To Study Selective Transport of Ag(I) Ion Using Polymer Inclusion Membranes Containing Thiuram Sulphide as a Carrier

A

Thesis Submitted

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Submitted by:

Shipra

(Regn No. 30702019)

Under the supervision of:

Dr. Ashok Kumar S.K.

Lecturer

School of Chemistry & Biochemistry

Thapar University, Patiala

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Shipra

Shipra

Candidate's Declaration

I hereby declare that the work being presented in the dissertation entitled **"To Study Selective Transport of Ag(I) Ion Using Polymer Inclusion Membranes Containing Thiuram Sulphide as a Carrier"**, in partial fulfillment of the requirements for the award of degree of Master of Science in Chemistry in the School of Chemistry and Biochemistry, Thapar University, Patiala, is my own work during the period of January 2009 to May 2009, under the supervision of Dr. Ashok Kumar S.K., Lecturer, School of Chemistry and Biochemistry, Thapar University, Patiala. I have not submitted the matter embodied in this dissertation for the award of any other degree.

Patiala

Date: 26/6/09.

Shipra

Shipra

This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

Dr. Ashok Kumar S.K.
Project Supervisor,
Lecturer (SCBC),
Thapar University

Susheel Mittal 29/6/09

Dr. Susheel Mittal
Head, SCBC
Thapar University

Certificate

This is to certify that the project entitled **"To Study Selective Transport of Ag(I) Ion Using Polymer Inclusion Membranes Containing Thiuram Sulphide as a Carrier"**, being submitted by Ms. Shipra in partial fulfillment of the requirements for the award of degree of Master of Science in Chemistry in the School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonifide work carried out under the supervision of Dr. Ashok Kumar S.K. and that no part of this project has been submitted for the award of any other degree.

Dr. Ashok Kumar S.K.
Lecturer,
Thapar University

Dr. Susheel Mittal 29/6/09
Head, School of Chemistry and Biochemistry,
Thapar University

29/6/09
Dr. R.K. Sharma
Dean, Academic Affairs,
Thapar University

Thesis Abstract

This work studies the mechanism of active transport of silver (I) through a polymeric inclusion membrane containing Thiuram sulphides having sulphur donor atoms namely Tetramethyl thiuram monosulphide (TMTMS) and Tetraethyl thiuram disulphide (TETDS). Membrane transport studies were performed in a two compartment cell. The CTA/2-NPOE containing thiuram sulphides membrane exhibited uphill transport of silver (I) against concentration gradient. The influences of the aqueous and membrane components on the permeability of silver (I) were studied to show its transport phenomenon. In the presence of thiosulphate ion as a suitable stripping agent in the strip solution, transport of silver occurs almost quantitatively after 120 min with recovery efficiency of 90 ± 4%.

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LIST OF ABBREVATIONS

AAS	Atomic absorption spectrophotometer
A	Membrane area
BLM	Bulk liquid membrane
C	Metal ion concentration at a given time in the source phase
C_i	Initial concentration of metal ion in the source phase
D2EHPA	di-(2-ethylhexyl)phosphoric acid
ELM	Emulsion liquid membrane
ECIL	Electronic corporation India limited
J	Permeation flux
J_i	Initial flux
k	Rate constant
M	Metal ion
o-NPOE	*Ortho*-Nitrophenyl octyl ether
P	Permeability coefficient
ppm	parts per million
PIMs	Polymer inclusion membranes
PVC	Poly(vinyl chloride)
rpm	Rotation per minute
RF	Recovery factor
S	Selectivity coefficient
s^{-1}	Per second
SLM	Supported liquid membrane
SX	Solvent extraction
t	Time of transport
TOA	Trioctyl amine
TDPNO	4-(1-n- tridecyl)pyridine N-oxide
TBP	Tertiary butyl phosphine
TETDS	Tetraethyl thiuram disulphide
TMTMS	Tetramethyl thiuram monosulphide
V	Volume of feed solution

Chapter – 1

INTRODUCTION

The rapidly increasing environmental consciousness has led to considerably tightened environmental standards in many countries. This is because in the near future, the production of hazardous waste from industries will become a serious problem all over the world. These resources including inorganic solids or sludge containing metal were generated by many types of industries such as metal finishing, electronic, electrical, electroplating, machinery and other chemical industries. So, the sources of metal wastes are diverse in nature. In 1984, a National Survey under U.S. Resource Conservation and Recovery Act reported that more than 264 million tons of hazardous wastes were generated by approximately 14,000 generators (1). The industrial effluents are usually treated to precipitate the toxic metals and the sludge so generated is dumped as land filled. Due to strict environmental regulations and conserve the natural resources, now it is necessary to develop a new techno-economical process for the recycling treatment of these effluents.

1.1 Common Methods for Silver Recovery

One of the hazardous waste generators is photographic industry which includes the manufacturing process, graphic arts, engineering and medicine (2). Beside silver the waste generated also contain other heavy metals like iron, zinc, lead, copper, nickel and chromium (3). Mainly silver existed in these waste as insoluble halide, soluble silver thiosulphate complex, silver ion or elemental silver depending on the type and the stage of the process. The silver content of the environmental samples is increased with the increasing use of silver compounds and silver containing preparations in industry and medicine (4). Silver can enter the environment via industrial waste waters because it is open as an impurity in copper, zinc, arsenic and antimony ores (5). The interaction of silver with essential nutrients, especially Se, Cu, Vitamin E and Vitamin B_{12}, have focused attention on potentially toxic nutrients. Thus, separation, concentration and sensitive determination of Ag^{+} ion are of increasing interest effective means of separation

of ions in solution. There are many methods which have been established commercially to recover silver from photographic wastes; these are precipitation, electrolysis, ion-exchange and reverse osmosis discussed in Table 1.

Table 1: Commonly available silver recovery methods

Method	Advantage	Disadvantage
Precipitation	- can attain 0.1 mg Ag/L - low investment	- complex to operate - silver recovered as sludge - treated solution can not be reused - potential hydrogen sulphide released
Electrolytic Recovery	- silver recovered as pure metal - high silver recovery	- sulphide formation possible - effulent has high silver content - not suitable for dilute Ag concentration (less than 100 ppm) because the plating efficiencies are very low. - High capital investment & critical operating conditions
Ion Exchange	- can recover 0.1 – 0.2 mg Ag / L	- only for diluted solutions - complex operation - high investment
Reverse Osmosis	- Also recovers other chemicals - Purified water is recyclable	- high investment - high operating cost

In this connection membrane technology can play very important role. Membrane technology is comparatively new and emerging area in the field of separation science.

1.2 Liquid Membranes

Liquid membrane technology is introduced and is identified as a subset of membrane science. This technology has attracted increasing attention for its potential capability in the field of separation and has been demonstrated as an effective tool in many applications (6-8). Several kinds of liquid membranes have been used in various disciplines such as chemical engineering, inorganic chemistry, analytical chemistry, physiology, biotechnology and biomedical engineering. Within these disciplines, the method has been applied to a wide variety of uses such as gas separation, organic compound removal, metal ion recovery, pollutant removal and bio-separation. The technology is particularly attractive when very dilute solutions are involved since the treating ratio between receiving phase and source phase can be drastically reduced.

In 1986, a process to recover zinc from waste streams at a textile plant in Austria was developed as the first liquid membrane process on a commercial scale (9). The attraction of liquid membranes for extraction processes is due to its several advantages. The molecular diffusion in liquids is generally several orders of magnitude faster than in solids. Liquid membranes can also be designed to be highly selective to specific solutes and relatively small quantities of carrier or extractant are needed. Therefore, low amounts of highly selective, relatively expensive agents can be used. Furthermore, a maximum driving force can be created, which avoids the use of multistage processes in liquid extraction. A major disadvantage of liquid membranes in comparison to solid membranes is the lack of the long term stability. Recently, due to their mechanical stability, PIMs provide a more effective method of separation than supported liquid membrane (SLM) and bulk liquid membrane (BLM) systems. PIMs also provide higher efficiency, selectivity and ease of use than the previously mentioned systems. The large surface area to volume ratio that is exhibited by PIMs affords than the potential to be used in nuclear and harmful metal waste remediation on an industrial scale.

1.3 Polymer Inclusion Membranes

PIMs are simple in structure. They consist of a polymer that provides mechanical strength, a carrier molecule which effectively binds and transports ions across the membrane, and a plasticizer that provides elasticity and acts as the solvent in which the carrier molecule can diffuse. The carrier molecule acts as a guest specific host that provides selective membrane permeability for a target species (10). The polymer cellulose triacetate (CTA) has many properties that facilitate it to be used as an effective polymer in the production of PIMs. These are thermoplastic polymers consisting of linear polymer strands devoid of cross-links between them. The mechanical strength of this films made with these polymers is determined by a combination of intermolecular forces and the process of entanglement (11). However, due to hydrolysis of the ester bonds in CTA, it is necessary to find polymers that would hold up in alkaline and acidic solutions. Polar interactions which are the strongest among these forces often result in a rigid polymer structure. The role of a plasticizer or the extractant, capable of acting as a plasticizer is to penetrate between the polymer strands and essentially neutralize their

polar groups with its own polar groups or and to increase the distance between the polymer strands and reduce the strength of the intermolecular forces acting between them (12).

1.4 Carriers

The factors that need to be considered in metal selectivity and capacity of extraction are the selection of carrier types and its concentration. High selectivity and capacity can only be achieved by selecting the right carrier and its concentration for target metal ions. An increase in carrier concentration will increase the extraction capacity, but to what extent needs to be optimized to avoid excessive use of carrier that is normally very costly. The types of carrier used in making PIMs are acidic, basic, neutral, solvating and chelating extractants. Table 1 and Table 2 shows early and recently reports on PIM carriers.

Acidic extractants: To extract a cation from an aqueous solution, it must be combined with an anion to form an uncharged complex. Acidic extractants are very effective for the separation of cations by exchanging their protons for the cations, Examples: Cyanex 272, Cyanex 302 and di-(2-ethylhexyl)phosphoric acid (D2EHPA).

Basic extractants: Metal extraction by a basic extractant has grown into one of the promising tools in aqueous separation chemistry and the extraction with basic carriers is based on the principle of ion association. These reagents can extract any metal capable of forming anionic complexes in aqueous solutions. In aqueous solutions, many metal ions can form a variety of anionic complexes with sulphate, cyanate, thiocyanate, chloride and a number of other anionic ligands. Examples of anionic metal complexes that commonly exist in solutions in hydrometallurgical and electroplating processes are $Cd(CN)_4^{2-}$, $AuCl_4^-$, Examples: tertiary amines, tri-n-octylamine (TNOA), Alamine 336.

Neutral extractants: Neutral extractants often extract uncharged metal complexes or cations together with anions in order to maintain the electrical neutrality in the membrane phase. For liquid membranes with neutral carriers, the concentration gradient driving force across the membrane phase must be accomplished by incorporating strong metal

complexing agents in the strip phase. Coupled transport is however also possible with macrocyclic carriers, Examples: Macrocyclic ligands and Organo-phosphoryl compounds.

Solvating extractants: This extractant rely on the power of oxygen containing organic extractants to solvate inorganic molecules or complexes. By such solvation the solubility of the inorganic species in the organic phase is greatly increased. Most commercially available neutral or solvating carriers are phosphorus-based extraction reagents such as tri-*n*-butyl phosphate (TBP), tri-*n*-octyl phosphine oxide (TOPO) and dibutyl butyl phosphonate (DBBP).

Chelating extractants: These contain donor groups capable of forming complexes with metal ions. In the majority of chelating extractive system it was observed that whenever the co-ordination number of the metal doubles its ionic charge, the chelate formed satisfies the co-ordination requirements of the metal and the metal is readily extractable into both polar and non-polar solvent. Examples: Hydroxyoximes and β-diketone.

