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Novel PVC Membrane Based Alizarin Sensor and its application; Determination of Vanadium, Zirconium and Molybdenum

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A fabrication of new potentiometric alizarin sensor based on the use of alizarin Red-S-CTAB (ARS-CTAB) ion pair, in poly (vinyl chloride) (PVC) matrix, is reported. Effect of various plasticizers (o-NPOE, DBP, DEP, DOP, TBP, & CN) and cation excluder, Cetryltrimethylammoniumbromide (CTAB) was studied. The best performance was obtained with a membrane composition of PVC: o-NPOE: ARS-CTAB: CTAB ratio (w/w; %) of 31:60:7:2. The sensor exhibits significantly enhanced selectivity towards alizarin over the concentration range 1.0×10^{-8} to 1.0×10^{-3} M with a lower detection limit of 3.0×10^{-9} M and a Nernstian slope of 59.8 mV decade^{-1} of activity. Influence of the membrane composition, and possible interfering ions was investigated on the response properties of the electrode. Fast and stable response, good reproducibility and long-term stability are demonstrated. The sensor shows response time of < 10 s and can be used for about 3 months without any considerable divergence in their potential response. Selectivity coefficients determined with matched potential method (MPM) indicate high selectivity for alizarin. The proposed electrode shows fairly good discrimination of alizarin from anions. It was successfully applied to determination of vanadium ion in water and soil samples, zirconium ion in alloy samples and molybdenum ion in geological samples using indirect potensiometry and the results obtained are comparable with those provided by AAS analysis. The electrode can be used in the pH range of 2.0 to 5.0 and mixtures containing up to 20% (v/v) non-aqueous content. It was used as an indicator electrode in potentiometric titration of alizarin against EDTA.

Keywords: Alizarin ions sensor, Potentiometry, PVC membrane, Ion-pair

1. INTRODUCTION

The sensors for the determination of anionic species attracted less attention inspite of their presence in a variety of chemical, clinical and environmental samples [1-9]. Due to their ease of preparation, simple operation, fast response, reasonable selectivity, and wide linear working concentration ranges the ion selective electrode is an attractive alternative method for determination of organic and inorganic species. These electrodes have proven useful for quantitative determination of anionic surfactants [1-3], molybdate anion [4], gibberellic acid [5], ethylenediaminetetraacetatobismuthate (III) anion [6], orthophosphate [7], cysteine [8] and flufenamic acid anion [9]. In addition, some modified calixarenes and macrocyclic receptors have been recently, developed and applied as sensing materials for selective determination of chromate, monohydrogen phosphate, carbonate and phosphate, respectively [10-13]. Many ion pairs have been reported or developed for the purpose of determination of anionic, cation and drugs species by incorporating the ion pair with PVC membrane [14-17]. It has already well documented that, alizarin Red S (Figure 1a) (1,2-dihydroxyanthraquinone-3-sulfonic acid, sodium salt) has been used as a selective reagent for Zirconium [18,19,20], Molybdenum [21], Vanadium [22], Cerium[23], Samarium and Neodymium [24], Lead, Zinc, Cobalt, Copper [25], Platinum, Uranium, Bismuth, Scandium, Mercury [26] and Chromium [27]. In such studies, alizarin has been extensively used for selective determination of some rare earths due to its high ability to chelate specific cations. Alizarin is a water soluble compound, for this reason, we synthesized a water-insoluble form of this indicator, Alizarin Red S-CTAB is a lipophilic ion pair (Figure 1b.), which made its possible use in PVC sensors. Alizarin ion selective sensors have been hardly used [28] and also the sensor reported for alizarin exhibit narrow working concentration range and show interferences to various anions such as ClO_4^- , CNS^-, and I^- . Thus, there is still a need for having a good sensor for alizarin and further efforts are required to develop it.

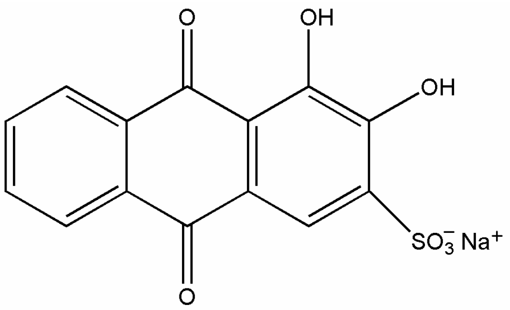

Figure 1a. Structural formulae of Alizarin Red S (1,2-dihydroxyanthraquinone-3-solphonic acid, sodium salt)

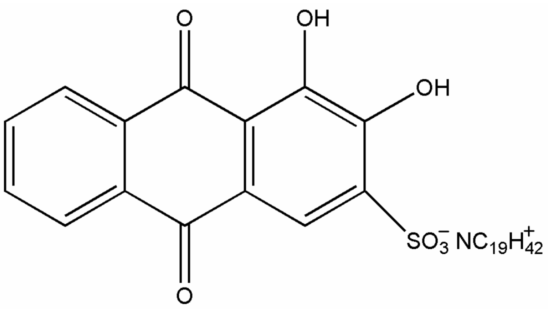

Figure 1b. Structural formulae of Alizarin Red S-CTAB ion pair.

