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Facilitated Transport of Cr(VI) Through a Bulk Liquid Membrane Containing *p-tert*-Butylcalix[4]arene Amine Derivative as a Carrier

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The facilitated transport of Cr(VI) through a bulk liquid membrane (BLM) is investigated, using the by *p-tert*-butylcalix[4]-arene amine derivative as mobile carrier. The transport efficiency of Cr(VI) by *p-tert*-butylcalix[4]arene amine derivative was investigated under various experimental conditions such as the influence of pH on the donor and the acceptor phase, effect of Cr(VI) and carrier concentration, the type of solvent, the stirring speed, and the temperature. The kinetic parameters (k_1, k_2, R_m^{max}, t_{max}, J_d^{max}, J_a^{max}) were calculated for the interface reactions assuming two consecutive, irreversible first order reactions. The activation energy values are calculated as 5.94 and 12.51 kJ mol^{-1} for extraction and reextraction, respectively. The values of the calculated activation energy indicate that the process is diffusionally controlled by species.

Keywords bulk liquid membrane; Cr(VI); kinetic model; *p-tert*-butylcalix[4]arene

INTRODUCTION

The extensive use of chromium in leather tanning, metallurgy, electroplating, and other industries has resulted in the release of aqueous chromium, which is a major environmental problem when it is found in wastewater, groundwater, or soil. Chromium occurs most frequently as Cr(VI) or Cr(III) in aqueous solutions (1,2). Although Cr(III) is less toxic than Cr(VI), its discharge is still regulated and many environmental authorities make no distinction between the Cr(III) and Cr(VI) (2). The high toxicity and carcinogenicity of Cr(VI) make this one of the most alarming and urgent metals that need to be controlled (3–5). For this reason, the removal of Cr(VI) from aqueous solutions is studied.

The different methodologies for the recovery or removal of Cr(VI) from aqueous solutions have been developed utilizing ion-exchange (6), solvent extraction (7,8), non-disperse solvent extraction (9,10), and membrane-based technologies. The membrane based methods (i.e., nanofiltration (11), micellar enhanced ultrafiltration (12), facilitated transport through bulk liquid membrane (BLM) (5,13,14), supported liquid membrane (SLM) (15,16), polymer inclusion membrane (PIM) (17), emulsion liquid membrane (ELM) (18), activated composite membrane (ACM) (19,20), etc.) have been used for the separation of Cr(VI) from aqueous phase.

The calixarenes are a major class of supramolecular hosts. One of the important properties of calixarene is its ability to recognize cationic and anionic species, as well as neutral molecules. These receptors have the possibility to form interesting complexes both with metal cations and biological compounds by exhibiting extractability and selectivity. Many studies have been published dedicated to calixarenes, particularly in the molecular inclusion of biological substrates, such as amines and amino acids (21–25). Various applications of calixarenes also refer to purification, chromatography, catalysis, enzyme mimics, ion selective electrodes, phase transfer, transport across membranes, ion channels, and self-assembling monolayers (26–33).

We have previously reported the synthesis of *p-tert*-butylcalix[4]arene based receptors as novel extractants for $Cr_2O_7^{2-}$ anions (34,35). Thus, *p-tert*-butylcalix[4]arene derivatives are expected to be mobile carrier for the liquid membrane transport of Cr(VI) ions. In the present study, we investigated the transport of $Cr_2O_7^{2-}$ anions through the bulk liquid membrane 5,11,17,23-tetra-*tert*-butyl, 25,27-bis(benzylamino etoxy)-26,28-dihydroxycalix[4]arene as the carrier. Several important parameters (temperature, concentration, pH, stirring rate, and solvent) that affect the transport rate in the liquid membrane system were studied.

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MATERIALS AND METHODS

Materials

The chemical reagents used in bulk liquid membrane experiments were potassium dichromate, acetic acid,

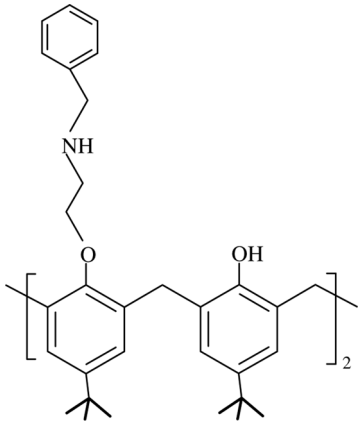

FIG. 1. Chemical structure of *p-tert*-butylcalix[4]arene amine derivative as the carrier used to extract Cr(VI) ions.

phosphoric acid, boric acid, sodium hydroxide, dichloromethane, chloroform, and carbon tetrachloride, all from Merck Co. (Darmstadt, Germany). The potassium dichromate aqueous solutions were prepared in B. Robinson buffer solution at pH 2–6 (36). The carrier (as presented in Fig. 1) used in the study was synthesized according to the method described in the literature (37).

