A novel precipitate-based manganese(II) sensor

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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), NH₄(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.

Koryta¹ has reviewed the sensitivity of a number of electrodes towards Mn(II) ions. In a recent paper Midgley and Mulcahy² 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 MnSO₄ and kept immersed in a solution of 0.01 mol dm⁻³ MnSO₄ 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 $30^{\circ} \pm 1^{\circ}$ 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 MnSO₄ 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.

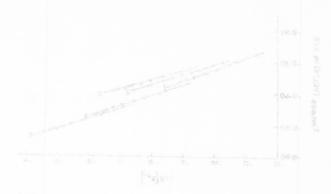
The selectivity coefficients were determined³ as 0.1 for divalent Zn, Mg, Cu, Ca and Ba ions and as 0.5, 0.04 and 0.2 for Fe(II), Al(III) and $NH_4(I)$ ions, respectively.

To examine the applicability of the electrode for the determination of Mn(II) ion, the precipitation titration of Mn(II) against Na(NH₄)₂PO₄ was performed using the prepared electrode as an indicator electrode and SCE as the reference electrode. For this purpose MnSO₄ 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(NH₄)₂PO₄ 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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[4] P. B. et Ennis V. 2018, [16] [2] at different contrements of values (7.96 to 11.98, at 22 c.0.17C, [1] pH 7.96, [2] pH of values (7.96 to 11.98, at 22 c.0.17C, [1] pH 7.96.

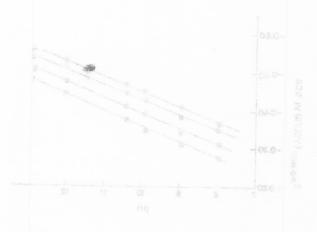


Fig. 2.—Plots of E_{BARS} versus pH at constant [Naple, a 28 \pm 0.1°C [(1) 4.4 × 10⁻⁸ M (2) 3.5 × 10⁻⁴ M (2) 8.3 × [10 M and (4) 1.3 × 10⁻⁴ M

mination of pH in the range of 7.96 to 11.98 51 lbc presence of S²

The potentials of the electrode have been intervented as a function of [S⁻¹] at different temperalatter tranging from 5-25°C, using three different concentrations (4.4 × 10°, 3.2 × 10°, au-S.3 × 10°, M) or Na₂S in aqueerus, aque-alcebric S⁰% v(v) and alkeline media. The values of F° of efferent temperatures are listed in Table 1. The different temperatures are listed in Table 1. The temperature coefficient, ($\partial E^{\circ}/\partial T$), has been detemperature coefficient, ($\partial E^{\circ}/\partial T$), has been denud the values are presented in Table 1. The thermodynamic functions $\Delta G^{\circ}/\Delta T$ and ΔS° for F6have been calculated² at 25 ± 0.1°C and the vathes are listed in Table 1. The therhave been calculated² at 25 ± 0.1°C and the vabas been calculated following the method of has been calculated following the method of mod⁻¹ which is in close agreement with the literature' values of – 66.9 kJ mol⁻¹.

Fards 1 – E* Values and Temperature Coefficients di Pd-PdS Electrode in Aqueons, Wate -Valuerol 20% v v and Afsel ac zH 2.96-11.98, Solicitous of S²

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Table — Values of A.C., A.P. and A.C. of PH-PdS Electroide in Aques us, Aques alcoholic, SC. v. 9) and

Solubary product K_{p} of PLE cas been calcutant from the standard free energy change of the requiremer PdS(s) which (raq) + S (raq) by means of the expressions in K_{p} — ΔG^{*} Fit. Since the value of ΔG^{*} of PdS has dready been calculated as 65.1 kJ and 1 and using the interature values³ of ΔG^{*} for S^{*} in and CP (rap as 85.77 kJ mol⁻¹ and 176.5 kJ mol⁻¹ respectively the value of K_{p} works due to be 1.16 × 10⁻⁵⁸ at 25 ± 0.1°C.

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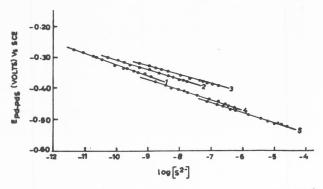


Fig. 1-Plots of E_{Pd-PdS} versus $\log[S^{2-}]$ at different (controlled) pH values (7.96 to 11.98) at 25 ± 0.1 °C [(1) pH 7.96, (2) pH 8.95, (3) pH 9.91, (4) pH 10.38 and (5) pH 11.98]

