Effect of Mass Transfer Resistance of Polymeric Surfactant on Transport of Metal through Bulk Liquid Membrane Interface

Diptendu Das*

Atomic Energy Regulatory Board, Mumbai, India

Abstract: This research work deals with an investigation on the reduction of mass transfer coefficient due to the presence of polymeric surfactant/ polycondensate layer in the liquid membrane. Mo(VI) is chosen as target species which are to be removed from feed solution using Bulk Liquid membrane (BLM) in presence of polymeric surfactant and extractant. Mathematical model is developed for simulation of kinetics of Mo(VI) extraction using BLM. Study reveals that for efficient Mo(VI) extraction, reduction of stripping rate is not at all desirable. Abil EM 90 is found best suitable polymeric surfactant as it has least mass transfer resistance of Mo(VI) transport in strip phase. This study is very useful for selecting suitable polymeric surfactant/ polycondensate layer for stabilising liquid emulsion membrane for metal extraction/recovery purpose.

Keywords: Polymeric surfactant, Bulk liquid membrane transport, Semipermeable membrane, Mass transfer coefficient, Interfacial polycondensation.

1. INTRODUCTION

Liquid membrane is a semi permeable barrier between two liquid phases. The interstitial immiscible liquid phase is called membrane and the other two liquid phases are called source or feed and extract or strip phases. Normally feed and strip phases are aqueous and membrane phase is organic, Also the reverse configuration is possible. The organic phase contain metal extractant or carrier. Liquid membrane are three types i) Supporting Liquid Membrane (SLM), where semipermeable membrane is solid ii) Liquid Emulsion Membrane (LEM), strip phase is emulsified and iii) Bulk Liquid Membrane. Bulk liquid membrane (BLM) consists of a bulk aqueous feed phase, and strip (extract) phase separated by a bulk organic, water–immiscible liquid phase. The mass transfer coefficient for transport of Mo(VI) (Molybdenum VI) through Bulk liquid membrane is studied in this paper because there are many advantages of BLM among the other two types . Bulk liquid membrane is relatively simple in operation, and easy to determine experimental concentration in all three phases *i.e.* feed (aqueous), membrane (organic) and extract/strip (aqueous) phase. Bulk Liquid Membrane (BLM) is not used commercially because of very low mass transfer area per unit volume as compare to other type of liquid membrane (Supported Liquid Membrane , SLM or Liquid emulsion Membrane , LEM) which possess large mass transfer area per unit volume . However, BLM is easy to model and mass transfer area can be easily measured. Polymeric surfactants are used to stabilise emulsion droplets by adsorbing water –in –oil (W/O) interface at very low concentrations and reduce interfacial tension to a very low value (c.a. 0.1mN/m). Another technique to stabilize emulsion is to interfacial polycondensation (IP)Techniques, where instead of direct addition to polymeric surfactant in the system polymerization takes place in the W/O interface. In this research work Mo(VI) is the target species to be removed from feed solution .BLM is used in this study to predict mass transfer coefficient of Mo(VI) transport in presence of polymeric surfactant . Polymeric surfactants are used to stabilise LEM systems. The objective of this study is to find out best suitable polymeric surfactant for LEM system with least mass transfer resistance.

Many investigators carried out research work on the solvent extraction of Mo(VI) from aqueous media using different carrier such as alamine [1, 2, 9, 10], Di-2-ethylhexylphosphoric acid [3, 4, 14], n-Tributyl Phosphate, [8, 11, 13, 15] Di-2-ethylhexylphosphoric acid,t 2-Ethylhexyl ester [5]. Equilibrium extraction of Molybdenum from perchloric acid solution was studied by [12, 13] using Tributyl Phosphate (TBP) as carrier. Molybdenum is poorly extracted by with dilute TBP from nitrate solution , in contrast to chloride media from which it readily passes into 1-10% TBP in saturated hydrocarbon hydrocarbon diluents in the form of Molybdenum chloride $MoO_2Cl_2.(H2O)_3.2TBP$ [6] carried out Molybdenum extraction from supersaturated solution (Mo initial conc. 22gl-1) in nitric acid medium with 100%TBP as carrier and achieved Distribution Coefficient (Ratio of concentration of Mo in organic phase with aquoeos phase), D_{Mo} =7. However when [6] used 50% TBP in Isopara L (diluents) distribution coefficient, D_{Mo} =0.003 was achieved in nitric acid

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*Address correspondence to this author at the Atomic Energy Regulatory Board, Mumbai, India; Tel: +91-22-25990407; Fax: +91-22-25990400;
E-mail: diptendu49@gmail.com

