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Effect of substituent on working of potentiometric sensors for lanthanum

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ABSTRACT

La(III) selective electrodes have been prepared by using 2-Hydroxy-N-(2'-hydroxyphenyl) benzalideneimine (as I) and 5-Bromo-2-hydroxy-N-(2'-hydroxyphenyl) benzalideneimine (as II) as electro active materials and epoxy resin as a binding material. The electrodes were prepared with composition 50% electro active material and 50% binder. An excellent response was shown by (I) in the concentration range of 10^{-6} M - 10^{-1} M La (III) ions with a sub Nernstian slope of 14 mV/decade. It has a fast response time of 10 seconds and can be used for at least six months without any considerable potential divergence. The response shown by electrode (II) was also in the concentration range of 10^{-6} M - 10^{-1} M La (III) ions with a sub Nernstian slope of 7 mV/decade. It also has a fast response time of 10 seconds and can be used for at least four months without any considerable potential divergence. Effect of internal solution has been studied and the electrodes were successfully used in partially non-aqueous medium, too. Selectivity coefficients have been determined by FIM method, with respect to alkali, alkaline earth, some transition and rare earth metal ions. Electrode (I) can be used in the pH range of 2.85-7.5 and electrode (II) shows pH range of 2.9-8.9. Both the electrodes have been used as indicator electrodes in the potentiometric titration of La (III) ions against Tartaric acid.

Key words: Selectivity coefficient, Fixed interference method (FIM), Potentiometric titration, (Ion selective electrode) ISE.

INTRODUCTION

The increased use of ion sensors in the fields of agriculture, environment, medicine etc. is encouraging the analytical chemists to develop new sensors for fast, accurate, reproducible and selective determination of various ions. In this study, a new Lanthanum selective membrane sensor was proposed and used for determination of trace amounts of Lanthanum. Lanthanum has no known biological role. The element is not absorbed orally, and when injected its elimination is very slow. Lanthanum carbonate is used in medication to absorb excess phosphate in cases of

end stage renal failure [1]. Lanthanum has pharmacological effects on several receptors and ion channels [2]. Lanthanum ions accelerate hydrolysis of phosphate ester binding by 13 orders of magnitude which infers that phosphate diester in DNA may also suffer such destruction. Genotoxicity of La (III) in human peripheral blood lymphocytes has also been reported. Lanthanum chloride causes changes in lipid peroxidation, the redox system and ATPase activities in plasma membranes of rice seeding roots [3, 4]. Lanthanum oxide is used widely in preparation of gasoline cracking catalysts, carbon arcs, polishing compounds etc. It is also used to remove sulfur, carbon and other electronegative elements from iron and steel [5]. Various other uses of lanthanum and its compounds have been reported [6 – 10]. Exposure to high levels may cause some health problems. Thus the determination of La (III) is warranted by a window of useful and toxic ions.

Methods for low level determination of rare earth metal ions in solution include isotopic dilution, mass spectroscopy, neutron activation analysis, ICP-MS, ICP-AES [11] etc. These are either time consuming or too expensive. In comparison potentiometric method based on ion selective electrodes (ISEs) offers fast response time, ease of preparation, reasonable selectivity, dynamic linear range and is less expensive.

Some reports available for ion sensors detecting La(III) ions in low limits are based on 1,3,5-Trithia cyclohexane[12], N-{Hexahydro cyclopentapyrol-2[(1H-yl)amino] carbonyl}-4-methylbenzenesulphonamide[13] ,Bis(2-mercaptoanil)diacetyl [14], Bis (thiophenol) phenylen-1,3-diamine [15], 2,2'-Dithiodipyridine [16], N-2,4-Dimethylphenyl-N'-ethyl formamidine [17], Bis(2-methyl benzaldehyde) butane-2,3-dihydrazone [18], N,N'-Adipylbis(5-phenylazo salicyl-aldehyde hydrazone [19], Bis (5-nitro-2-furaldehyde) butane 2,3-dihydrazone [20], N-(2-Pyridal)-N'-(4-methoxy phenyl)-thiourea [21], 4-methyl-2-hydrazinobenzothiazole [22], 8-Amino-N-(2-hydroxybenzylidene) naphthylamine [23], 3-Hydroxy-N-(pyridine-2-ylmethylene)-2-naptho hydrazide [24], N-(1-Pyridin-2- ylmethylene)-2-fluorohydrazide [25], Dicyclohexano-18-crown-6 [26].

In the present work, we have tried to introduce a new highly sensitive and selective membrane sensor for fast monitoring of lanthanum ions in various samples. The effect of substituent on emf. using a bromo derivative of the same electro active material .has also been studied. Schiff's bases derived from salicylaldehyde are among the polydentate ligands that form very stable complexes with different cations **[**27 – 29].

MATERIALS AND METHODS

2.1 Materials used

Salicylialdehyde, 5-Bromo salicylialdehyde and o-aminophenol needed for the preparation of 2-Hydroxy-N-(2'-hydroxyphenyl) benzalideneimine and 5-Bromo-2-hydroxy-N-(2'-hydroxyphenyl) benzalideneimine, Lanthanum (III) nitrate & other rare earth nitrates were obtained from CDH chemicals, India. All the chemicals were of analytical grade and hence, were used as such. A solution of lanthanum (III) nitrate was standardized against EDTA solution using Xylenol orange as an indicator. Double-distilled deionized water was used throughout the experiments.

2.2 Instrument
EMF measurements were made using potentiometer (Microsil EQ/602, India) with an accuracy of 0.1mV.

2.3 Preparation of Exchanger I
2-Hydroxy - N-(2' - hydroxyphenyl) benzalideneimine was prepared by refluxing an ethanolic solution of salicylaldehyde (20 mmol in 25ml) with an ethanolic solution of o- aminophenol (20 mmol in 25 ml) for 1.5 hr. The red precipitate obtained on cooling was filtered, washed with ethanol , recrystallized from ethanol and dried.

2.4 Preparation of Exchanger II
A solution of 5- bromosalicylaldehyde (20 mmol) in 25 ml ethanol was mixed with 25 ml of an ethanolic solution of o-aminophenol (20 mmol) in 1:1 molar ratio. The resulting solution was stirred on a magnetic stirrer at room temperature for 1 hr. The orange precipitate so obtained was collected by filtration, washed, recrystallized from ethanol and dried.

2.5 Preparation of Epoxy Membrane
A number of membranes were prepared using varying amount of epoxy resin as a binding material. Desired amount of finely powdered exchanger was mixed thoroughly with araldite in varying amounts (w/w) to make a near homogeneous paste, which was then, spread between the folds of butter paper. Glass plates were kept below and above the paper folds as supports. A pressure of 2.0 Kg/cm^2 was applied over the glass plates for 24 hours and left to dry. The sheet of membrane, thus obtained was then, dipped in distilled water to remove the paper from the membrane surface.

2.6 Storage of Electrodes
Electrodes were stored in distilled water when not in use for more than one day. These were activated by keeping immersed in the 0.1 M La^{3+} ion solution for two hours, to compensate for any loss of metal ions in the membrane phase that might have taken place due to a long storage in distilled water. Electrodes were then washed thoroughly with distilled water before use.

