

A heterogeneous precipitate based potassium membrane ion selective electrode-its preparation and analytical application

J. THAMARAI SELVI

Department of Chemistry,
Avinashilingam Institute for Home Science and Higher Education for Women,
Coimbatore- 641043 Tamilnadu (INDIA)

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Abstract

A new potassium ion-selective membrane electrode has been developed based on heterogeneous precipitate and the membrane was developed using epoxy resin. An analytically useful potential changes occur in the 1 to 10^{-3} M concentration range of KCl. The slope of the linear portion (1×10^{-1} - 1×10^{-3} M) was 55mv/decade. The stable potentiometric signals are obtained within a short period of 7 seconds. In the presence of 1×10^{-4} M potassium no interference was observed for Na^+ , Mg^{2+} , Ba^{2+} , Mn^{2+} , Ni^{2+} , Cu^{2+} , F^- , Cl^- , Br^- , I^- , SO_4^{2-} ions. The effect of pH and effect of medium have been standardized found to give better response life time of the electrode was approximately 3 months. This electrode has been used for the determination of potassium ion commercially available product.

Key words: Potassium ion selective electrode, Membrane electrode, Potassium ion, Epoxy resin.

Introduction

Potassium ion is necessary for the function of all living cells. Potassium ion diffusion is a key mechanism in nerve transmission and potassium depletion in animals including humans results in Cardiac dys functions. Potassium is found in especially high concentration with in plant cells.

Direct potentiometric measurements

provide a rapid and convenient method for determining the activity of various cations and anions. The technique requires only a comparison of the potential developed in a cell containing the indicator electrode in the analyte solution, with its potential when immersed in one or more standard solution of known analyte concentration.

Ion selective electrodes (ISE) are important for potentiometric methods as they

have certain advantages such as they have good selectivity and give specific and sensitive results in short time, electrodes can be prepared rapidly they can simply be produced with a very low cost and above all they allow us to available the solution without pretreatments. Some of them are in solid state¹⁻³, some of them are prepared using PVC membrane^{4,5}.

In this study, a simple heterogeneous precipitate based membrane have been prepared along with the potentiometric performance of these sensors, effect of pH, effect of medium, response time and selectivity coefficient with respect to different interfering ions have been studied.

Experimental process

Preparing memberane electrode :

10ml of 1N zinc sulphate (LR Grade, Reachem Laboratory Chem Pvt. Ltd) was mixed with 10ml of 1N potassium ferrocyanide (LR Grade, E.merck India Ltd.). A white precipitate was obtained. It was filtered and dried in air for 24 hours and powdered.

About 0.2g of powdered precipitate was thoroughly mixed with epoxy resin and the paste was applied on Whatmann filter paper No.42. This was spread uniformly over the filter paper to obtain 0.9mm thickness of the electro active material with matrix. This was left in air to dry for 48 hours to get an electro active membrane. A circular piece of this membrane was cut and fixed with resin at one end of the hollow glass tube.

All measurements were carried out with cell of the type:

Internal reference Electrode(Cu wire)	Internal reference solution(1M CuSO ₄ solution)	Ion selective membrane	Sample solution (1M to 1x10 ⁻⁴ M KCl	External reference electrode (SCE)
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For potential measurements Equip – Tronics EQ- 602 potentiometer is used and Ag/AgCl as reference electrode. Reagent grade chemicals were used without further purification. Stock solutions were prepared with doubly distilled water, measurements were made at room temperature 32±2°C. All reagents used in the study were from Reachem and E-Merk.

Results and Discussion

Electrode response :

The electrodes were first conditioned in 1M solution of KCl for one week till attained stable equilibrium after which it was used for the determination of characteristic study of the electrode. The electrode potential for a series of standard solutions of KCl concentration in the range of 1M to 1x10⁻⁴ (Table 1).

Standard electrode potential (E⁰) electrodes were determined by extrapolation method was found to be -0.024 V. The Nernst

slope value was found to be 55mV/decade (Graph 1).

ELECTRODE RESPONSE

Table 1

Concentration of potassium chloride solution (M)	E.M.F (Volts)
1	-0.024
1×10^{-1}	-0.020
1×10^{-2}	-0.015
1×10^{-3}	-0.009
1×10^{-4}	-0.009

Effect of membrane thickness :

In order to understand whether the electrode sensitivity depends on the membrane thickness electrode membrane prepared using different size of thickness (0.5mm, 0.7 mm, 0.9 mm). It was shown that 0.9 mm thickness of the electro active material with matrix shows higher sensitivities towards potassium ion.