Table 2: Examples of PIM carriers reported in the literature

Type of carriers	Examples	Target solutes	References
Basic			
Quaternary amines	Aliquat 336	Au(III), Cd(II)	(13,14)
Tertiary amines	TOA, other tri-alkyl amines	Cr(VI), Zn(II)	(15,16)
Pyridine and derivatives	TDPNO	Ag(I), Cr(VI)	(17)
Acidic and chelating			
Hydroxyoximes	LIX 84	Cu(II)	(18)
Hydroxyquinoline	Kelex 100	Cd(II)	(19)
β- Diketones	Benzoylacetone	Sc(III),Y(III)	(20)
Alkyl phosphoric acids	D2EHPA, D2EHDTPA	Pb(II), Ag(I)	(21)
Neutral solvating			
Phosphoric acid esters	TBP	U(VI)	(22)
Phosphonic acid esters	DBBP	As(V)	(23)

Table 3: Reported PIM studies using macrocyclic and macromolecular carriers

S.No.	Macrocyclic carriers	Target species	Base polymer/ Plasticizer	References
1.	Pyridino-and bipyridino podants	Ag(I)	CTA/2-NPOE	(24)
2.	Calix[4]arene	Ag(I)	CTA/2-NPOE and TBEP	(25)
3.	Acyclic polyether diamide	Ag(I)	CTA/2-NPOE and TBEP	(26)
4.	N-benzylated macrocyclic	Ag(I)	CTA/2-NPOE	(27)
5.	Dibenzo 18-crown-6	Ag(I)	CTA/2-NPOE	(28)
6.	Dibenzo 18-crown-6	Cu(II)	CTA/2-NPOE	(29)
7.	DB18C6, DA18C6	Ag(I)	CTA/2-NPOE	(30)
8.	Diazadibenzocrown ethers	Pb(II)	CTA/2-NPOE	(31)
9.	Diphosphaza-16-Crown-6 Derivatives	Zn(II)	CTA/2-NPOE	(32)
10.	B-Cyclodextrin(B-CD) polymers	Cu(II)	CTA/2-NPOE	(33)
11.	Bathophenanthroline	Zn(II), Cu(II)	CTA/various plasticizers	(34,35)
12.	di-tert-butylcyclohaxano-18-crown-6(BuDC18C6)	Sr(II)	CTA/2-NPOE	(36,37)
13.	Acyclic polyether	Ba(II)	CTA/PVC/NPOE	(38)
14.	Calix[6]arene	Ba(II)	CTA/NPOE-TBEP	(39)
15.	1,3-calix[4]arene-biscrown-6	Cs^+	CTA/2-NPOE	(40,41)
16.	Isoguanosine	Cs^+	CTA/2-NPOE	(42)
17.	Dibenzo-16-crown-5-oxyacetic acids	Na^+	CTA/2-NPOE or 2-NPPE	(43)
18.	4-N-butylcarboxamido benzo-15-crown-5	K^+	Sol-gel	(44)

1.5 Research Problem

One of promising extractant is thiuram sulphide family. The extraction of silver was very high even at a low concentration of TETDS. The bulk liquid membrane extraction results (45) show that 73 % of silver extracted with 0.005 M concentration. With 0.05 M, the extraction of silver was almost 100 %. It is expected that this is due to the existence of excess free extractant in the process. In addition, tetraethylthiuram disulphide is also very selective to silver. However, this reagent only dissolved in a non-polar solvent, like $CHCl_3$, toluene, dichloromethane or 1,2 dichloroethane. Therefore, safety and environmental regulations make it less preferable in extractant selection especially in global era. But more safely and convient factors in polymer based liquid membrane led us to prepare PIMs using these extractants.

Chapter – 2

LITERATURE REVIEW

Carrier mediated transported through supported liquid membrane is currently recognized as a potentially valuable technology for selective separation and concentration of toxic and valuable metal ions. In this thesis, a review of the fundamental aspects concerning metal ion transport and influencing factors are surveyed in terms of membrane efficiency like (permeability, selectivity and stability) of liquid membranes. These membranes includes polymer inclusion membranes (PIMs) and supported liquid membranes (SLMs) (46). A remarkable increase in the application of liquid membranes, especially those of a new type (i.e. polymer inclusion membranes, PIMs), in separation processes of metal ions and small organic compounds has been observed (10). PIMs are formed by casting using as a support cellulose triacetate (CTA) or Poly(vinyl chloride) from an organic solution to form a thin, stable film. This casting solution also contains an ion carrier and a membrane plasticizer (2-NPOE). The resulting membrane is used to separate the source and receiving phases (47).The composition and morphology of PIM membranes are distinctively different from SLM, the actual bulk diffusion mechanisms within the membrane can be quite different. Since the carrier is not covalently bound to the base polymer, it may be assumed that the actual diffusion mechanism in PIM membranes is intermediate between mobile carrier diffusion and fixed site jumping (48). It is also used in fabricating ion selective electrodes. In sensing fast ion exchange or metal ion complexation is required at the sample solution/membrane interface in order to establish a fast interfacial electrical potential difference. While only negligible transport of the metal containing species through the membrane within time frame of the measurement is allowed. For separation purposes, fast interfacial reactions are required but also high diffusion co-efficients of the metal containing species within the membrane are desirable in order to achieve mass transport from the source to the receiving phase within a reasonable time frame (49).

2.1 Transport Mechanism

One or more driving forces facilitate the transport of the particular species through the membrane. Species can be transported from a region of high solute concentration to a region of low solute concentration by diffusion, following the first Fickean law:

$$J = - D (\partial c / \partial x)$$

Where $(\partial c / \partial x)$ = concentration gradient

J= flux

D= diffusion co-efficient

The flux 'J' is proportional to the concentration gradient across a phase with thickness 'x' (m). This means that the diffusion of a species through a liquid membrane will stop as soon as the concentration at both sides of the membrane become equal. This is called unfacilitated transport.

Two other transport mechanisms in liquid membrane processes can be distinguished.

1) **Type I facilitation:** In order to maintain the transport of solutes from bulk phase 'I' towards bulk phase II, the diffusing species react with a chemical reagent in the receiving phase resulting in a compound that can not move bulk towards phase I.
2) **Type II facilitation:** Another type of transport mechanism is needed in the case that the species to be removed are not soluble in the organic membrane phase. This type of transport is also called carrier mediated transport. The addition of a complexing agent to the membrane phase accelerates the transport of a specific component. Both coupled and uncoupled transport can be distinguished. The majority of liquid membranes for metal ion separation follow a coupled transport mechanism, which involves the presence of two components. Coupled transport can be further subdivided into:
   (a) Co-coupled transport: the two components are moving in the same direction.
   (b) Counter-coupled transport: the two components are moving in opposite direction.

2.2 Metal Ion Separations by SLMs and PIMs

A variety of synthetic carriers such as acidic, basic and neutral extractants are known which transport metal ions selectively across liquid membrane configurations and are widely used in the separation science and ion-selective electrodes. Some of the recent report work described in the following discussion. Tarditi *et al.* (50) reported the modelling of zinc (II) transport through a PC-88A SLM. Zinc has been permeated through a flat-sheet SLM, using 2-ethylhexylphosphoric acid and mono-2-ethylhexyl ester (PC-88A) in kerosene. Liquid–liquid experiments were conducted as a function of aqueous pH (1–6) to establish optimum conditions for both extraction and stripping of the metal. Asghar *et al.* (51) reported the highly selective transport of silver ion through a SLM using calix[4]pyrroles as suitable ion carriers. Thiosulfate used as a suitable metal ion acceptor in the strip phase and picrate ion as ion pairing agent in the source phase, transport of silver occurs almost quantitatively after 75 min. The selectivity and efficiency of silver transport from aqueous solution containing Cu^{2+}, Mg^{2+}, Ni^{2+}, Ca^{2+}, Zn^{2+}, Pb^{2+} were investigated. Bukhari *et al.* (52) reported the coupled transport of Ag(I) ions through triethanolamine–cyclohexanone-based supported liquid membranes. Facilitated transport of silver(I) ions in acidic medium, across a SLM by using triethanolamine (TEA) as carrier. Increase in H^+ concentration by increasing HNO_3 concentration from 0.5 to 1 M results into an increase in silver ions flux but a decrease in flux has been found beyond 1 M HNO_3 concentration in the feed, providing a maximum flux of 3.21×10^{-7} mol/m^2 s at 1 M HNO_3. Swain *et al.* (53) reported the extraction of Co(II) by SLM and solvent extraction using Cyanex 272 as an extractant. Cobalt has been extracted from dilute sulfate solution by SLM and solvent extraction (SX).

Kocherginsk (54) reported the copper removal from ammoniacal wastewater through SLM. LIX54, one of well-established extractants for copper, was used as a carrier in the liquid membrane phase to extract and transfer copper. Zaghbani *et al.* (55) reported the selective thiacalix[4]arene bearing three amide groups as ionophore for binary Pd(II) and Au(III) extraction by a SLM system. Seta *et al.* (56) reported the extraction and separation of metal cations in solution by SLM using lasalocid A as carrier. Flat-sheet SLM incorporating lasalocid A (a natural ionophore), were previously shown to be

permeable to metal cations (Cd^{2+} and Zn^{2+}) against a proton gradient (pH), which is the driving force of the process. This transport process has been extended to other metal species such as Pb^{2+}, Na^{+}, and Ag^{+} and also to the case where two metal species compete for transport. Jianshun *et al.* (57) reported the carrier-mediated transport of Platinum (IV) through a SLM impregnating 8-quinolinol derivatives as a mobile carrier. Platinum(IV) was extracted with LIX 26 from an HCl solution via an anion exchange reaction and stripped from the loaded organic phase by a weakly acidic solution (pH>1). Platinum(IV) was nearly quantitatively transported across an SLM impregnating 15% (v/v) LIX 26 and 10% (v/v) 1-octanol in kerosene from a feed solution of 1–2 M HCl into a weakly acidic product solution. Herman *et al.* (58) reported the Kinetics of carrier-mediated alkali cation transport through SLM. The effects of membrane solvent, co-transported anion, and support on the diffusion constant D_m, the extraction constant K_{ex} and the rate constant k have been studied.

Ruey *et al.* (59) reported the coupled transport of vanadium (1V) through SLM containing bis-(2-ethylhexyl)phosphoric acid. The transport process was mainly governed by interfacial chemical reaction and partly by combined membrane diffusion. Another work (60) reported by same group on the permeation of zinc and copper ions from sulfate solutions through SLM containing bis(2-ethylhexy1)phosphoric acid (D2EHPA) dissolved in kerosene as a mobile carrier at 25^{o}C. Theodorus *et al.* (61) reported the mechanism of facilitated membrane transport of salts through SLM containing synthetic ionophores in o-nitrophenyl octyl ether with potassium perchlorate and dibenzo-18-crown-6 as a support the microporous polypropylene membrane.

Miguel *et al.* (62) reported that the transport of Au(III) acid across polymer inclusion membranes (PIM) from concentrated hydrochloric media using Kelex 100(7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline)as carrier and 2-nitrophenyloctylether as plasticizer. Wang *et al.* (63) have studied the extraction of Cd(II) and Cu(II) from 2M hydrochloric acid solutions using a PVC-based membrane containing 30, 40 and 50% (w/w) Aliquat 336. The extraction of Cd(II) was found to be much higher than that for Cu(II) and the authors suggested this was because the $CdCl_3^-$ species was involved, which was present

in higher concentration than the $CuCl_3^-$ species. The competitive transport of Cd(II) and Pb(II) using a CTA/NPOE-based PIM containing TOMAC as carrier has been described by Hayashita (64). This work reported that the selectivity depended on the membrane surface area. For a small surface area (0.8 cm^2), Cd(II) was transported preferentially, however for a large surface area (15 cm^2) this was reversed. Hayashita explained this on the basis of accumulation of Cd(II) in the small surface area membrane that consumed most of the carrier thus inhibiting the transport of Pb(II). For the large surface area membrane containing a much larger amount of carrier, this did not occur and preferential transport of Pb(II) was observed.

Walkowiak *et al.* (65) have studied the transport of Cr(VI) through CTA-based membranes plasticized with 2-NPPE using a series of tertiary amines and Aliquat 336 as carriers. The source phase for this work was HCl at pH 2 and the receiving phase 0.1M NaOH. It was found the flux decreased with an increase in the hydrocarbon chain length of the amines used with the highest flux being obtained for TOA. This was further confirmed by Kozlowski and Walkowiak (66) who showed that the flux decreased linearly with an increase in the log *K* values of the tertiary amines. They reported that the flux for a similar PVC based PIM was lower than for the CTA-based membrane and could be attributed to the fact that PVC was more hydrophobic than CTA. In their study, Walkowiak et al. also investigated the competitive transport between Cr(VI) and Cr(III) using acidic chloride and sulfate solutions and the selectivity coefficient was found to be considerably higher for chloride than for sulfate.

Salazar-Alvarez *et al.* (67) have studied the transport of Pb(II) using a CTA-based membrane containing D2EHPA with a source phase containing 10 mM $NaNO_3$ at a pH between 2.85 and 3.45 and a 1.5 M nitric acid receiving phase. This system produced a high Pb(II) flux of 3.5 μ mol m^{-2} s^{-1} which was of the same order of magnitude as reported for the analogous SLM system by these authors. The transport of Pb(II) has also been studied by Lee *et al.* (68) using a synthesized lipophilic acyclic polyether dicarboxylic acid as the carrier of structure similar to the antibiotic monensin. The membrane composition was 76% (w/w) 2-NPOE, 18% (w/w) CTA and 6% (w/w) carrier.

Using a source phase at pH 4.5–5.5, 100% of the Pb(II) could be transported to a 0.1M nitric acid receiving phase with little transport of Cu(II) and no transport of Zn(II), Co(II) and Ni(II).

