Sodium Ion-Selective Membrane Electrode Based on Dibenzopyridino-18-Crown-6

Nahid Tavakkoli

Department of Chemistry, Isfahan Payame-Noor University, Isfahan 81655-718, I. R. Iran
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A sodium ion- selective electrode based on dibenzopyridino-18-crown-6 as membrane carrier was successfully prepared. The electrode exhibits a Nernstian response for Na$^+$ ions within the concentration range of 1.0×10^{-4}-1.0×10^{-1} M. The response time of the sensor is 20 s. The sodium ion-selective electrode exhibited comparatively good selectivities with respect to alkali, alkaline earth and some transition metal ions.

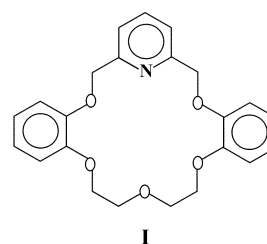**Key Words :** Sodium ion selective electrode, Crown ether, Potentiometry

Introduction

Since the first synthesis of macrocyclic crown ethers,[1] extensive amount of research work has been undertaken to study the thermodynamics and kinetics of their complexation reactions with cations.[2-4] In comparison, applications in analytical chemistry are still rather limited in spite of specific affinity and selectivity of crown ethers for a certain class of metal ions.[5-9] An interesting application of crown ethers is their potential use as ion-selective components (ion carriers) in liquid membrane electrodes.[6-10]

Potentiometric ion-selective membrane electrodes for Na$^+$ ion are steadily replacing flame photometry and other analytical techniques for monitoring sodium ion in various matrices.[11,12] Such determinations are normally conducted with the sodium glass membrane electrode. However, the use of glass membranes presents several difficulties, such as contamination of the glass membrane surface, high resistance, interferences from hydrogen ions and technical problems in the design of various configurations and shapes of cell assemblies.[13] Further, there is a continuing search for alternative and improved sensors.

The membrane sensors for Na$^+$ ion incorporate crown ethers,[14] bis-crown ethers,[13] poly(crown ethers)[10] and crown ether-phosphotungstic acid precipitates.[15] Owing to the high solubility of the most mono(crown ethers) in water, poly(crown ethers) and bis(crown ethers) have been used in most instances. However, it is time consuming to prepare poly(crown ethers) and bis(crown ethers) and electrodes made of the poly(crown ethers) have the great disadvantage that the response time is over 10 min.[10] The sodium ion selective PVC membrane electrode based on 12-crown-4-phosphotungstic acid precipitates was described.[15] This electrode gave a linear response with a Nernstian slope within the concentration range 10^{-1}-10^{-4} M NaCl. However, the Na$^+$ selectivity against K$^+$ was poor (log $K_{Na,K}^{pot}$ =0.72).

In this paper, we report the use of dibenzopyridino-18-crown-6 (DBPY18C6, I) as an excellent neutral carrier in the construction of a new Na$^+$ ion-selective electrode.

*e-mail: tavakoli@pnu3.ac.ir, Tel: +98-311-7380555; Fax: +98-311-7381002

I

Experimental Section

Reagents. Reagents grade dibutyl phthalate (DBP), *o*-nitrophenyl octyl ether (NPOE), dimethyl sebacate (DMS), high relative molecular weight PVC and tetrahydrofuran (THF) were purchased from Fluka chemical company and used as received. Dibenzopyridino 18-crown-6 (DBPY18C6), the chloride and nitrate salts of all cations used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P$_2$O$_5$. Triply distilled deionized water was used throughout.

Electrode Preparation. The general procedure to prepare the PVC membrane was to mix 93 mg of powdered PVC, 3 mg of DBPY18C6 and 186.5 mg of plasticizer as solvent mediator. The mixture was then thoroughly dissolved in 2 mL of THF. A pyrex tube (3 mm i.d.) was dipped into the resulting solution for a few min. Then the tube was pulled out from the solution and kept at room temperature for 24 h. The tube was filled with internal filling solution (2.0×10^{-2} M sodium chloride). The electrode was finally conditioned for 24 h by soaking in a 5.0×10^{-2} M NaNO$_3$ solution. A silver/silver chloride coated wire was used as an internal reference electrode.

Emf Measurements. All emf measurements were carried out with the following cell assembly: Ag-AgCl/internal solution (2.0×10^{-2} M NaCl)/PVC membrane/test solution/ Hg-Hg$_2$Cl$_2$, KCl (satd).

