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Fabrication of an Er^{3+} PVC membrane sensor based on oxalic acid bis[2-[(phenylamino)carbonyl]hydrazide]

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Abstract A highly selective and sensitive Er^{3+} sensor was constructed with a polyvinyl chloride matrix membrane containing oxalic acid bis[2-[(phenylamino)carbonyl]-hydrazide] as a neutral carrier, sodium tetraphenyl borate as a cationic additive and nitrobenzene as a plasticizing solvent mediator. The proposed sensor exhibits linear potential response with a Nernstian slope of 19.7 ± 0.4 mV decade^{-1} of activity in the Er^{3+} concentration range of 1.0×10^{-6} to 1.0×10^{-2} mol dm^{-3} in the pH range of 2.7–10.2. It has a very short response time (<10 s), a detection limit of 5.8×10^{-7} mol dm^{-3} and good selectivity relative to a wide variety of other metal ions including common alkali, alkaline earth, heavy and transition metal ions. The sensor can be used for at least 2 months without any considerable divergence in potentials. The proposed sensor was successfully applied as an indicator electrode for the potentiometric titration of 1.0×10^{-4} mol dm^{-3} of Er^{3+} ions with a 1.0×10^{-2} mol dm^{-3} EDTA. It was also used in the indirect determination of F^{-} ions in some mouthwash solutions.

Keywords Sensor · Potentiometry · Ion-selective electrode · PVC membrane

Introduction

The utility of ion-selective electrodes (ISEs) is being increasingly realized by analytical chemists in view of the rapid growth of industry and technology all over the world as they represent a rapid, accurate and low-cost method of analysis.

Lanthanides are widely distributed in low concentrations throughout the earth's crust [1]. Determination of rare earth compounds is considered necessary because of their applications in bioinorganic and inorganic chemistry, industrial use and also their enhanced discharge, toxic properties and other adverse effects. It is estimated that the erbium concentration of the earth's crust reaches 24 ppm. Its commercial sources are monazite and bastnasite. Although the conclusion of the investigators is to classify the rare earths as having a low acute toxicity rating, the studies of toxicity of various erbium compounds show that when inhaled, taken orally or injected into the blood stream, erbium salts can cause serious problems [2].

Voltammetry [3] has been used for the determination of trace amounts of erbium in alkali halides, and secondary ion mass spectroscopy [4] and Rutherford back-scattering techniques [5] have been used for the analysis of erbium profiles in lithium niobate crystals. Higher order derivative spectrometric procedures were developed for determination of erbium in selected rare earth mixtures [6–9]. Recently, preconcentrative ICP-MS and neutron activation analysis (NAA) procedures have been developed to ascertain the individual rare earth element concentration in seawater samples from various locations by using a spectrofluorometric method [10]. These methods are either time consuming, involve multiple sample manipulations or are too expensive for most analytical laboratories. Potentiometric membrane sensors have been shown to be very

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effective tools for the analysis of a wide variety of metal ions. They are very simple, fast, inexpensive and capable of reliable response in wide concentration ranges. However, detection limits of these methods are lower than for PVC membrane sensors. Little attention has been paid to the development of Er^{3+} membrane electrodes in recent years [11–13].

The aim of this research is fabrication of a selective and sensitive Er^{3+} membrane sensor, based on oxalic acid bis [2-[(phenylamino)carbonyl]hydrazide] (AOPH, Scheme 1) as a suitable ionophore for the potentiometric measurement of the Er^{3+} ion in a certain concentration range.