2.7 Distribution Studies
Distribution coefficients (K_d) for different metal ions such as La^{3+}, Ce^{3+}, Sm^{3+}, Nd^{3+} and Pr^{3+} were determined in aqueous solutions by keeping 20 mL of distilled water and 0.2 g of synthesized electro active material , overnight in a titration flask. Meanwhile intermittent shaking was done to attain the equilibrium. The strength of the exchanged metal ion solution was obtained by titrating against 0.1M EDTA standardized with $Pb(NO_3)_2$. Then the distribution coefficient was determined by using the formula-

$$\mathbf{K_d = (I- F) / F. V / W}$$

Where, I & F= Volumes of EDTA consumed by cations before and after equilibrium
V is the initial volume of the metal ion solution for analysis and W is the initial dry mass of ion exchanger.

2.8 EMF Measurements

The membrane was fixed to one end of glass tube of 1.8 cm (internal dia.) using epoxy resin. These were then equilibrated with 0.1M La^{+3} ion solution for 24 hours. The tube was filled with a solution of Lanthanum nitrate (0.1M) and immersed in a beaker containing test solutions of varying concentrations, keeping the level of inner solution higher than the level of outer solution to avoid any reverse diffusion of electrolyte. All the EMF measurements were carried out by using cell assembly:

SCE │0.1M La^{3+} │ │membrane│ │ test solution│ SCE

A digital potentiometer (Microsil EQ/602, India) was used for the potential measurements at 25 ± 0.1^0C. Activities were calculated according to Debye-Huckel equation [30]. Test solutions of La^{3+} were obtained by gradual dilution of 0.1M solution and their potential measurements were made in un-buffered solution.

RESULTS AND DISCUSSION

On the basis of distribution studies, the most promising property of 2-hydroxy-N-(2'-hydroxyphenyl) benzalideneimine was found to be high selectivity towards La^{3+} metal ions. The distribution coefficient (K_d) values are given in Table 1.

The effect of membrane composition on the response of the electrode was studied using membranes of different compositions as shown below:

S No.	Electro active material (%)	Epoxy resin (%)
1	70	30
2	60	40
3	50	50

The performance parameters, like slope of the calibration curve, measurement range and the response time were compared for prepared electrodes. Best response was shown by membrane having composition 50% electro active material and 50% binder. The results are given in Table 2. Results show that the electrode I show excellent response in the concentration range of $1x10^{-6}$-$1x10^{-1}$M La (III) ion with a sub Nernstian slope of 14.0 mV /decade. It has a response time of 10 s. Same composition was tried for bromo derivative of the electro active material for the purpose of comparison. In case of electrode II, we get the linear concentration range of $1x10^{-6}$-$1x10^{-1}$M La (III) ion with a sub Nernstian slope of 7.0 mV/ decade . It has a response time of less than 10 s. So these two electrodes are selected for further studies.

Potential measurements were made on the selected electrodes for different concentrations of La^{3+} ion solutions. EMFs were plotted against log of activities of the Lanthanum ion. Experiment was repeated five times to check the reproducibility of the electrode system. A standard deviation of ±1.0 mV was observed for electrode I and II. A representative calibration curve is shown in Figures 1 and 2. Detection limit was calculated according to IUPAC recommendation [31] from the intersection of the two extra-polated linear portions of the curve. The detection limit was found to be 1.0 $x10^{-7}$ and 7.9 $x10^{-7}$ for both the electrodes respectively.

The non-Nernstian behavior of the electrode may also be due to a possible discrepancy between the ions activities in the bulk and at the phase boundary, i.e. the uptake of the ions by the membranes results in a depletion zone of the analyte ion from the nearest diffusion layer. This is supported by earlier reports [32]. Response time for electrode I was 10 s while that for electrode II was 5-10s. The sensing behavior of the membranes remain unchanged when the potentials are measured either from low to high or from high to low concentration. The electrodes were stored in distilled water when not in use to avoid any change in the concentration in membrane phase.

3.1 Effect of Internal Solution Concentration

The effect of internal solution on the response of the proposed sensor for La^{3+} ion was studied by using 10^{-1} M to 10^{-3} M internal solution concentrations for electrode I as well as electrode II. The results are given in Tables 3 & 4 and Figures 3 & 4 respectively. The results show that a variation in concentration of the internal solution does not have any significant effect on the response of the electrode except for an expected change in the intercept of the curves as observed by Ganjali et al. [32] and Mittal et al [26].

3.2 Effect of pH

The influence of pH on the potential response of the electrode was studied at $2x10^{-2}$ M and $2x10^{-3}$ M over a pH range of 2.0- 12.0 for electrode I as well as II . The results are shown in Figures 5 and 6 respectively. pH was adjusted by introducing small drops of HCl (0.1 M) or NaOH (0.1 M) as per requirement. The potential is independent of the pH range 2.85-7.5 and 2.9-8.9 for both the electrodes respectively. Hence, this pH range may be chosen as the working pH range for the electrode assembly. The variation above and below this pH range may be due to the formation of $La(OH)_3$ and protonation of nitrogen atoms of exchangers, respectively.

3.3 Selectivity Coefficients and Analytical Properties of La^{3+} Selective Electrodes

Selectivity is one of the most important characteristics of electrode, which defines the nature of the device and extent to which it may be employed in the determination of a particular ion in the presence of other interfering ions. Potentiometric selectivity coefficients of the La^{3+} membrane electrodes were evaluated by the fixed interference method (FIM) [31] at $1.0x10^{-3}$ M and $1.0x10^{-4}$ M interfering ion concentrations. According to this method, a calibration curve is drawn for the primary ion with a constant interfering ion background. The linear portion of the curve is extrapolated until it intersects with the second linear part of the curve in the low concentration region. The selectivity coefficients are calculated from these two segments of the calibration curve by using formula:

$$K_{A,B}^{Pot} = \frac{a_A}{(a_B)^{z_A/z_B}}$$

Where, a_A is the activity of the primary ion and a_B the activity of the interfering ion. z_A and z_B are their respective charges. The results given in Tables 5 and 6, show potentiometric selectivity coefficients of sensors at two different interferying ion activities. Results are obvious that the electrodes have a reasonably good selectivity with respect to rare earth metal ions, considering the fact that all rare earths have identical sizes and properties. They also have a good selectivity over some common alkali, alkaline earth and transition metal ions.

3.4 Effect of Partially Non–aqueous Medium on the Working of La^{3+} Selective Electrodes

Both the electrodes were investigated in partially non-aqueous media using acetone, ethanol and methanol. The slope remains unaltered with the addition of non-aqueous solvents. Hence, the proposed sensors can be used in partially non–aqueous solvents. The results of the effect of various non–aqueous solvents on the functioning of two electrodes are given in the Tables 7 & 8 and Figures 7 & 8.

