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Design and Characterization of a Li-Selective Optical Sensor

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Abstract. An optical ion-sensing system based on a PVC membrane containing a Li^+ ionophore in combination with a H^+ selective chromoionophore (ETH 5294) is presented. It exhibits an absorbance response to Li^+ concentration in pH buffered solutions. The dynamic range and Li^+/Na^+ selectivity of this new optode system are discussed.

Key words. Optical sensor, Li ionophore, lithium selectivity.

1. Introduction

The very rapid developments in the interdisciplinary area of chemical sensors in the last 25 years are connected with the development of a new class of compounds, called ionophores, which select and complex specific ions and transport the complexes formed across the hydrophilic/lipophilic interphase. The most important feature of such inclusion compounds is the possession of polar, electron donor sites, responsible for the complexation and nonpolar sites responsible for their solubility in nonpolar solvents. An important factor which has to be considered in complexation is the effect of the ligand geometry. The cavity of the macrocyclic ligands, appropriate to the size of the guest, stabilizes the complex. The open chain ligands do not have a real molecular cavity, but when complexing they are able to wrap around the cation forming a pseudo-cavity.

Among the Li-complexing compounds reported so far, amides with bulky and lipophilic substituents, such as dicyclohexylamides, with the appropriate number of polar binding sites, seem to act favorably as ionophores for Li ion selective electrodes. The spatial arrangement of binding centers in amide podands is much more flexible than in the small, 12- or 13-membered crown ethers; podands can exchange the hydration shell of the Li cation slowly, in a stepwise way. Among many amides of quite similar structure studied by us tripodand **1**, with six coordinating centers, was found to have the best ionophoric properties in ion selective electrodes [8, 10, 13].

Over the past few years there has been great interest in the development of optical sensors as an alternative to the rather better known electrochemical sensors. They do not suffer from electrical interference and are considered safer in biomedical applications.

Although there are several different kinds of optical sensors the basic concepts in all of them is similar [1, 2, 3]. A very interesting optode system, first introduced by Simon's group in Zurich [4, 5, 6], is based on PVC membranes that incorporate a conventional, highly lipophilic neutral ionophore (without structure modification) in combination with a H^+ selective chromoionophore. The recognition mechanism involves an ion-exchange and the optode membranes respond to the activity ratio of the two ion species involved: a cation of interest and a counterion. Optical determination of ion activity can be carried out only if the activity of the counter ion is buffered to a constant value. The absorbance response in optodes depends on the ratio of sample activities of the two involved ionic species:

$$A = f(K_{\mathrm{exch}} a_{\mathrm{M}} / a_{\mathrm{H}})$$

where a_{M} and a_{H} are the activities of the ions in the sample solutions; K_{exch} is the equilibrium constant of the basic ion exchange process, including carrier complexation/decomplexation.

During the measurements in pH buffered solutions, at a constant ionic strength, the absorbance is finally influenced by the sample concentration (changes in activity coefficients could be neglected) as follows [7]:

$$A = f(c_{\mathrm{M}})$$

In this paper, an optimal lithium ion-sensing system based on a PVC membrane containing a Li^+ ionophore in combination with a H^+ selective chromoionophore is presented. It exhibits an absorbance response to Li^+ concentration in pH buffered solutions. The purpose of this study was to compare the properties of the obtained optode with the potentiometric sensor, lithium ion-selective electrode based on the same Li ionophore.

2. Experimental

2.1. REAGENTS

The ionophore **1** was prepared as described in Ref. [8]. The H^+-selective chromoionophore ETH 5294 was kindly made available by Professor Simon; the synthesis of this compound is described in Ref. [9]. Other membrane components: poly(vinyl chloride) PVC (high molecular), bis(1-butylpentyl) adipate (BBPA), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate and tetrahydrofuran (THF) were from Fluka. NaCl, LiCl and 1,1,1-tris(hydroxymethyl)propane (TRIS) were of reagent grade (from Merck). Aqueous solutions were prepared with doubly quartz-distilled water. All LiCl and NaCl solutions were prepared in a TRIS buffer of pH = 7.25 (0.01 M Tris/0.1 M HCl).