The goal of this work was to develop an ion selective electrode for alizarin detection and study its applicability in the potentiometric determination of some metal ions. The electrode based on Alizarin Red S-CTAB ion pair shows a stable and reproducible potentiometric response towards alizarin anion with a linear concentration range and fast response time. The sensor has been applied for the determination of Vanadium, Zirconium and molybdenum (as an example) with satisfactory results.

2. EXPERIMENTAL PART

2.1. Reagent and apparatus

All the reagents were purchased from Aldrich and used as received. For membrane preparation, high molecular weight polyvinyl chloride (PVC), o-nitrophenyl ether (o-NPOE), dibutylphthalate (DBP), acetophenone (AP), tributylphosphate (TBP), cetryltrimethylammoniumbromide (CTAB), sodium alizarin-sulphonate (Alizarin Red S) and tetrahydrofuran (THF) were used as received from Fluka. Reagent grade sodium salts of all anions used were highest purity available from SRL (Mumbai, India) and used without any further purification except for vacuum drying over P_2O_5. Anionic salt solution were prepared in doubly distilled water and standardized whenever necessary.

All potentiometric measurements were performed at room temperature using Thermo Orion 4 star pH meter with PVC membrane based alizarin Red-S electrode in conjunction with a SCE reference electrode.

2.2. Conditioning of membranes and potential measurements

The membranes were equilibrated for two days in 0.01 M alizarin Red S solutions. The potentials have been measured by varying the concentration of Alizarin Red S in the test solution in the range 1.0×10^{-10} to 1.0×10^{-2} M. The standard Alizarin Red S solution had been obtained by gradual dilution of 0.01 M Alizarin Red S solutions. The potential measurements were carried out at room temperature using saturated calomel electrodes (SCE) as a reference electrode with the following cell assembly:

SCE |test solution|| PVC membrane || 0.01 M Alizarin Red S| SCE

2.3. Fabrication of PVC membranes and sandwich PVC membranes

PVC membranes have been fabricated as suggested by Craggs et al. [29]. Membranes have been prepared by dissolving appropriate amounts of ionophore, cation additive (CTAB), plasticizers (DBP, o-NPOE, DOP, DEP, CN or TBP) and PVC in THF (5 mL). The components were added in terms of weight percentages. The homogeneous mixture obtained after complete dissolution of all components, was concentrated by evaporating THF at room temperature and then poured into polyacrylate rings placed on a smooth glass plate and glued to one end of a “Pyrex” glass tube. It is known that the sensitivity, linearity and selectivity obtained for the given ionophore depends significantly on the membrane composition and nature of plasticizer used [30]. Thus, the ratio of membrane ingredients, time of contact and concentration of equilibrating solution were optimized after a good deal of experimentation. Membranes which generate reproducible and stable potentials have been studied. The blank membranes having only PVC as membrane ingredients was also prepared and studied. While membrane having PVC plasticizer small potentials with slope of ≈5 mV were generated. The activities of ions were calculated from the modified form of the Debye-Huckel equation [31].

The sandwich membrane was fabricated by pressing two individual membranes (ordinarily one without ion-pair and one with the same components and an additional ion-pair) together immediately after blotting them individually dry with tissue paper. The obtained sandwich membrane was visibly checked for air bubbles before mounting on electrode body with the ion-pair-containing segment facing the sample solution. The combined segmented membrane was then rapidly mounted on to the electrode body and potentials were measured.

2.4. Synthesis of ion pair

The Alizarin Red-S-CTAB ion pair (Fig. 1) was prepared by the following method; 0.5g of Alizarin Red-S and 0.5g of CTAB were separately dissolve in 5 mL of dimethylformamide and then mixed. Then, 1mL of 0.5 mL HCL was added to the mixture. Under this condition, only the sulphonic group is dissociated, and thus, is capable of forming an ion pair, while the chelate-forming groups remain protected. Dilution of the mixture with water results in the precipitation of the ion pair in the form of a viscous oil. The ion pair was extracted by dichloromethane and dried at 70^{o}C.

2.5. Sample preparation

2.5. a. Determination of vanadium in water samples

A six times more concentration of alizarin was mixed with a 25 mL of tap water (spiked with 5, 100 and 500 ugL^{-1} of Vanadium). After complete color development the concentration of vanadium ion has been determined by indirect potentiometry using the proposed alizarin electrode.

