

Studies on the electrochemical and thermodynamic behaviour of Hg-HgS electrode in the presence of sulphide ions

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MS received 19 August 1987; revised 28 January 1988

Abstract. Mercury-mercury (II) sulphide electrode has been prepared and its electrochemical and thermodynamic behaviour has been studied in different media. The electrode is found to show Nernstian response to pS ($-\log [S^{2-}]$) over the range 5.19–10.38. In the pH range 7.96–11.98, at constant $[S^{2-}]$, its response is also Nernstian. The values of thermodynamic functions, viz., ΔG^0 , ΔH^0 , and ΔS^0 for the electrode reaction: $Hg_{(s)} + S^{2-}_{(aq)} \rightleftharpoons HgS_{(s)} + 2e$, have been determined. Further, the standard free energy of formation (ΔG_f^0) and solubility product constant (K_{sp}) of HgS in aqueous medium at $25 \pm 0.1^\circ C$ have also been determined.

Keywords. Mercury-mercury sulphide electrode; sulphide ions; thermodynamic behaviour.

1. Introduction

In earlier publications (Sharma and Singh 1982a,b) the electrochemical and thermodynamic behaviour of As-As₂S₃, Sb-Sb₂S₃, Mo-MoS₂, Sn-SnS and Pt-PtS electrode in the presence of sulphide ions has been reported. In the present paper we report the results of our investigation on the electrochemical and thermodynamic behaviour of Hg-HgS electrode in the presence of S²⁻.

2. Experimental

All the chemicals used were of analytical reagent grade. The experimental details relating to the preparation of pure H₂S, Na₂S solutions, buffers (BR) and measurement of potential etc. have already been mentioned in earlier publications (Sharma and Singh 1982a,b).

2.1 Preparation of the electrode

A platinum wire of 1.5 cm length and 0.5 mm diameter was fused in Pyrex tubing, cleaned and dried. During electrolysis the platinum wire (cathode) was fully dipped in 0.01 M aqueous acidified (HCl) solution of HgCl₂. Another platinum wire was used as the counter-electrode. A constant current of 5 milliamperes was passed from

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4 volt battery for about 10 minutes so that mercury was deposited on the cathode. The mercury electrode so prepared was washed with conductivity water and then kept immersed overnight in a saturated aqueous solution of pure H_2S so as to get a uniform coating of HgS on it. The electrode was again washed with conductivity water and kept immersed for another 24 hours to attain equilibrium potential. To ensure reproducibility over a long period of time the electrode was kept in conductivity water.

The potential of the electrode in solutions containing S^{2-} was measured (vs. SCE) under different experimental conditions by setting up a cell of the type:



The liquid junction potential contribution of the above cell should also be taken into consideration. However, according to Goates *et al* (1951a,b) the uncertainty of the assumption of complete elimination of the liquid junction potential by a saturated KCl salt bridge (as is the case with the present study) involves an error of 1–2 millivolts. In the present study this error can be safely neglected in comparison to the magnifide of cell e.m.f.

3. Results and discussion

3.1 Evaluation of the electrode

It was found that the potential of the Hg-HgS electrode in aqueous Na_2S solutions of different concentrations (3.9×10^{-5} , 5.9×10^{-4} , 3.9×10^{-3} and 2.1×10^{-2} M) at $25 \pm 0.1^\circ\text{C}$ became constant after three minutes in well-stirred solutions and remained steady upto 60 minutes. This shows that Hg-HgS electrode attains equilibrium potential fairly rapidly in well-stirred solutions.

The reproducibility of the electrode potential was ascertained by preparing the electrode five times using the same method and each time measuring its potential in aqueous solutions of Na_2S of different concentrations (3.9×10^{-5} , 5.9×10^{-4} , 3.9×10^{-3} and 2.1×10^{-2} M). It was found that the variation in the values of the electrode potential was within the limits of standard deviation (1.27×10^{-3}) thereby showing that the potential of the electrode is reproducible.

The stability of the electrode was ascertained by measuring its potential in aqueous solutions of Na_2S of varying concentrations at a constant temperature after an interval of one month. It was observed that the potential of the electrode remained steady upto six months thereby showing that the electrode is quite stable if handled carefully and kept in conductivity water after use.