2.2. PREPARATION OF THE OPTODE MEMBRANE

The optode membrane composition was 8.0 mg of ionophore **1**, 2.3 mg of chromoionophore ETH 5294, 4.5 mg of the sodium tetrakis[3,5-bis(trifluoromethyl) phenyl)] borate, 60 mg of PVC amd 120 mg of bis(1-butylpentyl) adipate (BBPA). All these components were dissolved in 1.5 mL of freshly distilled tetrahydrofuran (THF). 0.2 mL of this solution was injected onto a rotating quartz glass plate of 35 mm in diameter (W. Moller AG, Zurich); rotating frequency 600 rpm. After a spinning time of about 2 s the glass support with the optical sensing membrane was stored in air for 15 minutes for further drying. The thickness of the membrane prepared in this way is about 4 μm.

2.3. THE MEASUREMENTS

Absorbance measurements and spectra of the PVC-membranes were taken using a flow-through cell in a Perkin Elmer Model Lambda 2 double-beam spectrophotometer. All spectra were recorded at 21 ± 1 °C. The absorbance measurements were made at 660 nm, which corresponds to the protonated form of the chromoionophore.

Two identical glass plates with membranes of about 4 μm thickness were mounted into the measuring cell of the flow-through system. The reference cell of the spectrophotometer contained two glass plates without membranes.

3. Results and Discussion

Comparison was made between optical and potentiometric sensors based on the same Li-selective ligand **1**. The optical sensor uses a UV/VIS spectrophotometer as detector and does not need a separate reference device. Potentiometric sensors require a milivoltmeter (pH meter) and a Ag/AgCl or calomel reference electrode.

The PVC/BBPA optode membrane studied here contained **1**, a highly lipophilic ligand (L) [10] and a lipophilized H^+-selective chromoionosphore ETH 5294 (Ch), (Fluka No. 27086) [9]. Both compounds are shown in Figure 1. The third component of the optode membrane is a salt with the highly lipophilic anion R^-, sodium tetrakis[3,5-bis(trifluromethyl)phenyl]borate [11]. The concentration of the main components should be kept as follow:

$$c(\mathrm{Ch}) < c(\mathrm{R}^-) < c(\mathrm{L})$$

The basic principle of the PVC/BBPA Li optode membrane is shown in Figure 2. In pure Tris buffer solution of pH = 7.25 the chromophore ETH 5294 exists in the protonated form. After contact with aqueous lithium salt solutions of different concentrations the following equilibrium occurs:

$$\mathrm{Li}^+_{(\mathrm{aq})} + \mathrm{L}_{(\mathrm{org})} + \mathrm{R}^-_{(\mathrm{org})} + \mathrm{ChH}^+_{(\mathrm{org})} \rightleftharpoons \mathrm{LiL}^+_{(\mathrm{org})} + \mathrm{R}^-_{(\mathrm{org})} + \mathrm{Ch}_{(\mathrm{org})} + \mathrm{H}^+_{(\mathrm{aq})}$$

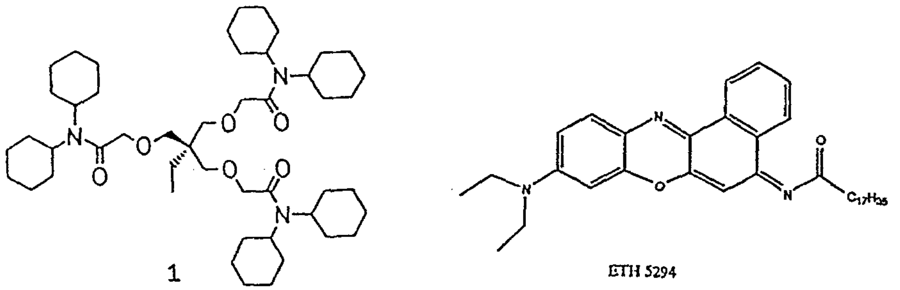
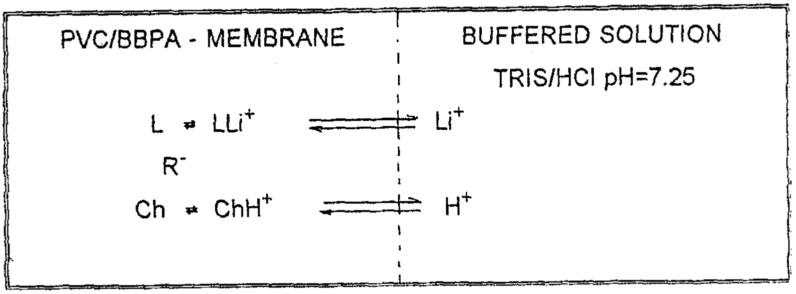


Fig. 1. Structures of ionophore **1** and chromophore ETH 5294.



