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Removal Of Chromate Ions From Waste Water With Coupled Transport Of Liquid Membranes At Different Stirring Speeds And Temperatures

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ABSTRACT

In this study, the non-steady state kinetics of the coupled transport of chromate (CrO_4^{-2}) ions through liquid membranes (n-hexane 90 %, chloroform 10 %) containing benzyltrimethyl ammonium chloride (BTMACl) as a carrier was examined at stirring speeds ranging from 100-250 rpm and temperatures 293-308 °K. In this study, the influence of stirring speed and temperature on the kinetic parameters(k_{1d} , k_{2m} , k_{2a} , t_{max} , R_m^{max}, J_d^{max}, J_a^{max}) have been investigated. The transport efficiency of chromate ions increased with increasing stirring speed. The membrane entrance and exit rate constants (k_{1d} , k_{2m} and k_{2a} respectively) were linearly depent on the stirring speed ratios of 100 to 250 rpm. The membrane entrance(k_{1d}) and exit rates (k_{2m} , k_{2a}) have been increased with temperatures. For maximum membrane entrance (J_d^{max}) and exit (J_a^{max}) fluxes, the activation energies of membrane entrance and exit permeate rates for chromate ions were calculated from the slopes of the two linear relationships : E_{ad} = 11.82 kcal/mol and E_{aa} = 8.38 kcal/mol, respectively. The values of the calculated activation energy indicate that the process is kinetic controlled at the membrane entrance and it is diffusionally controlled at the membrane exit .The membrane was stable during the transport experiments (no leakage of carrier or chromate ion-carrier complex to both aqueous phases and also, no supplementary water penetration into the membrane). This favours interfacial reaction of chromate ion and carrier.

KEYWORDS

Coupled transport;
Chromate ion transport;
Liquid membranes;
Membrane stability;
Chromate removal.

INTRODUCTION

In recent years, membranes processes have been often used in usual separation processes. Usual separating operations in the area of separation sciences are solvent extraction and ion exchange etc.[1]. It has been accepted that the liquid membrane processes are effective techniques for the separation of different species from dilute solutions and they play an important role in separation processes[2,3]. Their efficiency and economic advantages designate them as the optimal solutions of some important problems in science and technology, such as precious-metal recovery[4,5], toxic product(heavy metals, organic molecules)[1,6,7], anion ions, weak acids and bases, biologically important compounds and gaseous mixtures elimination from wastewaters, etc. Especially, for low concentrations of ions in water, below some hundreds of ppm, it is useful to employ liquid membranes so that high enrichment factors can be obtained[8].

In a study, membrane behaviour in chromate recovery using emulsion liquid membranes have been investigated[9]. In that work several surfactants have been used that allows to obtain the highest yield of extraction and recovery of the metal. The membrane behaviour with each surfactant and the analysis of the influence of the carrier concentration on the rate and on the yield of Cr(VI) extraction have been reported. Equilibrium and kinetics of Cr(VI) extraction with aliquat 336 has been studied[10]. It has been reported that solvent extraction as a useful technology fort he recovery of Cr(VI) from industrial effluents. They have studied the equilibrium and kinetics of the solvent extraction process based on a complex organic phase (0.5 % Aliquat 336.5 % n-decanol, and kerosene as diluent). In their work, the influence of the chromium(VI) concentration on the distribution coefficient has been fitted by a semiempirical model, which allows evaluation of the equilibrium conditions in the mass-transfer kinetic model. As a result of the study of the extraction reaction between chromium(VI) and Aliquat 336, the main parameters of the equilibrium and kinetic behaviour have been evaluated.

It is well known, that polymeric and liquid membranes are often used in molecule and ion transportation processes. However, some properties of polymeric membranes such as higher energy costs, lower permeate rate and selectivity limit the use of these types of membranes. The high selectivities permeate and separating efficiencies of liquid membranes are very important from the point of technological practice. Liquid membranes have broad application areas such as; gas treatment and purification, removal of toxic components, separation of fermentation products and wastewater treatment The maximum permissible limit of chromium in drinking water is about 0.05 mg/l[3,5].

In spite of many examples in the literature on cation separation, only few investigations on anion separation are known[11,12].. High chromate ion concentrations are present in industrial wastes of iron, steel, explosive production in municipal wastewater as well as in agriculture wastes. Another example of counter-transport processes, between chloride and hydroxide ions, is reported in literature[12]. In this latter article the transport mechanism was not enticaly clear and some complexities in the chemistry of facilitated diffusion were observed. Anions can also be removed by a co-transport mechanism. These ions are removed from waste water by chemical precipitation, ion exchange, reverse osmosis, electro dialysis, biological denitrification, and ultrafiltration processes[13,14,15].

In this study, the removal of chromate ions from aqueous streams with liquid membrane technique has been investigated. Among the other parameters (pH, acceptor phase type and medium concentration), the stirring speeds a in the range of 100 250 rpm, and temperature in the range of 293-308°K were chosen as process parameters. From the experimental results, it has been determined that the reaction was kinetic controlled at the membrane entrance and diffusion controlled at the membrane exit. The transport efficiency of chromate ions increased with increasing stirring speed and temperature. The membrane entrance and exit rate constants (k_{1d}, k_{2m} and k_{2a}, respectively) were increased with temperature, and linearly dependent on the stirring speeds. The kinetics of chromate ion transport could be analyzed in the formalism of two irreversible first order reactions.