3.2 Electrochemical behaviour of Hg-HgS electrode vis-a-vis its use in the quantitative determination of the sulphide ion

A series of aqueous solutions of Na_2S of different concentrations ranging from 3.9×10^{-5} to 2.1×10^{-2} M were used as test solutions and their pH values were measured with a pH meter (Toshniwal, CL 49) to permit the calculation of $[\text{S}^{2-}]$ using the equation (Laitinen and Hseu 1979).

$$[\text{S}^{2-}] = [\text{S}^{2-}]_0 / \left(1 + \frac{[\text{H}^+]}{K_2} + \frac{[\text{H}^+]^2}{K_1 K_2} \right) \quad (1)$$

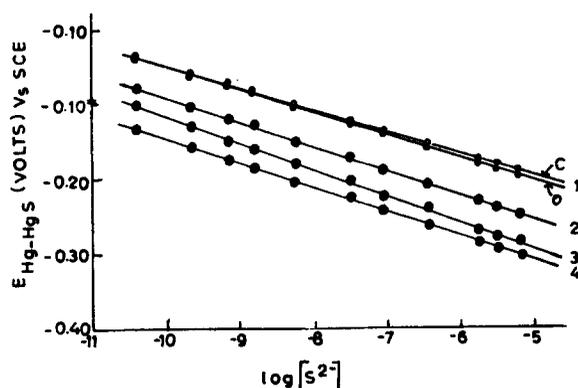


Figure 1. Plots of $E_{\text{Hg-HgS}}$ vs. $\log [S^{2-}]$ in aqueous, aquo-alcoholic (25%, 50% and 75% v/v) Na_2S solutions at $25 \pm 0.1^\circ\text{C}$. 1—aqueous (O = observed, C = calculated); 2—25% (v/v); 3—50% (v/v); 4—75% (v/v).

where $[S^{2-}]_t$ is the total concentration of sulphide present, i.e., $[S^{2-}]_t = [S^{2-}] + [\text{HS}^-] + [\text{H}_2\text{S}]$. K_1 and K_2 are the ionisation constants for H_2S , $K_1 = 9.23 \times 10^{-8}$ and $K_2 = 1.20 \times 10^{-15}$. The potential of the Hg-HgS electrode (vs. SCE) was measured as a function of $[S^{2-}]$ at $25 \pm 0.1^\circ\text{C}$. The plot of $E_{\text{Hg-HgS}}$ vs. $\log [S^{2-}]$ is linear (figure 1). The electrochemical equation to this linear plot at $25 \pm 0.1^\circ\text{C}$ is given below:

$$E_{\text{Hg-HgS}} = -0.451 - 0.030 \log [S^{2-}], \quad (2)$$

where the intercept potential value -0.451 V at $\log [S^{2-}] = 0$ is the sum of the standard potential (E^0) of Hg-HgS electrode and that of SCE from which E^0 of Hg-HgS electrode works out to be -0.692 V at $25 \pm 0.1^\circ\text{C}$. The experimental slope value is 0.030 V which is very close to the theoretical (Nernstian) value of 0.0296 V (at 25°C). The validity of the electrochemical equation (2) has been further checked by obtaining from it the calculated values of the potential of Hg-HgS electrode as a function of $[S^{2-}]$. In figure 1 the values of observed and calculated potentials of Hg-HgS electrode have been plotted against $\log [S^{2-}]$. It is seen that the difference between the observed and calculated values is nil for values of $\log [S^{2-}]$ lying between -10.40 to -8.5 , while for values of $\log [S^{2-}]$ beyond -8.5 there is a slight difference (0.6%) between the observed and calculated values. Thus, the Hg-HgS electrode can be successfully used in the quantitative determination of S^{2-} in given samples.

3.3 Effect of various experimental conditions on the working of Hg-HgS electrode

3.3a Effect of foreign ions: The effect of increasing concentrations (1×10^{-6} – 1×10^{-3} M) of some foreign ions viz., F^- , Cl^- , Br^- , I^- , HCO_3^- , CO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} and NO_3^- , on the working of the Hg-HgS electrode in 1.2×10^{-4} M aqueous Na_2S solution has been ascertained. The results show that there is hardly any difference in the potential of the electrode in the presence of F^- , Cl^- , Br^- , I^- , HCO_3^- and CO_3^{2-} . However, in the presence of $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} and NO_3^- some change in the potential of the electrode occurs. From this study it follows that the

Hg-HgS electrode can be successfully used in the quantitative determination of sulphide ion in the presence of impurities of F^- , Cl^- , Br^- , I^- , HCO_3^- and CO_3^{2-} ions in the given samples of Na_2S .

