

Highly selective oxalate –membrane electrode based on [CuL](ac)₂

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Abstract: The complexes of Cu(II) were synthesized with the new macrocyclic ligand. The newly synthesized azamacrocyclic ligand L: 5,15-dibromo-9,10,11,20,21,22-hexamethyl-1,8,12,19-tetraazadicoso- 9,11,20,22-tetraene was prepared by the reaction of 3-Methyl-2,4 pentadione and 5-bromo-2,6-diamino pyridine. All the complexes were characterized by the conductance measurements, magnetic susceptibility measurements, mass, I.R. electronic and EPR spectral studies. The molar conductance measurement of the complexes in DMF solution is corresponding to non-electrolytic nature. Thus these complexes may be formulated [M(L)X₂] [where M = Cu (II) and X = Cl⁻, CH₃COO⁻ and NO₃⁻]. On the basis of spectral studies, tetragonal geometry was assigned for Cu(II) complexes. Complex was then used as a good sensing material for oxalate ion selective PVC membrane sensor. The proposed potentiometric sensor showed a stable potential response to oxalate ion with Nernstian slope-29.0 mV decade⁻¹ over a wide linear concentration range of 5.0x10⁻⁷ - 6.0x10⁻¹M. The sensor was found to have a short response time of about 10-15 s and have an accepted life time. Application of the proposed sensor in analysis of oxalate ion in some water samples showed good results.

Key Words: Spectroscopic, potentiometry, sensor, oxalate ion, ion selective electrode, PVC membrane.

I. Introduction

The coordination chemistry has been considerably enriched due to the synthesis of metal complexes, in which the metal is coordinated through sulphur, nitrogen and oxygen [1]. Metal complexes have found widespread uses, especially, for the direct determination of ionic species in whole and diluted blood, serum, urine, tissue and intracellular samples [2]. Oxalate ion is one of the important nutrients in the human diet found principally in spinach, beet leaves, etc. Oxalate ion is primary chelator of calcium ion, so it forms chelates with dietary calcium, thus gives the complex unavailable for adsorption in the body and absorbed oxalate is also precipitated as insoluble salts that accumulate in the renal tissue. So, calcium oxalate is a most important phase in case of stone diseases [3]. Determination of oxalate ion in different food matrices is of great interest because a high oxalate level in the foodstuff may cause the formation of insoluble kidney stones as a result of unbalanced nutritional habits. The measurement of oxalate in urine is important in the diagnosis of hereditary and enteric hyper-oxaluria and in the evaluation and management of patients with urinary calculi (stones). Calculi are deposited chemicals in compact form and these concretions are frequently found in urinary tract. Therefore, the determination of oxalate ion in some biological material is important.

Calcium oxalate is the principal constituent of urinary tract stones in 60–80% of cases and the concentration of oxalic acid in urine is an important risk factor for calcium-containing stones. In addition to being excreted in excess in the hyperoxaluric syndromes, the mean urinary oxalate excretion is higher in patients with recurrent idiopathic stones than in normal subjects. Since even a small oxalate ion excess in an organism could lead to serious health problems, determination of oxalate ion is a very important task that requires the search for simple, accurate, reliable and low cost methods for its determination.

In this study, the construction and evaluation of a novel ion-selective electrode, with high selectivity toward oxalate based on PVC membrane of a compound is described.

II. Experimental Section

Reagents

PVC of high relative molecular weight, hexadecyltri-methylammonium chloride (HTAC), dibutyl phthalate (DBP), Tri-n-butylphosphate(TBP), n-butylacetate(BA), nitrobenzene(NB), Acetophenone(AP) and THF were obtained from Merck and were used as received except for vacuum drying over P₄O₁₀. All aqueous solutions were prepared with deionized, distilled water. Solution of anionic interferences, for selectivity studies, was prepared mostly from sodium salts in the water. Working solutions were prepared by successive dilutions with water.