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medium [7]. studied Molybdenum –Complex equilibrium they also observed that extraction with Tri-n-Butyl phosphate from hydrochloric acid is favoured by high acid concentration, but from a nitric acid medium it is impossible even at very high acid concentration [7]. achieved distribution coefficient, D_{Mo} =1.25 while molybdenum extraction carried out by 50%HCl in heptane in from 1MHCl aqueous media. In our previous work we have reported Mo(VI) extraction by Liquid Emulsion Membrane using TBP as an extractant [16]. However , no comparative studies on change of mass transfer coefficient of Molybdenum transport through membrane with or without presence of polymeric surfactant is available, hence study is carried out in our laboratory to find out change of Mo(VI) concentration in feed and strip phases in Bulk Liquid Membrane and its effect on mass transfer. Also simultaneously equilibrium study was carried out by 30 hrs shaking aqueous and organic phase for both feed and strip conditions separately. The aim of this work is to understand reduction of mass transfer coefficient due to presence of polymeric surfactant in the Bulk liquid membrane and to develop a mathematical model to determine mass transfer coefficient of Mo(VI) transport through BLM.

2. EXPERIMENTAL

2.1. Reagents and Solutions

The extractant n-TBP was used as supplied by the manufacturer M/s.Sigma Aldrich Co Ltd,. The average molecular weight of n-TBP is 266.42 and the density (20° C) is 979 kg m^{-3}. Light Paraffin oil diluent was also used as supplied by the manufacturer M/s. Mercks and viscosity 30cp, density800 kg m^{-3}; all other chemicals were of AR grade.

A 1000 mg L^{-1} stock solution of Mo(VI) was prepared by dissolving MoO_3 (Mercks) in dilute NaOH solution and it was further diluted to 0.1M HCl solution. The working solutions, containing various concentration of Molybdenum (VI) in 2 (N) HCl, were prepared by dilution of the stock Molybdenum solution in HCl-water solution.

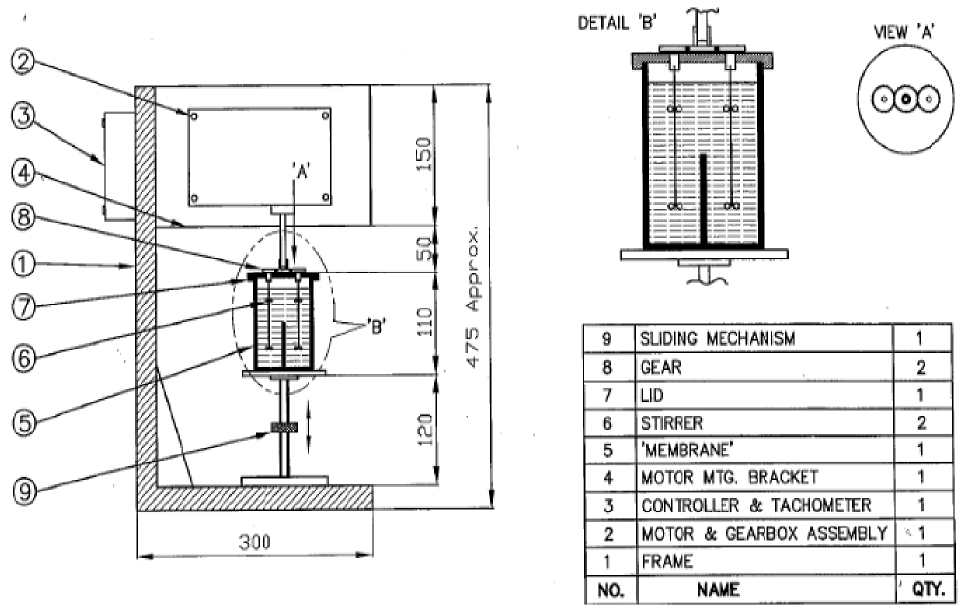
2.2. Apparatus

The extraction experiment were carried out with 10%(v/v) TBP in dodecane as organic phase. Extraction experiments were conducted in a laboratory scale Bulk Liquid Membrane (BLM) setup, which was in house fabricated as shown in Figure **1**.