Effect of medium:

In order to identify the conditioning medium, the proposed sensors were investigated in partially non-aqueous medium *i.e.*, ethanol for 25%, 50%, 75% with water. A standard solution containing 1M KCl is added with serious of 25%, 50%, 75% ethanol is taken. It was found that the potential of the electrode remains unaffected in the presence of a series of various percentage of ethanol (25%, 50%, 75%).

Effect of pH :

In order to identify the pH range the influence of pH on the potential response of the all the three electrodes were studied at 1M KCl solution over a pH range of 4.01 – 9.2. The pH was adjusted by using buffer solution. The potential is independent of the pH in the range of 4.01 – 9.2 of KCl solution. Hence the corresponding pH range may be chosen as the working pH of the electrode assembly.

Response time of the electrode :

The response time of the electrode was measured for various potassium concentrations when K^+ concentration was changed from 1×10^{-4} M to 1M the response of the electrode was less than 7 seconds.

Interference effect of various cations and anions :

The selectivity is an important characteristic of membrane sensors. It is measured in terms of potentiometric selectivity. It measures the response of the sensor towards the primary ion in the presence of secondary ion present in the sample solution. The selectivity co-efficient has been determined by using Fixed Interference Method (FIM) based on the semi-empirical Nicolski – Eisenman equation. In this method, the concentration of primary ion of KCl is varied where as the concentration of secondary interfering ion is kept constant in the test solution which is 1M concentration of interfering ion in the present case. The potentiometer selectivity co-efficient data of sensor for various interfering ions (cations and anions) are given in the tables 2 and 3. All the interfering ion shows the E.M.F value to the original value of E.M.F ± 5 .

Interference by Anions

Table 2

Anions (Interfering ion)	Electrode $K_{\text{potassium}}^{\text{pot}}, M$
F ⁻	-0.019
Cl ⁻	-0.019
Br ⁻	-0.019
I ⁻	-0.019
SO ₄ ²⁻	-0.030

Interference by Cations

Table 3

Cations (Interfering ion)	Electrode $K_{\text{potassium}}^{\text{pot}}, M$
Na ⁺	-0.019
Mn ²⁺	-0.030
Mg ²⁺	-0.030
Cu ²⁺	-0.030
Ni ²⁺	-0.030
Ba ²⁺	-0.030

Temperature study :

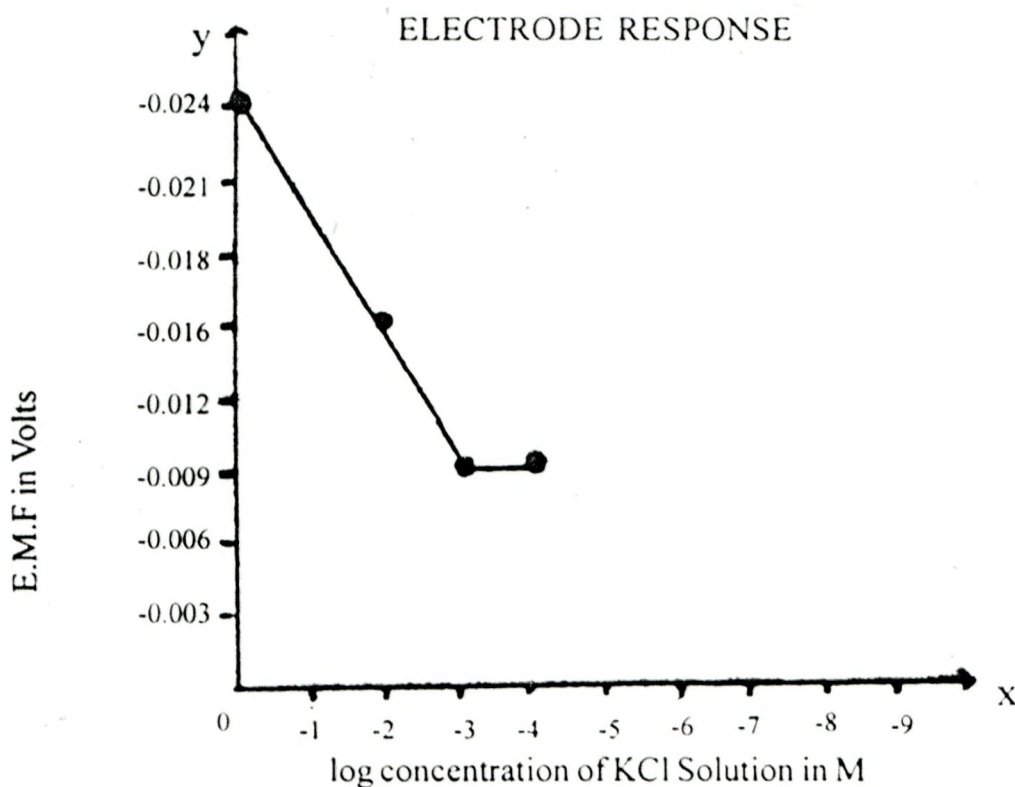
Effect of temperature on standard electrode potential (E°) of the proposed electrode in the presence of aqueous, ethanol and pH solution and determination of thermodynamic functions.