Synthesis of ligand

The ligand 5,15-dibromo-9,10,11,20,21,22-hexamethyl-1,8,12,19-tetraazadicoso- 9,11,20,22-tetraene [L] was synthesized by refluxing a hot ethanolic solution (20 mL) of 5-Bromo-2,6-diaminopyridine (2.1826 g,

0.02 mol) with a hot ethanolic solution (20 mL) of 3-methyl 2,4-pentanedione (2.2830 g, 0.02 mol) in a 2:2 molar ratio. This reaction mixture was refluxed for 11h at $70^{\circ}C$ in the presence of conc. HCl. On overnight cooling the contents at $0^{\circ}C$ a light brown crystalline compound was separated out. This was filtered, washed several times with cold ethanol and dried under vacuum over P_4O_{10}

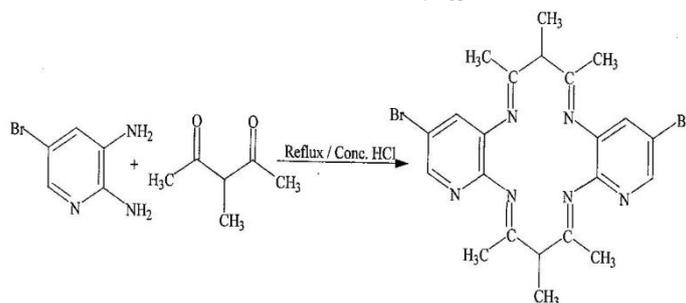


Figure 1. Synthesis of Ligand

Preparation of Complex Ionophore, $[CuL](ac)_2$

Hot ethanolic solution (20ml) of ligand (0.001mol) and hot ethanolic solution (20ml) of corresponding metal salt copper acetate (0.001 mol) were mixed together with constant stirring. The mixture was refluxed for 5-7 hours at $70^{\circ}-90^{\circ}C$. On cooling colored complex was precipitated out. It was filtered washed with cold EtOH and dried under vacuum over P_4O_{10} .

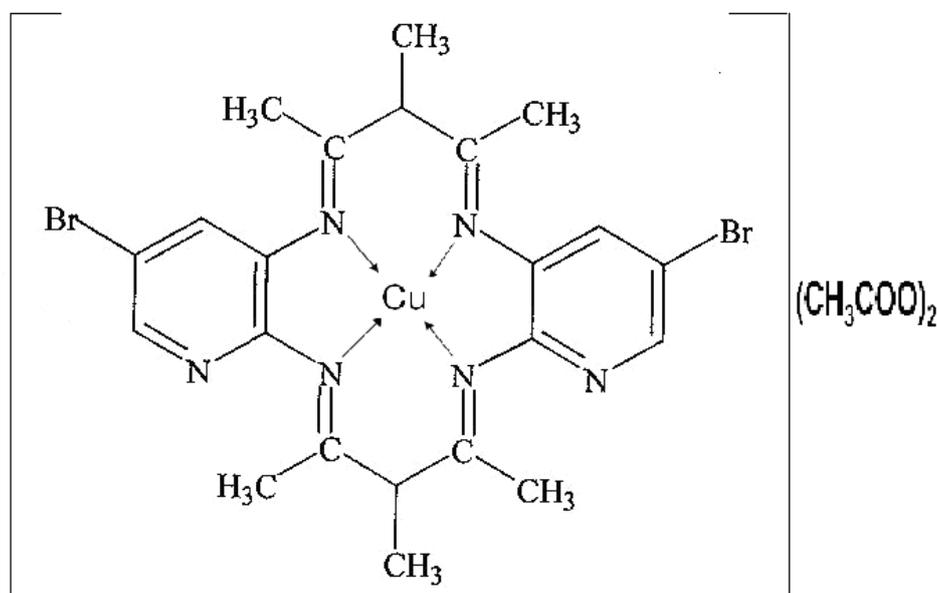


Figure 2 Ionophore, $[CuL](ac)_2$

CHN Analysis: Calcd for $C_{22}H_{24}N_6Br_2$, C, 37.00, H, 3.36, N, 11.77

Found: C, 37.00, H, 3.30, N, 11.10.