Results and discussion

The existence of ten donating atoms (four oxygen and six nitrogen) in the structure of AOPH was expected to increase both the stability and selectivity of its complexes with transition metal ions (especially lanthanide ions). Thus, in order to check the suitability of AOPH as an ion carrier for different metal ions, in preliminary experiments AOPH complexation with a number of metal ions, including mono-, di- and trivalent cations, was investigated conductometrically in acetonitrile solutions (1.0×10^{-4} mol dm^{-3} of cation solution and 1.0×10^{-2} mol dm^{-3} of ligand solution) at 25 ± 0.1 °C [14–16]. Each ion solution (25 cm^3) was titrated with 0.01 mol dm^{-3} of AOPH solution in order to obtain a clue about the stability and selectivity of the resulting complex. The conductance of the solution was measured after each addition. Addition of the ligand was continued until the desired ligand-to-cation molar ratio was achieved. The 1:1 binding of the cations with ligands can be expressed by the following equilibrium:

$$M^{n+} + L \xrightarrow{K_f} ML^{n+} \tag{1}$$
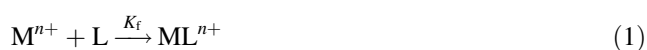
The formation constant of equilibrium, K_f, is given by:

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} \frac{f_{(ML^{n+})}}{f_{(M^{n+})}f_{(L)}} \tag{2}$$

where $[ML^{n+}]$, $[M^{n+}]$, $[L]$ and f represent the equilibrium molar concentration of complex, free cation, free ligand and the activity coefficient of the species indicated,
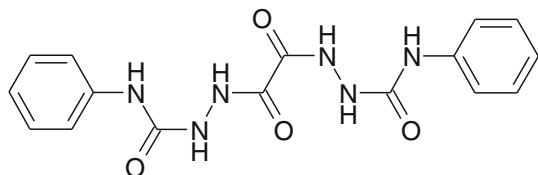
respectively. Under the dilute condition we used, the activity coefficient of the unchanged ligand, $f_{(L)}$, can be reasonably assumed as unity. The use of the Debye-Hückel limiting law of 1:1 electrolytes leads to the conclusion that the activity coefficient in Eq. 2 is canceled out. Thus, the complex formation constant in terms of the molar conductance can be expressed as:

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \tag{3}$$

where

$$K_f = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})} \tag{4}$$

Here, Λ_M is the molar conductance of the cation before addition of ligand, Λ_{ML} the molar conductance of the complex, Λ_{obs} the molar conductance of the solution during titration, C_L the analytical concentration of AOPH added and C_M the analytical concentration of the cation. The complex formation constants, K_f, and the molar conductance of complex, Λ_{ML}, were obtained by computer fitting of Eqs. 3 and 4 to the molar conductance-molar ratio data, using a nonlinear least-squares program KINFIT [17]. The logarithm of the formation constants (log K_f) of the resulting 1:1 complex between Er^{3+} ion and AOPH was calculated as 5.32 ± 0.34. The results of this experiment showed that stability of the Er–AOPH complex is higher than other cations tested. Thus, AOPH with the most stable complex with Er^{3+} ion is expected to act as a suitable ion carrier for the fabrication of an Er^{3+} sensor.

In the next experiment, AOPH was used as a suitable ionophore in the construction of polymeric membrane sensors for a variety of metal ions, including alkali, alkaline earth, transition and heavy metal ions. It is noted that the resulting Er^{3+} potential response showed a Nernstian behavior, while the slopes of the linear parts of the emf responses to other cations (including other lanthanide ions) were much lower than those expected by the Nernst equation.

In general, the presence of lipophilic anions in cation-selective membranes based on a neutral carrier not only diminishes the ohmic resistance and enhances the response behavior and selectivity, but also, in cases where the extraction capability is poor, increases the sensitivity of the membrane electrodes [18–22]. Obviously, from Table 1, the sensor slope in the absence of sodium tetraphenyl borate (NaTPB) is lower than the expected Nernstian value (membrane no. 1). Nevertheless, the addition of 2% NaTPB will increase the sensitivity of the electrode response considerably, so that the membrane electrode demonstrates a Nernstian behavior (membrane no. 3). However, the membranes with the composition of 30% PVC, 4% AOPH, 2% NaTPB and 64% nitrobenzene (NB) exhibit a Nernstian