2.5. b. Determination vanadium in soil samples

The soil samples were collected from Sidukul Industrial area Haridwar (S_1), Star paper mills Ltd Saharanpur (S_2) and Yamuna river sediment (S_3). An air dried homogenized soil sample (100 g) was weighed accurately and placed in a 100 mL Kjeldahl flask. The sample was digested in the presence of an oxidizing agent following the method recommended by Jackson [32]. The content of the flask was filtered through a whatman No. 40 filter paper into a 25 mL calibrated flask and made up to mark with de-ionized water.

2.5. c. Determination of zirconium in alloys

Dissolve 100 mg of alloy sample by heating with a mixture of 5 mL of concentrate nitric acid, 5 mL of concentrate hydrochloric acid and 5 mL of water. Evaporate the solution about 2 mL. The solution was filter through a whatman No. 40 filter paper into a 25 mL volumetric flask and make up to mark with de-ionized water.

2.5. d. Determination of molybdenum in geological samples

The geological samples were obtained from mineral testing laboratory, Earth science department IIT Roorkee. Sample (0.2g) was weighted into a platinum crucible; 1g of potassium hydrogensulphate was added and mixed. The mixture was fused at 550°C for 10 min, and then leached in a water bath with 10 mL of 4 M hydrochloric acid at 80°C until it melts. It was then crushed with a glass rod. After allowing the mixture to cool to room temperature and settle, 5 mL of the clear solution was transferred in to the beaker and adjust the pH about 3.6 by adding 5 mL of phthalate buffer, then 0.25 mL of 0.1 M citrate and 0.75 mL of 0.1 M EDTA as masking agents respectively.

3. RESULTS AND DISCUSSION

3.1. Response of different anions

In preliminary experiments, various PVC-membrane ion-selective electrodes with the synthesized ion pair were prepared and tested for different anions. The potential response of the electrode for different anions is shown in Fig. 2. The results exhibited significantly high selectivity to alizarin ion over other anions. Hence, ion pair was selected as a carrier for preparation of alizarin-selective electrode.

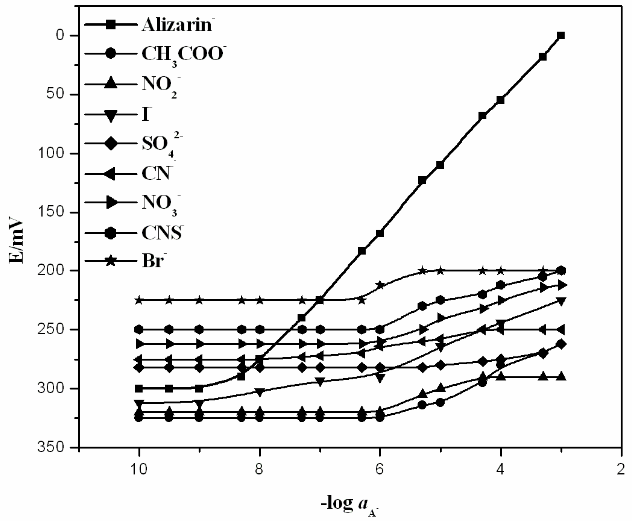

Figure 2. Variation of membrane potential with activity of alizarin ions of PVC based membranes of without plasticizers, with plasticizers, o-NPOE, DBP, DOP, DEP, CN and TBP.

Table 1. Optimized membrane compositions and their potentiometric response as in alizarin sensor.

Sensor no.	Composition (w/w, %)				Slope (mV decade^{-1} of activity)	Linear Range (M)	Detection limit (M)
	Ionophore	CTAB	Plasticizer	PVC			
1	0	3	64, DBP	33	N.M.	N.M.	0.0
2	6	0	62, DBP	32	52.8	7.5×10^{-5} to 1.0×10^{-3}	5.5×10^{-6}
3	6	3	0	91	64.5	6.3×10^{-4} to 1.0×10^{-3}	2.5×10^{-7}
4	6	3	60, DOP	31	65.3	7.8×10^{-5} to 1.0×10^{-3}	3.5×10^{-7}
5	6	3	60, CN	31	62.0	5.6×10^{-5} to 1.0×10^{-3}	1.5×10^{-8}
6	6	3	60, TBP	31	61.4	1.2×10^{-5} to 1.0×10^{-3}	5.0×10^{-6}
7	6	3	60, DBP	31	60.2	7.9×10^{-7} to 1.0×10^{-3}	5.0×10^{-6}
8	6	3	60, DEP	31	60.2	1.0×10^{-6} to 1.0×10^{-3}	5.0×10^{-7}
9	6	3	60, DEP	31	60.2	5.0×10^{-7} to 1.0×10^{-3}	2.5×10^{-7}
10	6	2	60, *o*-NPOE	32	59.6	6.4×10^{-7} to 1.0×10^{-3}	4.5×10^{-8}
11	6	1	61, *o*-NPOE	32	57.8	8.4×10^{-6} to 1.0×10^{-3}	5.0×10^{-7}
12	6	4	59, *o*-NPOE	31	62.3	5.7×10^{-7} to 1.0×10^{-3}	4.0×10^{-8}
13	5	2	61, *o*-NPOE	32	58.4	3.5×10^{-7} to 1.0×10^{-3}	3.1×10^{-8}
14	8	2	59, *o*-NPOE	31	59.2	7.3×10^{-7} to 1.0×10^{-3}	5.5×10^{-8}
15	7	2	60, *o*-NPOE	31	59.8	1.0×10^{-8} to 1.0×10^{-3}	3.0×10^{-9}

