cr (III) through liquid membrane are shown in Figure 5.

3.9 Effect of Diverse Ions

The effect of diverse ions those associated mostly with Cr (III) ion is given in Figure 6. The interference studies are made by measuring the absorbance of Cr (III) ion present in the receiving phase. The tolerance limit is set as the amount of foreign ions causing a change of ±0.0001 in the rate constant. Most of the ions do not interfere under the mentioned transportation conditions.

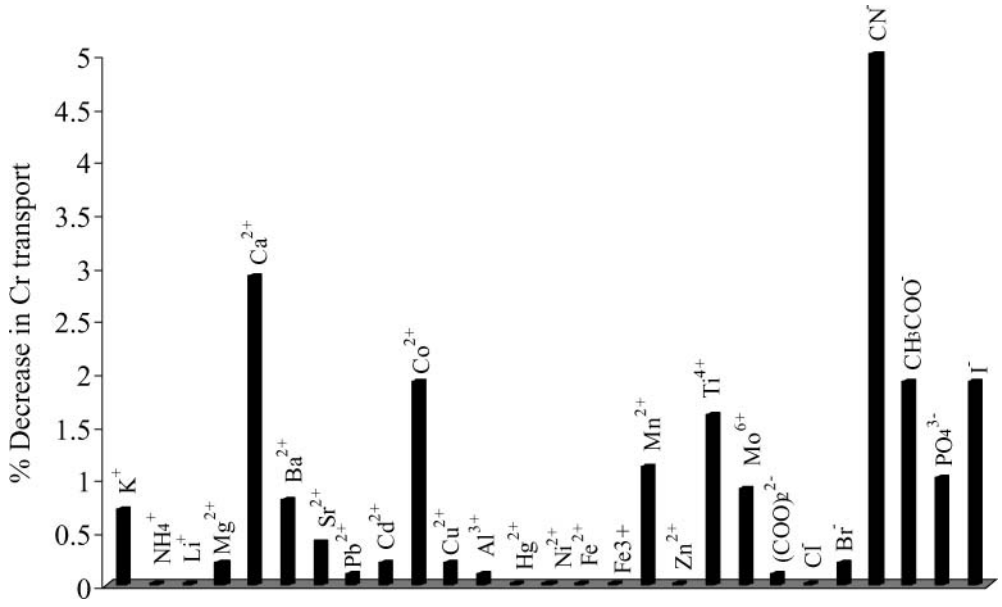


Fig. 6. Effect of diverse ions on % transport of Cr ion.

4 Conclusions

In conclusion, the synthesized chromogenic azacrown ether complexes strongly and selectively with Cr (III). It is an excellent carrier for the transport of Cr (III) and can be used as a highly efficient and selective method for this biologically important metal.

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