L - ionophore

Ch - chromophore

R^- - lipophilic anion (phenyl borate)

Fig. 2. Basic principle of the Li optode.

The assumption that a 1 : 1 lithium–ligand complex is formed is based on the NMR studies of Li complexes with dicyclohexylamides [12].

The neutral ligand forms reversibly a complex with a Li cation and has low water solubility, which minimizes the problem of leakage from the membrane. The lipophilicity of all components is very important; the optode membrane is very thin (4 μm) when compared with the electrode membrane (0.1 mm), and in order to obtain a stable sensor, the components should not be easily washed out from the membrane. Therefore, immobilization of the chromophore and also other membrane components is, unlike in electrodes, desirable in optodes.

Various possibilities were investigated before deciding on the final composition of the optode membrane. Different buffer solutions were tested and the most suitable was Tris buffer, since there is no interference with the lithium ions.

The absorbance of the chromoionophore was determined at the wavelength of maximum absorption of its protonated form, at 660 nm. Figure 3 shows the

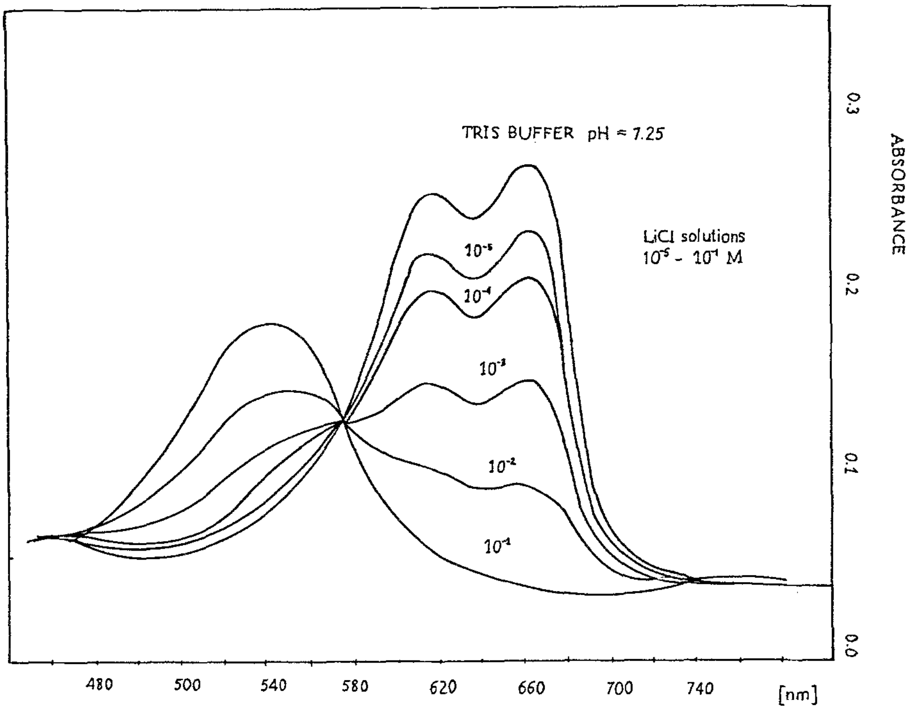


Fig. 3. Absorption spectra of optode membranes after equilibration with solutions of different LiCl concentration in TRIS buffer of pH = 7.25.

absorption spectra after equilibration with pH-buffered solutions of different LiCl concentration. The measured changes in absorbance, being a result of deprotonation of the lipophilic pH indicator is correlated with lithium or sodium ion activity in the bulk sample solution. At 0.1 M LiCl concentration the pH indicator exists in the unprotonated form. Figure 4 shows the calibration curves (the absorbance vs activity) obtained for Li^+ and Na^+ cations. The dynamic concentration range for lithium cation is between 10^{-4}–10^{-1} at pH = 7.25. The estimated selectivity for Li^+ over Na^+, expressed as $\log K^{\mathrm{opt}}_{\mathrm{Li/Na}}$ is -1.8.

