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Study on Competitive Transport of Heavy Metal Ions Through Liquid Surfactant Membrane

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Abstract: In the present work an attempt has been made to develop a mathematical model for competitive transport of Cr(VI) and Mo(VI) through liquid surfactant membrane from acidic solution using Alamine-336 and Caustic Soda as extractant and stripping reagent respectively. A reaction front has been assumed to exist within the emulsion globule in the proposed model. It has been assumed that, an instantaneous and irreversible reaction takes place at the membrane-internal stripping phase interface between the solute and internal stripping reagent. Experiments on simultaneous extraction of Cr(VI) and Mo(VI), in batch mode, from aqueous solutions of Potassium Dichromate and Ammonium Molybdate have been carried out with the initial concentration of the solutes between 50–100 mg/l. Experiment on emulsion stability has also been performed to arrive at a reasonably stable emulsion composition. Effect of initial solute concentration on distribution coefficient has also been found experimentally and fitted by a semiemperical model that has been used in the computer simulation of the simultaneous extraction process. It has been found that the experimental results are within reasonably close proximity with the simulated curves.

Keywords: Heavy metalions, liquid surfactant membrane, competetive transport

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INTRODUCTION

By virtue of its large surface area for mass transfer, short diffusion path, good permeability characteristics, simultaneous extraction, and stripping (1), liquid surfactant membrane (ELM) is viewed as a potentially viable technique for separation of organic and inorganic contaminants, heavy metal from waste waters. Dr. Norman Li (2) first invented and used the technique for separation of hydrocarbons in 1968. Emulsion liquid membrane is made by first making a primary emulsion (oil/water or water/oil) and then dispersing the same into a third phase, either oil or water, thereby forming a multiple emulsion of the type O/W/O or W/O/W as the case may be. The dispersed phase usually has a droplet size of 0.5–10 µm while, that for the emulsion globules is between 0.1–0.2 mm. in diameter (3). ELM technique has been predominately applied in the areas of extraction of heavy metal ions (viz. copper, cobalt, zinc, nickel, molybdenum, mercury, chromium (4–11) etc. from aqueous solutions, industrial effluents). Removal of weak acids e.g. phenol (12–14) and weak bases e.g. ammonium (15, 16) amines (17), separation of hydrocarbons have also been reported. This technique has also been applied in biochemical and biomedical fields viz. encapsulation of enzymes, extraction of fatty acids, detoxification of blood etc. (18–24). In majority of the work water-in-oil (W/O) type of emulsion have been used.

Facilitated transport processes have been described by *Distributed resistance* models in which it is assumed that, the diffusional resistance is distributed throughout the emulsion drop. Among the distributed resistance models (viz. Reversible Reaction Model, Advancing Reaction Front Model etc.) advancing reaction front (or shrinking core) model has found wide application (25–29). In this model it is assumed that the internal reagent reacts instantaneously with the solute and the reaction is irreversible.

In this work competitive transport mechanism of a binary system (Chromium and Molybdenum) through liquid emulsion membrane at low concentrations has been studied. Chromium and Molybdenum mixture find wide application in special category steel specifically manufactured for certain elements (steel tubes) used in the aircrafts. Chromium has wide applications in industries such as, electroplating, tannery etc. Besides Cr(VI) is also identified as a toxic substance because of its carcinogenic effect on living bodies.

High molecular weight amines have the potential of removing heavy metal ions including the toxic ones at low concentrations. Alamine-336, a straight chain tri-alkyl amine has reasonably good selectivity for Cr(VI), Mo(VI) and a host of other metal ions. It extracts anionic species such as $(Cr_2O_7)^{-2}$ and $(Mo_7O_{24})^{-6}$of the metals at low pH (~2) while stripping takes place at predominantly basic pH range. The simultaneous extraction and stripping reactions (30, 31) involving chromium and molybdenum in LEM are as follows:

$$[R_3N]_{org} + H^+Cl^- = [R_3NH^+Cl^-]_{org} \tag{1}$$

$$2[R_3NH^+Cl^-]_{org} + K_2Cr_2O_7^{-2} = [(R_3NH^+)_2Cr_2O_7^{-2}]_{org} + [2KCl]_{aq} \tag{2}$$

$$\begin{aligned} &6[R_3NH^+Cl^-]_{org} + (NH_4)_6[Mo_7O_{24})^{-6}] \\ &\quad = 6[R_3NH^+(Mo_7O_{24})^{-6}]_{org} + 6(NH_4)Cl \end{aligned} \tag{3}$$

The complexes break down with reaction with a base NaOH in the following manner:

$$\begin{aligned} &[(R_3NH^+)_2Cr_2O_7^{-2}]_{org} + 4[Na^+OH^-] \\ &\quad = 2(R_3N)_{org} + 2[Na_2CrO_4]_{aq} + 3H_2O \end{aligned} \tag{4}$$

$$\begin{aligned} &6[R_3NH^+(Mo_7O_{24})^{-6}]_{org} + 6NaOH \\ &\quad = 6(R_3N)_{org} + Na_6(Mo_7O_{24}) + 6H_2O \end{aligned} \tag{5}$$

Attempts have been made in this work to explain the facilitated transport mechanisms and competitive nature of the binary system with respect to the following parameters: the *pH* of the system, distribution coefficients of both Cr(VI) and Mo(VI) between organic and aqueous phases, external phase solute concentration, treat ratio, volume fraction, and concentration of the internal phase by performing batch experiments. A mathematical model has been developed based on shrinking core model to describe the simultaneous extraction and stripping of Cr(VI) and Mo(VI) through LEM using Alamine-336 as the carrier and caustic soda as the stripping agent. The model equations have been solved by numerical computations to obtain the solute concentration profile in the external phase and the shrinking profile of the unreacted core (reaction front) with time. The experimental values of distribution coefficient of the solutes between organic and aqueous phases have been used to solve the model equations.

