

Full Paper

Application of Graphite Coated Potassium-Selective Electrode in Determination of Potassium in Real Samples

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Received: 13 July 2014 / Received in revised form: 10 September 2014 /

Accepted: 22 September 2014 / Published online: 31 October 2014

Abstract- A graphite coated ion selective electrode (GCISE) based on Dibenzo-18-Crown-6 (DB18C6) as a neutral carrier in a Poly Vinyl Chloride (PVC) matrix was fabricated for the determination of K⁺ ions. The GCISE exhibited a Nernstian slope of 55.3 mV per decade for K⁺ ion over a wide concentration range of 1.0×10⁻⁵ to 1.0×10⁻¹M. The lower detection limit is 5.4×10⁻⁶M of KCl. This GCISE had a short response time of 10s, and could be used in a pH range of 2.4 to 9.5. Matched potential method (MPM) was used for determination of selectivity coefficient. High selectivity was obtained over 10 various metal ions. The GCISE was reproducible and stable for a period of two weeks. It was successfully applied in determination of potassium in Oral Rehydration Salts (O.R.S) and mineral water.

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

1. INTRODUCTION

Potentiometric detection based on ion selective electrodes, as a simple method, offers several advantages such as speed and ease of preparation and procedures, simple instrumentation, relatively fast response, wide dynamic range, reasonable selectivity and low cost. These characteristics have inevitably led to electrodes for several ionic species, and the

list of available electrodes has grown substantially over the last few years [1-8]. The potassium ions have been determined in several matrices using different techniques such as, the remogravimetry [9], inductively coupled plasma-atomic emission spectrophotometry [10], turbidimetric in-flow injection analysis [11,12], spectrophotometry [13], chromatography [14] and electroanalytical methods [15-20]. PVC membrane electrodes are one of subdivisions of potentiometric electrodes which are widely used and have different application in analysis of various ionic species [21-27]. From study of complexation behaviour of the ions with macrocyclic compounds [28,29], it was found that the potassium ions form a strong complex with dibenzo18crown6. 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 electrone-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. We report on the fabrication of a graphite coated electrode (GCE) for K^+ ions and its characteristics, which have been studied for an evaluation of its usefulness in determination of potassium ions in real samples. Ones of important aspects of using a GCE is use of graphite powder as internal electronic conductor. This electrode was successfully applied in determination of K^+ ions in mineral water and oral rehydration salts (ORS).

2. EXPERIMENTAL

2.1. Apparatuses

Potentiometric and pH measurements were made with a pH/mV meter model (213 HANA, 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, U.S.A), Sodium-Tetra-Phenyl-Borate ($NaTPB$), Di-Butyl-Phthalate (DBP), benzylacetate (BA), dimethyl sebacate (DMS), Tetra-Hydro-Furan (THF)(Merck, Co, Germany), graphite, and Dibenzo-18-Crown-6 (DB18C6) were purchased from Aldrich chemical Co, U.S.A. Salt of metal chlorides (all from Merck) were of the highest purity available without modification. Oral Rehydration Salts (O.R.S) manufactured by Rouz Darou

pharmaceutical Co, (Tehran-Iran), Mineral water cheshmeh product of argnoosh special economic zone phase 2 industrial.

2.3. GCISE Preparation

Varying amounts of the ionophore (DB18C6), anion excluder NaTPB and PVC were dissolved in about 3mL of THF along with the solvent mediator plasticizer (DBP) to obtain different compositions. The solvent was evaporated slowly at room temperature until an oily concentrated mixture was obtained [30,31]. A graphite about 1mm diameter and 5 mm length, sealed into the end of a Teflon tube, and filled with an internal filling powder graphite, which did not need any internal solution. GCISE was obtained by dipping graphite into this mixture, until a thin film coating was formed. This film was allowed to dry for 5 h in air. The electrode was finally conditioned for 24 h in a 1×10^{-1} M of potassium chloride (KCl) solution.

2.4. Potential measurement

For potential measuring, the desired GCISE filled with an internal filling graphite powder and then was connected to potentiometer with a silver wire. For this purpose, an Ag/AgCl electrode was used as external reference electrode. Solution with different concentrations of KCl (10^{-7} - 10^{-1} M) was prepared and their potential was measured at 25 °C.