The influence of the stirring speed and the temperature on the kinetic parameters has been also investigated[16,17].

EXPERIMENTAL

Materials

The chemical reagents used in these experiments are K_2CrO_4 (Merck, > 99.5 %) as source phase, benzyltrimethyl ammonium chloride,$C_{10}H_{16}ClN$ as carrier ion, (Fluka, > 99 %), n-hexane, C_6H_{14} (Fluka, > 99.7 %) and chloroform, $CHCl_3$ (Fluka, > 99 %) as organic phase (10% $CHCI_3$ + 90% C_6H_{14}) and hydrochloric acid, HCl (Merck, 37 %) as acceptor phase. The aqueous solutions were prepared using demineralised water.

Kinetic procedure

Coupled transport experiments were conducted using a thermostated (TECHNE mark, model TE-8D) apparatus shown in figure 1. The initial compositions of the phases are consist of the donor phase which was an aqueous K_2CrO_4 solution (initial chromate ion concentration, C_{d0} = 99.5 mg/l, or 8.58 x 10^{-4}M). The donor (d, 50 ml) and acceptor (a, 50 ml) water phases were stirred at variable speeds by a mechanical stirrer (IKA mark, model RE 166). The organic membrane phase was made up by dissolving carrier (benzy trimethyl ammonium chloride, $C_{carrier}$ = 10^{-3}M) in the chloroform(10%) and n-hexane(90%) solution (density<1 gr/cm^3). The membrane phase (m, 250 ml) which has a density less than 1, in was stirred magnetically (HEIDOLPH mark, model MR 3003 SD). The acceptor phase was 2M HCl solution. Stirring speed of membrane phase was kept at 150 rpm during all experimental study, and stirring speeds of acceptor phase and donor phase were 100, 150, 200 and 250 rpm during experimental study that related to stirring speed and the experiments was made at 298°K temperature. However, stirring speed of acceptor phase was kept at 200 rpm during experimental study in the range of 293-308°K. The duration of a kinetic run was about 450 minutes.

Samples (0.5 ml) were taken from both phases (acceptor and donor phases) at 30 minutes regular time intervals, and concentration analysis of chromate ions were carried out by a UV (Model: 160 A, Shimadzu) spectrophotometer (error <1%). In our experimental system, organic membrane phase was took place above donor and acceptor phases. Whenever the interface come into nonexistance at relatively high stirring speeds, hydrodynamic non-stabilities occurred. Furthermore, while, the stirring speeds exceeded 350 rpm, the phases were mixed with each others by the affects of stirring speeds(or impression), as a result of that interface thickness of the donor and acceptor phases were increased largely. Relatively, in higher stirring speeds, the interface was disappeared into a nonexistance and thus, hydrodynamic non-stabilities were come into existance[16,18].

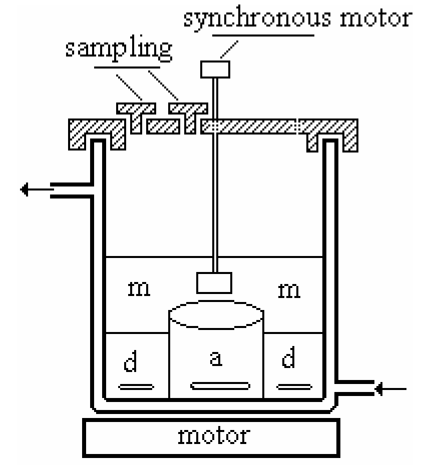

Figure 1: Apparatus used for coupled chromate ion transport through liquid membranes

RESULTS AND DISCUSSIONS

If a membrane is considered as a semipermeable barrier between two phases, then the diffusion coefficients in liquids are typically order of magnitude higher than in polymers, so a larger flux can be obtained. Further enhancement can be accomplished by using a nonvolatile complexing agent (carrier) in the liquid. This carrier molecule can selectively and reversibly react with the solute, and this reversible reaction provides a means of enhancing the solute flux and improves the selectivity at the same time.

In this study, it was considered that two consecutive irreversible first-order reactions were formed at coupled transport with liquid membrane system of chromate ions and so the kinetic equations were written as follow:

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

where C_d, C_m and C_a are the CrO_4^{-2} concentrations in donor, membrane and acceptor phases, respectively and C_{d0} is the initial (at t = 0) CrO_4^{-2} concentration in donor phase.

Since the concentration changes are very small, it was thought that writing in R notation is more practical, and so dimensionless reduced concentrations are used for practical reasons: $R_d = C_d / C_{d0}$, $R_m = C_m / C_{d0}$ and $R_a = C_a / C_{d0}$ can be written. Samples were taken from acceptor aqueous phase and thus, chromate analyses were made. CrO_4^{-2} concentration in organic phase was determined from mass balance equation. Mass balance equation with R notation may be written as follows:

$$R_d + R_m \frac{V_m}{V_d} + R_a \frac{V_a}{V_d} = 1 \tag{3}$$

where V_a, V_d and V_m are the volumes of the acceptor, donor and membrane phases, respectively.

