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Transport of Molybdenum Across a Bulk Liquid Membrane Using 8-Hydroxy Quinoline as a Carrier

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ABSTRACT

8-Hydroxy quinoline was used successfully as a carrier for the transport of molybdenum across a bulk liquid membrane of chloroform. The pH of the feed solution was adjusted to 5.5. A mixture of 0.1-M nitric acid and 0.2-M hydrogen peroxide served as receiving phase for the maximum transport of the metal ion. Under the optimized experimental conditions, 80% of molybdenum was transported across the membrane in 5 hr and the value increased to 95% in 24 hr. Addition of 1,10 phenanthroline to the feed solution had a synergistic effect and caused a pronounced acceleration of the transport, while the effect of Dibenzo 18 crown 6 was insignificant. The transport of molybdenum was made selective by the addition of suitable masking agents to the feed solution. Most of the

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common interfering metal ions were masked by the addition of EDTA. The interference from tungsten was eliminated with citrate and the co-transport of uranium was minimized by the addition of ammonium carbonate to the feed solution.

Key Words: Molybdenum transport; Bulk liquid membrane; 8-Hydroxy quinoline as carrier.

INTRODUCTION

Molybdenum and its alloys find many industrial applications due to high melting points, high mechanical strength, high thermal conductivity, and corrosion resistance. They are frequently used in electronics and aviation industry.[1] Molybdenum is used as a catalyst in many chemical and petrochemical industries. It is used in nuclear medicine for the production of carrier free ^{99m}Tc of high specific activity. Separation of molybdenum from excess of uranium and fission products is very important in the nuclear industry.[2]

Ion exchange, precipitation, liquid–liquid extraction, and membrane separation are the commonly used techniques for the separation of a given metal ion from a mixture. Various methods for separation of molybdenum from other metal ions include liquid–liquid extraction using di (2-ethyl hexyl) phosphoric acid,[3] 1,10 phenanthroline,[4] dibenzo 18 crown-6,[5] tri *n*-butyl phosphate,[6] ion exchange,[7] bulk,[8] and supported liquid membranes.[9,10] The membrane separation method is of recent interest[11] due to its several advantages over the other separation methods. It is cost effective, energy efficient, and offers a high preconcentration factor with a possible high degree of selectivity. The solid membranes are not very attractive due to low transmembrane flux but the carrier-facilitated transport of metal ions across a liquid membrane has been studied widely primarily due to the simplicity of operation. Chelating agents generally serve as carriers in the facilitated uphill transport of metal ions. 8-Hydroxy quinoline is known to form a stable chelate with many metal ions. It is used as a gravimetric reagent for the quantitative precipitation of Mo(VI). We have, in the present study, used it as carrier for Mo(VI) across a bulk liquid membrane. The synergistic effect of 1,10 phenanthroline and dibenzo 18 crown 6 on the transport of Mo(VI) by oxine was also examined. The effect of the variation of pH, carrier concentration, and stripping agents on the transport was studied to arrive at optimum transport conditions. The study also demonstrates that the selective transport of molybdenum from various binary mixtures of Mo(VI) with transition metal ions and UO_2^{2+} can be accomplished by making use of appropriate masking agents in the feed solution.

EXPERIMENTAL

Reagents

- Ammonium molybdate (E. Merck, GR)—Weighed quantity of the solid was dissolved in deionized water to make standard stock solution.
- 8-Hydroxy quinoline (oxine), 1,10 phenanthroline and dibenzo 18 crown 6 (DB18C6) were obtained from E. Merck, Germany.
- Solutions of metal ions were prepared by dissolving weighed amount of their chloride or nitrate salt (analytical reagent grade) in dilute hydrochloric acid.
- Membrane phase was prepared by dissolving appropriate amount of carriers in chloroform (E. Merck, India) such that the concentration of oxine in chloroform was 1×10^{-3} M. All other reagents used were of analytical grade.

