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# Why Do Uranyl Salophene Ionophores Lose Phosphate Selectivity in Time? The $^1$H NMR and UV/Vis Studies

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$^1$H NMR and UV/Vis studies on the interaction of uranyl complex of salophene (bis-salicylaldehyde-phenylenediimine) with nitrite, nitrate, sulphate, dihydrogenphosphate and fluoride anions are described. Only in the case of phosphate and fluoride ions an interaction was noticed. In the case of the former ion the changes in spectra were attributed to destruction of ionophore. The degradation of the ionophore is caused by the formation of uranyl phosphate, followed by hydrolysis of the Schiff base. Also the consecutive reaction might shift the hydrolysis equilibrium. NMR and UV/Vis studies aiming at the explanation of the mechanism of salophene decomposition are described.

**Key words**: uranyl salophene, phosphate selectivity, ion-selective membranes

Uranyl complexes of bis-salicylaldehyde-phenylenediimine, known as uranyl salophenes, have been studied as potential ionophores for anions since 1992 [1]. The electrodes with high selectivity towards some hydrophilic anions were constructed. Depending on the substituents present in the structure of salophene, selectivity of electrodes for nitrite, dihydrogenphosphate or fluoride was achieved. However, it is still unclear why these anions induce very high potentiometric response of the membranes containing uranyl salophenes and why this response decays in time. A short lifetime is the main problem in successful construction of anion-sensitive sensor [2]. The selectivity of membranes drops down after some days in the case of some uranyl salophenes. Only recently, derivatives with a lifetime of at least three months were reported [3]. The knowledge of the origins of the selectivity drop would be very valuable from the practical point of view. Investigations described here are the part of our research on phosphate sensor based on uranyl salophenes. During studies on the potentiometric selectivity, some NMR and UV/Vis experiments were performed in order to get an insight into the interaction between uranyl salophenes (the structures of investigated salophenes are depicted in Figure 1) and selected anions: $Cl^-$, $SO_4^{2-}$, $NO_3^-$, $NO_2^-$, $F^-$ and $D_2PO_4^-$. The latter three anions are known to induce the highest potentiometric response of sensors [3,4,5] after introduction to the polymeric mem-

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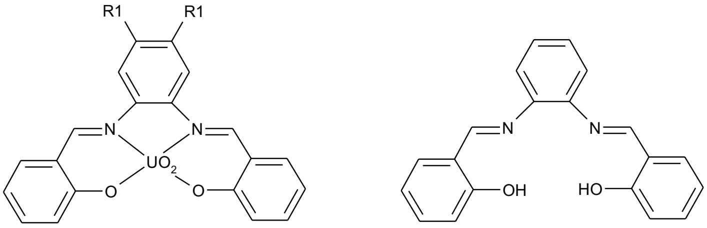
branes. In our $^1$H NMR experiments we used THF-$d_8$/$D_2O$ mixture as a solvent to simulate the organic-aqueous conditions of the polymeric membrane.

## EXPERIMENTAL

**Chemicals**: All hydrogen containing chemicals, except the sulphuric acid, were used in deuterated form. The sodium salts, except $AgNO_3$, were used. All chemicals were purchased from Sigma-Aldrich. Salophene (3) and uranyl salophenes (1, 2) were prepared according to previously described methods [4].

**$^1$H NMR spectra** were taken on the Varian 300 MHz spectrometer. If not stated otherwise the solvent consisted of 0.75 ml THF-$d_8$ and 0.25 ml $D_2O$. 2 mg of salophene (3) or uranyl salophene (1) or (2) were added. For the experiments with anion – uranyl salophene interaction, sulphuric acid was added to the solution of (1), (2) or (3) to reach the concentration of $10^{-4}$ M. Next, 2 mg of solid sodium or potassium salt of $Cl^-$, $SO_4^{2-}$, $NO_3^-$, $NO_2^-$, $F^-$, $D_2PO_4^-$ or $AgNO_3$ were added and spectrum recorded. Solid-liquid extraction was realized by adding 2 mg of uranyl salophene (1) to 1 ml of $D_2O$ followed by consecutive spectra recording every three days. For the liquid-liquid extraction 2 mg of derivative (1) were dissolved in 1 ml of $CD_2Cl_2$ and 0.1 ml of $D_2O$ was added. The spectra were recorded as previously.



**1.** R1=H
**2.** R1-$OC_{12}H_{25}$

**3.**

**Figure 1.** Structures of investigated salophene derivatives.

**GC-MS analysis**: The aqueous phase after solid-liquid extraction: salophene (3) – 0.1 M $NaH_2PO_4$ solution, was subjected to GC-MS analysis on gas chromatograph HP 5890 Series II, Hewlett Packard connected to mass selective detector HP 5971, Hewlett Packard. The chromatographic column HP-5, Hewlett Packard (5% methyl groups, 30 m) was used.