The side and top view of the Schematic of BLM set up is shown Figure **2**

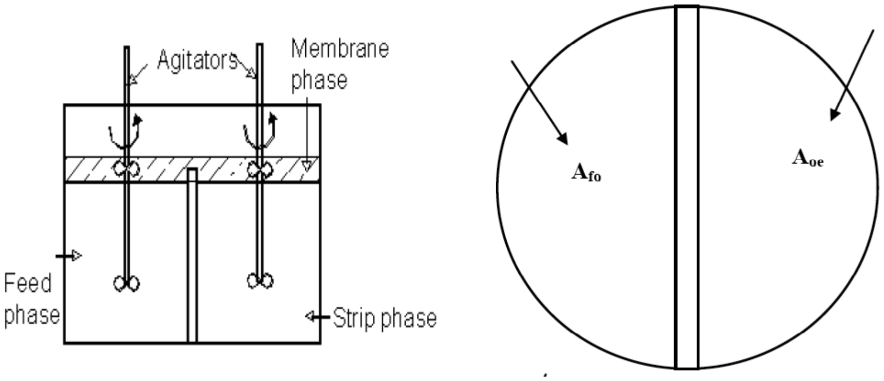
2.3. Experimental Procedure of Bulk Liquid Membrane (BLM)

All experiments were conducted in 50 mL capacity BLM vessel, equipped with a stirrer, under atmospheric pressure. Molybdenum trioxide was dissolved in desired qty in a few mL of sodium hydroxide solution



NO.	NAME	QTY.
9	SLIDING MECHANISM	1
8	GEAR	2
7	LID	1
6	STIRRER	2
5	'MEMBRANE'	1
4	MOTOR MTG. BRACKET	1
3	CONTROLLER & TACHOMETER	1
2	MOTOR & GEARBOX ASSEMBLY	1
1	FRAME	1

Figure 1: BLM Experimental set up Assembly details.



(a) Side view (b) Top view

Figure 2: Schematic of Bulk Liquid membrane setup. [Top view of circular cross section for the BLM [A_{fo}=Feed/organic interfacial area(17cm^2), A_{oe} =organic/extract interfacial area(17cm^2)].

and diluted with milliQ water and made the solution slightly acidic by adding hydrochloric acid. All the equilibrium studies were conducted in 250 mL beaker. 25mL organic phase and 25mL aqueous phase containing various concentration (10-50ppm) of Mo(VI) were poured in 250 mL beaker and continuously agitated for 30hr in a shaker with const. speed and temperature (29^{0}C) to attain equilibrium. The equilibrium concentration of Mo(VI) in aqueous feed phase was measured using thiocyanate method by UV Spectrophotometer (M/s Thermo Electronics, Model Helios alpha) at wavelength of 465nm . The concentration of Mo(VI) in organic phase was calculated from the mass balance. The distribution coefficients of Mo(VI) extraction were estimated from the ratio of equilibrium Mo(VI) concentration in organic phase to the equilibrium concentration of Mo(VI) in aqueous phase. The Mo(VI) extraction experiments were carried out using various solvents such as dodecane and paraffin. Extraction experiments were conducted in a laboratory scale BLM setup fabricated as shown in Figure **1**. Since membrane (organic) phase is lighter than feed/strip phases, therefore feed and strip phases were bottom of BLM compartment separated by a polyacrylic separating wall. Aqueous feed and strip phases were poured in such a way that the level of these liquid remains well below the top of the polyacrylic barrier and both the phases remain isolated by the separating wall. The organic/membrane phase is then poured from the top in such a way that the height of the membrane phase covers both feed and extract phases and create a bridge between the feed and extract phase for possible mass. The feed , organic and stripping/extract phases, were mechanically stirred at 30 rpm, respectively, at room temperature so that at any cost aqueous/organic phase interfaces does not get disturbed. Once the feed solution (50 mL) and the organic (25mL) and stripping (50mL) phases were placed in their corresponding chambers and the extraction begins.

2.3. Mass Transport Model

Mo (VI) form complexes with ligand TBP at the W/O (feed/organic) interface. In hydrochloric acid solution, Mo (VI) would be in chloride form and thus $MoO_2Cl_2.n$ TBP complex forms at feed/organic interface and the complex is soluble in organic phase. At alkaline medium dissociation of $MoO_2Cl_2.n$TBP complex takes place at organic/strip interface. The concentration profile of Mo(VI) transport is described in Figure **3**

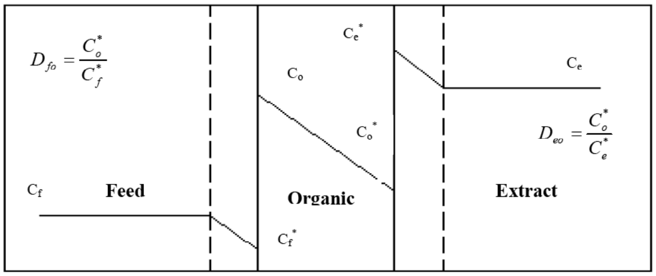


Figure 3: Concentration profile diagram for Mo(VI) extraction through BLM.