2.5. Analytical procedure

2.5.1. The calibration graphs

Suitable increments of standard KCl solution were added to 50 mL of 1×10^{-7} M KCl solution to cover the concentration range from 1.0×10^{-7} to 1.0×10^{-1} M. In the case of concentrated solutions, separate solutions were used. In this solution a potential was recorded after 10 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 (1.0×10^{-3} M) 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 M NH_4Cl 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. Electrode response characteristics

The potential responses of graphite coated ion-selective electrode (GCISE) for solutions containing each cation separately were obtained, and the results are shown in Fig. 1. As this figure exhibits, this electrode has a better response to potassium than to the other cations. The electrode properties of DB18C6-based ISE were highly influenced by the complexing ability of the DB18C6 with the K^+ ion, which were dependent considerably on the relative size of cavity of ionophore and ion.

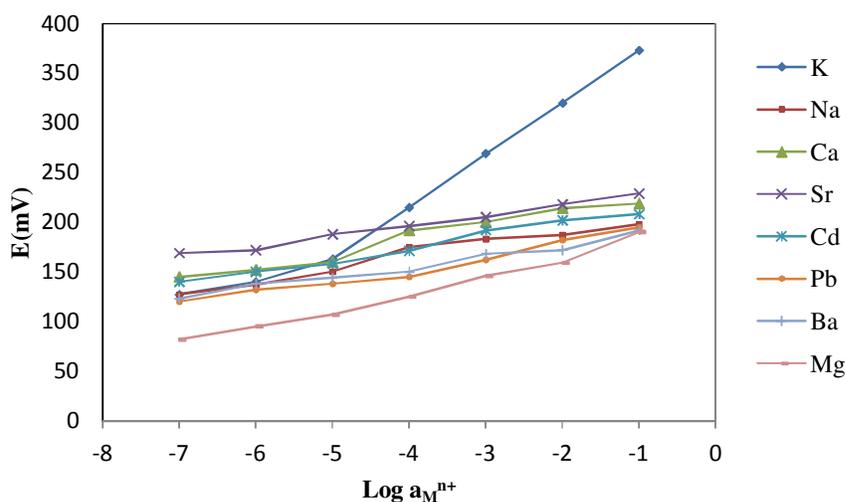


Fig. 1. The potential responses of various cations on GCISE

3.2. Optimization of membrane composition

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 [32,33], 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 electrode responses showed that DBP membrane has better respond.

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 [34,35]. 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.

Finally, membrane no.3 with composition of 32% PVC, 3.3% DB18C6, 62.7% DBP and 2% NaTPB was selected to design the electrode. The GCISE with optimum composition showed a liner response with slope of 55.3 ± 0.2 mV per decade in concentration range of 1.0×10^{-5} to 1.0×10^{-1} M for KCl solutions. In this work, detection limit of electrode was 5.4×10^{-6} M which was calculated by extrapolating the two segments of the calibration curves.

Table 1. Optimization of the PVC membrane ingredients

Membrane number	Composition in ratio (w/w)				Detection Limit (M)	Slope (mV per decade)
	PVC	plasticizer	DB18C6	NaTBP		
1	32	BA,62.7	3.3	2	1.0×10^{-5}	34.6 ± 0.5
2	32	DMS,62.7	3.3	2	1.0×10^{-5}	18.3 ± 0.4
3	32	DBP,62.7	3.3	2	5.4×10^{-6}	55.3 ± 0.2
4	32	DBP,63	3	2	8.5×10^{-6}	50.8 ± 0.4
5	32	DBP,64	2	2	5.0×10^{-5}	41.1 ± 0.4
6	32	DBP,65	1	2	8.0×10^{-5}	45.3 ± 0.6
7	32	DBP,62	4	2	1.0×10^{-5}	38.9 ± 0.4
8	32	DBP,66	-	2	-	7.9 ± 0.6

3.3. The effect of pH

The effect of pH of test solution on the response of the electrode was investigated in a 1.0×10^{-4} M (KCl) solution and the results for pH value of 1.0 up to 10.0 are shown in Fig. 2. The pH adjustments in solutions were made with NH_3 or HCl solutions. The response of electrode is independent from pH in the range of about 2.4 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 ion carrier and formation of some hydroxyl complexes of K^+ ion in solution, respectively.