**The UV/Vis spectra** were taken on diode array Carl-Zeiss Specord S10 using quartz cuvettes. Water was used as a reference. Membranes containing 2% uranyl salophene (1), tetradecyloammonium bromide TDAB (20% mol *vs* uranyl salophene), PVC (33%) and *o*-nitrophenyl-octyl ether (*o*-NPOE) as plasticiser (65%) were prepared according to standard procedure [2]. For each ionophore four membranes (7 mm in diameter) and four solid samples (1 mg) were conditioned (solid-liquid extraction) in water or 0.1 M aqueous solutions of NaCl, $NaNO_3$, $NaH_2PO_4$ (3 ml volume in each case). The pH of all samples was adjusted to 4.5 by addition of $H_2SO_4$ (except phosphate solution). 2 ml of aqueous phase was pipetted to quartz 5-ml cuvette (1 cm in optical path) for every spectrum recording, and after recording recycled to the conditioning vial.

## RESULTS AND DISCUSSION

In general, moieties containing imine bond are susceptible to acidic hydrolysis. At first the hydrolytic pathway was checked as a potential reason of the potentiometric selectivity decrease. The influence of the presence of sulphuric acid on uranyl salophene (1) stability was investigated up to the concentration of $10^{-4}$ M. The maximum concentration of acid used corresponds to the concentration of $H_3O^+$ ions in the aqueous solutions applied for potentiometric measurements of membranes containing uranyl salophenes [3]. The $^1$H NMR spectra did not change (Fig. 2a) unless $AgNO_3$ was added to the solution containing sulphuric acid and uranyl salophene (1). In this case, $^1$H NMR spectrum changed drastically, *i.e.* new groups of aromatic signals appeared. In addition, the intensity of metimine proton ($\delta = 9.4$) decreased and new peaks ($\delta = 10.1$ and $\delta = 8.1$) appeared at the expense of the former (Fig. 2b). Within two hours a mirror was formed on the walls of the NMR tube. The presence of silver nitrate alone did not result in any changes in the spectrum and the mirror formation. Appearance of a mirror indicates the presence of salicylaldehyde, which reduces silver from silver nitrate (analogous to Tollens' test). The consumption of salicylaldehyde (for reduction of silver ions) drives the equilibrium of decomposition reaction of the salophene to the right (see Figure 3). However, in the absence of this additional driving force the decomposition of salophene (1) is negligible.

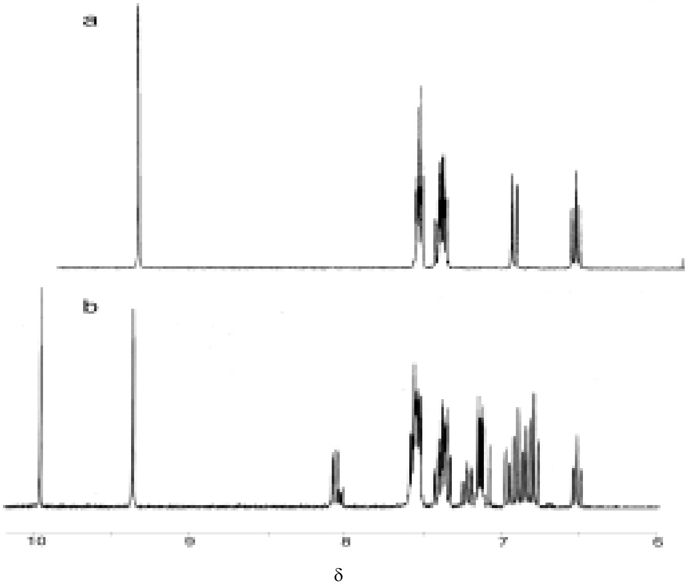


**Figure 2.** $^1$H NMR spectra of uranyl salophene (1) in THF-$d_8$/$D_2O$ (3:1 v/v) mixture, (a) in the presence of sulphuric acid $10^{-4}$ M, and (b) in the presence of sulphuric acid $10^{-4}$ M and $AgNO_3$.

The $^1$H NMR spectrum presented in Figure 2b contains probably the signals corresponding to the mixture of substrate of the reaction depicted in Figure 3, *i.e.* Schiff base (3) and the products of its decomposition, *i.e.* salicylaldehyde and *o*-phenylenediamine. Moreover, these products may undergo further irreversible reactions. It was proved by UV/Vis experiments, that the *o*-phenylenediamine is easily oxidized in acidic aqueous environment resulting in the formation of oligomeric products. For these reasons the interpretation of the spectrum presented in Figure 2b is very complicated and the proper identification of each single signal is practically impossible.