The following assumptions were taken into account in the development of a mass transfer model in the two compartment cell with bulk liquid membrane

1. The Molybdenum complex (MoO_2Cl_2.nTBP) formation chemical reactions at the feed/organic interface is very fast, which indicates diffusional

mass transfer resistance at the feed/organic interface is important

2. The Molybdenum complex dissociation chemical reactions at the organic/strip interface is very fast, which indicates diffusional mass transfer resistance at the organic/extract interface is important.

3. All the three phases are well mixed and hydrodynamic conditions at both interfaces *i.e*. feed/organic and organic/strip are identical (stirrer speed in feed , organic and extract phase kept same)

4. Both the interfaces feed/organic and organic/extract are in equilibrium

5. Due to sample collection for Mo(VI) analysis change of volume of feed , membrane and the stripping is negligible

6. Concentration of Mo(VI) complex in the strip solution is zero

The model equation for mass balance of feed , organic and strip(extract) are as follows

$$V_f \frac{dC_{Mo,f}}{dt} = -k_{fo}A_{fo}\left(C_{Mo,f} - \frac{C_{Mo,o}}{D_{fo}}\right) \quad (1)$$

$$V_o \frac{dC_{Mo,o}}{dt} = k_{fo}A_{fo}\left(C_{Mo,f} - \frac{C_{Mo,o}}{D_{fo}}\right) - k_{oe}A_{oe}\left(C_{Mo,o} - D_{eo}C_{Mo,e}\right) \quad (2)$$

$$V_e \frac{dC_{Mo,e}}{dt} = k_{oe}A_{oe}\left(C_{Mo,o} - D_{eo}C_{Mo,e}\right) \quad (3)$$

In this equation, $C_{Mo,o}$ $C_{Mo,f}$ $C_{Mo,e}$ are the concentration of Mo(VI) in organic, feed and strip(extract) phase respectively , V_o represents volume of organic phase, k_{fo} is the mass transfer coefficient and A_{fo} is the interfacial area at the feed/organic interface, Distribution coefficient, D_{fo} between feed and organic equilibrium and Distribution coefficient, D_{eo} between extract and organic phase. Similarly k_{oe} is the mass transfer coefficient and A_{oe} is the interfacial area at the organic/extract interface.

the initial boundary conditions are

At t=0

$$C_{Mo,f} = C^0_{Mo,f}\,; \quad C_{Mo,o} = C^0_{Mo,o} = 0\,; \quad C_{Mo,e} = C^0_{Mo,e} = 0 \quad (4)$$

where, $C^0_{Mo,f}$, $C^0_{Mo,o}$ and $C^0_{Mo,e}$ are the initial concentrations of *Mo(VI)* in the feed, organic and strip phase respectively. The transport of Mo(VI) can be explained by the following steps:

i) diffusion of MoO_2^+ from the bulk of feed solution to the aqueous source boundary layer,

ii) reaction between MoO_2Cl_2 and TBP carrier at the Feed-organic interface,

iii) diffusion of metal-ligand complexes ($MoO_2Cl_2.2TBP$) from the feed-organic interface through the membrane,

iv) stripping of Mo(VI) at the Organic-extract phases and diffusion of them to the bulk of the strip solution,

v) diffusion of the regenerated carrier back through the organic to the feed –organic interface, after which the process is repeated.

2.4. Results and Discussion

2.4.1. Equilibrium Studies

Equilibrium extraction and stripping studies were carried out by shaking the organic phase with aqueous phase for overnight. The distribution coefficient of Mo(VI) were estimated by measuring equilibrium concentration of organic phase with aqueous phase. From the equilibrium studies it was observed that the equilibrium concentration of Mo(VI) in organic phase and metal concentration in aqueous phase varies nonlinearly. The Distribution Coefficient, D_{fo} of Mo(VI) was found in the range of 0.8-0.9 for extraction study Distribution Coefficient for stripping equilibria study shows value of , D_{oe} of Mo(VI) ≈ 0.1

2.4.2. Evaluation of the Mass Transfer Coefficient without Surfactant

Experiments were performed to measure the concentration vs. time profile of Mo(VI) in feed phase and strip phase using BLM. Initial concentration of Mo(VI) in aqueous feed phase was 50 ppm and initial acidity of the feed phase was 2(N)HCl. Figure **4** depicts the typical changes in Mo(VI) concentration in feed and strip phases as a function of time, when no surfactant was added in the system. BLM stirrer speed was kept at 30 rpm for all experiments.

