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SELECTIVE TRANSPORTATION OF MOLYBDENUM FROM MODEL AND ORE THROUGH POLY INCLUSION MEMBRANE

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ABSTRACT. The extraction of molybdenum from the aqueous solution through poly inclusion membrane (PIM) containing tri-caprylylmethylammonium chloride (Aliquat-336) as a carrier has been investigated. A solution of molybdenum in phosphoric acid was used as a feed side while sodium hydroxide was used as stripping reagent. The results indicate that maximum flux value was obtained at 0.16 M Aliquat-336. Increase in H_3PO_4 concentration from 0.05 to 1.5 M results into an increase in molybdenum ions. The maximum flux of 3.00×10^{-6} mol/m²s through PIM was found at 1.5 M H_3PO_4 . The optimized conditions were applied for removal of Mo(VI) from ore and more than 97 % Mo(VI) was extracted.

KEY WORDS: Molybdenum extraction, Poly inclusion membrane, Aliquat 336

INTRODUCTION

Molybdenum (Mo) is essential in trace quantity for all living organism. Due to high melting point of Mo, its compounds are used in industrial processes such as corrosion control, textile dyeing, leather tanning process, oxidation process, metallurgy, electroplating, cement, paper making, paints, ink and pigments, catalyst in oil industry, photographic industry, alloying agent in cast iron and super alloys, mechanical strength and thermal conductivity [1, 2]. Similar to many metals and their compounds [3–23], Mo compounds also find application in the field of catalysis. The utility of Mo is increasing extensively as the modernization of nanostructured material is going on, particularly molybdenum sulfides (MoS_x) are favorable options to platinum for the electrochemical generation [4] of hydrogen from water [2].

Generally, Mo occurs in the form of molybdate (MoO_4^{2-}) ions and its major oxidation state is Mo(VI) which forms oxyanions in acidic media [24], and appears to be toxic when its concentration is higher than $5 \mu g L^{-1}$ [25]. Due to high commercial demand of Mo concentration and also its serious consequences to the human health, there is a need of its removal from waste water (industrial discharges), air (coal combustion) and soils (waste disposal) [26].

Many hydrometallurgical potential are working to extract and separate the content of molybdenum from aqueous solutions. Therefore, various conventional techniques are used for the removal of Mo from ground and surface water. These methods include fractional crystallization, ion exchange [27], solvent extraction [28], precipitation [29], chromatography and conventional solvent extraction processes. These techniques have their own limitations such as less efficiency, high capital and operating cost, secondary sludge formation, complex and sensitive operating conditions. Therefore, more effective and efficient methods are required to seek out these difficulties.

Among these techniques, the removal of metals by membrane technique is getting popular nowadays. The different kinds of membranes used in this technique include bulk liquid membrane (BLM), emulsion liquid membrane (ELM), supported liquid membrane (SLM), activated composites membrane (ACM) and polymer inclusion membrane (PIM) [30, 31]. Among these, supported liquid membrane (SLM) has been extensively studied due to its high transport rates, has low capital and operating cost as well as low energy consumption and good

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selectivity, therefore, being a very interesting alternate technique to overcome the SX downsides [32–34]. But the main problems related with SLM which hinders their use in practical applications are the lack of membrane stability, permeability and low flux value which minimize the use of SLM. Alternatively, several authors have reported that polymer inclusion membrane (PIM) shows good long-term stabilities [35]. Recently, a comparison between SLM and PIM performance has been reported by Paugam and Buffle [36] in which Cu(II) facilitated transport across both types of membranes using lauric acid as a carrier has been investigated. However, stability of these two membranes system has not been reported earlier. In a similar way, Schow *et al.* [37] compared the fluxes of K^+ through a cellulose triacetate (CTA)-2-nitrophenyloctyl ether (NPOE) PIM containing crown ether as a carrier with other supported liquid membranes. Literature reported that PIM fluxes, permeability and stability were three times greater than those exhibited by the thin sheet and hollow fiber SLM. Beside the more efficiency of PIM over SLM, PIM have long-term life and durability [35]. The literature present to date for the separation of Mo(VI) in the field of liquid membrane is very limited which has been summarized in Table. 1.