Scheme 1

Table 1 Optimization of the membrane ingredients

No.	Composition (wt%)				Linear range (mol dm^{-3})	Slope (mV decade^{-1} of activity)	R^2	DL (mol dm^{-3})
	PVC	Plasticizer	AOPH	NaTPB				
1	30	NB, 66	4	0	1.0×10^{-2} to 1.0×10^{-6}	10.2 ± 0.2	0.752	1.0×10^{-6}
2	30	NB, 65	4	1	1.0×10^{-2} to 1.0×10^{-6}	15.6 ± 0.5	0.863	9.1×10^{-7}
3	30	NB, 64	4	2	1.0×10^{-2} to 1.0×10^{-6}	19.7 ± 0.4	0.995	5.8×10^{-7}
4	30	NB, 63	4	3	1.0×10^{-2} to 1.0×10^{-6}	16.8 ± 0.6	0.868	1.0×10^{-6}
5	30	NB, 66	2	2	1.0×10^{-2} to 1.0×10^{-6}	14.1 ± 0.4	0.703	1.0×10^{-6}
6	30	NB, 65	3	2	1.0×10^{-2} to 1.0×10^{-6}	18.6 ± 0.3	0.882	1.0×10^{-6}
7	30	NB, 63	5	2	1.0×10^{-2} to 1.0×10^{-6}	21.9 ± 0.3	0.985	1.0×10^{-6}
8	30	BA, 64	4	2	1.0×10^{-2} to 1.0×10^{-6}	19.4 ± 0.5	0.913	1.0×10^{-6}
9	30	AP, 64	4	2	1.0×10^{-2} to 1.0×10^{-6}	19.2 ± 0.3	0.897	1.0×10^{-6}
10	30	DBP, 64	4	2	1.0×10^{-2} to 1.0×10^{-6}	18.7 ± 0.5	0.907	1.0×10^{-6}
11	30	NB, 68	0	2	1.0×10^{-2} to 1.0×10^{-4}	7.8 ± 0.3	0.795	1.0×10^{-4}
12	30	NB, 70	0	0	1.0×10^{-2} to 1.0×10^{-3}	4.5 ± 0.5	0.763	1.0×10^{-3}

potential response. As can be seen from Table 1, the optimum amount of ionophore (AOPH) was 4% (no. 3).

Several important features of the PVC membranes, such as the properties of the plasticizer, the plasticizer/PVC ratio, the nature and amount of ionophore, and especially the nature and amount of the additive used are reported to influence the sensitivity and selectivity of the ion-selective electrodes significantly [22–26]. Thus, different compositions of the Er^{3+}-selective membrane were optimized, and the results are given in Table 1. Previous reported works revealed that the membrane prepared with a plasticizer/PVC ratio about 2.2 shows the best performance. Since the nature of the plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules, and the state of ligand [22–26], it was expected to play a key role in determining the selectivity, working concentration range and response time of the membrane electrode. Among four different solvent mediators tested, NB is superior with respect to dibutyl phthalate, benzyl acetate and acetophenone. All the used plasticizers have a nearly low donocity number (DN) but different dielectric constants (DC). NB is used as a plasticizer because of having a higher dielectric constant than the others. The higher DC of NB helps the better extraction of the polar Er^{3+} ion, which is a cation with high charge density from the aqueous layer to the organic layer of the membrane and causes a better and faster response.