Table 1. Distribution coefficient values for various metal ions

Sensor	2-Hydroxy-N-(2'-hydroxy phenyl) benzalideneimine				
Metal ions	Pr(III)	La(III)	Ce(III)	Nd(III)	Sm(III)
Distribution coefficient (K_d)	25.26	**42.86**	19.04	35.13	31.57

Table 2. Optimization of substituted and unsubstituted membranes

Electro-active material	**% of electro-active material**	**Binder**	**Slope, mV/ decade**	**Measuring Range, M**	**Response Time, s**
2-Hydroxy-N-(2'-hydroxy phenyl) benzalideneimine	50(%)	Epoxy	14.0	$1.0x10^{-6} – 10^{-1}$	10
5-Bromo-2-hydroxy-N-(2'-hydroxy phenyl) benzalideneimine	50(%)	Epoxy	7.0	$1.0x10^{-6} – 10^{-1}$	10

Table 3. Effect of internal solution concentrations on response of La^{3+} ion-selective electrode based on (I)

Composition of membrane	**50%**		
Internal soln. concentration, M	$1.0x10^{-1}$	$1.0x10^{-2}$	$1.0x10^{-3}$
Electro active material	2-Hydroxy-N-(2'-hydroxyphenyl) benzalideneimine		
Slope, mV/decade	14.0	13.0	13.6
Response time, s	10	10	10

3.5 Potentiometric Titration

The practical utility of both the membrane sensors were tested by their use as indicator electrodes for the titration of 20 ml of 10^{-3} M La^{3+} ions vs. $5.0x10^{-3}$ M Tartaric acid. The emf data was plotted against volume of tartaric acid added. The titration curve for electrode I is shown in Figure13. Figure 14 shows the results of 20 ml of 10^{-3} M La^{3+} ions vs. $5.0x10^{-3}$ M Tartaric acid titration for electrode II.

Table 4. Effect of internal solution concentrations on response of La^{3+} ion-selective electrode based on (II)

Composition of membrane	**50%**		
Internal soln. concentration, M	$1.0x10^{-1}$	$1.0x10^{-2}$	$1.0x10^{-3}$
Electro active material	5-Bromo-2-hydroxy-N-(2'-hydroxyphenyl) benzalideneimine		
Slope, mV/decade	7.0	6.3	7.6
Response time, s	10	10	10

Table 5. Selectivity coefficient values for La^{3+} selective electrode for various interfering ions by FIM (10^{-4}M)

Interfering ion (B)	Selectivity coefficient values $K_{A,B}$	
	2-Hydroxy-N-(2'-hydroxyphenyl) benzalideneimine	5-Bromo-2-hydroxy-N-(2'-hydroxyphenyl) benzalideneimine
Nd(III)	3.97×10^{-5}	1.25×10^{-3}
Sm(III)	3.15×10^{-4}	1.75×10^{-4}
Eu(III)	3.97×10^{-5}	1.25×10^{-3}
Ce(III)	1.58×10^{-3}	0.5×10^{-3}
Fe(III)	3.2×10^{-4}	0.5×10^{-5}
Al(III)	0.63×10^{-4}	3.97×10^{-5}
Ca(II)	1.1×10^{-1}	1.0×10^{-3}
Na (I)	1.0×10^{-3}	2.5×10^{-2}

Table 6. Selectivity coefficient values for La^{3+} selective electrode for various interfering ions by FIM (10^{-3}M)

Interfering ion (B)	Selectivity coefficient values $K_{A,B}$	
	2-Hydroxy-N-(2'-hydroxy phenyl) benzalideneimine	5-Bromo-2-hydroxy-N-(2'-hydroxyphenyl) benzalideneimine
Nd(III)	3.97×10^{-3}	0.5×10^{-2}
Sm(III)	0.5×10^{-2}	1.5×10^{-2}
Eu(III)	0.5×10^{-2}	1.0×10^{-2}
Ce(III)	0.9×10^{-3}	0.5×10^{-2}
Fe(III)	0.79×10^{-3}	0.5×10^{-3}
Al(III)	0.5×10^{-2}	0.99×10^{-3}
Ca(II)	0.5×10^{-1}	0.5×10^{-2}
Na (I)	$0.39x\ 10^{-2}$	0.5×10^{-2}

Table 7. Effect of partially non –aqueous media on the working of La^{3+} selective electrode based on 2-Hydroxy-N-(2'-hydroxy phenyl) benzalideneimine

Solvent	Percentage, v/v	Slope, mV/decade	Measuring range, M
Acetone	30%	13.5	1.0×10^{-7}
	20%	13.0	1.0×10^{-7}
	10%	13.5	5.01×10^{-7}
Ethanol	30%	14.0	5.01×10^{-7}
	20%	12.5	5.01×10^{-7}
	10%	13.0	3.16×10^{-7}
Methanol	30%	12.0	1.0×10^{-7}
	20%	14.5	1.0×10^{-7}
	10%	14.0	5.01×10^{-7}

Table 8. Effect of partially non –aqueous media on the working of La^{3+} selective electrode based on 5-Bromo-2-hydroxy-N-(2'-hydroxyphenyl) benzalideneimine

Solvent	Percentage, v/v	Slope, mV/decade	Measuring range, M
Acetone	30%	8.0	5.01×10^{-7}
	20%	7.5	3.16×10^{-7}
	10%	8.0	1.99×10^{-7}
Ethanol	30%	6.0	1.0×10^{-7}
	20%	7.5	5.01×10^{-7}
	10%	8.0	3.16×10^{-7}
Methanol	30%	6.5	3.16×10^{-7}
	20%	7.0	1.0×10^{-6}
	10%	7.5	1.99×10^{-7}

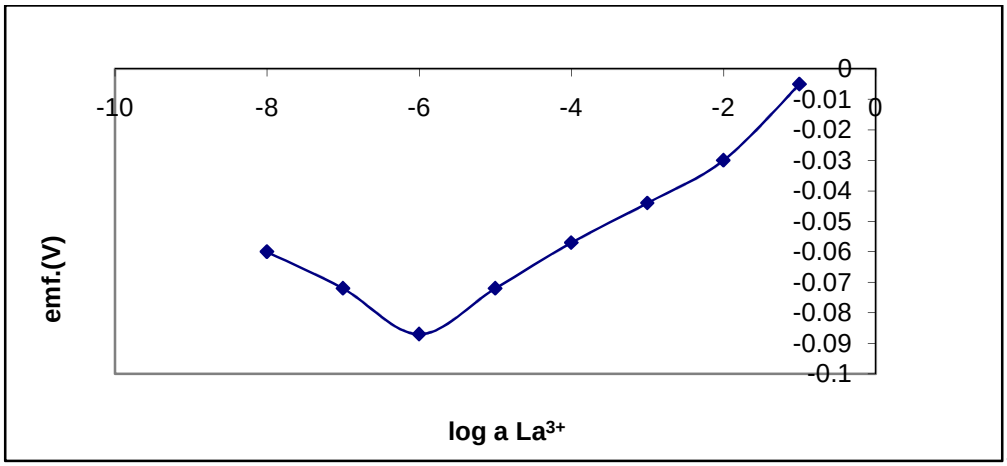


Figure 1. Calibration curve for La^{3+} selective electrode based on 2-Hydroxy-N-(2'-hydroxyphenyl) benzalideneimine