MATHEMATICAL DESCRIPTION

In this work an unsteady state mathematical model, based on the model developed by Ho et al. (25) is proposed for separation of Cr(IV) and Mo(IV) ions using liquid surfactant membrane. At the outer interface of the emulsion globules, solutes (Cr and Mo ions) from the external aqueous phase react with the complexing agent (Alamine 336) contained in the membrane phase and form oil soluble metal ion-carrier complexes. The complexes thus formed diffuse through the membrane phase until dissociated by reaction with the internal stripping agent (NaOH) contained in the emulsion globules. The solute is immediately consumed by NaOH. The reactions are instantaneous and irreversible in nature. The reaction products being oil insoluble, can not diffuse back through the organic membrane phase. As a result they remain entrapped in the internal droplets. The solute molecules can not diffuse beyond those globules in which NaOH has been completely exhausted. This indicates that there would be a reaction front separating the *as yet* unreacted NaOH and the reaction product droplets. As the reaction progresses, the reaction front shrinks further until the stripping reagent is completely exhausted. This model has been based on certain assumptions such as Fig. 1:

- Due to considerable viscosity difference between the aqueous internal phase and the membrane phase and presence of surfactant in the membrane phase, the internal circulation of droplets within the emulsion globule is neglected.
- Concentration gradient within the internal droplets is neglected.
- The effect of non-uniform size distribution of emulsion globules in the continuous phase is neglected and the system is assumed to be mono-disperse with globules of average size.
- Coalescence and re-dispersion of the emulsion globules are neglected due to lowering of membrane-external phase interfacial tension by the surfactant.
- The hydrodynamic condition inside the vessel (the stirrer geometry, the stirrer speed and the ratio of impeller to vessel diameter) is such that the system is well mixed and therefore the mass transfer resistance around the emulsion globule is neglected.
- Emulsion rupture and swelling are neglected.
- In the present context Cr(VI) and Mo(VI) exist in hexavalent form in the aqueous phase. One mole of Cr complex an six moles of Mo complex react with four moles and six moles of internal reagent respectively at the reaction front.

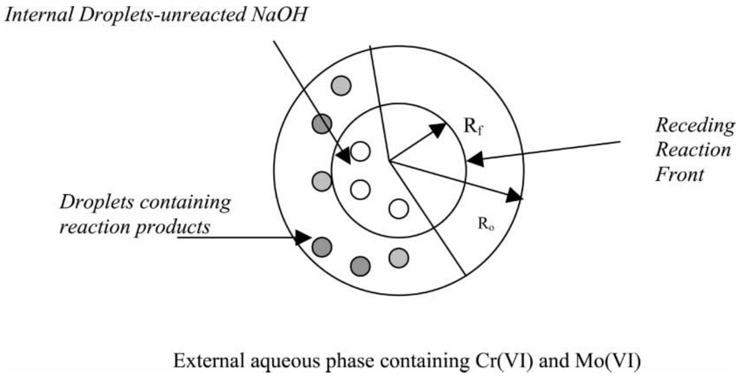

Figure 1. Schematic diagram of advancing front model.

The material balance equations for the solutes in the external phase are:

$$-d\frac{C_0}{dt} = \frac{3V}{V_0} \cdot \frac{Deff}{R_0} \cdot \frac{\partial Cm}{\partial r}\bigg|_{r=R_0} \tag{6}$$

$$\frac{-dC_0'}{dt} = \frac{3V}{V_0} \cdot \frac{Deff'}{R_0} \cdot \frac{\partial Cm'}{\partial r}\bigg|_{r=R_0} \tag{7}$$

The initial conditions are,

$$C_0 = C_0^* \quad \text{at} \quad t = 0 \tag{8}$$

$$C_0' = C_0^{**} \quad \text{at} \quad t = 0 \tag{9}$$

Material balance of solutes in the membrane phase ($R_0 > r > Rf$):

$$\frac{\partial Cm}{\partial t} = \frac{Deff}{(1-\varphi)}\left[\frac{\partial^2 Cm}{\partial r^2} + \frac{2}{r}\frac{\partial Cm}{\partial r}\right] \tag{10}$$

$$\frac{\partial Cm'}{\partial t} = \frac{Deff}{(1-\varphi)}\left[\frac{\partial^2 Cm'}{\partial r^2} + \frac{2}{r}\frac{\partial Cm'}{\partial r}\right] \tag{11}$$

The initial and boundary conditions are:

$$Cm(0, r) = 0 \tag{12}$$

$$Cm'(0, r) = 0 \tag{13}$$

$$Cm(t, R_0) = Cm_{r=Ro} = C_D \cdot C_0 \tag{14}$$

$$Cm'(t, R_0) = Cm'\big|_{r=Ro} = C_D' \cdot C_0 \tag{15}$$

$$Cm(t, R_f) = 0 \tag{16}$$

$$Cm'(t, R_f) = 0 \tag{17}$$

$$\frac{\partial Cm}{\partial r}\bigg|_{r=Rf=0} = 0 \tag{18}$$

$$\frac{\partial Cm'}{\partial r}\bigg|_{r=Rf=0} = 0 \tag{19}$$

The rate of consumption of internal reagent is

$$\left[\frac{-d}{dt} 4/3\pi\, R_f^3 \varphi C_i\right] = m4\pi R_f^2\ Deff \cdot \frac{\partial Cm}{\partial r}\bigg|_{r=Rf} + 4\pi\, R_f^2 m' Deff' \cdot \frac{\partial Cm'}{\partial r}\bigg|_{r=Rf} \ldots . \tag{20}$$

where,

$$t = 0, \quad R_f = R[\text{value of } m, m' \text{ depend upon reaction stoichiometry}] \ldots\ldots \tag{21}$$

$$\frac{-dR_f}{dt} = \frac{1}{\varphi}\left[\frac{Deff}{C_i}\frac{\partial Cm}{\partial r}\bigg|_{r=Rf} + \frac{Deff'}{C_i} \cdot \frac{\partial Cm'}{\partial r}\bigg|_{r=Rf}\right] \cdots \tag{22}$$