The EMF value of the proposed electrode was measured at different temperatures ranging from 5-30°C.

Effect of temperature

Table 4

Medium	E° (volts) at different temperature						$\delta E/\delta T$ V/K ^o
	278 k	283 k	288 k	293 k	298 k	303 k	
Aqueous	-0.019	-0.020	-0.022	-0.024	-0.026	-0.028	-1.8×10^{-5}
Ethanol							
25% Ethanol	-0.025	-0.027	-0.029	-0.029	-0.030	-0.031	-1.2×10^{-5}
50% Ethanol	-0.022	-0.021	-0.024	-0.025	-0.026	-0.027	-1.0×10^{-5}
75% Ethanol	-0.014	-0.011	-0.017	-0.018	-0.019	-0.021	-1.4×10^{-5}
pH study							
pH-4.02	-0.024	-0.020	-0.028	-0.031	-0.033	-0.035	-1.8×10^{-5}
pH—7	-0.022	-0.017	-0.026	-0.028	-0.030	-0.031	-1.8×10^{-5}
pH-9.2	-0.019	-0.012	-0.021	-0.023	-0.025	-0.027	-1.6×10^{-5}



Graph-1
Plot of cell E.M.F (V) Vs log concentration of KCl (M)

The relationship is linear in all cases in accordance with the equation

$$E^{\circ} = \Delta H^{\circ}/nF + T(\delta E/\delta T)_p$$

The value of temperature co-efficient in Table-4 in aqueous, ethanol, acidic and alkaline media have been used in the calculation of ΔG° , ΔH° and ΔS° at 25°C of the proposed electrode and the results are tabulated in Table 5.

Table 5

Medium	ΔG° K.cal/mole	ΔH° K.cal/mole	ΔS° e.u
Aqueous	2235.58	-48224.26	-173.7
Ethanol			
25% Ethanol	2734.16	-30905.73	-115.8
50% Ethanol	2364.25	-25669.00	-96.5
75% Ethanol	1688.75	-37557.80	-135.1
pH study			
pH-4.02	2846.75	-47613.10	-173.7
pH-7	2589.41	-47870.43	-173.7
pH-9.2	2171.25	-42681.95	-154.4

Analytical applications :

To assess the applicability of the sensors to real samples an attempt was made to determine potassium ion in commercially available products (tooth paste and fanta). The recovery of potassium ion in sample analysis was found to be quantitative with maximum recovery of 99%.

References

1. Laksh.R.L., "Electro analytical techniques", 209-214 (2004).
2. Bakker. E., Buhlmann. P. and Prestsche, Chem. Rev, 97(1997)30383; (6) Buhlmann P., Pretsch E.; Bakker E., *Chem. Rev*; 98: 15993 (1998).
3. Chandras. Agarwal H., Singh C.K., Sindhu S. R. and Kumar P., *Ind. J. Chem*, 44A (2005) 2060; (b) Nandad, Chouhan HPS & Maiti B; *Ind.J.Chem*; 43A :1685 (2004).
4. Polymer Science, Synthesis, Qualitative and Quantitative analysis of macromolecules Siddaramaiah.CBS publishers, New Delhi, India (First edition)(2005).