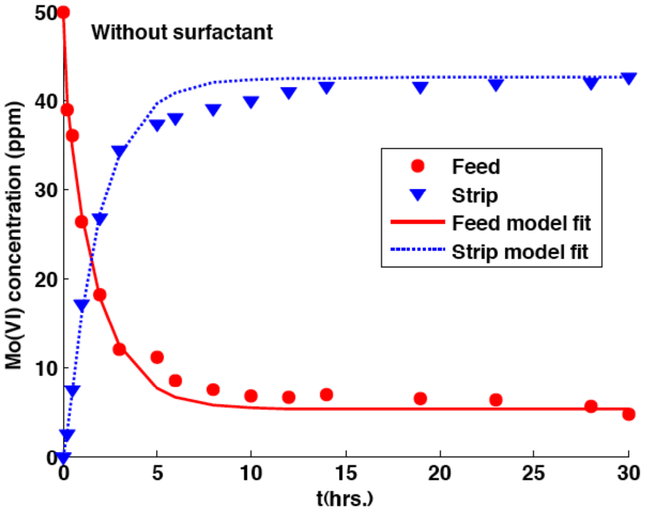


Figure 4: Mo(VI) concentration changes as a function of time in feed and strip phase (without surfactant). [Initial Mo(VI) in feed phase, $C^0_{Mo,f}$ =50ppm, Aqueous feed phase acidity 2(N) HCl, Organic phase 10%TBP in Dodecane (No surfactant added in the system].

Figure **4** shows a possible transport scheme for Mo(VI) using this BLM . Such a process is called carrier mediated or facilitated transport in Liquid membrane with mobile carrier. The above experimental data is fitted into the developed model and individual mass transfer coefficient of feed/organic interface , $k_{fo} = 1.01\times10^{-5}\, m/s$ and mass transfer coefficient of organic/strip interface $k_{fo} = 0.927\times10^{-5}\, m/s$ are determined

2.4.3. Evaluation of Mass Transfer Coefficient with Polymeric Surfactant (Pluronic F127)

Next we have mixed polymeric surfactant Pluronic F127 (PEO-PPO-PEO) 1000 ppm in both feed phase and strip phase. Figure **5** shows the typical changes in Mo(VI) concentration in aqueous feed and strip phases as a function of time when Pluronic F-127 concentration was maintained 1000ppm(w/v) in the aqueous feed and strip phase. It can be seen that Mo(VI) concentration in the feed phase decreased quickly in the initial stage (about 3hrs) and then nearly becoming constant after 10 hrs. Strip phase Mo(VI) concentration increased slightly at lower rate and then remain steady state at around 15 hrs time.

Main objective of this study is to find out effect on mass transfer coefficient. It is observed from the model fit that by addition of polymeric surfactant feed phase mass transfer is substantially reduced (k_{fo} and k_{oe} were reduced to $0.167\times10^{-5}\, m/s$ and $0.107\times10^{-5}\, m/s$). It was also observed that organic-extract (strip) phase mass transfer coefficient substantially reduces due to addition of polymeric surfactant pluronic F127 into the aqueous phase.

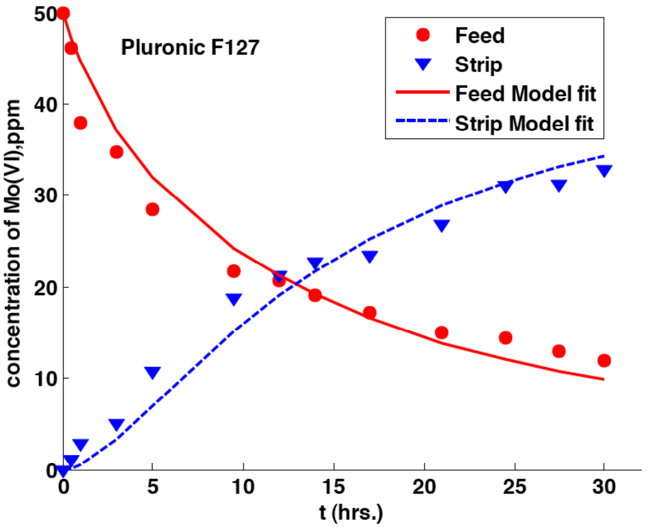


Figure 5: Mo(VI) conc. profile as a function of time in BLM (polymeric surfactant Pluronic F127 1000 ppm) ,[Initial Mo(VI) in feed phase, C^0_f =50ppm, Aqueous feed phase acidity 2(N) HCl, Organic phase 10%TBP in Dodecane].

