# Voltammetric Studies on Micro-, Ultramicro- and Ultramicro-array Electrodes Part I: Measurement of Diffusion Coefficient

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The efficacy of the micro-, ultramicro- and ultramicro-array electrodes in the determination of diffusion coefficient was investigated. Ferocene was used as the probe. It was found that the micro-electrode (r = 600 $\mu$m) gives the best result in 0.1 M electrolyte with the scan rate in the range 2 V/sec to 20 mV/sec, while ultramicro-electrode gave best result in the scan range of 50 mV/sec or less. The effect of concentration of electrolyte on diffusion coefficient was also investigated. Ultramicro-array electrode showed interesting behavior.

An electroanalytical technique widely used to investigate electrochemical (faradaic as well as nonfaradaic) processes is voltammetry [1]. Conventionally, electrodes of small dimension have been used in this technique. Within last decade, attention is being paid to the usage of electrodes of submicro dimension (radius < 100 $\mu$m) - termed ultramicroelectrode [2].

For a conventional voltammetric study, a supporting electrolyte is added to the sample solution to suppress the migration current and to minimize resistance which could otherwise create problem in electrode potential measurement. It would be desireable to avoid the addition of the supporting electrolyte, if possible [3]. In some cases, a supporting electrolyte may be totally insoluble (as in nonpolar solvents); nevertheless, an electrochemical study in such solvent may give valuable information. Also, at high scan rate (say, >100 V/sec), the voltammogram at the conventional size electrode, may be a distorted one because of solution resistance or charging current. The IR drop distorts the voltage axis of the voltammogram. It has recently been shown that the problem of IR can be minimised with the use of electrode of micrometer radius. The current is suffeciently small at these electrodes and hence undistorted cyclic voltammogram can be obtained in solution with low concentration of supporting electrolyte. The problem of charging current on these ultramicro electrodes is not too profound either [2g].

One of the useful quantities which can be obtained from voltammetric measurements is


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diffusion coefficient. For a chemical reaction to take place, there has to be an encounter between two reacting moieties. This encounter is subject to mass transfer mode for transport. The mode of transport where atom or molecules move under the concentration gradient - diffusion - becomes particularly important when other modes of transport are suppressed or eliminated. Polarography, an electrochemical technique, is based on recording the diffusion current. In biological system / biological matrices, diffusion may become important for biological reactions. Thus a knowledge of the diffusion coffecient and the mode of its measurment become important.

Electrochemical methods have been used for the determination of diffusion coefficient [5]. Voltammetry can be and has been used to obtain diffusion coefficient of molecules in solution and gels [6]. The use of ultramicro electrode [2,7] has opened a new field of high speed voltammetry (in solution of low or zero concentration of elctrolytes). These ultramicro electrodes can be used in the determination of diffusion coffecients [8]. In the present study, some measurements of diffusion coefficient have been carried out on micro (r>500 $\mu$m), submicro- (50 < r < 100 $\mu$m), ultramicro- (r = 10 $\mu$m) and ultramicro array electrodes, of various materials (platinum, gold or graphite paste), at various scan rates (100 V/sec. down to 20 mV/sec.) and in solution containing 0.1 to 0.0000 M of electrolyte.

The peak current of a cyclic voltammogram at micro size electrode (r>500 $\mu$m) is given [1, page 218] by the expression:

$$i_p = (2.69X10^5)^{1/2}\ n^{3/2}\ AD^{1/2}\ v^{1/2}C_u \qquad \ldots (1)$$

with n = 1 and $C_u$ = concentration of the redox couple. $C_u$ in $10^{-6}$ mole/cm$^3$, $i_p$ in microamp, r in micron and $v$ in V/sec, the diffusion coefficient can be expressed as:

$$D = (i_p)^2 / (7.24X10^{-6}\ A^2\ v) \qquad \ldots (2)$$

Diffussion coefficient can be determined from the limiting current obtained at ultramicro electrode (low scan rate, spherical diffusion) using the expression [8,9]:

$$i_l = 4FDCr \qquad \ldots (3)$$

## EXPERIMENTAL

Acetonitrile (Fluka AG) was passed through a column of activated alumina [10]. Dichloromethane (BDH, purity 98%), tetra n-butyl ammonium perchlorate (Fluka AG) and ferrocene (BDH) were used directly as received. Gold wire (radius 10 $\mu$m - code No. 16001468-c-660-A64-C7) was a gift from Carrier Telephone industries, Islamabad, Pakistan. Graphite fine powder (E. Merck) was used directly as received.

