

SalphenH₂ as a Neutral Carrier for the Uranyl Ion-Selective PVC Membrane Sensor

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The complexation of *N,N'*-4,5-(ethylenedioxy)benzenebis(salicylideneimine), (salphenH₂) with uranyl ion was studied in acetonitrile solution spectrophotometrically, and the formation constant of the resulting 1 : 1 complex was evaluated. The salphenH₂ ligand was used as an ionophore in plasticized poly(vinyl chloride) (PVC) matrix membrane sensor for uranyl ion. The prepared sensors exhibited a near Nernstian response, 28.0-30.9 mV/decade for uranyl ion over the concentration range 1.0×10^{-2} to 1.0×10^{-6} M with a limit of detection of 3.2×10^{-7} M. The proposed electrode could be used at a working pH range of 1.5-4.0.

Key Words : Uranyl ion sensor, Potentiometry, PVC membrane, SalphenH₂ ionophore

Introduction

Uranium is extensively used in the nuclear industry and is highly radioactive. It presents in low level ($10^{-5} \sim 10^{-3}$ M) in wash streams coming out of nuclear reactors. Thus the constant monitoring of the streams for the presence of uranium in high activity content is essential.^{1,2} Several analytical methods, such as spectrophotometry and fluorometry have been used for uranium quantification.³

On the other hand, the potentiometric sensor based on ionophore-impregnated PVC membrane has the specific advantages of covering a wide range of concentrations, elimination of prior separation from the impurities, high sensitivity, accuracy and precision, and low cost.⁴ Efforts made so far developing uranyl-selective electrodes make use of organo-phosphorous compounds,⁵⁻⁸ a thiourea-based resin,⁹ a calix[6]arene derivative^{10,11} and some acyclic and cyclic polyethers.¹²

The Schiff base, salphenH₂ derived from salicylaldehyde and *ortho*-diamine as N₂O₂-tetradentate ligand has been known to form very stable complex with uranyl ion. SalphenH₂-uranyl complexes behave as electrically neutral and hard Lewis acids, which have been applied to the recognition of anions¹³⁻¹⁵ and neutral molecules,¹⁶⁻¹⁸ and also ditopic devices.¹⁹⁻²⁰ However, despite the extensive reports on the synthesis and characterization of the salphenH₂-uranyl complexes, to our best knowledge, no one has reported on the use of salphenH₂ molecules as ionophores in

uranyl ion-selective electrode.

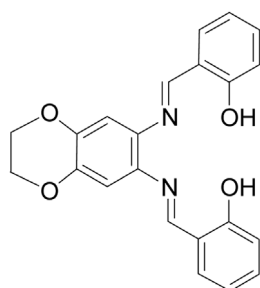
In the present work, we found that the recently synthesized lipophilic salphenH₂ can form highly selective 1 : 1 complex with uranyl ion in acetonitrile solution. Thus, we examined the salphenH₂ as a neutral ionophore for the preparation of PVC-based membrane sensors for UO₂²⁺. The proposed membrane resulted in the theoretical response characteristics and excellent selectivity for uranyl ion.

Experimental Section

Reagents. Potassium tetrakis(4-chlorophenyl)borate (KTpClPB), *o*-nitrophenyl octyl ether (*o*-NPOE) and high relative molecular weight PVC were obtained from Fluka. Dioctylphthalate (DOP), tris(2-ethylhexyl) phosphate (TEHP) and tetrahydrofuran (THF) were purchased from Aldrich. All other chemicals were of analytical grade reagents. All solutions were prepared in doubly distilled water and solutions of different concentrations were made by diluting 0.1 M stock solutions prepared from the corresponding metal nitrates and maintained at a pH of 3.5 by addition of nitric acid.

Synthesis of salphenH₂. SalphenH₂ was prepared by four-steps using a known procedure based on nitration of 1,2-(ethylenedioxy)benzene followed by catalytic hydrogen and Schiff-base condensation with salicylaldehyde.²¹ The product was purified by silica-gel column chromatography (ethyl acetate/*n*-hexane, 1 : 4); yield, 72%; mp : 203-204 °C; Mass, *m/z* (rel abundance), 374 (M⁺, 100), 357 (20.30), 318 (40.32), 281 (34.81), 269 (14.07), 268 (74.12), 254 (13.81), 238 (6.56), 212 (14.58), 187 (6.98), 170 (9.19); ¹H-NMR (300 MHz, CDCl₃) δ 4.32 (s, 4H, 2CH₂O), 6.88-6.93 (m, 2H, ArH), 7.03-7.05 (dd, 2H, ArH), 7.27 (s, 2H ArH), 7.32-7.37 (m, 2H, ArH), 8.57 (s, 2H, NCH), 13.09 (s, 2H, ArOH); Anal. Calcd for C₂₂H₁₈N₂O₄: C, 70.58; H, 4.85; N, 7.48; O, 17.09. Found: C, 71.13; H, 4.63; N, 7.50; O, 17.23.