2.4.4. Evaluation of Mass Transfer Coefficient with Interfacial Poly Condensation Film at the W/O Interface

Next we have we have added monomer in both organic and aqueous phase and allowed to form an interfacial film at the W/O interface, this technique is called, Interfacial Poly condensation (IP) technique. The objective of this experiment is to analyse the reduction of mass transfer coefficient due to presence of interfacial film at the W/O interface. Khare *et al*. 2003 studied interfacial Polycondensation (IP) phenomenon by using Meta Phenylene Di-amine(MPD) in aqueous phase and Trimesolyl Chloride (TMC) 0.1% in organic phase and they observed formation of solid polymeric films at the interface between aqueous and immiscible organic solutions. Similar way we have added 1% (w/v)MPD in aqueous phase and 0.1% (w/v)Trimesolyl Chloride (TMC) in organic phase and interfacial polycondensation reaction occurred between monomeric reactants present in the two phases. MPD monomer diffuses through the growing IP film and reacts with TMC on the organic phase. The trifunctional nature of nature of TMC enables formation of a cross linked poly amide at the W/O interface.

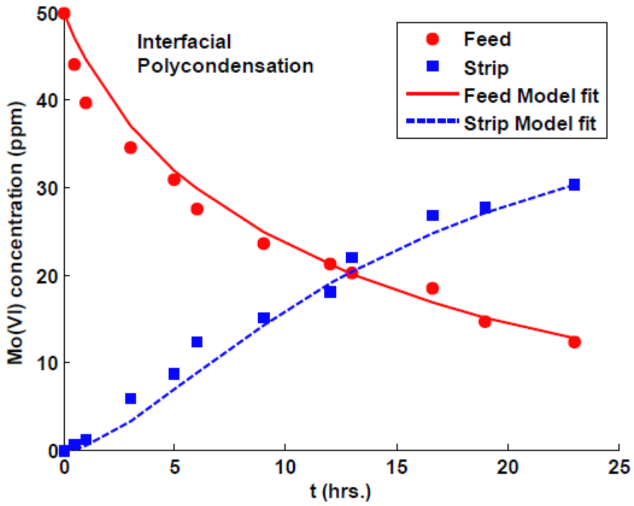


Figure 6: Mo(VI) conc. profile as a function of time in the BLM (Interfacial polycondensation polyamide film at W/O interface)[MPD 1% added aq. Phase TMC 0.1% added in organic phase, Initial Mo in feed phase, C_f^0 =50ppm, Aqueous feed phase acidity 2(N) HCl, Organic phase 10%TBP in Dodecane,].

We have sampled from aqueous feed and strip phase at different time interval and analysed for Mo(VI) concentration and concentration of Mo(VI) in organic phase derived by mass balance as describe in Figure **6** . Above experimental Mo(VI) concentration-time data was fitted in the model [Eq.1-4] and mass transfer coefficients were determined. It was observed that due to interfacial film formation mass transfer coefficient was substantially reduced (k_{fo} and k_{oe} were reduced to $0.129\times10^{-5} m/s$ and $0.134\times10^{-5} m/s$) but the result was comparable to Pluronic F127 . Hence Interfacial poly condensation technique can be used for stabilizing liquid emulsion membrane.

2.4.5. Evaluation of Mass Transfer Coefficient with Polymeric Surfactant (Abil EM90)

Next we have mixed polymeric surfactant Abil EM 90 (PDMS-PEO) 1000 ppm(w/v) in organic phase (10%(v/v) TBP in Dodecane).

Figure **7** shows the Mo(VI) concentration time profile of feed and strip phase after addition of Abil EM90 in the organic phase. It has been noted that almost feed-organic phase mass Transfer coefficient 90% reduces(k_{fo} reduced from $1\times10^{-5} m/s$ to $0.102\times10^{-5} m/s$), however organic -strip phase only 20% of mass transfer coefficient was reduced (k_{oe}= $0.807\times10^{-5} m/s$

2.4.6. Evaluation of Mass Transfer Coefficient with Polymeric Surfactant (Hypermer -A60)

Next we have mixed polymeric surfactant Hypermer A-60 (PEO-PMMA) 1000 ppm(w/v) in organic phase 10%(v/v) TBP in dodecane. Figure **8** shows the concentration time profile of Mo(VI) in feed and strip phase after addition of polymeric surfactant HypermerA60 in the system. It has been noted 30% mass transfer coefficient feed-organic phase was reduced(k_{fo} was reduced from $1\times10^{-5} m/s$ to $0.7\times10^{-5} m/s$), however 70% of mass transfer coefficient in organic-strip phase was reduced (k_{oe}= $0.294\times10^{-5} m/s$)