Figures 3-6 and 8-11 show that chromate ion accumulates in the membrane phase during the transport process. As a consequence, the concentration gradient of chromate ion varies permanently and therefore non-steady state kinetics will govern the whole transport process. Such kinetic behaviour may be observed whenever the amounts of carrier and anion ions are comparable with each other[16,19]. Using reduced concentrations, the following rate equations may be written for the above-proposed kinetic scheme (Eq.2):

$$\frac{dR_d}{dt} = -k_1 R_d \equiv J_d \tag{4}$$

$$\frac{dR_m}{dt} = k_1 R_d - k_2 R_m \tag{5}$$

$$\frac{dR_a}{dt} = k_2 R_m \equiv J_a \tag{6}$$

At this transport system, if differential equations (4), (5), (6) are integrated and rearranged(when $k_1 \neq k_2$), the following equations are obtained (Frost, et.al.,1953)[20].

$$R_d = \exp(-k_1 t) \tag{7}$$

$$R_m = \frac{k_1}{k_2 - k_1}\left[\exp(-k_1 t) - \exp(-k_2 t)\right] \tag{8}$$

$$R_a = 1 - \frac{1}{k_2 - k_1}\left[k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)\right] \tag{9}$$

where the k_1 (k_{1d}) and k_2 (k_{2m}, k_{2a}) values are the apparent membrane entrance and exit rate constants, respectively. It is apparent that R_d decreases monoexponentially with time, R_a follows a monotonically increasing sigmoid-type curve while the time variation of R_m presents a maximum. Then, the maximum value of R_m (when $dR_m/dt = 0$) and t_{max} may be written as follow;

$$R_m^{max} = \left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} \tag{10}$$

$$t_{max} = \left(\frac{1}{k_1 - k_2}\right) \ln \frac{k_1}{k_2} \tag{11}$$

R_a versus t yields an increasing sigmoid curve. It has an inflection point (when $d^2R_a / dt^2 = 0$)

$$R_a^{infl} = 1 - \left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} \left(1 + \frac{k_2}{k_1}\right) \tag{12}$$

occurring at[23] :

$$t_{infl} = t_{max} \tag{13}$$

First order time differentiation of Eqns. (7) to (9) leads to the final forms of flux equations

$$\frac{dR_d}{dt} = -k_1 \exp(-k_1 t) \tag{14}$$

$$\frac{dR_m}{dt} = \frac{k_1}{k_2 - k_1} \cdot \left[k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)\right] \tag{15}$$

$$\frac{dR_a}{dt} = \frac{k_1 k_2}{k_2 - k_1}\left[\exp(-k_1 t) - \exp(-k_2 t)\right] \tag{16}$$

The complexity of these equations prevents simple comparison of kinetics which observed for different membrane materials. Therefore, it is useful to examine and compare maximum release rates which can be attained in a given experimental condition. Substituting t in Eqns. (14) to (16) by its maximum value(Eqns. (17) and (19)) one obtains[16].

$$\left.\frac{dR_d}{dt}\right|_{max} = -k_1 \left(\frac{k_1}{k_2}\right)^{-k_1/(k_1-k_2)} \equiv J_d^{max} \tag{17}$$

$$\left.\frac{dR_m}{dt}\right|_{max} = 0 \tag{18}$$

$$\frac{dR_a}{dt}\Big|_{max} = k_2 \left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} \equiv J_a^{max} \tag{19}$$

We see that at $t = t_{max} = t_{infl}$, the system is in steady state since the concentration of chromate ion in the membrane (R_m) does not vary with time (Eqn. 18) because the maximum penetration (J_d) and exit (J_a) fluxes are equal but having opposite sign[17].

$$-J_d^{max} = +J_a^{max} \tag{20}$$

The actual numerical analysis was carried out by non-linear curve fitting using a STATISTICAL (Version:6) program. The first rate constant, k_1 , was obtained from eq. (7) using the donor phase data (k_{1d}), while the membrane exit rate constant, k_2, may be obtained either directly from the acceptor phase kinetic data (k_{2a}) using eq. (9) or indirectly from the membrane phase data calculated on the basis of eq. (8) (k_{2m}). In both cases k_{1d} value, obtained from eq. (7) which was used in the calculations. The obtained kinetic parameters for different stirring speeds and temperatures (k_{1d} , k_{2m} , k_{2a} , R_m^{max}, t_{max}) are given in TABLE 1 and 2.

There is a basic mechanism for this enhanced coupled transport. In coupled transport the carrier agent couples the flow of two or more species, e.g. chromate ion and chloride ion. In this case the carrier must contain, of course, ionizable-chloride groups. Chromate ion can be transported against its concentration gradient provided that the concentration gradient of chlorides is sufficiently large. The mechanism of coupled transport of chromate ion is given in figure 2. QCl represents the chloride carrier. At the interface d/m, chromate ion reacts with two chloride ionizable carrier molecules (QCl), liberating two chloride ions. Then, the Q_2CrO_4 complex diffuses through the membrane. At the interface, m/a, the carrier molecules are protonated and chromate ions are liberated into the receiving phase. Finally, neutral carrier diffuses back across the membrane. Thus, chromate ions move from left to right and electrical neutrality is maintained by the movement of chloride ions in the opposite direction. A simple theoretical approach can be used to obtain kinetic equations for coupled transport system, we must also consider the equilibrium existing at the two interfaces(membrane-water phases).