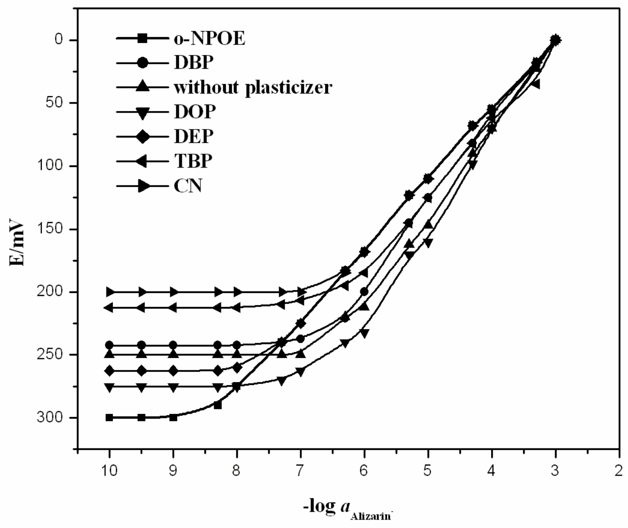

Figure 3. Potential responses of ion-selective membrane sensor for various anions.

3.2. The effect of membrane composition on potential response of the alizarin sensor

Potential of the membranes were investigated as a function of alizarin ion activity in the range 1.0×10^{-10} to 1.0×10^{-3} M and the results obtained are compiled in Tables 1 and Fig. 3. The electrodes with no carrier (containing PVC, plasticizer and CTAB) displayed insignificant sensitivity towards alizarin Red-S. The influence of plasticizer on the response characteristics of the alizarin electrode was investigated by using six plasticizers of different polarities including *o*-NPOE, DBP, DOP, DEP, CN and TBP. The sensor no. 3 having membranes without plasticizer exhibits a narrow working concentration range of 6.3 × 10^{-4} to 10^{-3} M with a sub Nernstian slope (64.5 mVdecade^{-1} of activity). Improvement in sensors performance was observed by the addition of plasticizer. Among the several membranes tested for each of the carriers, the membranes incorporating *o*-NPOE showed better potentiometric responses, i.e., higher sensitivity and wider linearity of the calibration plots (sensor nos. 10 and 15). It seems that *o*-NPOE, as a low polarity and a relatively high mobility, with respect to other plasticizers examined, provides appropriate conditions for incorporation of highly lipophilic alizarin ion. The addition of lipophilic cationic additive in anion selective membranes is necessary to introduce permselectivity [33]. The influence and concentration of the membrane additives was also investigated by incorporating CTAB into the membranes. The potentiometric sensitivity of the membranes based on ion-pair was greatly improved in the presence of CTAB as a lipophilic cationic additive, compared to the membranes with no additive at all. Previous studies have shown that there is an optimal concentration of lipophilic ionic additives in the membranes and that gives the best electrode performance. The effect of CTAB concentration in the membrane was investigated at several additive/ion-pair mole ratios. The sensor with CTAB/ion-pair mole ratio is ~ 0.55 for the carrier exhibited maximum sensitivity over a wide range of alizarin concentration.

3.3. Calibration characteristics

A membrane among the different membranes compositions has membrane with ion-pair (ARS-CTAB) /CTAB/PVC/ *o*-NPOE in (w/w, %) 7/2/31/60 showed highest sensitivity and widest linear range and were selected as the optimum composition for further studies (Fig. 4). These sensors exhibit the maximum working concentration range of 1.0 × 10^{-8} to 1.0 × 10^{-3} M with a slope of 59.8 mVdecade^{-1} of activity (Sensor no. 15, Table 1).

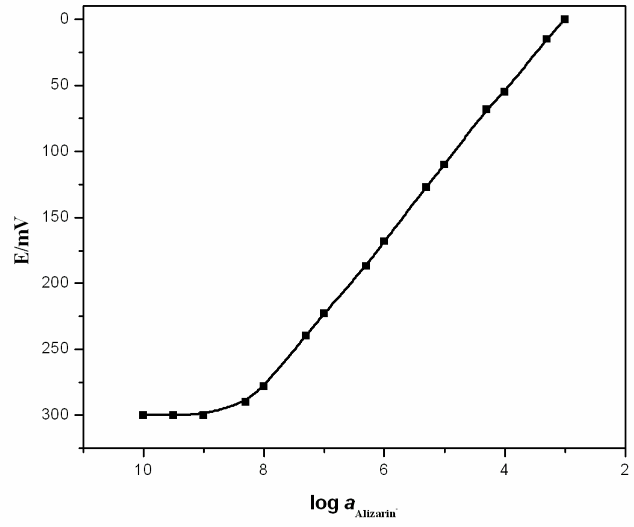

Figure 4. Calibration plot of alizarin-selective sensor based on Alizarin Red S-CTAB ion pair.