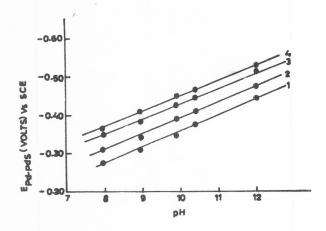


Fig. 2–Plots of E_{Pd-PdS} versus *p*H at constant [Na₂S] at 25±0.1°C [(1) 4.4×10^{-5} *M*, (2) 3.5×10^{-4} *M*, (3) 5.3×10^{-3} M and (4) 1.3×10^{-2} M

mination of pH 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 [S²⁻] at different temperatures ranging from 5-25°C, using three different $(4.4 \times 10^{-5}, 3.5 \times 10^{-4})$ concentrations and 5.3×10^{-3} M) of Na₂S 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, $(\partial E^{\circ}/\partial T)_{P}$ has been determined from the linear plots of E° versus T(°K) and the values are presented in Table 1. The thermodynamic functions ΔG° , ΔH° and ΔS° for Pd-PdS electrode, in different media containing S^{2-} , have been calculated² at 25 ± 0.1 °C and the values are listed in Table 2. From these data, the standard free energy of formation, $\Delta G_{\rm f}^{\circ}$ 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 literature⁵ 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 (pH 7.96-11.98) Solutions of S2-

| | | $E^{\circ}(V)$ | | | Temp. coeff. |
|--------|---|--|--|---|---|
| 278 K | 283 | 288 | 293 | 298 | $\times 10^3$ (V/K) |
| | Aq | ueous me | dium | | |
| -0.786 | -0.791 | -0.798 | -0.804 | -0.815 | -1.42 |
| A | quo-alcol | holic (50% | v/v) medi | um | |
| -0.795 | -0.799 | -0.810 | -0.815 | -0.826 | -1.53 |
| | All | kaline med | lium | | |
| | | | | | |
| -0.751 | -0.760 | -0.765 | -0.771 | -0.782 | - 1.41 |
| -0.766 | -0.770 | -0.779 | -0.785 | -0.796 | - 1.51 |
| -0.791 | -0.795 | -0.805 | -0.811 | -0.821 | -1.50 |
| -0.815 | -0.821 | -0.830 | -0.836 | -0.845 | -1.40 |
| -0.829 | -0.834 | -0.846 | -0.849 | -0.859 | - 1.66 |
| | -0.786 A -0.795 -0.751 -0.766 -0.791 -0.815 | $\begin{array}{r} Aq\\ -0.786 & -0.791\\ Aquo-alcol\\ -0.795 & -0.799\\ All\\ -0.751 & -0.760\\ -0.766 & -0.770\\ -0.791 & -0.795\\ -0.815 & -0.821 \end{array}$ | 278 K 283 288 Aqueous met -0.786 -0.791 -0.798 Aquo-alcoholic (50 % -0.795 -0.799 -0.810 Alkaline met -0.751 -0.760 -0.765 -0.766 -0.770 -0.779 -0.791 -0.795 -0.805 -0.815 -0.821 -0.830 | 278 K 283 288 293 Aqueous medium -0.786 -0.791 -0.798 -0.804 Aquo-alcoholic (50% v/v) medi -0.795 -0.799 -0.810 -0.815 Alkaline medium -0.751 -0.760 -0.765 -0.771 -0.766 -0.770 -0.779 -0.785 -0.791 -0.795 -0.805 -0.811 -0.815 -0.821 -0.830 -0.836 | 278 K 283 288 293 298 Aqueous medium - 0.786 - 0.791 - 0.798 - 0.804 - 0.815 Aquo-alcoholic (50% v/v) medium - 0.795 - 0.799 - 0.810 - 0.815 - 0.826 Alkaline medium - 0.751 - 0.760 - 0.765 - 0.771 - 0.782 - 0.766 - 0.770 - 0.779 - 0.785 - 0.796 - 0.791 - 0.795 - 0.805 - 0.811 - 0.821 - 0.815 - 0.821 - 0.830 - 0.836 - 0.845 |

Table 2 – Values of ΔG° , ΔH° and ΔS° of Pd-PdS Electrode in Aqueous, Aquo-alcoholic (50% v/v) and Alkaline media at 25 ± 0.1 °C

| Arkanne media at 25 ± 0.1 C | | | | | |
|-----------------------------|--|---|---|--|--|
| Medium | ΔG° kJ mol ⁻¹ | ΔH° kJ mol ⁻¹ | ΔS° J mol ⁻¹ | | |
| Aqueous | 153.9 | 74.9 | -274.0 | | |
| Aquo-alcoholic | 156.0 | 71.1 | -296.6 | | |
| (50% v/v) | | | | | |
| Alkaline | | | | | |
| (pH) | | | | | |
| 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 | | |
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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: $\ln K_{\rm sp} = -\Delta G^{\circ}/RT$. Since the value of $\Delta \tilde{G}_{\rm f}^{\rm o}$ of PdS has already been calculated as -68.1 kJ mol⁻¹ and using the literature values⁵ of $\Delta G_{\rm f}^{\circ}$ for S²⁻_(aq) and Pd²⁺_(aq) as 85.77 kJ mol⁻¹ and 176.5 kJ mol⁻¹ respectively the value of $K_{\rm sp}$ works out to be 1.16×10^{-58} at $25 \pm 0.1^{\circ}$ C.

References

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