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A Comparative Study of Linked 2, 2'-Dipyridylamine Ligand System as an Ion Selective Electrode for Ag (I) Ions

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The linked 2, 2'-dipyridylamine derivatives have been explored as neutral carrier ionophores for preparing poly (vinyl chloride) based electrodes selective to Ag(I) ions. Based on the stability constants determined by sandwich membrane method and the energy minimization studies using CAChe software, the ionophore was found selective for Ag (I) ions. Different compositions of the membrane were studied. The best performance was found with the electrode composition (w/w) ionophore (3%): PVC (33%): o-NPOE (64%). This electrode exhibits Nernstian response with a slope of 59mV/decade of activity in the concentration range 5.5×10^{-6} - 1.0×10^{-1}M of Ag (I). The electrode shows satisfactory performance over a pH range of 2.0 – 9.5, with a fast response time of 14s. Response of the electrode was highly selective to Ag(I) ions over a number of uni-, di- and trivalent metal cations. Also, the electrode has been used successfully as an indicator electrode in potentiometric titrations of Ag (I) ions

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Keywords: 2, 2'-dipyridylamine, potentiometry, selectivity, stability constant, Ag (I) ions.

1. INTRODUCTION

2,2'-dipyridylamine (dpaH) is an aromatic amine, in some ways similar to 2,2'-bipyridine (bpy), but the central amine unit introduces several differences: (i) dpaH coordinates with six-membered chelate rings instead of five-membered rings for bpy; (ii) the coordinated pyridine rings are not necessarily forced to near coplanarity as in bpy; (iii) the ligand field strength of dpaH is greater than ethylenediamine. The two-pyridine rings of dpaH are flexible in their coordination with metal centers. Hence, the coordination chemistry of 2, 2'-dipyridylamine (dpa) and its derivatives has been the focus of a considerable number of investigations [1]. For example, mono-, di- and tri-dpa derivatives have been reported [2-4] in which secondary nitrogen of each dpa is directly bound to an aryl core with such species being employed in studies that range from metal coordination and supramolecular chemistry to synthesis of new luminescent materials. Neutral dipyridylamine has been shown to form discrete complexes with silver. Potentiometric electrodes are especially suited for analytical determinations of metal ions, as they offer advantages such as selectivity, sensitivity, good precision, simplicity and low cost. Silver is used widely in production of coins, jewelry and tableware, electrical apparatus, mirrors, electrodes and chemicals for photographic processes. Also, it is used in the production of dental amalgams and burn skin treatment creams as silver sulfadiazine cream because of its antibacterial properties [5-7].

2. EXPERIMENTAL PART

2.1. Reagents

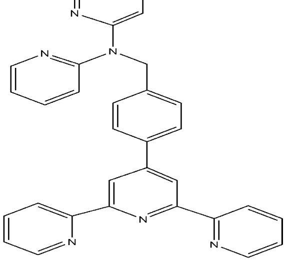
High molecular weight polyvinylchloride (PVC), *o*-nitrophenyloctylether (*o*-NPOE) and tetrakis (p-chlorophenyl) borate (KTpClPB), tetrahydrofuran (THF) were purchased from Aldrich (India) and used as received. Metal salt solutions of concentration 0.1M were prepared by dissolving AR grade metal nitrates in double distilled water and standardized wherever necessary. Working solutions of different concentrations were prepared by serial dilutions.