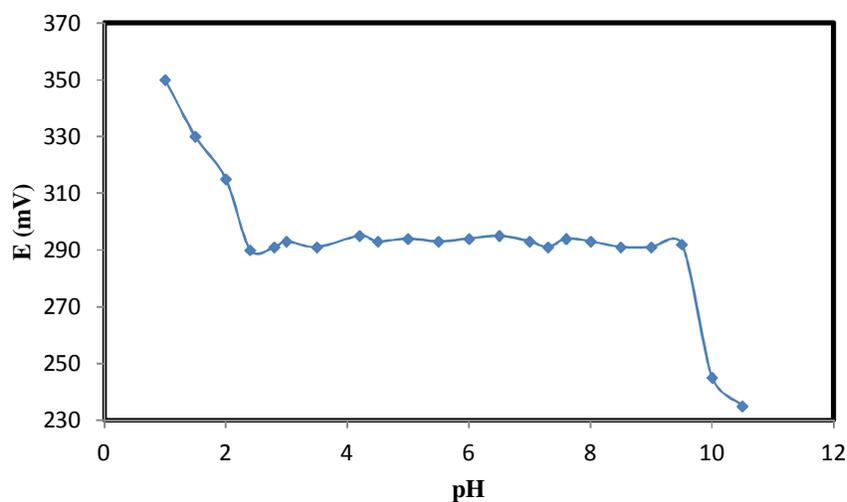


Fig. 2. Effect of pH of the test solution on the potential reading (1.0×10^{-4} M KCl) Solution at 25°C

3.4. Response time of the electrode

The average time required the electrode to reach a potential within ± 1 mV of final equilibrium value after successive immersion of a series of K^+ ion solutions, each having a 10-fold difference in concentration, was measured [36-37]. The static response time of the electrode obtained was 10 s for solutions from 1.0×10^{-5} to 1.0×10^{-3} M. A potential-time plot for the electrode is given in Fig. 3.

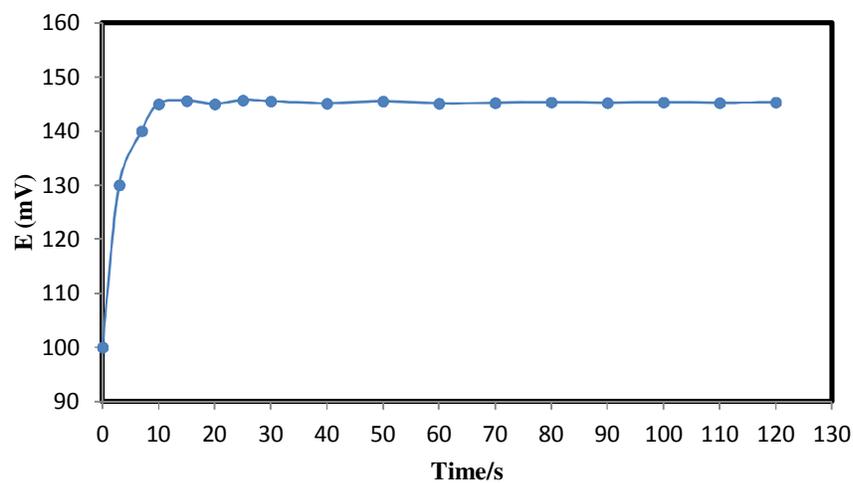


Fig. 3. Response time profile of K^+ -GCISE (membrane no.3) for concentration 1.0×10^{-5} to 1.0×10^{-3} M

3.5. life time, Reproducibility and Repeatability of electrode

The proposed electrode can be used for two 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 found. In PVC membrane electrodes after several time of usage, the membrane ingredients leak from the organic layer and affect the membrane response. To evaluate the reproducibility of the proposed electrode, five electrodes with similar compositions (as no. 3. in Table 1) were prepared and the responses of these electrodes to K^+ ion concentration were tested. The results are shown in Fig. 4. The slope of each electrode was determined and average slope with standard deviation was 54.7 ± 0.3 mV per decade. In the repeatability study, the calibration curves of one electrode in 7 days were obtained. The average slope with standard deviation that obtained was 54.7 ± 0.3 mV per decade.