Table 1. Literature review of extraction of Mo(VI) through membrane.

Feed phase	Membrane/method	Membrane phase	Strip phase	Reference
$Na_2MoO_4 \cdot 2H_2O$	Liquid emulsion membrane (LEM)	Alamine 336	$Na_2CO_3 \cdot 2H_2O$	[38]
$Na_2MoO_4 \cdot 2H_2O/H_2SO_4$	SLM	Alamine 336/ kerosene	$Na_2CO_3 \cdot 2H_2O$	[39]
$Na_2MoO_4 \cdot 2H_2O$ $Na_2WO_4 \cdot 2H_2O$	Liquid liquid membrane	Primary amine N1923	NaOH	[40]
MoS_2 /nitric acid	Hollow fiber contactor	Alamine 336/n-hexane		[41]
Na_2MoO_4	Liquid emulsion membrane (LEM)	Aliquat 336, TBP, TOA, D_2EHPA , alamine, Primene JMT/dodecane	NaOH	[42]
$Na_2MoO_4 \cdot 2H_2O$	Liquid liquid extraction	bis(2,4,4-Trimethylpentyl) dithiophosphinic acid/ kerosene	$(NH_4)_2CO_3$	[43]
Mo, V, Ni	Liquid-liquid extraction	Alamine 336/kerosene	Na_2CO_3	[44]

SLM: Supported liquid membrane, Alamine 336: tri-octyl/decylamine, Aliquat 336: tricaprylylmethylammonium chloride/trioctylmethylammonium chloride, TOA: tri-octylamine.

In the literature, there are limited reports on SLM method for extraction of Mo(VI). However, no literature is present for the extraction of Mo(VI) using PIM methods. In the present work we want to improve an extraction efficient of Mo(VI) from model and ore samples. In this method membrane of polyvinyl chloride was used with quaternary ammonium chloride (Aliquat 336) as a carrier and phosphoric acid was used as a feed side. The transport of Mo(VI) is explained on the basis of a two migrating species model. The performance of membrane system and the effects of carrier concentration, acid concentration, pH and stripping agent on membrane permeability have been investigated. Further, the model system was applied on the real sample to estimate the efficiency of the system.

EXPERIMENTAL

Chemicals

The extractant tricaprylylmethylammonium chloride ($C_{25}H_{54}ClN$, commercially known as Aliquat 336) (98%), poly (vinyl chloride) (PVC) and tetrahydrofuran (C_4H_8O abbreviated as THF) (99%) was purchased from Merck. The ammonium molybdate ($(NH_4)_6Mo_7O_{24}$, 99%), hydrochloric acid (HCl 36%), phosphoric acid (H_3PO_4 85%) and sodium hydroxide (NaOH 99%) were obtained from Fluka Company. All the solutions were prepared in double distilled water.

Membrane PIM

Poly inclusion membrane was prepared by intermixing of PVC polymer, Aliquat 336 as a carrier and THF as a solvent. The obtained membrane having porosity (ϵ) 80%, pore size $\Phi = 0.12\text{--}0.22$ μm and thickness (d_0) of 28 μm .

Instrumentation

The metal ion concentration was determined by UV spectrophotometer (resolution 0.001 mg/L, accuracy ± 0.1 mg/L) at 350 nm (BMS model 1602, Hopkinton, USA). The pH measurement was carried out by pH meter NeoMet model 200L digital (Seoul, South Korea). The SEM analysis was carried out by Scanning Electron Microscope model JSM-5910 JEOL (Tokyo, Japan). The TG analysis for PVC/Aliquat-336 PIMs was carried out using a TGA-X model Pyris Diamond Series TG/DTA (Perkin Elmer, USA).

