Polymer Membranes based on Ionophore-impregnated for Nutrients Detection by Electrochemical Methods

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ABSTRACT

Polymer membranes are becoming ever more attractive for trace analysis based on ionophore-impregnated; offering a wide variety of potential for an even wider variety of applications. Here we report a series of macrocyclic compounds with different substituents; which have been examined for their potential to detect potassium phosphate in the presence of other potassium counter ions. The ion selective electrode based on dibenzo-18-crown-6 exhibited a near Nernstian response for potassium phosphate over a wide concentration range of 5×10^{-5} mol/l^{-1} to 1×10^{-1} mol/l^{-1} with a low limit of detection of 3.2×10^{-6} mol/l^{-1}. The resulting electrode exhibited a shelf life of 40 days with negligible drift. The ensemble was use used to determine K^+ ions in a range of real samples the results of which showed a strong correlation with the data obtain from the same samples via atomic absorption spectroscopy. The use of dibenzo-18-crown-6 showed the potential towards a method for the quantitative determination of potassium phosphate in water samples.

Keywords: Crown ethers, Ion selective electrode, Potassium phosphate, Dibenzo-18-crown-6, Ionophore, Polymer membrane

INTRODUCTION

Potassium and phosphorus are among the nutrients plants and other organisms need to flourish, hence potassium phosphate delivers both and as such is a common substituent of fertilizer. The over use of such fertilizers result in the contamination of rivers and water supplies, thus issues of water quality still continue to attract the attention of researchers [1]. This has led to an increased level of interest in potentiometric based sensors because of their selectivity, ease of use in the field and long shelf life [2,3]. Ion-selective Electrodes (ISEs) are widely applied in analytical chemistry and have a steeped history of use to determine the activity of specific ions [4,5]. Currently over a billion ISE measurements are performed world-wide in a large variety of fields; including physiology [6], process control [7], environmental analysis [8], pollution monitoring, food processing [9] and water quality [10].

There is increasing interest in the development of ion-selective sensors for detecting electrolytes such as K^+ [11]. To date, several potassium sensors based on plasticized membranes, containing different ionophores have been developed [12]. Most of them however are based on vancomycin [13,14], or crown ethers [15,16] and report the results of a single crown ether rather than a direct comparison. Macrocyclic compounds, because of their selective receptor properties and their ease of structural modification, have also been engaged as ionophores in the assembly of ion selective electrodes for the determination of alkali, alkaline and many transition metal ions [17]. Crown ether macrocycles provide a simple receptor model and are well matched as hosts due to their conformational flexibility and the presence of multiple binding sites in their structures [18,19]. The complexing properties of crown ether derivatives depend on the comparative size of the ions being detected to the size of the crown ether ring as well as the number and variety of heteroatom's and functional groups [20,21]. Here, we report on the production of a range of potassium phosphate sensors based on crown ethers. The resulting sensors have been evaluated for their effectiveness in the determination of potassium ions in solutions.

EXPERIMENTAL SECTION

Reagents

All chemicals were of analytical grade and purchased from Aldrich unless stated otherwise. All potassium salts were purchased from Fluka along with the benzo-18-crown-6, and benzo-15-crown-5. The ionophores structures reported here have been illustrated in Figure 1.
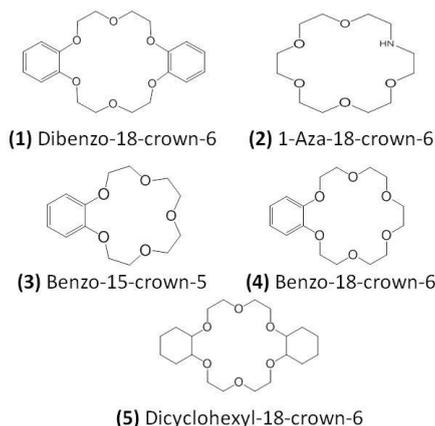
(1) Dibenzo-18-crown-6   **(2)** 1-Aza-18-crown-6

(3) Benzo-15-crown-5   **(4)** Benzo-18-crown-6

(5) Dicyclohexyl-18-crown-6

Figure 1: The structures of the ionophores

Preparation of the sensor membrane

The plasticizer dibutyl phthalate (DBP) was chosen because it yielded the largest dynamic range for the sensor (data not shown). The membrane composition was carefully chosen because the sensitivity of the ISE not only depends on the nature of ionophore used, and the properties of the plasticizers, but also significantly on the membrane composition and additives used.