Apparatus

The experimental set up is similar to literature (13). The standard bulk liquid membrane apparatus is a cylindrical glass cell (5.0 cm, i.d.) holding a glass tube (3.5 cm, i.d.) for separating of the two aqueous phases. The experiments were carried out by using a thermostated (PolyScience 912, USA) apparatus to keep the temperature controlled. pH measurements were made with a pH meter (Microprocessor pH 537, Germany) using a combined glass electrode The membrane phase was stirred including a Teflon coated magnetic bar by magnetic stirrer (Yellow line MST basic, Germany). A UV-Vis spectrophotometer (Shimadzu 1201 V, Japan) was used for the measurement of the chromium concentration in the donor and acceptor phases at 360 nm.

Kinetic Procedure

In the experiments, the membrane phase (50 mL), containing the carrier in an organic solution was placed at the bottom of the cell and stirred magnetically at 300 rpm. The donor phase (40 mL) contained Cr(VI) solution buffered with B. Robinson buffer at pH 2 was added slowly inside cylinder. The acceptor phase (40 mL) containing B. Robinson buffer at pH 5 was placed outside the cylinder. In experiments, variation of Cr(VI) concentration with time was directly determined in both donor (C_d) and acceptor phases using a UV-Vis Spectrometer at regular time intervals for a 6 h period. The corresponding change of Cr(VI) ion concentration in the membrane phase was determined from the material balance between the phases. 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(VI) concentration in the donor phase while C_d, C_m, and C_a represent the Cr(VI) concentration in the donor, membrane, and acceptor phases, respectively. The material balance with respect to the reduced concentrations can be expressed as $R_d + R_m + R_a = 1$. When the R_d, R_m, and R_a values are inspected, the results suggest that the Cr(VI) ion transport obeys the kinetic laws of two consecutive irreversible first-order reaction according to the kinetic scheme (5,13,14,38–41).

$$C_d \xrightarrow{k_1} C_m \xrightarrow{k_2} C_a \tag{2}$$

where k_1 and k_2 are pseudo-first-order apparent rate constants of the extraction and reextraction, respectively. In this study, the experimental results show that $k_1 > k_2$ and $k_1 < k_2$ in some cases. In case of $k_1 > k_2$, the penetration of Cr(VI) into the membrane takes place at higher speed than its release from the membrane. The kinetic scheme Eq. (2), for consecutive irreversible reactions can be described by the following rate equations (42–46).

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

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

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

where J represents the flux. When $k_1 \neq k_2$, integrating Eqs. (3)–(5), gives the following expressions:

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

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

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

where k_1 and k_2 values are the apparent extraction and reextraction rate constant, respectively. The kinetic parameters k_1 and k_2 were obtained by fitting Eqs. (6)–(8) to the experimental obtained data. The observed experimental results reveal that R_d decreases exponentially with time, accompanied by a simultaneous increase of R_a, whereas R_m presents at maximum at intermediate times.

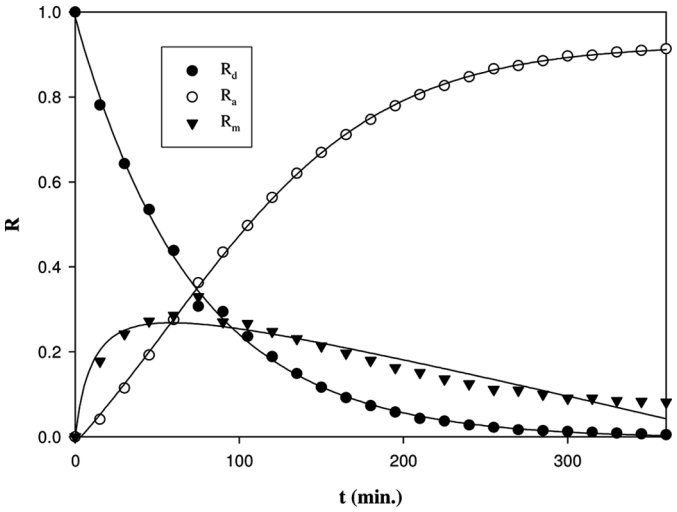

FIG. 2. Time dependence of R_d, R_m, and R_a for transport of Cr(VI). Theoretical curves calculated from Eqs. (6)–(8). Donor phase: 3×10^{-4} M $K_2Cr_2O_7$ solution buffered at pH 2; acceptor phase: buffered at 5; membrane phase: 1×10^{-4} M carrier in chloroform, 300 rpm and 298 K.

