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Cross-Sensitive Potentiometric Sensors based on Anti-Crown $(C_6HgF_4)_3$

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Abstract: A In this work we explore the possibility of using anti-crown ether $(C_6HgF_4)_3$ as a membrane-active component for potentiometric cross-sensitive sensors. Anti-crown ligands were already employed as ionophores in plasticized polymeric membranes, however the results of these studies are contradictory. In order to clarify the electrochemical sensitivity patterns of anti-crown based sensors we have studied plasticized polymeric membranes containing cation and anion-ex1changing additives and various solvents-plasticizers. We explored the electrochemical sensitivity of these membranes in a wide variety of aqueous solutions of inorganic salts. Alkaline, alkaline-earth and d-elements salts with different anions were studied. It was found that the sensors based on anti-crown $(C_6HgF_4)_3$ exhibit cationic sensitivity and no considerable anionic responses were observed.

Keywords: anticrown; multisensor arrays; potentiometric sensors

1. Introduction

In this work we explore the possibility of using so called anticrown compound $(C_6HgF_4)_3$ as a membrane-active component for potentiometric cross-sensitive sensors. Anticrown ethers are macrocyclic organometallic compounds consisting of mercury atoms or tin atoms separated by carbon atoms, including fluorinated macrocycles and mercury-carborands.

The chemistry of anticrowns is very extensive and it is a rapidly grown field of research. Recently it was reported that $(o\text{-}C_6F_6Hg)_3$ is readily coordinated with bromide and iodide anions to yield the following complexes: $\{o\text{-}[(C_6F_6Hg)_3Br]^-\}$ and $\{o\text{-}[(C_6F_6Hg)_3I]^-\}$. When anticrowns interact with halogens they formed polydecker wedge-shaped sandwiches: $[(\cdots(C_6F_6Hg)_3\cdots X\cdots)_n]^{n-}$, where X = chloride and bromide anions [1]. The ability of anticrown ethers to coordinate with single-charge anions attracted the attention of analytical chemists. Several attempts have been made to create the sensors based on anticrown ethers to detect anions. For example, mercury-carborand was used as an ionophore for the determination of chloride ions [2]. The authors made a PVC-plasticized membranes consisting of NPOE as plasticizer, TDDMA-Cl as anion exchange additive and mercurycarborand-3 as an ionophore. It was experimentally shown that the sensors have near-Nernstian response when interacting with Cl^- in a wide range of concentrations and detection limits were in micromole range. It was also found that the presence of TDDMA-Cl in the membrane causes an increase in sensor sensitivity. Another study explored three mercury anticrown ether to develop the sensors for Me_4N^+ cation [3]. The authors of the article synthesized three different PVC-plasticized membranes with various plasticizers: bis(2-ethylhexyl) sebacate (DOS), dioctyl phthalate

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(DOP), dibutyl phthalate (DBP). Potassium tetrakis(4-chlorophenyl)-borate (KTpClPB) was used as a cation-exchanger. A near-Nernstian response of 54.2 mV/dec towards Me_4N^+ cation was observed when DOS was employed as a plasticizer. With other plasticizers, the responses were worse. The electrode with the ionophore was more sensitive, the response was: 54.9 mV/dec.

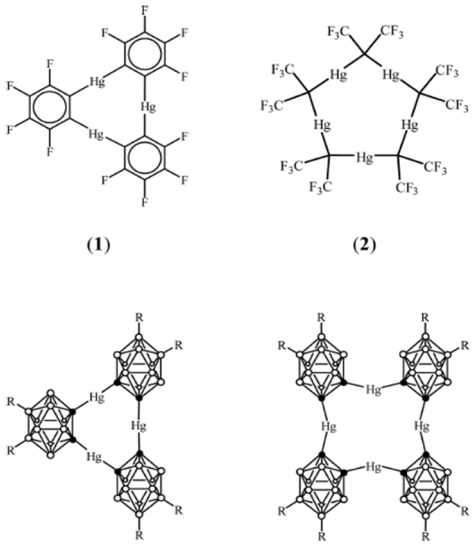

Figure 1. Structural formulas of typical anticrown ethers based on fluorinated macrocycles and mercury-carborund [1]. (1) – containing 3 mercury atoms, (2) – containing 4 mercury atoms.