Copper transport using a CTA membrane has been studied by de Gyves *et al.* (69) using LIX 84 and TBEP 30% (w/w) as plasticizer. The source phase contained copper(II) sulfate or chloride at pH 4–6 in acetate buffer with 1M H_2SO_4 or 1M HCl as the receiving phase. Maximum permeability for Cu(II) was obtained at pH 5 with no difference between sulfate and chloride for the source phase. However, higher permeability was obtained using H_2SO_4 in the receiving phase rather than HCl. A comparison between carrier-facilitated transport of Cu(II) in a CTA-based PIM and a SLM has been reported by Paugam *et al.* (70). The carrier used was lauric acid with TBEP acting as plasticizer for the PIM and as the diluent for the SLM. The source phase was buffered to pH 6.0 using *N*-morpholinoethane and the receiving phase was 5×10^{-4} M cyclohexanediaminetetraacetic acid (CDTA) at pH 6.4. The selective removal of Zn(II) from other transition metal ions such as Co(II), Ni(II), Cu(II) and Cd(II) using PIMs has been studied by Ulewicz *et al.* (71). Their system used a CTA membrane containing D2EHPA and 2-NPOE as plasticizer. Separation was achieved by pH control of the source phase with 1.0M HCl as the receiving phase. Best selectivity for Zn(II) was achieved using the source phase at pH < 2, which was in accordance with the solvent extraction properties of D2EHPA for these metal ions. In another study Baba *et al.* (72) have also demonstrated that Cu(II) can be preferentially transported in the presence of Pd(II) across a PVC-based PIM using D2EHPA as the carrier and plasticizer from a source phase at pH 3–4 (acetate buffer) to a receiving phase of 1.0 M HCl.

Jenkins (73) have studied the transport of rare earth metal ions through CTA-based membranes containing a series of β-diketones as carriers and with 2-NPOE and TBEP as plasticizers. Selectivity was controlled by the pH of the source phase and they found that Sc(III) was transported at a lower pH than both Y(III) and La(III) which was most likely due to the difference in ionic radii. At pH values 5.1 and 6.1, high fluxes were obtained

but there was no significant difference in transport amongst the rare earth metal ions except for Sc(III).

Bloch *et al.* (74) prepared a membrane of composition of 25% (w/w) PVC and 75% (w/w) TBP for permeating uranyl ion. In these experiments, the receiving solution was pure water and the source solution contained 0.02 M $UO_2(NO_3)_2$ with the concentration of HNO_3 varying in the range from 2 to 8 M. Matsuoka *et al.* (75) have studied the transport of uranyl nitrate using a CTA-based membrane containing 0.5 mL of TBP for every 0.3 g of the base polymer CTA. The authors reported an uphill transport of uranyl nitrate from a source solution containing 3.5mMof UO_2^{2+} and 1M HNO_3 to a receiving solution containing an initially equal concentration of UO_2^{2+} (i.e. 3.5 mM) and 1M Na_2CO_3. Kusumocahyo *et al.* (76) have developed PIMs consisting novel solvating carriers namely octyl(phenyl)-N,N-diisobutylbarbamoylmethyl phosphine oxide and N,N,N',N'-tetraoctyl-3- oxapentanediamide denoted as CMPO and TODGA, respectively, for the removal of $Ce(NO_3)_3$ from low radioactivity wastewater.

Lamb *et al.* (24) have studied the transport of Ag(I) through CTA/2-NPOE membranes containing a series of pyridinoand bipyridino-podands. These carriers have hydrophilic palmitoyl tails making them insoluble in aqueous solutions and highly soluble in the membranes thus conveying excellent homogeneity and stability. These podands have three pyridine nitrogen atoms in tridentate coordinating positions and have strong binding properties for the Ag(I) ion. Thus, only Ag(I) transport from a perchlorate solution in the presence of Cd(II), Zn(II), Co(II), Ni(II), Pb(II) and Cu(II) to awater receiving phase was observed. A similarly high transport selectivity for Ag(I) compared to Pb(II) and Cd(II) has been observed by Kim *et al.* (25) for a series of calix[4]azacrown ether derivatives (B) immobilized in aCTA-based PIM plasticized with 2-NPOE and TBEP. In another study, Kim *et al.* (26) also investigated the transport of Ag(I) in PIMs and SLMs using acyclic polyether ligands having diamide and diamine end-groups (C). They found again highly selective transport of Ag(I) in the presence of Cd(II), Zn(II), Co(II), Ni(II), Pb(II), and Cu(II). In addition, the transport of Ag(I) was considerably faster in PIMs than in

SLMs. Only one carrier showed some transport of a metal ion (i.e. Pb(II)) other than Ag(I).

Above comprehensive survey of literature shows that thiuram sulphides have not been used as a carrier in making polymer inclusion membranes for silver ion extraction. Hence, this work describes characterization of thiuram sulphides as polymer inclusion membranes for silver ion extraction.

Chapter – 3

METHODOLOGY

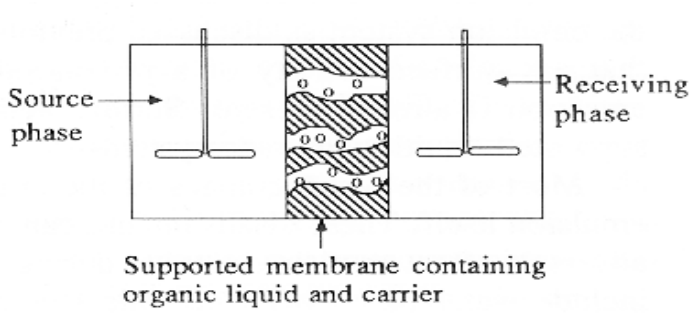
3.1 Reagents

Tetraethyl thiuram disulphide (TETDS), Cellulose triacetate (CTA), 2-nitrophenyl octyl ether (2-NPOE) were purchased from Sigma-Aldrich, U.S.A. Working solutions for metal ions were prepared by dissolving their nitrate salts in double distilled water. All other reagents used were of analytical grade.

3.2 Polymer Inclusion Membrane Preparation

A dichloromethane solution of cellulose triacetate, plasticizer (2-nitrophenyloctyl ether) and thiuram sulphides as the ion carrier was prepared. 0.1 g of cellulose triacetate was dissolved in 10 mL of DCM for more than 30 minutes. This CTA solution was added to a mixture of thiuram sulphide solution in DCM with 0.1 mL of 2-NPOE. After shaking for 30 minutes and resulting solution reduced to 3-4 mL. This CTA membrane solution was casted into film on the flat bottom glass ring (30 mm diameter). The Petri dish was then covered loosely with a watch glass and left for 24 hours at room temperature. After drying, membrane was peeled off from the glass plate. Then membrane was tightly clamped between two cell compartments.

3.3 Transport Studies



Transport experiments were conducted in a permeation cell in which the membrane film (at surface area of 2.5 cm^2) was tightly clamped between two cell compartments. Both i.e. the source and the receiving phases (70 mL each) were mechanically stirred at 600 rpm. The receiving phase was 0.1 M HCl, 0.1 M $Na_2S_2O_3$, 0.1 M $NaClO_4$, 0.1 M oxalic acid. The PIM experiments were carried out at the ambient temperature of 27 ^{0}C. Small samples (1mL each) of the aqueous receiving phase were removed periodically via sampling port with a syringe and analysed to determine Ag^+, Cu^{2+}, Zn^{2+}, Ni^{2+}, Hg^{2+} concentrations by atomic spectroscopy method using single beam Atomic Absorption Spectrophotometer (ECIL,4503,India). .

The **kinetics of** PIM transport can be described by a first order reaction in metal ion concentration (77):

$$\ln(C/C_i) = - kt \ldots\ldots\ldots\ldots\ldots\ldots (3.1)$$

where,

'C' is the metal ion concentration at a given time in the source phase (M),

C_i is the initial concentration of metal ion in the source phase (M),

k is the rate constant (s^{-1}),

and 't' is the time of transport (s/min/hour).

To calculate 'k' values, the plots of ln (C/C_i) vs time were performed. The relationship of ln (C/C_i) vs time was linear.

Permeability: This measures the quantity of a solute transported through a specific area of membrane surface in a unit of time and is defined as

$$P = - (V/A) K \ldots\ldots\ldots\ldots\ldots\ldots (3.2)$$

Where,

P = permeability coefficient ,

V = volume of feed solution,

A = membrane effective area,

The **initial flux** (J_i) was determined by as

$$J_i = P. C_i \ldots\ldots\ldots\ldots\ldots\ldots (3.3)$$

To describe the efficiency of metal ion removed from the source phase, the **recovery factor** (RF) was calculated :

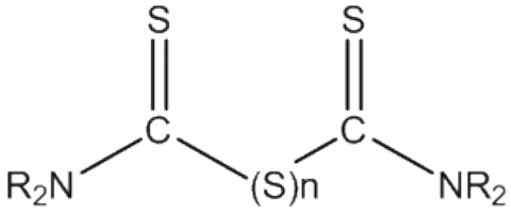
$$RF = (C_i - C)/ C_i \times 100\ \% \ldots\ldots\ldots(3.4)$$

The **selectivity coefficient** 'S' was defined as the ratio of initial fluxes for M_1 and M_2 metal ions, respectively

$$S =(J_i\ M_1)/(J_iM_2) \ldots\ldots\ldots\ldots\ldots\ldots(3.5)$$

3.4 Response Mechanism

The dithiocarbamates which belong to the organic sulphur compounds possess strong metal binding properties and a capacity to form chelates with many metals as a non-selective complexing agents. On the other hand, the use of thiuram sulphides which contain two moieties of dithiocarbamates would have an enhanced selectivity to metal ions due to the appropriate positions of their two dithiocarbamate groups. Further, the dithiocarbamate derivatives are less soluble in organic solvents, while these thiuram sulphides are soluble in organic solvents. Thiuram sulphides make a useful alternative to the dithiocarbamate derivatives, where it can be used to extract metal from the aqueous phase.



(I) Tetramethylthiuram monosulphide (TMTMS) n=1, $NR_2 = N(CH_3)_2$
(II) Tetraethylthiuram disulphide (TETDS) n=2, $NR_2 = N(C_2H_5)_2$

TETDS having a disulphide bond also possesses extensive resonance stability to silver selectivity. It also contains two moieties of dithiocarbamates that will enhance the silver selectivity due to the approximate positions of their two dithiocarbamate groups. However, other metal ions in small amounts are also co-extracted as well as silver ions by TETDS because the C-N bond in the dithiocarbamate has a polar character which enhances the reactivity of the dithiocarbamate molecule.

Chapter-4

RESULTS & DISCUSSION

4.1 The Effect of Carrier Concentration on Silver Ion Transport

In order to determine the effect of the thiuram sulphide carriers on the transport rate the membranes containing the various content of TETDS. The metal ion concentrations in the feed solution are linearly decreased with the contacting time on semi-logarithmic plot Figure (1a). These results indicate that the kinetics of the transport process for silver ions follows first order kinetics Figure (1b) and follows very good linearity which is confirmed by R^2 values (R^2=0.96). The amounts of CTA and plasticizer kept constant i.e.100 mg each to get flat sheet polymeric membrane. The permeability coefficients 'P' were calculated, shows that there is permeability of silver increases gradually with increasing amount of TETDS and shows highest permeability i.e. 167 x 10^{-3} cm s^{-1} at a composition of (w/w) CTA:o-NPOE:TETDS 100mg: 100mg: 3mg and further increasing concentration in the membrane media decreases gradually, this may be due to saturation of membrane active sites. Table 4, shows optimization of membrane ingredients and their kinetic parameters. The membrane containing no TETDS does not show any appreciable transport taking place. This may be due to non permeability of the membrane to metal ions.

4.2 Effect of Stripping Medium

The permeability of the membrane system for Ag^+ ion is considerably dependent on the nature of stripping agent for Ag^+ ion used in the receiving phase (Table 5). In the presence of thiosulphate in the receiving phase, 95 % of Ag^+ ion transported through the membrane during 120 min shown in Fig. 1(a). Results show that highest rate constant, permeability and flux favours when the stripping medium is sodium thiosulphate Fig. 1(b). This is due to good complexing ability of sodium thiosulphate and silver ions in the stripping medium while in the case of water, hydrochloric acid (0.1M) and oxalic acid (0.1M) transportation was found to be 32%, 47% and 31% respectively (Fig. 2(a), 3(a),

4(a)). This lower percentage of silver may be due to weak complexing ability than membrane complex constituents. This makes lower in rate constant, permeability and flux in comparison to thiosulphate medium (Fig. 2(b), 3(b), 4(b)). Also, the time took in all the cases were approximately 120-210 minutes to get maximum transport. The optimum concentration of thiosulphate in the receiving phase was also investigated (Table 6) and found to be 0.1 M.

4.3 Effect of pH in the Source Phase on Silver Transport

The influence of pH source phase on the transport efficiency of Ag^+ ion was studied in the pH range 3–10 and it was found that maximum Ag^+ transport occurs at 5-7 pH range (Table 7). On either side of 5-7 pH there is a decrease in transport. This may be due to protonation of the carrier in the membrane phase leading to leaching of the carrier from the membrane phase. The pH of receiving phase did not disturb because of the thiosulphate solution decomposes in acidic solution. The results shows that thiosulphate has an important role for silver transport and acidic receiving solution is not suitable for silver transport itself.