The polyvinyl chloride (PVC) membrane was prepared by thoroughly mixing the PVC powder (928 mg), DBP (185.5 mg) and the ionophore (2.8 mg) in anhydrous Tetrahydrofuran (THF) 10 ml. The resulting clear mixture was poured into a glass ring (3 cm I.D) which was placed on a clean glass surface. The THF was allowed to evaporate for 48 h at room temperature in order to obtain membranes with reproducible characteristics. The resulting PVC template membranes ($\approx$ 500 nm thickness) were sectioned with a cork borer (9.0 mm I.D) and clued to polyethylene tubes (12 cm length, 7.0 mm I.D) using THF. The resulting membranes were then immersed in an appropriate potassium solution (1×10^{-2} mol/l^{-1}, pH 9) until use.

Construction of the electrodes

The electrodes consist of a glass Ag/AgCl (1.0 mm diameters) internal reference electrode, to which the polyethylene tube was attached at one end. The polyethylene tube was filled with an internal reference solution (potassium phosphate 1×10^{-2} mol/l^{-1}) at pH 9. The indicator electrodes were conditioned by soaking in a potassium solution (1×10^{-2} mol/l^{-1}) for 24 h and stored in the same solution when not in use [22]. When testing the electrode at a range of pH values the pH of the internal electrode solution was also changed.

Potential measurements

All potentiometric measurements were made at room temperature using a portable Orion (Model 290) pH/mV meter. An Orion double junction Ag/AgCl reference electrode (Model 90-02) containing 10 wt% potassium chloride in the outer compartment was used in conjunction with the proposed electrode. The sensor design consists of an internal reference solution (potassium phosphate 1×10^{-2} mol/l^{-1}) at pH 9, which is separated from the solution of interest by a PVC ionophore modified membrane.

The potential of potassium ion solutions were measured within a concentration range of 5×10^{-5} to 1×10^{-1} mol/l^{-1}. Each solution was stirred and the potential reading was recorded after stabilization to $\pm$ 0.2 mV. The lower limits of detection were determined from the intersection of the linear segments of the calibration graph, calculated as recommended by the International Union of Pure and Applied Chemistry (IUPAC) [23,24].

RESULTS AND DISCUSSION

Performance characteristics of the sensor

The potentiometric response of the ISE modified with ionophore (1) was investigated against the potassium phosphate. Appropriate aliquots of the stock solution were introduced to the cell and the corresponding potentials determined. The potential readings were plotted against the logarithmic values of the concentration over a range of 5×10^{-5} to 1×10^{-1} mol/l^{-1} (Figure 2).
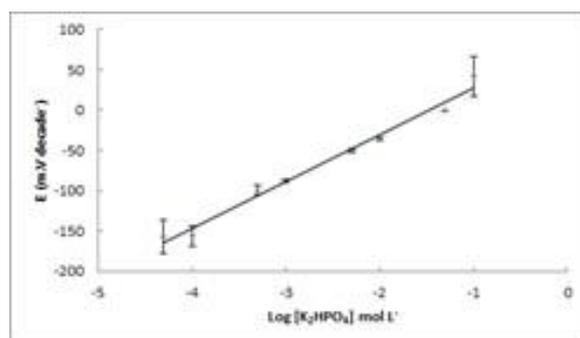

Figure 2: Potential response of the potassium ISE containing ionophore (1) *vs.* Ag/AgCl reference electrode for increasing concentrations of potassium phosphate ion at pH 9 (n=3 and error bars (where visible) indicate the standard deviation)

The slope of the calibration line was 58.1 ± (1.1) mV per decade and the limit of detection was 3.2×10^{-6} mol/l^{-1}; when the error bars are considered it can be seen that the low concentration have increased errors this is thought to be due to the associated increase in response time for the sensor [25].

Lifetime of the electrode

For analytical applications, the dynamic response time is an important factor for any ISE [26] and it can be defined as the time in which a stable potential is achieved [27]. In high concentration, the response time was longer ($\approx$ 60 s) than at lower concentrations ($\approx$ 35 s). This is because the potassium ions are known to transfer, with a reversible nature, from the aqueous solution under test to the membrane phase and again to the internal solution and hence at higher concentrations the diffusion of the species across the membrane are hindered; as a consequence the electrode needs a longer duration to achieve equilibrium [28,29].