Procedure

Transport studies were carried out using a permeation cell described elsewhere.[12] The feed compartment contained 10 mL of ammonium molybdate solution or a binary mixture of Mo(VI) and another metal ion adjusted to pH 5.5. A mixture of nitric acid and hydrogen peroxide made up to 25 mL volume served as the receiving solution. Chloroform solution (50 mL) of 10^{-4} M of oxine formed the membrane phase. The membrane phase was continuously stirred with a magnetic stirrer and the concentration of molybdenum in both feed and receiving solution were measured after 5 and 24 hr. The measurement was carried out using UV-visible spectrophotometer model 210A (Shimadzu, Japan). Eriochrom Black T was the chromogenic reagent and the measurement was carried out at 380 nm.[11]

RESULTS AND DISCUSSION

The solution chemistry of molybdenum is complicated due the existence of various species at different acidity of the solution. However, in neutral or slightly acidic solution, irrespective of the species present, Mo is present mostly as Mo(VI). Oxine is a versatile chelating agent that forms a complex with many metal ions. Hence, it is often used as an extracting agent or as a gravimetric reagent for their determination. The reagent has a nitrogen atom in the heterocyclic ring. A phenolic –OH group adjacent to nitrogen makes it suitable for chelate formation with the metal ion. The nitrogen gets protonated at lower pH and the phenolic –OH dissociates in the alkaline solution. On account of this, it has low solubility in the aqueous phase between pH 5 and 9. It reacts with Mo(VI) under neutral pH conditions to form an insoluble complex having the composition $MoO_2(oxine)_2$.[13] Although the complex is insoluble in aqueous medium, it has sufficient solubility in chloroform so that it could be successfully used in the present study as carrier for the transport of Mo(VI) across a bulk liquid membrane. The organic membrane phase was kept in contact with Mo(VI) at pH 5.5 while the permeated ion was stripped out as peroxo complex in the acidic receiving phase. The optimum pH of 5.5 for the feed solution was decided on the basis of the pH variation studies carried out in the range of 5 to 9. It was observed that the transport of molybdenum(VI) in this range was independent of the pH of the feed solution.

Various stripping agents, like SCN^-, PO_4^{3-}, and H_2O_2, were tried for the effective stripping of molybdenum from the membrane phase. It was observed that H_2O_2 in combination with HNO_3 gave the best result. This is in agreement with the observation made by Rezvanianzadeh et al.[8] during their transport studies on molybdenum using di (2-ethyl hexyl) phosphoric acid as a carrier. The acidity of the receiving phase was varied to achieve maximum transport. Figure 1 shows that the maximum transport of molybdenum was obtained when the nitric acid concentration of the receiving phase was kept at 0.1 M.

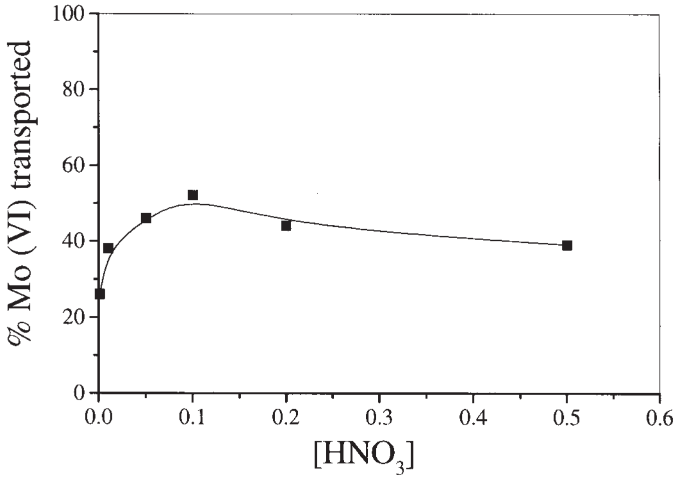

Figure 1. Amount of molybdenum transported as a function of HNO_3 concentration (moles/l) in the receiving phase: feed, 10^{-3} M ammonium molybdate at pH of 5.5; carrier, 10^{-4} M oxine.

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The effect of the variation of hydrogen peroxide is shown in Fig. 2. In the absence of H_2O_2, the transport was very low but it reached maximum when the concentration of the stripping agent was 0.2 M.