Preparation of PVC membrane. PVC-matrix ion-selective membranes were prepared by the method described elsewhere.²²⁻²⁴ Table 1 summarized the compositions of uranyl-selective membranes examined in this study. The membrane components ~1.0 wt% ionophore salphenH₂, ~66



SalphenH₂

Table 1. Formulation and electrochemical properties for UO_2^{2+} -ISEs based on salphenH₂

| Electrode Type | Membrane mass composition / mg | | | | Slope (mV/decade) | Detection Limit (M) |
|----------------|--------------------------------|------|--------|----------------------|-------------------|---------------------|
| | Plasticizer | PVC | Ligand | KTpCIPB ^a | | |
| E1 | NPOE(119.0) | 59.4 | 1.8 | — | 31.5 | 10 ^{-6.0} |
| E2 | TEHP(118.9) | 59.4 | 1.8 | — | 28.0 | 10 ^{-6.5} |
| E3 | NPOE(119.7) | 59.3 | 1.8 | 0.8 | 30.9 | 10 ^{-6.5} |
| E4 | TEHP(118.8) | 59.9 | 1.8 | 0.9 | 30.8 | 10 ^{-6.5} |

^aPotassium tetrakis(4-chlorophenyl)borate

wt% plasticizer (TEHP or *o*-NPOE), ~33 wt% PVC and KTpCIPB (~30 mol% with respect to the ionophore), were mixed and dissolved in 5.0 mL THF. The resulting THF solution was poured onto a glass ring with an inner diameter of 35 mm resting on a smooth glass plate. THF was allowed to evaporate for 48 h standing at room temperature. Transparent PVC membranes were obtained with a thickness of ~0.2 mm. A 9.0 mm diameter piece was cut out from the PVC membrane and mounted in a lab-made Ag/AgCl electrode body. An Ag–AgCl inner electrode and a filling solution consisting of 10⁻² M $\text{UO}_2(\text{NO}_3)_2$ + 10⁻² M NaCl internal solution were used. The sensor was conditioned for 24 h by soaking in 10⁻² M $\text{UO}_2(\text{NO}_3)_2$ solution, rinsed well with distilled water and stored in air when not in use.

Sensor potential measurement. The potential differences between the ISEs and the reference electrode (Orion sleeve-type double junction Ag/AgCl reference electrode; model 90-02) were measured using a PC equipped with high-impedance input 16-channel analog-to-digital converter (KOSENTECH, Busan, Korea). The response of the sensor for uranyl ions was examined by measuring electromotive force (EMF) of the following electrochemical cell: Ag|AgCl|sat. KCl|sample solution|PVC membrane|10⁻² M $\text{UO}_2(\text{NO}_3)_2$ + 10⁻² M NaCl solution|AgCl|Ag. Dynamic response curves and calibration plots were obtained through the step addition of standard solutions to 100 mL of background electrolyte at 25 °C. The solutions were magnetically stirred during the recording of all emf values. The selectivity coefficients $K_{\text{UO}_2, \text{B}}^{\text{pot}}$ were determined by separate solution method using the reduced form of the Eisenman equation.²⁵

$$\log K_{\text{UO}_2, \text{B}}^{\text{pot}} = (E_1 - E_2) / S(n/z - 1) \log[a]$$

E_1 is the potential measured in 10⁻² M solution of the interfering ion, E_2 is the potential measured in 10⁻² M UO_2^{2+} solution, S is the calibration slope, n and z are electrical charges of uranyl and interfering ions, respectively, and a is the concentration of the ions used (10⁻² M). The detection limits of the electrodes were also estimated according to the method suggested in IUPAC recommendation.²⁵ The pH of the uranyl ion solution was adjusted by adding an appropriate amount of 1.0 M nitric acid or sodium hydroxide.

Spectrophotometric measurement. All UV-vis spectra and the absorbance measurements were carried out on a HP 8453 spectrophotometer at room temperature. The ionic strength of all salphenH₂ and uranyl nitrate solutions in acetonitrile was adjusted by 0.1 M tetramethylammonium chloride.