The initial condition for this reaction is:

$$\mathrm{R_f = R_0} \quad \text{at} \quad \mathrm{t = 0}$$

Let's define dimensionless variables:

$$\mathrm{X = r/R_0}, \quad \mathrm{X = R_f/R_0}, \quad \tau = \frac{\mathrm{Deff \cdot t}}{\mathrm{R^2}}, \quad \beta = \frac{\mathrm{Deff}\,'}{\mathrm{Deff}} \tag{23}$$

$$\mathrm{E} = \frac{\mathrm{3V}}{\mathrm{V_0}}, \quad \theta_0 = \mathrm{C_0/C_0^*}, \quad \theta_0' = \mathrm{C_0'/C_0^{**}} \tag{24}$$

$$\theta_\mathrm{m} = \mathrm{Cm/C_0^*}, \quad \theta_\mathrm{m}' = \mathrm{C_m'/C_0^{**}} \tag{25}$$

$$\theta_\mathrm{i} = \mathrm{Ci/C_0^*}, \quad \theta_i' = \mathrm{C_i'/C_0^{**}} \tag{26}$$

Applying these quantities the above equations can be written in dimensionless form.

The material balance (in the external phase) equation therefore becomes

$$\frac{-\mathrm{d}\theta_0}{\mathrm{d}\tau} = \mathrm{E}\frac{\partial\theta_\mathrm{m}}{\partial \mathrm{x}}\bigg|_{\mathrm{x}=1} \tag{27}$$

$$\frac{-\mathrm{d}\theta_0{}'}{\mathrm{d}\tau} = \mathrm{E}\beta\frac{\partial\theta_\mathrm{m}'}{\partial \mathrm{x}}\bigg|_{\mathrm{x}=1} \tag{28}$$

where, θ_0, $\theta_0{}' = 1.0$ at $\tau = 0$.

The diffusion equations in the external phase are:

$$\frac{\partial\theta_\mathrm{m}}{\partial\tau} = \frac{1}{(1-\varphi)}\left[\frac{\partial^2\theta_\mathrm{m}}{\partial \mathrm{x}^2} + \frac{2}{\mathrm{x}}\cdot\frac{\partial\theta_\mathrm{m}}{\partial \mathrm{x}}\right] \tag{29}$$

$$\frac{\partial\theta_\mathrm{m}'}{\partial\tau} = \frac{\beta 1}{(1-\varphi)}\left[\frac{\partial^2\theta_\mathrm{m}'}{\partial \mathrm{x}^2} + \frac{2}{\mathrm{x}}\cdot\frac{\partial\theta_\mathrm{m}'}{\partial \mathrm{x}}\right] \tag{30}$$

$$\theta_\mathrm{m}(0, \mathrm{x}) = 0, \quad \theta_\mathrm{m}'(0, \mathrm{x}) = 0 \tag{31}$$

$$\theta_\mathrm{m}(\tau, \mathrm{x} = 1) = \theta_\mathrm{m}|_{\mathrm{x}=1} = \mathrm{C_D} \cdot \theta_0 \tag{32}$$

$$\theta_\mathrm{m}'(\tau, \mathrm{x} = 1) = \theta_\mathrm{m}'|_{\mathrm{x}=1} = \mathrm{C_D'} \cdot \theta_0' \tag{33}$$

$$\theta_\mathrm{m}(\tau, \mathrm{x_f}) = 0,\ \theta_\mathrm{m}'(\tau, \mathrm{x_f}) = 0 \tag{34}$$

$$\frac{\partial\theta_\mathrm{m}}{\partial \mathrm{x}}\bigg|_{\mathrm{X=X_f=0}} = 0 \tag{35}$$

$$\frac{\partial\theta_\mathrm{m}'}{\partial \mathrm{x}}\bigg|_{\mathrm{X=X_f=0}} = 0 \tag{36}$$

$$\frac{-\mathrm{dx_f}}{d\tau} = \frac{\mathrm{m}}{\varphi\theta_\mathrm{i}}\cdot\frac{\partial\theta_\mathrm{m}}{\partial \mathrm{x}}\bigg|_{\mathrm{x=x_f}} + \frac{\beta}{\varphi\ \theta_\mathrm{i}'}\frac{\partial\theta_\mathrm{m}'}{\partial \mathrm{x}}\bigg|_{\mathrm{x=x_f}} \cdots \tag{37}$$

where $\tau = 0$, $\mathrm{x} = 1$.

The coupled equations (27)–(30)and (37) have been solved by numerical computations using an implicit finite difference technique. A central difference scheme has been used for integration along dimensionless radial distance X and Euler's method for integration along dimensionless time τ. The grid sizes in τ and X direction have been chosen by trail to obtain good convergence. As none of the equations referred to above can be solved independently, an iterative process has been adopted for each time step. The computational procedure for each time step is as follows:

1. Values of $\theta_{0,}$ θ'_0 and X_f have been assumed to be equal to those in the previous time step.
2. The assumed values of $\theta_{0,}$ θ'_0 and X_f have been substituted in equations (29) and (30). The simultaneous linear algebric equation having tridiagonal matrix of coefficients obtained by representing the above equation in finite difference form have been solved by matrix inversion and multiplication method to obtain $\theta_{m,}$ θ'_m as a function of X.
3. Checks have been made whether the values of X_f and $\theta_{m,}$ θ'_m thus obtained satisfy equation (37). If not, a new estimate for X_f has been made and the procedures from step (ii) onward have been repeated until satisfactory matching was obtained.
4. $\theta_{0,}$ θ'_0 have been calculated from equations (27, 28) and calculated and assumed values of $\theta_{0,}$ θ'_0 have been matched by an iterative process similar to that adopted in step (iii) for solving $X_{f.}$

EXPERIMENTAL PROCEDURE

The constituent materials of the liquid membrane used in this study are as follows: Kerosene oil (24 gm) as the solvent (locally procured, b.p-150–240°C, density-0.798 gm/ml), Surfactant.- Span-80 (3 wt%) to stabilize water-in-oil emulsions (HLB value 4.3), Poly-butyl Succinimide (2 wt%) as membrane strengthening agent (Lubrizol, India, sp.gr. 0.93 and viscosity-270 cst.), Alamine 336 (Henkel, USA) as the complexing agent (0.25 wt% to 4 wt%, a straight chain tri-alkyl amine, density- 0.81 gm/ml at 25°C, avg. mol.wt.- 392). Stable emulsion formulation has been found experimentally. An emulsion prepared with 3 wt% Span 80 and 2 wt% LZ-890 has been found to be reasonably stable as long as the experiments were performed. In extraction experiments the external aqueous phase contained Potassium Dichromate ($K_2Cr_2O_7$) and Ammonium Molybdate [$(NH_4)_6(Mo_7O_{24})$, $4H_2O$, Merck, 99.99% pure] as source ofsolutes Cr^{+6}:/Mo^{+6} in the range of 50:50 to 50:100 mg/l.