TABLE 1: Kinetic parameters for coupled transport of chromate ions through liquid membranes at different stirring speeds

Stirring speed, ω (rpm)	$K_{1d}\cdot10^3$ (min^{-1})	$K_{2m}\cdot10^3$ (min^{-1})	$K_{2a}\cdot10^3$ (min^{-1})	R_m^{max}	t_{max} (min)	k_{1d}/k_{2m}
100	3.64	3.16	4.11	0.394	294.6	1.1519
150	4.5	3.71	4.65	0.404	244.4	1.2129
200	4.75	3.88	4.81	0.282	232.6	1.2242
250	5.29	4.48	5.53	0.400	205.2	1.1808

$$2QCl + CrO_4^{-2} \Leftrightarrow Q_2CrO_4 + 2\,Cl^- \tag{1}$$

All the experimental determinations of organic membrane phase have been made at the similar experimental conditions, except the mixing velocity and temperature. In experiments that carried out with appropriate stirring speeds, by reducing to a minimum the thickness of film layer between donor and acceptor phases which contact with organic membrane phase, the increase of transport efficiency of chromate ions had been considered. In donor, membrane and acceptor phases, for various steering speeds, the chromate concentrations with time have given in figures 3-5. As can be seen from these figures, the experimental data and theoretical curves are with in a good agreement. Typical reduced kinetic curves for donor, membrane and acceptor phases at different stirring speeds were given in figure 6. As can be seen in this figure, the theoretical

TABLE 2: Non-steady state kinetic parameters for coupled transport of chromate ions through liquid membranes at different temperatures (k_{1d} , k_{2m} , k_{2a} , t_{max} , R_m^{max},J_d^{max},J_a^{max})

Temp., T,(°K)	$k_{1d}\cdot10^3$ (min^{-1})	$K_{2m}\cdot10^3$ (min^{-1})	$K_{2a}\cdot10^3$ (min^{-1})	R_m^{max}	t_{max} (min)	$J_d^{max}\cdot10^3$	$J_a^{max}\cdot10^3$
293	4.21	3.38	4.32	0.4089	264.56	1.382	1.569
298	4.43	3.61	4.54	0.4061	249.62	1.466	1.649
303	4.64	3.82	4.73	0.4041	237.15	1.544	1.723
308	4.98	4.20	5.15	0.4000	218.39	1.678	1.863

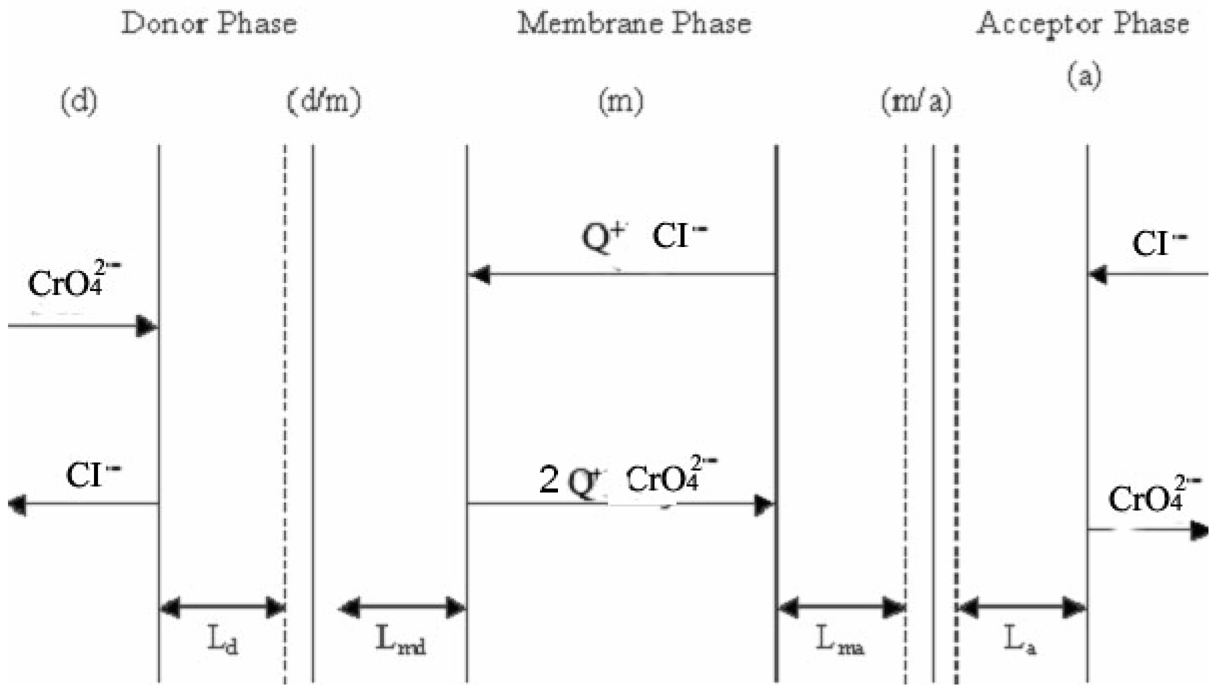

Figure 2: A Schematic view of coupled transport of chromate ions with liquid membrane system

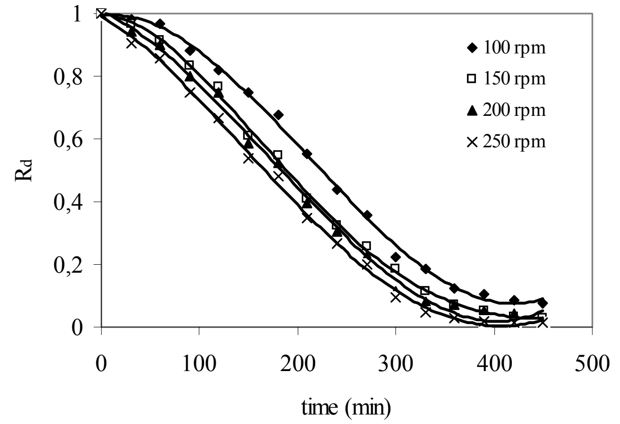

Figure 3: Time variation of reduced concentration of chromate ions in the donor phase (R_d) during coupled transport through liquid membranes at different stirring speeds: 100 (♦) rpm, 150 rpm (□), 200 rpm (▲), 250 rpm (×). Theoretical curves are calculated from Eq.(7)