The variation of R_d, R_m, and R_a with time through the liquid membrane is shown in Fig. 2.

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

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

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

By considering the first-order time differentiation of Eqs. (6)–(8) at $t = t_{max}$, one obtains:

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

$$\left.\frac{dR_m}{dt}\right|_{\max} = 0 \tag{12}$$

$$\left.\frac{dR_a}{dt}\right|_{\max} = k_2 \left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} \equiv J_a^{\max}. \tag{13}$$

We see that at $t = t_{max}$, the system is in steady state, because the concentration of Cr(VI) in the membrane does not vary with time Eq. (12). Because the maximum entrance ($J_d^{\max}$) and exit ($J_a^{\max}$) fluxes are equal but having opposite signs:

$$-J_d^{\max} = J_a^{\max} \tag{14}$$

The actual numeric analysis was carried out by nonlinear curve fitting using Sigma-Plot software program. The activation energy values were obtained from the Arrhenius equation by using the k_1 and k_2 values at different temperature.

$$\ln(k) = \ln(A) - \frac{E_a}{RT} \tag{15}$$

RESULTS AND DISCUSSIONS

It is well known that the liquid membrane technique is composed of two processes in a single stage: extraction of an ion from aqueous donor solution to organic phase containing the carrier molecules (membrane) and the back extraction of this ion from the membrane to the aqueous acceptor phase. The overall transport process is a mixture of diffusion steps, complexation/decomplexation reactions at two independent and possibly different interfaces.

Effect of Carrier Concentration

The experiments were carried out at different initial carrier concentrations 1×10^{-5}, 5×10^{-5}, 1×10^{-4}, and 5×10^{-4} M in $CHCl_3$ at 298 K and 300 rpm (Fig. 3). Cr(VI) ion increases with an increase in the carrier concentration up to 5×10^{-4} M in the membrane. It is quite obvious from Eqs. (3)–(5) that the flux is related to the carrier concentration. At a lower carrier concentration the interface between the donor phase and the membrane is not saturated by the carrier (42). Therefore, the higher carrier concentration flux values increased from 2.86 to 16.20×10^{-2} mol/m^{2}s (Fig. 3). In addition, a blank experiment was performed with no present carrier in the membrane. No detectable movement of the Cr(VI) ions through the liquid membrane was found in the blank experiment, suggesting

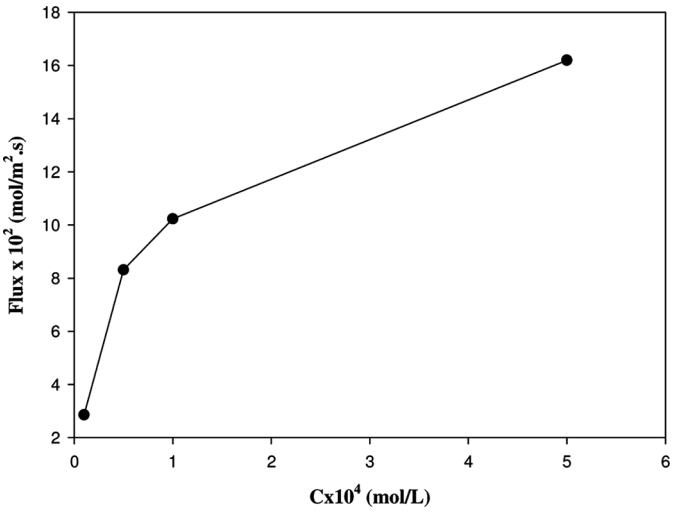

FIG. 3. Influence of carrier conentration on Cr(VI) flux. Donor phase: 3×10^{-4} M $K_2Cr_2O_7$ solution buffered at pH 2; acceptor phase: buffered at 5; membrane phase: 1×10^{-4} M carrier in chloroform and 298 K.