The primary emulsion (W/O) was prepared by gradually dripping NaOH soln in to the oil membrane in a beaker using a high speed stirrer at 4600 RPM for about 25 minutes. The stirrer (REMI, India) was fitted with turbine type stainless steel blades and special stainless steel perforated jacket to ensure better mixing of oil and water. The resultant milky white emulsion was then dispersed in the external aqueous phase (containing solutes) in a glass mixer-settler (7 inches dia.) fitted with baffles for better mixing, a stop-cock for easy sampling and a variable speed turbine type glass stirrer rotating at a speed of 150 rpm to ensure proper mixing as also to minimize emulsion rupture. Samples, drawn at fixed intervals, were filtered before analyzing for chromium and molybdenum using a UV spectrophotometer following standard procedures. pH of the external phase was maintained at around 2 by dripping dil.HCL in to the mixer-settler. Equilibrium experiments have been carried out in separating flasks with the solute concentration varying between 25–100 mg/l of Cr(VI): Mo(VI) taken together in the proportion of 1:1 (oil: aqueous phase by volume).

ESTIMATION OF MODEL PARAMETERS

Emulsion Globule Size

The emulsion globule size (Sauter mean) has been calculated using the correlation of Ohtake et al (29) as below:

$$d_{32} = 0.12(\mathrm{We})^{-0.5} d_1 \tag{38}$$

The value of the interfacial tension has been determined by a tensiometer as 13 dynes/cm and the Sauter mean diameter has been calculated to be 0.0782 cm.

Effective Diffusivity

The diffusivity of Alamine-Chromium and Molybdenum complexes have been calculated by correlation developed by Wilke and Chang (32) as following:

$$D_m = \frac{(117.3 \times 10^{-18})(\omega M)^{0.5} T}{\mu_m \cdot (V_B)^{0.6}} \, m^2/\sec.$$

The solvent association factor ω has been taken to be 1. The viscosity of the membrane phase has been experimentally determined to be 0.0028 kg/m · sec. The molar volume of the solutes have been estimated using Le-Bas formula (32) and the values are 0.507 m^3/kg mole (alamine-chromium complex–V_B) and 0.51 m^3/kg · mole (alamine-molybdenum complex–V_B'). The molecular weight of the solvent kerosene has been determined to be 142.3. Values of diffusivity of the complexes in the membrane phase thus calculated are: 0.22343 × 10^{-9} m^2/sec and 0.22672 × 10^{-9} m^2/sec respectively. In both the cases of complexation (Cr and Mo) the molar volume of the complex is largely dominated by that of the tertiary amine. Using correlation of Jefferson-Witzell-Sibbitt (33) the effective diffusivity of the complex in emulsion has been calculated. In the present context it is as follows:

$$D_{eff.} = 10^4 \cdot D_m \left[\frac{4(1+2\,p)^2 - \pi}{(1+2\,p)^2} \right] cm^2$$

where, $p = 0.403(\varphi)^{-0.33} - 0.5$.

The effective diffusivity of the complexes thus calculated are: 0.151405×10^{-5} m^2/sec and 0.15388×10^{-5} m^2/sec for Cr-alamine and Mo-alamine complexes respectively.

Distribution Coefficient

From the experimentally determined equilibrium solute concentrations in the aqueous phase values of distribution coefficients of the solutes between organic and aqueous phases have been calculated as follows:

$$C_D = \text{Solute conc. in org. phase/ Solute conc. in aq. phase}$$

The calculated values of distribution coefficients (for Cr and Mo) have been correlated with aqueous phase solute concentration at equilibrium by linear regression method. The following equations have been obtained:

$$\text{For Cr(VI)} \ - C_D = 29.36202\ C_S^{-0.52462} \quad \& \ R^2 = 0.98198$$

$$\text{For Mo(VI)} - C_D = 21.6703\ C_S^{-0.48476} \quad \& \ R^2 = 0.95873$$

Logarithmic values of distribution coefficient (C_D) of chromium(VI) and molybdenum(VI) at pH2 have been plotted against logarithmic value of equilibrium aqueous phase solute concentration (C_S) along with the experimental results as shown in Fig. 2. It is evident that distribution coefficient of both the metal ions decrease with increasing internal phase solute concentration. Molybdenum shows a lower distribution coefficient (C_D) than that of chromium. This is shown in Fig. 3. This difference in distribution coefficient may influence the extraction characteristics of the species.