The emf response of the polymeric membrane at varying Er^{3+} concentrations (Fig. 1) indicates a Nernstian slope of 19.7 ± 0.4 mV decade^{-1} of activity, over a very wide concentration range of erbium ions from 1.0×10^{-6} to 1.0×10^{-2} mol dm^{-3}. The detection limit was 5.8×10^{-7} mol dm^{-3} as determined from the intersection of the two extrapolated segments of the calibration plots. The standard deviation of ten replicate measurements was
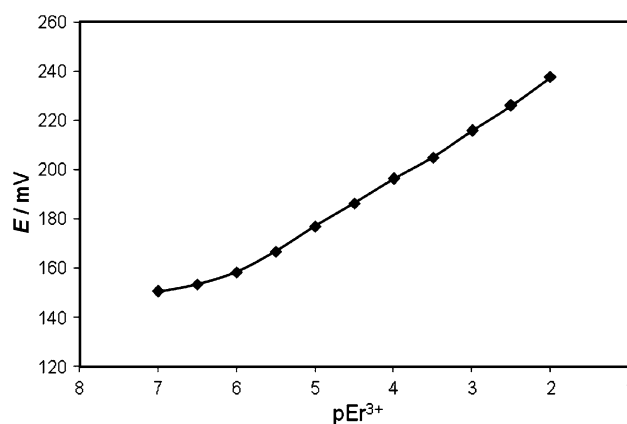
Fig. 1 Calibration curves of the AOPH-based erbium electrode

± 0.4 mV. All measurements were carried out in 0.1 mol dm^{-3} of sodium acetate buffer with pH 4. The proposed PVC-based membrane sensor could be used for at least 2 months (use for 1 h daily).

In order to study the effect of pH on the performance of the sensor, the potentials were determined in the pH range of 1.0–12.0 (pH was adjusted by using concentrated NaOH or HCl) at a concentration of 1.0×10^{-3} mol dm^{-3} of Er^{3+} ion. The results are depicted in Fig. 2. As seen, the potential response of the sensor remains constant in the pH range of 2.7–10.2. At lower pH than 2.7, an increase in potential was observed. This is due to the response of the membrane to the hydronium ion (protonation of nitrogen atoms in acidic media). At higher pH values than 10.2, a decrease in potential due to the formation of insoluble erbium hydroxide was observed.

Dynamic response time of the membrane was measured at various concentrations (0.01, 0.001, 0.0001, 0.00001 and 0.00001 mol dm^{-3}) of the Er^{3+} solutions, and the results
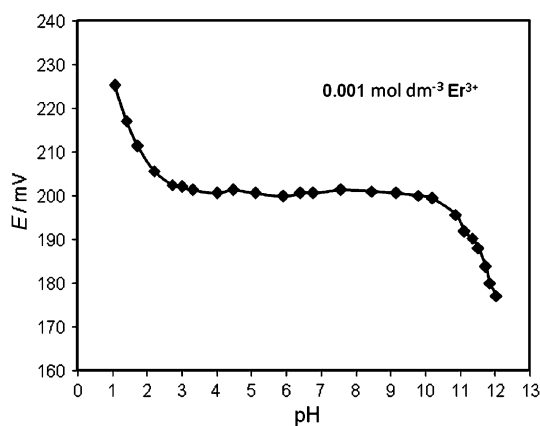
Fig. 2 pH effect of the test solution (1.0×10^{-3} mol dm^{-3} of Er^{3+}) on the potential response of the Er^{3+} ion-selective electrode
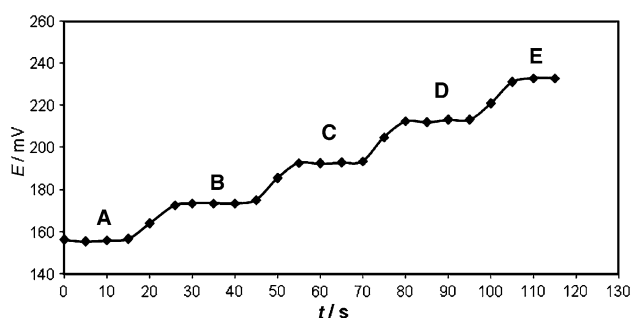

Fig. 3 Dynamic response time of the erbium electrode for step changes in the Er^{3+} concentration: *A* 1.0×10^{-6} mol dm^{-3}, *B* 1.0×10^{-5} mol dm^{-3}, *C* 1.0×10^{-4} mol dm^{-3}, *D* 1.0×10^{-3} mol dm^{-3}, *E* 1.0×10^{-2} mol dm^{-3}

are shown in Fig. 3. As can be seen from Fig. 3, in the whole concentration range the sensor reaches its equilibrium response very fast (<10 s).