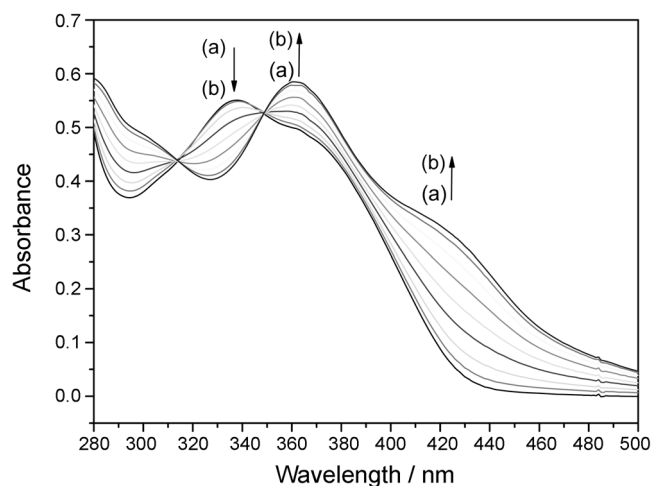


Figure 1. Electronic spectra of a 1.0×10^{-5} M solution of salphenH₂ in acetonitrile in the presence of increasing concentrations of UO_2^{2+} from 0.00 (a) to 2.5×10^{-5} M (b).

Results and Discussion

In preliminary experiments, UV-vis spectra for the salphenH₂ were measured in acetonitrile to elucidate its uranyl complex behaviour, which results a decrease in the salphenH₂ absorbance and produces a new absorbance peak at a longer wavelength (bathochromic shift). In order to determine the stoichiometry and stability of the resulting salphenH₂ complex with uranyl ion, the spectra of a series of solutions containing a constant concentration of ionophores

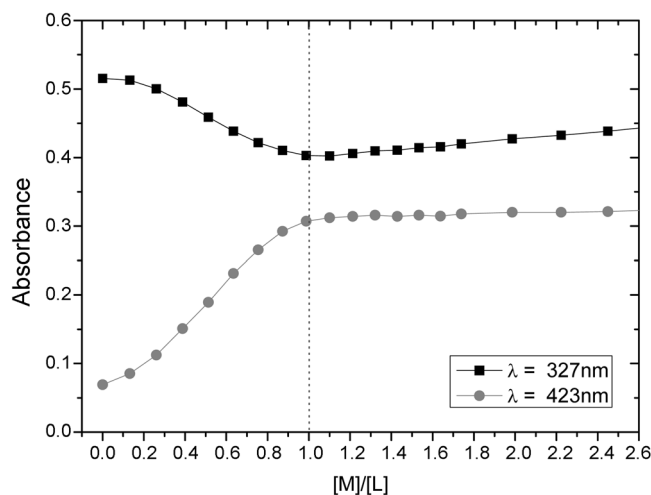


Figure 2. Spectrophotometric titration curves for salphenH₂ with UO_2^{2+} ion in acetonitrile.

(5×10^{-5} M) at room temperature and varying amounts of the metal ion were obtained (Figure 1). As can be seen, the complexation was accompanied by a relatively strong shift of the absorption band of the salphenH₂, with $\lambda_{\text{max}} = 327$ nm, towards longer wavelengths $\lambda_{\text{max}} = 357$ and 423 nm. From the results, the titration curves showing absorbance vs $[\text{UO}_2^{2+}]/[\text{salphenH}_2]$ mole ratio plots were obtained at 327 and 423 nm. As can be seen from Figure 2, the titration curves reveal distinct inflection points at mole ratio 1 : 1, suggesting the formation of 1 : 1 (uranyl to salphenH₂) complex in both wavelength. The 1 : 1 stoichiometry for the parallel system was also confirmed by Job's method. From the titration data the stability constant value (K_s) for the 1 : 1 complex was calculated by KINFIT program²⁶ to be 6.0×10^4 .

Plasticized PVC matrix membrane sensors incorporating salphenH₂ as ionophore in the presence of different solvent mediators (TEHP or *o*-NPOE) and KTpCIPB as an anion excluder were prepared and their performance characteristics were evaluated according to IUPAC recommendations.²⁵ The results are summarized in Table 1. The results showed that uranyl sensor based on salphenH₂ with TEHP and *o*-NPOE plasticizer gives a good potential response for uranyl nitrate with a theoretical Nernstian or near Nernstian slope, 28.0-30.9 mV/decade over the concentration range of 1.0×10^{-2} to 1.0×10^{-6} M and a detection limit of $10^{-6.5}$ M uranyl ion.

