UO_2^{2+} Ion-Selective Membrane Electrode Based on a Naphthol-Derivative Schiff's Base 2,2'-[1,2-Ethandiyl bis(nitriloethylidene)]bis(1-naphthalene)

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Received September 2, 2003

A new PVC membrane electrode for UO_2^{2+} ion based on 2,2'-[1,2-ethanediyl bis (nitriloethylidene)]bis(1-naphthalene) as a suitable ionophore was prepared. The electrode exhibites a Nernstian response for UO_2^{2+} ion over a wide concentration range (1.0×10^{-1}-1.0×10^{-7} M) with a slope of 28.5 ± 0.8 mV/decade. The limit of detection is 7.0×10^{-8} M. The electrode has a response time of < 20 s and a useful working pH range of 3-4. The proposed membrane sensor shows good discriminating abilities towards UO_2^{2+} ion with regard to several alkali, alkaline earth transition and heavy metal ions. It was successfully used to the recovery of uranyl ion from, tap water and, as an indicator electrode, in potentiometric titration of UO_2^{2+} ion with Piroxycam.

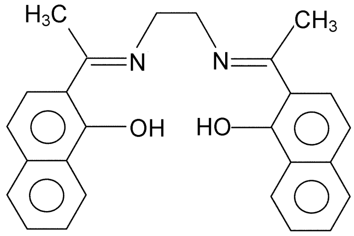
Key Words : UO_2^{2+} ion-selective electrode, PVC membrane, Schiff's base, Potentiometry

Introduction

A large number of ion-selective electrodes based on natural or synthetic ionophores, which form selective complexes with the ions of interest, have been reported over the last three decades.[1-4] There has been an increasing interest in the preparation of molecular carriers possessing electrical neutrality, lipophilic character and capability to selectively and reversibly bind metal ions to induce a selective permeation of one metal ion through the membrane electrodes.[1,4-6] The Schiff's bases derived from salicyladehyde (Salens) are among the polydentate ligands that form very stable complexes with different cations.[7-9] The resulting Salen complexes have attracted increasing attention, mainly due to their peculiar properties[8-10] and their reactivity mainly in the area of binding of small molecules.[11,12] We have recently reported the successful of some Schiff's base complexes with Fe^{3+},[13] Zn^{2+} [14] and Cd^{2+} [15] complexes as suitable carriers for the preparation of new potentiometric sensors for I^-, SO_4^{2-} and SCN^- ions, respectively.

Due to the relatively high mobility of uranium in surface and near surface environments, its measurement in trace amounts in natural waters could used as a basis for geochemical exploration[16] and some industrial processes.[17-19] Thus, in the last decade, several uranyl ion-selective electrodes have been introduced,[20-28] and search for suitable ionophores for the preparation of new UO_2^{2+} membrane sensors of high selectivity and very low limit of detection is still a challenging task. In this work we discovered that the Schiff's base 2,2'-[1,2-ethanediylbis(nitriloethylidene)]bis(1-naphthalene) (Salen I) can be used as an excellent ionophore to prepare a highly selective and sensitive PVC-membrane sensor for UO_2^{2+} ion.

Salen I



Experimental Section

Reagents. Reagent grade nitrophenyl octyl ether (NPOE), dimethyl sabacate (DMS), dioctyl phthalate (DOP), dibutyl phthalate (DBP), sodium tetraphenylborate (NaTPB), potassium tetrakis(4-chlorophenyl)borate (KTClPB), high relative molecular weight PVC and tetrahydydrofuran (THF) were purchased from Fluka chemical company and used as received. Reagent grade nitrate salts of the cations used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying. Salen I was synthesized and purified as described elsewhere.[29] Doubly distilled deionized water was used throughout.

Electrode Preparation. Membrane electrodes were prepared by thorough mixing of 4.0 mg of Salen I, 30.5 mg of powdered PVC, 63.5 mg of plasticizer DOP and 2.0 mg of additive NaTPB in 2 mL of THF. The resulting clear mixture was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3 mm o.d. on top) was dipped into the mixture for about 10 s so that a nontransparent membrane of about 0.3 mm thick was formed. The tube was then pulled out from the mixture and kept at room temperature for about 2 h. The tube was then filled with an internal filling solution (1.0×10^{-3} M UO_2^{2+}). The electrode was finally conditioned in a 1.0×10^{-3} M solution of uranyl ion overnight.