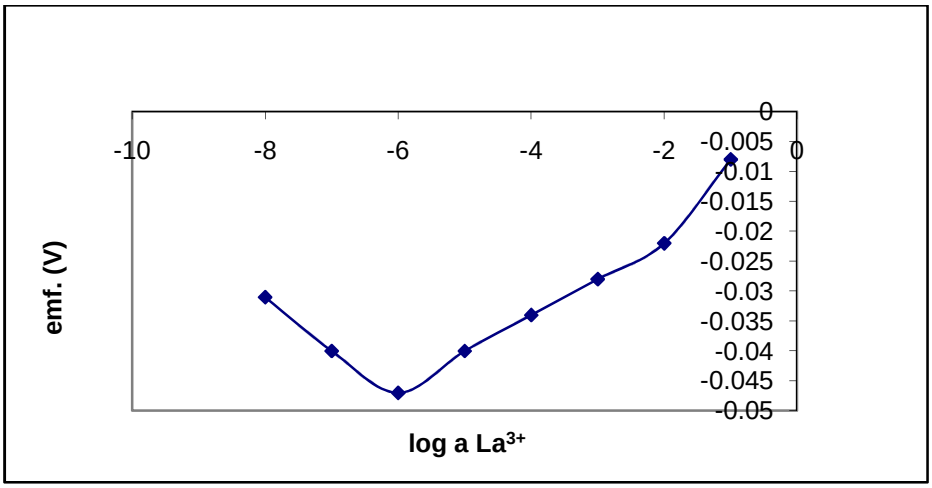


Figure 2. Calibration curve for La^{3+} selective electrode based on 5-Bromo-2-hydroxy-N-(2'-hydroxyphenyl) benzalideneimine

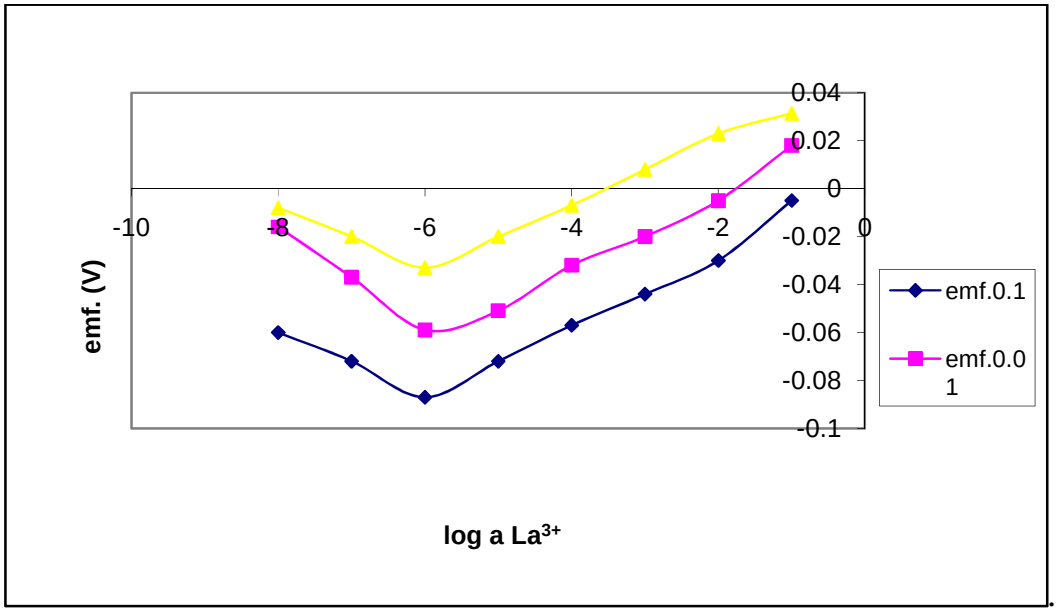


Figure 3. Effect of internal solution on the potential response of the La^{3+} selective electrode based on 2-Hydroxy-N-(2'-hydroxyphenyl) benzalideneimine

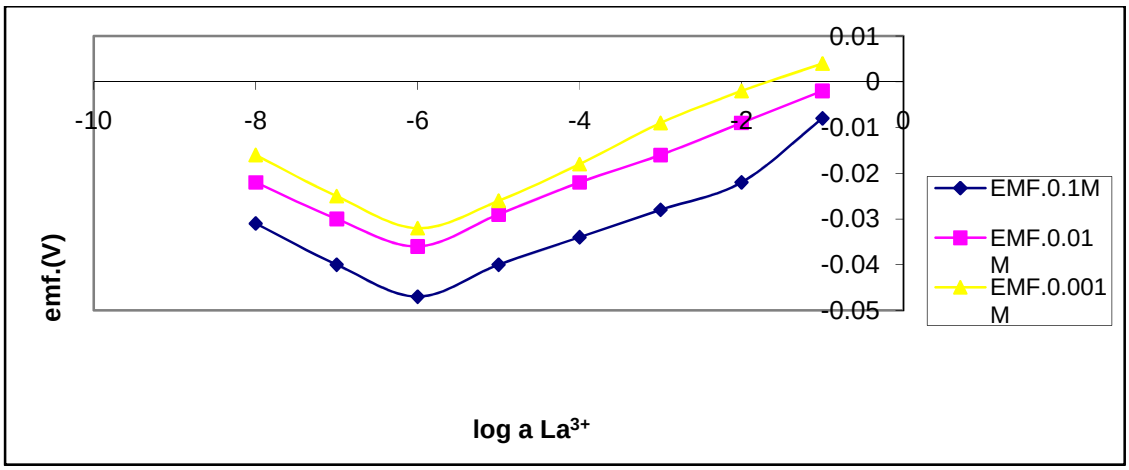
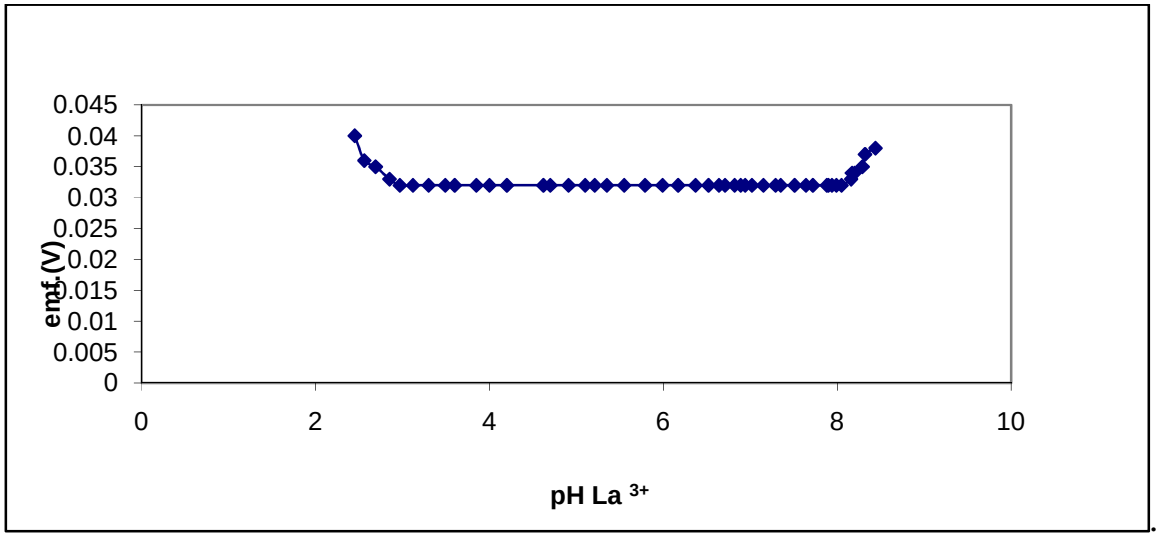