RESULTS AND DISCUSSION

Effect of pH of the External Aqueous Phase

Experimental results of the effect of pH of the external aqueous phase on extraction characteristics are shown in Fig. 4 for pH values of ~2 and 10. It is evident that lower pH value favors greater extraction of the metal ions from external phase. Extraction practically ceases at pH 10. It also

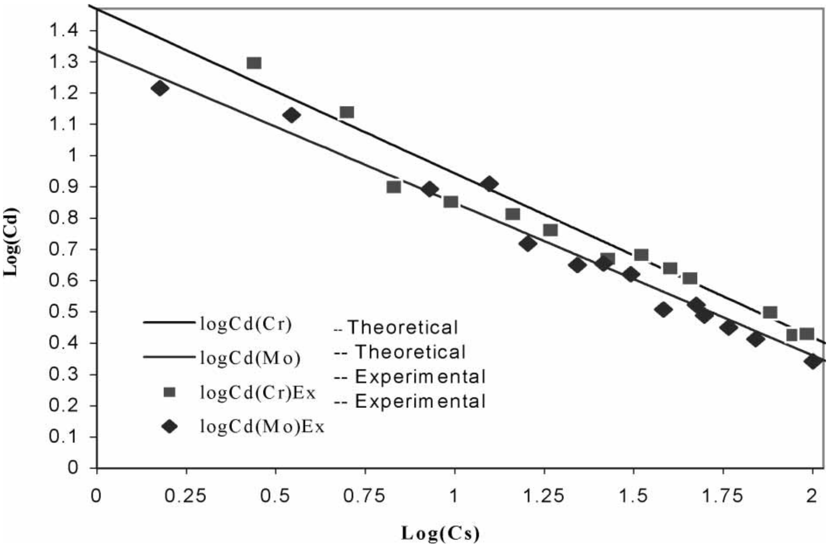

Figure 2. Distribution coefficient as a function of equilibrium aqueous phase solute concentration (pH-2).

appears that there is a competition in extraction between the metal ions: extraction of Cr(VI) is more as compared with that of Mo(VI). This is because the value of distribution coefficient of Mo(VI) is less than that of Cr(VI) as seen in Fig. 3.

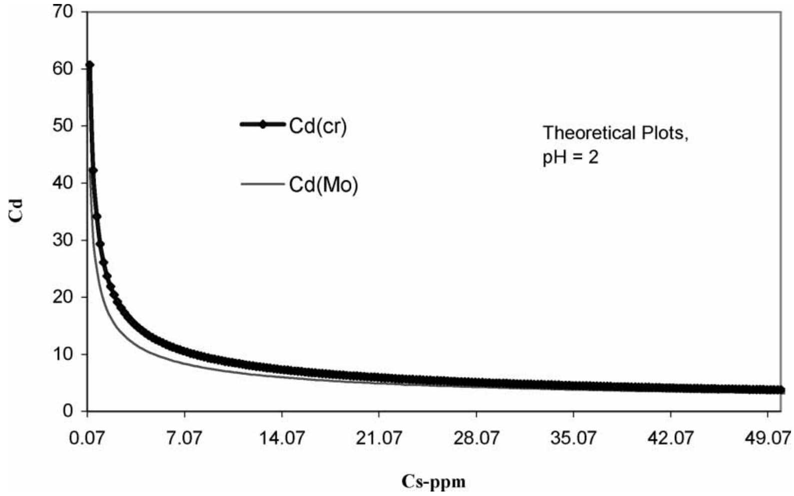

Figure 3. Variation of distribution coefficient (Cd) of Cr^{+6} & Mo^{+6} with equilibrium solute concentration (Cs) in the external phase.

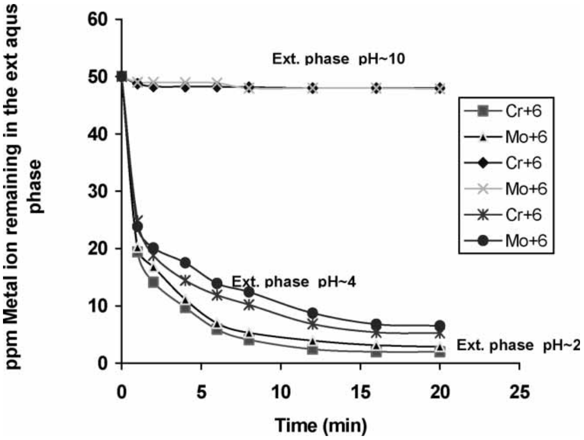

Figure 4. Effect of external phase pH on extraction of Cr^{+6} and Mo^{+6}.

Model Parameters

The following parameters have been used in the proposed model to study competitive transport between Cr^{+6} and Mo^{+6}:

1. Effect of internal reagent concentration (dimensionless variable. θ_i),
2. Effect of volume fraction of internal phase (φ),
3. Effect of initial solute concentration in external phase (Co, Co′) and
4. Effect of volume ratio of emulsion phase to external aqueous phase (E) on extraction rate as also on the time profile of the reaction front movement.

The experimental data obtained for these parameters have been compared with the theoretical curves and presented in Figs. 5–12.Values of the operating parameters for the extraction runs are given in Table 1 below along with calculated values of quantities such as D_{eff}, D'_{eff}, R_0, C_D, C'_D etc.

Effect of Internal Reagent Concentration [C_i(N)] on Simultaneous Extraction of Cr(VI) and Mo(VI)

It is apparent from the experimental results (Figs. 5 and 6) that increase in internal phase concentration causes increase in extraction rate of the metal ions. This is because with increase in NaOH concentration more solute-complex molecules can readily react because of the availability of NaOH molecules near the surface of the emulsion drops increases. It indicates that, the molecules do not have to travel far into the internal droplets—therefore

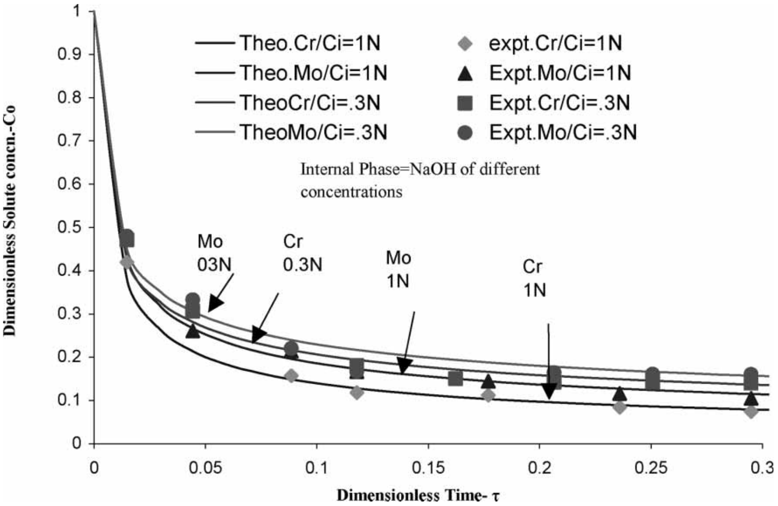

Figure 5. Effect of internal phase concentration on simultaneous extraction of Cr^{+6} & Mo^{+6}.