Emf Measurements. All emf measurements were carried out with the following cell assembly:

Ag-AgCl/KCl (3 M) | internal solution, 1.0×10^{-3} M $UO_2(NO_3)_2$ | PVC membrane | test solution | Hg-$HgCl_2$, KCl (satd)

The emf observations were made relative to a double-junction saturated calomel electrode (SCE, Philips) with the chamber with an ammonium nitrate solution. A double-junction silver/silver chloride electrode (Metrohm) containing a 3 M solution of KCl was used as the internal reference electrode. Activities were calculated according to the Debye-Hückel procedure.

Results and Discussion

The Schiff's bases derived from salicyladehyde polydentate ligands (Salens) have been shown to form stable complexes with UO_2^{2+} ion.[30,31] The resulting uranyl complexes have been used as neutral ionophores for the preparation of $H_2PO_4^-$ [31] and NO_2^- anions.[32] Salen I is an O_2-N_2 donating Schiff's base which is insoluble in water. Thus, in contrast to water soluble Salen derivatives acting as a bivalent anion in chelate formation with transition metal ions,[8,9,12] the naphthol derivative Salen I used in this study presumably acts as a neutral chelating agent in the membrane system.[33]

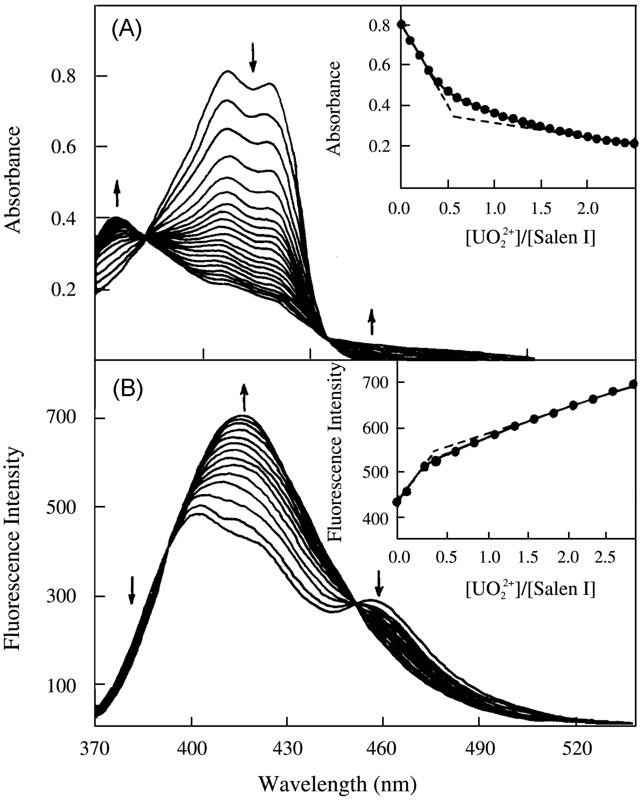


Figure 1. Absorption (A) and fluorescence (B) spectra of a 5.0×10^{-5} M solution of Salen I in acetonitrile upon addition of increasing amount of uranyl ion. The corresponding mole ratio plots are shown in the insets of A and B.

In order to obtain a clue about the stoichiometry and stability of the Salen I- uranyl ion complex, in preliminary studies, we investigated the complexation of Salen I with UO_2^{2+} ion in acetonitrile solution both spectrophotometrically and spectrofluorimetrically. In these experiments, the Salen I concentration in acetonitrile was kept constant at 5.0×10^{-5} M and a concentrated UO_2^{2+} solution in the same solvent was added while the absorbance and fluorescence intensity of the resulting solution at various UO_2^{2+}/Salen I mole ratios were measured, until a desired mole ratio is reached. The corresponding spectra and the resulting mole ratio plots are shown in Figure 1. As is obvious from Figure 1, both the absorption and fluorescence spectra of Salen I show distinct changes upon complexation with uranyl ion in solution. In both cases, the resulting mole ratio plots are indicative of the formation of a stable 2 : 1 (Salen I : UO_2^{2+}) complex in acetonitrile solution. The overall stability constant of the 2 : 1 complex was evaluated from the computer fitting of absorbance and fluorescence intensity vs cation-to-ligand mole ratio to the corresponding equations.[34,35] The resulting log β_2 values are 10.8 ± 0.3 (spectrophotometry) and 11.1 ± 0.4 (spectrofluorimetry). Based on the above observations, we decided to examine the capability of Salen I as a very suitable UO_2^{2+} complexing agent for the construction of a new uranyl ion-selective electrode.