TABLE 1
The kinetic parameters for transport of Cr(VI) ions at different carrier concentrations

Concentration (M)	$k_1 \times 10^2$ (min.$^{-1}$)	$k_2 \times 10^2$ (min.$^{-1}$)	R_m^{max}	t_{max} (min.)	$J_d^{max} \times 10^3$ (min.$^{-1}$)	$J_a^{max} \times 10^3$ (min.$^{-1}$)
0.1×10^{-4}	0.13	0.78	0.11	275.40	−0.90	0.90
0.5×10^{-4}	0.69	0.88	0.32	127.95	−2.85	2.85
1×10^{-4}	1.41	1.63	0.34	68.93	−5.56	5.56
5×10^{-4}	3.72	3.81	0.36	26.55	−13.85	13.85

Donor phase: 3×10^{-4} M $K_2Cr_2O_7$ solution buffered at pH 2; acceptor phase: buffered at pH 5; membrane phase: $0.1–5 \times 10^{-4}$ M carrier in chloroform, 300 rpm and 298 K.

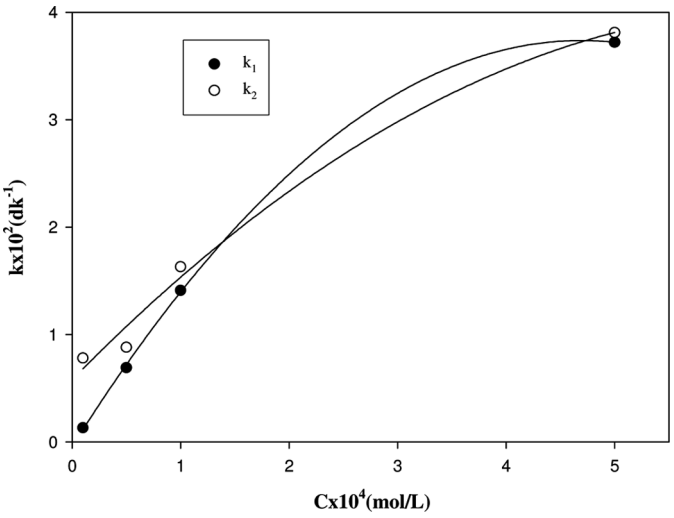

FIG. 4. Carrier concentration dependence of k_1 and k_2 for transport of Cr(VI) ions. Conditions of experiments, see Table 1.

that the transport of Cr(VI) ions through the liquid membrane is fulfilled by the carrier. Therefore the carrier is essential to transport the Cr(VI) ions from the donor phase.

The kinetic parameters for transport of Cr(VI) ions are presented in Table 1 and Fig. 4. As it is seen, the transport rate, k_1 and k_2 increase and t_{max} decreases with an increase in carrier concentration. Figure 4 shows that k_1 and k_2 values increase with an increase in carrier concentration in the organic phase from $1 \times 10^{-5}–5 \times 10^{-4}$. When the obtained data was compared with Ref. (13), the obtained data is an agreement with results in Ref. (13) that Cr(VI) transport was increased with increase in carrier concentration. The optimum concentration was obtained as 1×10^{-4} M and in this optimum value, kinetic parameters $(k_1, k_2, R_m^{max}, J_d^{max}, J_a^{max})$ were found to be higher than that of in Ref. (13), whereas t_{max} was obtained at lower values. This difference can come from either different carriers used and the optimum conditions were found to be different for both works. It had been reported that in controlled conditions, k_1 increases with increasing carrier concentration, showing small and fractional exponent value (43). This obviously can be assumed from Eqs. (6)–(8) that the reduced dimensionless concentration is related with the carrier concentration.

Effect of pH of the Donor and Acceptor Phase

In order to investigate the effect of the pH parameter the transport experiments of chromium(VI) ions (initial concentration 3×10^{-4} mol/L) from acidic medium through chloroform membrane containing *p-tert*-butylcalix[4]arene amine derivative, into a $K_2Cr_2O_7$ solution and the pH of the donor phase in the range of 2–4 were carried out. The pH of the acceptor phase containing B. Robinson buffer solution adjusted to 5. The experimental results are collected in Table 2. The results revealed that the maximum

TABLE 2
The kinetic parameters for transport of Cr(VI) ions at different donor phase pH

pH of donor phase	$k_1 \times 10^2$ (min.$^{-1}$)	$k_2 \times 10^2$ (min.$^{-1}$)	R_m^{max}	t_{max} (min.)	$J_d^{max} \times 10^3$ (min.$^{-1}$)	$J_a^{max} \times 10^3$ (min.$^{-1}$)
2	1.41	1.63	0.34	68.93	−5.56	5.56
3	0.31	0.91	0.19	180.34	−1.76	1.76
4	0.08	0.76	0.08	327.64	−0.63	0.63

Donor phase: 3×10^{-4} M $K_2Cr_2O_7$ solution buffered at pH 2–4; acceptor phase: buffered at pH 5; membrane phase: 1×10^{-4} M carrier in chloroform, 300 rpm and 298 K.