2.2. Apparatus

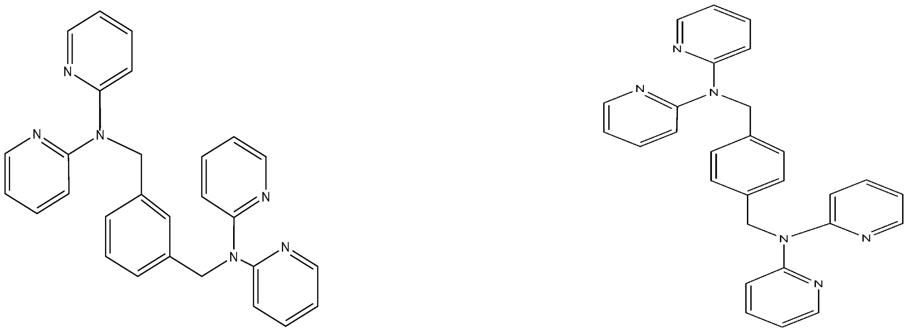
Potentials were measured with an Equip-Tronics (EQ-602, accuracy, ±0.1mV) potentiometer (Mumbai, India) and pH of the solution was monitored simultaneously with a conventional glass pH electrode.

3. RESULTS AND DISCUSSION

Ionophores with donating nitrogen atoms in their structure, insolubility in water, high molecular weight were expected to act as a suitable ion carrier as reported in literature [8,9]. To investigate the suitability of the ionophore for comparison purposes, three ionophores; ‘tpydpa’, ‘mdpa and ‘pdpa’ were used (Figure 1).



Di-2-pyridylaminoethyl-4-terpyridylbenzene **(tpydpa)**



1,3-Bis(di-2-pyridylaminoethyl) benzene **(mdpa)** 1,4-Bis(di-2-pyridylaminoethyl) benzene(**pdpa)**

Figure 1. Structures of ionophores, tpydpa, mdpa, pdpa

3.1. Energy minimization studies of ionophores with some metal ions using CAChe software

Energy minimization studies of the metal-ionophore complexes were carried out with different metal ions carried with the help of CAChe 6.01 software using MM3 calculations.

Table 1. Energy minimization of different ionophores (tpydpa, mdpa, pdpa) with some metal ions for 1:1 and 1:2 complexes

Metal Ion	**Energy Values (kcal/ mol)**					
	tpydpa		mdpa		pdpa	
	1:1	1:2	1:1	1:2	1:1	1:2
Without metal ion	88	88	52	52	52	52
Ag^{+}	441	236	165	601	675	597
Pb^{2+}	244	544	131	781	131	776
Hg^{2+}	291	538	187	709	187	689
Zn^{2+}	216	481	164	656	164	650

Figure 2. Optimal conformation of the ionophore tpydpa before complexation

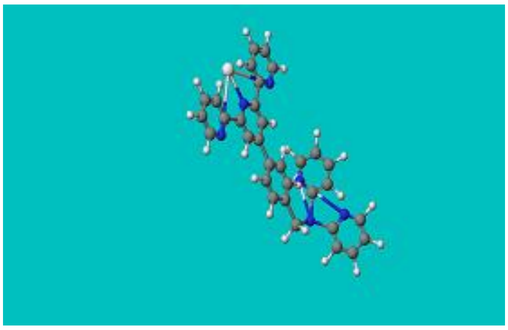


Figure 3. Optimal conformation of the ionophore tpydpa after complexation

The results are shown in Table 1 using 1:1 and 1:2 complexations metal ionophore interactions (Figures 2 and 3). Assuming, both coordinate as well as weak interactions between the ionophores and the metal ion. However, the experimental results are in agreement with weak-weak interactions between the metal ion and the ionophore.

3.2. Determination of the Formation Constant

In order to use the ionophore for a particular metal ion its interactions with different metal ions were studied by sandwich membrane method. In this method, fused segmented sandwich membrane yield information about the activity ratio on both sides of the membrane. It requires membrane potential measurement [10] on two layer sandwich membrane, where only one side contains the ionophore and other side of the membrane does not contain the ionophore.

