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New potentiometric sensors for rare earth metals based on commercial calcium ionophores †

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Abstract: PVC-plasticized sensor membranes based on ETH 129 and ETH 5234 were developed and their potentiometric performance was evaluated in acidic solutions of some REM ions and compared to that of well-established neutral ligands, such as tetraoctyldiglycolamide (TODGA). Sensor membranes were synthesized using poly(vinyl chloride) as polymeric matrix, o-nitrophenyloctyl ether (NPOE) as a solvent-plasticizer, ionophore, and chlorinated cobalt dicarbollide (CCD) or fluorinated tetraphenyl borate derivatives (TFPB) as the cation exchanger. Sensors based on calcium ionophores exhibited good sensitivity across the linear concentration range of pC=3 to pC=5 M with the Nernstian slope towards REM ions at pH 2 and with the detection limit of around 0.1-0.5 mg/l of REMs. The ETH 5234-based sensor demonstrated more remarkable sensitivity compared to the ETH 129-based sensor due to its high lipophilicity. Furthermore, the sensitivity of the sensor based on ETH 5234 looked rather similar to the ligands such as TODGA. The effect of lipophilic CCD and KTFPB cation exchangers on the potentiometric response of the sensors was studied. The results revealed that the sensors containing CCD demonstrated superior sensing characteristics compared to those including TFPB.

Keywords: electrochemical ion sensors; potentiometric sensitivity; ionophores; rare earth metals; ETH 129; ETH 5234

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1. Introduction

Extensive use of rare earth metals (REMs) in different industries such as electronics, superconductors, ceramics, gasoline cracking catalysts, and alloys making has increased the concerns on the environmental fate of these elements [1,2]. The environmental and biological effects of REMS are problems of the greatest importance since the accumulation of these metals in the food chain is detrimental to plants, animals, and human health [3,4]. Therefore, the determination of REMs is a significant issue. Spectroscopic techniques such as ICP-MS, ICP-AAS, and ICP-AES are typically used for REM measurements. Despite high precision, low detection limit, and reproducibility of the results, these methods require high capital costs, time-consuming preparation of samples, and trained staff. Potentiometric sensor analysis is one of the potential alternatives to sophisticated analytical instruments. Potentiometric sensors with polymeric plasticized membranes containing neutral ligands are capable of precise, fast, and direct quantification of target analytes [5]. Various ligands with diamide functions have been used for the construction of REM-sensitive sensors [5]. The chemical structures of some of these diamides are very similar to calcium II (ETH 129) and calcium IV (ETH 5234) ionophores suggested in 80's and successfully commercialized by Fluka Company. Thus, we have hypothesized that these commercial calcium ionophores can provide noticeable potentiometric sensitivity to REM ions. To confirm the validity of this hypothesis, the potentiometric sensors based on these two ligands were prepared and their potentiometric behavior for three lanthanides (including lanthanum, europium, and lutetium) was studied.

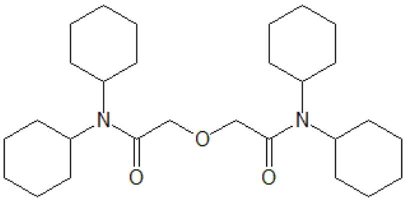
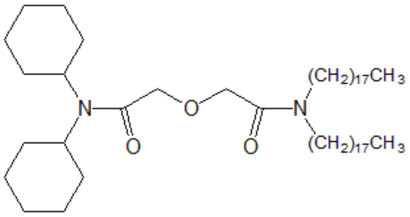
The aim of this study was finding cost-effective and reliable ligands alternative to the expensive compounds for the detection of lanthanides.