IR Characterization:

IR (KBr) (ν cm^{-1}): does not show any band at 1700 cm^{-1} corresponding to $\nu_{(C=O)}$ and bands at 3380 cm^{-1} and 3250 cm^{-1} are corresponding to $\nu_{as(NH_2)}$ and $\nu_s(NH_2)$ of 3-methyl-2,4-pentanedione and free primary amino groups of 2,6-diaminopyridine, respectively. This suggests the complete condensation of amino groups with the ketonic group. IR spectrum shows a strong band at 1607 cm^{-1} which is assigned to $\nu_{(C=N)}$ stretching vibration (azomethine linkage). This confirms the macrocyclic ligand formation. In addition, the bands at 1430 cm^{-1} , 631 cm^{-1} and 479 cm^{-1} appeared in the spectrum, which are due to the pyridine-ring-deformation, in-plane-ring-deformation and out-of-plane-ring deformation respectively. The spectrum also shows the band at 2959 cm^{-1} due to the C-H stretching, 3018 cm^{-1} corresponding to the asymmetric stretching vibration of CH_3 groups and 3098 cm^{-1} is characterized to C-H stretching vibration of aromatic ring.

NMR spectra:

1H NMR (300MHZ, 298K), The spectrum displays a singlet at ca. δ 1.25 ppm (s, 12H, 4N=C-CH₃a) due to the four methyl groups present at corners.

The six-methyl protons give another signal as doublet at ca. δ 2.7-2.9 ppm (d, 6H, 2C-CH₃b) due to the coupling with Hc proton.

The spectrum displays a quartet signal at ca. δ 3.0 ppm (q, 2Hc) because of splitting of the signal by methyl group proton.

Two signals as a doublet and a triplet at ca. δ 7.06 ppm (d, 2Hd) and at ca. δ 7.36 ppm (t, 4He) respectively are obtained in the spectrum due to the two types of non-equivalent pyridine ring protons.

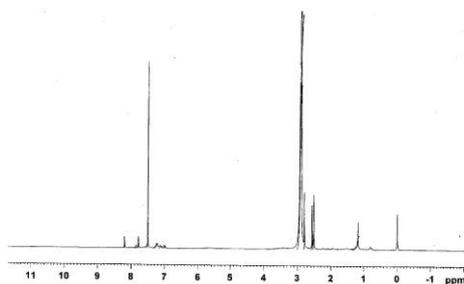


Figure 3 1H NMR of Ligand

Mass spectra:

Confirmed the proposed formula by showing a peak at 266 amu and 268 amu corresponding to the macrocyclic moiety $[(C_{22}H_{26}N_6)^+]$ and split up of bromine molecule. It also shows a series of peaks corresponding to various fragments their intensities give an idea of the stability of the fragments. Two broad bands are observed due to split up of bromine molecule.

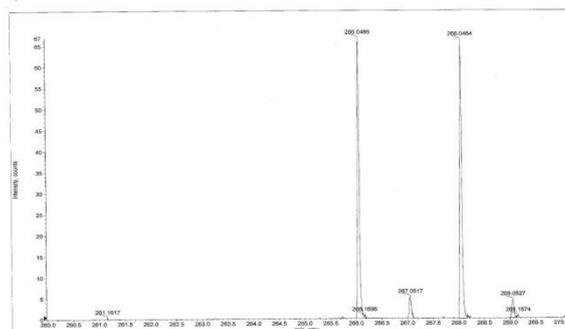


Figure 4 Mass spectra of Ligand

Electrode preparation

Different compositions of membrane ingredients, including ionophore, the plasticizers DBP, BA, AP, NB, TBP, the additive HTAC and PVC [Table 1], were thoroughly dissolved in 10 ml THF. The resulting solution was carefully cast in to a glass dish of 2 cm diameter for slow evaporation at room temperature to obtain membrane of about 0.3 mm thickness with optimum composition and behavior. The membrane was cut and pasted to the one end of pyrex tube with the help of araldite. The electrode was then filled with an internal solution of $1.0 \times 10^{-2}M$ oxalate. The prepared electrodes were finally conditioned by soaking in a $1.0 \times 10^{-2} M$ oxalate solution for 24 h.