The membrane electrode E2 based on salphenH₂/TEHP exhibited sub-Nernstian response of 28.0 mV/decade while the membrane electrode E1 containing salphenH₂/*o*-NPOE which leads to polar solvent medium exhibited super-Nernstian response of 31.5 mV/decade, however, both electrodes (E3 and E4) incorporated additive lipophilic salt, KTpCIPB displayed near-Nernstian response slope of 30.9 mV/decade (E3) and 30.8 mV/decade (E4) respectively. It has been known that the presence of lipophilic anionic additives in PVC-membrane ISEs based on electrically neutral carrier are necessary to improve the electrochemical properties and selectivity for the ISEs.²⁷ In this study, however, the addition of a lipophilic salts KTpCIPB to the

membrane slightly improved the Nernstian slope, but did not strongly affect the electrochemical properties.

The effect of pH on the response of the PVC membrane electrodes, E2 and E4 for uranyl ions is shown in Figure 3. The operational pH range was studied by varying the pH of the test solutions with nitric acid or sodium hydroxide at 1.0×10^{-2} M of UO_2^{2+} ion. Figure 3 shows a decrease in the sensor potential at higher pH (> 4.0) probably due to the formation of insoluble uranyl hydroxide interference caused by hydroxide ions.²⁸ An optimum pH 1.5 ~ 4.0 is recommended for potential measurement where the potential response is almost constant.

The dependence of the sensor potentials on the concentration of the internal solution that 10^{-2} M $\text{UO}_2(\text{NO}_3)_2 + 10^{-2}$ M NaCl appears to be the optimum concentration of the internal solution to obtain the best response function. The dynamic response time was determined by immersion of the sensor in different concentrations of uranyl nitrate. The electrode reaches its equilibrium response (± 0.1 mV) in a relatively short time (< 1 min) for uranyl concentration of $> 10^{-4}$ M.

As shown in Figure 4, electrode E2 prepared with plasticized PVC membranes doped with salphenH₂ respond to uranyl ion over other cations including alkali metal ions (Na^+ , K^+) and NH_4^+ , alkaline earth metal ions (Ca^{2+} , Mg^{2+}) and transition metal ions (Ni^{2+} , Zn^{2+} , Cd^{2+} , Cu^{2+} and Pb^{2+}) as function of wide range of concentration, 10^{-1} M - 10^{-6} M. The E2 electrode exhibited wide linear concentration range of 10^{-2} M - 10^{-6} M with a detection limit of $10^{-6.5}$ M and a response slope of 28.0 mV/decade. All of the other cations under investigation show negligible responses.

The most important characteristic of a membrane sensor is its relative response for the primary cation over other cations present in the solution, which is expressed in terms of potentiometric selectivity coefficients ($K_{\text{UO}_2^{2+}, \text{B}}^{\text{pot}}$). Selectivity coefficients of the uranyl membrane sensor were calculated by the separate solutions method²²⁻²⁵ using aqueous 10^{-2} M solutions of metal nitrates and were shown in Figure 5.

The role of membrane plasticizer on the potentiometric

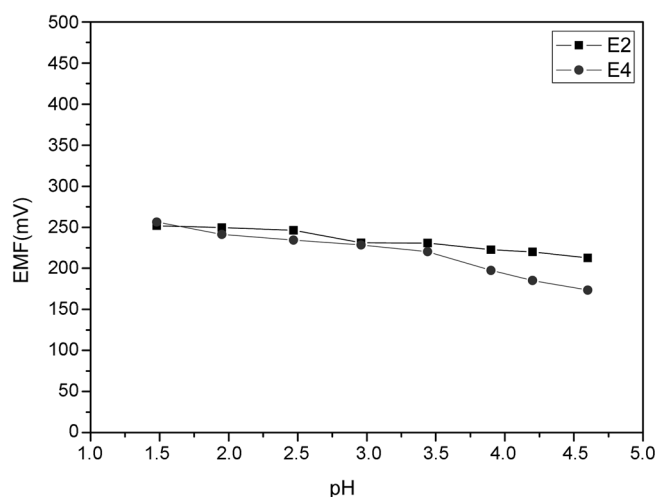


Figure 3. Potentiometric pH response for the UO_2^{2+} -ISE based on salphenH₂; E1 (■), E4 (●) in Table 1, respectively.