3.4. Effect of internal solution

The influence of the concentration of internal solution on the potential response of the polymeric membrane electrode for alizarin ion was studied. The concentration was varied from (1.0 × 10^{-1} to 1.0 × 10^{-5} M) and the potential response of the sensors has been observed. It was found that the best results in terms of slope and working concentration range have been obtained with internal solution of activity 1.0 × 10^{-2} M. Thus, 1.0 × 10^{-2} M concentration of the reference solution was quite appropriate for the smooth functioning of the proposed sensor.

3.5. Influence of pH on the on sensors performance

The influence of pH on the response of the potential was examined by use of 10^{-4} M and 10^{-5} M Alizarin Red-S solutions over the pH range 1.5-8.0. To adjust the pH, very small volumes of HNO_3 and NaOH were used. The results for ion pair are shown in Fig. 5, which indicated that the sensor exhibits a better response and extended linearity at lower pH values. In alkaline media, the potentiometric response properties of the electrode slightly deteriorated due to hydroxide may be deprotonation of alizarin ion. The working pH range is 2.0-5.0.

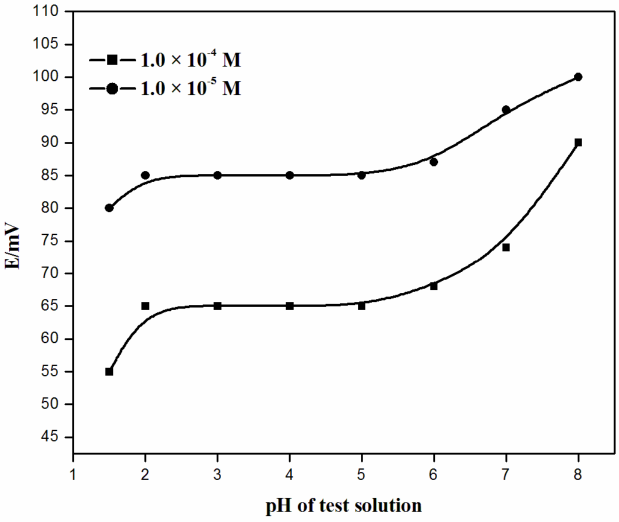

Figure 5. Effect of pH on potential response of the alizarin ion-selective sensor.

3.6. Lifetime of proposed sensor

The lifetime of the sensor (no. 15), which is a measure of sensor durability, was studied over a 4 months period. During this period, the electrode was daily used over extended period (2 h per day), and its slopes and detection limits have been measured. After 3 months changes were observed in the slope (from 59.2 to 58.6 mV/decade of activity) and detection limit (1.9 × 10^{-7} to 2.5 × 10^{-5} M). The reproducibility of the proposed alizarin sensor was also investigated. The standard deviations of 10 replicate measurements at 1.0×10^{-3} and 1.0×10^{-4} M were ± 0.24 and ± 0.38 mV/decade, respectively. The ion pair is sufficiently lipophilic i.e. insolubility in aqueous solution. This factor imparts no leaching (loss of components) from the membrane and produces a long and stable response. After life time period the membrane became mechanically weak, therefore deviation in potential occurs and slight gradual decrease in slope. It is important to emphasize that sensors were stored in 0.01 M alizarin solutions when not in use.

3.7. The Dynamic response time behavior of the proposed electrode

Dynamic response time is an important factor for Alizarin sensitive sensor. In this study, the practical response time has been recorded (for sensor no. 15) by changing solutions with different alizarin Red-S^- concentrations. The measurement sequence was from the lower (1.0×10^{-6} M) to the higher (1.0×10^{-3} M) concentration. The actual potential versus time traces is shown in Fig. 6. As it is seen, the electrode reached the equilibrium response in a very short time of about 10 s. To evaluate the reversibility of the electrode, a similar procedure in the opposite direction was adopted. The measurements have been performed in the sequence of high-to-low from (1.0×10^{-4} to 1.0×10^{-5} M) sample concentrations. The results showed that, the potentiometric response of the electrodes was reversible; although the time needed to reach equilibrium values (40 s) were longer than that of low-to high sample concentrations.