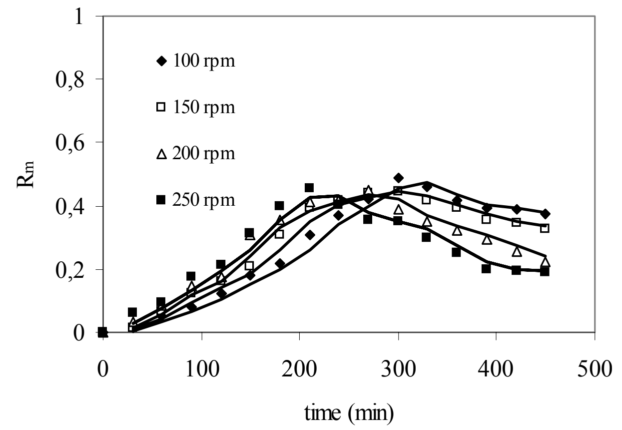

Figure 4: Time variation of reduced concentration of chromate ions in the membrane phase (R_m) during coupled transport through liquid membranes at different stirring speeds: 100 (♦) rpm, 150 rpm (□), 200 rpm (▲), 250 rpm (×). Theoretical curves are calculated by Eqn. (8)

and experimental data values are fitted on to each other, and also, repetition of this curves is well (m, 15 %). The determined rate coefficients, (k_{1d} , k_{2a} and k_{2m}) at various stirring speeds are shown in figure 7. As shown in figure 7 the rate coefficients, (k_{1da} , k_{2a} and k_{2m}) are changed linearly with stirring speeds. The experiments had been carried out in steering speeds range of 100-250 rpm. As can be seen from figure 7, stirring speed has a linear affect on the transport rate in transport process. The rate determining step is the diffusion of the carrier chromate complex (Q_2CrO_4) from thin l_{md} to l_{ma} film layers. The thickness of these layers are decreased with increasing stirring speeds. Transport rate can be controlled by

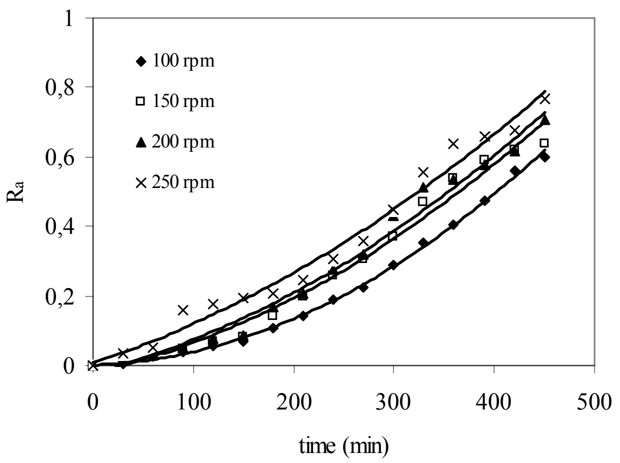

Figure 5: Time variation reduced concentration of chromate ions in the acceptor phase (R_a) during coupled transport through liquid membranes at different stirring speeds: 100 (♦) rpm, 150 rpm (□), 200 rpm (▲), 250 rpm (×). Theoretical curves are calculated by Eqn. (9)

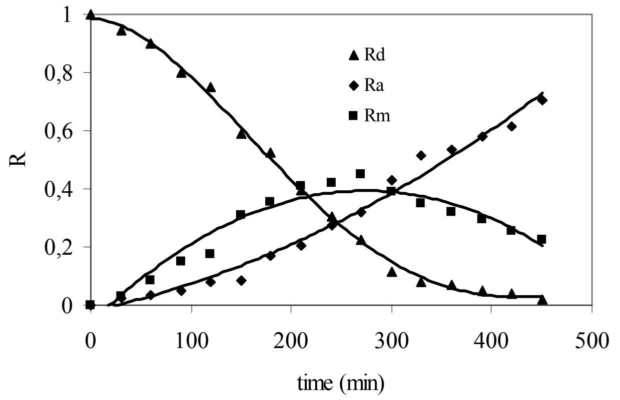

Figure 6: Time dependence of reduced concentration of chromate ions, R_d(▲), R_a(♦), R_m(■) phases in coupled transport through liquid membranes(ω = 200 rpm, T= 291°K). Theoretical curves are calculated from eqns. (7), (8) and (9), respectively

controlling the thicknesses of these layers. At higher stirring speeds (ω = 350 rpm), the phases are mixed with each other and then, these thin layers disappeared. This case has been seen from some other literatures, similarly[19,20,22]. Consequently, when TABLE 1 and figure 7 examined, according to these data, the effect of steering speed on coupled transport of chromate ions has seen to be lineer. The interfaces in coupled transport system is decomposed by deforming in higher steering speeds (ω = 350 rpm). Therefore, to study in higher steering speeds does not become appropriate in transport systems [16,18].