A model 624 Metrohm digital research pH meter was used for the potential measurements. The emf observations were made relative to a double junction saturated calomel electrode (SCE, Philips) with the chamber filled with an ammonium nitrate solution. Activities were calculated according to the Debye-Huckel procedure.
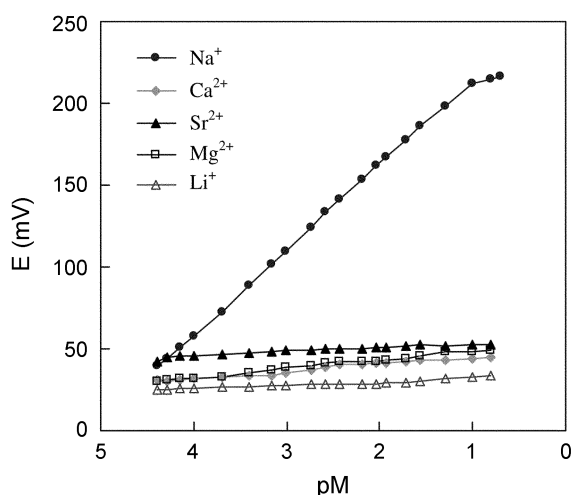
Figure 1. Potential response of various metal ion- selective electrodes based on DBPY18C6.

Results and Discussion

In preliminary experiments, DBPY18C6 was used as a neutral carrier to prepare PVC membrane ion − selective electrodes for Na^+, Li^+, Ca^{2+}, Sr^{2+}, Mg^{2+} ions. The potential responses of various ion − selective electrodes based on the macrocycle used are shown in Figure 1. As seen, except with the Na^+ ion-selective electrode, the slope of the corresponding potential − pM plots is much lower than the expected Nernstian slope. However, sodium ion shows the most sensitive potential response in the series, most probably due to selective complexation of the ligand with sodium ion and the fast complexation-decomplexation kinetics at the solution- membrane interface.[16]

It is well known that the sensitivity and selectivity of the ion-selective sensors not only depend on the nature of ionophore used, but also significantly on the membrane composition and the properties of the plasticizer employed. Thus, the influences of the membrane composition and the nature of plasticizer on the potential response of the Na^+ sensor were investigated and the results are summarized in Table 1.

Several plasticizers including DBP, NPOE and DMS, which are often used with PVC membrane electrodes were evaluated. Since the nature of plasticizer influences the

Table 1. Effect of membrane composition on the potential response of the Na^+-ion selective electrode

Number	Composition%			slope mV/decade
	ligand	PVC	Plasticizer	
1	1.1	33	65.9 DBP	51.2
2	1.1	33	65.9 NPOE	39.0
3	1.1	33	65.9 DMS	58.5
4	2.0	33	65.0 DMS	50.2
5	0.5	33	66.5 DMS	40.0
6	3.0	33	64.0 DMS	49.5

dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands,[17,18] it is expected to play an important role in determining the ion-selective characteristics. As it is seen from Table 1, among different plasticizers examined, DMS results in the best sensivity and widest linear range.

The dependence of the electrode response (slope) on the amount of carrier was also examined. In the case of the carrier-type ion-selective electrodes, the mechanism of electrode response depends mainly on the extraction equilibrium in the vicinity of the interface between the membrane and aqueous layer.[19,20] In spite of these considerations, a carrier content of 1.1% was chosen as the optimum condition (No. 3, Table 1), because the surface condition of the PVC membrane deteriorated as a result of decreasing and increasing the carrier content.

The influence of the concentration of internal solution on the potential response of the Na^+ ion-selective electrode was studied. The NaCl concentration was changed from 1×10^{-3} to 1×10^{-1} M and the emf -pNa plot was obtained. It was found that the variation of the concentration of internal solution does not cause any significant difference in the electrode's potential response, except for an expected change in the intercept of the resulting near-Nernstian plots. A 2.0×10^{-2} M concentration of the reference solution is quite appropriate for smooth functioning of the electrode system.

The influence of the pH of the test solution on the potential response of the sensor was tested at 1.0×10^{-2} M Na^+ concentration. Potentials were found to stay constant from pH 4 to 11. The observed drift at pH < 4 could be due to the protonation of the crown ethers in the membrane, which results in their losing their abilities to complex with sodium ions.