Permeator cell

The transport experiment through PIM was carried in a permeation cell made-up from acrylic sheets in which the membrane film tightly clamped between two cell compartments. Each compartment of a permeation cell had an effective surface area of 23.79 cm^2 . The maximum capacity of each half cell was 300 mL. Both the source and receiving aqueous phases were provided with a vertical mechanical stirrer in the range of 1000-1500 rpm to avoid concentration polarization at the membrane interfaces.

Membrane preparation

The PVC membranes were prepared according to the procedure reported by Sugiura *et al.* [45]. PVC and Aliquat 336 were dissolved in 10 mL tetrahydrofuran by using magnetic stirrer to avoid aggregation. The solution was poured into a Petri dish, covered with a glass funnel in order to avoid the contamination with dust and left for 24 h at room temperature to allow the complete evaporation of solvent. The PIM membranes obtained were appeared as flexible, transparent, homogenous and good strength thin films. Membranes of different concentration of PVC and Aliquat 336 were prepared.

SEM analysis

Information about membrane morphology was obtained by scanning electron microscopy (SEM), images being noted with an electron microscope. In order to analyze the surface morphology of PIM, the samples were prepared by freezing the membrane under liquid nitrogen and were fractured, resulting in a clean break fracture image to view their cross section. The samples were mounted onto an aluminum support using a C graphite double scotch, and coated with a 15 nm gold layer by sputtering.

Procedure

The membrane was tightly clamped in between the two compartments of the permeator cell, feed and strip compartments, to be filled with feed and stripping solutions respectively. The electric stirrer was used in each compartment to stir the solution at 1500 rpm to avoid polarization of concentration. In the experiments, various molybdenum(VI) ions (conc. 0.05–2 M) and NaOH (0.05–1.5 M) concentrations were used as feed and strip solutions, respectively. After every 60 min, 1 mL of aliquot from the feed and the stripping solutions were withdrawn. A yellow color stable complex was obtained by mixing of 1 mL of solution with 1 mL of N,N'-bis(2-hydroxy-5-bromo-benzyl)1,2-diaminopropane(1:1) and left for 10 min after 10 min, the absorbance of solution analyzed by UV spectrophotometer at 350 nm [46].

Flux calculation

Mass flux J ($\text{mol}\cdot\text{cm}^2\cdot\text{s}^{-1}$) of the metal ions through PIM transferred from the feed side to stripping side through membrane was determined by using following relation (Eqs. 1 and 2):

$$\text{Flux} = \frac{\text{Concentration change of metal ion } (\text{mol}/\text{dm}^3) \times \text{solution volume in feed or strip } (\text{dm}^3)}{\text{Effective membrane area } (\text{m}^2) \times \text{dt}} \quad (1)$$

$$J = \frac{\Delta n}{S \Delta t} \quad (2)$$

where Δn represents the variation in the mole number of the metal ions in the receiving solution during reference time Δt , and S is the effective membrane area.

Permeability coefficient

The permeability coefficient (P) was calculated as:

$$p = \frac{\left[\ln \left(\frac{\text{initial feed concentration}}{\text{feed concentration at time } (t)} \right) \right] \times \text{volume in feed phase}}{\text{Effective membrane area} \times \Delta t} \quad (3)$$

where, Δt indicates the total permeation time interval in seconds.

Percent extraction

Molybdenum extraction extent, %E (Mo), was calculated according to Equation 4, where the subscripts 'in' and 'eq' indicate initial and equilibrium conditions, respectively, and 'aq' denotes aqueous solution.

$$\% E(\text{Mo}) = \frac{[\text{Mo}]_{\text{aq, in}} - [\text{Mo}]_{\text{aq, eq}}}{[\text{Mo}]_{\text{aq, in}}} \times 100\% \quad (4)$$

RESULTS AND DISCUSSION*Effect of Aliquat-336 concentration*

The concentration of Aliquat-336 in the liquid membrane phase of poly inclusion membrane has critical role on removal of metal ions. To observe the effect of Aliquat-336 concentration on transport of Mo(VI) through PIM, various concentrations of Aliquat-336 in the range from 0.044 to 0.2 M were studied. In the experiment, the Mo(VI) concentration in feed solution was kept at 5.21×10^{-4} M in 1.0 M of H_3PO_4 and the NaOH concentration in strip solution was fixed at 1.0 M.