III. Measurements of potentials:

Emf measurements

All emf measurements were carried out with the following assembly:

$Ag|AgCl|$ internal solution ($1 \times 10^{-2}M$ oxalate)|PVC membrane| test solution || $Hg-Hg_2Cl_2, KCl$ (saturated). Potentials were measured with digital potentiometer EQ-602 Equiptronics (accuracy, 0.001 V,

India). The pH measurements were carried out on digital pH meter. Auto ranging Conductivity meter/TDS meter TCM-15 (Toshniwal Instruments Mfg. Pvt. Ltd Ajmer).

Activities were calculated according to the Deby-Hückle procedure [4].

The solutions were stirred and potential readings were recorded when they reached the steady state values. The data were plotted as observed potential against the logarithm of the oxalate concentration. Potentiometric selectivity ($K_{Oxalate, A^-}$) were determined by the fixed interference method (FIM).

IV. Results and Discussion

Potential Response

In the preliminary experiments, the potentiometric responses for various anions were investigated with the membrane electrode, based on $[CuL](ac)_2$ in a PVC matrix without any amount of additive. It should be noted that ionic additives are ion exchangers, which themselves induce a selective response if no or only an insufficient amount of ionophore is present. In this case, all the electrodes were conditioned in $1.0 \times 10^{-2} M$ solution of the corresponding anion. As it is obvious from the **Figure 5** that with the exception of oxalate ion, all the tested anions showed negligible responses in the concentration range of $5.0 \times 10^{-7} - 6.0 \times 10^{-1} M$, due to their very weak interactions with ionophore. This is, most probably, due to the specific interaction between oxalate and, $[CuL](ac)_2$. The electrode, based on, $[CuL](ac)_2$, exhibits an excellent performance as an anion sensor for oxalate ion with a Nernstian response to the concentration of oxalate in the range of $5.0 \times 10^{-7} - 6.0 \times 10^{-1} M$.

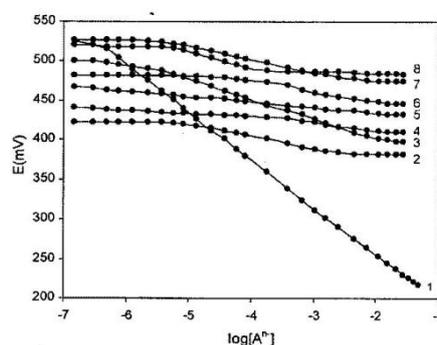


Figure 5. Potential responses of various anion selective electrodes based on complex, $[CuL](ac)_2$ (1) $C_2O_4^{2-}$ (2) SCN^- (3) I^- (4) SO_4^{2-} (5) NO_3^- (6) Cl^- (7) NO_2^- (8) Br^-

UV-Vis study

The preferential response towards oxalate ion is believed to be associated with the coordination of oxalate ion with the central metal of the ion-carrier $[CuL](ac)_2$. With UV-Vis spectra, of $1.0 \times 10^{-4} mol L^{-1}$ $[CuL](ac)_2$ in DMSO were obtained with and without the presence of $1.0 \times 10^{-4} mol L^{-1}$ oxalate ion as illustrated in **Figure 6**, it was possible to distinguish the interactions between the central metal and oxalate. The substantial increase in the absorbance at 204 nm after the contact of the carried solution with oxalate-containing phase suggested that the absorbing species had increased in size and axial coordination was thought to take place.

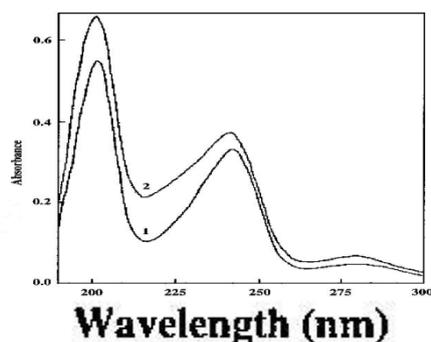


Figure 6 UV-Vis spectra of $1.0 \times 10^{-4} mol L^{-1} [CuL](ac)_2$ in DMSO in the absence (1) and presence (2) of $1.0 \times 10^{-4} mol L^{-1}$ oxalate.