3.3b *Effect of medium*: The electrochemical behaviour of Hg-HgS electrode has been studied in alcoholic solutions of Na_2S in the concentration range 3.9×10^{-5} to 2.1×10^{-2} M. The potential of the electrode (vs. SCE) has been measured as a function of $[S^{2-}]$ in 25%, 50% and 75% (v/v) aquo-alcoholic solutions. In all the cases, the plots of E_{Hg-HgS} vs. $\log [S^{2-}]$ are linear (figure 1) thereby showing that this electrode can be successfully used in the quantitative determination of sulphide ion concentration in aquo-alcoholic medium. The electrochemical equations to the linear plots can be represented as under:

$$E_{Hg-HgS} = -0.423 - 0.033 \log [S^{2-}], \text{ in 25\% aquo-alcoholic solution,}$$

$$E_{Hg-HgS} = -0.435 - 0.032 \log [S^{2-}], \text{ in 50\% aquo-alcoholic solution,}$$

$$E_{Hg-HgS} = -0.457 - 0.031 \log [S^{2-}], \text{ in 75\% aquo-alcoholic solution.}$$

The values of E^0 of the electrode in 25%, 50% and 75% (v/v) aquo-alcoholic solutions work out to be -0.664 , -0.676 and -0.698 V respectively and the experimental slope values are 0.033 , 0.032 and 0.031 V respectively. From these slope values it is evident that the response of the electrode to $[S^{2-}]$ in aquo-alcoholic solutions is fairly Nernstian.

3.3c *Effect of pH*: A series of Na_2S solutions of varying concentrations were prepared in BR buffers (pH 7.96–11.98), and the potential of the electrode was measured as a function of $[S^{2-}]$ at fixed (controlled) pH values (7.96–11.98). Plots of E_{Hg-HgS} vs. $\log [S^{2-}]$ at different pH values have been found to be linear (figure 2). At pH 7.96, 8.95, 10.38 and 11.98, the experimental slope values are

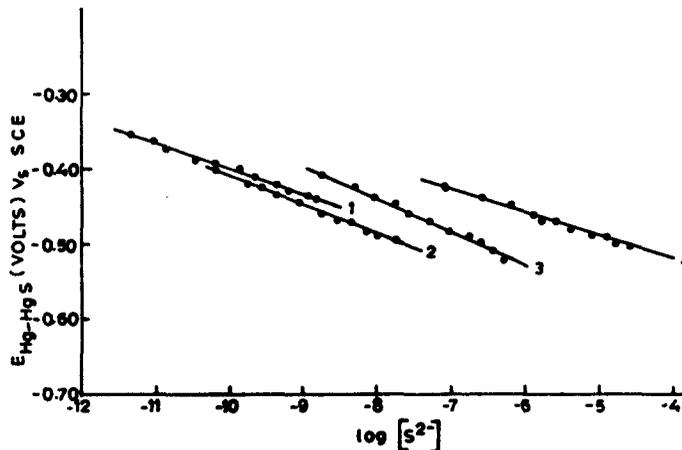


Figure 2. Plots of E_{Hg-HgS} vs. $\log [S^{2-}]$ at different (controlled) pH values (7.96–11.98) at $25 \pm 0.1^\circ C$. 1–pH 7.96; 2–pH 8.95; 3–pH 10.38; 4–pH 11.98.

0.033, 0.038, 0.038 and 0.030 V respectively. From these it appears that the electrode shows a Nernstian response to S^{2-} at the highest pH value (11.98) while at lower pH values (7.96–10.38) there is some deviation from the theoretical Nernstian value. Nonetheless the linear relationship between $E_{\text{Hg-HgS}}$ and $\log [S^{2-}]$ shows that this electrode can be used in the quantitative determination of S^{2-} in the pH range 7.96–11.98.