4.4 Life Time of the Membrane

The time dependence of silver transport through the liquid membrane under the optimal experimental conditions. An increase in time increased the percentage transport of silver ion to receiving phase and decreased the percentage of silver ion remaining in the source phase. According to the results (Table 8), the extraction of Ag^+ from the source phase into the organic membrane is fast and its release from the membrane phase into receiving phase also follow same trend. The silver transport seems to be completed within 120 minutes (approx.). The reproducibility of silver transport was investigated and the percent of silver ion transported after 3 hours from two replicate measurements was found to be 90 ±5.0%. The life time of the membrane was also investigated. Table 8, results show that after continuous use upto 7 days, 90 ±5.0% transport; after 7 days it start to decrease gradually and after 10^{th} day, transport decreases suddenly. This shows that the life time of CTA- thiuram sulphides based membranes was approximately 7-8 days. This problem can be due to the loss of the carrier and / or solvent from the membrane (NPOE), which

has an influence on both flux and selectivity. The major degradation membrane stability due to

(i) blockage of membrane pores by precipitation of a carrier complex at the surface
(ii) emulsion formation in the liquid membrane phase
(iii) pressure difference over the membrane
(iv) progressive weting of the pores in the membrane supported by the aqueous phase

4.5 Selectivity Co-efficient of Transport Study

The percentage transport of Ag^{+} in the presence of various binary mixtures of (Ag^{+} + Cu^{2+}) , (Ag^{+} + Ni^{2+}), (Ag^{+} + Zn^{2+}) and (Ag^{+} + Hg^{2+}) were investigated in Table 9. The results show that in presence of Ni^{2+} and Zn^{2+}, the transport of Ag^{+} ion is not affected too much because little deviation from the actual value i.e., from 90 to 87% while in the case of Cu^{2+} and Hg^{2+}ion, the percentage transport of silver found to be 39% and 68% respectively. This shows that some interference of Cu^{2+} ion and to certain extent Hg^{2+} is also interfering.

Table 4: Optimization of membrane ingredients to study kinetics parameters, permeability, flux and recovery factors for silver ions transport across PIMs

S.No.	Membrane Composition (mg) (w/w)			Transport phenomenon parameters			
	CTA	Plasticizer	Ligand	Rate constant k (10^{-3}) (sec^{-1})	Permeability P (10^{-3}) (cm s^{-1})	Flux J_i (10^{-7}) (mol cm^{-2} s^{-1})	Recovery factor (percentage)
1.	100	100	1	1.00	22	22	27
2.	100	100	2	0.85	18.9	18.9	50
3.	100	100	3	7.50	167	167	95
4.	100	100	4	3.80	84	84	77
5.	100	100	5	0.95	21.1	21.1	38
6.	100	--------	--------	No transportation of metal ion			
7.	100	100	--------	No transportation of metal ion			

Experimental conditions: Source phase, 70 ml of 1 x 10^{-4} M Ag^{+} : Receiving phase, 70 ml of 0.1M sodiumthiosulphate, time of transport carried out 300 minutes.

Table 5: Effect of stripping medium to study kinetics parameters, permeability, flux and recovery factor

Name of Stripping medium	Transport phenomenon parameters			
	Rate constant k (10^{-3}) (sec^{-1})	Permeability P (10^{-3}) (cm s^{-1})	Flux J_i (10^{-7}) (mol cm^{-2} s^{-1})	Recovery Factor (Percentage)
Water	1.7	37	37	32
HCl	2.6	57.96	57.96	47
Oxalic acid	1.6	35.6	35.6	31
Sodium thiosulphate	7.5	167	167	95

Experimental conditions: Source phase, 70 ml of 1 x 10^{-4} M Ag^+ : Receiving phase, 70 ml of 0.1 M stripping medium, time of transport carried out 300 minutes

Table 6: Effect of $Na_2S_2O_3$ concentration in receiving phase on silver transport

Concentration of $S_2O_3^{2-}$ (M)	0.1	0.01	0.001
% transported into receiving phase	95	38	35

Experimental conditions: Source phase, 70 ml of 1 x 10^{-4} M Ag^+ : Receiving phase, 70 ml of (10^{-1}, 10^{-2}, 10^{-3} M) sodiumthiosulphate, time of transport carried out 300 minutes.

Table 7: Effect of pH in source phase on silver transport

pH of source phase	3	4	5	6	7	8
percentage transport	75	80	88	90	93	85

Experimental conditions: Source phase, 70 ml of 1 x 10^{-4} M Ag^{+} : Receiving phase, 70 ml of 0.1M sodiumthiosulphate, time of transport carried out 300 minutes.

Table 8: Life time of thiuram based CTA membrane

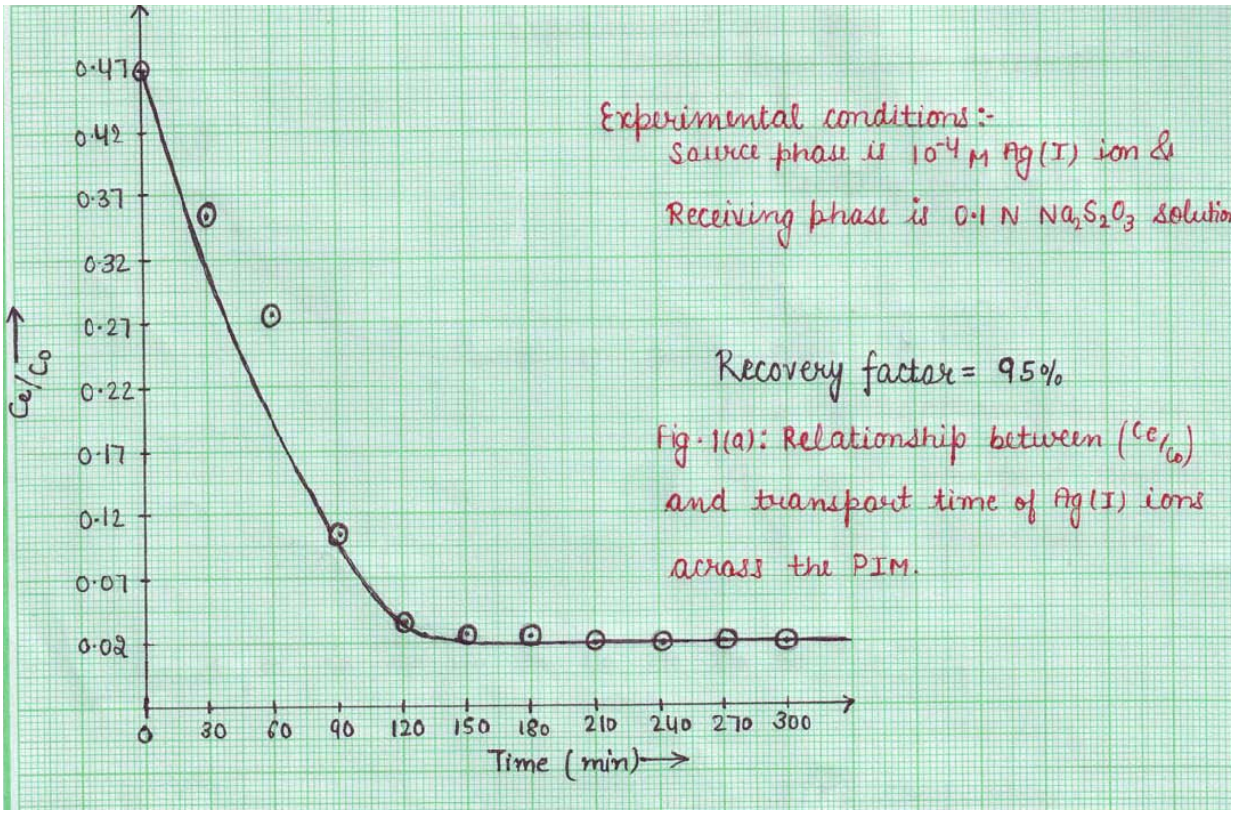
No. of days	1^{st}	2^{nd}	3^{rd}	4^{th}	5^{th}	6^{th}	7^{th}	8^{th}	9^{th}	10^{th}
percentage transported	95±4	92±3	90±3	90±4	90±4	87±4	86	85	80	74

Experimental conditions: Source phase, 70 ml of 1 x 10^{-4} M Ag^{+} : Receiving phase, 70 ml of 0.1M sodiumthiosulphate, time of transport carried out 300 minutes.

Table 9: Amount of Ag(I) transported from various bi-cation mixtures through PIMs

Interfering ion	Transport phenomenon parameters			
	Rate constant k (10^{-3}) (sec^{-1})	Permeability (P) (10^{-3}) (cm s^{-1})	Flux (J_i) (10^{-7}) (mol cm^{-2} s^{-1})	Recovery factor (percentage)
Ag^{+}	7.5	334	334	95
Ag^{+} + Cu^{2+}	1.3	28	28	39
Ag^{+} + Ni^{2+}	6.0	132	132	87
Ag^{+} + Zn^{2+}	3.0	66	66	87
Ag^{+} + Hg^{2+}	3.3	73	73	68

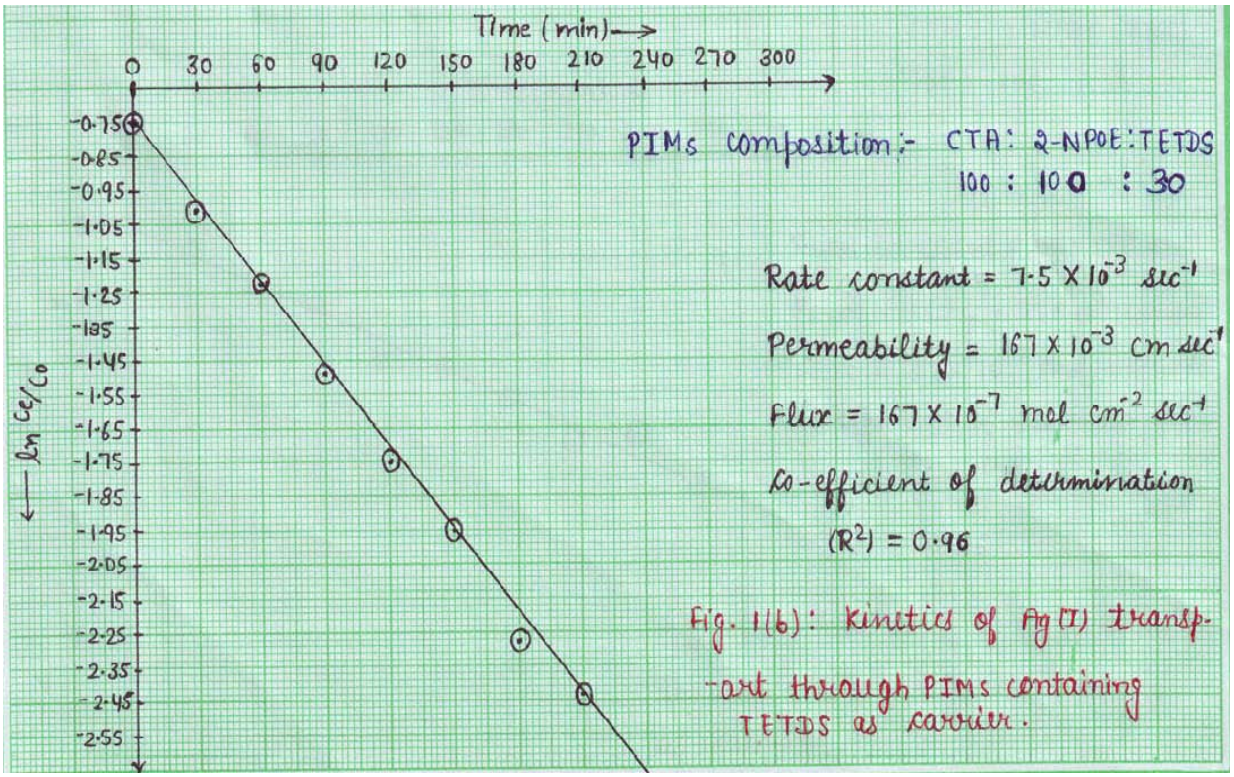
Experimental conditions: Source phase, 70 ml of 5 x 10^{-5} M of each cation: Receiving phase, 70 ml of 0.1M sodiumthiosulphate, time of transport carried out 300 minutes.



Experimental conditions :-
Source phase is 10^{-4} M Ag(I) ion &
Receiving phase is 0·1 N $Na_2S_2O_3$ solution

Recovery factor = 95%

Fig. 1(a): Relationship between (C_e/C_o) and transport time of Ag(I) ions across the PIM.



PIMs composition :- CTA : 2-NPOE : TETDS
100 : 100 : 30

Rate constant = 7.5×10^{-3} sec^{-1}

Permeability = 167×10^{-3} cm sec^{-1}

Flux = 167×10^{-7} mol cm^{-2} sec^{-1}

Co-efficient of determination
$(R^2) = 0.96$

Fig. 1(b): Kinetics of Ag(I) transport through PIMs containing TETDS as carrier.