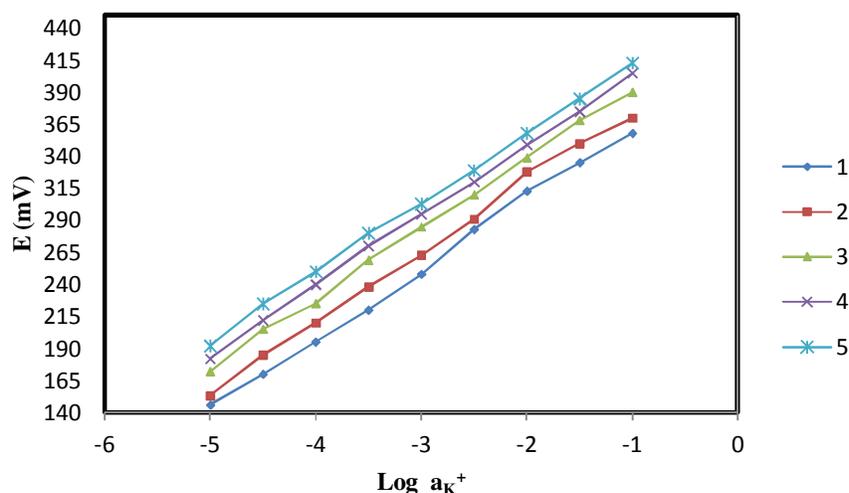


Fig. 4. Reproducibility of the electrodes (five) with similar composition (Membrane no.3)

3.6. Selectivity coefficients of K^+ -GCISE

The selectivity behavior is one of the most important characteristics of K^+ -GCISE. The potentiometer selectivity coefficients were evaluated by the matched potential method (MPM) [38,39]. The selectivity coefficients are shown in Table 2. 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, $K_{A,B} = a_A/a_B$.

Table 2. Selectivity coefficients $K_{A,B}$ of various interfering cations (B) with primary ion (A)

Interfering Ion	Log (K_{MPM})
Na ⁺	-2.15
Sr ²⁺	-3.00
Li ⁺	-3.85
NH ₄ ⁺	-3.00
Pb ²⁺	-4.20
Ni ²⁺	-3.82
Ba ²⁺	-3.01
Mg ²⁺	-4.00
Cd ²⁺	-3.91
Ca ²⁺	-3.62

In comparison with other reported K⁺ membrane electrodes, Table 3, the proposed electrode is superior to the previously reported ones in linearity range, Nernstian slope and detection limit.

Table 3. Comparison of the linear range (M), slope (mV per decade) and detection limit of the K⁺-GCISE (membrane no.3) and the previous reported ones

Properties	Ref. [40]	Ref. [41]	Present work
Slope (mV per decade)	53-57	53-55	55.3
Linear range (M)	8.0×10 ⁻⁵ to 1.0	4.0×10 ⁻⁵ to 1.0×10 ⁻²	1.0×10 ⁻⁵ to 1.0×10 ⁻¹
Detection limit (M)	4.0×10 ⁻⁵	1.9×10 ⁻⁵	5.4×10 ⁻⁶

3.7. Analytical applications

The Oral Rehydration Salt (ORS) and mineral water solutions were used for K⁺ ions determination by the GCISE as an indicator electrode using the standard addition method and the results are summarized in Table 4. As shows in Table 4, the results are comparable with the values obtained by flame photometry.

T-test method was used for accuracy test, that 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 4. Determination of the concentration (M) of K⁺ ion in ORS and mineral water by use of the K⁺-GCISE and comparison with the flame photometry method

Sample	Flame photometry (M)	*Potentiometry with K ⁺ -GCISE (M)	Calculated value t	●Critical value t
O.R.S	$(20.65 \pm 1.3) \times 10^{-3}$	$(21.37 \pm 1.5) \times 10^{-3}$	1.17	3.18
Mineral Water	$(0.3 \pm 0.02) \times 10^{-3}$	$(0.3 \pm 0.01) \times 10^{-3}$	0	3.18

*The results are based on four replicate measurements.

●The critical value of |t| for 95% confidence limits for three degree of freedom

4. CONCLUSION

Graphite coated ion-selective electrode (GCISE) fabricated in the present work holds promise for the analysis of potassium in various matrices, because it has good selectivity over a number of other metal ions. The main advantages of GCISE are simple construction and inexpensiveness compared to the conventional ISEs. GCISEs also have the big interesting advantages that do not need any internal solution.

Acknowledgment

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

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