Figure 1 shows that transport of Mo(VI) increases as the Aliquat-336 concentration increases from 0.044 to 0.2 M in THF and then decreases. The transport of Mo was negligible when the extraction experiment was performed using PVC film that had been cast from THF without Aliquat-336, which shows that the transport of Mo was fulfilled by extractant. Figure 2 shows that in membrane phase carrier has a significant effect on flux of Mo(VI). As the concentration of carrier increases beyond 0.16 M, the flux is insignificant due to enhanced friction of liquid membrane phase and high viscosity. Extraction of Mo(VI) increases with the increase in concentration of Aliquat 336 from 0.044 to 0.16 M as shown in Figure 1. Beyond 0.16 M the extraction of Mo(VI) decreases. This decrease in transport of Mo(VI) could be due to enhanced friction of liquid membrane phase due to high viscosity, as with increasing carrier concentration the viscosity of liquid membrane phase increases. Further studies were carried out with the 0.16 M of Aliquat-336 as optimum carrier concentration.

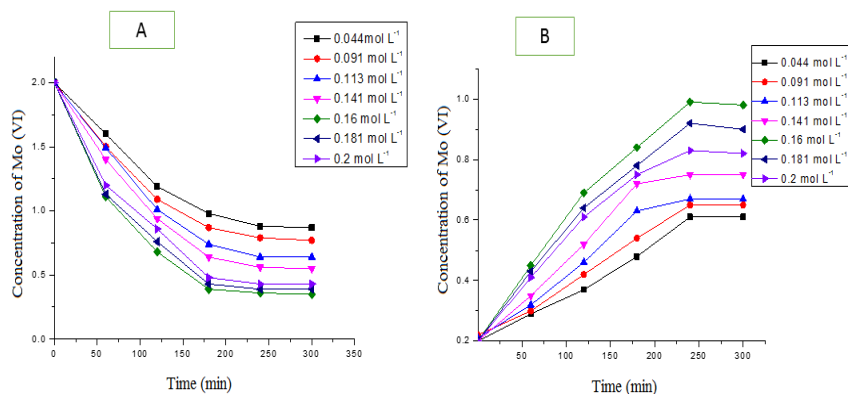


Figure 1. Effect of carrier concentration on transport of Mo(VI) concentration on feed solution (A) and strip solution (B) using poly inclusion membrane. Aliquat-336 = 0.044-0.2 M, Mo(VI) concentration in feed solution = 5.21×10^{-4} M, $\text{H}_3\text{PO}_4 = 1.0$ M, $\text{NaOH} = 1.0$ M.

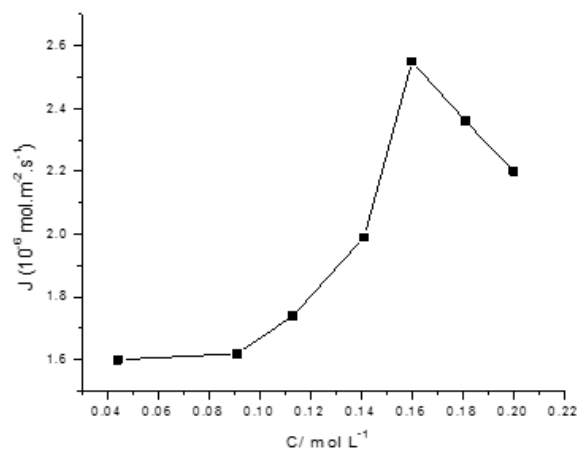


Figure 2. Effect of Aliquat 336 concentration on transport of Mo(VI) in stripping phase using poly inclusion membrane.