Figure 4. Effect of internal solution on the potential response of the La^{3+} selective electrode based on 5-Bromo-2-hydroxy-N-(2'-hydroxyphenyl) benzalideneimine

Internal solution – 10^{-1} M La
External solution – 10^{-2} M La



Internal solution – 10^{-1} M La
External solution – 10^{-3} M La

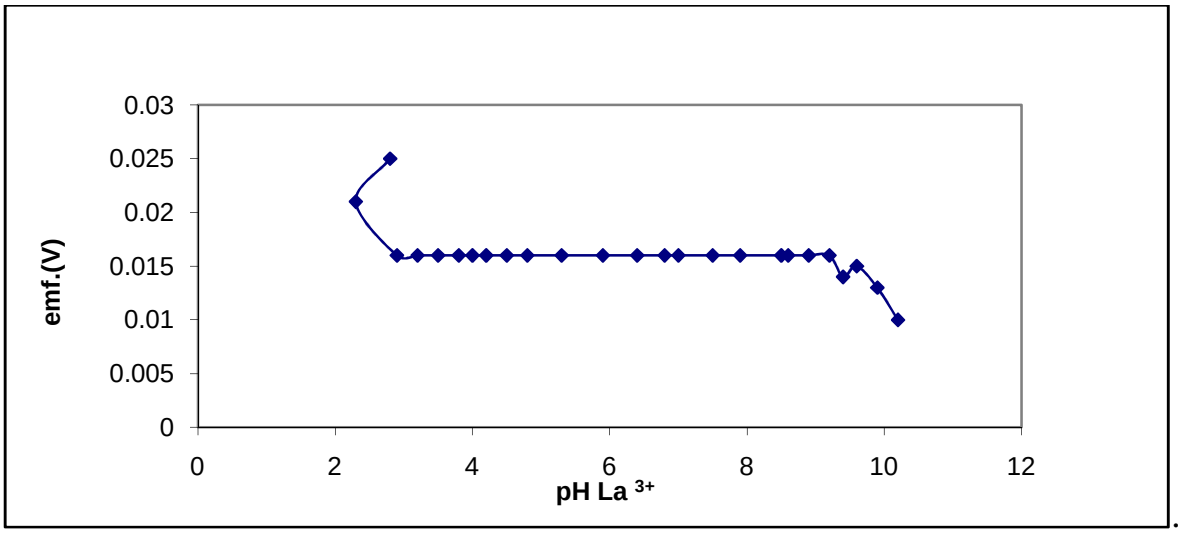
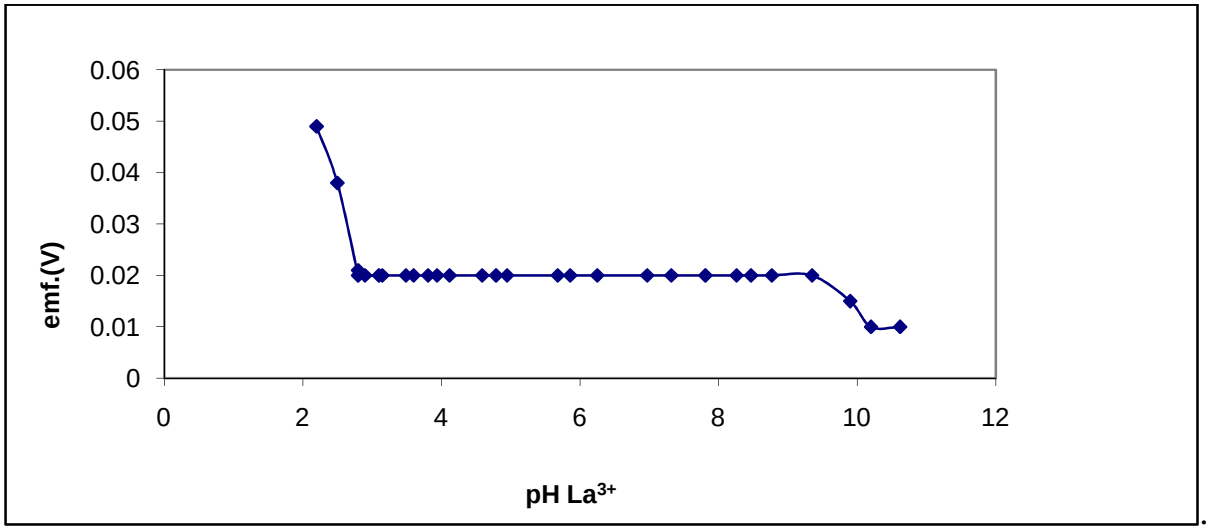


Figure 5. Effect of pH on the response of the La^{3+} selective electrode based on 2-Hydroxy-N-(2'-hydroxy phenyl) benzalideneimine

Internal solution – 10^{-1} M La (subs.)
External solution – 10^{-2} M La (subs.)



Internal solution – 10^{-1} M La(subs.)
External solution – 10^{-3}M La(subs.)

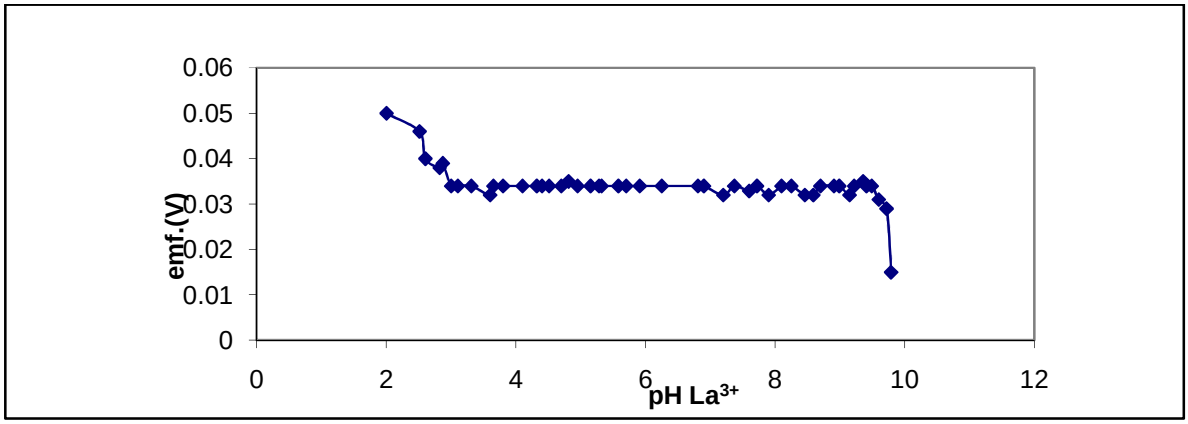


Figure 6. Effect of pH on the response of the La^{3+} selective electrode based on 5-Bromo-2-hydroxy-N- (2'-hydroxyphenyl) benzalideneimine