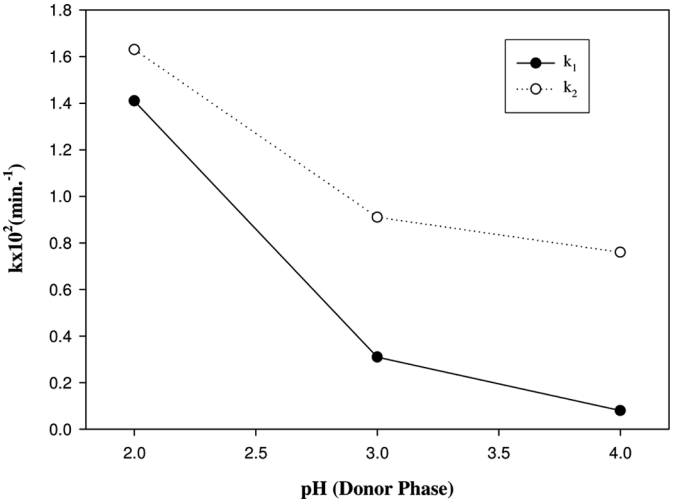

FIG. 5. Influence of pH of the donor phase for transport of Cr(VI) ions. Conditions of experiments see Table 2.

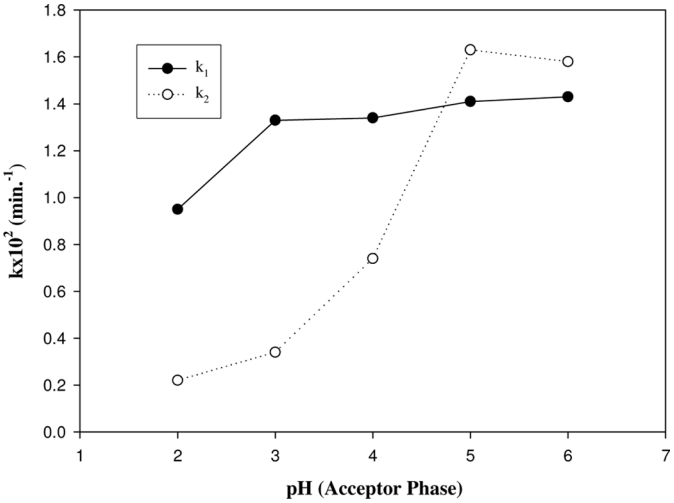

FIG. 6. Influence of pH of the acceptor phase for transport of Cr(VI) ions. Conditions of experiments see Table 3.

Cr(VI) ions transport occurs at pH 2 (Fig. 5). At higher pH values there was a decrease in the transport rate of Cr(VI) ions probably due to the incomplete protonation of the calix[4]arene amine moieties in the d/m interface. Thus, a pH of 2 was selected for the other experiments. When occurs the donor phase is at pH 2, the best complexation occurs in d/m interface.

The effect of pH of the acceptor phase on the efficiency of Cr(VI) ions transport was also studied. The experimental results are collected in Table 3 and they indicate that the transport rate increases with an increase in pH up to pH 5. At pH 6 value, the transport rate decrease (Fig. 6). Table 3 also shows that the extraction of the Cr(VI) ions from the donor phase to the membrane phase increases when the difference in the pH values increases. This result is in full agreement with previous studies (38,39). Alternatively, it can be expressed that the Cr(VI) transport is influenced with the pH of the donor and the acceptor phases and this is confirmed in this work (Tables 2 and 3) and the same conclusion was stated in Ref. (13). Therefore, the pH of the acceptor phase should be higher than the donor phase for the efficient transport of Cr(VI) ions (44–46). The pH of 5 was employed for further studies.

Effect of Cr(VI) Concentration in the Donor Phase

In order to assess the influence of the chromium(VI) concentration on its transport through BLM, the transport experiments were carried out at three different concentrations: 1.5, 3, and 6×10^{-4} M. The experimental results in Table 4 indicate that k_1 and k_2 increase with an increase in Cr(VI) concentration. As the Cr(VI) concentration increases, the complexation rate in d/m interface increase, and depending on this, the decomplexation rate in the m/a interface increase.

