

The plot of E vs log $(i_1 - i/i)$ is linear with the slope of 120 mv indicating that the first electron transfer is the slow step.

The effect of concentration is shown in table 2.

Table 2

Data taken from cyclic voltammograms of acrylonitrile in $\text{Bu}_4\text{NHSO}_4 + \text{Na}_2\text{HPO}_4 + \text{H}_2\text{O}$.

Electrode: 10 μm Hg disc.

$[\text{CH}_2=\text{CHCN}]$	mol dm^{-3}	0.1	0.25	0.5	0.75	1.0	1.5
$10^4 i_1 / [\text{CH}_2=\text{CHCN}]$	A mol^{-1} dm^3	20	19	17	18	10	9

These results suggest that the mechanism at high concentrations involves only 1e per molecule whereas at lower concentration 2 electrons are involved.

This is compatible with the observed formation of adiponitrile at high concentrations and of propionitrile at lower concentrations.

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POLAROGRAPHY OF THE COPPER ADENINE SYSTEM IN SULPHURIC ACID MEDIUM

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Introduction

It has been shown⁽¹⁾ that in the presence of adenine copper (II) ions in 0.25M H_2SO_4 are reduced at the mercury electrode in two distinct stages; this is a consequence of the interaction of adenine with copper (I) ions.

In attempt to clarify which are the reactions involved, the nature of the complexes formed and the respective formation constants a series of experiments using polarographic techniques (sampled DC and DP Polarography) was carried out.

Apparatus

A polarographic analyzer PAR Mod. 174-A with a PAR SMDE 303 stand with Ag/AgCl reference electrode and XY Recorder Mod. PM 8041 Philips was used.

The measurements were made at room temperature after deaerating with purified nitrogen for 12 minutes.

In DPP pulse amplitude was 25 mV and drop time 0.5 sec.

Chemicals

Adenine p.a. supplied by Merck was used without further purification. All other reagents were of analytical grade.

Results and discussion

In a typical experiment the polarogram of a solution of 10^{-4}M Cu(II) in 0.25M H_2SO_4 was recorded and a single reduction wave, corresponding to the 2 electron Cu(II) - Cu(0) reduction was obtained. Increasing quantities of adenine solution were then added until a Cu:Ade ratio of 1:1 was obtained. Under these circumstances two reduction waves were obtained, the first, at more anodic potentials than the original Cu(II) - Cu(0) reduction, corresponding to the reduction Cu(II) - Cu(I), and the second, at more cathodic potentials than the original Cu(II) - Cu(0) reduction, corresponding to the reduction Cu(I) - Cu(0) Hg. (Fig. 1.)

The half-wave potentials of these new waves became progressively

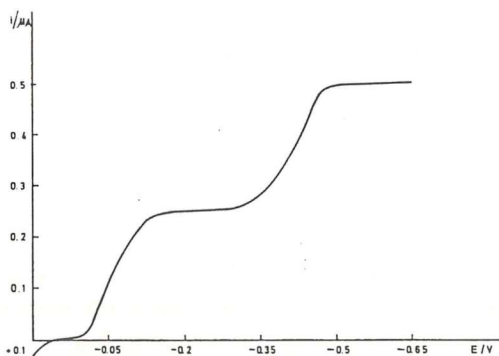


Fig. 1. Sampled DC polarogram of 10^{-4} CuSO_4 with 8×10^{-3} M Adenine in $0.25\text{M H}_2\text{SO}_4$.

more distant as the adenine concentration of the solution was increased. The first reduction wave was observed to move to more positive potentials and the second to more negative potentials.

Analysing the SDC polarograms with the use of E vs. $\log i/(i_d-i)$ graphs for the first reduction gave a straight line with a gradient of 56 mV. This gradient is close to the 59 mV theoretical value for reversible reactions. (Fig 2.)

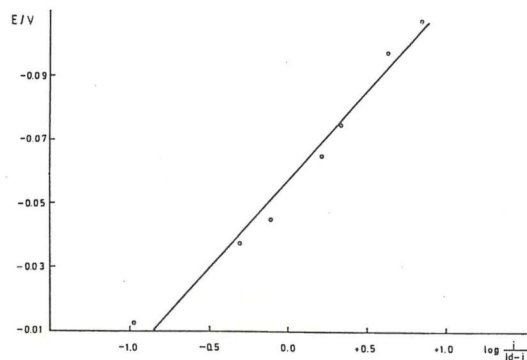


Fig. 2. E vs. $\log i/(i_d-i)$ for the first reduction wave of 10^{-4} M CuSO_4 , 8×10^{-3} M Adenine in $0.25\text{M H}_2\text{SO}_4$.

For the second polarographic wave the gradient obtained was 70mV, from which we obtain the value of $\alpha n = 0.84$ which indicates the quasi-reversible character of this reduction. (Fig 3.)