Effect of acid concentration

For the formation of complex $((\text{LH})_n \cdot [(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3]_{n+1})$, the H_3PO_4 plays an important role in the transport of Mo(VI), as it provides H^+ and PO_4^- ions. For the experiments, concentration of Aliquat 336 and concentration of NaOH were kept constant at 0.16 M and 1.0 M, respectively. The influence of H_3PO_4 concentration on extraction Mo(VI) was observed by changing the concentration of H_3PO_4 in the range from 0.05 M to 2.0 M. Figure 3 shows that the concentration of Mo(VI) decreases with the increase of H_3PO_4 from 0.05 M to 2 M. Figure 4 indicates that the flux of Mo(VI) increases as the concentration of H_3PO_4 increases from 0.05 M to 1.5 M. The transport of Mo(VI) decreases by further increasing the concentration of H_3PO_4 beyond 1.5 M. Beyond 1.5 the extraction of Mo(VI) decreases. The concentration of H^+ and PO_4^- in feed solution increases with the increase of H_3PO_4 concentration which in turn increases

the complex formation that eventually increases the transport of Mo(VI) ions. Reaction is inhibited in forward direction due to formation of $H_n \cdot [(NH_4)_3PO_4 \cdot 12MoO_3]_n$ type species owing the excessive quantity of H^+ and $H_2PO_4^-$ in feed phase. This study shows that the optimum concentration of H_3PO_4 for transport of Mo(VI) is 1.5 M.

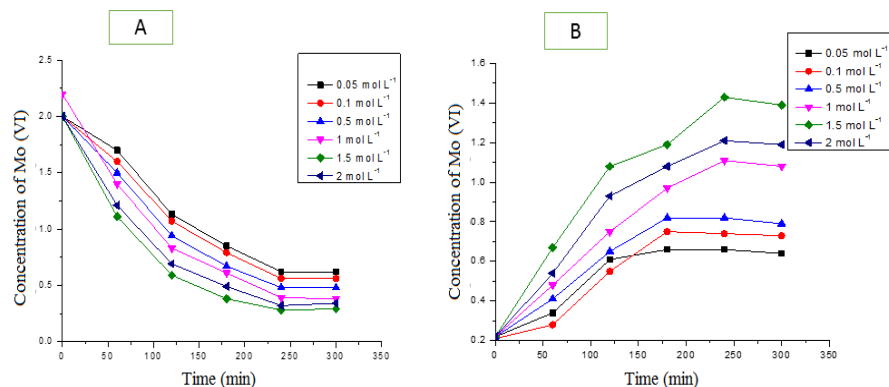


Figure 3. Effect of acid concentration on transport of Mo(VI) in feed solution (A) and strip solution and (B) using poly inclusion membrane. $H_3PO_4 = 0.05\text{--}2.0$ M, Aliquat 336 = 0.16 M, NaOH = 1.0 M, Mo(VI) concentration in feed solution = 5.21×10^{-4} M.

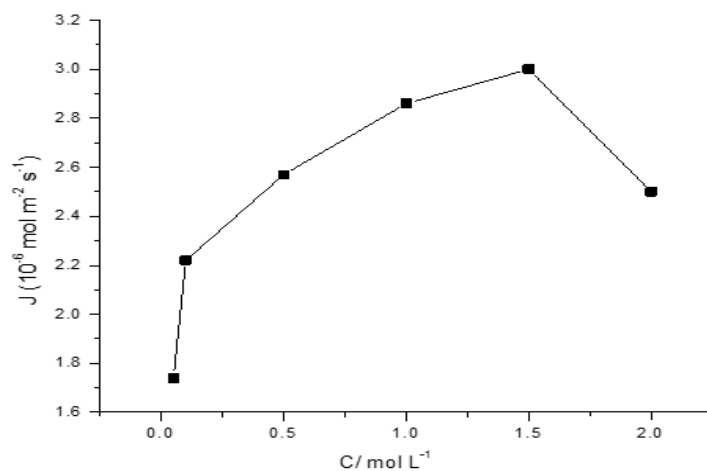


Figure 4. Effect of acid concentration on transport of Mo(VI) in stripping phase using poly inclusion membrane.