Thus, in preliminary experiments, Salen I was used as a potential neutral ionophore for the preparation of PVC membrane ion-selective electrodes for a variety of metal ions, including alkali, alkaline earth, transition and heavy

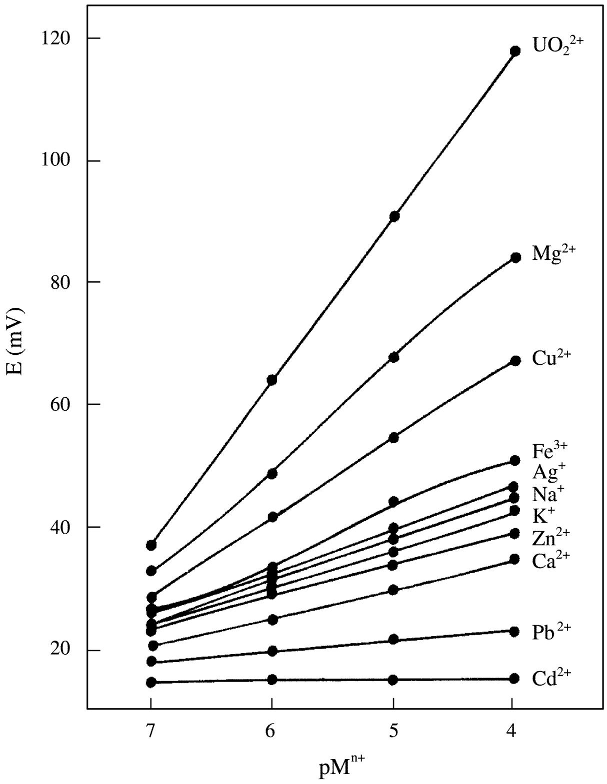


Figure 2. Emf-pM^{n+} plots for different cation-selective electrodes based on Salen I.

metal ions. The potential responses obtained for different ion-selective electrodes in the range of 1.0×10^{-4} to 1.0×10^{-7} M are shown in Figure 2. As can be seen, among different cations examined, UO_2^{2+} with the most sensitive response seems to be suitably determined with the membrane electrode based on the Schiff's base used.

Optimum membrane ingredients were tested by changing the plasticizer/PVC ratio from 0.5 to 2.5, while keeping the amount of ionophore constant (i.e., 4.0%). The most sensitive, reproducible and stable results were obtained at a plasticizer/PVC ratio of about 2. It is reported that the response characteristics of ion-selective electrodes are largely affected by the nature of plasticizer used.[13-15,20-28,36] This is due to the influence of the plasticizer on the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands.[36,37] Thus, in the present work, we examined DOP, DBP, DMS and NPOE as plasticizer while keeping the membrane composition and nature of other ingredients constant. The slopes of the resulting potential responses, in the UO_2^{2+} concentration range of 1.0×10^{-7} to 1.0×10^{-4} M, for the electrodes based on DOP, DBP, DMS and NPOE were found to be 28.5, 22.6, 18.2 and 20.9 mV/decade, respectively. Thus, DOP was selected as the best plasticizer for the preparation of UO_2^{2+}-selective PVC-membrane.

The optimization of permselectivity of the PVC-membrane electrodes is known to be highly dependent on the incorporation of additional membrane compounds.[36] In fact, it has been clearly demonstrated that the presence of the negatively charged lipophilic additives improves the potentiometric behavior of certain cation-selective electrodes. This is possible not only by reducing the ohmic resistance[38,39] and improving the response behavior and selectivity[40,41] but also, in cases where the extraction capability of the ionophore is poor, by enhancing the sensitivity of the membrane sensor.[42] Moreover, the lipophilic additives may catalyze the exchange kinetics at the sample-membrane interface.[43] In the present work, we tested NaTBP and KTClPB as lipophilic additives and found that the use of 2% NaTPB resulted in a Nernstian behavior (*i.e.*, slope = 28.5 mV/decade) and improved linearity, selectivity and stability of the electrode response. It should be noted that, in the absence of NaTPB, the slope of the resulting potential response was at the most 20.8 mV/decade. Thus, membranes with optimized PVC : DOP : Salen I : NaTPB percent ratio of 30.5 : 63.5 : 4.0 : 2.0 were prepared for further studies.