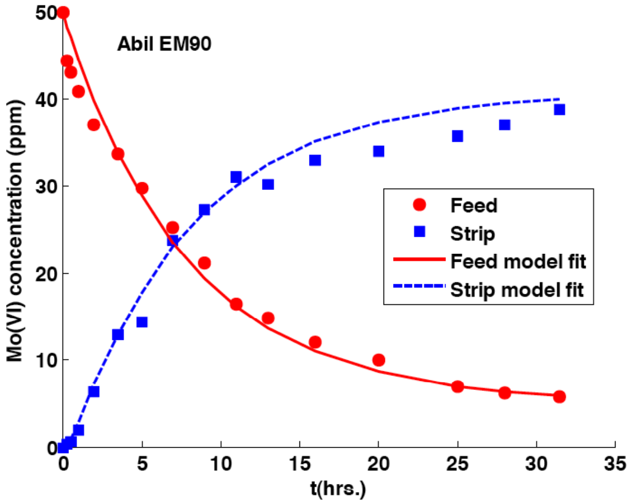


Figure 7: Mo(VI) conc. profile as a function of time in BLM (polymeric surfactant Abil EM90 conc.1000 ppm) [Initial Mo in feed phase, C_f^0 =50ppm, Aqueous feed phase acidity 2(N) HCl, Organic phase 10%TBP in Dodecane]

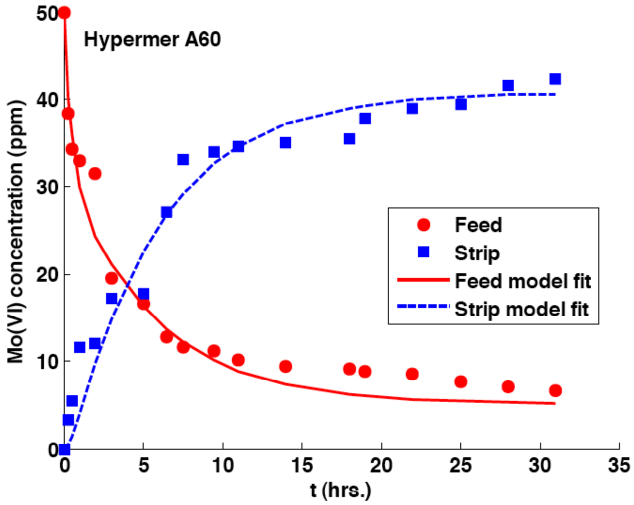


Figure 8: Mo(VI) conc. profile as a function of time in BLM (polymeric surfactant Hypermer A-60 conc. 1000 ppm) [Initial Mo in feed phase, C_f^0 =50ppm, Aqueous feed phase acidity 2(N) HCl, Organic phase 10%TBP in Dodecane].

2.4.7. Evaluation of Mass Transfer Coefficient with Polymeric Surfactant (Arlacel P-135)

Next we have mixed polymeric surfactant Arlacel P135 (PHS-PEO-PHS) 1000 ppm(w/v) in the organic phase contained 10% TBP(v/v) in dodecane . Figure **9** shows the Mo(VI) concentration time profile of feed and strip phase after addition of polymeric surfactant Arlacel P-135 into the system. It has been noted almost feed-organic phase 90% mass transfer coefficient was reduced (k_{fo} value was reduced from $1\times10^{-5} m/s$ to $0.1\times10^{-5} m/s$), however organic -strip phase side only 16% mass transfer coefficient was reduced (k_{fo} value was reduced from $927\times10^{-5} m/s$ to $0.793\times10^{-5} m/s$).