Another important characteristic of any ISE membrane is its stability over time [30]. The main reason for the limited lifetimes for carrier-based sensors results from the loss of plasticizer and or ionophores from the polymeric film, due to leaching into the sample solution [31]. Thus, the lifetime of a sensor based on ionophores in solvent polymeric membranes depends on the distribution coefficient of the ionophores and plasticizers between the aqueous and membrane phases [32]. The stability of the membrane was examined and the membrane was found to be stable over a period of 40 days without showing any significant divergence within the concentration range. The electrodes were stored in air and were re-equilibrated by dipping in a potassium phosphate solution (1×10^{-2} mol/l^{-1}) before use for at least 24 h. After using the electrode for 40 days a slight deviation was observed in response time and slope, which could be corrected by re-equilibrating the membrane with potassium phosphate (1×10^{-2} mol/l^{-1}) solution for 2-3 days. For this reason after use the membranes were stored in the said solution to enhance their lifetime.

Different crown ethers

Macrocyclic crown ethers are well known as selective carriers for various ions [33,34]. It is clear that both the types of donor groups and the cavity size influence the complexing ability of the ionophore toward potassium ions and consequently the potential response of the resulting membrane sensor [35]. Hence a range of ionophores with different electronegative functional groups and one ionophore (3) of a smaller cavity size were examined for their affect.

The plasticized PVC-based crown ether electrode containing ionophore (1) generated stable potential responses in solutions containing potassium phosphate (Figure 2). Therefore, the performance of the membrane electrodes based on this carrier for potassium phosphate in aqueous solutions was evaluated with a range of ionophores (1) to (5) in the PVC membranes. The potential response from the five different ionophore modified membrane electrodes, in the same composition, was measured; the resulting Nernstian response and their associated correlation coefficients have been illustrated in Figure 3.
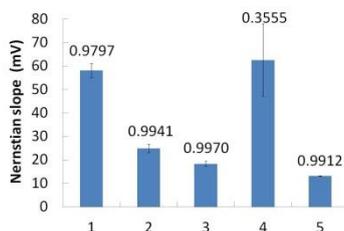

Figure 3: Nernstian response for a range of ionophores with their associated correlation coefficients (n=3 and error bars indicate the standard deviation)

Under the same experimental conditions, the best Nernstian response can be seen from ionophores (1) and (4). Both are 18-crown-6 ethers with benzo functional side groups. The dibenzo1-8-crown-6 (1) ether has a considerable smaller error associated with the measurements and the correlation coefficient is much higher. With the monobenzo ether having an unacceptably low correlation coefficient over a linear range of 5×10^{-5} -1 $\times 10^{-1}$ mol/l^{-1} suggesting that the higher lipophilicity of the benzene groups show a better compatibility with the membrane components [36]. Ionophores (2) and (5) have poor Nernstian responses, this is thought to be due to the absence of benzo groups on the macrocyclic ring in ionophore, which results in the enhanced configuration rigidity of these compounds within the membrane [37,38]. Ionophore (3) has a smaller crown size (15) and despite the presence of a benzo group also has an unacceptably low Nernstian response. However the ionophores (2), (3) and (5) do show a high correlation coefficient despite the low efficiency of electron transfer. Figure 3 illustrates that the macrocyclic compound (1) is the most suitable, from the range tested, ion carrier to modify the PVC membrane with. Hence, ionophore (1) was chosen for all further experiments.

The effect of pH

A range of pH values (6-12) were utilized to examine the effect of the pH on the selective behavior of potassium based (1) ionophore membrane sensor.
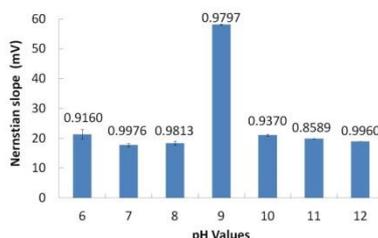

Figure 4: Nernstian response for ionophore (1) over a range of pH values with their associated correlation coefficients (n=3 and error bars (where visible) indicate the standard deviation)

As expected Figure 4 clearly illustrates that the pH has an effect on the response [39]. However, the ion-selective electrode is intended for use in the detection of ions in drinking water samples which typically show pH value variations 7-8. It can be concluded that the most suitable pH for potassium phosphate solutions is at pH 9 because of the significant effect on the electrode Nernstian response. Therefore, it is important to know/adjust the pH value of the samples before conducting ISE measurements. The electrode potential for solutions with a pH values lower than pH 9 may well be responding to hydrogen ions along with potassium. The deviation from the Nernst equation at pH values high than 9 is thought to be exhibiting Donnan failure [40,41] due to the increasing concentration of anions in the solution. At these pH values the potassium ionophore complex in the membrane behaves as an anion-exchanger rather than as cation exchanger, and as such is going to yield a response to the phosphate or hydroxyl anion.