2. Experimental Part

2.1. Reagents

Three-mercury anticrown ether was used as ionophore in all membranes. Anticrown was synthesized in A.N.Nesmeyanov Institute of Organoelement Compounds. The polymer matrix of the membranes was made of PVC (poly(vinylchloride)). o-nitrophenyloctyl ether (NPOE) and dioctyl sebacate (DOS) were used as a solvent-plasticizers. NaTpClPB was used as an anionic additive, and TDDMA-NO_3 was used as a cationic additive. All these substances were from SigmaAldrich in Selectophore grade. We made 3 membranes of each type to assess repeatability of the results.

2.2. ISE Preparation and Potentiometric Measurements

The composition of the sensor membranes is shown in Table 1. The membranes were made by mixing the following components: 200 mg plasticizer, 109 mg PVC, 17 mg of anticrown ether, 30 mg of NaTpClPB (membranes 2 and 5), 20 mg of TDDMA-NO_3 (membranes 3 and 6). The components where mixed with 5 ml THF using magnetic stirrer until completely dissolved. After that the mixture was put into a flat-bottom teflon beaker and left overnight for solvent evaporation. The disks 7 mm in diameter were cut from the parent membrane and glued into electrode bodies. After the glue dried, the housing was connected to the electrodes and filled with 0.01M NaCl solution. Finally the electrodes were soaked for a day in a solution of sodium chloride of the same concentration. Between subsequent measurements, the sensors were stored in the air. In total, we made 6 membranes and 18 sensors.

Table 1. Membrane compositions.

Sensor.	Component	Weight, g
1	PVC	0.1089
	DOS	0.2020
	Anticrown	0.0170
2	PVC	0.1090
	DOS	0.2024
	Anticrown	0.0171
	NaTpClPB	0.0030
3	PVC	0.1089
	DOS	0.2019
	Anticrown	0.0171
	TDDMA-NO_3	0.0020
4	PVC	0.1089
	NPOE	0.2054
	Anticrown	0.0172
5	PVC	0.1088
	NPOE	0.2026
	Anticrown	0.0171
	NaTpClPB	0.0030
6	PVC	0.1089
	NPOE	0.2010
	Anticrown	0.0046
	TDDMA-NO_3	0.0009

Solutions with a concentration of 1M were prepared by weight, and less concentrated solutions were prepared by sequential volume dilution of the parent solution. All solutions were prepared with bidistilled water.

The galvanic cell for the potentiometric measurements was the following:

Ag|AgCl, KCl(sat.)| analyzed solution | PVC membrane| NaCl, 0,01M , AgCl|Ag

The reference electrode was a silver chloride electrode filled with a saturated solution of potassium chloride. A glass electrode was used to control the pH during the experiment. All measurements were carried out at room temperature.

3. Results and Discussion

3.1. Anion Sensitivity

To study the anion sensitivity of the sensors, a series of measurements was carried out in aqeous solutions of Li_2SO_4, NaCl, NaOAc, NaF, $Ca(NO_3)_2$ in concentration range 10^{-6}–10^{-2}M. Based on the results of three parallel measurements, the slopes of the linear parts (10^{-5}–10^{-2}M) of the calibration curves were calculated. The sensor compositions 2 and 5 (Table 2) contain cation - exchange NaTpClPB, compositions 3 and 6-TDDMA-NO_3 contain anion-exchange additive.

Table 2. Response characteristics of the electrodes to anions (± 2mV/dec).