3.3d *Potential-pH relationship*: The response of the Hg-HgS electrode to pH in the presence of fixed $[S^{2-}]$, has been studied. It is seen that the plots of $E_{\text{Hg-HgS}}$ vs. pH are linear (figure 3). The electrochemical equations to the linear plots can be represented as below:

$$E_{\text{Hg-HgS}} = -0.556 - 0.031 \text{ pH},$$

$$E_{\text{Hg-HgS}} = -0.592 - 0.031 \text{ pH},$$

$$E_{\text{Hg-HgS}} = -0.667 - 0.033 \text{ pH},$$

$$E_{\text{Hg-HgS}} = -0.721 - 0.036 \text{ pH}.$$

It is thus seen that the Hg-HgS electrode can be used for the determination of pH in the range 7.96–11.98 in the presence of S^{2-} .

3.3e *Effect of temperature on standard electrode potential (E^0) of Hg-HgS electrode in aqueous, aquo-alcoholic (50% v/v) and alkaline solutions (pH 7.96–11.98) of Na_2S and determination of thermodynamic functions (ΔG^0 , ΔH^0 and ΔS^0)*: The potential of the electrode has been measured as a function of $[S^{2-}]$ at different temperatures ranging from 5–25°C, using three different concentrations (4.4×10^{-5} , 6.4×10^{-4} and 7.9×10^{-3} M) of Na_2S in aqueous, aquo-alcoholic (50% v/v) and alkaline media. The values of E^0 of the Hg-HgS electrode have been obtained in different media at different temperatures and listed in table 1. The temperature coefficient, $(\partial E^0/\partial T)_p$, has been determined from the linear plots of E^0 vs. $T(\text{K})$ (figure 4) and the values are presented in table 1. The thermodynamic functions (Daniels and Alberty 1966) ΔG^0 , ΔH^0 and ΔS^0 for Hg-HgS electrode, in different media containing S^{2-} , have been calculated at $25 \pm 0.1^\circ\text{C}$ and the values are listed in table 2.

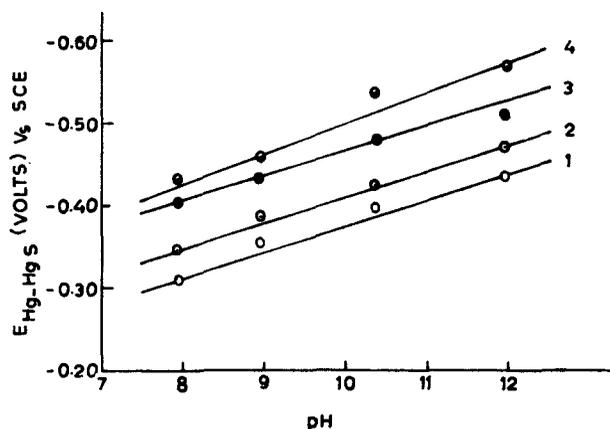


Figure 3. Plots of $E_{\text{Hg-HgS}}$ vs. pH at constant Na_2S at $25 \pm 0.1^\circ\text{C}$. 1– 7.4×10^{-5} M; 2– 5.6×10^{-4} M; 3– 8.4×10^{-3} M; 4– 2.4×10^{-2} M.

Table 1. Values of standard electrode potential (E^0) and temperature coefficient $(\partial E^0/\partial T)_p$ of the Hg-HgS electrode in aqueous, aquo-alcoholic (50% v/v) and alkaline (pH 7.96–11.98, BR buffer) solutions of S^{2-} .

Medium	E^0 (volts) at different temperature (K)					Temp. Coeff. $(\partial E^0/\partial T)_p$ (V/K) ($\times 10^{-3}$)
	278	283	288	293	298	
Aqueous	-0.665	-0.671	-0.680	-0.685	-0.692	-1.33
Aquo-alcoholic (50% v/v)	-0.652	-0.655	-0.660	-0.671	-0.676	-1.30
Alkaline (pH)						
7.96	-0.813	-0.816	-0.821	-0.829	-0.834	-1.42
8.95	-0.809	-0.814	-0.819	-0.831	-0.835	-1.36
9.91	-0.817	-0.823	-0.827	-0.835	-0.840	-1.33
10.38	-0.840	-0.844	-0.850	-0.859	-0.866	-1.66
11.98	-0.830	-0.835	-0.844	-0.851	-0.855	-1.25