Table 2. Formation constants for complexes of ionophores tpydpa, mdpa and pdpa with some metal ions

	Formation constant		
Metal ion	tpydpa	mdpa	pdp
Ag^+	13.28	5.71	5.20
Hg^{2+}	6.49	5.76	5.38
Ca^{2+}	6.42	6.91	5.13
Cu^{2+}	5.68	5.90	5.60
Co^{2+}	5.85	6.16	5.47
Fe^{3+}	5.99	6.20	3.76
Ni^{2+}	5.58	6.03	5.81
Pb^{2+}	6.10	6.10	-
Sr^{2+}	6.12	-	5.23
Cd^{2+}	5.89	5.42	5.81

The membrane potential E_M is determined by subtracting the cell potential for a membrane without ionophore from that for the sandwich membrane. The values obtained of ion-ionophore complex are shown in Table 2. This method allows convenient determination of ion-ionophore complexes within the membrane phase on the basis of transient membrane potential measurement on two layer sandwich membrane neglecting the ion pairs.

3.3. Electrode preparation and E.M.F. measurements

Stability constants and optimization of membrane ingredients (Table 3) of linked 2,2’-dipyridylamine derivatives indicated that only ‘tpydpa’ forms a strong interaction with silver metal ions compared to other derivatives. Hence, only tpydpa was subjected to further potentiometric studies**.** Membranes were prepared by dissolving appropriate amounts of powdered PVC, plasticizer, ionophore (tpydpa) according to Table 3 and were completely dissolved in 5 mL of THF. The components were added in terms of weight percentages. The homogenous mixture obtained after complete dissolution of all components was concentrated by evaporating THF slowly at 25° C so as to get an oily mixture.

Table 3. Optimization of membrane ingredients for tpydpa, mdpa and pdpa based ionophores

Electrode No.	Ionophore (% w/w)	Anionic Site (KTClPB) (% w/w)	o-NPOE (% w/w)	PVC (% w/w)	Detection Limit(M)	Slope (mV/decade)
E_1	1(tpydpa)	-	66.0	33.0	1x10^{-5}	41
E_2	3(tpydpa)	-	64.0.	33.0	1x10^{-5}	59
E_3	5(tpydpa)	-	62.0	33.0	1x10^{-5}	43
E_4	3(tpydpa)	1.1	62.9	33.0	1x10^{-4}	38
E_5	3(tpydpa)	2.2.	61.8	33.0	1x10^{-3}	62
E_6	3(tpydpa)	3.0	61.0	33.0	1x10^{-5}	58
E_7	2(pdpa)	-	65.0	33.0	1x10^{-4}	24
E_8	3(pdpa)	-	64.0.	33.0	5x10^{-6}	46
E_9	4(pdpa)	-	63.0	33.0	1x10^{-3}	39
E_{10}	3(pdpa)	2.2.	61.8	33.0	1x10^{-3}	62
E_{11}	3(pdpa)	3.0	61.0	33.0	1x10^{-5}	58
E_{12}	1(mdpa)		66.0	33.0	5x10^{-5}	29
E_{13}	3(mdpa)	-	64.0.	33.0	1x10^{-4}	52
E_{14}	5(mdpa)	-	62	33.0	1x10^{-5}	49
E_{15}	5(mdpa)	0.5	61.5	33.0	1x10^{-5}	28
E_{16}	7(mdpa)	-	60.0	33.0	1x10^{-4}	42
E_{17}	5(mdpa)	2.5	61.5	31.0	1x10^{-4}	47

The concentrated mixture solution was poured in a glass ring of diameter 20 mm placed on smooth glass plate. The concentrated mixture solution was then allowed to evaporate for 24 h at room temperature. Transparent membranes so obtained were cut to the size and glued on one end of a pyrex glass tube with araldite adhesive. The membrane was equilibrated with 0.1M silver nitrate solution.

The ratio of different membrane ingredients and the contact time were optimized to provide membranes which resulted in reproducible and stable potentials. Also, membranes having only PVC as the membrane ingredients (dummy membranes) were prepared to observe whether any background potentials were produced due to binding material or not. It was observed that potentials were not generated without the ionophore. The activities of metal ions were calculated by using modified form of the Debye-Huckel equation. All emf measurements were carried out with the following assembly: Hg/Hg_2Cl_2, KCl (satd)./Internal Solution ($1x10^{-1}$M $AgNO_3$)/PVC Membrane/Test solution/Hg-Hg_2Cl_2, KCl (satd). The concentrations of test solution were varied from $1x10^{-8}$M to $1x10^{-1}$M.