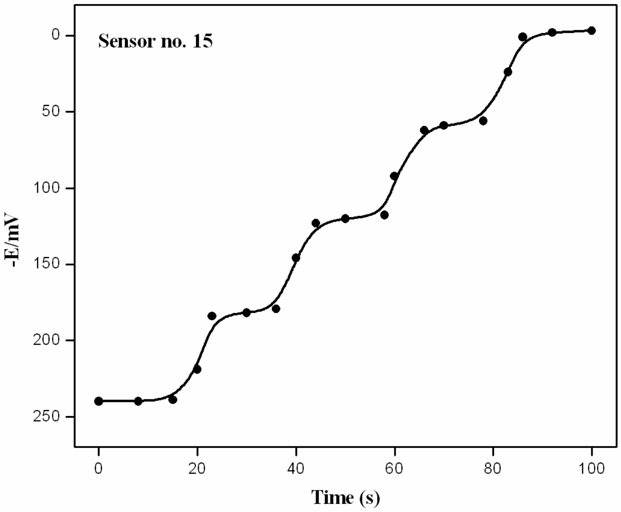

Figure 6. Dynamic response of the membrane sensor based on Alizarin Red S-CTAB ion pair.

3.8. Determination of formation constant

Formation constant of the ion–pair complex within the membrane phase is a very important parameter that dictates the practical selectivity of the sensor. In this method, two membrane segments are fused together, with only one containing the ion-pair, to give a concentration-polarized sandwich membrane. A membrane potential measurement of this transient condition reveals the ion activity ratio at both interfaces, which translates into the apparent binding constants of the ion–pair complex [38]. In this method complex formation constants obtained by neglecting ion pairing. As reported, the membrane potential E_M is determined by subtracting the cell potential for a membrane without ion-pair from that for the sandwich membrane. The formation constant is then calculated from the following equation:

$$\beta_{IL_n} = \left(L_T - \frac{nR_T}{Z_I} \right)^{-n} \exp \left(\frac{E_M z_I F}{RT} \right) \tag{2}$$

Where L_T is the total concentration of ion-pair in the membrane segment, R_T is the concentration of lipophilic ionicsite additives, n is the ion–ion-pair complex stoichiometry, and R, T and F are the gas constant, the absolute temperature, and the Faraday constant. The ion I carries a charge of z_I. The determined formation constants (log β_{ILn}) for the examined different complexes were recorded in Table 2. The elapsed time between sandwich fusion and exposure to electrolyte was typically <1 min. The potential was recorded as the mean of the last minute of a 5 min measurement period in the appropriate salt solution. The potential of such sandwich membranes remains free of diffusion-induced potential drifts for about 20 min. Standard deviations were obtained based on the measurements of sets of at least three replicate membrane disks that were made from the same parent membrane. A careful analysis of the data in Table 2 reveals that alizarin ion has significant anionic-binding characteristics.

Table 2. Formation constants of ion pair (alizarin Red-S-CTAB) in segmented sandwich-PVC membrane with different anions.

Anions	Formation constant (log β_{ILn})*
SCN^-	2.2
CN^-	2.3
Sal^-	1.8
ClO_4^-	1.5
I^-	1.8
NO_2^-	2.2
OH^-	2.0
Br^-	2.7
SO_4^{2-}	2.6
Cl^-	2.9
NO_3^-	3.1
HPO_4^{2-}	3.0
CH_3COO^-	2.8
Cit^{3-}	2.6
HCO_3^-	2.1
$C_2O_4^{2-}$	1.9
Alizarin	6.7

*R.S.D. < 1.3, n = 5

Table 3. Selectivity coefficients of alizarin selective sensor.

Interfering ion (B)	Selectivity coefficient (-log $k^{Pot}_{Alizarin^-,B}$) (MPM) Sensor No. 15	(FIM) Sensor No. 15
SCN^-	3.78	3.86
CN^-	3.85	3.90
Sal^-	3.05	3.07
ClO_4^-	2.96	3.01
I^-	3.01	3.08
NO_2^-	3.80	3.81
OH^-	3.3 1	3.68
Br^-	3.48	3.72
SO_4^{2-}	4.24	4.41
Cl^-	4.62	4.98
NO_3^-	4.52	4.82
HPO_4^{2-}	4.51	4.81
CH_3COO^-	4.56	4.85
Cit^{3-}	4.58	4.90
HCO_3^-	3.06	3.12
$C_2O_4^{2-}$	3.01	3.08

3.9. Selectivity of ion sensing membranes

The Selectivity is an important characteristic of a sensor that delineates the extent to which the device may be used in the estimation of analyte ion in the presence of other ions and extent of utility of any sensor in real sample measurement. In this work, the selectivity coefficients of the sensor toward different anionic species (A^{n-}) were evaluated by using both the matched potential method (MPM) [34, 35] and the fixed interference method (FIM) [36]. In the MPM, the selectivity coefficient ($K^{Pot}_{Alizarin,B}$) was determined by measuring the change in potential upon increasing the primary ion (Alizarin Red-S^-) activity from an initial value of a_{Alizarin} to a'_{Alizarin} and a_{B} represents the activity of interfering ion added to the reference solution of primary ion of activity a_{Alizarin} which also brings about same potential change. It is given by expression:

$$K^{pot}_{Alizarin,\ B} = \frac{\Delta a_{Alizarin}}{a_B} = \frac{a'_{Alizarin} - a_{Alizarin}}{a_B} \qquad (1)$$

Table 4. Comparison of the potentiometric parameters of the proposed Alizarin-sensor with the literature reported Alizarin sensor.

