pH DEPENDANCE OF THE POTENTIAL OF THE SILVER/SILVER SULPHIDE ELECTRODE

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Electrode potential of the silver-silver sulphide electrode has been determined by potential mediator method and pH dependance of the electrode potential has been studied in buffered medium with pH ranging from 6.6 to 9.1. An equation has been proposed to calculate the electrode potential if pH and concentration of the sulphide solution are known.

The silver–silver sulphide electrode, which responds to sulphide ion concentration in aqueous solution, has been studied by a number of investigators[1-5] without considering the pH of the sulphide solutions. The present paper is an attempt in this direction.

EXPERIMENTAL

The experiment was carried out by means of the cell

$$Ag / Ag_2S / Na_2S / / KCl / Hg_2Cl_2 / Hg.$$

The electrodes of the cell, the silver–silver sulphide and the saturated calomel electrodes, were prepared as recommended by Goates[3] and Clark[6], respectively.

Pure sodium sulphide was prepared by Botger's method[7]. The solution was standardised iodometrically and the solutions of desired concentrations were obtained by dilution method. Buffer solutions of known pH were made by mixing suitable aliquots of borax and potassium dihydrogenphosphate solutions. Potentiometric observations were made by PL 52 Toshniwal potentiometer and a thermostatic water bath was used to maintain the temperature of the solutions.

RESULTS AND DISCUSSION

In Figure 1 the electrode potential of the silver-silver sulphide electrode (E) has been plotted against logarithm of sulphide ion concentration (log $S^{''}$). The electrode potential has been observed to be linearly related to the logarithm of concentration in buffered solutions ranging from pH 6.6 to 9.1.

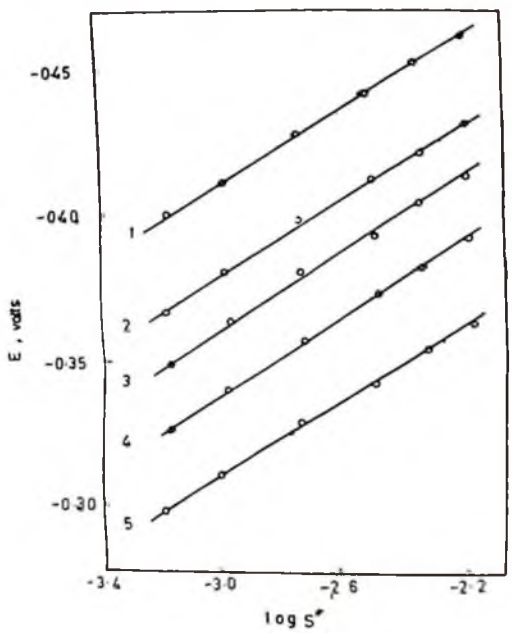


Fig. 1. Plots of E (volts) vs log $S^{''}$. Solutions 1, 2, 3, 4 and 5 are buffered at pH 9.1, 8.6, 8.0, 7.45 and 6.6 respectively at 25°C.

Plots of the electrode potential and pH of the sodium sulphide solutions (curve 1,2,3,4,5 and 6 of Figure 2), keeping sulphide ion concentration constant, are linear, showing thereby that the electrode potential is a linear function of pH also. It, therefore, indicates that the three variable viz. the electrode potential, logarithm of sulphide concentration and pH are interrelated through a linear relation.

In order to incorporate pH, the usual Nernst equation

$$E = E^{\circ} - [RT/nF] \ln S^{''}$$

for the electrode reaction

$$Ag_2S + 2e = 2Ag + S^{''}$$

may be considered as

$$E = \pi - [RT/nF] \ln (S'').^{\alpha} (H+)^{-\beta}$$

where α and β are arbitrary constants which are to be determined experimentally. The slope of the lines of Figure 1 and Figure 2 gave the values of α and β to be equal to 2.2 and 0.6, respectively.

