

Full Paper

Fabrication of Potassium Ion-selective Membrane Electrode as Immobilized Liquid based on Dibenzo-18-Crown-6 (DB18C6) as Ionophore

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Received: 1 March 2014 / Received in Revised form: 22 July 2014 /

Accepted: 8 August 2014 / Published online: 31 August 2014

Abstract- Precisely detection of specific ion in a solution with ion electrodes provides valuable clinical and chemical information. For this purpose, specific ion selective electrodes have been designed, which are able to detect the concentrations of specific ions as much as 10^{-5} M. In this study, we introduced a polyvinylchloride (PVC)-based membrane of Dibenzo-18-crown-6 (DB18C6), which exhibited good potentiometric response for K^+ over a wide concentration range of 1.0×10^{-5} to 1.0×10^{-2} mol L^{-1} . The best Nernstian slope for the desired electrode was 53 mV/decade of K^+ concentration. Matched potential method (MPM) was used for determination of selectivity coefficient. The response time for the K^+ selective electrode was 30 s. The electrode was used for a period of 4 weeks. Our results showed that the electrode can be used in wide pH range from 3.0 to 9.5. Electrode was successfully applied for determination of potassium in oral rehydration salts (ORS) and mineral water.

Keywords- K^+ ion, Selective electrode, PVC membrane, Dibenzo-18-crown-6

1. INTRODUCTION

Analytical methods for detection of potassium ions have significantly developed. Numerous articles have been published since 2010 on the subject of potassium determination in a wide variety of biological, environmental, and metallurgical samples.

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. 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. An interesting application of crown ethers is their potential use as ion-selective components (ion carriers) in liquid membrane electrodes [2-8]. Some of the electroanalytical methods found in literatures such as those in which hexacyanoferrate-modified electrodes have been used as ion-selective electrodes are very important [9-13].

Eftekhari [14] and Mortimer et al. [15] developed hexacyanoferrate-modified electrodes as a potentiometric sensor to determine potassium ions. The potassium is determined in biodiesel using flame atomic emission spectrometry and using ICP optical emission spectrometry [16,17]. These methods of analysis show low standard deviations and good reproducibility, but involve costly equipments and long time of analysis.

In the present study, the proposed method has some important advantage. For example, the electrode proved to be successful, and provided a rapid, simple and low cost potentiometric method for the determination of K^+ ion in pure solution mineral water and in pharmaceuticals. From study of the complexation behavior of the ions with macrocyclic compounds [18,19], it was found that the potassium ions form strong complex with Dibenzo18crown6.

In the primary conductance study for complexation, the stability constant value ($\log K_f$) of K^+ -DB18C6 complex was calculated that showed this ionophore was used as a sensing material in concentration of K^+ ion membrane electrode. The ISE response is attributed to the electron-exchange mechanism at the membrane-contact interface and ion exchange at the membrane solution interface. This electrode is based on incorporation of an ion-pair complex of the tetraphenylborate anion (TPB^-) with potassium cation (K^+) in a polyvinylchloride matrix.

2. EXPERIMENTAL

2.1. Apparatuses

Potentiometric and pH measurements were made with a pH/mV meter model 213 HANA, (City, Romania) with ± 0.1 mV precision. The glass cell where the K^+ indicator PVC membrane electrode was located; consisted of two Ag/AgCl double junction reference electrodes as internal and external reference electrodes.

2.2. Materials and Reagents

Analytical reagent grade chemicals and doubly distilled water were used for preparing all aqueous solutions. High molecular weight Poly Vinyl Chloride powder (PVC) (Aldrich Chemical Co, USA), Sodium-Tetra-Phenyl-Borate (NaTPB), Di-Butyl-Phthalate (DBP), benzylacetate (BA), dimethyl sebacate (DMS), Tetra-Hydro-Furan (THF) (Merck, Co, Germany), and Dibenzo-18-Crown-6 (DB18C6) were purchased from Aldrich chemical Co, USA. Salt of metal chlorides (all from Merck) were of the highest purity available without modification. Oral Rehydration Salts (ORS) manufactured by Modava Pharmaceutical Co, (Tehran-Iran) and mineral water produced by Pahre product of Irancola Iranshahr factory were prepared.

2.3. Preparation of PVC membrane Electrodes

Different amounts of ionophore with appropriate percentage of PVC, plasticizer and additives were dissolved in 5 to 8 ml of tetrahydrofuran (THF). The solution was poured into a Pyrex tube of 2 cm diameter, and was mixed well. Afterwards, THF was evaporated slowly until an oily concentrated mixture was obtained. Then, a Pyrex tube was dipped into the mixture for about 20 s, so that a transparent membrane (of about 0.3 to 0.5 mm in thickness) was formed. The tube was then removed from the mixture and kept at room temperature for about 10 h, and filled with an internal filling solution (1.0×10^{-2} mol L⁻¹ of KCl). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-1} mol L⁻¹ KCl [20-22].