Ref. no.	Ionophore name	Linear Range (M)	Slope (mV/decade of activity)	pH range	Selectivity coefficients (-log $k^{Pot}_{Alizarin^-,B}$)	Response time (s)
[23]	Alizarin S & its salt (Trioctylmethylammonium chloride, triheptyldodecyl ammonium iodide)	2.0×10^{-4} to 5.0×10^{-7}	57	2 to 4.2	NO_3^- (5.03), SCN^- (3.55), ClO_4^- (2.44), I^- (3.72), *by MPM method.*	30
[This work]	Alizarin Red S-CTAB (Ion pair)	1.0×10^{-8} to 1.0×10^{-3}	59.8	2 to 5	SCN^- (3.78), CN^- (3.85), Sal^- (3.05), ClO_4^- (2.96), I^- (3.01), NO_2^- (3.80), OH^- (3.31), Br^-(3.48), SO_4^{2-} (4.24), Cl^- (4.62), NO_3^- (4.52), HPO_4^{2-} (4.51), CH_3COO^- (4.56), Cit^{3-}(4.58), HCO_3^-(3.06), $C_2O_4^{2-}$(3.01); *by MPM method*	<10

Table 5. Performance of sensor no. 15 in partially non-aqueous media.

Non-aqueous content (%v/v)	Working concentration range (M)	Slope (mV decade^{-1} activity)
0	1.0×10^{-8}-1.0×10^{-3}	59.2
Methanol		
10	1.0×10^{-8}-1.0×10^{-3}	59.8
20	5.0×10^{-8}-1.0×10^{-3}	59.8
30	4.2×10^{-7}-1.0×10^{-3}	58.4
35	1.5×10^{-7}-1.0×10^{-3}	56.5
Ethanol		
10	1.0×10^{-8}-1.0×10^{-3}	59.8
20	6.1×10^{-8}-1.0×10^{-3}	59.0
30	3.8×10^{-7}-1.0×10^{-3}	58.2
35	5.2×10^{-6}-1.0×10^{-3}	55.9
Acetonitrile		
10	1.0×10^{-8}-1.0×10^{-3}	59.8
20	5.3×10^{-8}-1.0×10^{-3}	59.8
30	5.3×10^{-7}-1.0×10^{-3}	57.6
35	5.3×10^{-7}-1.0×10^{-3}	57.0

In the present studies a_I and a'_I were kept at 1.0×10^{-4} and 5.0×10^{-4} M alizarin$^-$ and a_B was experimentally determined. FIM is the most widely used procedure as per IUPAC recommendation for determining selectivity coefficients [37]. In the FIM, the selectivity coefficient was evaluated from potential measurement on solutions containing a fixed concentration of interfering ion (1.0×10^{-3} M) and varying amount of alizarin$^-$ ions. The values of selectivity coefficient so determined are compiled in Table 3. A value of selectivity coefficient equal to 1.0 indicates equal response to both primary ion and interfering ions. If the value of selectivity coefficient is smaller than 1.0 it shows that the sensor is selective to the primary ion over the interfering ions. It is seen from the Table 3, that the selectivity coefficients determined by both the methods are sufficiently smaller than 1.0 indicating that the present sensor are significantly selective to alizarin Red-S ion over all the interfering ions. Thus sensor no. 15 was compared with some reported Alizarin selective sensors (Table 4). It is seen that the selectivity, working concentration range and `pH range of the proposed sensor toward Alizarin is better as compared to reported sensors.

3.10. Solvent effect

The real sample may contain non-aqueous content, so the performance of the sensor was also investigated in partially non-aqueous media using 10%, 20%, 30%, and 35% using non-aqueous content in methanol-water, ethanol-water and acetonitrile-water mixtures up to 20% (v/v) non-aqueous contents. However, it is clear from Table 5 above 20% non-aqueous content, potentials show drift with time. The drift in potentials in the organic phase may be probably due to leaching of ionophore at higher organic content.

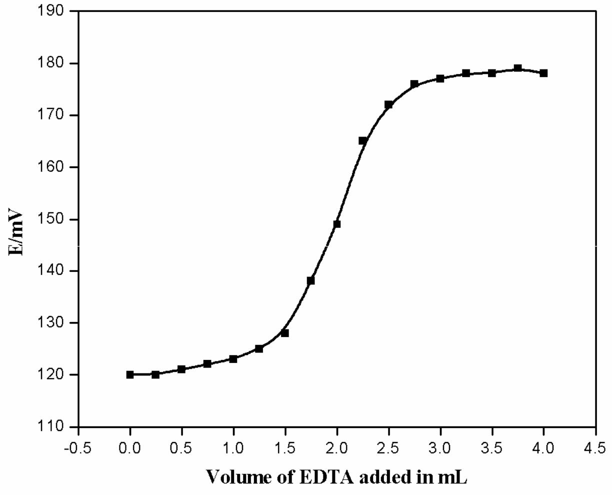

Figure 7. Potentiometric titration curve for 20 mL of 1.0×10^{-4} mol L^{-1} Alizarin with 1.0×10^{-3} molL^{-1} EDTA using the proposed sensor (no. 15).