Effect of membrane composition

It is well known that the sensitivity as well as selectivity, linearity and selectivity, obtained for a given ionophore, depends significantly on the membrane composition, nature and the amount of additive used [5-31, 37-48]. The composition of membranes with different proportional ingredients the performance and characteristics of the electrode are given in **Table 1**. Our experience on using several plasticizers including BA, AP and DBP for preparation of membrane showed that plasticizer DBP perform best as it exhibits the widest working concentration range and near-Nernstian slope. Plasticizer influence both dielectric constant of membrane, mobility of ionophore enhance its interaction with ion. The effect of ionophore amount on the functioning of oxalate membrane was investigated. It is seen from **Table 1** that among different membrane compositions tested, the membrane No. 6, with 5% ionophore, 31% PVC, 63% DBP and 1% HTAC, offers the widest linear range with a Nernstian slope of -29.0 ± 1.0 mV per decade over the concentration range of 5.0×10^{-7} - 6.0×10^{-1} M of oxalate ion solution as recommended by the IUPAC [33, 34]. Results have shown which of the plasticizer/PVC ratios produced maximum sensitivity [32].

Table 1. Evaluation of different membrane composition of oxalate ion-selective electrode

No:	Composition wt(%)				Slope (mVdecade ⁻¹)
	PVC	Plasticizer	I	HTAC	
1	32	64, TBP	4	0	-22
2	32	64, DBP	4	0	-26
3	32	64, BA	4	0	-20.2
4	32	64, NB	4	0	-21.3
5	32	64, AP	4	0	-20.1
6	31	63, DBP	5	1	-29.0
7	31	62, DBP	5	2	-26.6
8	31	62, DBP	6	1	-25.7
9	31	62, TBP	6	1	-21.4

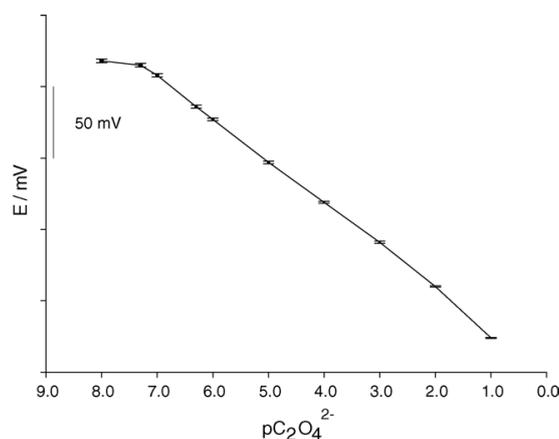


Figure 7 Potentiometric response of the oxalate ion-selective electrode based on $[CuL](ac)_2$ towards oxalate anion.

Optimization of pH.

The pH dependence of the membrane electrode was tested over the pH range of 2-12 at an oxalate concentration of 1.0×10^{-1} M and the results are shown in **Figure 8**. The results show that the sensor is suitable for oxalate determination with the wide pH range of 2.0-10.5. In high pH media, probably OH^- will compete with oxalate ion, whereas in acidic media ($pH < 2.0$), the drift in the potential may be due to the instability of the ionophores due to the nitrogen sites protonation (or formation of oxalic acid). The working pH range, over which the electrode can be used (2.0-10.5), covers the physiological conditions ($pH 7.2-7.6$). However, in highly alkaline media, the potential increases.

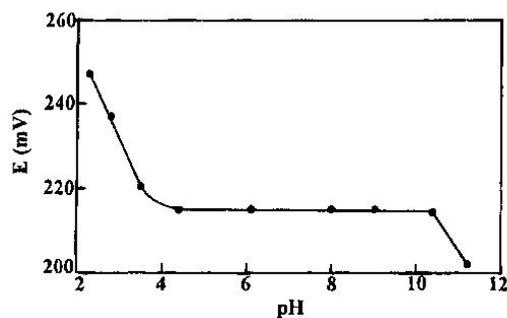


Figure 8. The influence of pH on the potential response of the optimized Oxa-ISE for (a) 1.0×10^{-2} M oxalate concentration

The influence of the concentration of the internal solution

The influence of the concentration of the internal solution on the potential response of the polymeric membrane electrode was also studied.