X-ray analysis of the free ligand and its lithium complex, LLi^+, shows that in the complex Li cation and six oxygen atoms are inside the lipophilic shell, therefore the complex is even more lipophilic than the free ligand [13]. The lipophilicity of the membrane components, which is important in ion selective electrodes, is even more important in very thin optode membranes. The lipophilicity of the Li ionophore **1** is high: $\log P_{TLC} = 13.8$ (calculated by the Hansch method, $\log P = 12.1$) [10]. The electrode based on this ligand has excellent properties and lasts several months. It has been calculated that an ionophore of such high lipophilicity has a theoretical lifetime of 40,000 h, even when used for measurements in blood serum [10]. Practically, after 8 months of using the electrode in water electrolyte solutions the characteristic did not change significantly.

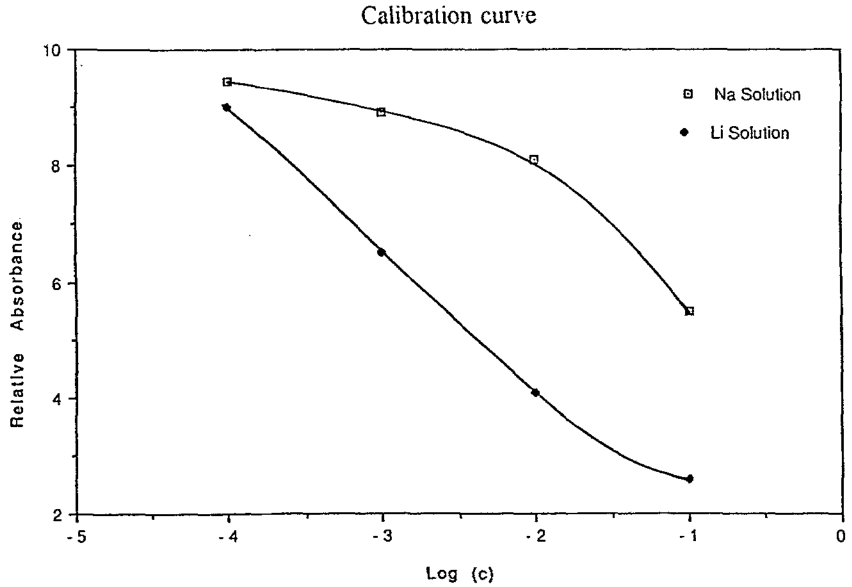


Fig. 4. Calibration curves for Li and Na ions: absorbance at 660 nm as a function of log a_M/a_{H^+}.

TABLE I. Comparison of both sensors: Li optode and Li electrode.

Properties	PVC/BBPA Li^+-optode	PVC/BBPA Li^+-electrode
Working range −[log c]	4–1	5–1
Selectivity log $K_{Li/Na}$	−1.8	−2.05
Response time	10 sec	20 sec
Life time	hours/days	weeks/months
Membrane thickness	4 μm	100 μm

The response time of the optode is shorter than of the electrode. It is only a few seconds and the optode reacts very rapidly to the changing concentration of the solutions. Selectivity for lithium over sodium estimated by the separate solution method (SSM) is not exactly the same: log $K^{opt}_{Li/Na} = -1.8$ and log $K^{pot}_{Li/Na} = -2.05$. The concentration (activity) range, expressed as −log $c_{Li} = 4 - 1$ in the optode is larger in the electrode − log $c_{Li} = -$ 1.

The positive charge of ChH^+ is located on the surface of the molecule, changing its lipophilicity. The weak point of the optode described here is leakage of the chromophore, especially in its protonated form. The lipophilicity of ETH 5294 is estimated as log $P_{TLC} = 18$ (in basic form) and only 10 (in protonated form). The comparison of both sensors is given in Table I.

4. Conclusions

The present study shows that both sensors, the Li optode and the Li electrode, possess good signal stability. They can be treated as alternatives, however their characteristic are not exactly the same.

Our first Li optode should be improved and we are doing further work on its technology. A crucial drawback to be overcome is the short life time of the optode. Another choice of membrane material, such as plasticizer or polymer or use of a different chromophore might solve the problem. This is being investigated.

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