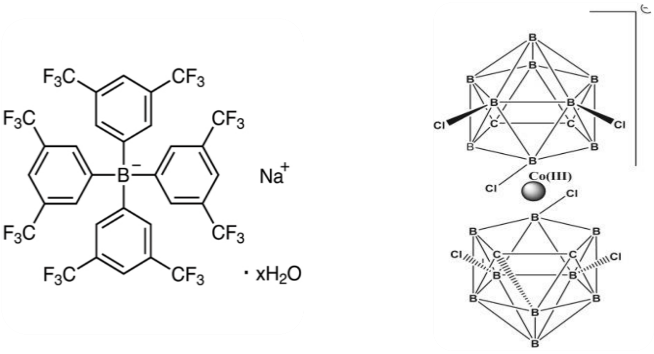
2. Experimental

2.1. Reagents and chemicals

The polymeric membrane matrix of electrodes was composed of poly(vinyl chloride) (PVC) (33 wt.%) as a polymeric matrix and 2 - nitrophenyloctyl ether (NPOE) as a plasticizer (62–64 wt.%). 10 mmol/kg sodium tetrakis[3,5-bis(trifluorometyl)phenyl]borate (NaTFPB) were used as cation-exchangers (0.89 wt.%). All sensor membranes contained 50 mmol/kg of one of the calcium commercial ligands listed in Table 1. PVC, NPOE, NaTFPB, and ligands were obtained from Merck (Darmstadt, Germany) in Selectophore® grade. CCD was provided by Katchem (Prague, Czech Republic). Tetrahydrofuran (THF) as a solvent was also purchased from Merck and used as received. Nitrate salts of metals were purchased from Sigma-Aldrich (Germany) and were used without further purification. Doubly distilled water was used for solution preparation. The chemical structures of the cation exchangers are illustrated in Figure 1.

Table 1. The chemical structure of the studied ligands.

Sensor	Ligand	Chemical structure
S1	ETH 129	
S2	ETH 5234	



a b

Figure 1. The chemical structure of cation exchangers: a. TFPB, b. CCD.

2.2. Sensors preparation

The sensor membranes and the corresponding electrodes were prepared using the standard protocol explained in literature [5–7] and then were filled in with 0.01M NaCl solution and immersed in the same solution for 48 h before measurements to equilibrate sensor membranes with aqueous solutions. Three identical sensors of each membrane composition were prepared.

2.3. Potentiometric measurements

Following galvanic cell was used during experimental studies:

Cu|Ag|AgCl, KClsat|sample solution|membrane|NaCl, 0.01M|AgCl|Ag|Cu

The potential values of sensors were measured with 0.1mV precision against the standard reference electrode using a multi-channel digital voltmeter connected to a PC for data acquisition. The measurement time was 3 minutes for each sample solution. After each measurement sensors were washed with several portions of distilled water until initial readings in water were observed. Solutions were magnetically stirred to eliminate mass transport resistance and reduce the response time of the sensors.

2.4. Sensors characteristics

Calibration of the sensors was carried out in solutions containing 10^{-7} and 10^{-3} M of each metal ions at pH 2 (by nitric acid) to suppress hydrolysis. The sensitivity values of sensors were calculated as the slopes of the linear parts of the calibration curves and were averaged over at least three measurements measurements for three replica sensors with the same membrane composition. Lower detection limit values of sensors were determined according to the standard protocol recommended by IUPAC (1976) by finding the intersection between two linear segments of each calibration curve of the studied ions.

3. Results and discussion

The response curves of the studied sensors for the studied lanthanide ions are illustrated in Figure 2 to Figure 4. All sensors showed the linear response at the concentration range of 10^{-5} to 10^{-3} M of the target ions. Sensitivity values of sensors S1 and S2 for La^{3+} were 13 and 16, for Eu^{3+} were 11 and 18, for Lu^{3+} were 6 and 19 mV/dec. The sensitivity pattern of the sensor S2 based on ETH 5234 looked rather similar to the previously studied ligand (TODGA) which showed sensitivity values 10 mV/dec for La^{3+}, 16 mV/dec for Eu^{3+}, and 20 mV/dec for Lu^{3+} and increasing by the increase in lanthanide molecular weight [8]. Sensor responses were stable and reproducible, and standard deviations of the reported values did not exceed 2 mV/dec towards the studied ions over three replicated measurements in three identical electrodes. According to Figure 2 to Figure 4 it can be noticed that sensor S2 based on ETH 5234 showed pronounced sensitivity for the studied ions. The higher sensitivity may be attributed to the presence of lipophilic side chains in ETH 5234 ligand. To improve the sensitivity of sensor S1 for the detection of the studied lanthanides, chlorinated cobalt dicarbollide (CCD) was used as a cation-exchanger rather than TFPB. The sensitivity values of sensor S1 for La^{3+}, Eu^{3+}, and Lu^{3+} were 13, 13 and 9, respectively which showed that CCD improves sensing characteristics of the polymeric membrane.