2.4. Potential measurement

For potential measuring of the desired ion selective electrode, the concentration of 0.01 M of the same cation was saturated with silver nitrate solution, and then was connected to potentiometer with a silver wire. For this purpose, an Ag/AgCl electrode was used as external reference electrode. The voltage is theoretically dependent on the logarithm of the ionic activity, according to the Nernst equation. Solution with different concentrations of KCl (10^{-7} to 10^{-1}) was prepared, and their potential was measured at 25 °C. Subsequently, the potential curve was drawn versus log cation activity, and the slope of the line was calculated. According to the Nernst equation, when the slope of the desired cation is equals with $0.0591/n$, the electrode is a selective electrode for the ion.

2.5. Analytical procedure

2.5.1. Calibration graph

Suitable increments of standard KCl solution were added to 50 mL of 1×10^{-7} mol L⁻¹ KCl solution to cover the concentration range from 1.0×10^{-7} to 1.0×10^{-1} mol L⁻¹. In the case

of concentrated solutions, separate solution was used. In this solution a potential was recorded after 30 s, at 25 °C, after each addition. The unknown concentration was determined from the calibration graph. The electrode potentials (E_{elec}) were calculated from the emf values and plotted versus $\log a_{\text{K}^+}$.

2.5.2. Standard addition method

Small increments of a standard potassium hydrochloride solution ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) were added to 50 mL aliquot samples of various O.R.S solution and mineral water concentrations. The change in potential reading (at a constant temperature of 25 °C) were recorded for each increment and used to calculate concentration of K^+ sample solution. The potentiometric measurements were carried out in $0.01 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$ solution to maintain the ionic strength constant and the pH range adjustment. For the analysis of potassium formulations, ORS powder was dissolved in 50 mL of distilled water and the standard addition technique was applied as described above.

3. RESULTS AND DISCUSSION

3.1. PVC Membrane Composition Selection

It is well known that the sensitivity and selectivity of the ion-selective electrodes 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 K^+ electrode were investigated and the results are summarized in Table 1.

Several plasticizers including DBP, BA and DMS, which are often used with PVC membrane electrodes were evaluated. Since the nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands [23,24], 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, the best electrode responses was observed in membrane having DBP.

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 [25,26]. In spite of these considerations, a carrier content of 3.3% 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 electrodes behavior showed that the best Nernstian slope is 53.0 mV/decade. Finally, membrane no.3 with the composition of 32% PVC, 3.3% DB18C6, 62.7% DBP and 2% NaTPB was selected to design the electrode (Table 1). A linear response towards the K^+

concentration was from 1.0×10^{-5} to 1.0×10^{-2} mol L⁻¹. Detection limit of K⁺ selective electrode, which was calculated by extrapolating the two segments of calibration curves, was 5.06×10^{-6} mol L⁻¹.

Table 1. Optimization of the PVC membrane ingredients

Membrane number	Composition in ratio (w/w)				Detection Limit (mol L ⁻¹)	Slope (mV/decade)
	PVC	plasticizer	DB18C6	NaTPB		
1	32	BA,62.7	3.3	2	1.0×10^{-5}	26.5±0.6
2	32	DMS,62.7	3.3	2	1.0×10^{-5}	39.3±0.4
3	32	DBP,62.7	3.3	2	5.4×10^{-6}	53.0±0.8
4	32	DBP,63	3	2	8.5×10^{-6}	47.1±0.2
5	32	DBP,64	2	2	5.0×10^{-5}	41.5±0.6
6	32	DBP,65	1	2	8.0×10^{-5}	28.2±0.3
7	32	DBP,62	4	2	1.0×10^{-5}	40.5±0.1
8	32	DBP,66	-	2	-	11.9±0.6

3.2. Calibration Graph study

The potentiometric response of the ISE to K⁺ ions was tested by measuring the electrode potentials for a series of standard solution of KCl (Fig.1). The average slope was 53 mV/decade, slightly lower than the Nernstian value. The detection limit was 5.06×10^{-6} mol L⁻¹ which was calculated by extrapolating the two segments of calibration curves. The electrode exhibited a linear response to potassium ions in the concentration range of 1.0×10^{-5} to 1.0×10^{-2} mol L⁻¹. In comparison with other reported K⁺ membrane electrodes (Table 2), the proposed electrode is superior to the previously reported ones in linearity range, Nernstian slope and detection limit.