less resistance. As a result, faster extraction takes place. As the system approaches equilibrium the extraction curves gradually flatten out indicating decreased extraction rate. On the other hand, with increase in extraction rate (from 0.3 N to 1 N NaOH) the reaction front movement evidently slows

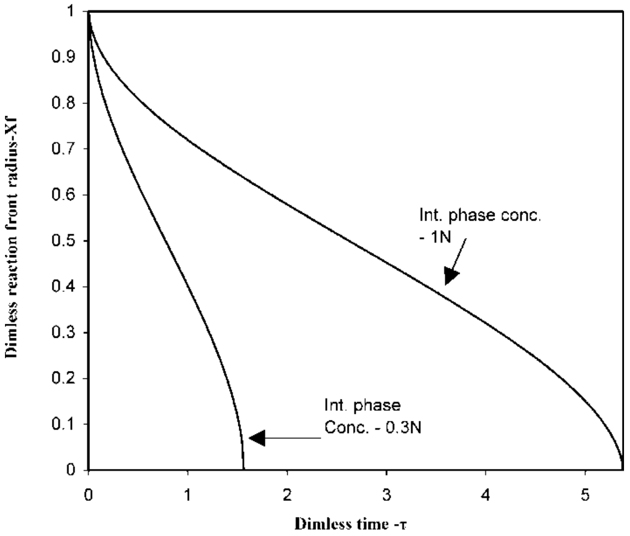

Figure 6. Simultaneous extraction of Cr-Mo-effect of internal phase concentration front movement.

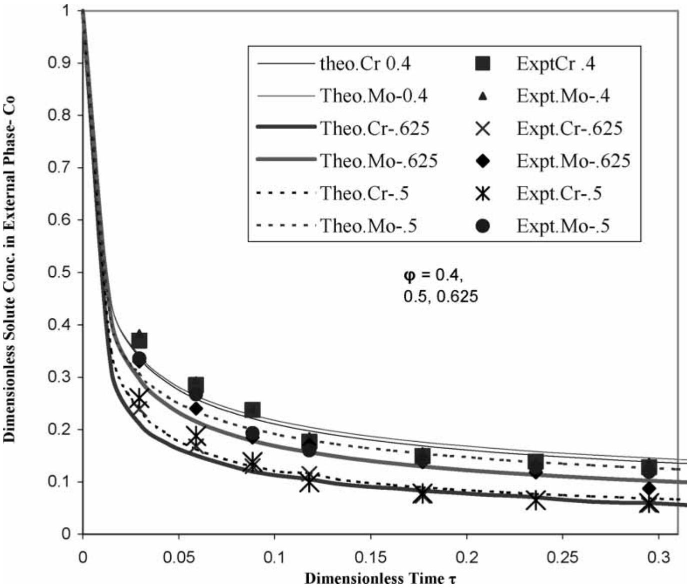

Figure 7. Simultaneous extraction of Cr^{+6} & Mo^{+6}-effect of internal phase vol. fraction.

down. (Fig. 6) In both the cases considered here (C_i- 0.3 & 1 N) the competitive nature of transport is evident. Extraction of chromium is more than that of molybdenum (Fig. 6). This is due to greater distribution coefficient of Cr(VI) as compared to that of Mo(VI).

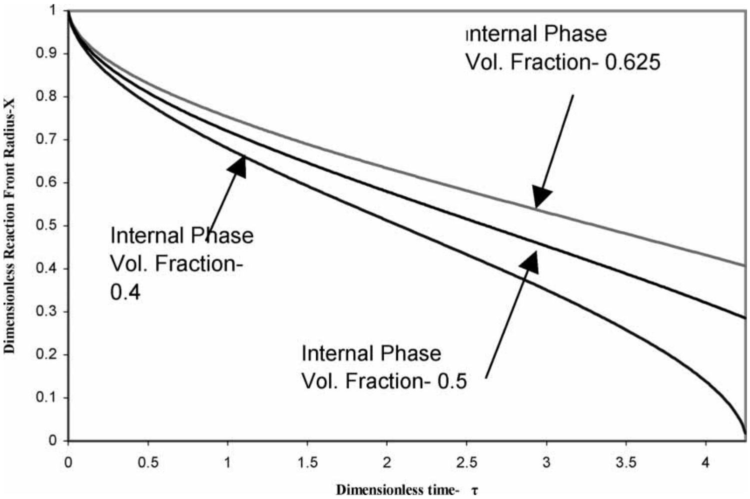

Figure 8. Simultaneous extraction of Cr^{+6} & Mo^{+6}-effect of internal phase vol. fraction.

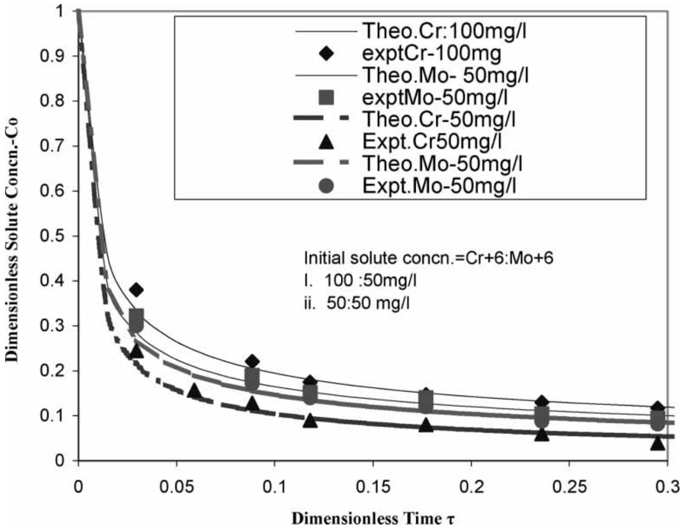

Figure 9. Effect of initial solute concentration on simultaneous extraction of Cr^{+6} & Mo^{+6}.

