



## A new Potassium ion-selective electrode based on dibenzo-18-crown-6 (DB18C6) as ionophore

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Potassium is a vital element in biological fluids of the human body. The daily monitoring of its concentration may be one of the most important indices in the early diagnosis of heart disorder, myocardial infarction, insult and other diseases [1]. PVC-based membrane of DB18C6 as ionophore with sodium tetraphenyl borate (NaPhB) as anion excluder and dibutylphthalate (DBP) as plasticizing solvent mediator was prepared and investigated as  $K^+$ -selective electrode. The various amounts of ionophore (1.3 – 3.3 wt%), NaTPB (0.95 – 1.41 wt%), plasticizers (63.75 – 65 wt%) and PVC (33-34.8 wt%) were dissolved in 6-8 mL of tetrahydrofuran and the solution was mixed by magnetic stirrer. After solvent evaporation overnight, the membrane was mounted on the end of a pyrex tube by dipping method [2]. The potentials were measured by direct potentiometry with the help of calomel electrodes as external reference electrode. A  $1.0 \times 10^{-2}$  M potassium chloride solution was taken as an inner reference solution and Ag/AgCl electrode were used as internal reference electrodes. The potential readings of the electrodes were recorded after the potential had reached steady state. Influences of the membrane composition, pH, and possible interfering ions were investigated on the response properties of the electrode. The performance of the electrodes was examined by measuring the potentials of the primary ion solutions with a concentration range of  $10^{-8}$  –  $10^{-1}$  M. Calibration plots were constructed by plotting the potential change versus the logarithm of the activity of the cation present in the sample solution. The response of the electrode is linear with a near Nernstian slope of 53.0 mV/decade over an  $K^+$  ion concentration range of  $1 \times 10^{-5}$  to  $1.0 \times 10^{-2}$  M and a detection limit of  $1.26 \times 10^{-5}$  M. The response time of the sensor for  $K^+$  concentrations ranging from  $1 \times 10^{-5}$  to  $1.0 \times 10^{-2}$  M is between 1-2 min. Separate solution method (SSM) was used for determination of selectivity coefficients [3,4]. The selectivity relative to transition and heavy metal ions is good. The electrode could be used for a period of 2 to 3 weeks without considerable alteration in its potential. The electrode is suitable for use within the pH range of 1–10. All pH adjustments were made with HCl and  $NH_3$ .

### References

- [1] Goldberger and Goldberger, 1970.
- [2] M. Ganjali, R. Nemat, F. Faridbod, P. Norouzi, F. Darviche, Int. J. Electrochem. Sci., 3(2008)1290.
- [3] M. de Souza Castilho, N. Ramos Stradiotto, Talanta 74(2008)1633.
- [4] P. R. Buck, E. Lindner, Pure Appl. Chem., 66(1994)2527.

## Polymeric membrane and coated graphite mercury(II)-selective electrodes based on 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane as an excellent Ionophore

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Recently, several greatly selective and sensitive poly(vinyl chloride) (PVC)-membrane ISEs for various metal ions have been reported [1,2]. In this study, the coated graphite electrode (CGE) for determination of mercury(II) was prepared based on 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (kryptofix5) as an excellent sensing material is successfully developed. It is well established that some important features of the PVC membranes such as the properties of the plasticizer, the plasticizer/PVC ratio, the nature and amount of the ion carrier, and particularly the nature and amount of the additives used, significantly influence the sensitivity and selectivity of the ion-selective electrodes [3]. The construction, performance characteristics, and application of a novel mercury(II) membrane sensor are reported in this paper. Different aspects for the preparation of Hg(II) sensors based on kryptofix5 were optimized. Effects of various plasticizers was studied in detail and improved performance was observed. In our preliminary studies, to examine the interactions between  $Hg^{2+}$  cations and the ligand, complex formation between the ligand and mercury(II) cations was investigated. The best performance was obtained for the membrane sensor having a composition of 30% poly(vinyl chloride) (PVC), 65% dibutyl phthalate (DBP), 5% 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (kryptofix5) and 2% sodium tetraphenyl borate (NaTPB). The electrodes exhibit Nernstian slope of  $30.8 \pm 0.3$  mV per decade for  $Hg^{2+}$  ions over wide concentration range ( $1.0 \times 10^{-2}$  to  $1.0 \times 10^{-7}$  M). The CGE have detection limits of  $5.0 \times 10^{-7}$  M, and response times of about 15s and can be used for at least 2 months without noticing any considerable potential divergence. The potentiometric response is independent of the pH of the test solution in the pH range 3.0–8.0. The potentiometric selectivity coefficient values as determined by match potential method (MPM) indicate excellent selectivity for  $Hg^{2+}$  ions over interfering cations. In addition, the proposed electrode revealed good selectivities over a wide variety of other cations including alkali, alkaline earth, transition and heavy metal ions. The CGE was used as indicator electrode in the potentiometric titration of  $Hg^{2+}$  ions with EDTA. The sensor possessed the advantages of short conditioning time, fast response time and, especially, good selectivity towards the transition and heavy metal ions as well as some mono, di and trivalent cations such as  $Na^+$ ,  $K^+$ ,  $Pb^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Mg^{2+}$ ,  $Fe^{3+}$ ,  $Al^{3+}$  and  $Cr^{3+}$ . The sensor accuracy was investigated by the potentiometric titration of a  $Hg^{2+}$  solution with sodium sulfide and sodium chloride as well as the monitoring of Hg(II) cations. As a result, the developed sensor provided satisfactory results after its application in the  $Hg^{2+}$  determination in waste water samples.

### References

- [1] G.H. Rounaghi, and A. Ghaemi, Electrochemical Society, 4(2012) 159.
- [2] G.H. Rounaghi, R. Mohammad Zadeh Kakhki, and H. Sadeghian, Electrochimica Acta, 56(2011) 9756-9761.
- [3] S.K. Mittal, S.K. Ashokkumar, H. Sharma, E-J. Chem. 7(2010) 849.

## Complexation and thermodynamic study of 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane with $Hg^{2+}$ cation in mixed non-aqueous solvents

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Cyclic polyethers (crown ethers) are selective complexing agents for the cations [1-3]. They are utilized to extract cations from aqueous solutions into hydrophobic, nonpolar organic solvents and to carry these cations selectively through solvent-polymeric liquid membranes [4,5]. The complexation processes between mercury(II) metal cation with macrocyclic ligand, 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (kryptofix5), were studied in acetonitrile-methanol (AN-MeOH), acetonitrile-tetrahydrofuran (AN-THF), acetonitrile-methylacetate (AN-MeOAc) and acetonitrile-nitrobenzene (AN-NB) binary solvents, at different temperatures using conductometric method. The conductance data show that the stoichiometry of the complexes formed between this macrocyclic ligand and  $Hg^{2+}$  cation in most cases is 1:1 (ML). The values of stability constants of the 1:1 [M:L] complex was determined from conductometric data using a GENPLOT computer program [6]. The results revealed that, the stability constant of (kryptofix5. $Hg^{2+}$ ) complex in pure organic solvents varies in the order: NB>MeOAc>AN>MeOH>THF and in the case of binary mixed solutions at 25°C it follows the order: AN-NB>AN-MeOAc>AN-