Variation of carrier concentration in the range between 10^{-3} M and 10^{-4} M did not show any significant change in the transport of molybdenum. The overall transport of molybdenum(VI) is a combination of two equilibria, at the feed and receiving compartments, i.e., absorption and stripping of the cation. Variation in the carrier concentration in the membrane phase may alter the absorption of Mo(VI) into the membrane phase but the net transport need not necessarily be governed by the absorption alone. If the stripping process is slow, then, it will be the rate-controlling factor for the overall transport. The insensitivity of the carrier concentration to the overall Mo(VI) transport may be attributed to the slow decomplexation and stripping of Mo(VI) from the membrane phase. So, the concentration of oxine in the membrane was arbitrarily chosen as 10^{-4} M for all transport experiments. Under the optimized conditions, 80% of the molybdenum transported from the feed compartment in 5 hr and the quantity increased to 95% in 24 hr.

The leaching out of the carrier from the membrane phase into both the feed and receiving solutions was tested. In the feed side, the leaching was negligibly small, presumably due to the pH conditions. The carrier in the form of metal complex (in the membrane phase) is insoluble in water and does not

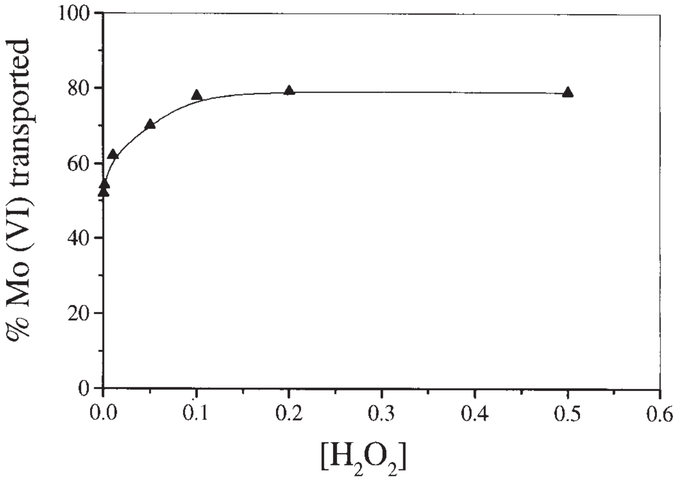


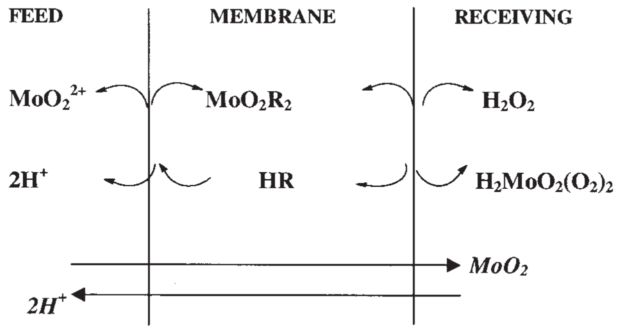
Figure 2. Amount of molybdenum transported as a function of H_2O_2 concentration (moles/l) in the receiving phase: feed, 10^{-3} M ammonium molybdate at pH of 5.5; carrier, 10^{-4} M oxine.

leach out as such. Although, there was some leaching on prolonged stirring, the amount was not significant in a limited period of 5 hr.

Based on the results obtained in the present study and the observation made by other researchers,[8,14–16] a coupled mechanism is proposed for the transport of molybdenum across the bulk liquid membrane. At the feed side, the carrier oxine forms a chelate $MoO_2(oxine)_2$ at the water–membrane interface. It dissolves in the membrane phase and gets distributed throughout the organic solvent. At the interface between membrane and the receiving phase, the stripping agent H_2O_2 forms a more stable and water soluble complex, $H_2MoO_2(O_2)_2$,[17] and releases the molybdenum into the receiving solution. The carrier anion receives proton from the acidic receiving phase and diffuses back into the organic membrane as neutral carrier. The released carrier becomes available at the membrane–feed interface for maintaining the continuity of the transport of molybdenum till its concentration is too low to form complex with the carrier. This is represented in Sch. 1.