Effect of Volume Fraction of Internal Phase(φ) on Simultaneous Extraction of Cr(VI) and Mo(VI)

Change in internal phase volume fraction (φ) affects the simultaneous extraction of chromium and molybdenum as is evident from the experimental results

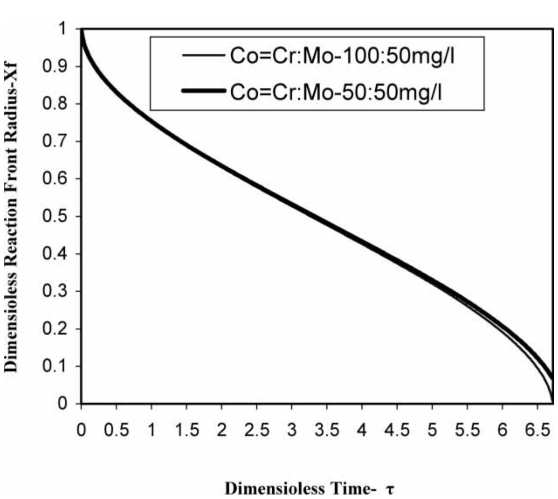

Figure 10. Effect of initial solute concentration on simultaneous extraction of Cr^{+6} & Mo^{+6}.

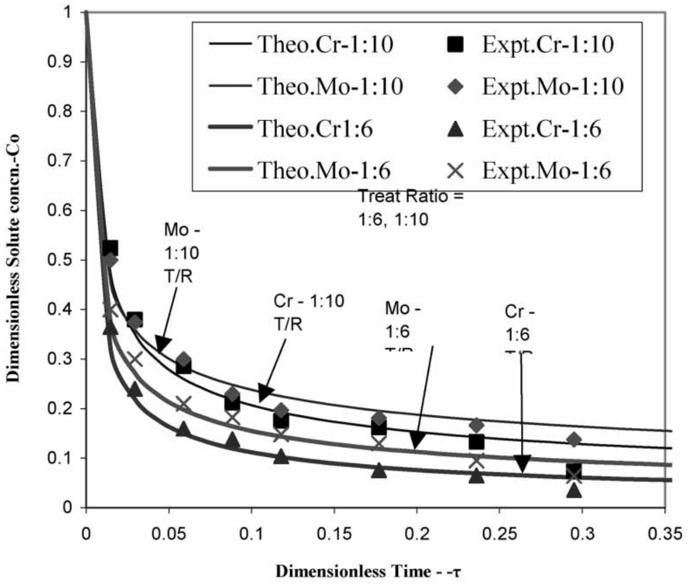

Figure 11. Effect of treat ratio on extraction of Cr^{+6} & Mo^{+6}.

depicted in Figs. 7 and 8. Lower volume fraction of internal phase means a decreasing number of NaOH molecules at the reaction front. This results in longer diffusional path for the solute-complex molecules to travel to react with the NaOH molecules. This results in more resistance to mass transfer

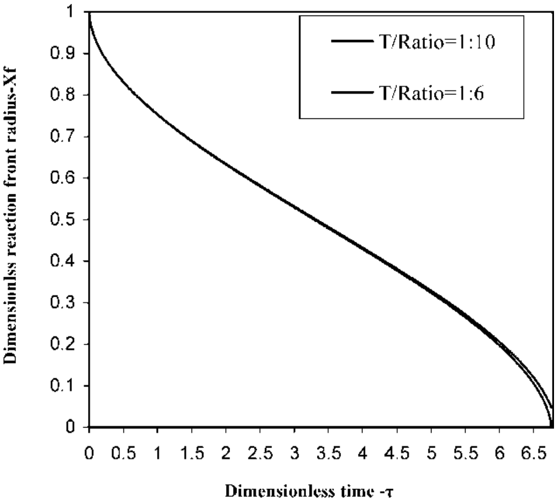

Figure 12. Effect of treat ratio on simultaneous extraction of Cr^{+6} & Mo^{+6}.

Table 1. Operating parameters for experiments on extraction of Cr^{+6} & Mo^{+6} in acidic medium

Figure	C_o, C_o'-mg/l	φ	E	C_i(N)	θ_i, θ_i'
5&6	50 mg/l each	0.50	0.2	0.3 N, 1 N	333.33,,1111 and 576.9, 1923
7&8	50 mg/l each	0.4, 0.5, 0.625	0.2	0.75 N	1111 & 1923
9&10	50 mg/l & 50 &100 mg/l	0.5	0.2	0.75 N	1111 & 1923
11&12	50 mg/l each	0.5	0.3, 0.5	0.75 N	1111 & 1923

($C_D = 29.36202 \times C_S^{-0.52462}$, $C_D' = 21.6703 \times C_S^{-0.48476}$, $R_o = 0.0736$ cm, $D_{eff}/R_o^2 = 2.4759 \times 10^{-4}$ m^2/sec, $D_{eff}'/R_o^2 = 2.3163 \times 10^{-4}$ m^2/sec).

and decreasing extraction rate (Fig. 7). On the other hand, the reaction front movement becomes faster with decreasing volume fraction of the internal phase (Fig. 8). Here too the extraction of the metal species show competitive transport characteristics. In the three cases considered here, it is seen that extraction of Cr(VI) is more than that of Mo(VI) due to difference in distribution coefficient of the species.