Effect of stripping solution on metal transport

Various concentration of NaOH in the range of 0.05 M to 2.0 M were used to observe the influence of NaOH on transport of Mo(VI). As the concentration of NaOH increases, the transport of Mo(VI) is also increases as shown in Figure 5. This is true up to 1 M of NaOH concentration, on further increasing the concentration of NaOH beyond 1 M, the extraction of Mo(VI) decreases. Figure 6 indicates that the flux of Mo(VI) ions also show a maximum value

at 1 M NaOH. On further increasing the NaOH concentration in strip solution increases, the concentration of OH^- also increases, that enhances the decomposition of complex at strip membrane interface this may due to formation of insoluble compound in excess of NaOH, and block the pores of poly inclusion membrane and supported liquid membrane and transport of Mo(VI) is controlled.

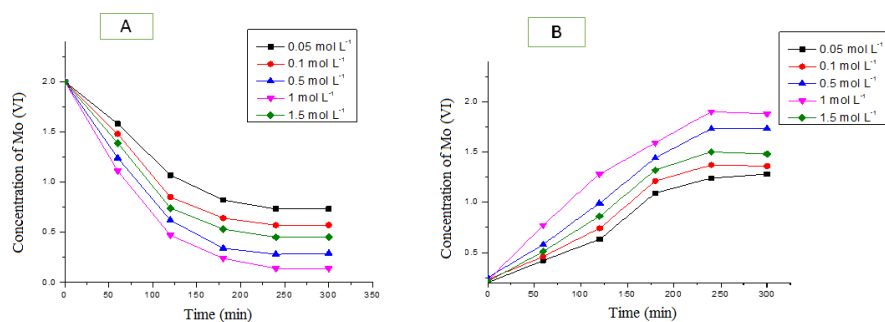


Figure 5. Effect of NaOH concentration on transport of Mo(VI) concentration in feed solution (A) and strip solution and (B) using poly inclusion membrane. NaOH = 0.05 M to 2.0 M, H_3PO_4 = 1.5 M, Aliquat 336 = 0.16 M, Mo(VI) concentration in feed solution = 5.21×10^{-4} M.

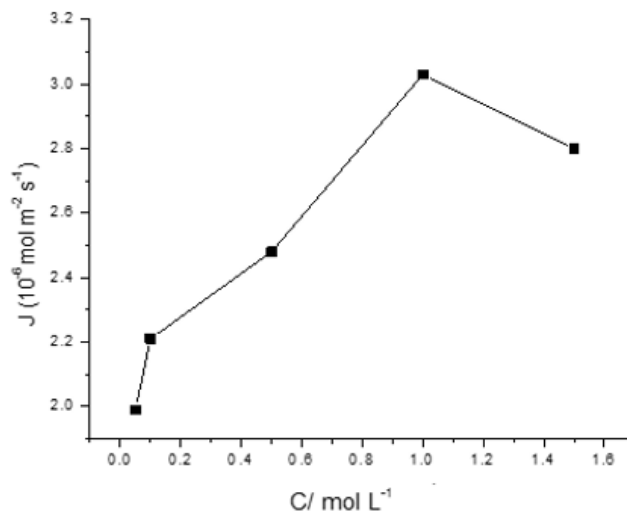


Figure 6. Effect of NaOH concentration on transport of Mo(VI) in stripping phase using poly inclusion membrane.

Effect of pH on Mo extraction

The effect of pH on feed solution was observed by changing the pH of solution in a range between 1 and 5 which was adjusted by addition of acid and base. The stripping side solution contained NaOH solution having a pH of around about 12. The extraction of Mo from aqueous

solution is pH dependent. This statement could be explained as the Mo(VI) in aqueous solutions present in the form of a series of species, e.g., MoO_4^{2-} , HMoO_4^- , H_2MoO_4 and MoO_2^{2+} , increasing in the above order as the acidity of the aqueous solution increases, so as the pH of solution increases, extraction of Mo decreases as shown in Figure 7 [47].