The most important characteristic of any polymeric membrane sensor is its relative response to the primary ion over other ions present in the solution (as interfering foreign cations), which is expressed in terms of potentiometric selectivity coefficients. In this work, selectivity coefficients were calculated by the matched potential method (MPM) and separate solution method (SSM) [27, 28]. According to the MPM method, a specified activity (concentration) of primary ions (A: 1×10^{-5} to 1.0×10^{-2} mol dm^{-3}) is added to a reference solution (1.0×10^{-6} mol dm^{-3} in 0.1 mol dm^{-3} sodium acetate buffer pH 4) and the potential is measured. In a separate experiment, interfering ions (B: 1×10^{-5} to 1.0×10^{-2} mol dm^{-3}) are successively added to an identical reference solution until the measured potential matches the one obtained before adding primary ions. The matched potential method selectivity coefficient, K^{MPM}, is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K^{\mathrm{MPM}} = \Delta a_{\mathrm{A}}/a_{\mathrm{B}}$.

In the separation solution method (SSM), the concentrations of a cell, comprising an ion-selective electrode and a reference electrode, are adjusted with two separate solutions: one containing the ion A (but no B) of a_{A} activity and the other containing the ion B (but no A) of activity, being as high as required to achieve the same measured cell voltage. From any pair of the a_{A} and a_{B} activities giving the same cell voltage, the value of K^{SSM} may be calculated from the equation:

$$K^{\mathrm{SSM}} = a_{\mathrm{A}}/a_{\mathrm{B}}^{\mathrm{ZA/ZB}}.$$

Response times, detection limits, dynamic ranges and interfering ions of this electrode are compared with those of the best previous Er^{3+} electrodes [11, 12], and the resulting values are given in Table 2. Obviously, the proposed sensor not only in terms of response time, detection limit and dynamic range, but also in terms of selectivity, is superior to the previously reported Er^{3+} ion-selective membrane electrodes.

Analytical application

The proposed Er^{3+}-PVC membrane electrode was found to work well under laboratory conditions. It was used as an indicator electrode in the potentiometric titration of a 1.0×10^{-4} mol dm^{-3} erbium ion solution with a standard 1.0×10^{-2} mol dm^{-3} of EDTA. The resulting titration curve is shown in Fig. 4. As seen, the sensor is capable of monitoring the amount of erbium ions.

Furthermore, the constructed sensor was used in indirect determination of fluoride ions in some mouthwash samples. Each sample (1.0 g) was taken and diluted with distilled water in a 100 cm^3 volumetric flask, and pH was adjusted to 4 by sodium acetate buffer (0.1 mol dm^{-3}). An aliquot of 25 cm^3 of this solution was titrated with Er^{3+} solution (1.0×10^{-3} mol dm^{-3}), while the proposed sensor was used as an indicator electrode. Due to the formation of the complex between the fluoride ion and erbium ion, the fluoride content of samples can be measured indirectly by using the proposed electrode. The results of triplicate measurements are summarized in Table 3. There is a satisfactory agreement among the declared fluoride content and the determined values by the sensor.