3.4. Effect of ionophore concentration

In preliminary experiments, membranes with and without carriers were constructed. The blank membrane showed insignificant selectivity towards Ag^+ and their responses were unreliable, whereas, in presence of proposed ionophore, 'tpydpa' the optimized membrane gave Nernstian response and remarkable selectivity for Ag^+ ion over several other metal cations. Preferential response towards Ag^+ ions is believed to be associated with selective coordination of ionophore to the Ag^+ ion. Ag^+ selective electrodes prepared with different amounts of ionophores have been evaluated in the Table 3. Since the sensitivity and selectivity of a given membrane electrode is significantly related to the composition of membrane, particularly, the amount of ionophore [11-16], the amount of ionophore, PVC and additive were varied to study their effect on the potential response of the proposed electrode. The data clearly indicates that composition of the electrode having ionophore less than or greater than 3% leads to non-Nernstian responses. This deviation in electrode response at higher and lower concentration of the ionophore is due to the loss of selectivity and enhanced interference of the lipophilic counter ions of the test solution as presumed in the phase boundary potential model of carrier based ISEs [17].

3.5. Calibration curve, response time and lifetime of electrode

The polymeric membrane electrodes for Ag^+ ion based on ionophore 'tpydpa' have been examined according to IUPAC recommendations [18] at various concentrations of inner filling solution of $AgNO_3$ solution in the range of $1.0x10^{-3}$M to $1.0x10^{-1}$M and the potential response of the electrode has been observed. It was observed that the best result in terms of slope and working concentration range has been obtained with inner filling solution of concentration $1.0x10^{-1}$M. The critical response characteristics of Ag (I) electrode were assessed according to IUPAC recommendations. E.M.F. of the membrane electrode at varying Ag(I) concentration shows a linear range from $1.0x10^{-5}$M to $1.0x10^{-1}$M with a Nernstian slope of 59 mV/decade. The detection limit was $5.0x10^{-6}$M as determined from the intersection of the two extrapolated segments of the calibration plots (Figure 4)

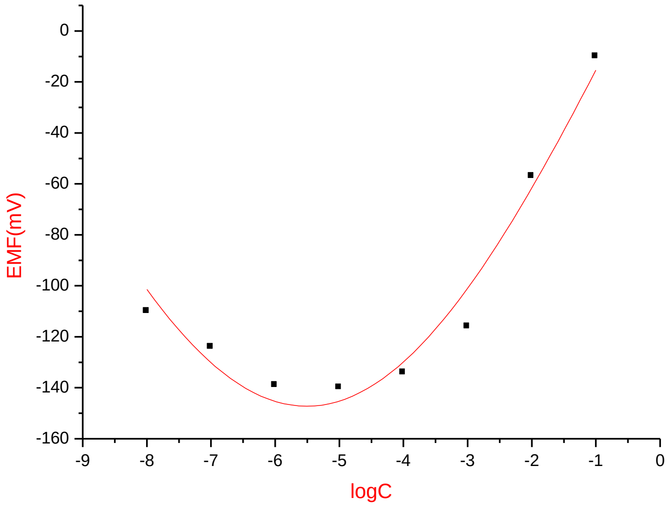


Figure 4. Calibration curve for Ag (I) ISE with tpydpa as ionophore

To study the distribution of membrane ingredients in membrane phase, scanning electron microscopic study was carried out at different stages of membrane composition. The images obtained in different cases are shown in figures 5. Figure 5(a) is the SEM image of the membrane containing PVC only. SEM images of the membrane containing PVC and o-NPOE, membrane containing PVC, o-NPOE and the ionophore ‘tpydpa’ and membrane containing PVC, o-NPOE and ionophore ‘tpydpa’ equilibrated with 0.1M $AgNO_3$ solution are shown in figures 5(b), 5(c) and 5(d) respectively. Figure 5(d) shows uniform complexation tpydpa with Ag(I) ions.