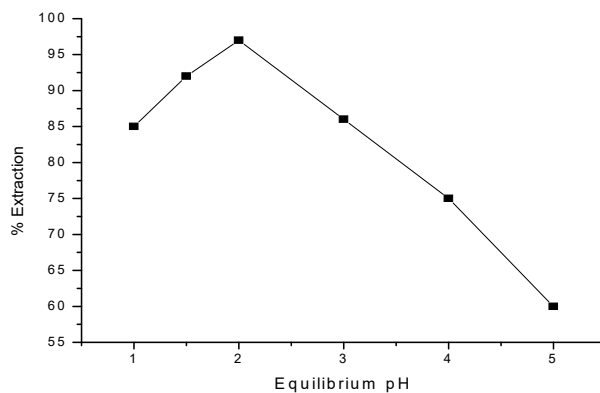


Figure 7. Effect of pH on transport of Mo(VI) using poly inclusion membrane.

Percent extraction

The experimentally observed results show that the % extraction of molybdenum increases at strip side when pH of feed solution was adjusted to 2 and extractant concentration 0.16 M using PIM. Beyond 0.16 M the extraction of Mo(VI) decreases. This decrease in transport of Mo(VI) due to high viscosity, as with increasing carrier concentration the viscosity of liquid membrane phase increases. About 99% of molybdenum extracted through PIM. The results are shown in Figure 8a.

The permeability coefficient was calculated using permeability equation, which was arranged in straight line form and slope of the $\ln C/C_0$ vs. time curve (Figure 8b) is equal to S/PtV^{-1} ; where the porosity of PIM is equal to 85%, S is the effective surface area of the membrane which is 27.8 cm^2 and V is the volume of feed solution which is 250 cm^3 . The average slope for PIM was calculated to be -0.0113 thus P was calculated as 19.91 cm s^{-1} .

SEM analysis

The morphology of PVC/Aliquat 336 membranes at various Aliquat 336 concentrations were studied and a typical image is given as Figure 8c. In order to do a characterization of the optimal 70% Aliquat 336/30% PVC membrane, we analyzed membrane, i.e. PIM after the extraction. The SEM studies were performed by analyzing the PIM's surfaces. PVC membranes with a low concentration of the Aliquat 336 carrier were characterized as dense thin films with no apparent porosity. As the concentration of Aliquat 336 increased above 50% (w/w), a clear porous membrane structure with irregular shape pores and pore sizes of a few micrometers or less were examined. It was speculated that this transformation in the interior structure could explain the apparent increase in metal ion transport through the membranes reported by several other studies [48] when the Aliquat 336 concentration reached 50% (w/w). The SEM image of the 70% Aliquat 336/30% PVC PIM presents a surface with small drops of Aliquat 336 uniformly distributed throughout the PIM (Figure 8c). As it can be seen from Figure 8c, the dimensions of these liquid domains increase with the increasing of the Aliquat 336 content in PIM. This

supports the idea of coalescence of the liquid domains at high Aliquat 336 concentrations to create liquid pathways which assure the transport process by such PIMs, which occurs by a relay mechanism [49, 50].