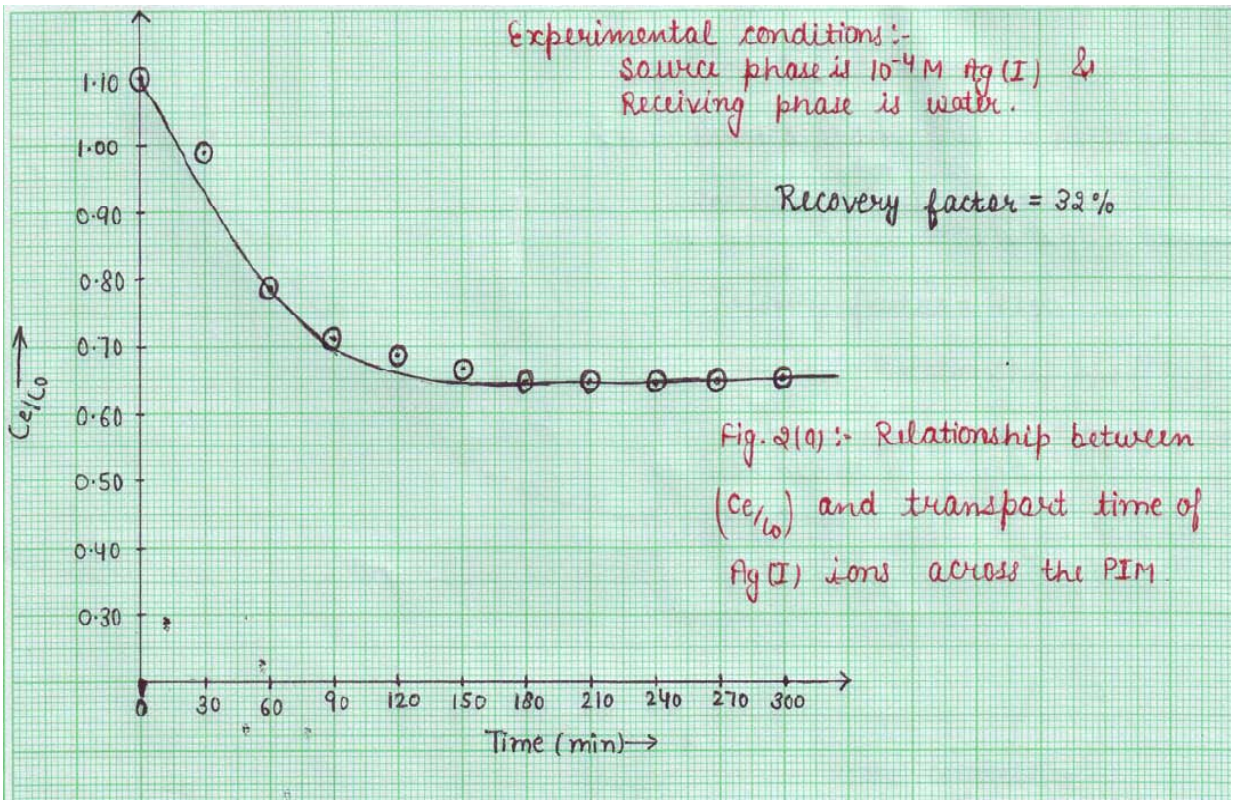


Fig. 2(a) :- Relationship between (C_e/C_o) and transport time of Ag (I) ions across the PIM.

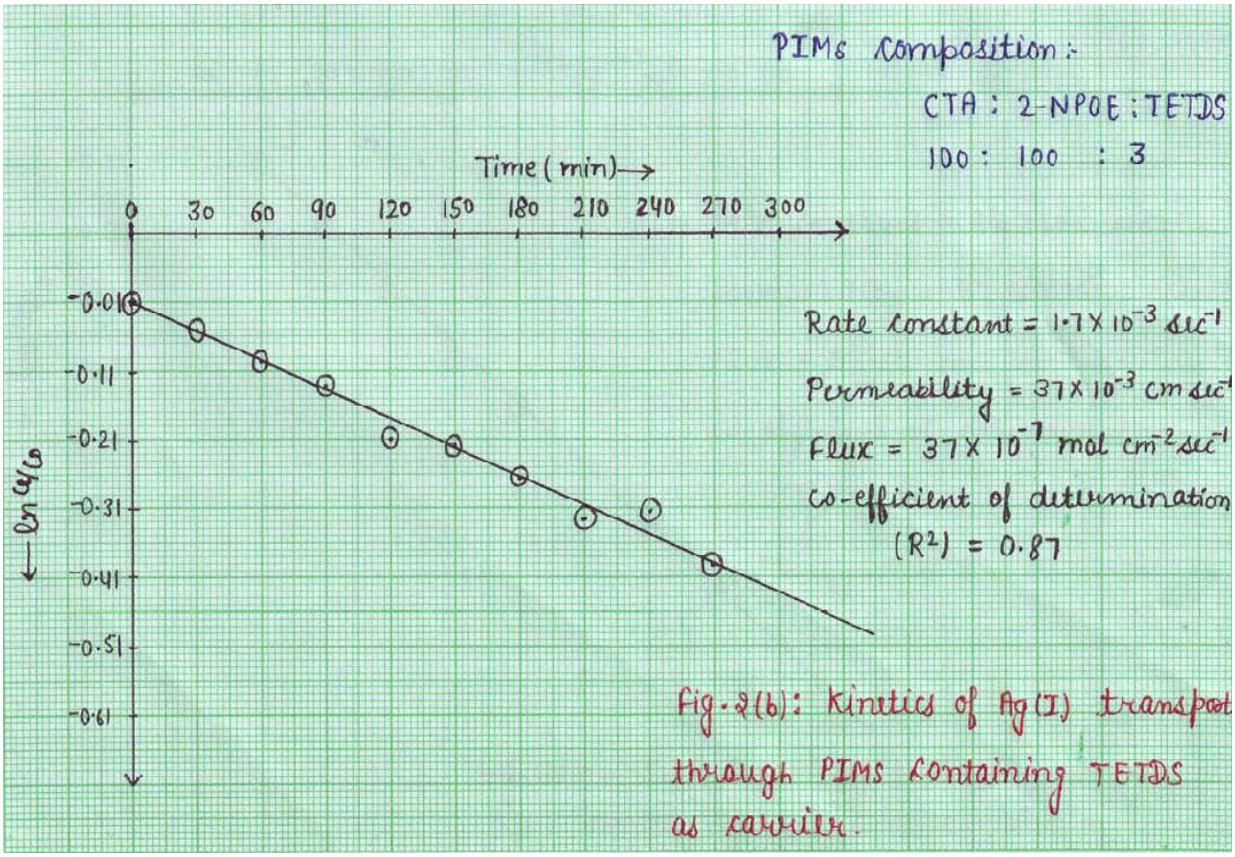
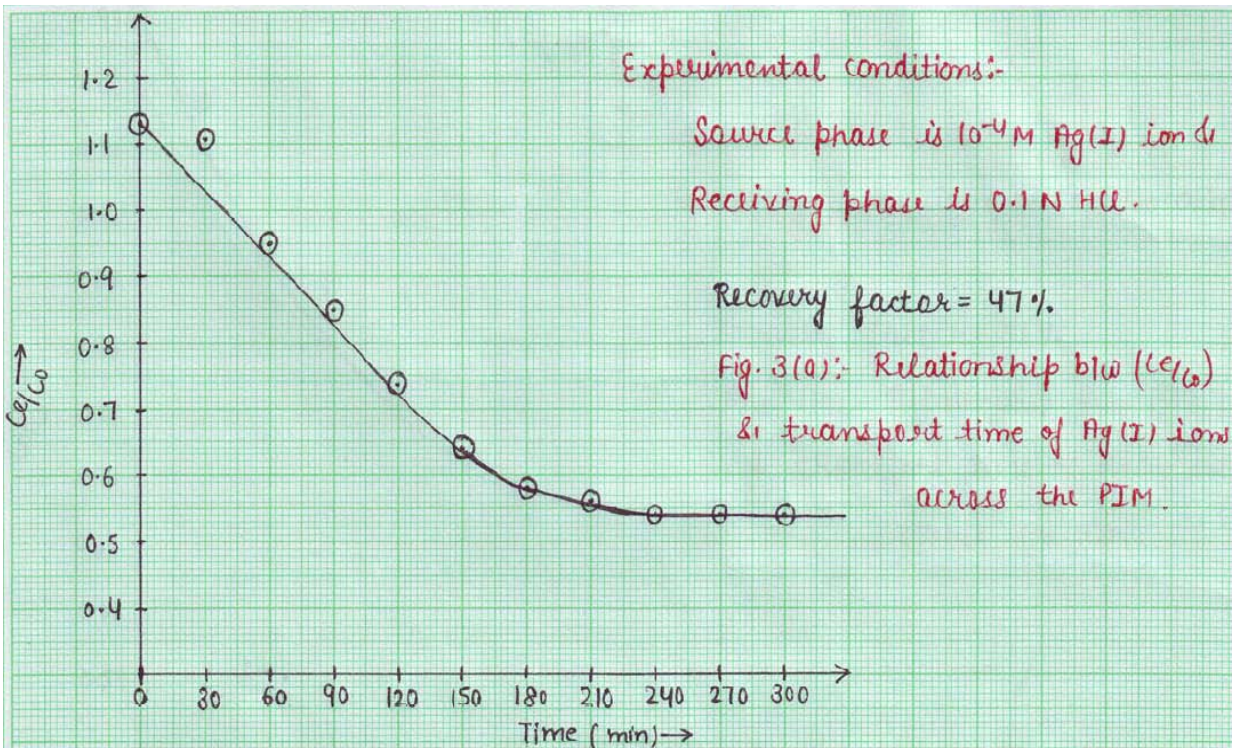
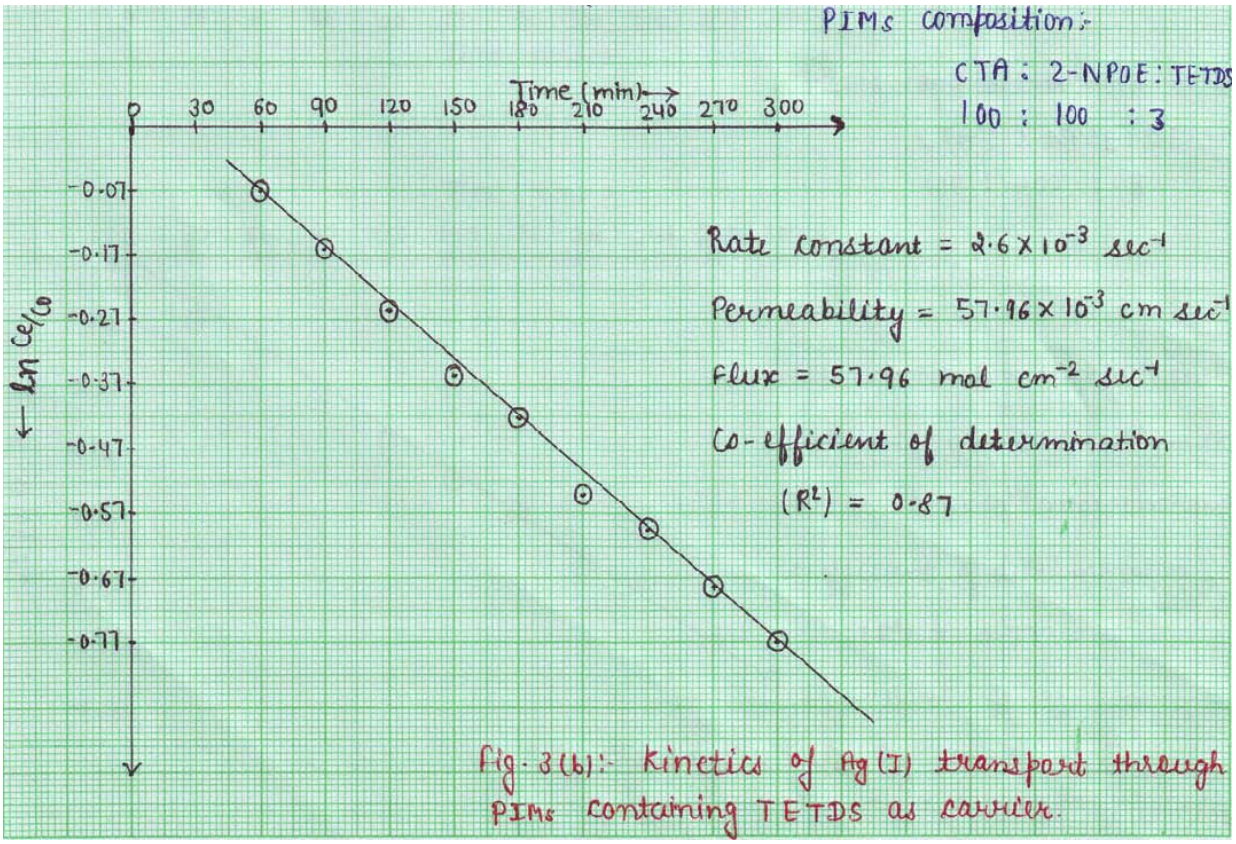
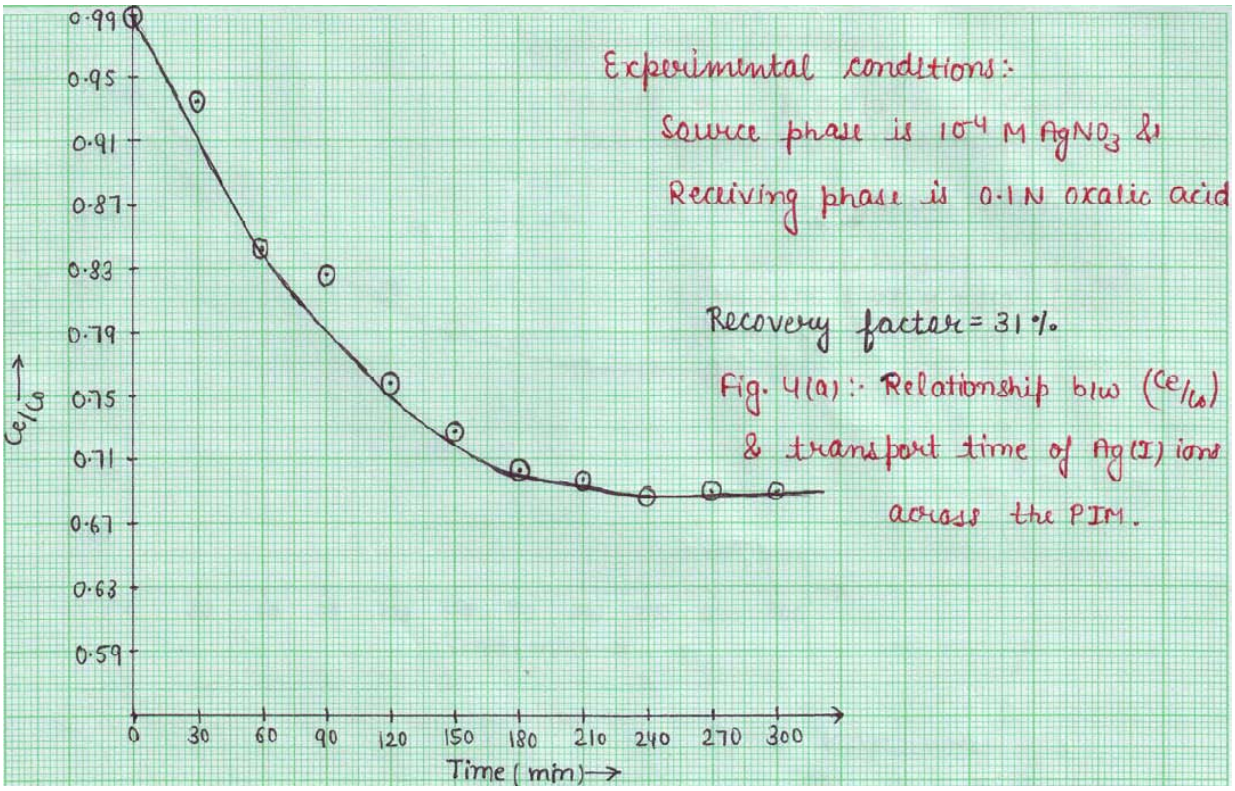