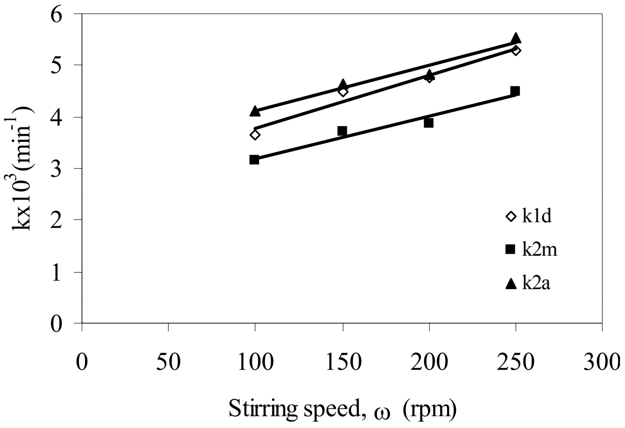

Figure 7: k_{1d}, k_{2m}, k_{2a} for chromate ions at different stirring speeds: k_{1d}(◊), k_{2m}(■), k_{2a}(▲). Theoretical curves calculated from eqns.,(7), (8) and (9), respectively

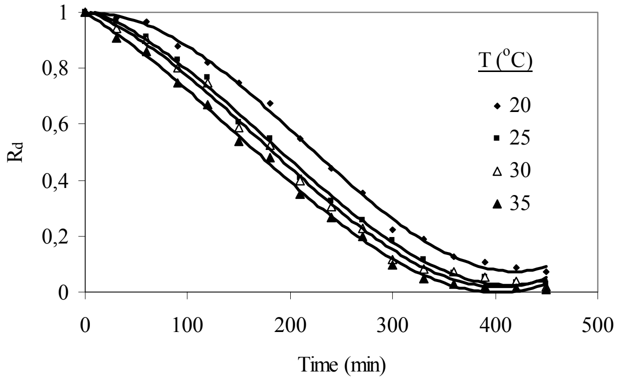

Figure 8: Time variation of reduced concentration of chromate ions in the donor phase(R_d) during coupled transport through liquid membranes at different temperatures: 20°C (♦), 25°C(■), 30 °C(Δ), 35 °C(▲). Theoretical curves are calculated from Eq.(7)

The variation of reduced chromate ion concentrations for various temperatures with time in donor, membrane and acceptor phases were shown in figures 8, 9, 10, and 11, respectively. Coupled transport of chromate ion experiments was executed at temperatures ranges of 293-308°K and the membrane entrance (k_{1d}) and exit rates (k_{2m} , k_{2a}) increased with increasing temperatures. A numerical analysis between membrane exit rates k_{2m} and k_{2a} can be ex-

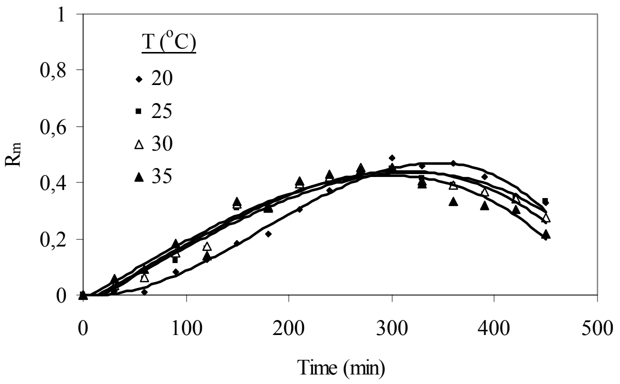

Figure 9: Time variation of reduced concentration of chromate ions in the membrane phase (R_m) during coupled transport through liquid membranes at different temperatures: 20°C (♦), 25°C (■), 30 °C(Δ), 35°C(▲). Theoretical curves are calculated by Eqn. (8)

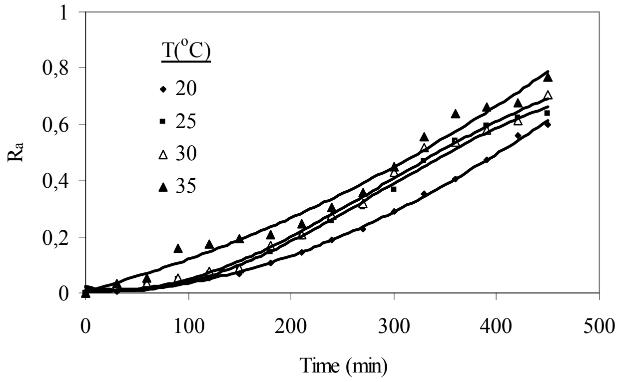

Figure 10: Time variation reduced concentration of chromate ions in the acceptor phase (R_a) during coupled transport through liquid membranes at different temperatures: 20°C(♦), 25°C(■), 30 °C(Δ), 35°C(▲). Theoretical curves are calculated by Eqn. (9)

pressed with temperature values. In addition to temperature, mixing velocity should be optimized at different experimental conditions for CrO_4^{-2} ions transport with liquid membranes.