A number of cations interfered in the transport of molybdenum. Table 1 shows the interferences of different ions. On account of the versatile complexing ability of oxine, many metal ions compete with molybdenum and lower its transport. However, the co-transport of most of the interfering ions could be effectively minimized by the addition of EDTA to the feed solution. Tungsten(VI) and U(VI) showed serious interferences that could not be masked with EDTA. The interference from W(VI) could be eliminated by masking it with citrate, whereas the addition of ammonium carbonate to the feed solution effectively prevented the co-transport of UO_2^{2+}.

Reagents like 1,10 phenanthroline and dibenzo 18 crown 6 have been used as extracting agents for the extraction of Mo(VI) from acid medium.[5,6] It was then of interest to examine the synergistic effect of these reagents on the



Scheme 1. Schematic representation of molybdenum transport, where R represents oxine.

Table 1. Transport of molybdenum in the presence of interfering ions.

Interfering ion	Percentage of Mo(VI)		Masking agent
	Without masking	With masking	
—	79.6		Nil
Ca^{2+}	58.9	74.3	EDTA
Mg^{2+}	62.1	76.4	EDTA
Cu^{2+}	38.7	62.1	EDTA
Ni^{2+}	62.4	70.1	EDTA
Zn^{2+}	58.1	64.3	EDTA
Fe^{3+}	54.2	73.1	EDTA
UO_2^{2+}	32.2	49.6	EDTA
		69.3	$(NH_4)_2CO_3$
W(VI)	50.2	78.3	Citrate

Note: Feed, 10^{-3} M ammonium molybdate at pH of 5.5; carrier, 10^{-4} M oxine; receiving, 0.1 M HNO_3 + 0.2 M H_2O_2; transport time, 5 hr.

permeation of Mo(VI) across the liquid membrane under the present experimental conditions. Table 2 gives the results of the transport of molybdenum in the presence of these reagents. When 1,10 phenanthroline alone was used as carrier, the permeation of molybdenum was very poor under the present experimental conditions but the reagent, in combination with oxine, showed a pronounced accelerating effect on the transport of molybdenum. Although the total quantity of molybdenum transported in 24 hours' time was marginally higher, the percentage of metal ion transported in 5 hr increased from 80% to 89%. This accelerating effect may be attributed to the complexing ability and synergistic effect of hydrophobic phenanthroline resulting in the facile absorption and of the metal ion in the membrane. Similar

Table 2. Effect of carriers in the transport of molybdenum (VI).

Carrier	Concentration (M)	Percentage Mo(VI)
Oxine	10^{-4}	79.6
1,10 phenanthroline	10^{-2}	4.1
DB18C6	10^{-3}	<1
Oxine + DB18C6	$10^{-4} + 10^{-3}$	81
Oxine + 1,10 phenanthroline	$10^{-4} + 10^{-2}$	89

Note: Feed, 10^{-3} M ammonium molybdate at pH of 5.5; receiving, 0.1 M HNO_3 + 0.2 M H_2O_2; transport time, 5 hr.

synergistic effect and enhancement of transport have been observed in the transport of UO_2^{2+} using calixarene as carrier and TOPO as the synergistic agent.[18] The crown ether failed to bring about such enhancement in the transport, presumably due to its poor complexing ability toward molybdenum.

CONCLUSION

8-Hydroxy quinoline, normally used as a gravimetric reagent for the quantitative determination of Mo(VI), can be successfully used as a carrier for the transport of molybdenum across a bulk liquid membrane of chloroform. The transport was maximum when the pH of the feed phase was maintained at 5.5 and a mixture of hydrogen peroxide and nitric acid was used as a stripping solution in the receiving compartment of the permeation cell. About 95% of molybdenum was transported in 24 hr. Oxine in combination with 1,10 phenanthroline showed a remarkable acceleration in the transport, while the effect of DB18C6 was insignificant. The selectivity in the transport of molybdenum was accomplished by the addition of proper masking agents to the feed solution. The co-transport of transition metal ions was minimized with EDTA, while that of W(VI) and U(VI) was prevented by masking them with citrate and carbonate, respectively. The study suggests that a liquid membrane system may be useful for the separation of molybdenum from tungsten and uranium.

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