Thus, two similar membranes were prepared under optimal membrane composition and each electrode was filled with an internal solution of varying oxalate ion concentration (1.0×10^{-2} and 1.0×10^{-3} M). Then, the electrodes were conditioned by soaking in the same solutions of oxalate. Finally, plot of the emf oxalate selective electrode versus $p_{[oxalate]}$ was investigated for each electrode. The results are shown in **Figure 9**, which shows that the concentration of the internally filled solution has a negligible effect on the potential response of the electrode, except for the expected plots, which showed that the variation in the concentration of the internal solution changes the linear range and intercept of the resulting plots. Thus, based on the results, the concentration of 1.0×10^{-3} M was selected for further studies.

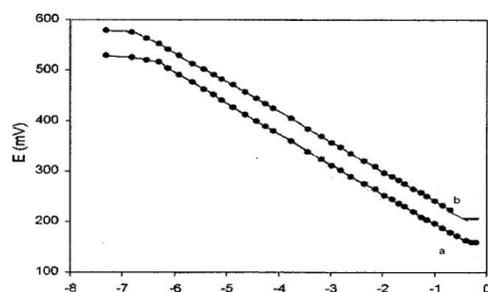


Figure 9. The influence of the concentration of internal solution on the potential response of the optimized Oxa-ISE: (a) 1.0×10^{-2} M, (b) 1.0×10^{-3} M.

Response characteristics of oxalate-selective electrode.

The response time of electrochemical cells, containing ion-selective membrane electrodes, is considered to be one of the most critical and limiting factors in the chemical and biochemical applications of potentiometric sensors. Since, the composition of the membranes in ion-selective electrodes remains approximately constant; the diffusion processes of ions passing through the membrane become negligible in the absence of interfering ions. As a result, the dynamic response characteristic is governed by the transport processes in the aqueous diffusion layer, *i.e.*; the response time depends on the shape and condition of the membrane surface as well as the composition of the sample. Furthermore, it is markedly influenced by the direction of the change in activity in the sample solution. Also, the response time of membrane selective electrodes, containing lipophilic salts, can be reduced by minimizing the aqueous diffusion layer (fast stirring, flowing the sample and micro-electrodes) and by using samples of higher activities. The t_{90} response time, as recommended by IUPAC, was used (where t_{90} is the time required for the electrode to reach 90% of the steady-state value). Under these conditions, t_{90} was found to 5-15 s for all the ranges of oxalate concentration. The response time of the electrode increases when concentration of oxalate is lowered, as illustrated in **Figure 10**. This is caused by the increased thickness of the diffusion layer near the membrane of electrode [35].

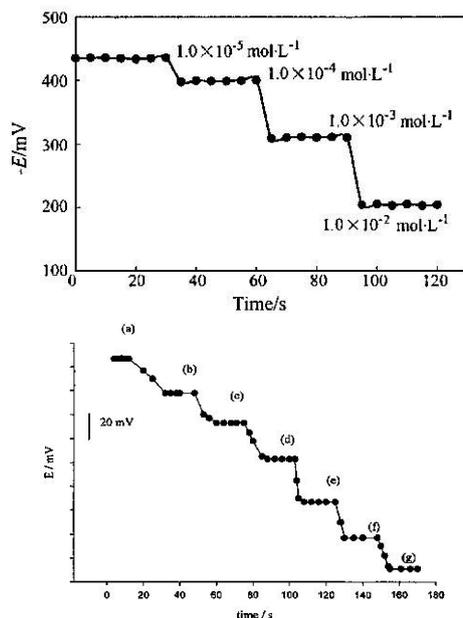


Figure 10. Response time of the optimized Oxa-ISE for stepwise changes in the concentration of oxalate: a) 1.0×10^{-6} M, b) 1.0×10^{-5} M, c) 1.0×10^{-4} M, d) 1.0×10^{-3} M, e) 1.0×10^{-2} M and f) 1.0×10^{-1} M.