Fig. 2(b) : Kinetics of Ag (I) transport through PIMS containing TETDS as carrier.


Experimental conditions:-
Source phase is 10^{-4} M Ag(I) ion &
Receiving phase is 0.1 N HCl.
Recovery factor = 47 %.
Fig. 3(a):- Relationship b/w (C_e/C_o) & transport time of Ag(I) ions across the PIM.
C_e/C_o
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0 30 60 90 120 150 180 210 240 270 300
Time (min)→


PIMs composition:-
CTA : 2-NPOE : TETDS
100 : 100 : 3
Time (min)→
0 30 60 90 120 150 180 210 240 270 300
-0.07
-0.17
-0.27
-0.37
-0.47
-0.57
-0.67
-0.77
$\ln C_e/C_o$
Rate constant = 2.6×10^{-3} sec^{-1}
Permeability = 57.96×10^{-3} cm sec^{-1}
Flux = 57.96 mol cm^{-2} sec^{-1}
Co-efficient of determination
(R^2) = 0.87
Fig. 3(b):- Kinetics of Ag(I) transport through PIMs containing TETDS as carrier.



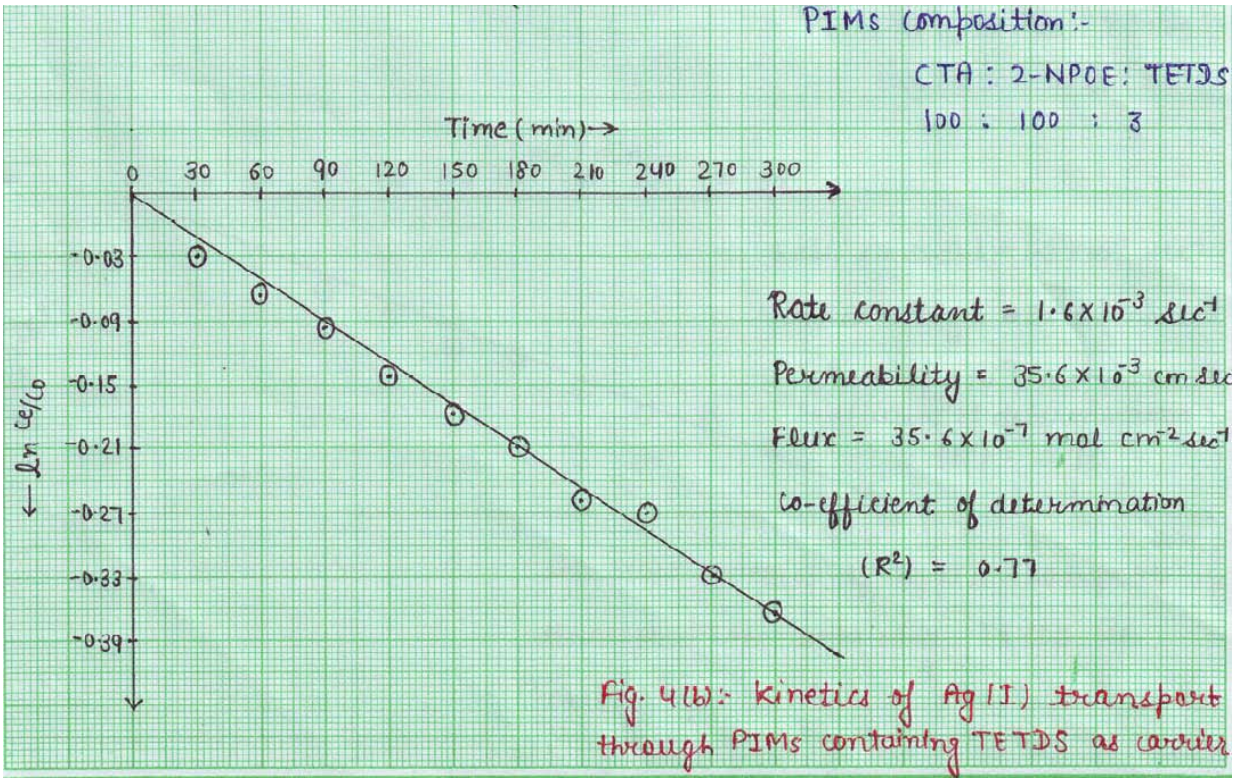
Experimental conditions:-

Source phase is 10^{-4} M $AgNO_3$ &

Receiving phase is 0·1 N oxalic acid

Recovery factor = 31 %.

Fig. 4(a):- Relationship b/w ($Ce/_{Co}$) & transport time of Ag(I) ions across the PIM.



PIMs composition:-

CTA : 2-NPOE : TETDS

100 : 100 : 3

Rate constant = $1·6 \times 10^{-3}$ sec^{-1}

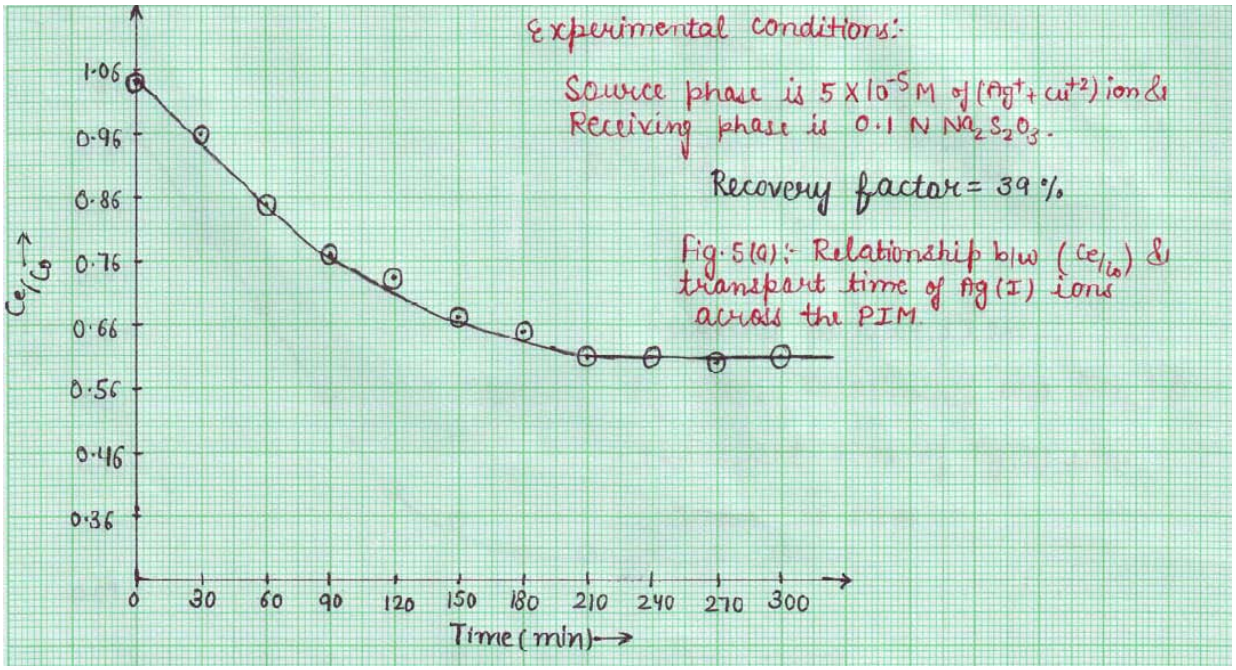
Permeability = $35·6 \times 10^{-3}$ cm sec

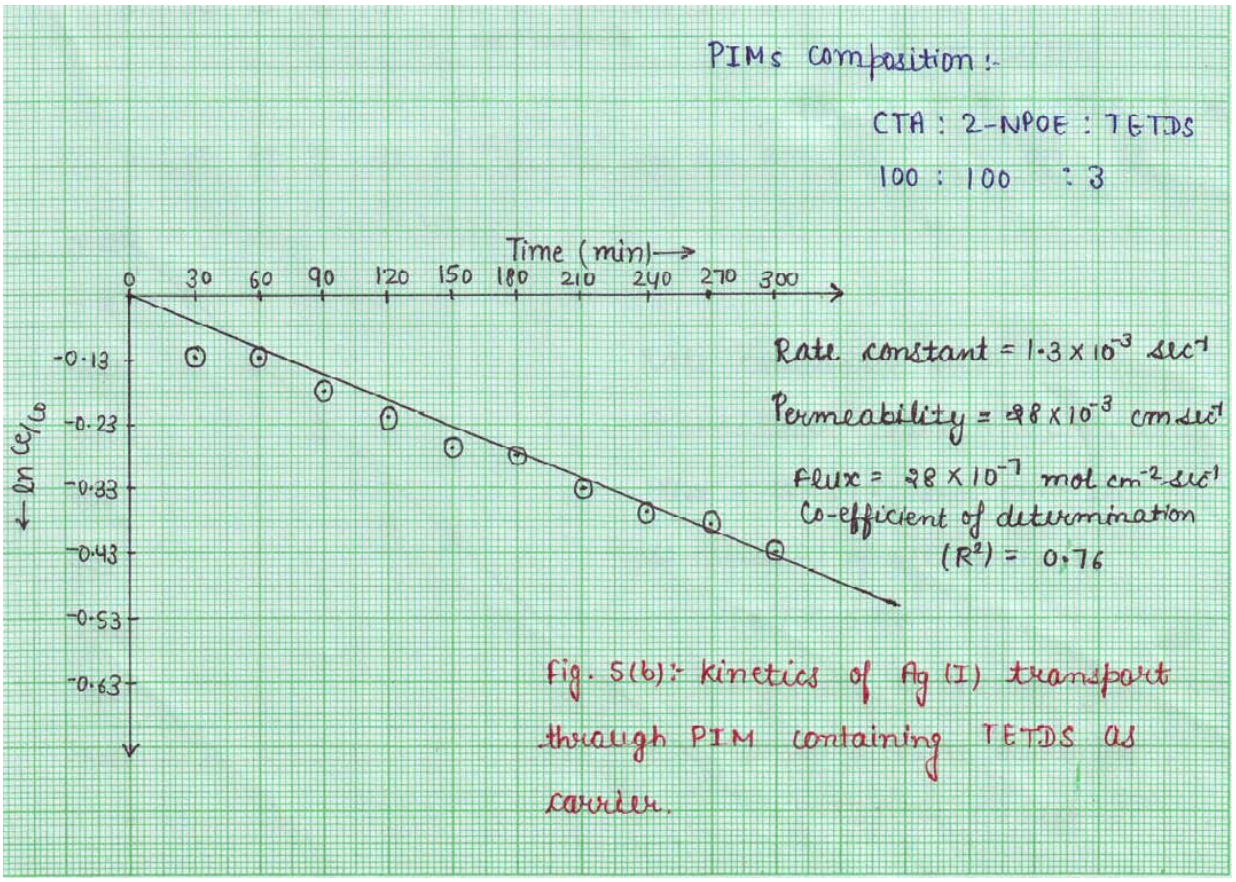
Flux = $35·6 \times 10^{-7}$ mol cm^{-2} sec^{-1}