Sensor	Cl^-	F^-	OAc^-	NO_3^-	SO_4^{2-}
1	5	9	8	4	6
2	16	18	14	19	11
3	−27	−1	−6	−3	−2
4	34	31	32	5	35
5	29	39	32	15	41
6	−41	−8	−10	−11	−3

As one can notice the developed sensors in most cases do not have a pronounced sensitivity to anions. The sensitivity values obtained for chloride for sensors of composition 6 (−40.85 mV/dec with NPOE plasticizer) are the closest to the theoretical values. The sensors without any ion-exchanging additive showed cation sensitivity, thus we suggested that three mercury anticrown ether promotes cation sensitivity.

3.2. Cation Sensitivity

Further we studied sensitivity of the electrodes to cations. A broad variety of inorganic cations was studied: Li^+, Na^+, Mg^{2+}, K^+, Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Sr^{2+}, Cd^{2+}, Cs^+, Pb^{2+}, La^{3+}, Eu^{3+}, Lu^{3+}. The measurements were performed in the concentration range: 10^{-7}–10^{-3} M for lanthanides solutions, other salts were in concentration range 10^{-6}-10^{-2}M. The slopes were calculated for the concentration range of 10^{-5}–10^{-2}M (10^{-5}–10^{-3}M for La^{3+}, Eu^{3+}, Lu^{3+}).

Table 3. Cation sensitivities of the electrodes (± 2mV/dec).

Sensor	Li^+	Na^+	Mg^{2+}	K^+	Ca^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
1	6	5	−1	23	4	−2	−3	8
2	11	16	9	44	19	12	11	10
3	−2	−27	−3	1	−3	−4	−3	2
4	35	34	4	39	5	15	10	13
5	41	29	10	44	15	15	12	14
6	−3	−41	−7	−6	−11	−2	−17	−10
	Zn^{2+}	Sr^{2+}	Cd^{2+}	Cs^+	Pb^{2+}	La^{3+}	Eu^{3+}	Lu^{3+}
1	−3	−3	1	36	2	−1	0	−1
2	9	13	8	51	19	1	2	2
3	−3	−5	0	12	−1	−1	−2	−4
4	13	13	11	42	23	3	3	2
5	12	14	13	47	17	0	0	1
6	−6	−4	−2	−12	−2	0	−1	−2

It can be seen that the sensors have pronounced cross-sensitivity to cations. The sensors of compositions 3 and 6 in most cases showed anion sensitivity, apparently due to the presence of the anion exchanger. The sensor with a cation exchange additive based on the plasticizer DOS (composition 2) was more sensitive to all the cations than the sensor without an additive with the same plasticizer (composition 1). For example, for the Cs^+ and Pb^{2+} the slope for sensor 1 are 35.8 mV/dec and 2.1 mV/dec, for sensor 2 are 51.2 mV/dec and 18.7 mV/dec. Comparing sensors based on different plasticizers, 2 and 5, plasticizers DOS and NPOE, we can say that for most of the cations: Li^+, Mg^{2+}, Ni^{2+}, Cu^{2+}, Sr^{2+}, $Cd2^+$, the values of the slope of the electrode function are higher for the sensor based on o-nitrophenyloctyl ether (composition 5). For example, for Cd^{2+}, slope for sensor 2 is 8.4 mV / dec, and for sensor 5 is 12.9 mV / dec. At the same time, it is worth noting that the observed sensitivity values in most cases are far from the theoretical values. The developed sensors didn't show sensitivity to the La^{3+}, Eu^{3+}, and Lu^{3+} cations.

4. Conclusion

We studied the possibility of using a three-mercury anticrown as an ionophore. Also, the electrochemical sensitivity of developed sensor membranes in solutions of inorganic anions and cations was studied. It was found that the presence of three mercury anticrown ether in the polymer plasticized membrane promoted the cation sensitivity of sensors.

In general, the developed sensors may have a potential in the development of potentiometric multi-sensor systems, however, further studies are needed to confirm that there is some benefit of using anticrown compounds as ionophores, since the observed

sensitivities are following the lipophilicity of the cations (the highest values are observed for cesium and lead).

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