The influence of internal solution concentration was investigated by changing the concentration of UO_2^{2+} from 1.0×10^{-2} to 1.0×10^{-4} M and measuring the potential response of the proposed electrode. It was found that variation of the concentration of the internal solution does not cause any significant difference in the potential response of the electrode, except for an unexpected change in the intercept of the resulting Nernstian plots. A 1.0×10^{-3} M concentration of internal UO_2^{2+} solution is quite appropriate for proper functioning of the electrode.

The static response time of the electrode was studied by plotting the emf response of the electrode versus time, at various concentrations of the uranyl ion, and it was found to be < 20 s over the entire concentration range tested. This is actually the average time required for the electrode to reach a potential within ± 1 mV of the equilibrium value after successive immersion of a series of UO_2^{2+} ions, each having a tenfold difference in concentration. The optimum conditioning time for the membrane electrode in a 1.0×10^{-3} M $UO_2(NO_3)_2$ solution was 20 h, after which it generated stable potentials in contact with uranyl ion solutions. The membrane electrode was used practically for 2 months, at stretch, without any significant change in response time, slope or detection limit.

The influence of pH of test solution on the potential response of the proposed electrode at an uranyl concentration of 1.0×10^{-4} M was also investigated, in a pH range of 2.0-9.5. The pH was adjusted by introducing small drops of 0.1 M solutions of nitric acid or sodium hydroxide. The results revealed that the potential response is independent of the pH of test solution at a pH range 3.0-4.0. At higher pH values, the hydroxyl complexes of UO_2^{2+} ion can be formed or precipitate out[44] and, therefore, the emf diminished significantly. On the other hand, at pH < 3.0, the membrane suffered a strong interference from hydrogen ion due to the protonation of the Schiff's base.

The emf response of the membrane electrode at varying concentration of UO_2^{2+} ion (Figure 3) indicated a rectilinear range from 1.0×10^{-7} to 1.0×10^{-1} M. The slopes of the calibration curves were 28.5 ± 0.9 mV/decade. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 7.0×10^{-8} M. The standard deviation of ten replicate potential measurements was ± 0.5 mV.

In addition to the Nernstian behavior, linear dynamic range, detection limit and response time, the selectivity of the potentiometric membrane electrodes is also of fundamental importance in their practical applications. To assess

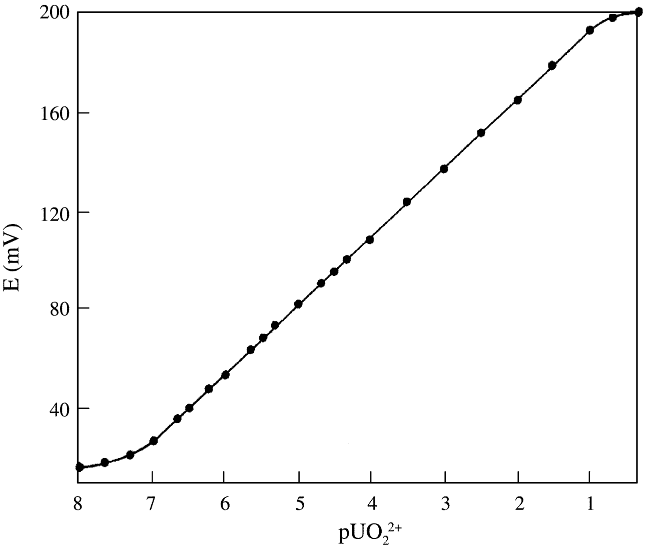


Figure 3. Calibration graph for the UO_2^{2+} ion-selective electrode.