The highest transport efficiency was reached at 303-308°K. At 293°K lower membrane efficiencies are present. Moreover, the chromate ion concentrations are relatively high in membrane. Furthermore separating efficiency may be characterized with R_a values. At all temperatures, except 293°K and at stirring speed of 100 rpm, it is observed that R_a is grater than 0.60. At coupled transport of chromate ions,

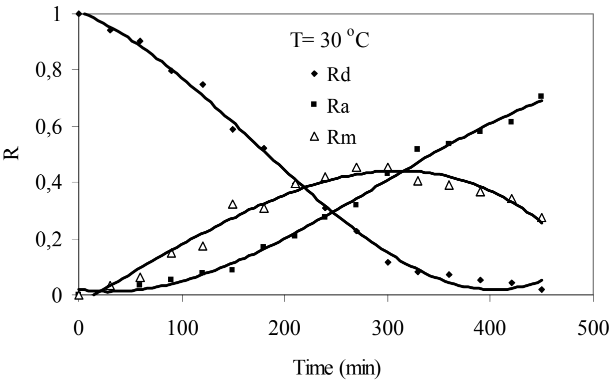

Figure 11: Time dependence of reduced concentration of chromate ions, R_d(♦), R_a (■) R_m(Δ) phases in coupled transport through liquid membranes(T= 303°K). Theoretical curves are calculated from eqns., (7), (8) and (9), respectively

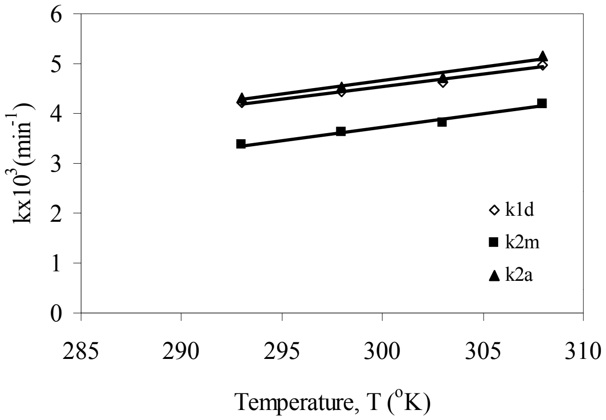

Figure 12: k_{1d}, k_{2m}, k_{2a} for chromate ions at different temperatures: k_{1d}(◊), k_{2m}(■), k_{2a}(▲). Theoretical curves calculated from eqns., (7), (8) and (9), respectively

highest R_a values are obtained at 250 rpm, and 308°K as seen in figures 5 and 10. Activation energies are calculated which take into consideration J_d^{max} and J_a^{max} from experiments which were carried out at four different temperatures (293, 298, 303 and 308°K). The determined rate coefficients, (k_{1d} , k_{2a} and k_{2m}) at various temperatures are shown in figure 12. The rate coefficients, (k_{1da} , k_{2a} and k_{2m}) are changed linearly with temperatures. The experiments had been carried out in temperature range of 293-308°K. As can be seen from figure 12, temperature has a linear affect on the transport rate in transport process.

For diffusion controlled processes, the activation energy (E_a) values are quite low, while there is a strong effect of temperature on actual rate constants (Figures 13 and 14). E_a values are rather higher at chemically controlled processes. For this reason the activation energy (E_a) is used as an indicator at diffusion or chemical reaction control steps of a reaction at membrane processes. For diffusion controlled processes, E_a values are lower than 10 kcal /mol. But according to the literature at chemically controlled processes, E_a values are higher than 10 kcal /mol[23]. Thus, it is considered that the transport of chromate ions is kinetic controlled at the membrane entrance and it is diffusion controlled at the membrane exit. It was concluded that temperature have an affect on the kinetic constants which have obtained for the coupled transport of chromate ions. Since the coupled transport of chromate ions, was formed with the consecutive irreversible reactions, calculating the activation energy of the transport process with respect to membrane entrance and exit rates is not proper. Thus, it was used maximum membrane entrance flux (J_d^{max}) and membrane exit permeate flux (J_a^{max}) values for transport process including k_1 and k_2 (Eq. 21). Activation energy values were obtained from the maximum logarithmic plots of membrane exit flux and membrane entrance plots (J_a^{max}) versus (1/T) plots which are given in figures 13 and 14.