To assess the precision of the technique, parameters of the repeatability and reproducibility were investigated. Precision was carried out by eight determinations at three different concentrations. For this purpose, eight replicate standard samples of 0.5, 5 and 50 mg dm^{-3} were measured by the proposed sensor. Then, the mean concentration of each set was found to be 0.51, 5.08 and 50.3 mg dm^{-3} and with associated RSD values of 1.9, 1.5 and 0.6%, respectively. To evaluate the reversibility of the electrode, the

Table 2 Comparison of selectivity coefficients (log K^{MPM}), detection limit, response time and linearity range of proposed Er^{3+} sensor and the previously reported Er^{3+} ion-selective electrodes

	Ref. [11]	Ref. [12]	This work	
Linearity range (mol dm^{-3})	1.0×10^{-6} to 1.0×10^{-2}	1.0×10^{-5} to 1.0×10^{-2}	1.0×10^{-6} to 1.0×10^{-2}	
Detection limit (mol dm^{-3})	6.6×10^{-7}	5.0×10^{-6}	5.8×10^{-7}	
Response time (s)	~ 10	<10	~ 10	
Selectivity coefficients	MPM	MPM	MPM	SSM
Na$^+$	−3.49	−3.00	−3.42	−3.53
K$^+$	–	−2.96	−3.38	−3.42
Ca^{2+}	−3.26	−2.68	−3.66	−3.67
Ni^{2+}	−3.19	–	−3.43	−3.45
Co^{2+}	–	–	−3.42	−3.47
Pb^{2+}	−3.34	−2.85	−3.48	−3.45
Cr^{3+}	−3.06	–	−3.46	−3.45
Fe^{3+}	−3.24	–	−2.27	−2.30
Sm^{3+}	−2.11	−0.52	−2.64	−2.67
Lu^{3+}	−3.14	–	−2.60	−2.63
Eu^{3+}	−3.00	–	−2.66	−2.65
Tm^{3+}	−2.51	−1.43	−2.65	−2.63
Tb^{3+}	−2.66	–	−2.59	−2.64
Gd^{3+}	–	−2.43	−2.68	−2.67
Dy^{3+}	−2.09	−1.49	−2.59	−2.58
Nd^{3+}	−2.07	–	−2.51	−2.54
La^{3+}	−2.44	−1.52	−2.54	−2.56
Ho^{3+}	−2.60	−2.46	−2.63	−2.65
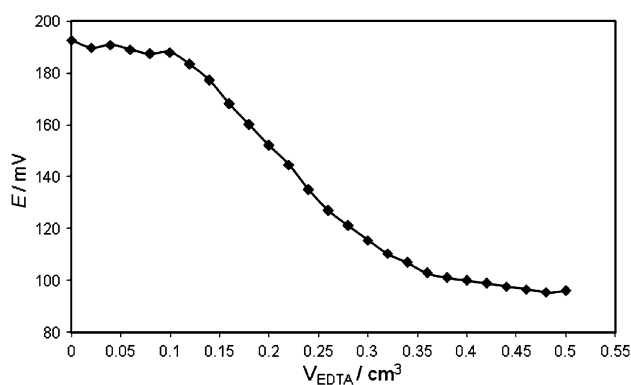
Fig. 4 Potential titration curve of 20.0 cm^3 from a 1.0×10^{-4} mol dm^{-3} Er^{3+} solution with 1.0×10^{-2} mol dm^{-3} of EDTA

practical potential response of the modified electrode was recorded by changing solutions with different erbium ion concentrations from 1.0×10^{-4} to 1.0×10^{-5} mol dm^{-3}. The measurements were performed in the sequence of high-to-low sample from the highest concentration to the lowest, and the results showed that the potentiometric responses of the sensor were reversible and had no memory effect, although the time needed to reach equilibrium values was longer than that when the solution sequence was reversed in low-to-high sample concentrations. It is well documented that, in the case of high-to-low concentrations, the time needed to attain a stable potential is larger than that required for the case of low-to-high concentrations (for a ten-fold change in the cation concentration).

