VOLTAMMETRIC STUDIES OF THE COPPER-CAFFEINE SYSTEM

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Introduction

In studies(1) carried out so far with this system we have used in differential pulse polarography (DPP) 0.25M sulphuric acid as supporting electrolyte and a pulse amplitude of 25mV. Under these conditions two peaks are observed when the ratio of [copper] to [caffeine] is equal or less than 1. When this ratio is larger only a single peak occurs corresponding to the reduction Cu(II)=Cu(0).

It was observed that decreasing the potential scanning rate and increasing the pulse amplitude both resulted in an attenuation of the distortion and an increase in the sensitivity.

On the other hand, in low sulphuric acid concentration (supporting electrolyte) two DPP peaks were observed corresponding to the staged reduction of the copper ions, even when the [copper]/[caffeine] ratio was larger than 1.

The response of the system ($[Cu^{2+}]=2x10^{-3}M$ and $[caffeine]=10^{-3}M$) as a function of the concentration of the supporting electrolyte was also studied. Table 1 shows that the most appropriate concentration of the supporting electrolyte is that for which the height of the reduction peaks of the copper-caffeine system is essentially independent of the the supporting electrolyte concentration.

Table 1 — Effect of the H_2SO_4 concentration on the differential pulse polarography peak current for reductions of Cu(II)=(Cu(I) (first peak) and Cu(I)=Cu(0) (second peak) in the presence of caffeine

Concentration (M) H_2SO_4	first peak (μA)	sec. peak (μA)
0.01	67.5	26.25
0.05	65.0	20.0
0.10	62.5	12.5
0.15	62.5	12.5
0.20	62.5	12.5
0.22	62.5	12.5

Experimental

A PAR model 174A Polarographic Analyzer was used in conjunction with a Phillips 8041 XY recorder. A PAR model 175 Universal programmer was used for cyclic voltammetry.

A three electrode cell was used with the mercury electrode operating as the working electrode, a platinum electrode as auxiliary and a silver/silver chloride as the reference electrode. The reagents caffeine, sulphuric acid and the copper (II) salt were analytical grade. The solutions were prepared in deionised water.

The solutions were deaerated for 12 minutes with oxygen-free nitrogen, the determinations were carried out at room temperature and the supporting electrolyte was 0.1 M sulphuric acid.

A 0.5 second drop time was used with a 2mV/sec scanning rate and a 100 mV pulse amplitude.

The half-wave potential was determined from DPP peak(2) using the equation:

$$E_{1/2}=E_p-\frac{\text{pulse amplitude}}{2}$$

Results and discussion

Under these experimental conditions no reduction peak of caffeine was detected in the potential range studied. However, in a solution containing $2\text{x}10^{-3}$M copper (II) and 10^{-3}M caffeine two reduction peaks were observed corresponding to the reductions copper (II) to copper (I) and copper (I) to copper (0). This staged reduction of copper (II) ions in the presence of caffeine is due to the stabilization of copper (I) species by complexation with caffeine.

By increasing caffeine concentration and maintaining copper concentration constant, the peak potential (E_p), of the copper (II) species shifts to more positive potentials, while the peak potential (E_p) of copper (I) shifts to more negative values. A simultaneous decrease in the peak height of the copper (II) species was observed in relation to the height of the incomplexed copper (II) species. Fig. 1.

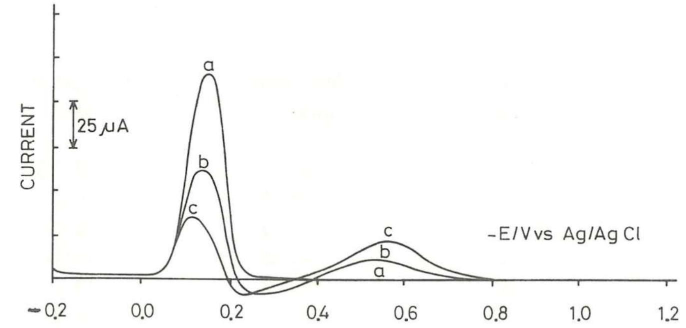

Fig 1. Differential pulse polarograms of $2.0\text{x}10^{-3}$M copper nitrate in presence of caffeine: *a* no caffeine; *b* $1.0\text{x}10^{-3}$M caffeine; *c* $1.0\text{x}10^{-2}$M caffeine.