$$\ln(J) = \ln(A) - \frac{E_a}{R}\left(\frac{1}{T}\right) \qquad \textbf{(21)}$$

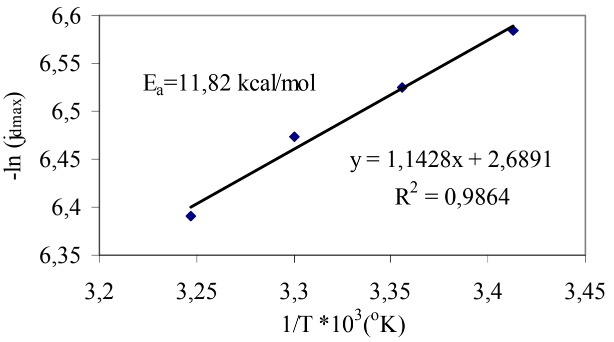

Figure 13: Arrhenius plot of chromate ion transport at J_d^{max}

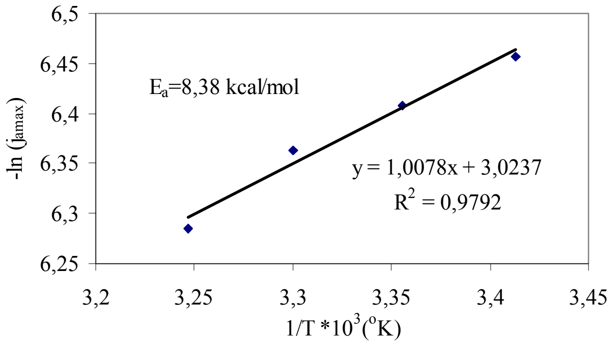

Figure 14: Arrhenius plot of chromate ion transport at J_a^{max}

Calculated activation energies for membrane entrance and exit permeate rates for chromate ions are E_{ad} = 11.82 kcal /mol and E_{aa} = 8.38 kcal /mol, respectively. Those calculated activation energies indicate that temperature have an affect on the transportation rate constants of chromate ion. It may be assumed that the temperature effect is mainly exerted on the maximum membrane entrance and exit fluxes of the coupled transport reactions which taking place in the reaction zones of ionic interfaces. The values of the activation energy obtained for the two transport stages revealed that the first step is kinetic and second step is most probably controlled by species diffusion. With liquid membrane processes, chromate ions are effectively and successfully removed from aqueous solutions. Stirring speed and temperature have an important affect on transport of chromate ions and especially, it is observed that transport rate constants are increased with stirring speed and temperature. In addition to temperature and stirring speed, an investigation on pH of different organic solvents and physicochemical specialties of phases may be useful. Moreover, as the stirring speed increases R_m^{max} slightly incerases, t_{max} decreases, while temperature is increased, R_m^{max} slightly decreases and t_{max} decreases, and chromate ions are rapidly transported into membrane, and so less accumulation appears in the membrane.

CONCLUSIONS

In this coupled transport system, interfaces between phases are deformed and decomposed with higher stirring speeds. Thus, to study with higher stirring speeds is not suitable. During the study, the obtained experimental results, k_{1d} , k_{2m} and k_{2a} kinetic constants, and other kinetic parameters, R_m^{max}, t_{max}, J_a^{max} , J_d^{max} and k_{1d} / k_{2m} values which are calculated by benefit from these constants had given in TABLES 1 and 2. According to UV spectrum of each phases, in acceptor phase, neither carrier nor carrier-chromate complexes are existed at the end of the experiments. This observation was suitable, also for the donor phase, as well. The non-existence of BTMACl salt in both aqueous phases is clearly demonstrated that BTMACl salt is well adsorbed on organic phase and it can not penetrates into the aqueous phase. It was observed that, transport reaction of chromate ion is formed between aqueous phase and membrane interface. Consequently, the thicknesses of film layers which can not be analysed with human eye, are decreased in higher steering speeds. Furthermore, the transport rate can be increased with the control of film layer thicknesses.The values of the apparent activation energy indicate that the process is kinetic controlled at membrane entrance and diffusionally controlled at membrane exit.

As a result of this experimental study, we can say that, the stirring speed and temperature have a linear effect on coupled transport of chromate ions. In this transport system which has been discussed so far, the rate limiting step is kinetic and diffusion of chromate- carrier complex (Q_2CrO_4) into the l_{md} and l_{ma} film layers, respectively.

Nomenclature

C	Chromate ion concentration ($mol \cdot L^{-1}$)
C_a	Chromate ion concentration in the acceptor phase ($mol \cdot L^{-1}$)
C_d	Chromate ion concentration in the donor phase ($mol \cdot L^{-1}$)
C_{d0}	Chromate ion concentration in the donor phase at t = 0 moment ($mol \cdot L^{-1}$)
C_m	Chromate ion concentration in membrane phase ($mol \cdot L^{-1}$)
$C_{carrier}$	Carrier concentration ($mol \cdot L^{-1}$)
E_a	Activation energy ($kcal \cdot mol^{-1}$)
E_{ad}	Activation energy for membrane entrance rate (($kcal \cdot mol^{-1}$)
E_{aa}	Activation energy for exit permeate rate ($kcal \cdot mol^{-1}$)
J_a^{max}	Maximum value of membrane exit flux ($mol.m^{-2}.min^{-1}$)
J_d^{max}	Maximum value of membrane entrance flux ($mol.m^{-2}.min^{-1}$)
k_1	Mmembrane entrance rate constant (min^{-1})
k_2	Membrane exit rate constant (min^{-1})
k_{1d}	Membrane entrance or leak to membrane rate rate constant (min^{-1})
k_{2a}	Membrane exit rate constant (min^{-1})
k_{2m}	Membrane exit rate constant (min^{-1})
R	Reduced chromate ion concentration (dimensionless)
R_a	Reduced chromate ion concentration in the acceptor phase (dimensionless)
R_d	Reduced chromate ion concentration in the donor phase (dimensionless)
R_m	Reduced chromate ion concentration in the membrane phase (dimensionless)
R_m^{inf}	Reduc. chromate ion conc. in acceptor phase corresponding to infl. point of function (dimensionless)
R_m^{fin}	R_d at the end of reaction time(dimensionless)
R_m^{max}	max. reduced chromate ion concen. of mem. phase(dimensionless)
t	Time (min.)
t_{inf}	Time corresponding to inflection point of the function (min.)
t_{max}	Time which chromate ion concentration becoming maximum (min.)
T	Temperature (°K)
BTMACl	Benzyl trimetyl ammonium chloride
V_a	Volume of acceptor phase (cm^3)
V_d	Volume of donor phase (cm^3)
V_m	Volume of membrane phase (cm^3)
ω	Stirring speed (rpm)

Subscripts

a	Acceptor phase
d	Donor phase
d_0	Iinitial chromate ion concentration
m	Membrane phase

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