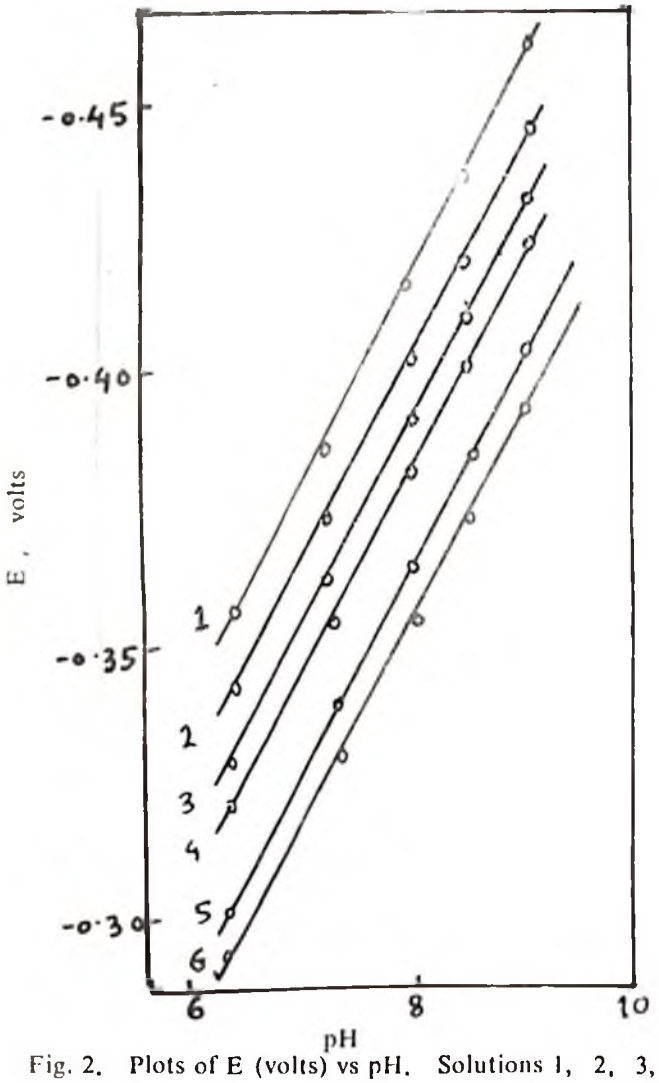


Fig. 2. Plots of E (volts) vs pH. Solutions 1, 2, 3, 4, 5 and 6 have log S'' at —2.2, —2.35, —2.5, —2.75, —3.0 and —3.2, respectively at 25°C.

π is a constant, but differs from standard electrode potential, E°, which depends on the nature of the electrode. The π represents a better value of the constant as pH has also been taken into consideration and its value has been worked out to be —0.270 volts at 25°C.

Table 1. Comparison of calculated and observed values of the potential of the silver-silver sulphide electrode with buffered sodium sulphide solution at 25°C.

log S''	pH	EAg—Ag_2S in mV Observed (a)	Calculated (b)	Difference (a—b)
—3.25	9.1	—388	—387	1
—3.25	8.6	—369	—369	0
—3.25	8.0	—349	—347	2
—3.25	7.45	—327	—327	0
—3.25	6.6	—297	—297	0
—3.05	9.1	—401	—400	1
—3.05	8.6	—381	—382	1
—3 05	8 0	—362	—362	0
—3.05	7.45	—340	—340	0
—3.05	6.6	—310	—310	0
—2.80	9.1	—426	—420	6
—2.80	8.6	—399	—402	3
—2.80	8 0	—381	—380	1
—2.80	7.45	—358	—360	2
—2.80	6.6	—328	—330	2
—2.55	9.1	—433	—431	2
—2.55	8.6	—412	—413	1
—2.55	8 0	—391	—391	0
—2.55	7 45	—370	—371	1
—2.55	6.6	—340	—341	1
—2.40	9.1	—444	—443	1
2.40	8.6	—423	—425	2
—2.40	8.0	—403	—403	0
—2.40	7.45	—382	—383	1
—2.40	6.6	—354	—353	1
—2.25	9.1	—454	—452	2
—2.25	8.6	—433	—434	1
—2.25	8.0	—414	—412	2
—2.25	7.45	—391	—392	1
—2.25	6.6	—362	—362	0

It is evident from Table 1 that there is little difference between calculated and observed values of the electrode potential with sodium sulphide. Statistical examination of these data showed this difference to be insignificant.

Acknowledgement

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REFERENCES

1. A.A. Noyes and E.S. Freed, J. Am. Chem. Soc. 42 (1920) 476.
2. G. Scagliarini and P. Pratesi, Atti accad Lincei, 11 (1930) 193.
3. R.J. Goates, A.G. Cole, E.L. Gray and N.D. Faux, J. Am. Chem. Soc. 73 (1951) 707.
4. K.E. Wrabets. Z. Electrochem., 60 (1956) 722.
5. V.A. Kremer and E.L. Veil, U.S.S.R. 109 Feb. 25 (1958) 853.
6. W.M. Clark, "Determination of hydrogen ions," III ed. The Williams and Wilkins Co., Baltimore, Md., 1928, p485
7. Botger, Ann. of d Chem., 223 (1884) 335.