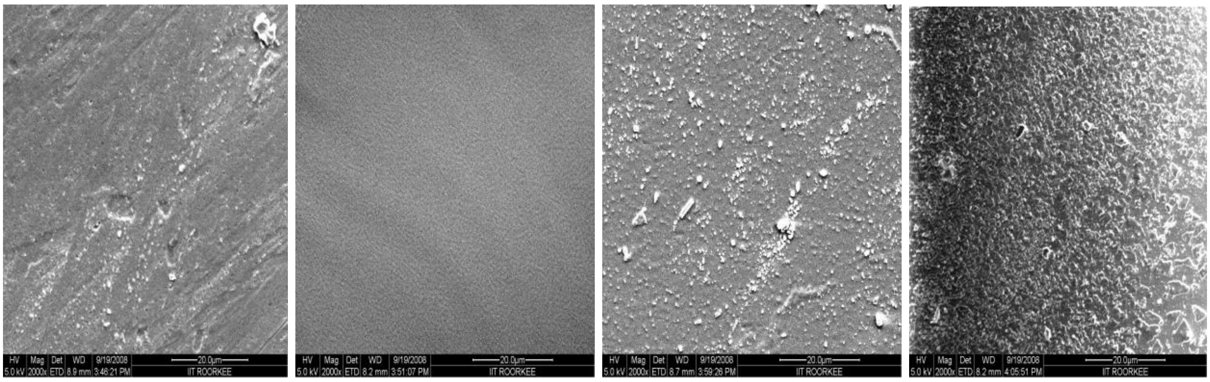


Figure **5(a)** Figure **5(b)** Figure **5(c)** Figure **5(d)**

Figure 5. SEM images of the membranes at different stages

3.6. Effect of pH on the response of Ag (I) selective electrode

pH dependence of the electrode response of the was studied in the pH range of 2.0 - 9.5 in the solution. pH of the solution was adjusted using NaOH (0.1M) and HNO_3 (0.1M) and the results are shown in the Figure 6. The potential response of the electrode remains constant in the pH range of 2.0 – 9.5. At higher pH values, the potential decreases. The sharp changes at higher pH may be due to the formation of some hydroxyl complexes of Ag (I) ions thereby causing interference. At lower pH values, the potential increases due to the membrane response to hydronium ion and Ag (I) ions.

