REFERENCES

[1] J. Buffle, A.M. Mota, M.L. Simões Gonçalves, J. Electroanal. Chem., 223 (1987) 235.

[2] M.L. Simões Gonçalves, M.M. Correia dos Santos, Sci. Total Environm. (submitted).

[3] J. Buffle and A. Cominoli, J. Electroanal. Chem., 121 (1981) 273.

[4] J. Buffle, Complexation Reaction in Aquatic Systems, Ellis Chorwood, Chichester, in press.

[5] J. Heyrovsky, Principles of Polarography, Czechoslovak Academy of Sciences, Prague 1965.

ULTRAMICROELECTRODES: SMALL IS BETTER

M.I. Montenegro * and D. Pletcher +

* Centro de Quimica Pura e Aplicada da Universidade do Minho
Largo do Paço, 4719 Braga Codex, Portugal

+ Department of Chemistry, The University
Southampton SO9 5NH, U.K.

In recent years, microelectrodes have attracted attention in many fields of electrochemistry and their popularity has grown rapidly due to a recognition of the significant advantages to be derived from their applications[1,2].

The use of very small electrodes made of carbon fibre or a thin metal wire has several advantages as a result of their very specific properties, (i) since they are very small (diameter < 100 μm) they draw very small currents, thus decreasing the effect of uncompensated iR drop and allowing measurements to be made in very concentrated solutions of electroactive species, or in highly resistive media; (ii) high rates of steady state diffusion can be obtained allowing the study of fast electron transfer reactions and coupled chemistry, (iii) the faradaic/charging current ratio is enhanced.

We have been interested in applying microelectrodes to a series of systems in order to determine the kinetics of fast heterogeneous electron transfer reactions by using fast sweep cyclic voltammetry[3]. In very short timescale experiments, the linear diffusion flux totally predominates over the spherical diffusion field and it is possible to use the equations and dimensionless plots of Nicholson and Shain to obtain the kinetic parameters.

Figure 1 shows a cyclic voltammogram recorded at a Pt microelectrode for ferrocene in CH_3CN at a scan rate of 1000 Vs^{-1}.

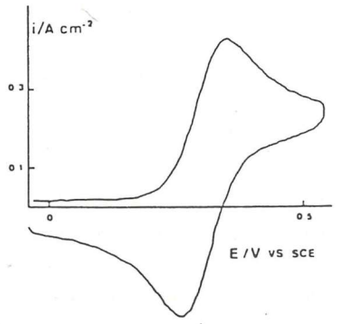

Figure 1. Cyclic voltammogram recorded at a Pt microelectrode, radius 5μm for 10 mmol dm^{-3} ferrocene in 0.5 mol dm^{-3} Bu_4NBF_4 in CH_3CN at a potential scan rate of 1000 Vs^{-1}.

The peak separations at various scan rates and for several concentrations are shown in table 1 demonstrating that the data are indeed free from distortions by iR drop.

Table 1

Data taken from cyclic voltammograms of ferrocene in Bu_4NBF_4 + CH_3CN. Electrode 10μm Pt disc.

$[Cp_2Fe]$/mmol dm^{-3}	Ep mv at v/Vs^{-1}		
	500	1000	3000
2	80	90	115
5	90	100	115
10	85	90	110
20	85	90	110
k/cm s^{-1}	1.10	1.13	1.13

Our interests have also been directed to the study of electrochemical systems that work in highly concentrated solutions of the electroactive species. A typical example is the so-called "Baizer process" which produces adiponitrile by electrodimerization of acrylonitrile[4]. The fact that this reaction only occurs at very high concentrations of acrylonitrile excludes the application of conventional electrochemical techniques. However, we have found that microelectrodes provide reliable data which can be utilized to study the mechanism for the dimerization process.

Figure 2 shows a linear potential scan recorded at a mercury microelectrode with a slow potential scan rate. A reduction wave, $E_{1/2}$=-2.03V vs SCE is clearly observed and the plateau region can be predicted although a further reduction reaction is seen at a potential close to the commencement of the plateau region.

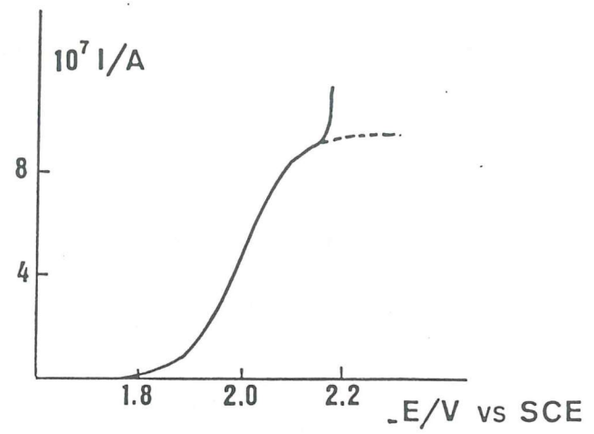

Figure 2 . i-E curve recorded at a Hg microelectrode, radius 5 μm for acrylonitrile 1.5 M in 0.4% Bu_4NHSO_4, 15 % Na_2HPO_4 in H_2O at a potential scan rate of 50 mVs^{-1}.

The plot of E vs log $(i_l - i/i)$ 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 $Bu_4NHSO_4 + Na_2HPO_4 + H_2O$.

Electrode: 10 μm Hg disc.

$[CH_2=CHCN]$	mol dm^{-3}	0.1	0.25	0.5	0.75	1.0	1.5
$10^4\ i_l / [CH_2=CHCN]$	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 proprionitrile at lower concentrations.

References

(1) M. Wightman, Anal. Chem. *53*, 9 (1981) 1125A.

(2) M.I. Montenegro, Portugaliae Electrochimica Acta, *3* (1985) 165.

(3) M.I. Montenegro and D. Pletcher, J. Electroanal. Chem., *200* (1986) 371.

(4) D. Pletcher, Industrial Electrochemistry, Chapman and Hall, London, 1982.

POLAROGRAPHY OF THE COPPER ADENINE SYSTEM IN SULPHURIC ACID MEDIUM

J.E.Simão and H.M.Tavares, Centro de Química Pura e Aplicada, University of Minho, 4719 Braga Codex, Portugal.

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 analizer 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 circunstances 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