TABLE 3
The kinetic parameters for transport of Cr(VI) ions at different acceptor phase pH

pH of acceptor phase	$k_1 \times 10^2$ (min.$^{-1}$)	$k_2 \times 10^2$ (min.$^{-1}$)	R_m^{max}	t_{max} (min.)	$J_d^{max} \times 10^3$ (min.$^{-1}$)	$J_a^{max} \times 10^3$ (min.$^{-1}$)
2	0.95	0.22	0.74	248.57	−0.90	0.90
3	1.33	0.34	0.62	136.63	−2.15	2.15
4	1.34	0.74	0.48	98.97	−3.56	3.56
5	1.41	1.63	0.34	68.93	−5.56	5.56
6	1.43	1.58	0.35	66.50	−5.52	5.52

Donor phase: 3×10^{-4} M $K_2Cr_2O_7$ solution buffered at pH 2; acceptor phase: buffered at pH 2–6; membrane phase: 1×10^{-4} M carrier in chloroform, 300 rpm and 298 K.

TABLE 4
The kinetic parameters for transport of Cr(VI) ions at different chromate concentrations in the donor phase

Concentration (M)	$k_1 \times 10^2$ (min.$^{-1}$)	$k_2 \times 10^2$ (min.$^{-1}$)	R_m^{max}	t_{max} (min.)	$J_d^{max} \times 10^3$ (min.$^{-1}$)	$J_a^{max} \times 10^3$ (min.$^{-1}$)
1.5×10^{-4}	0.78	0.53	0.44	154.41	−0.23	0.23
3×10^{-4}	1.41	1.63	0.34	68.93	−5.56	5.56
6×10^{-4}	1.56	1.79	0.34	59.85	−6.13	6.13

Donor phase: 1.5–6 $\times 10^{-4}$ M $K_2Cr_2O_7$ solution buffered at pH 2; acceptor phase: buffered at pH 5; membrane phase: 1×10^{-4} M carrier in chloroform, 300 rpm and 298 K.

TABLE 5
The kinetic parameters for transport of Cr(VI) ions at different stirring rates

Stirring rate (rpm)	$k_1 \times 10^2$ (min.$^{-1}$)	$k_2 \times 10^2$ (min.$^{-1}$)	R_m^{max}	t_{max} (min.)	$J_d^{max} \times 10^3$ (min.$^{-1}$)	$J_a^{max} \times 10^3$ (min.$^{-1}$)
100	0.87	0.55	0.45	142.99	−2.51	2.51
200	1.14	0.91	0.41	98.13	−3.73	3.73
300	1.41	1.63	0.34	68.93	−5.56	5.56

Donor phase: 3×10^{-4} M $K_2Cr_2O_7$ solution buffered at pH 2; acceptor phase: buffered at pH 5; membrane phase: 1×10^{-4} M carrier in chloroform, 100–300 rpm and 298 K.

Effect of Stirring

The influence of the stirring speed on Cr(VI) ions transport was studied in order to optimize uniform mixing of the solution and to minimize the thickness of aqueous boundary layers. In the present investigation, the stirring rate of the membrane phase was carried out at three different stirring rate, 100, 200, and 300 rpm at 298 K when the carrier concentration was 1×10^{-4} M in $CHCl_3$. The results are presented in Table 5, and indicate that the stirring rate affects the transport rate of Cr(VI) through the liquid membrane. As shown in Table 5, the membrane entrance (k_1) and exit (k_2) rate constants are increased by the rising stirring rate. This statement is similar to the obtained kinetic parameters in Ref. (13) and however, some differences for the kinetic parameters was found due to different conditions applied on both works. According to these results, the flux increases with increasing stirring rate due to decrease of the thickness of the diffusion boundary layers at both interfaces of the membrane. The membrane entrance (k_1) and exit (k_2) rate constants is plotted versus at different stirring speeds in Fig. 7. It can be seen that the membrane entrance (k_1) and exit (k_2) rate constants increased with increasing stirring speed.

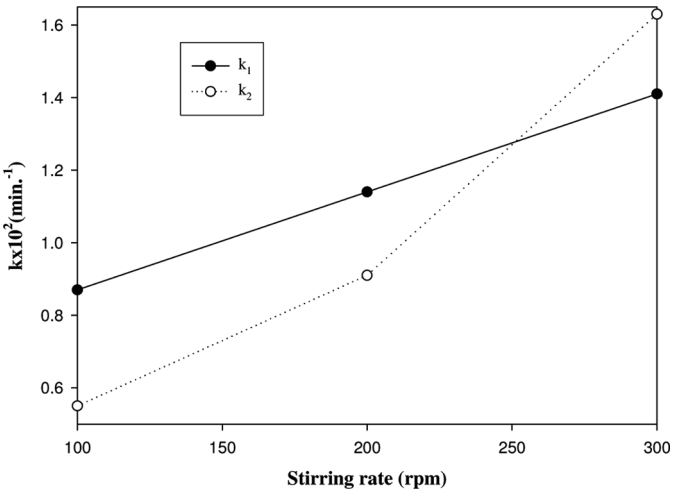

FIG. 7. Stirring rate dependence of k_1 and k_2 for transport of Cr(VI) ions. Conditions of experiments, see Table 5.