Conclusion

A highly selective erbium membrane electrode based on oxalic acid bis[2-[(phenylamino)carbonyl]hydrazide] (AOPH) as an ion carrier was reported. The sensor showed a Nernstian behavior over a wide concentration range of 1.0×10^{-6} to 1.0×10^{-2} mol dm^{-3} erbium ions with a detection limit of 5.8×10^{-7} mol dm^{-3} and a fast response time of <10 s. The sensor works well in a pH range of 2.7–10.2. Consequently, the proposed sensor is superior to the previously reported sensors in terms of response time, detection limit, concentration range and selectivity.

Experimental

Reagent grade benzyl acetate (BA), nitrobenzene (NB), dibutyl phthalate (DBP), acetophenone (AP), high relative

Table 3 Determination of fluoride ions in mouth wash solutions

Sample	Labeled (mg dm^{-3})	Found ISE[a] (mg dm^{-3})
Sodium fluoride mouthwash solution (Aquafresh, Brentford, UK)	1,350	1,381[b] ± 18
Sodium fluoride mouthwash solution (Eurodont, DuroDont GmbH)	1,450	1,478[b] ± 23

[a] Proposed Er^{3+} sensor

[b] Results are based on three measurements

molecular weight PVC, sodium tetraphenyl borate (NaT-PB) and tetrahydrofuran (THF) were purchased from Aldrich and used as received. Chloride and nitrate salts of the cations used (from Merck and Aldrich) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. Triply distilled deionized water was used throughout.

All electromotive force (emf) measurements were carried out with the following cell assembly: Ag/AgCl | internal solution (1 × 10^{-3} mol dm^{-3} $ErCl_3$) | PVC membrane | test solution | Hg_2Cl_2, KCl (saturated). A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25.0 ± 0.1 °C. The activities were calculated according to the Debye-Huckel procedure [29].

Melting points were recorded with an Electrothermal 9100 instrument. Bruker DRX-Avance was used to obtain ^1H NMR (300.1 MHz) and ^{13}C NMR (75.5 MHz) spectra. IR spectra were recorded on a Perkin-Elmer 1600 infrared spectrophotometer.

Oxalic acid bis[2-[(phenylamino)carbonyl]hydrazide]

Phenylcarbamic acid chloride (2 mmol, 0.31 g) was dissolved in hot ethanol, and oxalyl hydrazide (1 mmol, 0.118 g) was added to the solution. The mixture was refluxed for 1 h. Then the solid product was collected and crystallized from aceton/ethanol (1:1). Mp = 163–165 °C (Ref. [30] 254–256 °C); ^1H NMR: $\delta = 6.31$ (2H, d, $J = 7.3$ Hz, 2CH), 6.95 (2H, t, $J = 7.1$ Hz, 2CH), 7.15–7.20 (4H, m, 4CH), 8.33 (2H, s, 2CH), 15.65 (2H, br, 2NH), 12.21 (2H, br, 2NH) ppm; ^{13}C NMR: $\delta = 118.41$, 120.21 (2CH), 122.30 (C), 126.66, 129.41 and 159.40 (2CH), 160.95 (C), 169.17 (C=O) ppm; IR (KBr): $\bar{v} = 3,332, 3,320, 3,316, 3,310$ (NH), 1,655, 1,600, 1,610 (C=O), 1,550, 1,480, 1,272, 1,105, 1,030, 950, 840, 690 cm^{-1}.

General procedure to prepare the PVC membrane

Different amounts of the ionophore (AOPH) along with appropriate amounts of PVC, plasticizer (NB) and additive (NaTPB) were dissolved in tetrahydrofuran. The solution was mixed well. The resulting mixture was transferred into a glass dish of 2 cm diameter, and the solvent was

evaporated slowly until an oily concentrated mixture remained. A Pyrex tube (3–5 mm o.d.) was dipped into the mixture for about 10 s so that a transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 12 h. The tube was then filled with an internal filling solution (1.0 × 10^{-3} mol dm^{-3} $ErCl_3$). The electrode was finally conditioned for 24 h by soaking in a 1.0 × 10^{-3} mol dm^{-3} $ErCl_3$ solution [31–47].

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