Effect of Initial Solute Concentration (Cr^{+6} & Mo^{+6}) on Simultaneous Extraction of Cr^{+6} & Mo^{+6}

The results of this experiment (Figs. 9 and 10) indicate variations in extraction rates due to variation in initial solute concentration in the external aqueous phase. Extraction is faster in case of lower initial concentration [Co′ (Cr:Mo) = 50:50 mg/l]. It slows down as the initial concentration is increased [Co (Cr:Mo) = 50:100 mg/l, (Fig. 9)]. This may be explained in the following manner: the solute moves towards the emulsion globule by the process of diffusion. At low initial solute concentration since the driving force for mass transfer is low, molecules take a longer time to reach the emulsion globule. However, this is compensated by increase in distribution coefficient with decrease in initial solute concentration. Therefore the solutes dissolve faster in the membrane phase due to this increment in distribution coefficient. As a result, the reaction front movement remains almost unaffected (Fig. 10). On the other hand, although increased solute concentration results in faster diffusion towards the emulsion globule, but due to decreased distribution coefficient the extraction rate decreases. In either case it appears that the reaction front does not get affected. It is also seen that extraction of Cr^{+6} is more than that of Mo^{+6} ion in two cases considered here (Fig. 9). This competitiveness is because of the higher value of distribution coefficient of Cr^{+6}.

Effect of Volume Ratio of Emulsion Phase to External Aqueous Phase

The volume ratio of emulsion to external phases (treat ratio) is represented in dimensionless form as $E = 3 \times V/V_o$ where V is the volume of the emulsion phase and V_o is that of the external aqueous phase. In this experiment values of E are: 0.3 and 0.5. As the value of E increases there happens to be more emulsion globules present in the entire mass of fluid in which emulsion phase has been dispersed in external aqueous phase than at a lower value of E. More globules mean increasing surface area for mass transfer that in turn means faster extraction (Fig. 11). On the other hand, it appears from Fig. 12 that reaction front movement is not affected with change in E value. This is also corroborated by the fact that the model equation (37) as discussed above is independent of E. Here too the competition between chromium and molybdenum in terms of extraction is apparent in the two cases considered.

COMPARISON BETWEEN EXPERIMENTAL AND COMPUTED RESULTS

The analysis of deviation between the experimental and computed results of dimensionless external phase concentration, θ_0 as a function of dimensionless time, τ indicate that, the average absolute deviation for individual parameters are: 0.058 & 0.06, 0.07 & 0.069, 0.056 & 0.069 and 0.064 &0.057 for Cr(VI) and Mo(VI) respectively for initial value of $\theta_0 = 1$. The values indicate that the simulated curves are within close proximity of the experimental data.

CONCLUSIONS

In the present work characteristics of competitive transport of multicomponent system (Cr^{+6} and Mo^{+6}) by facilitated transport mechanism through liquid surfactant membranes has been studied using a high molecular weight amine as carrier and caustic soda as stripping agent. It has been found that,

1. The simultaneous extraction of chromium and molybdenum is influenced by variation in pH value of the external aqueous phase. With increase in pH value extraction rate slows down for both the metals since the distribution coefficients of the metal ions decreases with ascending pH value.

2. There seems to be a competition between the species when extracted simultaneously. Extraction of Cr(VI) has been found to be higher than that of Mo(VI) in all the experiments carried out.

This appears to be due to the difference in distribution coefficient values, which for Cr^{+6} is more than that of Mo^{+6}. An unsteady state mathematical models for simultaneous batch extraction of $Cr^{+6} - Mo^{+6}$ has been proposed. The model has been derived from the advancing reaction front model proposed by Ho et al. Effect of various parameters on transport mechanism has been found to be as follows:

1. The extraction is faster with an increase in the value of dimensionless variable E due to availability of larger surface area for mass transfer.
2. Extraction is favoured and reaction front movement slows down by an increase in concentration of internal reagent.
3. Extraction becomes faster with increase in volume fraction.
4. Increase in initial solute concentration decreases extraction rate because increase in solute concentration at a particular pH means decrease in distribution coefficient.

NOMENCLATURE

$C_{D,}\ C_D'$	Distribution coefficient of the solutes (Cr & Mo) between membrane and external phase
C_s, C_s'	Equilibrium solute concentrations in aqueous phase
C_i	Concentration of internal reagent, gm moles/cc
$C_{m,}\ C_m'$	Concentration solutes in the membrane phase, gm moles/cc
C_0, C_o'	Concentration solutes in the external phase, gm moles/cc
C_0^*, C_o^{**}	Initial solute concentrations in the external phase, gm moles/cc
$D_{eff.}$, D_{eff}'	Effective diffusivity of the solute-carrier complex in the membrane phase based on membrane phase concentration, cm^2/sec
D_m	Diffusivity of solute in membrane phase, m^2/s
d_{32}	Sauter mean dia. of emulsion globule, cm
We	Weber no. $= \rho\, N^2 d_I^3/\sigma$
d_I	Impeller dia., cm
V_B, V_B'	Molal volume of alamine-Cr & alamine-Mo complexes, $m^3/kg \cdot mole$
M	Molecular wt. of membrane phase, $kg/kg \cdot mol$
N	Stirrer speed, rps
T	Temperature, K
E	$3V/V_0$ (dimensionless parameter)

m	Moles of internal reagent reacting with moles of solute as complex at the reaction front
n	Number of emulsion globules
R_f	Reaction front radius, cm
R_0	Sauter mean emulsion globule radius, cm $\sum n_j R_j^3 / \sum n_j R_j^2$
R	Radial position inside an emulsion globule
t	Time, sec
V	Total volume of the emulsion, cc
V_0	External phase volume, cc
X	r/R_0 (dimensionless parameter)
X_f	R_f/R_0 = dimensionless reaction front radius

Greek Letters

ϕ	Volume fraction of internal aqueous phase in the emulsion
θ_i, $\theta_i^{'}$	Dimensionless initial concentration of internal reagent = C_i/C_0^*, C_i' / C_0^*
θ_m, $\theta_m^{'}$	Dimensionless membrane phase solute concentration = C_m/C_0^*, $C_m^{'}/C_0^{**}$
$\theta_{0,}$ $\theta_0^{'}$	Dimensionless external phase solute concentration = C_0/C_0', $C_0^{/}/C_0^{**}$
τ	Dimensionless time = $D_{eff}\, t/R_0^2$
μ_m	Viscosity of membrane phase, kg/m.s
ω	Solvent association factor

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