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Electrochemical & Thermodynamic Behaviour of Palladium-Palladium Sulphide Electrode in Presence of Sulphide Ions

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The Pd-PdS electrode is reversible in respect of S^{2-} in aqueous, aquo-alcoholic and alkaline media. The plot of $E_{Pd\text{-}PdS}$ versus $\log[S^{2-}]$ is linear showing that the electrode can be successfully used in the quantitative determination of S^{2-} in aqueous, aquo-alcoholic and alkaline media. The values of $E°$, $(\partial E°/\partial T)_P$ and thermodynamic functions; viz. $\Delta G°$, $\Delta H°$ and $\Delta S°$ for the electrode reaction: $Pd_{(s)} + S^{2-}{}_{(aq.)} \rightleftharpoons PdS_{(s)} + 2e$, and the solubility product have been determined.

Herein we report the preparation, evaluation and application of hitherto not investigated Pd-PdS electrode.

All the chemicals used were of AR grade. The Pd-PdS electrode was prepared by the method described in an earlier publication[1]. The potential of the electrode in solutions containing S^{2-} was measured under different experimental conditions by setting up a cell of the type (A)

Pd-PdS/S^{2-} ‖ (saturated) KCl/Hg_2Cl_2, Hg
(A)

The electrode was kept immersed in doubly distilled water after use.

The potential of Pd-PdS electrode was measured in well-stirred solutions of Na_2S of varying concentrations (1.0×10^{-5} to 1.0×10^{-2} *M*) at 25 ± 0.1°C. The electrode attained equilibrium potential within 3 min thereby showing that the response of the electrode towards S^{2-} is fairly rapid. The potential of the electrode remained steady upto eight months, indicating that the electrode is highly stable. The reproducibility of the electrode potential was ascertained by preparing the electrode six times using the same method and each time measuring its potential as a function of $[S^{2-}]$. It was found that the variation in the electrode potential was within the limits of standard deviation (1.2×10^{-3}).

The plot of $E_{Pd\text{-}PdS}$ versus $\log[S^{2-}]$ with SCE as a reference electrode is linear from which E° of Pd-PdS electrode works out to be -0.815 V at 25 ± 0.1°C. The experimental slope value is 0.030 V which is very close to the theoretical (Nernstian) value of 0.0296 V (at 25°C). From the experimental slope it is inferred that two electrons per mole of S^{2-} are involved in the electrode reaction.

The potential of the electrode in 1.2×10^{-4} *M* Na_2S did not vary much in the presence of increasing concentrations (from 1×10^{-6} to 1×10^{-3} *M*) of some foreign ions, viz. F^-, Cl^-, Br^-, I^-, HCO_3^- and CO_3^{2-}. However, in the presence of $S_2O_3^{2-}$, SO_4^{2-} and NO_3^- some change in the potential of the electrode occurred. It is thus clear that Pd-PdS electrode is highly specific to S^{2-} and that it can be successfully used in the quantitative determination of S^{2-} in the presence of impurities such as F^-, Cl^-, Br^-, I^-, HCO_3^- and CO_3^{2-} ions.

The potential of the electrode (vs SCE) was measured as a function of $[S^{2-}]$ (from 1.0×10^{-5} to 1.0×10^{-2} *M*) in 25%, 50% and 75% (v/v) water-ethanol mixtures. In all the cases, the plots of $E_{Pd\text{-}PdS}$ versus $\log[S^{2-}]$ were linear thereby showing that this electrode can be successfully used in the quantitative determination of $[S^{2-}]$ in aq. ethanol medium. The values of E° of the electrode in 25%, 50% and 75% (v/v) water-ethanol mixtures are: -0.792, -0.826 and -0.876 V respectively and the experimental slope values are 0.029, 0.031 and 0.030 V respectively. From these slope values it is evident that the response of the electrode to $[S^{2-}]$ in aquo-alcohol is Nernstian.

A series of Na_2S solutions of varying concentrations were prepapred in BR buffers (*p*H 7.96 to 11.98), and the potential of the electrode was measured as function of $[S^{2-}]$ at fixed (controlled) *p*H values in the range of 7.96 to 11.98. Plots of $E_{Pd\text{-}PdS}$ versus $\log[S^{2-}]$ at different *p*H values are linear (Fig. 1). At *p*H 7.96, 8.95, 9.91, 10.38 and 11.98, the experimental slope values are 0.033, 0.030, 0.029, 0.033 and 0.030 V respectively. From these it appears that the electrode shows a fairly Nernstian response to $[S^{2-}]$. Therefore, this electrode can be successfully used in the quantitative determination of S^{2-} in the *p*H range of 7.96-11.98.

The response of Pd-PdS electrode to *p*H in the presence of Na_2S solution has also been studied. It is seen that the plots of $E_{Pd\text{-}PdS}$ versus *p*H are linear (Fig. 2) and their slopes are Nernstian. Thus Pd-PdS electrode can be used for the deter-

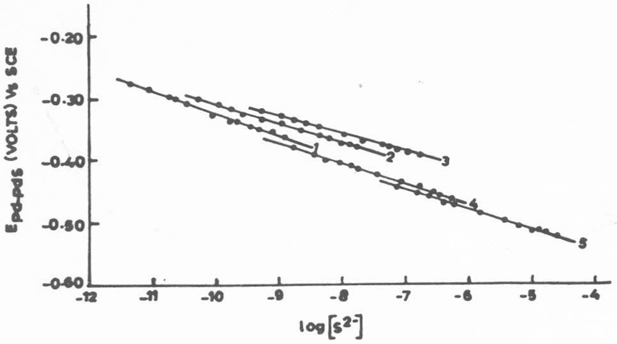

Fig. 1-Plots of $E_{Pd\text{-}PdS}$ versus log[S^{2-}] at different (controlled) *p*H values (7.96 to 11.98) at 25 ± 0.1°C [(1) *p*H 7.96, (2) *p*H 8.95, (3) *p*H 9.91, (4) *p*H 10.38 and (5) *p*H 11.98]

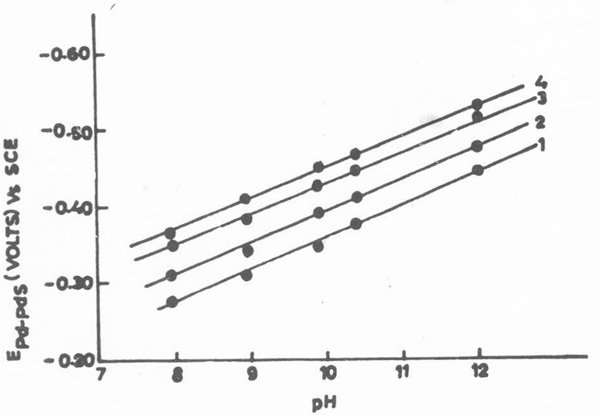

Fig. 2 – Plots of $E_{Pd\text{-}PdS}$ versus *p*H at constant [Na_2S] at 25 ± 0.1°C [(1) 4.4 × 10^{-5} *M*, (2) 3.5 × 10^{-4} *M*, (3) 5.3 × 10^{-3} *M* and (4) 1.3 × 10^{-2} *M*]

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. × 10^3 (V/K)
	278 K	283	288	293	298	
	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

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, ΔG_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}.

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 ΔG_f° of PdS has already been calculated as −68.1 kJ mol^{-1} and using the literature values[5] of ΔG_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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