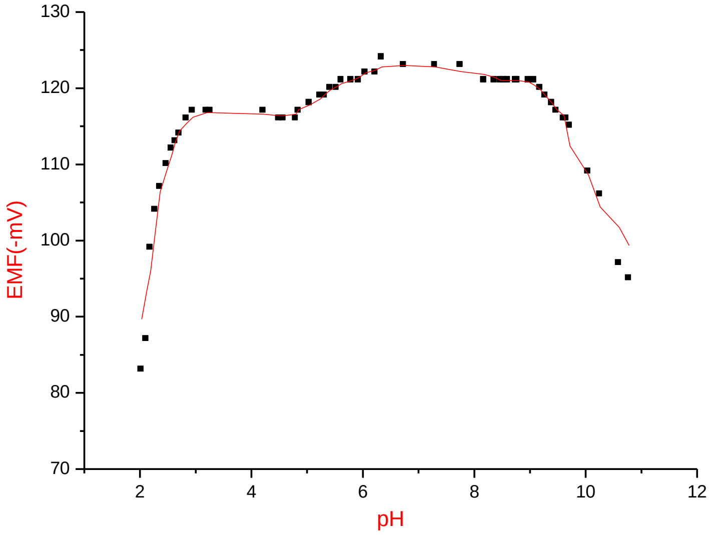


Figure 6: Effect of pH on response of electrode

3.8. Effect of interfering ions on electrode performance and selectivity

Selectivity is the term which is used to describe utility of ion selective electrode. It gives the response of ion selective electrode for the primary ion in presence of secondary ion present in the solution, which is expressed in terms of potentiometric selectivity coefficients. Potentiometric selectivity coefficient ($K^{Pot}_{Ag, B}$) describes preference by the membranes for Ag^+ relative to an interfering ion B. In this work selectivity coefficients were determined by fixed interference method (FIM) as per IUPAC recommendations [19, 20]. Selectivity coefficients were determined from the potential measurements on solutions containing fixed concentration of interfering ion ($1x10^{-2}$M) and varying concentrations of silver ions. The values of selectivity coefficient so determined are compiled in Table 4**.**

Table 4. Potentiometric Selectivity Coefficients for Ag(I) ISE based on ‘tpydpa’ by FIM

Metal Ion	**K^+**	**Mg^{2+}**	**Ca^{2+}**	**Sr^{2+}**	**Co^{2+}**	**Ni^{2+}**	**Fe^{3+}**	**Cu^{2+}**	**Zn^{2+}**	**Hg^{2+}**	**Cd^{2+}**	**Pb^{2+}**
log $K^{Pot}_{Ag,B}$	-0.6	-1.8	-1.8	-2.1	-2.6	-1.8	-2.2	-2.0	-1.9	-1.8	-1.8	-1.9

Mercury is known to interfere in the determination of Ag^{+} ions but in case of proposed electrode the level of interference of Hg^{2+} is the same as that of other bivalent ions like Cd^{2+}, Zn^{2+} and Pb^{2+}. The selectivity coefficients values are of the order 10^{-2} for divalent and trivalent metal ions (except Na^{+} and K^{+}) which indicate that these ions will cause negligible interference on the functioning of proposed silver electrode. Table 5 shows the comparison of the proposed electrode with the reported electrode [21-37]. Therefore, the proposed electrode can be used for the determination of Ag^{+} ions in the presence of certain interfering ions.

Table 5. Comparison of proposed silver selective electrode with the reported electrodes

S.No	Ionophore	Working Conc. Range (M)	pH Range	Slope (mV/decade)
1	p-tertbutyl calix[4] arene [21]	1.0x10^{-5}-1x10^{-1}	1.0-6.0	58.0
2	3-(2-pyridylethylimino)-2-butanoneoxime [22]	5.0x10^{-5}-7.9x10^{-1}	-	59.0
3	2,2'-dithiobis(benzothiozole) [23]	8.3x10^{-7}-9.4x10^{-2}	2.0-7.5	59
4	Polystyrene based Me6(14) diene2HClO$_4$ [24]	5.0x10^{-6}-1.0x10^{-1}	2.5-9.5	53.0
5	Schiff base of [bis 5-(4-nitrophenyl azo)salisylaldimine] 1,8-diamino, 3,6-dioxooctan (BNSAO) [25]	2.7x10^{-6}-1.9x10^{-2}	2.5-70	56.0
6	Tweezer-type and non-tweezer-type ionophores [26]	1.0x10^{-9}-1.0x10^{-3}	-	60.0
7	tert-Butylcalix[4]arene tetra(allyl ether) [27]	1.0x10^{-4}-1.0x10^{-1}	-	58.0
8	Methyl-2-pyridyl ketone oxime (MPKO) [28]	1.0x10^{-6}-1.0x10^{-1}	2.5-8.5	59.8
9	Schiff base p-tert-butyl Calix[4]arene derivatives containing N and O as binding sites[29]	1.0x10^{-5}-1.0x10^{-1}	1.0-10.0	60.0
10	Calix[2]furano[2]pyrrole [30]	1.0x10^{-6}-1.0x10^{-2}	2.8-12.0	57.1
11	bis(dialkyldithiocarbamates) [31]	1.0x10^{-6}-1.0x10^{-3}	2.0-7.0	59.0
12	hexathia-18-crown-6 [32]	6.0x10^{-6}-3.2x10^{-3}	2.0-7.5	59.0
13	Benzothiazole Calix[4]arene [33]	1.0x10^{-6}-1.0x10^{-2}	2.0-8.0	57.0
14	Schiff base–p-tert-butylcalix[4]arene [34]	1.0x10^{-5}-1.0x10^{-1}	1.0-5.6	59.7
15	5,10,15-Tris(pentafluorophenyl)corrole[35]	5.0x10^{-6}-1.0x10^{-1}	4.0-8.0	54.8
16	2-aminothiophenol based dipodal [36]	1.0x10^{-4}-1.0x10^{-1}	3.3-8.0	60.0
17	5,6:17,18-dibenzo,11,12-(4-nitrobenzo)-2,3-bishydroxyimine)-7,16-dithia-10,13-dioxo-4,19-diazacyclooctadecane(N$_2$S$_2$O$_6$)[37]	2.5x10^{-5}-1.0x10^{-1}	5.0-9.0	58.5
18	This work	5.5x10^{-6}-1.0x10^{-1}	2.0-9.5	59.0