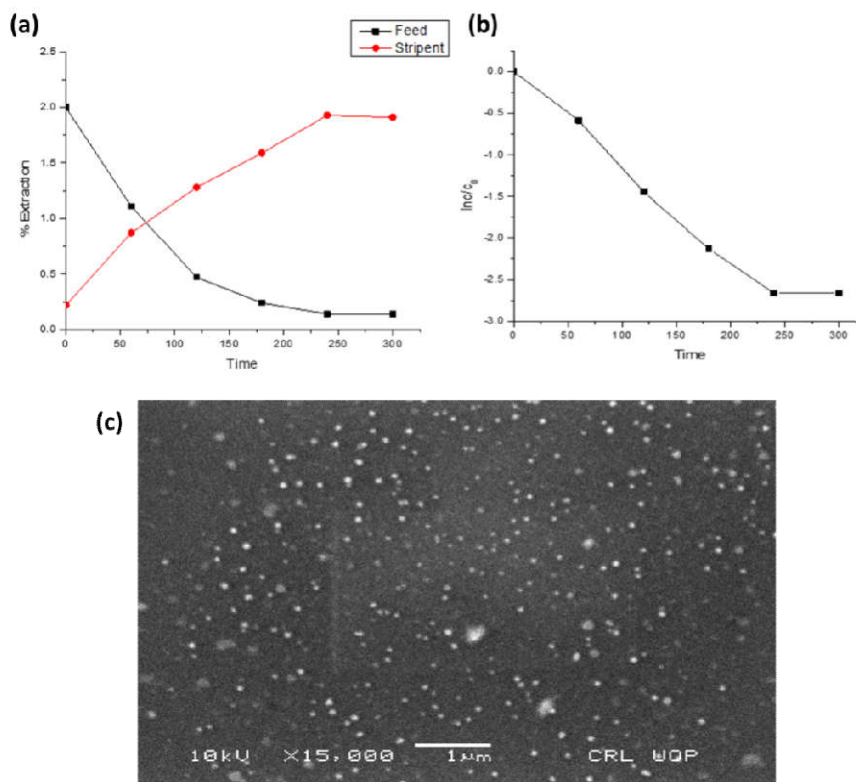


Figure 8. Extraction (%) of Mo(VI) in feed and stripping phase using poly inclusion membrane (a), plot of $\ln C/C_0$ vs. time at 0.16 mol L^{-1} Aliquat 336 concentration (b), and typical SEM image of PIM after extraction of Mo(VI) (c).

Selectivity of Mo from ore

The sample from molybdenum was taken as shown in Table 2 which was grinded to powder and then dissolved in phosphoric acid. Four different types of metals which include iron cobalt nickel and copper were selected as interfering ion in this study. The selectivity of molybdenum extraction by Aliquat 336 from ore solutions containing molybdenum, iron, cobalt nickel and copper were analyzed using optimum condition which are presented in Table 2. The ore contains more than five times in excess concentration of nickel along with cobalt than then the molybdenum concentration. After applying the optimum condition for the extraction of molybdenum was 97% while the other co-extraction were decreased significantly which are given in the Table 2. Therefore, Aliquat 336, like TOA is selective enough for metals recovery, and it is possible to separate these metals from other impurities. Other elements like B, Ti, V, and Sn, which are present in ore, but do not interfere in the extraction of Mo(VI).

Table 2. Analysis of ore sample before and after extraction through poly inclusion membrane (PIM).

Metal ion	Before extraction (M)	After extraction (M)	% Extraction
Mo	4.21×10^{-4}	4.1×10^{-4}	97.00
Fe	2.69×10^{-5}	7.5×10^{-7}	02.78
Co	3.21×10^{-3}	6.3×10^{-4}	19.62
Ni	2.45×10^{-3}	7.1×10^{-4}	28.97
Cu	7.28×10^{-6}	4.0×10^{-7}	05.49

CONCLUSIONS

It is proved from the experiment that molybdenum(VI) has been selectively extracted from receiving phase containing phosphoric acid aqueous solution and ore by PIM system. PVC is used as a support for tricaprylylmethyl ammonium chloride a basic carrier and which depends on the extractant concentration in organic phase. Extraction of molybdenum increases with increase in carrier concentration at 1.5 M acid concentration and 1 M stripping solution (pH = 2). The extraction of Mo(VI) by Aliquat 336 appears to proceed according to an anionic exchange mechanism. It was concluded that PIM was quite more stable and 99% of Mo was extracted through PIM. The optimized conditions were applied for extraction of Mo(VI) from ore where the actual percentage of Mo(VI) which was less than 7% and about 97% was recovery.

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