Effect of Temperature

The effect of temperature on the transport of Cr(VI) ions through the liquid membrane containing 1×10^{-4} M of carrier in $CHCl_3$ was examined at 293, 298, 303, and 308 K. The experimental results are shown in Table 6. It is quite obvious that the kinetic parameters k_1 and k_2, as well as J_d^{max} and J_a^{max} decreases with an increase in the temperature. The obtained results are different from the values which are found in Ref. (13). In Ref. (13), the kinetic parameters (k_1, k_2, J_d^{max}, and J_a^{max}) are increased with increasing temperature. In both studies this result can be different using carriers. The activation energy values were obtained from the Arrhenius equation by using the k_1 and k_2 values at different temperatures. An Arrhenius-type plot is followed perfectly in Fig. 8. The activation energy values are found to be as 5.94 and 12.51 kJ mol^{-1} for extraction and reextraction, respectively. For diffusion-controlled processes, the activation energy values are quite low, while for chemical-controlled processes, the activation energy

TABLE 6
The kinetic parameters for transport of Cr(VI) ions at different temperatures

Temperature (K)	$k_1 \times 10^2$ (min.$^{-1}$)	$k_2 \times 10^2$ (min.$^{-1}$)	R_m^{max}	t_{max} (min.)	$J_d^{max} \times 10^3$ (min.$^{-1}$)	$J_a^{max} \times 10^3$ (min.$^{-1}$)
293	1.50	1.74	0.34	61.84	−5.93	5.93
298	1.41	1.63	0.34	68.93	−5.56	5.56
303	1.37	1.47	0.35	70.45	−5.22	5.22
308	1.33	1.37	0.36	74.08	−4.96	4.96

Donor phase: 3×10^{-4} M $K_2Cr_2O_7$ solution buffered at pH 2; acceptor phase: buffered at pH 5; membrane phase: 1×10^{-4} M carrier in different solvents, 300 rpm and 293–308 K.

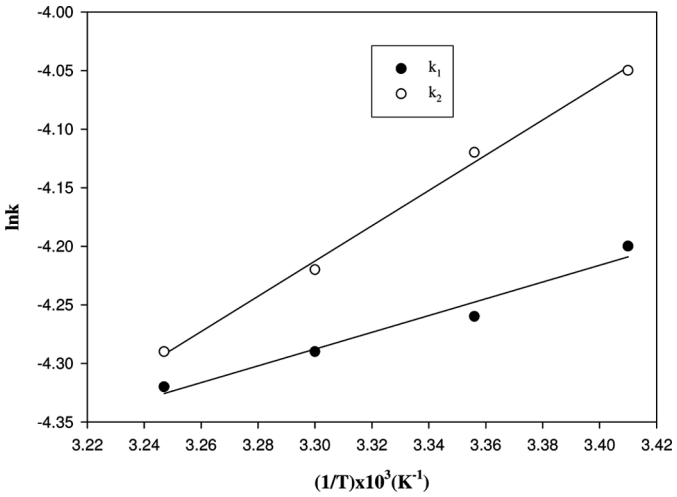

FIG. 8. Arrhenius plots for transport of Cr(VI) in liquid membrane. Conditions of experiments, see Table 6.

values are much higher because of the usually stronger influence of the temperature on the rate constants. Thus, the values of activation energy obtained for a given process can serve as an indicator whether diffusion or chemical reaction is the rate-controlling step. For diffusion-controlled processes, the value of the activation energy is below 5 kcal/mol, whereas those for the chemical reactions have been reported to be above 10 kcal/mol (47–48). The calculated activation energy shows that the transport of Cr(VI) ions is diffusion controlled processes (49).

Effect of Solvent

The experiments were accomplished with three different solvents: CH_2Cl_2, $CHCl_3$ and CCl_4. The kinetic parameters are shown in Table 7, indicate that the highest efficiency has been obtained with CH_2Cl_2. It is also found that the membrane entrance and exit rate constants, as well as the flux values vary in order of $CH_2Cl_2 > CHCl_3 > CCl_4$. In the ion transport, the polarity and viscosity of solvents are very important. Due to the highest polarity and the lowest viscosity of CH_2Cl_2, it is the most effective solvent. This result is in harmony with the previous studies (13,38,39).