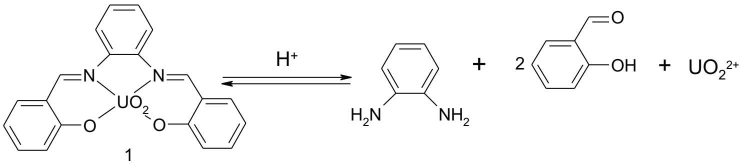


**Figure 3.** Scheme of proposed decomposition of uranyl salophene under acidic conditions.

Only the appearance of the new peak at $\delta = 10.1$ may be attributed to the proton of the salicylaldehyde (this peak was observed in the $^1$H NMR spectrum of the pure salicylaldehyde).

The main goal of our research was to examine the influence of the presence of different anions on the equilibrium depicted in Figure 3. Sulphuric acid was added to the solutions containing uranyl salophene (1) and the examined salts (except the phosphate salt) to reach the acid concentration of $10^{-4}$ M. Only in the case of fluoride and phosphate ions a significant change in the $^1$H NMR spectra was observed (Fig. 4 a,b). The peaks in aromatic region got broader upon addition of sodium fluoride, which might indicate the complexation reaction (Fig. 4a) between uranyl salophene (1) and fluoride anion. The broadening of the peaks may suggest slow on the NMR time scale kinetics of the complexation reaction. Even after 10 days no additional peaks, which could be attributed to decomposition of uranyl salophene (1), were observed in the spectrum.

Upon addition of potassium dideuteriumphosphate to the solution of (1), a yellowish precipitate resulted immediately. The $^1$H NMR spectra changed drastically in aromatic region (Fig. 4b). Moreover, the metimine proton peak decreased, while a new proton signal arose at $\delta = 10.1$. In a control experiment the "parent" Schiff base (3) was used instead of its uranyl complex (1) in order to investigate the role of the uranyl cation in the decomposition. The character of changes in the $^1$H NMR spectra was the same as in the case of complex, but there was no precipitation observed. The precipitate formed in the presence of uranyl salophene complex is one of the uranyl phosphates, probably monodeuteriumphosphate. In the case of uranyl salophene complex (1) after the removal of uranyl from the complex, salophene (the Schiff base) is hydrolyzed. This is possible, due to acidic conditions resulting from the presence of dideuteriumphosphate. The parallel reaction took place, in which the stabilizing factor-uranyl ion was removed.

It is interesting, that when tetrabutylammonium salts were used instead of the potassium salts, the decomposition of (1) was far slower upon addition of phosphate ions. This can be attributed to lower dissociation of tetrabutylammonium salts in comparison with potassium ones. As a result the effective concentration of phosphate ions, which causes the decomposition, is lower than in the case of sodium salt. In a previous report on uranyl salophenes [6], the $^1$H NMR spectra were recorded in water-free environment with ammonium salts, and in this case no decomposition was observed. In a non-polar $CDCl_3$ solvent, ammonium salt was very poorly dissociated, which means that neutral salt, instead of its anion, might have been complexed (the

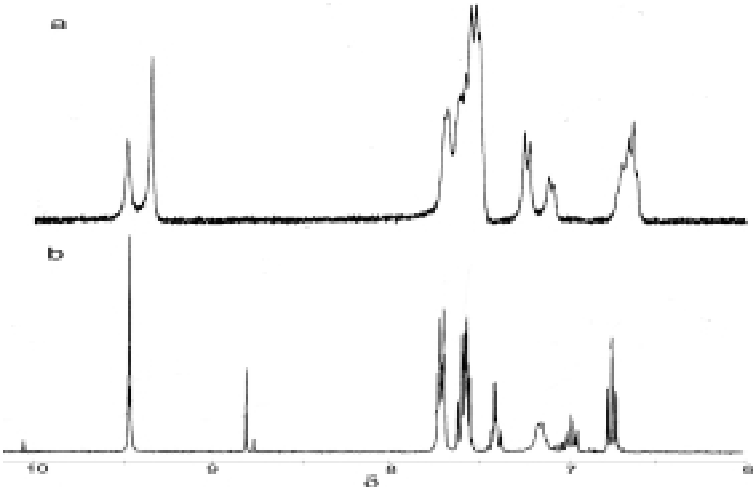


**Figure 4.** $^1$H NMR spectra of uranyl salophene (1) in THF-$d_8$/$D_2O$ (3:1 v/v) mixture, (a) after addition of solid KF and (b) after addition of solid $KD_2PO_4$.

shift was observed in the spectra). However, from the practical point of view, the presence of water and free ions, instead of non-ionized salts, should be taken into account.