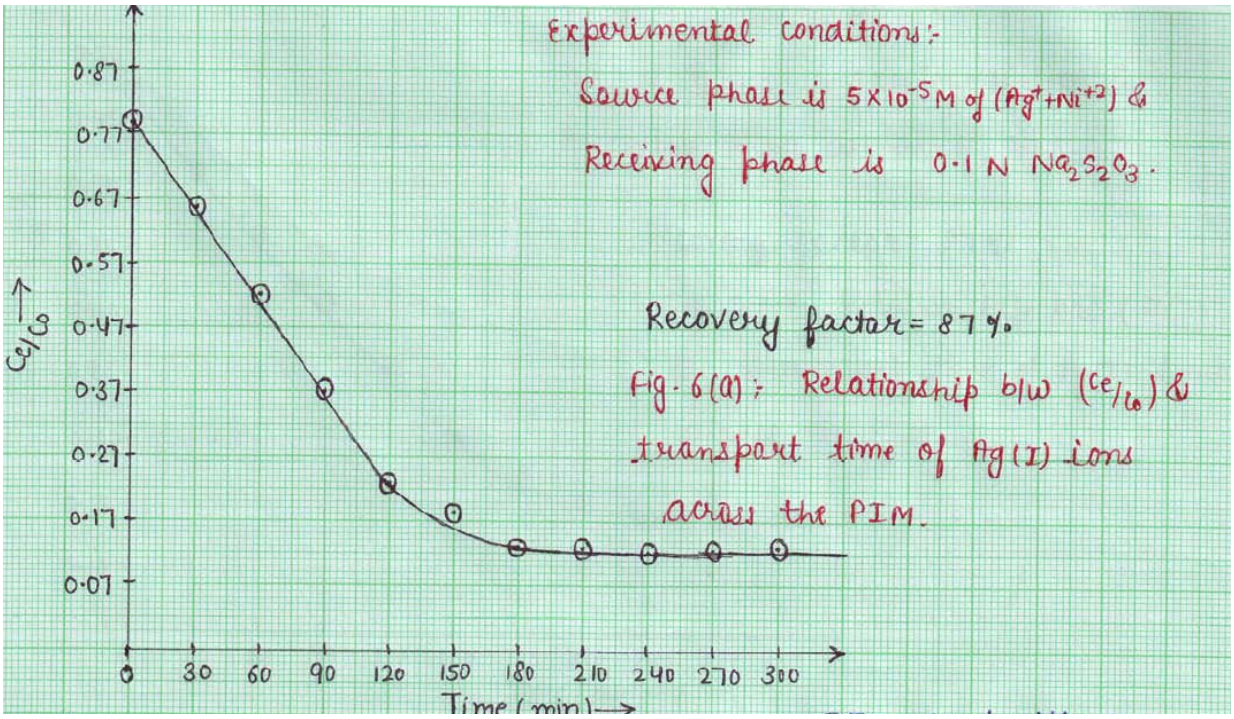
Co-efficient of determination

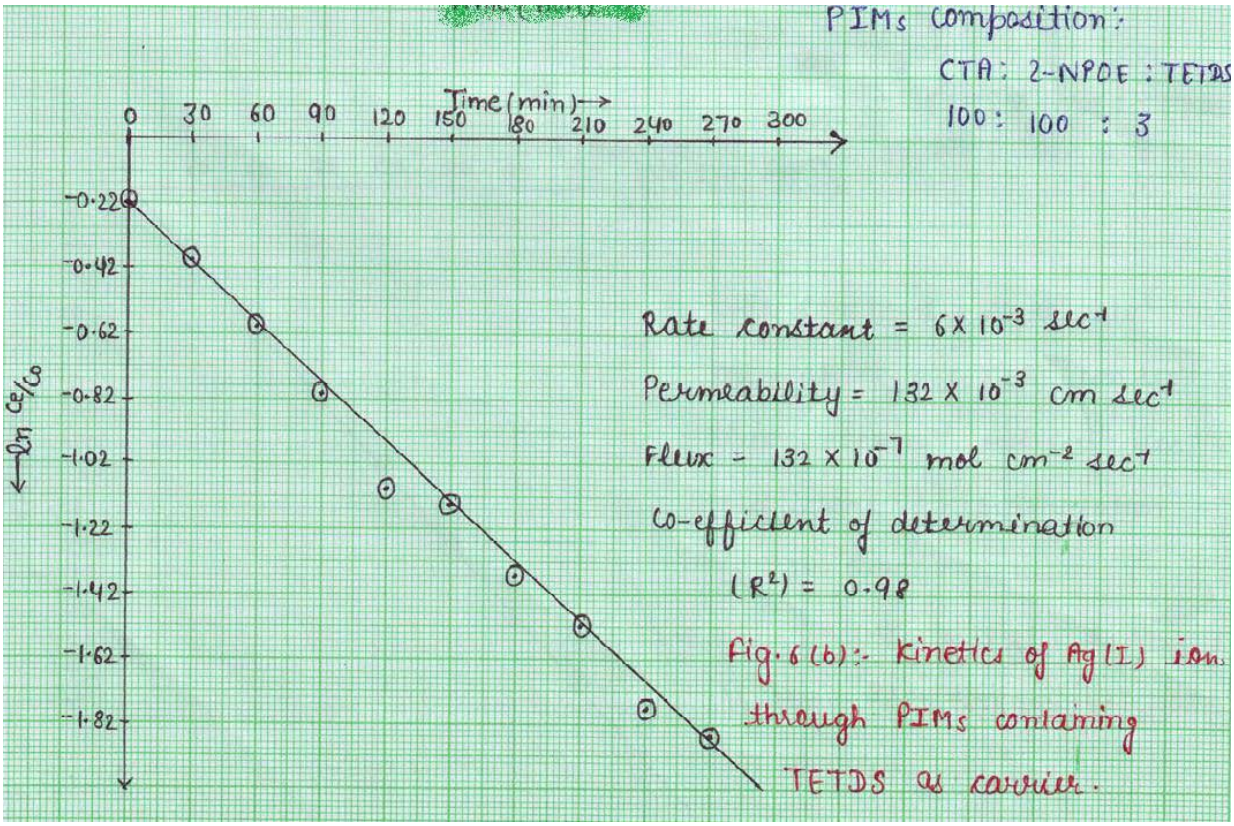
(R^2) = 0·77

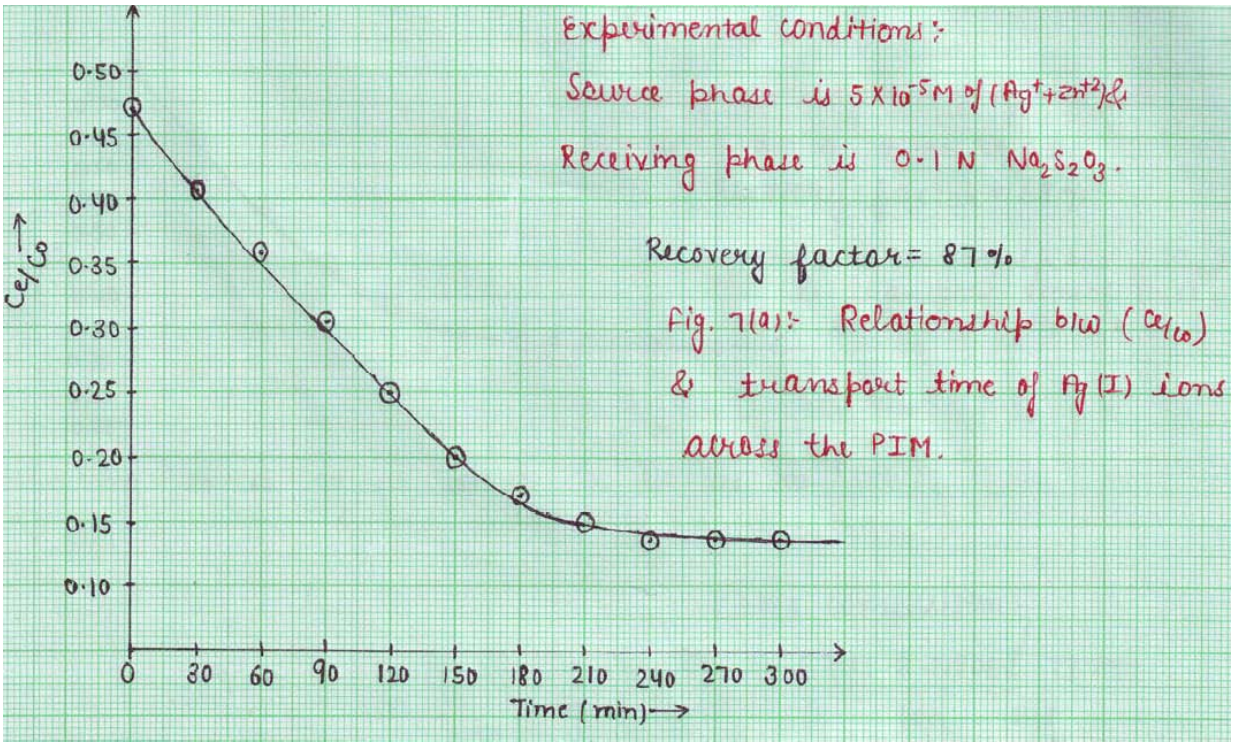
Fig. 4(b):- Kinetics of Ag(I) transport through PIMs containing TETDS as carrier

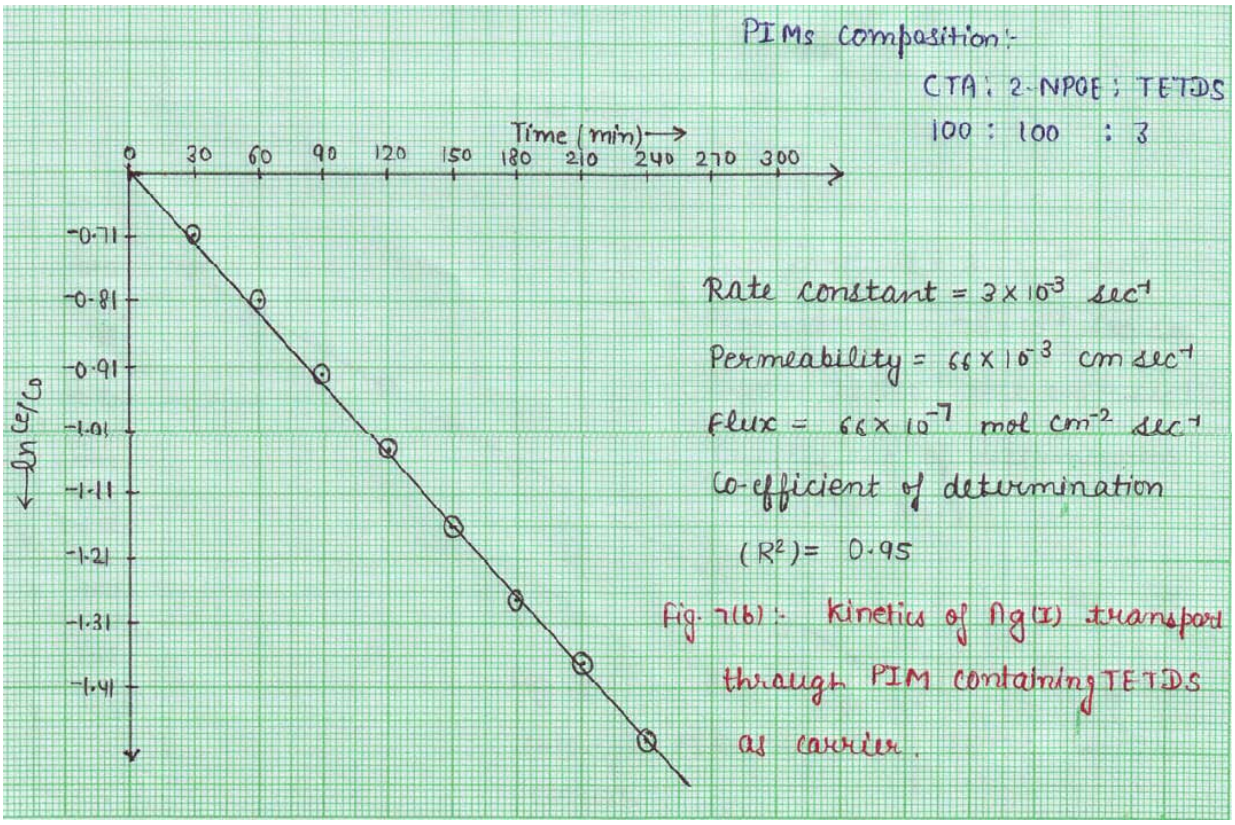

Experimental conditions:-
Source phase is 5×10^{-5} M of $(Ag^{+} + Cu^{+2})$ ion &
Receiving phase is 0.1 N $Na_2S_2O_3$.
Recovery factor = 39 %
Fig. 5(a):- Relationship b/w $(Ce/_{Co})$ & transport time of Ag (I) ions across the PIM
$Ce/_{Co}$ →
1.06
0.96
0.86
0.76
0.66
0.56
0.46
0.36
0 30 60 90 120 150 180 210 240 270 300
Time (min) →