Suggested Mechanism

The suggested mechanism for the transport of Cr(VI) ion through bulk liquid membrane, which operated in this study, is shown schematically in Fig. 9. The investigations carried out showed that Cr(VI) could well be transported into *p-tert*-butylcalix[4]arene amine derivative under acidic condition and then stripped into a slightly acidic solution. The amine derivatives bind chromate at lower pH values and release at higher pH values. Therefore, the pH of the acceptor phase should be higher than the donor phase for the efficient transport of Cr(VI) ions (44–46).

As known, the chromate ions may exist in the aqueous phase in different ionic forms ($HCrO_4^-, CrO_4^{2-}, Cr_2O_7^{2-}, HCr_2O_7^-$). CrO_4^{2-} ions prevail in basic or slightly acidic solution while $Cr_2O_7^{2-}$ convert into $HCr_2O_7^-$ ions in acidic aqueous solution at lower Cr(VI) concentrations. Therefore, in this study, Cr(VI) ions will exist as

TABLE 7
The kinetic parameters for transport of Cr(VI) ions at different solvents

Solvent	$k_1 \times 10^2$ (min.$^{-1}$)	$k_2 \times 10^2$ (min.$^{-1}$)	R_m^{max}	t_{max} (min.)	$J_d^{max} \times 10^3$ (min.$^{-1}$)	$J_a^{max} \times 10^3$ (min.$^{-1}$)
CH_2Cl_2	2.02	6.18	0.19	26.89	−11.72	11.72
$CHCl_3$	1.41	1.63	0.34	68.93	−5.56	5.56
CCl_4	0.39	0.20	0.49	348.08	−1.00	1.00

Donor phase: 3×10^{-4} M $K_2Cr_2O_7$ solution buffered at pH 2; acceptor phase: buffered at pH 5; membrane phase: 1×10^{-4} M carrier in different solvents, 300 rpm and 298 K.

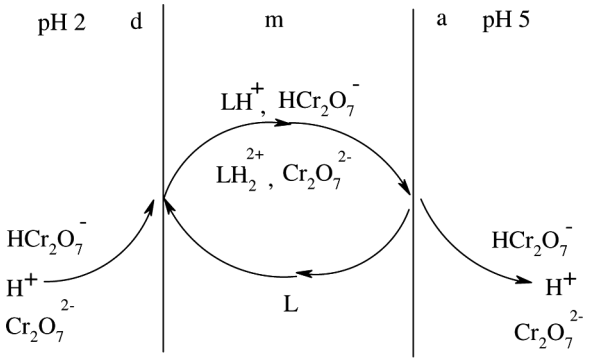

FIG. 9. Suggested mechanism for the transport Cr(VI) through bulk liquid membrane, containing *p-tert*-butylcalix[4]arene amine derivative as carrier.

$HCrO_4^-/Cr_2O_7^{2-}$ at low concentration in acidic aqueous solution. This has allowed us to consider this simultaneous extraction of 1:1 complexes according to the following equilibria (37).

$$[L]_m + [H^+, HCr_2O_7^-]_d \leftrightarrow [LH^+, HCr_2O_7^-]_m \quad (16)$$

$$[L]_m + [2H^+, Cr_2O_7^{2-}]_d \leftrightarrow [LH_2^{2+}, Cr_2O_7^{2-}]_m \quad (17)$$

The complex thus formed diffuses across the membrane towards the m/a interface as a result of concentration gradient. At the m/a interface, in slightly acidic condition, the cationic carrier is converted into a neutral carrier due to the breakage of complex. This is confirmed by the presence of Cr(VI) ions in the acceptor phase. The neutral carrier diffuses back across the membrane to donor solution-membrane interfaces where the cycle repeats.

CONCLUSIONS

The facilitated transport Cr(VI) through BLM is investigated using the by *p-tert*-butylcalix[4]arene amine derivative as mobile carrier. The efficiency of the method depends on various parameters, i.e., the pH of the donor and acceptor phase, effect of Cr(VI) and carrier concentration, type of solvent, stirring speed, and temperature. The kinetic parameters of BLM studies were analyzed assuming two consecutive, irreversible first-order reactions and also activation energy values of interfacial transport of extraction and reextraction have been determined. The possible mechanism of transport was also discussed.

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