Table 1. Selectivity coefficients of various interfering ions

Reference	Logarithm of Selectivity Coefficient											
	Na^+	K^+	Ag^+	Mg^{2+}	Ca^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}	Cd^{2+}	Fe^{3+}
This work	−1.9	−2.0	−1.5	−1.2	−1.5	−3.1	−3.0	−2.1	−1.8	−2.9	−3.4	−1.7
20	–	–	–	–	−2.0	−3.0	–	−2.8	–	–	–	+0.36
22	−2.1	–	–	−2.1	−2.6	−2.8	2.0	2.2	–	–	–	−0.23
25	−0.30	−0.47	–	−0.49	−0.49	–	−0.60	−0.60	–	−0.60	–	−0.66
26	+1.60	+0.38	–	−2.0	−1.9	−1.9	−1.8	−1.8	–	−1.6	–	−2.4
27	–	–	–	–	–	−1.20	−1.32	−1.47	–	–	–	−0.78
28	<−4	−1.8	–	<−4	<−4	−2.8	−1.9	−1.9	–	<−4	–	−1.4

the selectivity of the proposed urany ion-selective electrode over other cations, M^{n+}, the method of matched potential method (MPM) was employed.[45] This is a recently recommended procedure which gets ride of the Nicolski-Eisenman equation for the determination of potentiometric selectivity coefficients, including non-Nernstian behavior of interfering ions, inequality of charged and activity dependence of potential values.

According this method,[45] a specified activity (concentration) of the primary ion A (5.0×10^{-6} M UO_2^{2+}) is added to a reference solution (5.0×10^{-7} M UO_2^{2+}) and the potential is measured. In a separate experiment, the interfering ions B are successively added to an identical reference solution (from 5.0×10^{-6} M to 5.0×10^{-2} M M^{n+}), until the measured potential matches the one obtained before by adding the primary ions. The selectivity coefficient, $K_{A,B}^{MPM}$, is then calculated by the resulting primary ion to interfering ion activity ratio, $K_{A,B}^{MPM} = a_A/a_B$.

The resulting $K_{A,B}^{MPM}$ values obtained for the proposed uranyl ion-selective electrode are listed in Table 1. The selectivity coefficients for the previously reported uranyl ion-selective electrodes are also included in Table 1 for comparison, although this could be only a rough comparison because of different methods employed for the determination of the selectivity coefficients. As is obvious from Table 1, for all cations tested, the selectivity coefficients are in the order of 10^{-2} or smaller, which seem to indicate that disturbance produced by these ions in the functioning of the proposed electrode is negligible. It is noteworthy that, a comparison between the selectivity coefficients obtained for the proposed electrode with those previously reported for other uranyl-selective electrodes indicated that the proposed electrodes is superior, in the case of transition metal ion interferences. While, in the case of alkali and alkaline earth interferences, it is somewhat similar, in some cases, or weaker, in few others. Moreover, the linear range and limit of detection of the proposed electrode are significantly improved with respect to the previously reported PVC-membrane electrodes for uranyl ion.[20-28]

The proposed UO_2^{2+} ion-selective electrode was found to work well under laboratory conditions. The recovery of UO_2^{2+} ion from tap water samples in the range of 10 to 100 μg mL^{-1} by the electrode was found to be in the range of 98% to 101%. It was also successfully applied, as an indicator electrode, to the titration of 25.0 mL of 4.0×10^{-4} M UO_2^{2+} solution with 1.0×10^{-3} M Piroxycam and the resulting titration curve is shown in Figure 4. It is seen that the concentration of uranyl ion in solution can be accurately determined with the electrode.

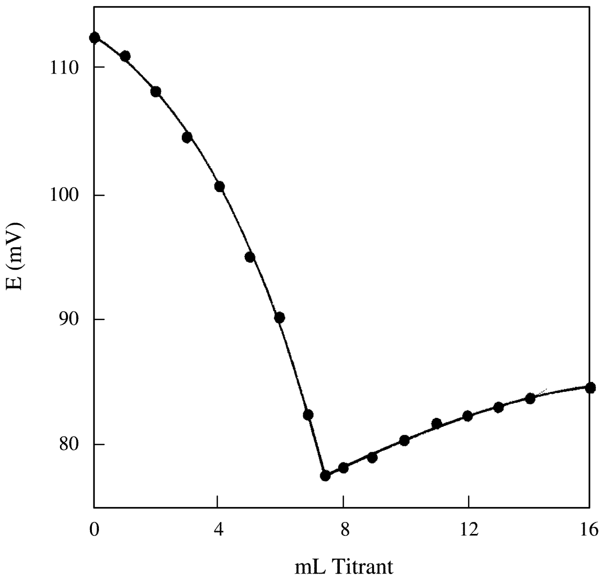


Figure 4. Potentiometric titration curve for 25.0 mL of 4.0×10^{-4} M UO_2^{2+} with a 1.0×10^{-3} M piroxycam, using the proposed sensor as an indicator electrode.

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