FORMAL POTENTIAL OF $V^{5+} - V^{4+}$ COUPLE IN CHLORIDE MEDIA

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The formal potential of V^{5+}—V^{4+} couple was determined potentiometrically at different concentrations of chloride ion. Plots of E vs log $[V^{5+}]$ / $[V^{4+}]$ were linear with a slope of 0.06 at 25°C at different $[Cl^-]$, confirming a one-electron transfer reaction Also the plot of E vs log $[Cl^-]$ was linear with a slope of 0.12 indicating the probable electrode reaction in chloride media to be $VCl_8^{3-} + e = VCl_6^{2-} + 2Cl^-$ The formal potential for V^{5+}— V^{4+} couple was calculated to be 0.9841 V at 25°C.

The oxidation potential of V^{5+} V^{4+} couple has been measured mainly in sulphuric acid medium by various workers, the earliest among them being Rutter[1] who gave a value of 0.92 V. Foester and Bottcher[2] reported a value of .0 V. A value of 1 2 V reported by Abegg, Auerbach and Lutter[3] in sulphuric acid was considered not reliable due to uncertain liquid junction potentials used during their work. Coryell and Yost[4] who studied the potentials of vanadic acid to vanadyl ion in hydrochloric acid solutions found it to vary with acid concentration and gave a value of 1.0753 V in 2.145 M HCl and 0.7653 V in 0.010 M HCl. The data of Coryell and Yost were recalculated by Carpenter[5] after correcting the small error in acid molarity and reported a value of 0.9996 V. In view of the different values reported for the potential of V^{5+}—V^{4+} couple in HCl in the literature, the authors have measured the potentials of V^{5+}— V^{4+} couple in chloride media, under various conditions to arrive at the correct formal potential and the type of species involved.

EXPERIMENTAL

All reagents were of AR grade. V^{5+} solutions were prepared by dissolving weighed quantities of ammonium meta vanadate in perchloric acid of known strength and determining the concentration by titrating against standard ferrous solution. V^{4+} solution was prepared by precipitating V^4 as hydroxide from a solution of vanadyl sulphate and dissolving the precipitate in perchloric acid of known strength. The exact concentration of V^{4+} was determined by titrating against standard potassium permanganate. A precision potentiometer was used for measuring the potentials against standard calomel electrode. The measurements were made at 25± 0.1°C. The Cl^- concentration was varied by adding concentrated solutions of standard sodium chloride. There was no change in potentials observed in air or in nitrogen atmosphere.

DISCUSSION

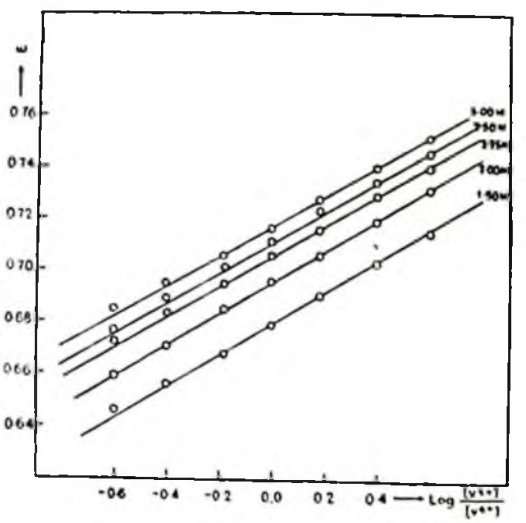
The present system could be represented in the following manner

$$VCl_x^{5-x} + e = VCl_y^{4-y} + (x-y)\,Cl^- \qquad (1)$$

The potential of such a system may be expressed as

$$E = E_o + \frac{RT}{nF}\log\frac{[(VCl_x)^{6-x}]}{[(VCl_y)^{4-y}]} - \frac{RT}{nF}\,\mathrm{Log}\,[Cl^-]^{x-y} \qquad (2)$$

The plot of E vs log $[V^{5+}]$ / $[V^{4+}]$ was linear with a slope of 0.060 ± 0.002 V (Fig. 1) for all concentrations



Plot of E vs log $[V^5/V^4]$ at various concentrations of Chloride.

of Cl^- confirming that the reaction is a one-electron transfer one. However, the experimentally determined potential, E was found to be dependent on chloride concentration. The plot of E vs log $[Cl^-]$ was linear with a slope of 0.12 suggesting that the value of (x-y) in expression (2) to be two. Substituting the value for y in terms of x as y = x—2, the expression (2) becomes

$$E = E_o + 0.06\log\frac{[(VCl_x)^{5-x}]}{[(VCl_{x-2})^{6-x}]} - 0.12\log[Cl^-] \quad .. \quad (3)$$

Salts of hexachlo vanadates (IV) have been reported by kitty and Nicholls[6] and Fowles and Walton[7] where

the anion was represented as $[VCl_6]^{2-}$ suggesting a value of 6 for y and since $x = y + 2$, the value of x in expression (1) should be 8. Coordination number eight for V^{5+} has been reported by Hill, Worsley and Helper[8] while Pope and Dale[9] observed that the larger size of V^{5+} permits variable coordination number in V^{5+} compounds.

In view of the above, the probable electrode reaction for the $V^{5+}-V^{4+}$ couple in chloride media may be written as :

$$VCl_8^{3-} + e = VCl_6^{2-} + 2\,Cl^- \quad \ldots (4)$$

Therefore the formal potential is given by

$$E_o = E + 0.12 \log [Cl^-] \quad \ldots (5)$$

Employing the value of SCE as 0.242 V the formal potential of $V^{5+}-V^{4+}$ couple comes out to be 0.9341 V.

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