Life Time

The life time of an ion-selective measuring system may be defined as the time interval between the conditioning of the membrane and the moment when at least one parameter of the functionality characteristics of the device changes detrimentally. For ion-selective membrane electrodes, the life time is mainly limited to the following two processes [36].

- The first process is the leaching out of carrier molecules from the membrane phase to the sample as an effect of a low partition coefficient at the sample/membrane interface.
- The second process is the extraction of the plasticizer by the sample and/or the degradation of the mobile ionic site additives of the membrane phase, which may catalyze the ion transfer. The electrode could be used for two months, without any measurable change in potential. During this time, the detection limit and slope of electrode remained almost constant.

The characteristic properties of the optimized membrane are summarized in **Table 2**.

Table 2. Characteristics of optimized oxalate-ISE

Linear range / M	$5.0 \times 10^{-7} - 6.0 \times 10^{-1}$ M
Slope / mVdecade⁻¹	-29.0 ± 1.0 mV per decade
pH range	2.0-10.5
Standard deviation of slope (mVdecade⁻¹)	± 1.0 mVdecade ⁻¹
Precision	At concentrations of 1.0×10^{-2} M and 1.0×10^{-3} M oxalate standard deviations were of ± 0.7 mV and ± 0.9 mV respectively.
Detection limit/M	1.0×10^{-7} M
Life time/month	> 2
Response time/s	10-15

Selectivity of the electrode

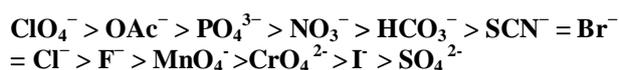
The basic parameter characterizing the analytical properties of each new electrode is its selectivity coefficient. Therefore, the coefficients of selectivity should be determined in a standardized way by a theoretically justified method which ensures the analytical usefulness of the values determined and enables the possibility of comparison of selectivity of different electrodes. The potentiometric selectivity coefficients ($K^{pot}_{oxalate, A^-}$) of the oxalate-selective electrode were determined by the fixed interference method (FIM), from potential measurements of solutions prepared with a fixed concentration of the interfering ions and varying

concentrations of $C_2O_4^{2-}$ [37-48]. The potentiometric selectivity coefficients of the proposed electrode are summarized in Table 3.

Table 3. Selectivity of coefficients, determined by use of the fixed potential method (FIM) for the oxalate-selective electrode

Interfering Ion	$\log K^{pot}_{oxa,A}$	Interfering Ion	$\log K^{pot}_{oxa,A}$
F^-	-4.1	PO_4^{3-}	-2.2
Cl^-	-4.0	ClO_4^-	-0.9
Br^-	-4.0	HCO_3^-	-3.0
I^-	-5.0	SO_4^{2-}	-5.0
SCN^-	-4.0	NO_2^-	-4.4
CO_3^{2-}	-3.0	MnO_4^-	-4.9
OAc^-	-2.0	NO_3^-	-3.0

According to the tabulated data in Table 3, the interfering effect of the ions is in the following order:



The selectivity is completely described by the distribution coefficients of the various anions between the sample solution and the membrane phase.

Effect of partially non-aqueous media

The performance of the proposed sensors was investigated in partially non-aqueous media using ethanol and acetone mixtures with water. The calibration plot of the electrode was obtained in the different mixture (v/v) of water-ethanol and water-acetone. From the data obtained, it was concluded that the membrane electrodes worked satisfactorily in solutions having a maximum of 20% (v/v) non-aqueous content. In these mixtures the working concentration range and slope remained unaffected, and only a little decrease was observed Figure 11. Therefore, the electrodes functioned well in the presence of up to 20% non-aqueous content. However, above 20% non-aqueous content, the slope and working concentration range were reduced, and the potentials showed drift and caused a significant interference in electrode and caused a significant interference in electrode functioning.

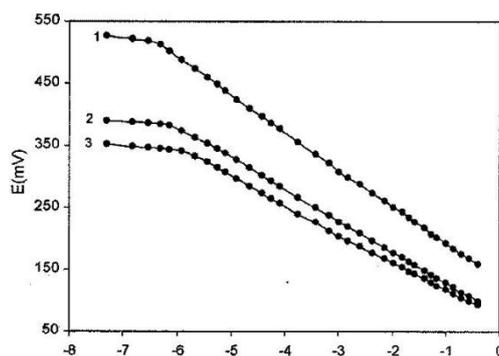


Figure 11. Effect of partially non-aqueous media on the calibration graph of oxalate-selective electrode : (1) aqueous media; (2) 20% acetone; (3) 20% ethanol.