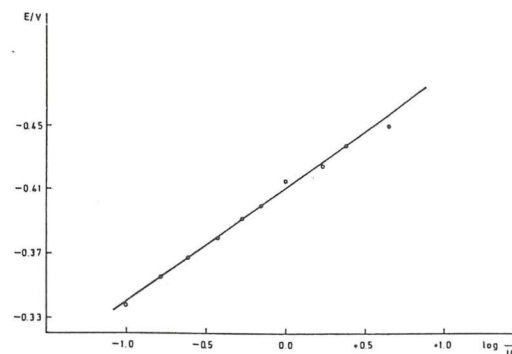
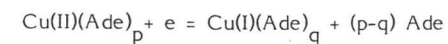


Fig. 3. E vs. $\log i/(i_d-i)$ for the second reduction wave of 10^{-4} M CuSO_4 , 8×10^{-3} M Adenine in $0.25\text{M H}_2\text{SO}_4$.

As the appearance of two polarographic waves (or two peaks in DPP) must result from the complexation of the copper ions with adenine, systematic studies of the variation of half-wave potentials with the adenine concentration were carried out.

Given that the reduction $\text{Cu(II)} - \text{Cu(I)}$ is reversible and that in the presence of adenine this reduction can be written as



the experimental data were studied with the aid of the expression (2,3)

$$\frac{\Delta E_{1/2}}{\log [\text{Ade}]} = - (p-q) \times 0.0591$$

which leads to the calculation of $(p-q)$. (Fig 4.)

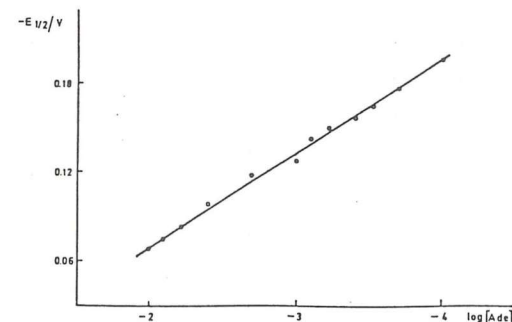
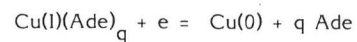


Fig. 4. $E_{1/2}$ vs. $\log [\text{Ade}]$ for the first reduction wave of 10^{-4} CuSO_4 in $0.25\text{M H}_2\text{SO}_4$ and various Adenine concentrations.

For the reaction



which is quasi-reversible we have

$$\frac{\Delta E_{1/2}}{\log [\text{Ade}]} = \frac{q}{\alpha n} \times 0.0591$$

The experimental results gave $p-q = -1$ and $q = 1$. Thus, for the concentrations used in our experiments, $0.25\text{M H}_2\text{SO}_4$; 10^{-4}M Cu^{2+} and adenine equal or greater than 10^{-4}M it seems that only the Cu(I) ion complexes significantly with adenine.

The expression (3,4)

$$E_{1/2} = (E_{1/2})_{\text{Cu}^+} - (E_{1/2})_{\text{C}} \text{Cu}^+ = \text{Cu}^+ \frac{q}{\alpha n} \times 0,0591 \log [\text{Ade}] + 0,0591 \log \beta \text{Cu}^+$$

was used to calculate the formation constant, βCu^+ , of the Cu(I)(Ade) complex, in which $(E_{1/2})_{\text{Cu}^+} \approx E^0 \text{Cu}^+/\text{Cu} = 0.166 \text{ V}$ (vs. Ag/AgCl electrode) and $q/\alpha n = 1.19$. The values calculated for $\log \beta \text{Cu}^+$ are given in the following table:

$[\text{Cu}^{2+}]$ M	$(E_{1/2})_{\text{Cu}^+}$ V	$[\text{Ade}]$ M	$-\text{Log} [\text{Ade}]$	$-(E_{1/2})_{\text{C}} \text{Cu}^+$	$(E_{1/2})_{\text{S}} \text{Cu}^+ -$ $-(E_{1/2})_{\text{C}} \text{Cu}^+$	$q/\alpha n$	$\log \beta \text{Cu}^+$
10^{-4}	0.166	10^{-4}	4.000	0.4325	0.5985	1.2	12.431
		2×10^{-4}	3.699	0.4525	0.6185		12.412
		3×10^{-4}	3.522	0.4650	0.6310		12.412
		4×10^{-4}	3.399	0.470	0.6360		12.358
		6×10^{-4}	3.222	0.4725	0.6385		12.218
		8×10^{-4}	3.097	0.4775	0.6435		12.163
		10^{-3}	3.000	0.4825	0.6485		12.136
		2×10^{-3}	2.699	0.4875	0.6535		11.906
		4×10^{-3}	2.398	0.4925	0.6585		11.675
		6×10^{-3}	2.222	0.4950	0.6610		11.534
		8×10^{-3}	2.097	0.4950	0.6610		11.409
		10^{-2}	2.000	0.4950	0.6610		11.312

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