The optimum equilibration time for the Na^+ ion-selective electrode based on DBPY18C6 is 24 h. It generated stable potentials when placed in contact with sodium ion solutions. The critical response characteristics of the electrode was
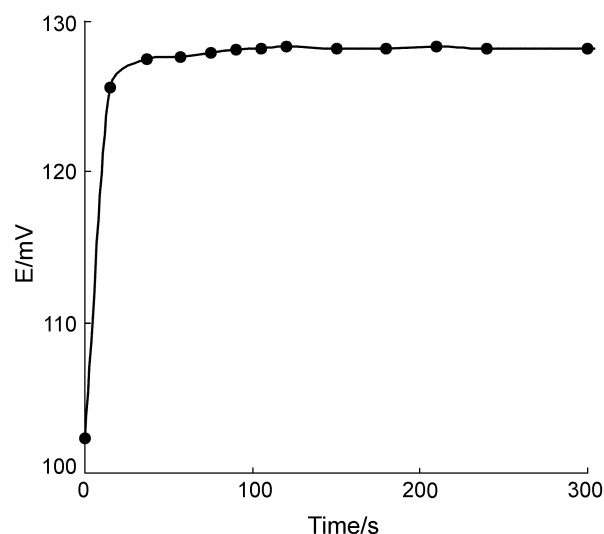

Figure 2. Response-time profile of the Na^+ ion-selective electrode based on DBPY18C6.

Table 2. Selectivity coefficients ($K_{Na,M}^{pot}$) of various interfering ions

Interfering ion	$\log K_{Na,M}^{pot}$
Li^+	-2.41
K^+	-0.67
Cs^+	-1.22
NH_4^+	-1.40
Mg^{2+}	-2.66
Ca^{2+}	-2.45
Sr^{2+}	-2.64
Ba^{+2}	-2.40
Ni^{2+}	-2.56
Co^{2+}	-2.37
Cd^{2+}	-2.20
Cu^{2+}	-2.41
Zn^{2+}	-2.28
Pb^{2+}	-0.52

assessed according to IUPAC recommendations.[21] The emf response of the PVC membrane at varying concentration of sodium ion (No. 3, Table 1) indicates a rectilinear range from 1.0×10^{-4} to 1.0×10^{-1} M ($r \geq 0.999$). The slopes of the calibration curves were 58.5 ± 0.5 mV/decade of Na^+ ion concentration. The limit of detection, as determined from the intersection of two extrapolated segments of the calibration graph, was 9.0×10^{-5} M.

The average time required for the Na^+ ion sensor to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of a series of sodium ion solutions, each having a 10-fold difference in concentration, was measured.[21] The static response time of the membrane sensor thus obtained was 20 s for concentrations $\leq 1.0 \times 10^{-1}$ M. A potential $-$ time plot for the electrode is given in Figure 2. It should be noted that the equilibrium potentials essentially remained constant for more than 5 min, after which only a very slow divergence was recorded. The standard deviation of 10 replicate measurements is ± 0.5 mV. The membrane sensors prepared could be used for at least 4 months without any measurable divergence.

The selectivity coefficients ($K_{Na,M}^{pot}$) were evaluated graphically by the mixed solution method[22] from potential measurements on solution containing a fixed amount of sodium (5×10^{-3} M) and a varying amount of the interfering ions (M^{n+}), according to the equation

$$K_{Na,M}^{pot} \, a_M^{1/n} = a_{Na}\{\exp[(E_2 - E_1)F/RT]\} - a_{Na} \qquad (1)$$

Where E_1 and E_2 are the electrode potentials for the solution of Na^+ ions alone and for the solution containing interfering ions and Na^+ ions respectively. According to eq. 1, the K_{Na}^{pot} values for diverse ions can be evaluated from the slope of the graph of $a_{Na}\{\exp[(E_2 - E_1)F/RT]\} - a_{Na}$ *Vs* $a_M^{1/n}$. The resulting values of the selectivity coefficients are summarized in Table 2.

As it is seen from Table 2, the bivalent alkaline earth ions exhibited almost no interference electrode. Among the alkali and transition metal ions, K^+ and Pb^{2+} caused only slight interference respectively.

The utility, sensitivity and selectivity of the proposed membrane electrode were verified by determining 15 μg mL^{-1} of Na^+ in synthetic mixtures containing 5-50 fold excess of different alkali and alkaline earth metal ions using the standard addition technique. Results with an average recovery of 99.1% and a mean standard deviation of 1.8% were obtained.

Conclusion

The sodium ion-selective electrode based on DBPY18C6 exhibits good sensitivity, a short response time (< 20 s), good reproducibility and good selectivity. In addition, it is very simple to prepare.

The optimized formulation of the membrane (*i.e.* 93 mg PVC, 186.5 mg DMS, 3 mg DBPY18C6) resulted in a linear concentration range of 1.0×10^{-4}-1.0×10^{-1} M with a slope of 58.5 mV/decade and a limit of detection of 9.0×10^{-5} M.

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