Analytical applications

The high degree of oxalate selectivity exhibited by the electrode based on compound $[CuL](ac)_2$ as carrier makes them to be potentially useful for monitoring concentration levels of oxalate in real samples. In order to assess the applicability of the membrane electrode for real samples, an attempt was made to determine $C_2O_4^{2-}$ in several water samples using the standard addition method. The proposed electrode was employed to determine the recovery of oxalate ion of water sample and the interfering effect of other anions and the results are given in Tables 4 and 5. The results indicate that the proposed electrode can be successfully employed for the determination of oxalate at normal concentrations in water samples. The quality of results was evaluated by performing a recovery test, spiking the water sample with standard oxalate solution.

Table 4. Determination of oxalate in water samples by Oxa-ISE

Sample No.	Initial (Oxalate added (M))	Found [Oxa-ISE (M) ^a]
1	1.27×10^{-5}	$1.15(\pm 0.55) \times 10^{-5}$
2	2.34×10^{-5}	$2.21(\pm 0.55) \times 10^{-5}$
3	3.43×10^{-5}	$3.24(\pm 0.55) \times 10^{-5}$

Table 5. Determination of oxalate in synthesis samples by Oxa-ISE

Concentration of different anions	Oxalate added (M)	Oxa-ISE (M) ^a
NO_3^- (1.0×10^{-4} M)	1.0×10^{-2}	$1.0(\pm 0.20) \times 10^{-2}$
CO_3^{2-} (1.0×10^{-4} M)		
SCN^- (1.0×10^{-4} M)		
SO_3^{2-} (1.0×10^{-4} M)		
Cl^- (1.0×10^{-3} M)		
ClO_4^{2-} (1.0×10^{-3} M)		

^aTMean value \pm standard deviation (n = 5).

Typical results for the titration for 10 ml of $0.001M C_2O_4^{2-}$ with $0.04M MnO_4^-$ is shown in **Figure 12**. As seen, the amount of $C_2O_4^{2-}$ ion in solution can be accurately determined with the electrode. The observation of an unsymmetrical titration curve is due to the fact that, before the end point, the potential shows a usual logarithmic change with the volume of titration added, while the potential response after the end point will remain almost constant due to the low concentration of free $C_2O_4^{2-}$ in solution. Therefore the end point can be obtained by extrapolation of the linear portions of the titration plot.

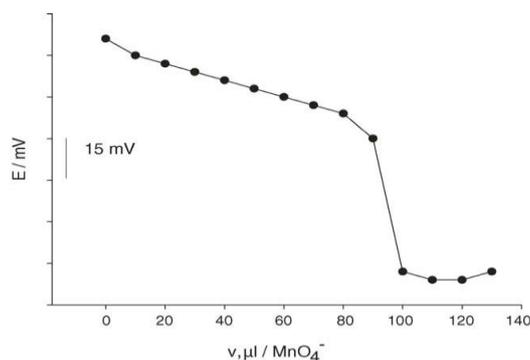


Figure 12 Application of the oxalate-selective electrode based on $[CuL](ac)_2$ to the potentiometric titration 10 ml of $0.001M C_2O_4^{2-}$ with $0.04M MnO_4^-$

V. Conclusion

New oxalate-selective membrane electrode has been prepared using $[CuL](ac)_2$. The electrode has been shown to have good operating characteristics (Nernstian response; reasonable detection limit; relatively high selectivity, especially with respect to the highly lipophilic anions; wide dynamic range; fast response; applicability over a wide pH range). These characteristics and the typical applications presented in this paper, make the electrode suitable for measuring the oxalate content in water samples, without a significant interaction from concomitant anionic species. The results show that there was a coordination interaction between oxalate and the proposed carrier, which played an important role in the response characteristics and selectivity of the electrodes.

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