The detection limit (LOD) of the sensors response function for the studied lanthanide ions were averaged over three replicas and were about pC=5 to pC=6 (0.1-0.5 mg/l)

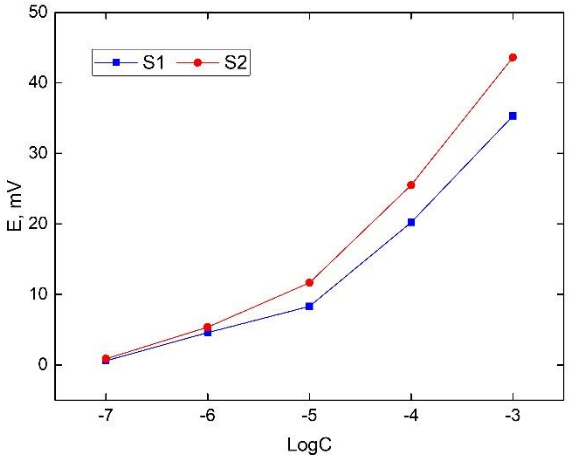


Figure 2. Potentiometric response curve for lanthanum at pH=2.

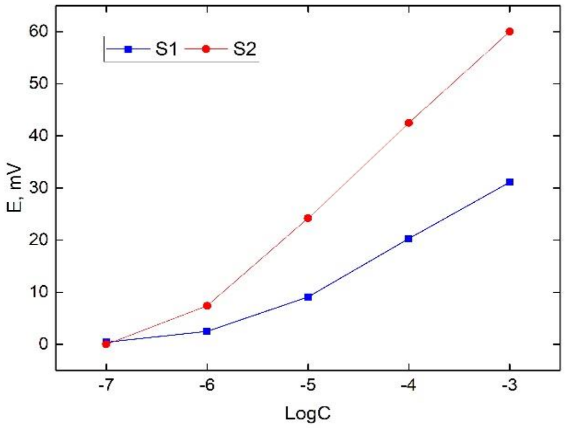


Figure 3. Potentiometric response curve for europium at pH=2.

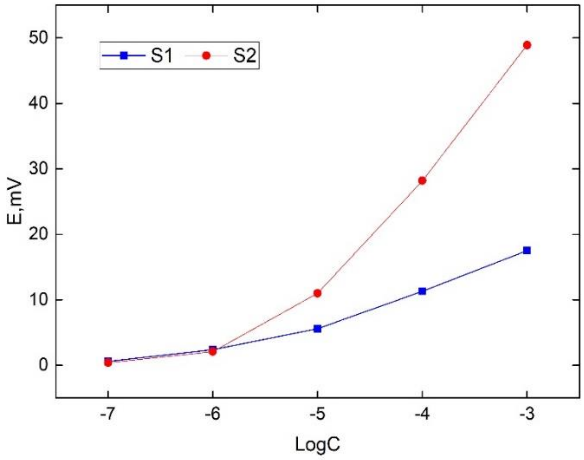


Figure 4. Potentiometric response curve for lutetium at pH=2.

4. Conclusions

In this study, the possibility of using commercial calcium ionophores for the determination of lanthanum, europium, and lutetium as REMs was presented for the first time. Reproducible and stable results, high sensing performance, and low detection limits make them promising alternatives to expensive ligands such as TODGA for technological monitoring purposes.

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Conflicts of Interest: The authors declare no conflict of interest.

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