4. ANALYTICAL APPLICATION OF ALIZARIN ELECTRODE

4.1. Titration of alizarin Red-S solution with a standard EDTA solution

The proposed alizarin membrane sensor (no. 15) was found to work well under laboratory conditions. It was applied successfully as an indicator electrode in the potentiometric titration of 20 mL of 1.0×10^{-4} $\mathrm{molL^{-1}}$ alizarin Red-S with 1.0×10^{-3} $\mathrm{molL^{-1}}$ EDTA and the resulting titration curve are shown in Fig. 7. As can be seen, the amount of alizarin can be determined with sensor.

4.2. Determination of vanadium in water and soil samples

The sensor was used for the determination of vanadium in tap water and soil samples using indirect potensiometry. The preparation of sample was done according to above procedure (2.5a, 2.5.b). These samples were immediately treated or stored for a short time in the dark at 4°C until analyzed. The results observed for analysis of water and soil samples are listed in Table 6 and 7; the recovery within 99.5 to 102.0 %. The results obtained were also compared with those from AAS analyzed. It is clear from the values in Table 6 and 7 that these were in a good agreement with those obtained by AAS. Hence, the sensor can be successfully employed for the estimation of vanadium ion.

Table 6. Determination of vanadium in water samples using proposed sensor.

Sample	Added (μgL^{-1})	Found by proposed sensor (μgL^{-1})	Found by AAS (μgL^{-1})	Recovery ± SD (%)
	6	6.05	5.86	100 ± 0.2
Roorkee City	100	101.05	99.52	99.9 ± 0.1
	500	502.0	500.32	100 ± 0.1

Table 7. Determination of vanadium in surface soil samples using proposed sensor.

Sample No.	Vanadium ($\mu g\ g^{-1}$) by proposed sensor	Found by AAS ($\mu g\ g^{-1}$)
S_1	0.02	0.03
S_2	0.05	0.07
S_3	0.06	0.06

4.3. Determination of zirconium in alloys

The sensor has been successfully applied for determination of zirconium in alloys using indirect potensiometry. The sample preparation was done according to procedure (2.5.c). The alizarin red-S has already been used as a complexing agent for Zirconium [18, 19, and 20] and normally a six-fold concentration of the alizarin reagent was used. In the present method the concentration of zirconium cations has been determined by indirect potensiometry using the proposed electrode. The results obtained are present in Table 8 and also validated using AAS. These results were compared with those from AAS analyzed. It can be seen that, the results obtained by the proposed electrode were in good agreement with those obtained by the AAS.

Table 8. Potentiometric determination of zirconium using proposed sensor in zirconium-oxygen alloys.

Sample No.	Suggested method, (μgL^{-1})	AAS (μgL^{-1})
1	5.4	6.8
2	12.2	14.8
3	28.4	15.0

4.4. Determination of molybdenum in geological samples

The sensor was successfully applied for determination of molybdenum in geological samples using indirect potensiometry. The sample preparation was done according to procedure (2.5.d). The alizarin red-S has already been used as a chelating agent for molybdenum [22]. The analytical result for geological sample was listed in Table 9; shows that these were in a good agreement with those obtained by AAS. Hence, the sensor can be successfully employed for the estimation of molybdenum ion.

Table 9. Determination of molybdenum in geological samples using proposed sensor.

Sample No.	Added (μg L^{-1})	Found by proposed sensor (μg L^{-1})	Found by AAS (μgL^{-1})
97834 (75-P-5)	0	25.4	24.4
	100.0	124.4	122.8
97893 (75-P-17)	0	56.2	54.2
	100	152	150
97895 (75-P-35)	0	51.4	49.4
	100	150	149

5. CONCLUSIONS

Our study has shown that alizarin Red-S-CTAB ion pair used as carrier, o-NPOE as a solvent mediator and PVC matrix as been developed. The electrode can be used to determine alizarin Red-S anions in the concentration range 1.0×10^{-8} to 1.0×10^{-3} M with a Nernstian slope of 59.8 mV decade^{-1} of activity. The electrode works in a relatively wide, independent pH range 2 to 5, and exhibits a fast response, high sensitivity and selectivity for alizarin anions. The proposed electrode was successfully applied to the determination of vanadium in water and soil, zirconium in alloys and molybdenum in geological samples by indirect potentiometry. The results obtained show a satisfactory agreement with those obtained using independent AAS method.

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