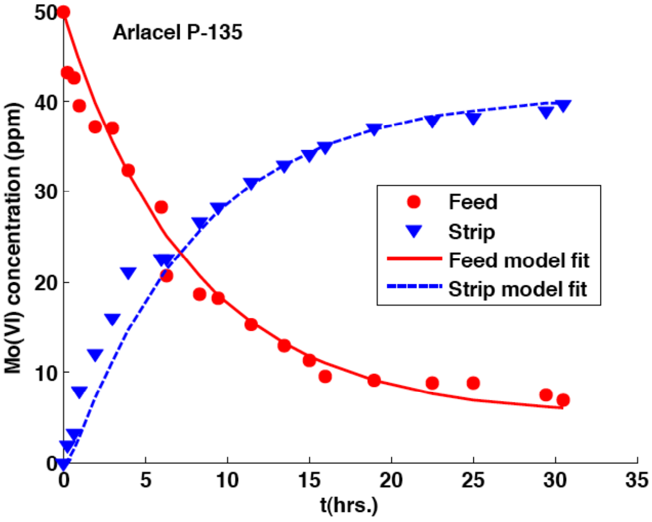


Figure 9: Mo(VI) conc. profile as a function of time in BLM (polymeric surfactant conc. Arlacel P-135 1000 ppm)[Initial Mo(VI) in feed phase, C_f^0 =50ppm, Aqueous feed phase acidity 2(N) HCl, Organic phase 10%TBP in Dodecane].

The rate equations of transport of the metal ions Mo(VI) (system of simultaneous differential equations 1, 2 and 3) were solved to get the analytical concentration versus time profiles for all the three phases (Feed, Organic and Strip). The simulation results are compared with experimental results at each measured point. All deviations between experimental and calculated values are squared and summed up to form objective function. This objective function was fed into least square fit minimiser routine using Levenberg-Marquardt algorithm that gives optimal mass transfer coefficient of acid and U(VI) . The tolerance value for function termination was set at 1×10^{-4}. We made a comparison on mass transfer coefficient in both extraction and stripping for various polymeric surfactants added into the BLM system. The results of reduction of mass transfer coefficients due to addition of polymeric surfactant into the organic –aqueous interface were shown in Figure **10**

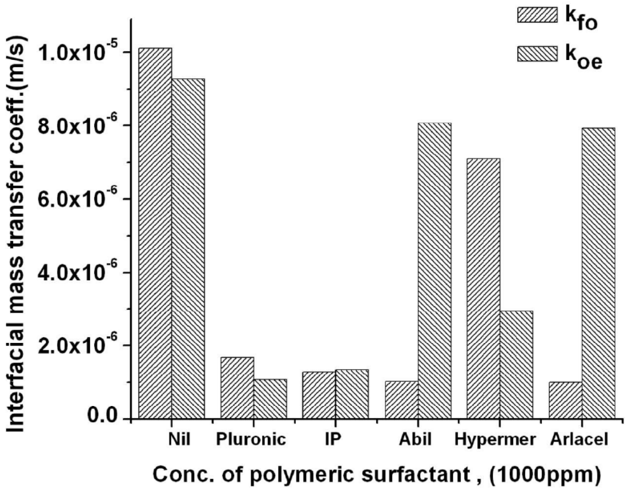


Figure 10: Comparison of mass transfer coefficient of Mo(VI) with and without polymeric surfactant.

2.5. ConclusionIn this research work, screening of polymeric surfactant was carried out based on interfacial resistance study. We have compared reduction of mass transfer rates with and without addition of polymeric surfactant into the organic-aqueous phase. After addition of polymeric surfactant in the organic-aqueous phase which cause lesser reduction of mass transfer coefficient is better surfactant for liquid membrane application. The result obtained showed that almost 90% extraction rate was reduced with addition of equal amount (1000 ppm) polymeric surfactant such as Abil EM 90 or Arlacel P-135 , whereas only 13-14% stripping rate was reduced. Similarly when equal amount of other polymeric surfactant such as Hypermer -A60 was added in the organic phase although extraction rate reduced only by 21% where as stripping rate was reduced substantially almost 68%. Again we observed Interfacial poly condensation film caused reduction of mass transfer rate in both extraction and stripping side around 80% , hence this film thickness may not be useful for Mo(VI) extraction , may be lesser film thickness is better , again in that case there would be stability issues . Similarly, when we have added Pluronic F127 (1000) ppm in aqueous phases we found that both side mass transfer coefficient ($k_{fo,}$ k_{oe}) were reduced around 90%, which indicates both extraction and stripping rate reduction substantially. Thus we can conclude that for efficient metal extraction, reduction of stripping rate is not at all desirable because equilibrium is attained. Hence, Abil EM 90 or Arlacel P-135 are better polymeric surfactant for Mo (VI) extraction case study as there was minor (13-14%) reduction of mass transfer coefficient, k_{oe} in the stripping side even though there was substantial (80%) reduction in extraction rate due to reduction of mass transfer coefficient, k_{fo} in feed/ organic interface side . Thus it can be concluded through interfacial resistance study that screening of polymeric surfactant should be carried out based on lesser mass transfer reduction rate and higher stability. This method could be utilised for selection of best suitable polymeric surfactant in liquid membrane applications.

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