Like copper (I) ions also copper (II) ions can complex with caffeine. Therefore the corresponding half-wave potentials depend on the caffeine concentration. The variation of the half-wave potential of the copper (II) complex $(E_{1/2})_{c,Cu^{2+}}$ for the first peak (Cu(II)=Cu(I)) with increasing caffeine concentration can be seen in Table 2 and Fig. 2,

Table 2 - Half-wave potentials ($E_{1/2}$) for Cu(II)=Cu(I) (first peak) and Cu(I)=Cu(0) (second peak) in the presence of caffeine.

[Caffeine] (M)	-log [Caffeine]	$-E_{1/2}$ (1º peak) (V)	$-E_{1/2}$ (2º peak) (V)
$1.0\text{x}10^{-2}$	2.000	0.1600	0.6100
$2.0\text{x}10^{-2}$	1.700	0.1475	0.6175
$2.3\text{x}10^{-2}$	1.638	0.1450	0.6200
$2.5\text{x}10^{-2}$	1.602	0.1525	0.6200
$2.7\text{x}10^{-2}$	1.569	0.1450	0.6200
$3.0\text{x}10^{-2}$	1.523	0.1450	0.6250
$4.0\text{x}10^{-2}$	1.398	0.1425	0.6300
$5.0\text{x}10^{-2}$	1.301	0.1375	0.6375
$6.0\text{x}10^{-2}$	1.222	0.1350	0.6400
$7.0\text{x}10^{-2}$	1.155	0.1300	0.6450
$8.0\text{x}10^{-2}$	1.097	0.1270	0.6475
$9.4\text{x}10^{-2}$	1.027	0.1225	0.6475
$9.7\text{x}10^{-2}$	1.013	0.1200	0.6525

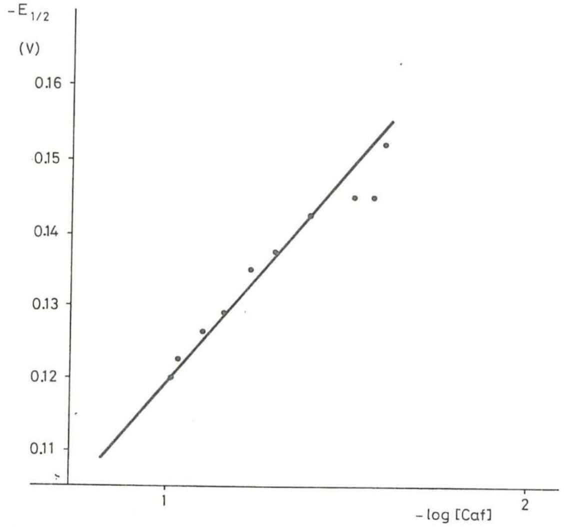

Fig 2.: Variation of the half-wave potential $(E_{1/2})_{c,Cu^{2+}}$ with the log [caffeine] for the first reduction.

from which the relation between $(E_{1/2})_{c,Cu^{2+}}$ and the caffeine concentration is calculated:

$$(E_{1/2})_{c,Cu^{2+}}=-0.062+0.0576 \log [\text{Caffeine}]$$

Fig. 3 and Table 2 show the variation of the half-wave potential of complexed copper (I), $(E_{1/2})_{c,Cu^{+}}$ for the second peak, Cu(I)=Cu(0), with increasing caffeine concentration, from which the relation between $(E_{1/2})_{c,Cu^{+}}$ and the caffeine concentration is calculated:

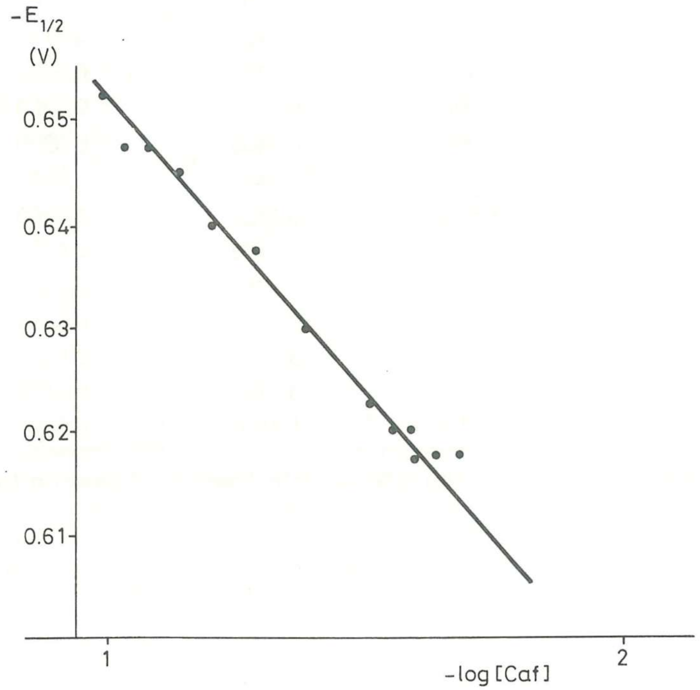

Fig. 3 Variation of the half-wave potential with the log [Caffeine] for the second redution.

$$(E_{1/2})_{c,Cu^{+}}=-0.711-0.0585 \log [\text{Caffeine}]$$

Applying the method of Subrahmanya(3) to calculate the stability constants by means of the expressions:

$$(1)\ (\Delta E_{1/2})=(E_{1/2})_{c,Cu^{2+}} - (E_{1/2})_{s,Cu^{2+}}=0.059 \log \frac{\beta^{+}}{\beta^{2+}} -(p-q)x0.059 \log [\text{Caff}];$$

$$(2)\ (\Delta E_{1/2})=(E_{1/2})_{c,Cu^{+}} - (E_{1/2})_{s,Cu^{+}}=-0.059 \log \beta^{+} - qx0.059 \log [\text{Caff}].$$

where $(E_{1/2})_c$ and $(E_{1/2})_s$ are the half-wave potentials respectively of the complexed ion and the aqueous ion, β^{2+} is the stability constant of the Cu (II)-caffeine complex, β^{+} is the stability constant of the Cu(I)-caffeine complex and p and q are the ligand numbers of Cu(II) and Cu(I) complexes respectively, we get the results shown in Fig. 4 and Fig. 5.

The plots of $(\Delta E_{1/2})$ as a function of log [caffeine] allow the stability constants and the ligand numbers to be obtained from the intercepts and the gradients of the lines, respectively.

From these data the following figures were obtained:

$\log \beta^{2+}=12.33$ $p=2$
$\log \beta^{+}=14.53$ $q=1$

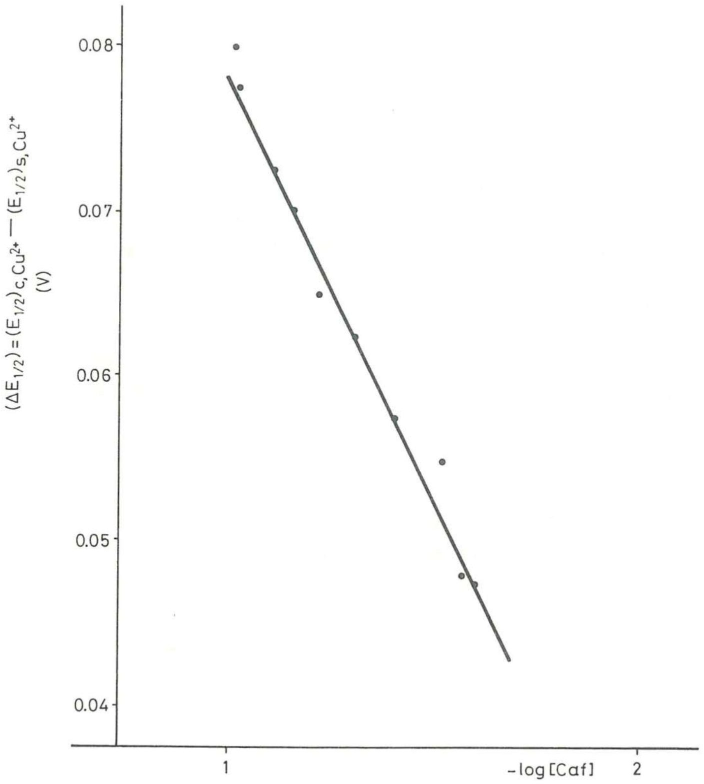

Fig. 4 Shift of the half-wave potential $(\Delta E_{1/2})$ *vs* log [caffeine] for the Cu(II)=Cu(I) reduction.

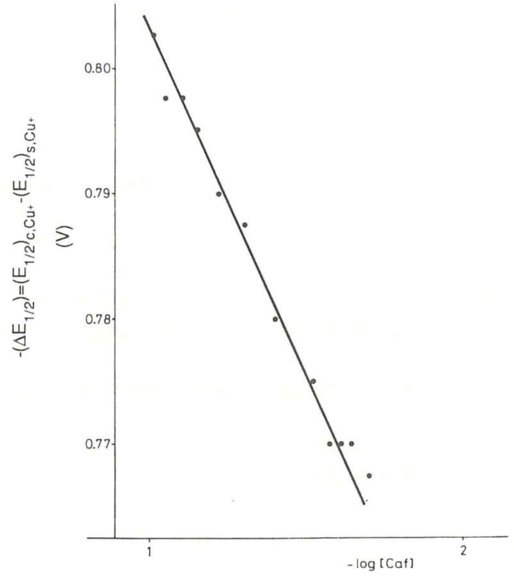

Fig.5 Shift of the half-wave potential ($\Delta E_{1/2}$) υs log [caffeine] for the Cu(I)=Cu(0) reduction.

It should be kept in mind that these values of the stability constants and ligand numbers were calculated for caffeine concentrations between 10^{-2}M and 10^{-1}M. At lower caffeine concentrations in the electrolyte solutions used the variations of half-wave potentials are very small, which may probably indicate the existence of a series of complexes.

Comparing these results with those obtained in 0.25M sulphuric acid, we notice that the ligand numbers have changed from p=1 to p=2 and q=2 to q=1 and that the stability constants of the complexes formed are higher,namely, β^{2+} is about 10 times greater and β^{+} is about 50 times greater.

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ELECTRON-TRANSFER REACTIONS IN VINYLIDENE AND DERIVED CARBYNE COMPLEXES OF RHENIUM

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ABSTRACT

The vinylidene complexes <u>trans</u>-[ReCl(=C=CHR)(dppe)$_2$] (R=Bu^t, C_6H_5, C_6H_4Me-<u>4</u> or CO_2Me; dppe = $Ph_2PCH_2CH_2PPh_2$) and the derived carbyne compounds <u>trans</u>-[ReCl(≡C-CH$_2$R)(dppe)$_2$]$^+$ undergo, by cyclic voltammetry, in tetrahydrofuran (or acetonitrile), at a Pt electrode, a single-electron reversible oxidation. The electrochemical P_L ligand parameter has been estimated for these ligands.

The carbyne complexes are obtained by protonation of the homologous vinylidene species, but the latter are regenerated upon cathodic reduction of the former.

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