B-1525 Sturrock

ANNUAL REPORT ON PROGRESS PRF 1516-A5

During the past year Mr. Higgins and the principal investigator continued experimental work along the lines suggested in the original proposal. The results were suggestive, but inconclusive and it was decided to employ some additional experimental techniques. For this purpose additional equipment was constructed and the crucial experiments are now underway.

Tentative values for the rate of the electrode reaction of copper(II) in pyrophosphate solution have been determined by potential step measurements. These values are the same order of magnitude as the rates in potassium nitrate solution. This definitely establishes the fact that the electron transfer is not the limiting step in electrode reaction of copper(II) in pyrophosphate. Data are presently being obtained which will indicate the presence or absence of specific adsorption and allow theoretical calculation of the double layer (Frumkin) effect on the rate of electrode reaction.

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ABSTRACT OF FINAL REPORT

PRF NO. 1516-A5

TITLE: Investigation of Specific Adsorption by Ligands as a Cause of Polarographic Irreversibility. INVESTIGATOR(S): Peter E. Sturrock INSTITUTION: The Georgia Institute of Technology

Electrode reactions of Copper(II)-pyrophosphate solution at mercury and copper amalgam electrodes were studied by a variety of techniques. No appreciable specific adsorption of reactant or products was found. The potential step technique was employed to determine the kinetic parameters of the electrode reaction which were then corrected for double layer effect. The extreme irreversibility observed in the D.C. polarograms for alkaline solutions is attributed to a static \bigvee_0 (Frumkin) effect.

FINAL REPORT

B-1525 Sturrock American Chemical Society

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TITLE: Investigation of Specific Adsorption by Ligands as a Cause of Polarographic Irreversibility. INVESTIGATOR(S): Peter E. Sturrock INSTITUTION: The Georgia Institute of Technology

Electrode reactions of Copper(II)-pyrophosphate solutions at mercury and copper amalgam electrodes were studied by a variety of techniques including: D.C. polarography, A.C. polarography, triangular sweep polarography, chronopotentiometry, single and double step chronocoulometry, potential step, and drop-time curves.

Experiments with chronocoulometry, triangular sweep polarography, drop-time curves, and streaming electrode potentials, indicate that neither the reactant nor products of the electrode reaction are specifically adsorbed to an appreciable extent.

The potential step technique was employed to determine the kinetic parameters of the electron exchange reaction as a function of pH and ionic strength. In the presence of $1 \pm \text{KNO}_3$ the exchange current density varies between 7.6 x 10^3 amp. cm.⁻² at a pH of 3 and 1.7 x 10^{-6} amp. cm.⁻² at pH values greater than 9. The transfer coefficient is 0.51 for both pH values. At lower concentrations of supporting electrolyte, the kinetic parameters are profoundly affected by the resulting changes in the statucture 3 of the double layer. Data from the drop-time curves were used, together with the Gouy-Chapman theory, to calculate the potential drop across the diffuse double layer. These values were combined with the rational potentials to obtain the potentials at the outer Helmholtz plane. The D.C. polarograms, performed at various pH values and concentrations of supporting electrolyte, were then analyzed for the static $\frac{1}{\sqrt{0}}$ (Frumkin) effect. This analysis indicates that different electrode reactions occur on the positive and negative sides of the electrocapillary maximum (E. C. M.).

On the positive side of the **c**. C. M., $Cu(P_2O_7)_2^{6-}$, which is the predominant species in alkaline solution, is directly reduced and its concentration at the outer Helmholtz plane is greatly enhanced over the concentration in the bulk of the solution because of the positive charge on the electrode. On the negative side of the E. C. M., $Cu(P_2O_7)_2^{6-}$ is strongly repelled by the negative charge of the electrode. The species, $Cu(P_2O_7)^{2-}$, is the predominant species undergoing electrode reaction. It is present, in low concentration, in the equilibrium mixture of the bulk solution and can also be formed by splitting off $P_2 O_7^{4-}$ from $Cu(P_2O_7)_2^{6-}$. At high concentrations of supporting electrolyte this decomposition reaction results in a kinetic polarographic At lower salt concentrations, even $Cu(P_2O_7)^{2-}$ is signifwave. icantly repelled by the negatively charged electrode and the dip, typical of the Frumkin effect, is observed in the polarographic wave.

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