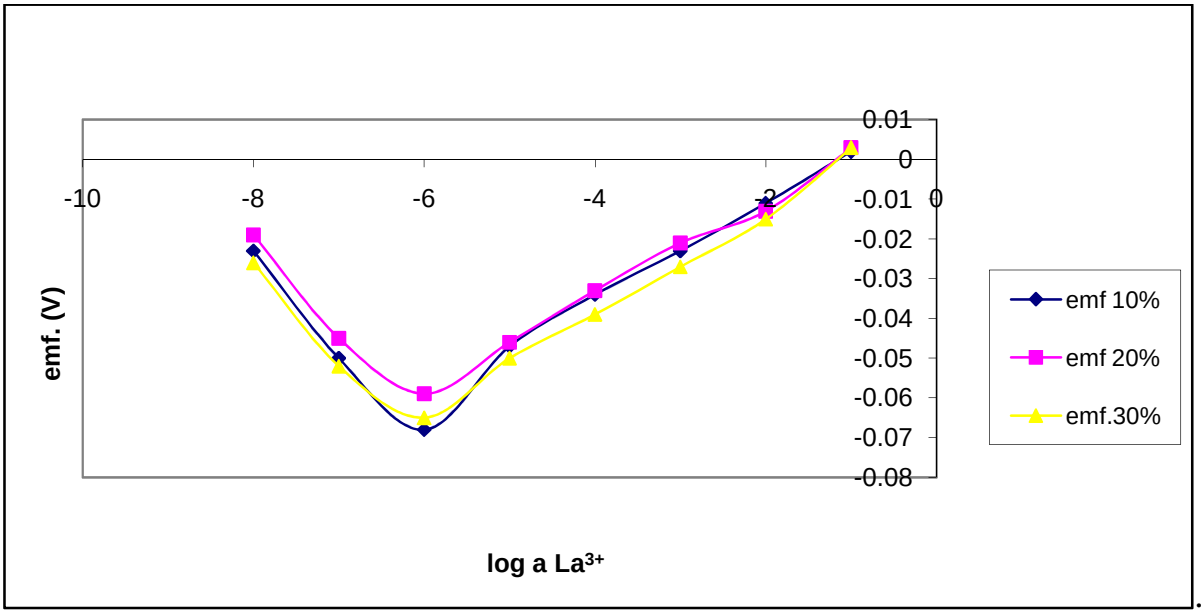


Figure 7. Effect of ethanol-water medium on the working of La^{3+}selective electrode based on 2-Hydroxy-N-(2'-hydroxyphenyl) benzalideneimine

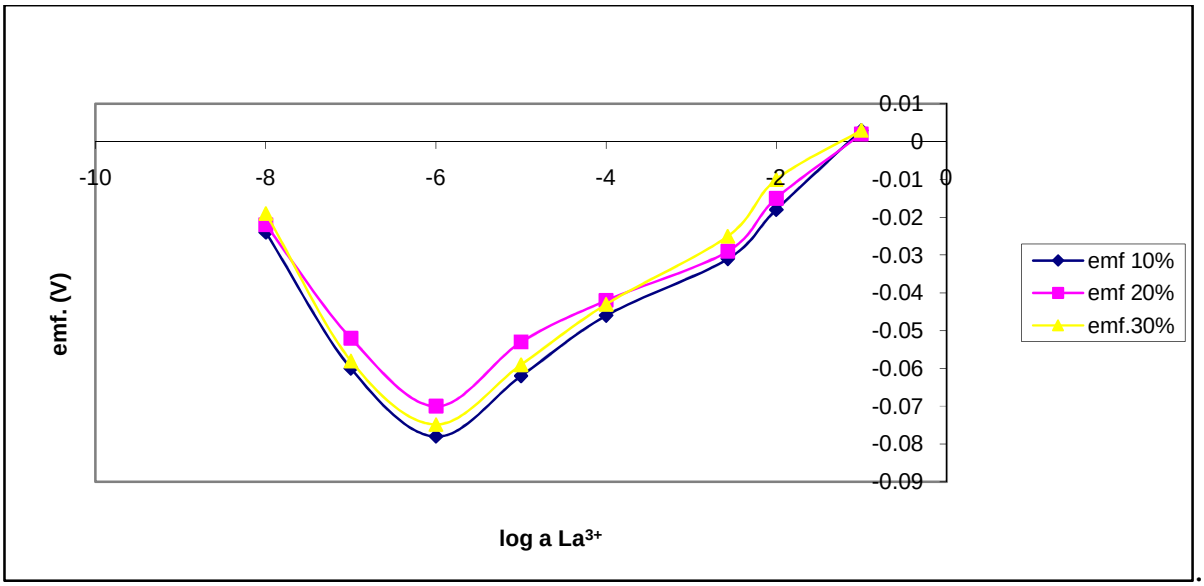


Figure 8. Effect of methanol-water medium on the working of La^{3+} selective electrode based on 2-Hydroxy-N-(2'-hydroxyphenyl) benzalideneimine

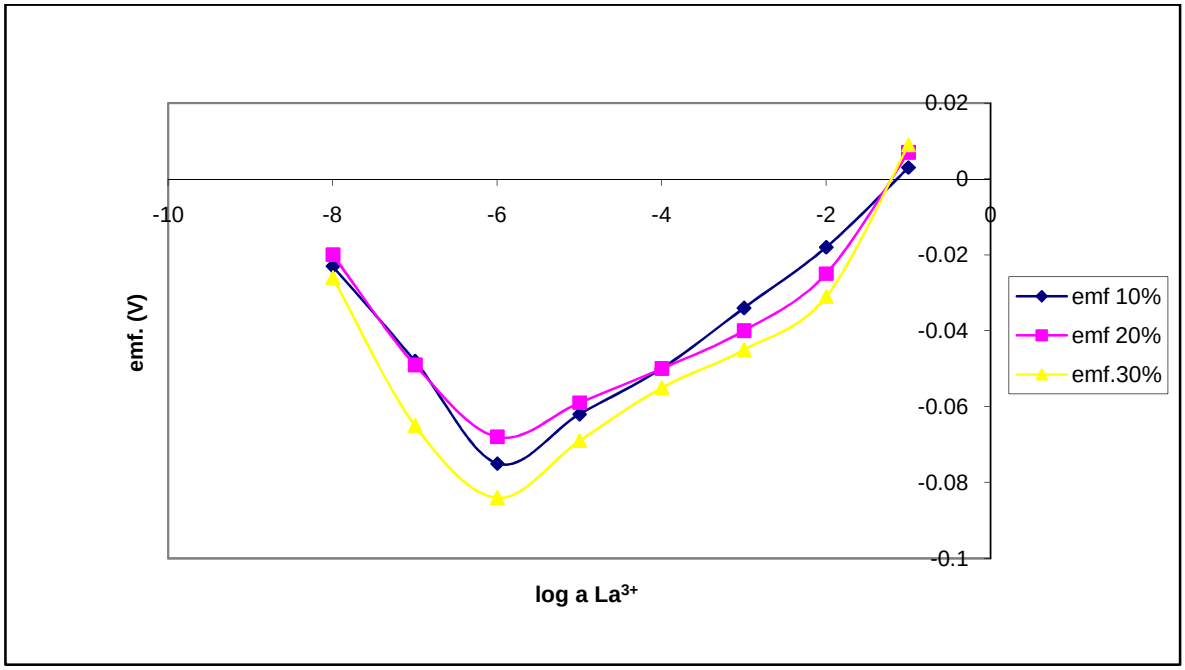


Figure 9. Effect of acetone-water medium on the working of La^{3+} selective electrode based on 2-Hydroxy-N-(2'-hydroxyphenyl) benzalideneimine