The selectivity coefficients [42,43] of the electrode ($k_{i,j}$) were determined by a separate solution method using the respective potassium salts. The concentrations were adjusted to 10 mM. The values were calculated using.

$$Log\ K_{i,j}{}^{Pot} = \left(E_{j-}E_i\right)/S + \log c_i - \log cj^{1/zj}$$

where Ei and Ej represent the potential readings measured for K^+ and the interfering ion, respectively, S is the theoretical slope of the electrode for K^+ (59.2 mV at 25°C), ci and cj are the concentrations of K^+ and the interfering ion, respectively and zj is the charge of the interfering ion.

The values of the selectivity coefficients w e r e measured against alkali metal ions for ionophore (1) using a separate potential method according to the Table 1 below.

Table 1: The selectivity coefficient of interfering ions on electrode based on ionophore (1)

Interfering ions	Log Kij
K^+	-0.342
Rb^+	-0.342
Na^+	-0.418
Cs^+	-0.416
Li^+	-0.508
$NH_4{}^+$	-0.315

Effects of the counter ion

The most important characteristic of any ion-selective sensor lies in its ability to distinguish a primary ion. Within this work the selectivity was desired for not only the primary ion but the primary ion with a particular counter ion, namely potassium phosphate. To this end a series of common potassium ions where selected and evaluated for their response to ionophore (1) at pH 9, as can be seen from Figure 5.
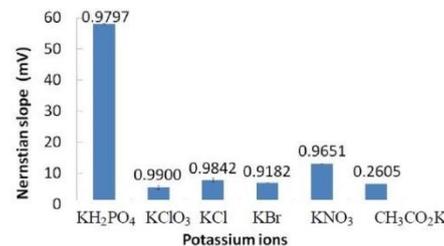

Figure 5: Nernstian response for ionophore (1) against a range of potassium ions with their associated correlation coefficients (n=3 and error bars (where visible) indicate the standard deviation)

Figure 5 illustrates that the ISE utilizing ionophore (1) is clearly selective towards potassium with phosphate as a counter anion. The electrode response toward the counter anion occurs in the following order $PO_4{}^{3-} > NO_3{}^- > ClO_4{}^- > Cl^- > Br^- > CH_3COO^-$. This anti-Hofmeister pattern clearly reveals the mechanism and recognition of $PO_4{}^{3-}$ as a counter anion for the ionophore (1) [44].

The quantification of the potassium ion in a range of real samples was determined. The unknown concentrations of the samples were confirmed *via* Atomic Absorption Spectroscopy (AAS) (Figure 6). Potential measurements were carried out with the ISE having a membrane of the ionophore (1) and DBP as a plasticizer in a PVC matrix.
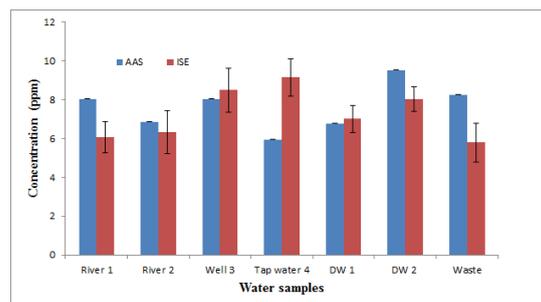

Figure 6: Water samples measurements for ionophore (1) in ISE method with comparison with AAS method (n=3 and error bars (where visible) indicate the standard deviation)

Linear regression analysis of potassium concentrations measured by the electrode based on ionophore (**1**) against values obtained by AAS showed a good correlation albeit with increased error bars.

CONCLUSION

Here we reported the characteristics of an electrochemical method utilizing a range of crown ethers as ionophores within a PVC membrane. The electrodes were constructed for the determination of potassium phosphate, with dibenzo-18-crown-6 (ionophore (1)) proving to be the most effective ionophore with a shelf life of 40 days. It responded in a near Nernstian fashion, and showed a low detection limit of 3.2×10^{-6} mol/l^{-1} and a fast response time over a concentration range of 5×10^{-5} to 1×10^{-1} mol/l^{-1}. The resulting electrode signifies a significant advancement in the construction of a potentiometric device for the determination of potassium phosphate concentrations in solution as can be seen from the comparison of the ISE results to that of AAS (Figure 6).

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