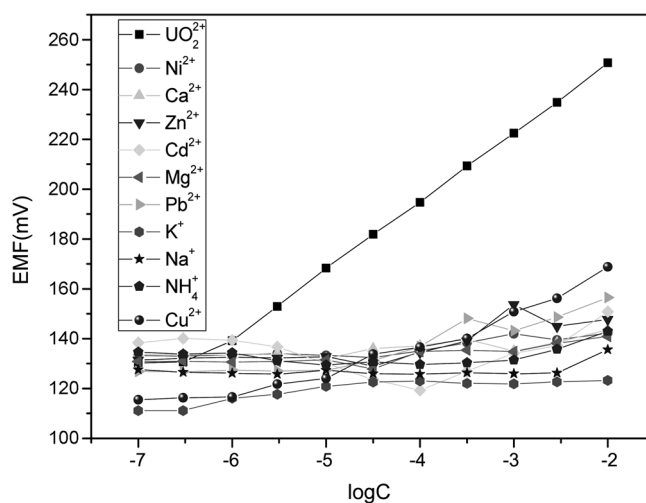


Figure 4. Potential responses of the membrane electrode E2 (see Table 1) for UO_2^{2+} and other interfering ions.

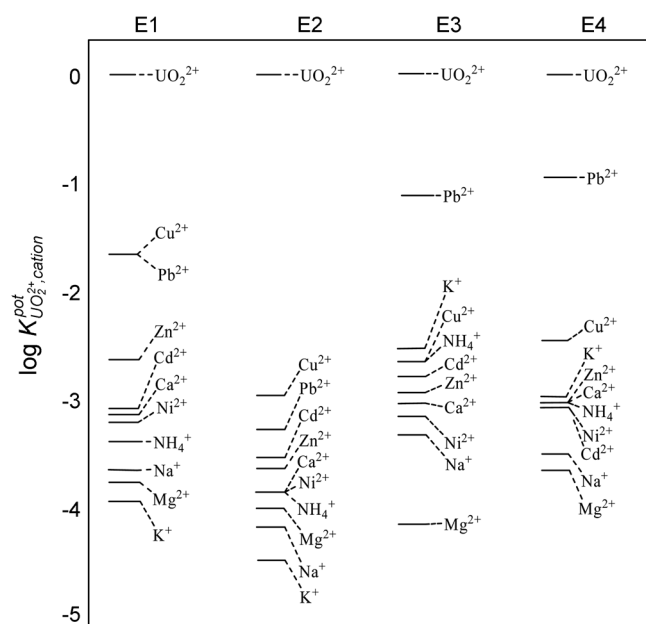


Figure 5. Comparison of the selectivity coefficients for E1-E4 (see Table 1).

selectivity of PVC membranes was examined using 1.8 mg (1.0 wt%) salphenH₂ without lipophilic anion and two plasticizers of different dielectric constants (*o*-NPOE, $\epsilon = 23.9$; TEHP, $\epsilon = 4.0$). As shown in Figure 5, the uranyl selectivity is better for membranes plasticized with low dielectric constant solvent, TEHP (column II) than with high dielectric solvent, *o*-NPOE (column I). In contrast, the uranyl selectivity of liquid membrane electrodes based on salphenH₂ with lipophilic anion, KTpCIPB (30 mol% relative to ionophore) (column III and IV) is not clearly marked off as function of solvent polarity. As suggested recently,²⁹ no simple rule can account for the change in selectivity due to plasticizer for membranes formulated with ionophores that form complexes with given cations. In general, It is likely that the selectivity for ion-exchanger-based membranes is dependent both on the ratio of single cation partition coefficients and relative cation-ionophore complexation in different dielectric constant plasticizers.²⁹

Consequently, all the electrode E1-E4 used in this study were demonstrated to show relatively good selectivity towards uranyl ion over a number of metal ions except Cu²⁺ and Pb²⁺. Especially, for E2 membrane electrode based on salphenH₂ without lipophilic anion, KTpCIPB, the selectivity coefficients are of the order of less than 10⁻³ and smaller emphasizing the highly selective behaviour of the proposed membrane electrode for UO₂²⁺ ion over all of the cations investigated.

Conclusions

We found that salphenH₂ is able to recognize uranyl ion in acetonitrile as demonstrated by spectrophotometric titration showing 1 : 1 complexation with the formation constant (K_s) of 6.0×10^4 . The PVC membrane sensor incorporating

salphenH₂ exhibited good Nerntian response (slope range: 28.0-30.9 mV/decade) over the concentration range of $1.0 \times 10^{-2} - 1.0 \times 10^{-6}$ M. The proposed electrode (E2) exhibited excellent selectivity for uranyl ion over a range of inorganic cations including the species which were known to interfere uranyl ion sensing seriously.

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