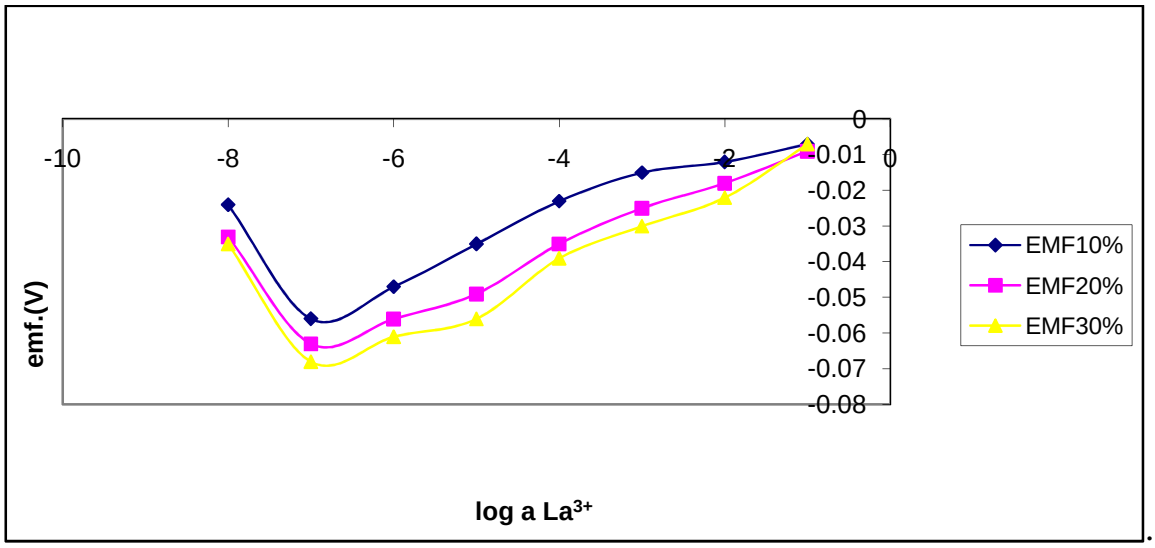


Figure 10. Effect of ethanol-water medium on the working of La^{3+} selective electrode based on 5-Bromo-2-hydroxy-N-(2'-hydroxyphenyl) benzalideneimine

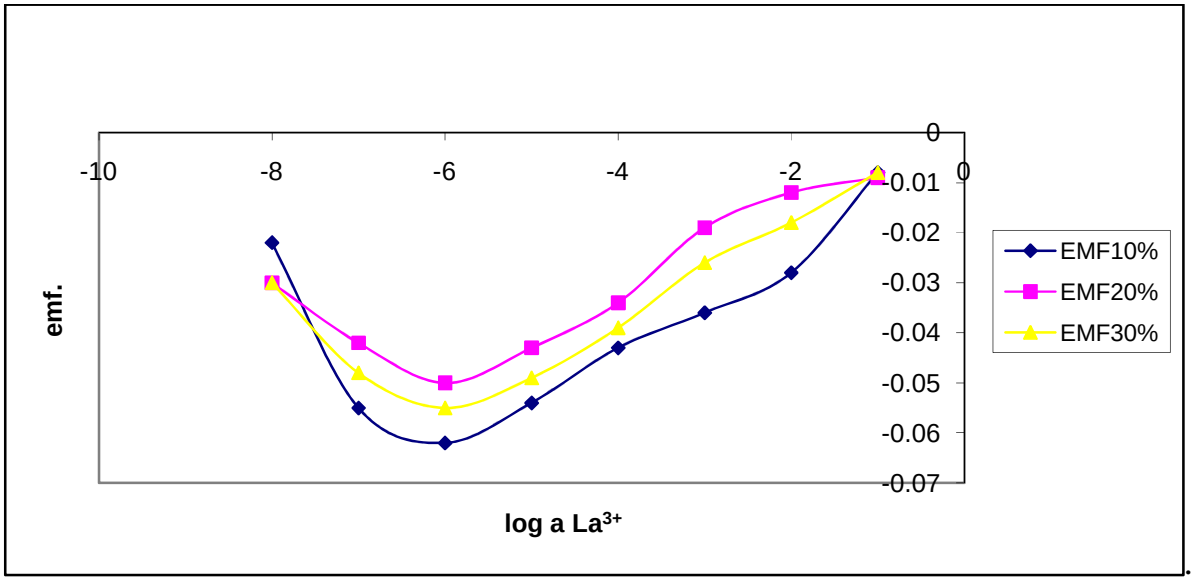


Figure 11. Effect of methanol-water medium on the working of La^{3+} selective electrode based on 5-Bromo-2-hydroxy-N-(2'-hydroxyphenyl) benzalideneimine