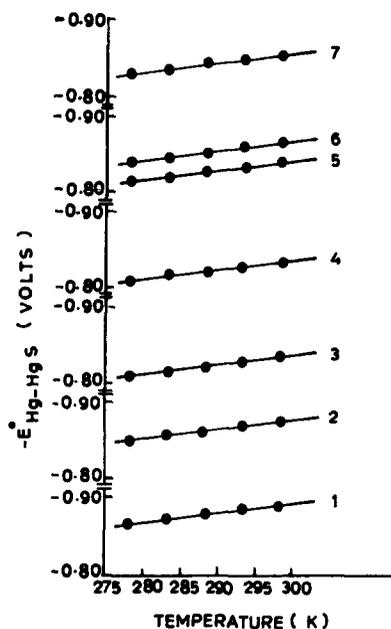


Figure 4. Plots of $E^0_{\text{Hg-HgS}}$ vs. $T(K)$ in aqueous, aquo-alcoholic (50% v/v) and alkaline (pH 7.96–11.98) solutions of Na_2S . 1–aqueous; 2–aquo-alcoholic (50% v/v); 3–pH 7.96; 4–pH 8.95; 5–pH 9.91; 6–pH 10.38; 7–11.98.

3.4 The standard free energy of formation (ΔG_f^0) of HgS

The standard free energy of formation, ΔG_f^0 , of HgS can be calculated following the method of Goates *et al* (1951). Now, ΔG^0 for the electrode reaction, $Hg_{(s)} + S^{2-}_{(aq)} \rightleftharpoons HgS_{(s)} + 2e$ is $31.3 \text{ kcal mol}^{-1}$ (vide table 2) at $25 \pm 0.1^\circ\text{C}$ in aqueous medium. A positive value of ΔG^0 shows that the above electrode reaction is non-spontaneous in the forward direction and that in the backward direction

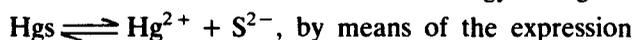
Table 2. Values of various thermodynamic functions of the Hg-HgS electrode in aqueous, aquo-alcoholic (50% v/v) and alkaline media at $25 \pm 0.1^\circ\text{C}$

Medium	ΔG^0 (kcal mol ⁻¹)	ΔH^0 (kcal mol ⁻¹)	ΔS^0 (e. u.)
Aqueous	31.3	13.0	-61.3
Aquo-alcoholic (50% v/v)	30.5	12.6	-59.9
Alkaline pH			
7.96	37.9	18.4	-65.5
8.95	37.8	19.1	-62.7
9.91	38.1	19.9	-61.3
10.38	39.3	16.5	-76.5
11.98	38.8	21.6	-57.6

it would be spontaneous with $\Delta G^0 = -31.3 \text{ kcal mol}^{-1}$. Thus $-31.3 = \Delta G_f^0(\text{HgS}_{(s)}) - [\Delta G_f^0(\text{Hg}_{(s)}) + \Delta G_f^0(\text{S}^{2-}_{(aq)})]$. As ΔG_f^0 of $\text{Hg}_{(s)}$ (element) is zero and taking ΔG_f^0 for $\text{S}^{2-}_{(aq)}$ as $20.5 \text{ kcal mol}^{-1}$ (at 25°C) (*Lange's handbook of chemistry 1979*), the value of ΔG_f^0 of HgS (black) works out to be $-10.8 \text{ kcal mol}^{-1}$. This is in arrangement, within the limits of experimental error with the literature value (Glasstone 1947) of $-11.4 \text{ kcal mol}^{-1}$.

3.5 Solubility product constant (K_{sp}) of HgS

It can be calculated from the standard free energy change of the reaction:



$$\ln K_{sp} = \frac{-\Delta G^0}{RT}$$

Since the value of the ΔG_f^0 of HgS has already been calculated as $-10.8 \text{ kcal mol}^{-1}$ using the literature value (*Lange's handbook of chemistry 1979*; Glasstone 1947) of ΔG_f^0 for S^{2-} and Hg^{2+} as $20.5 \text{ kcal mol}^{-1}$ and $39.42 \text{ kcal mol}^{-1}$, respectively, the value of K_{sp} can be obtained from the above expression. This works out to be 1.4×10^{-52} . The value of K_{sp} for HgS reported by Goates *et al* (1951) is 9×10^{-52} while the literature value (Lurie 1975) is 1.6×10^{-52} . Thus, the value of K_{sp} obtained in the present study is much closer to the literature value.

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