3.9. Effect of mixed solvents

In some cases, sample to be analyzed may be contaminated with non-aqueous media and hence to study the effect of non-aqueous media the proposed electrode was subjected to performance in partially non aqueous media using methanol, ethanol, dimethylsulphoxide and dimethylformamide mixed with water. The membrane does not undergo any appreciable change in working concentration range and in the slope up to 30 % of the non-aqueous content in the mixed solvent media. The results are shown in Table 6.

Table 6. Effect of Mixed Solvent Media on slope and Concentration range of the Ag(I) ISE

Solvent	Non Aqueous Content (% v/v)	Slope(mV/decade of activity)	Concentration Range (M)
Water	0	59	$5.5x10^{-6}$ - $1.0x10^{-1}$
Methanol	10	59	$5.5x10^{-6}$ - $1.0x10^{-1}$
	20	59	$5.5x10^{-6}$ - $1.0x10^{-1}$
	30	59	$5.5x10^{-6}$ - $1.0x10^{-1}$
Acetone	10	62	$5.5x10^{-6}$ - $1.0x10^{-1}$
	20	62	$5.5x10^{-6}$ - $1.0x10^{-1}$
	30	63	$5.5x10^{-6}$ - $1.0x10^{-1}$
DMF	10	61	$5.5x10^{-6}$ - $1.0x10^{-1}$
	20	62	$5.5x10^{-6}$ - $1.0x10^{-1}$
	30	60	$5.5x10^{-6}$ - $1.0x10^{-1}$
DMSO	10	61	$5.5x10^{-6}$ - $1.0x10^{-1}$
	20	61	$5.5x10^{-6}$ - $1.0x10^{-1}$
	30	63	$5.5x10^{-6}$ - $1.0x10^{-1}$

4. APPLICATIONS

4.1. Potentiometric titrations

The electrode has been applied successfully for the end point determination of Ag (I) ions both in the potentiometric titrations.

The titration exhibits 1:1 stoichiometry of the complex. Therefore, the proposed membrane electrode can be used as an indicator electrode for potentiometric determination of Ag (I) ions both in potentiometric titrations.

5. CONCLUSION

This work demonstrates that the electrode no. **E_2** is good for quantification of silver ion. The electrode exhibits excellent potentiometric performance. The best composition of the electrode was found to be: Ionophore (3%): PVC (33%): o-NPOE (64 %). It responds to Ag^+ in Nernstian fashion , presents good selectivity over most of the cations of conventional Ag^+ electrodes proposed earlier and showed a low detection limit and good working range. This is characterized by long term potential stability and was successfully applied as indicator electrode in argentometric titrations.

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