Table 2. Comparison of the linear range (mol L⁻¹), slope (mV/decade) and detection limit of the K⁺-ISE (membrane no.3) and the previous reported ones

Properties	Ref. [14]	Ref. [27]	Present work
Slope (mV/decade)	53-57	53-55	53.0
Linear range (mol L ⁻¹)	8.0×10^{-5} to 1.0	4.0×10^{-5} to 1.0×10^{-2}	1.0×10^{-5} to 1.0×10^{-2}
Detection limit (mol L ⁻¹)	4.0×10^{-5}	1.9×10^{-5}	5.06×10^{-6}

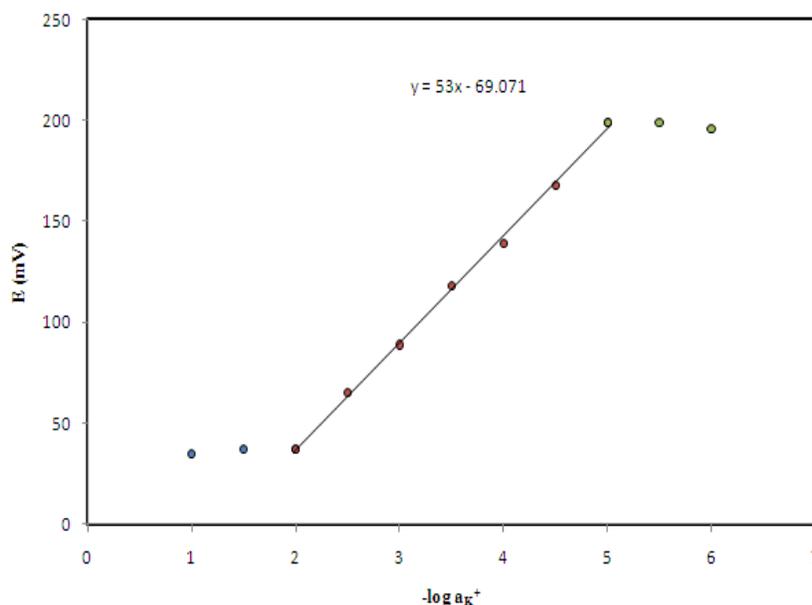


Fig. 1. Calibration curve of ion selective electrode, results are based on four replicate measurements

3.3. Study of electrode properties

The properties of potassium ion selective electrode including response time, life time, selectivity and pH range applicability are evaluated and the results are as follow. These properties are the most important characteristics that are considered in clinical uses of ISEs.

3.3.1. Response Time

Response time is the required time for the electrode to achieve values within ± 1 mV of the final equilibrium potential after successive immersion in the sample solutions [27,28]. It is an average time to record the potential carefully. This time for K^+ selective electrode was 30 s in concentrated solutions.

3.3.2. Life-time

The proposed electrode can be used for four weeks without any considerable change in potential response. After this time, a slight gradual decrease in the slope and an increase in the detection limit is observed. In PVC membrane electrodes after several time of usage, the membrane ingredients leak from the organic layer and affect the membrane response. The results are shown in Table 3.

Table 3. Life time of the K⁺ selective electrode (membrane no.3)

Week	Slope (mV/decade)	Detection Limit (mol L ⁻¹)
First	53.0	5.06×10 ⁻⁶
Second	52.6	6.00×10 ⁻⁶
Third	50.8	9.50×10 ⁻⁶
Fourth	50.0	5.00×10 ⁻⁵
Fifth	41.2	1.00×10 ⁻⁴

3.3.3. Selectivity

The selectivity behavior is one of the most important characteristics of K⁺-ISE. The potentiometer selectivity coefficients, were evaluated by the matched potential method (MPM) [30,31], and the results are shown in Table 4. According to the MPM, a specified activity of primary ion (A) is added to a reference solution and the height of potentiometric peak is measured. In a separate experiment, the interfering ions (B) are successively added to an identical reference solution, until the measured peak height matches to the one obtained before by adding primary ions. The MPM selectivity coefficient ($K_{A,B}$), is then given by resulting primary ion to interfering ion activity ratio, $K_{A,B} = a_A/a_B$.

There is a good correspondence between the formation constant and the selectivity coefficient order, because the selectivity of an ion-selective electrode is mainly related to the stability of the complex between ion and ionophore.

