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A novel precipitate-based manganese(II) sensor

Naheed Faizan & M C Chattopadhyaya*
Department of Chemistry, University of Allahabad, Allahabad 211 002

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A new heterogeneous precipitate-based Mn(II) selective electrode has been prepared. The electrode is selective for Mn(II) ions in the presence of Zn(II), Cu(II), Mg(II), Fe(II), Ca(II), Ba(II), Al(III), NH_4(I). It gives a linear response in the concentration range of 1×10^{-1} to 5×10^{-6} mol dm^{-3} and can be used as an indicator electrode in the precipitation titration of Mn(II) against phosphate ion.

Koryta[1] has reviewed the sensitivity of a number of electrodes towards Mn(II) ions. In a recent paper Midgley and Mulcahy[2] described a Mn(IV) oxide electrode as an Mn(II) sensor and also reported the selectivity coefficient of this electrode towards Fe(III) and Pb(II) ions. In this note a new heterogeneous precipitate-based Mn(II) ion selective electrode is described.

Preparation of electrode

Manganisum sulphate (200 mg, Sarabhai-Merck) was dissolved in a minimum amount of 10% acetic acid solution. The solution of 8-hydroxyquinoline (450 mg) (BDH) was prepared in hot ethyl alcohol. When these two solutions were mixed a yellowish precipitate of $Mn(C_9H_6ON)_2$ was obtained which was filtered off, washed with distilled water and dried in air for 24 hr. This compound (100 mg) was mixed with epoxy resin (400 mg) (Araldite, Ciba-Giegy Ltd) on a Whatman filter paper No. 42. The paste dispersed on filter paper uniformly to produce layer of about 0.1 mm in thickness which was dried to form a membrane. This membrane was dipped in a solution of 0.1 mol dm^{-3} $MnSO_4$ for 24 hr to remove the adhering filter paper.

A small piece of membrane was fixed to one end of a glass tube of about 15 cm in length with the help of Araldite and dried. The tube was filled with 0.1 mol dm^{-3} solution of $MnSO_4$ and kept immersed in a solution of 0.01 mol dm^{-3} $MnSO_4$ for a week. A saturated calomel electrode (SCE) was immersed through the open end of the tube for electrical contact.

The emf values (versus SCE) were measured at $30° \pm 1°$ with a Philips *p*H meter (model-PR 9405 M). Solutions were stirred with magnetic stirrer.

A series of standard solutions of $MnSO_4$ in the concentration range of 1×10^{-1} to 5×10^{-6} mol dm^{-3} was prepared and the *p*H of each adjusted to 4 by adding acetate buffer in the ratio of 20:1. The potential of each solution (vs SCE) was measured with the help of the electrode prepared. A linear response was obtained in this concentration range and the slope was 20 mV per decade change in the concentration in first week; in second week the slope was 25 mV per decade change in concentration.

The response time of the electrode was obtained by noting the response, when the concentration of $MnSO_4$ was suddenly changed from 0.01 to 0.001 mol dm^{-3}. Within 30 sec 75% of total potential was reached when concentration was changed. After 40 sec potential was stabilised and remained constant thereafter. The electrode potential remained unchanged in the *p*H range of 3-13.

The selectivity coefficients were determined[3] as 0.1 for divalent Zn, Mg, Cu, Ca and Ba ions and as 0.5, 0.04 and 0.2 for Fe(II), Al(III) and NH_4(I) ions, respectively.

To examine the applicability of the electrode for the determination of Mn(II) ion, the precipitation titration of Mn(II) against $Na(NH_4)_2PO_4$ was performed using the prepared electrode as an indicator electrode and SCE as the reference electrode. For this purpose $MnSO_4$ solution (10 ml, 0.1 mol dm^{-3}) was taken in a beaker, diluted with distilled water and titrated against 0.1 mol dm^{-3} $Na(NH_4)_2PO_4$ solution. After each addition of titrant, the potential was measured. A break in titration curve was observed at the equivalence point.

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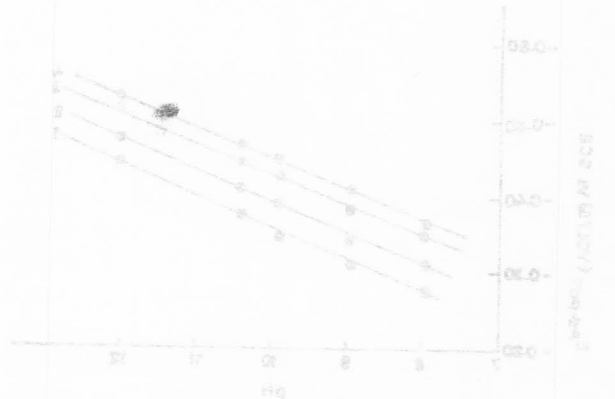