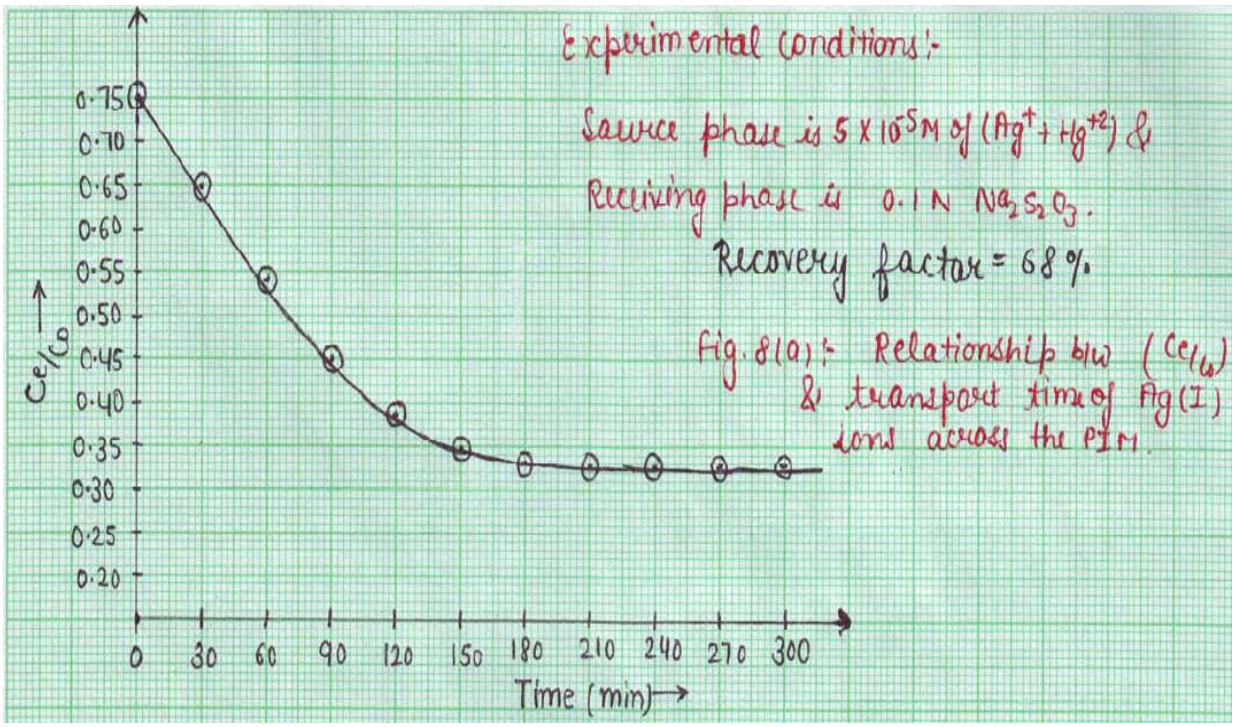

PIMs composition :-
CTA : 2-NPOE : TETDS
100 : 100 : 3
Time (min) →
0 30 60 90 120 150 180 210 240 270 300
-0.13
-0.23
-0.33
-0.43
-0.53
-0.63
← ln $Ce/_{Co}$
Rate constant = 1.3×10^{-3} sec^{-1}
Permeability = 28×10^{-3} $cm\,sec^{-1}$
Flux = 28×10^{-7} $mol\,cm^{-2}\,sec^{-1}$
Co-efficient of determination
$(R^2) = 0.76$
Fig. 5(b):- Kinetics of Ag (I) transport through PIM containing TETDS as carrier.

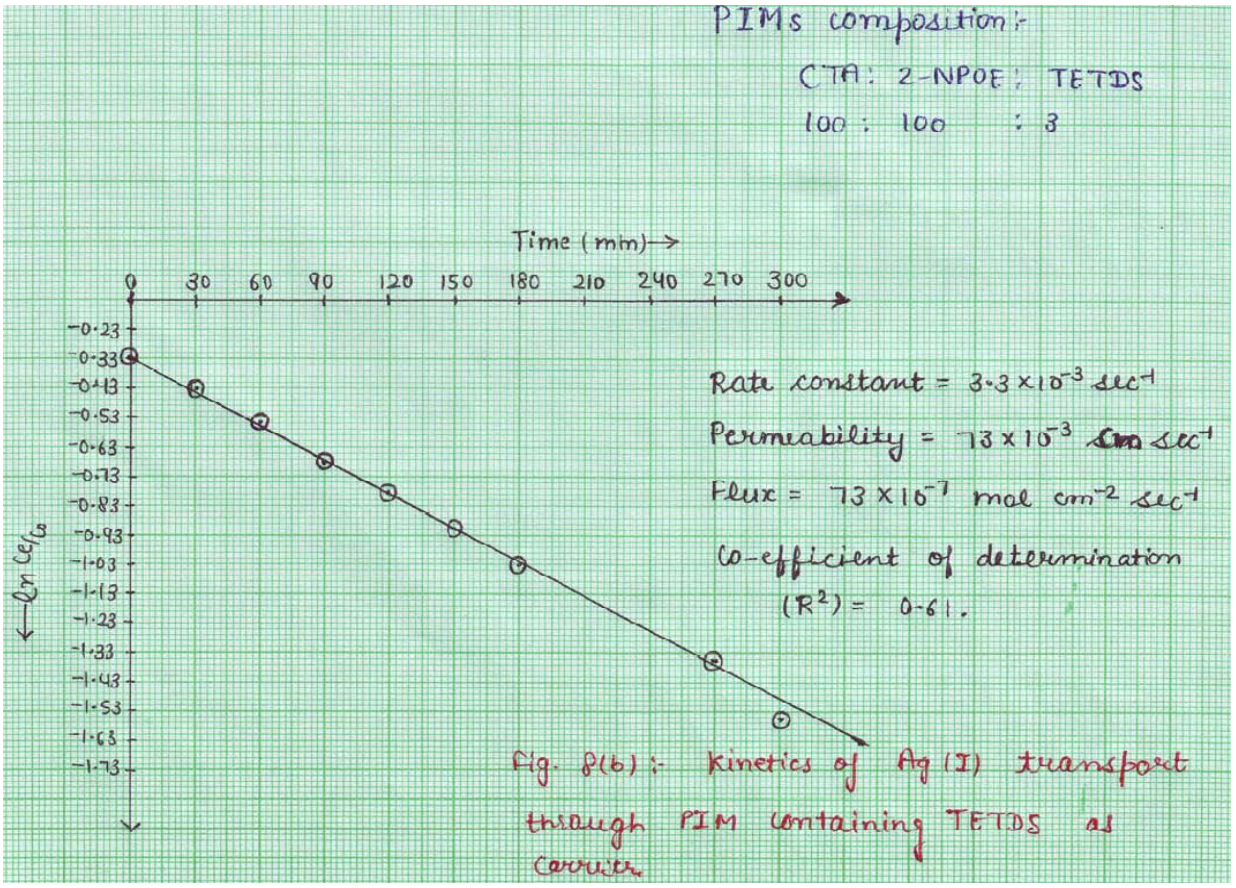

Experimental conditions:-
Source phase is 5×10^{-5} M of (Ag^{+}+Ni^{+2}) &
Receiving phase is 0.1 N $Na_2S_2O_3$.
Recovery factor = 87 %.
Fig. 6(a): Relationship b/w (C_e/C_o) & transport time of Ag(I) ions across the PIM.
C_e/C_o
0.87
0.77
0.67
0.57
0.47
0.37
0.27
0.17
0.07
0 30 60 90 120 150 180 210 240 270 300
Time (min)


PIMs Composition:
CTA : 2-NPOE : TETDS
100 : 100 : 3
Time (min)
0 30 60 90 120 150 180 210 240 270 300
$\ln C_e/C_o$
-0.22
-0.42
-0.62
-0.82
-1.02
-1.22
-1.42
-1.62
-1.82
Rate constant = 6×10^{-3} sec^{-1}
Permeability = 132×10^{-3} cm sec^{-1}
Flux = 132×10^{-7} mol cm^{-2} sec^{-1}
Co-efficient of determination (R^2) = 0.98
Fig. 6(b):- Kinetics of Ag(I) ion through PIMs containing TETDS as carrier.


Experimental conditions:-
Source phase is 5×10^{-5} M of (Ag^{+}+Zn^{+2})&
Receiving phase is 0.1 N $Na_2S_2O_3$.
Recovery factor = 87%
Fig. 7(a):- Relationship b/w (C_e/C_o) & transport time of Ag (I) ions across the PIM.
C_e/C_o
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0 30 60 90 120 150 180 210 240 270 300
Time (min)


PIMs composition:-
CTA : 2-NPOE : TETDS
100 : 100 : 3
Time (min)
0 30 60 90 120 150 180 210 240 270 300
$\ln C_e/C_o$
-0.71
-0.81
-0.91
-1.01
-1.11
-1.21
-1.31
-1.41
Rate constant = 3×10^{-3} sec^{-1}
Permeability = 66×10^{-3} $cm\ sec^{-1}$
Flux = 66×10^{-7} $mol\ cm^{-2}\ sec^{-1}$
Co-efficient of determination (R^2) = 0.95
Fig. 7(b):- Kinetics of Ag (I) transport through PIM containing TETDS as carrier.


Experimental conditions:-
Source phase is 5×10^{-5} M of $(Ag^{+} + Hg^{+2})$ &
Receiving phase is 0.1 N $Na_2S_2O_3$.
Recovery factor = 68 %.
Fig. 8(a):- Relationship b/w $(C_e/_{C_0})$ & transport time of Ag(I) ions across the PIM.
$C_e/_{C_0}$
0·75
0·70
0·65
0·60
0·55
0·50
0·45
0·40
0·35
0·30
0·25
0·20
0 30 60 90 120 150 180 210 240 270 300
Time (min)→


PIMs composition:-
CTA : 2-NPOE : TETDS
100 : 100 : 3
Time (min)→
0 30 60 90 120 150 180 210 240 270 300
−0·23
−0·33
−0·43
−0·53
−0·63
−0·73
−0·83
−0·93
−1·03
−1·13
−1·23
−1·33
−1·43
−1·53
−1·63
−1·73
$\ln C_e/_{C_0}$
Rate constant = 3.3×10^{-3} sec^{-1}
Permeability = 73×10^{-3} cm sec^{-1}
Flux = 73×10^{-7} mol cm^{-2} sec^{-1}
Co-efficient of determination (R^2) = 0.61.
Fig. 8(b):- Kinetics of Ag(I) transport through PIM containing TETDS as carrier.

CONCLUSIONS AND FUTURE SCOPE

This work describes an efficient and selective method for the transport of Ag^{+} ion through a PIM membrane containing thiuram sulphide as a carrier. The receiving phase contains $S_2O_3^{2-}$ ion, which was found to play an important role in the transport process. The amount of silver transported across the PIM after 120 minutes was 90 ± 5% and exhibits very good linearity (R^2=0.96). The selectivity and efficiency of silver ion transported from aqueous solutions containing equimolar mixtures of Zn^{2+}, Cu^{2+}, Ni^{2+}, Hg^{2+} were investigated. Results show only Cu^{2+} and Hg^{2+} exhibits some interference. The future scope of this work is attempting to optimize a process means move deeply into its physicochemical properties to subject for commercialization and volume reduction of stripping medium. .

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