
the electrochemical behaviour of copper in aqueous media

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1. A literature survey of the different theories of corrosion and passivity of copper in different media (acidic, alkaline and neutral) is given with particular emphasis on the effect of aggressive ions as well as the use of organic inhibitors. 2. The potential of the copper electrode was followed in oxygenated solutions of the sodium salts of carbonate, bicarbonate, monohydrogen phosphate, chromate, borate, tungstate, _-chloride, bromide and sulphate, respectively, of varying concentrations. The steady state potential, E_{ss} , varies with concentration of the anions (mentioned in 2) according to 4. When the aggressive ions Cr^{6+} and NO_3^- were added to the carbonate, chromate and borate solutions, in which copper electrode was previously equilibrated, sigmoidal E_{ss} - $\log C$ curves were obtained. The inflexion of these curves occur at larger addition of the aggressive ions, the higher of the concentration of the inhibitive anion in solution. The two parameters are related as: $\log C_{inh} = K_1 + n \log C_{agg}$. For the exponent "n" it was found that its value depends primarily on the type of the inhibitor and is higher in borate solution than in carbonate and chromate. ii- Its value for NO_3^- is greater than that for Cr^{6+} in the borate solutions. 5. The dissolution of copper in HNO_3 was determined by measuring the temperature rise using the thermometric technique. The rate of dissolution was found to increase on increasing the acid concentration according to an autocatalytic mechanism involving the formation of $Cu(NO_3)_2$. 6. Addition of monomethyl-, dimethyl-, trimethyl-, monoethyl-, diethyl-, triethyl- amines and hydrazine decreases the dissolution rate of Cu in $6M HNO_3$ by adsorption on the metal surface and/or by altering the autocatalytic dissolution reactions. On the other hand, NO_3^- , ClO_4^- and IO_4^- alter the rate of dissolution through the interference with the cathodic areas. These ions are assumed to compete with some cathodic depolarizing components for adsorption on the metal surface. 7. Cyclic voltammograms were constructed in Na_2CO_3 solutions as a function of the final electrode potential, electrolyte concentration and scanning rate. 8. The effect of addition of increasing concentrations of Cl^- ions on the cyclic voltammetry of Cu was studied in Na_2CO_3 solutions of different concentrations. It was found that the integrated charges under the cyclic voltammograms increase markedly with increasing the NO_3^- ion concentrations, due to the propagation of pitting corrosion. The difference of the charges amounts to that in the presence and absence of NO_3^- ions is taken as a measure of the extent of pitting corrosion to take place. 9. E_{ss} varies with the NO_3^- ion concentration according to 19. from the potentiodynamic polarization

measurements. It was found that the critical potential for pitting to take place varies with the Cl^- ion concentration according to a sigmoidal S-shaped curve¹⁰. Addition of inorganic inhibitive anions, e.g. CrO_4^{2-} , WO_4^{2-} , KPO_4 and B_4O_7 shift the critical pitting potential into the noble direction indicating increased resistance to pitting corrosion¹¹. Sufficient concentrations of the inhibitive anions cause complete pitting inhibition. The concentration of the inhibitive inorganic anions that can withstand the corroding action of a certain concentration of Cl^- ion can be deduced from the equation $\log \text{inh} = \log K + n \log \text{Cl}^-$ where K and n are constants.