

## Polarographic Irreversibility of the Copper(II) Pyrophosphate System

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The polarographic waves of a number of complex ion systems are known to be irreversible in alkaline solution. One such system is the copper(II)-pyrophosphate complex, formally represented as  $\text{Cu(Py)}_2$ . Below pH 6 a reversible polarographic wave is obtained for the system. As the pH approaches 9 the wave becomes split into two parts, and the normal diffusion current is not attained until the electrode potential is at least -1.3 volts versus S.C.E. In addition to the varying behavior of the reduction wave, the appearance of the polarogram of an alkaline solution of the complex is affected by the concentration of the supporting electrolyte, through the influence of the latter upon the electrical double layer. In this work potassium nitrate was used as the supporting electrolyte. As its concentration is decreased a maximum appears on the rising portion of the wave, and is followed by a pronounced minimum before the current finally rises to its diffusion-limited value.

Both relaxation and steady-state techniques were used to study the combined effects of pH and supporting electrolyte concentration. Techniques employed included the potential step method, chronocoulometry, triangular sweep voltammetry, drop-time electrocapillary measurements, and regular and A.C. polarography. Hanging drop and dropping mercury electrodes were used exclusively.

Since it was initially hypothesized that perhaps adsorption was the cause of the irreversibility, double-layer capacity data were obtained from triangular sweep voltammetry of the sodium nitrate-sodium pyrophosphate system. No adsorption of pyrophosphate was detected by this method, or by searching for the Esin-Markov effect for pyrophosphate. The value of the potential of a streaming mercury electrode in 0.1 and 0.2 F solutions of sodium pyrophosphate was a constant -0.428 volts versus S.C.E., actually less than the -0.435 volts expected in the absence of anionic adsorption, and this discrepancy was attributed to a slight cationic adsorption.

Near the end of the investigation, evidence supporting the existence of the specific adsorption of nitrate ion on mercury was published, and subsequent correlation with data taken in the present study confirmed that fact. The value of the ECM in 1 F  $\text{KNO}_3$  solution was confirmed to be -0.519 volts versus S.C.E.

Chronocoulometry and double-step chronocoulometry, selective for the detection of adsorption of electroactive species, were employed to determine whether any of the copper pyrophosphate complex is adsorbed. The greatest possible amount of adsorption was found to be only about  $0.5 \times 10^{-10}$  moles  $\text{cm}^{-2}$ . Thus it may be said that no detectable adsorption of the copper pyrophosphate complex occurs. Inspection of drop time electrocapillary curves for alkaline solutions of potassium nitrate, some with copper pyrophosphate and some without, showed no noticeable differences at any potential among the various curves. This is additional evidence against the existence of specific adsorption of the complex.

A previous report, plus evidence found in the present study, indicate that in alkaline solution the rate of the electrochemical reaction is controlled by the rate of dissociation of the 2:1 complex to form the reducible species, the latter being  $\text{Cu(Py)}^{2-}$  in the absence of substances which form complexes with copper pyrophosphate ions. By employing the potential step method it was possible to measure the parameters of the electrochemical reduction step in both acid and alkaline solutions. The values found for the parameters for 1 F  $\text{KNO}_3$  of pH = 9.34 are the following:  $i_a^0 = 0.596 \times 10^{-3}$  amp.  $\text{cm}^{-2}$ ,  $k_a^0 = 0.38 \times 10^{-3}$  cm.  $\text{sec}^{-1}$ ,  $\alpha = 0.4$ . At pH = 3.0 the values are  $i_a^0 = 6.92 \times 10^{-3}$  amp.

$\text{cm.}^{-2}$ ,  $k_s^0 = 3.90 \times 10^{-2} \text{ cm. sec.}^{-1}$ ,  $\alpha = 0.3$ . These apparent values tended generally to increase with decreasing  $\text{KNO}_3$  concentration and pH.

Double layer corrections were applied to the above results. These calculations yielded so-called true values of the parameters, as follows. At pH = 9.34,  $i_t^0 = 1.21 \times 10^{-6} \text{ amp. cm.}^{-2}$ ,  $k_t^0 = 6.7 \times 10^{-6} \text{ cm. sec.}^{-1}$ ,  $\alpha = 0.5$ . At pH = 3.0,  $i_t^0 = 1.07 \times 10^{-2} \text{ amp. cm.}^{-2}$ ,  $k_t^0 = 5.94 \times 10^{-2} \text{ cm. sec.}^{-1}$ ,  $\alpha = 0.5$ .

The apparent values of the kinetic parameters at pH 3 are only 20 per cent less than values, also uncorrected for double layer effects, reported in the literature for reduction of copper(II) from 1 F  $\text{KNO}_3$  solution. Thus it is thought that the complex is weak in acidic solution, particularly in the presence of 1 F sodium ion. This conclusion is strengthened by the results obtained for the ionic charge  $z$  on the reducible species in the bulk of the solution. These values were obtained as a by-product of the application of double layer corrections. At pH 9,  $z = 2$ , while at pH 3,  $z = +1$ .

A series of polarograms of the copper pyrophosphate complex was taken for varying concentrations of potassium nitrate. From the polarograms, values for an apparent rate constant  $v^*$  were computed from the formula of Koutecky for a kinetic polarographic current. Values for  $\psi_0 = f(C, E)$  were obtained from electrocapillary measurements and the Gouy-Chapman theory. In each case the value for  $\phi = 0$  was taken as the experimental point of zero charge for that solution. The values of  $v^*$  and  $\psi_0$  were then plotted as functions of  $\phi$  and the concentration, in the manner of Gierst (4). The results obtained from a graphical determination of  $\alpha$ ,  $z$ , and  $v^0$  from this plot are as follows. From the potential region of positive electrode charge,  $\alpha = 0.4$ ,  $z = -1.2$ ,  $v^0 = 8.0 \times 10^{-4} \text{ cm. sec.}^{-1}$ . From the potential region of negative electrode charge,  $\alpha = 0.1$ ,  $z = -0.32$ ,  $v^0 = 8.7 \times 10^{-4} \text{ cm. sec.}^{-1}$ .

In the region of positive electrode charge, observation of the  $v^*$  versus  $\phi$  curve for 1 F  $\text{KNO}_3$  indicates that the rate is nearly independent of  $\phi$ , and it is thought that in this potential region only the 1:1 complex is reduced. At more negative values of  $\phi$  both the mono- and di-ligand complexes are thought to undergo reduction, and the observed rate slowly increases until finally, at very negative potentials, the rate becomes diffusion controlled. In the region of positive electrode charge the value obtained for  $z$  is approximately equal that obtained from the relaxation experiments. The value for  $\alpha$  is moderately less. In the potential region of negative electrode charge, both  $\alpha$  and  $z$  are surprisingly small. This is attributed to the simultaneous reduction of more than one complex species, in addition to double layer effects.

The evidence indicates, therefore, that the effects are different on the two sides of the point of zero charge. The low value of  $\alpha$  at negative  $\phi$  indicates via the Frumkin equation that the effect of  $\phi$  on  $v^*$  is considerably lessened in this potential range. This is to be expected if both the 1:1 and 2:1 complexes are reduced in this region, since the 2:1 complex has an even larger negative charge than does the 1:1, and then the reactant, the adsorbed nitrate ions, and the electrode are all negative, and the  $\psi$  effect should then be at its maximum.