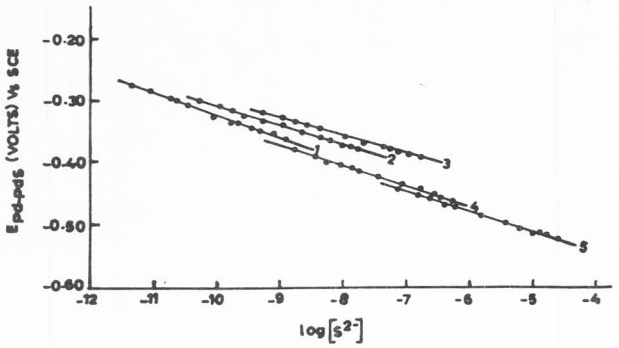

Fig. 1-Plots of $E_{Pd\text{-}PdS}$ versus $\log[S^{2-}]$ at different (controlled) *p*H values (7.96 to 11.98) at 25 ± 0.1°C [(1) *p*H 7.96, (2) *p*H 8.95, (3) *p*H 9.91, (4) *p*H 10.38 and (5) *p*H 11.98]

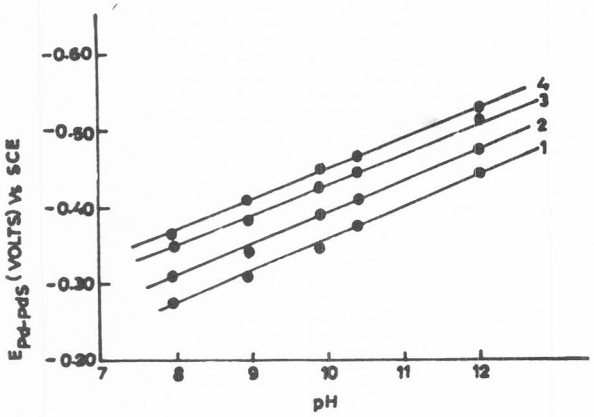

Fig. 2 – Plots of $E_{Pd\text{-}PdS}$ versus *p*H at constant $[Na_2S]$ at 25 ± 0.1°C [(1) 4.4×10^{-5} *M*, (2) 3.5×10^{-4} *M*, (3) 5.3×10^{-3} *M* and (4) 1.3×10^{-2} *M*]

mination of *p*H in the range of 7.96 to 11.98 in the presence of S^{2-}.

The potentials of the electrode have been measured as a function of $[S^{2-}]$ at different temperatures ranging from 5-25°C, using three different concentrations (4.4×10^{-5}, 3.5×10^{-4} and 5.3×10^{-3} *M*) of Na_2S in aqueous, aquo-alcoholic (50% v/v) and alkaline media. The values of E° of Pd-PdS electrode obtained in different media at different temperatures are listed in Table 1. The temperature coefficient, $(\partial E°/\partial T)_P$ has been determined from the linear plots of E° versus T(°K) and the values are presented in Table 1. The thermodynamic functions $\Delta G°$, $\Delta H°$ and $\Delta S°$ for Pd-PdS electrode, in different media containing S^{2-}, have been calculated[2] at 25 ± 0.1°C and the values are listed in Table 2. From these data, the standard free energy of formation, $\Delta G_f°$ of PdS has been calculated following the method of Goates *et al.*[3,4] This works out to be −68.1 kJ mol^{-1} which is in close agreement with the literature[5] values of −66.9 kJ mol^{-1}.

Table 1 – E° Values and Temperature Coefficients of Pd-PdS Electrode in Aqueous, Water-Ethanol (50% v/v) and Alkaline (*p*H 7.96-11.98) Solutions of S^{2-}

	E° (V)					Temp. coeff.
	278 K	283	288	293	298	$\times 10^3$ (V/K)
Aqueous medium						
	−0.786	−0.791	−0.798	−0.804	−0.815	−1.42
Aquo-alcoholic (50% v/v) medium						
	−0.795	−0.799	−0.810	−0.815	−0.826	−1.53
Alkaline medium						
(*p*H)						
7.96	−0.751	−0.760	−0.765	−0.771	−0.782	−1.41
8.95	−0.766	−0.770	−0.779	−0.785	−0.796	−1.51
9.91	−0.791	−0.795	−0.805	−0.811	−0.821	−1.50
10.38	−0.815	−0.821	−0.830	−0.836	−0.845	−1.40
11.98	−0.829	−0.834	−0.846	−0.849	−0.859	−1.66

Table 2 – Values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ of Pd-PdS Electrode in Aqueous, Aquo-alcoholic (50% v/v) and Alkaline media at 25 ± 0.1°C

Medium	$\Delta G°$ kJ mol^{-1}	$\Delta H°$ kJ mol^{-1}	$\Delta S°$ J mol^{-1}
Aqueous	153.9	74.9	−274.0
Aquo-alcoholic (50% v/v)	156.0	71.1	−296.6
Alkaline (*p*H)			
7.96	147.2	69.0	−271.9
8.95	150.2	66.5	−291.2
9.91	154.2	71.9	−289.1
10.38	159.8	82.0	−269.8
11.98	162.7	70.4	−320.0

Solubility product (K_{sp}) of PdS has been calculated from the standard free energy change of the reaction: $PdS(s) \rightleftharpoons Pd^{2+}(aq) + S^{2-}(aq)$ by means of the expression: $\ln K_{sp} = -\Delta G°/RT$. Since the value of $\Delta G_f°$ of PdS has already been calculated as −68.1 kJ mol^{-1} and using the literature values[5] of $\Delta G_f°$ for $S^{2-}{}_{(aq)}$ and $Pd^{2+}{}_{(aq)}$ as 85.77 kJ mol^{-1} and 176.5 kJ mol^{-1} respectively the value of K_{sp} works out to be 1.16×10^{-58} at 25 ± 0.1°C.

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