The effect of the presence of -$OC_{12}H_{25}$ substituents, conjugated with the uranyl group, was also investigated. The substituents were placed in the phenylenediimine ring (Fig. 1). Their influence on the lifetime of membranes containing this ionophore was explained so far by means of lipophilicity. But in the system under study: homogeneous mixture of THF-$d_8$ and $D_2O$, the lipophilicity does not seem to play any role in the recognition process, because there is no organic-aqueous boundary. The decomposition of uranyl salophene (2) was far slower than uranyl salophene (1) under the same experimental conditions. It took two days to destroy the imine bonds. The result may be explained by an electronic stabilization of the salophene–uranyl complex. Ether groups decrease partial positive charge on the uranyl centre through electron-donating effect. This makes the uranyl cation less eager to leave the complex and form uranylphosphate. Macroscopic manifestation of this phenomenon is the increased lifetime of potentiometric sensors containing ionophore (2) in comparison with (1).

The organic-aqueous mixture, used in previously described experiments, is still a homogenic solution, while in membrane systems another factor – nonhomogeneity – plays an important role. One may suggest that the decomposition of uranyl salophenes does not take place in two-phase systems. To confirm it, $^1$H NMR experiments were performed, which proved the decomposition of uranyl salophene, both solid and in the form of dichloromethane solution, upon contact with aqueous phosphate solution. The presence of salicylaldehyde in an aqueous phase was also proved by GC-MS analysis, when solid uranyl salophene (1) was extracted by an aqueous $NaH_2PO_4$ solution.

The extraction of solid or dissolved in PVC membrane uranyl salophene (1) by aqueous solutions of chloride, nitrate and dihydrogenphosphate sodium salts was followed by UV/Vis spectroscopy. Only in the case of the latter solution, the spectra of the aqueous phase changed during extraction. The characteristic peaks of salicylaldehyde in water ($\lambda = 320$ nm, $\lambda = 260$ nm) and peaks of the products of *o*-phenylenediamine/$NaH_2PO_4$ reaction ($\lambda = 440$ nm, $\lambda = 290$ nm) were found in these spectra (Fig. 5). Observation of changes in the region of the band with maximum at $\lambda = 440$ nm supplied the major information about the process. It was proved that the presence of the peak mentioned accompanies a chemical reaction, in which *o*-phenylenediamine and phosphate ions are involved. The former is known as a very unstable reagent, undergoing autooxidation and polymerization. These processes include formation of azo-groups, which results in absorption of light in the visible range. In the presence of $H_2PO_4^-$, the product of this reaction is yellow. Its solubility in water decreases as oligomers get longer. Since the reaction is slow, the peak at 440 nm continuously decays in days. Presented UV/Vis studies confirmed the pathway of the ionophore decomposition, upon contact with aqueous phosphate anions solution, depicted in Figure 3.

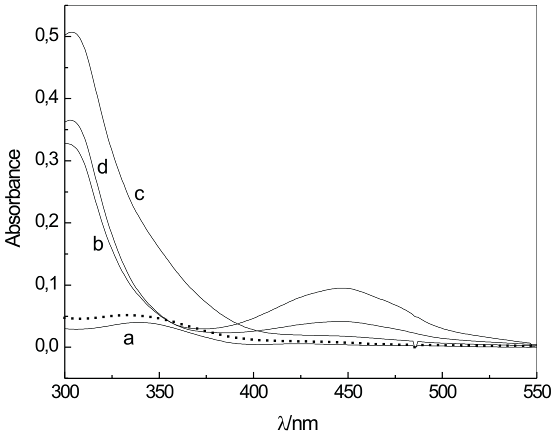


**Figure 5.** UV/VIS spectra of the aqueous phase after the conditioning of the membrane with (1) in $NaH_2PO_4$: a) 1 day, b) 7 days, c) 22 days, d) 57 days and: ----- after 22 days in pure water.

## CONCLUSIONS

It was proved that in the presence of an additional driving force the equilibrium of the uranyl salophene (1) decomposition might be significantly shifted. Both parallel (precipitation of uranyl phosphate) and consecutive (oxidation of salicylaldehyde) reactions with respect to decomposition reaction from Figure 3 were shown to shift the equilibrium to the right. Thus, it may be concluded that interaction with phosphate ions can lead to the decrease of potentiometric membrane selectivity, because destruction of ionophore occurs. The interaction may vary with the structure of salophene: the decomposition of the derivative (2) with -$OC_{12}H_{25}$ substituents was slower than uranyl salophene (1) under the same experimental conditions (similar results were obtained during long-term potentiometric studies of membranes containing uranyl salophenes (1) and (2) [3]). This may shed a new light on the optimization procedure of salophene-based ionophores. Not only lipophilic, but also electron-donating effect of substituents to the ionophore/membrane durability should be considered in the future. So far the electron-withdrawing or electron-donating effects were only regarded as responsible for the selectivity of ionophore [3]. The research is now focused on tuning of both electronic and lipophilic properties of uranyl salophene derivatives to obtain a highly selective and durable phosphate sensor.

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