Table 4. Selectivity coefficients ($K_{A,B}$) of various interfering cations (B) with primary ion (A)

Interfering ion	Log (K_{MPM})
Na ⁺	-2.70
Sr ²⁺	-3.30
Li ⁺	-3.90
NH ₄ ⁺	-4.10
Pb ²⁺	-3.09
Ni ²⁺	-3.52
Ba ²⁺	-4.00
Mg ²⁺	-3.10
Cd ²⁺	-4.50
Ca ²⁺	-3.70

3.4. Effect of pH

The working pH range of the proposed membrane electrode was described. In addition, significant changes in potential value were reported for this electrode. The behavior of the ISE was studied in concentration of K^+ $1.0 \times 10^{-3} \text{ mol L}^{-1}$ over the pH range of 1 up to 10 (Fig. 2). Adjustments of the pH were made using concentrated HCl or NH_3 . The response of electrode is independent from pH in the range of about 3.0 to 9.5, which can be taken as the working pH range of the electrode. The observed changes of potential at lower and higher pH values could be due to the protonation of the ionophore and formation of some hydroxyl complexes of K^+ ion in solution, respectively.

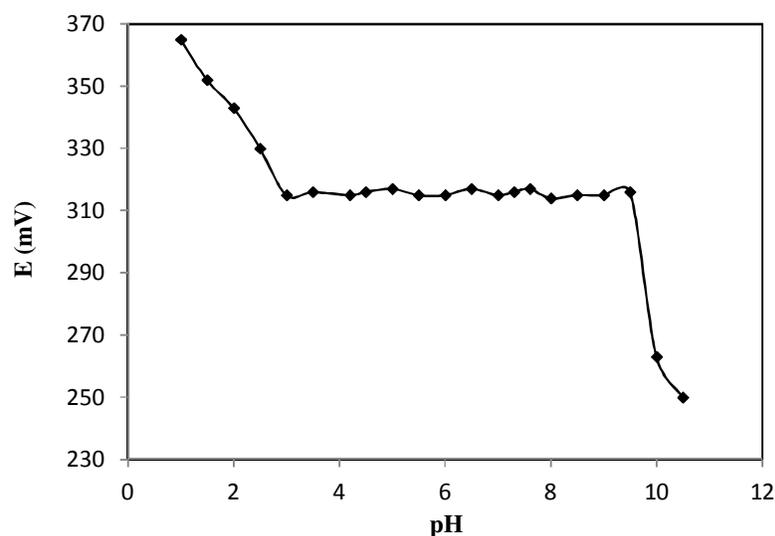


Fig. 2. Effect of pH of the test solution on the potential reading ($1.0 \times 10^{-3} \text{ mol L}^{-1}$ KCl) Solution at 25°C

3.5. Precision and accuracy

Repeatability is one of the most important features of an ion selective electrode. For repeatability monitoring of the membrane electrode, 2 standard samples were measured. All parameters including the Nernst slope, life-time, response time, and effect of pH should be maintained constant. The relative standard deviation (RSD%) values by PVC membrane were not exceeding 4.1%. The results of this study were confirmed with flame photometry.

3.6. Analytical applications

The Oral Rehydration Salt (ORS) and mineral water solutions were used for K^+ ions determination by the ISE as an indicator electrode using the standard addition method and the results are summarized in Table 5. As shows in Table 5 the results are comparable with the values obtained by flame photometry.

T-test method used for accuracy test, that the mean values were obtained at 95% confidence limits for three degree of freedom and the results showed that calculated t-test did not exceed the critical values.

Table 5. Determination of the concentration (mol L^{-1}) of K^+ ion in ORS and mineral water by K^+ -ISE and comparison with the flame photometry method

Sample	Flame photometry (mol L^{-1})	*Potentiometry by K^+ -ISE (mol L^{-1})
ORS	$(19.2 \pm 1.5) \times 10^{-3}$	$(18.7 \pm 1.3) \times 10^{-3}$
Mineral Water	$(0.96 \pm 0.2) \times 10^{-3}$	$(0.91 \pm 0.5) \times 10^{-3}$

*The results are based on four replicate measurements

4. CONCLUSION

The potassium ion-selective electrode based on DB18C6 exhibited good sensitivity, and a short response time (~ 30 s). The optimized formulation of the membrane composition was composed of 32% PVC, 3.3% DB18C6, 62.7% DBP and 2% NaTPB, which resulted in a linear concentration range of 1.0×10^{-5} to 1.0×10^{-2} mol L^{-1} with a slope of 53.0 mV/decade and a detection limit of 5.06×10^{-6} mol L^{-1} . Potentials of the electrode were found to stay constant across the range of pH 3 to 9.5. The electrode enabled the potassium determination in real samples.

Acknowledgment

This work was funded by grant number 892/2/453 from the University of Sistan and Baluchestan, Iran.

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