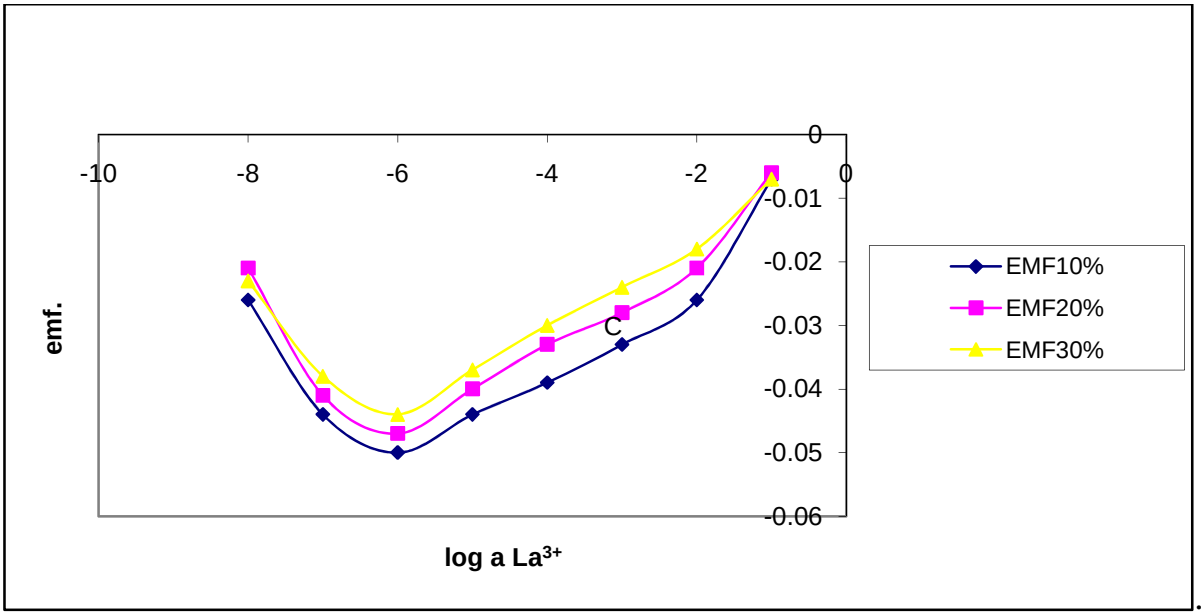


Figure 12. Effect of acetone-water medium on the working of La^{3+} selective electrode based on 5-Bromo-2-hydroxy-N-(2'-hydroxyphenyl) benzalideneimine

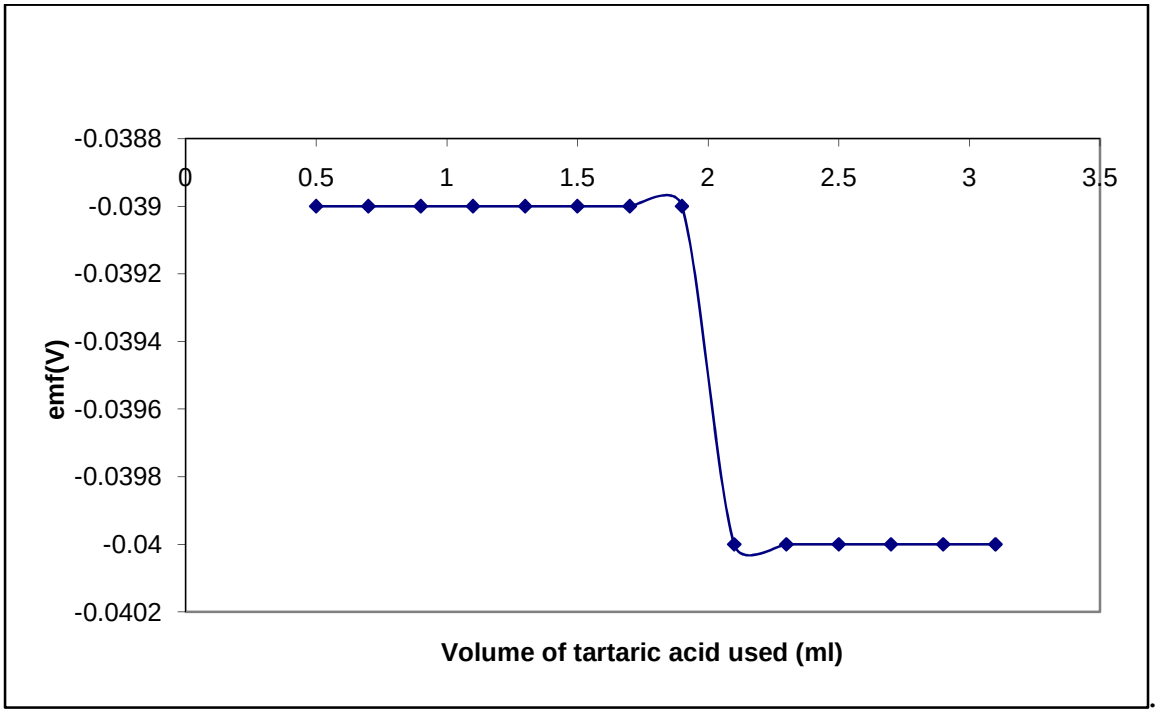


Figure 13. Potentiometric titration curve using proposed sensor based on 2-Hydroxy-N-(2'-hydroxy phenyl) benzalideneimine as an indicator electrode

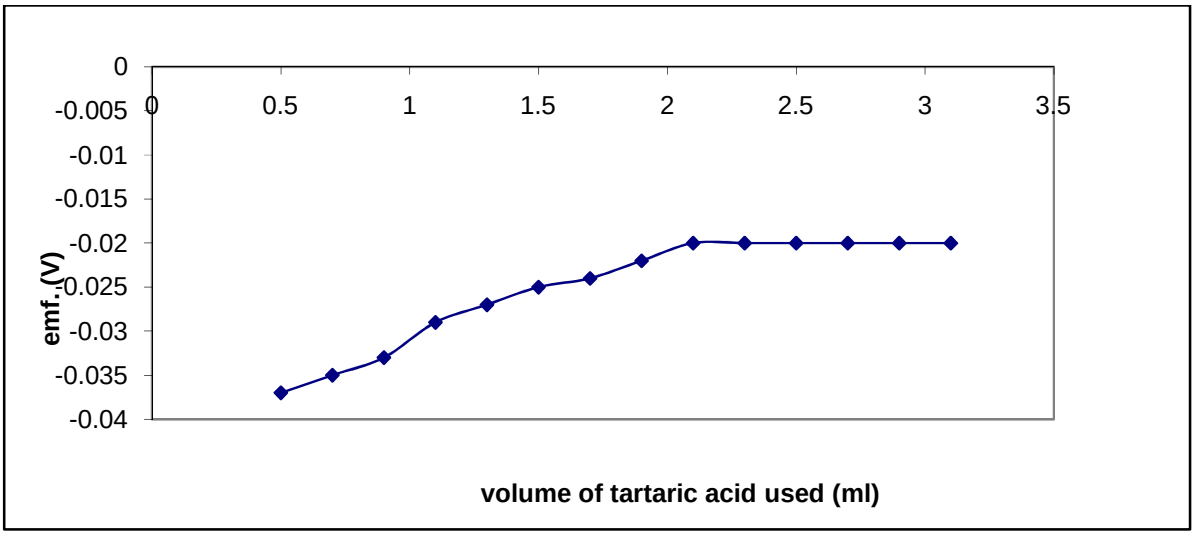


Figure 14. Potentiometric titration curve using proposed sensor based on 5-Bromo-2-hydroxy-N-(2'-hydroxyphenyl) benzalideneimine as an indicator electrode

CONCLUSION

2-Hydroxy-N-(2'-hydroxyphenyl) benzalideneimine (as I) and 5-Bromo-2-Hydroxy-N-(2'-hydroxyphenyl) benzalideneimine (as II) can both be successfully used as electro active materials for making a La^{3+} selective membrane electrode. The electrodes have reasonably good

lifetime, detection limit, pH range, selectivity coefficient and can be successfully used in partially non aqueous media . They can also be used as indicator electrodes. However on comparing the performance of the two sensors, it can be concluded that the one based on 2-Hydroxy-N-(2'-hydroxyphenyl) benzalideneimine (as I) is better in terms of response time and Nernstian response.

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