Polarographic Analyser 174 (for low scan rate) and Potentiostat model 173, Universal Programmer 175 of EG & G Princeton Applied Research Instruments were used in conjunction with Houston RE0074 X-Y

recorder and Tektronic Storage Oscilloscope EU - 510N with plug - in- units 5A2N differential amplifier and 5B10N Time Base amplifier. Conductivity Bridge MC1MKV, of Electronic Instrument Ltd. England, was used for conductivity measurement (for IR drop).

Counter electrode was a platinum wire (length 1.5 to 2 cm, r = 600 $\mu$m) sealed in a glass tube with epoxy. Reference electrode was custom made saturated calomel eletrode.

Test (working) electrodes were the following:
(a) platinum disc electrodes (600,100,75 $\mu$m),
(b) gold disc electrodes (r = 600, 10 $\mu$m)
(c) gold array electrode (constructed from gold wires of radius 10 $\mu$m) and
(d) graphite paste electrodes (r = 600,50 $\mu$m).

Radii of platinum and gold disc eletrodes were measured with the help of a screw gauge while the radii of graphite paste and ultramicro (gold) electrodes were measured with a travelling microscope. Platinum and gold electrodes were fabricated by sealing pieces of wire of desired radius in glass capillaries. The electric connection was made through a pool of mercury (or by directly soldering a copper wire). These discs were polished with alumina polisher prior to each measurement.

Gold array electrode was fabricated by sealing eight wire pieces (r of each = 10.0 $\mu$m, length 12.5 cm) between two pieces of microscopic slides (1 cm x 1.5 cm) using Araldite epoxy (CIBA-GIEGY). The slide piece separated when placed in dichloromethane overnight, leaving Araldite in the form of a thin soft membrane. The membrane was again sealed between slide pieces (1.0 x 1.2 cm) with the help of Araldite. The two ends were exposed-one for electrical connection and the other for exposure to the solution. A boat of sliver foil (BDH 0.13 mm, 1.0 $cm^2$) was made and glued to the copper wire through conducting silver epoxy. Araldite epoxy was applied at the edges of silver foil. Thus the membrance containing gold wires sealed in slide pieces was mounted in the expanded end of a capillary glass tube with Araldite epoxy (fig. 1).




**Fig.1: Gold Array Electrode**

Graphite paste (disc) electrode (r = 50 $\mu$m) was prepared by mulling 15 g graphite powder with 9 ml of Nujol until the entire mixture appears uniformly wetted. Jets were

drawn with capillary glass tubes (one end was jet, the other end broad). Graphite paste was applied at the narrow (jet) end of glass tube and pressed with the tip of pin head and thin wires. Electric connection was made through copper wires.

**Measurements**

Cyclic Voltammetry was carried out as described earlier [11]. Scan rates employed were 100, 10, 2, 0.5, 0.1 and 0.02 V/sec. Tetra butyl ammonium perchlorate (TBAP) concentration was maintained at 0.1, 0.01, 0.001 & 0.0001 M and also 0.0000 M (zero concentration). Conductivity measurements were carried out by following the instruction provided with the instrument.

## RESULTS AND DISCUSSION

Ferrocene was used as probe redox couple. 0.1 to zero concentration of TBAP was the electrolyte used. Diffusion coefficient of ferrocene was calculated from the peak current (eq.1) or limiting current (eq.3) as the case be.

**Effect of Size and Scan Rate (0.1 M TBAP)**

Diffusion coefficient calculated using various electrodes are summerised in the Table 1.

Using platinum and gold electrodes of dimension 600 $\mu$m, the diffusion coefficient of ferrocene, calculated from eq 2, in the scan range 2 V/sec to 20 mV/sec came out to be $2.58\pm0.75 \times 10^{-5}$ cm$^2$/sec. The reported values are $2.40 \times 10^{-5}$ cm$^2$/sec [12] and $2.00 \times 10^{-5}$ cm$^2$/sec [13]. The platinum submicro electrode (r = 100 $\mu$m) gave D = $4.50\pm0.55 \times 10^{-5}$ cm$^2$/sec in the scan range 10 to 2 V/sec. The value of D obtained at this electrode at lower scan rate and other submicro- & ultramicro- electrodes in all scan range (100 V/sec-20 mV/sec) were of the order of $10^{-4}$ cm$^2$/sec. The behavior of graphite paste micro electrode and ultramicro array electrode was interesting. Diffusion coefficient obtained using the graphite paste microelectrode (r = 600 $\mu$m) was smaller by a factor of 3-4; D was $6.50\pm0.50 \times 10^{-6}$ cm$^2$/sec suggesting that electrochemical area was different from the geometric area. The diffusion coefficient obtained using ultramicro array electrode (8 electrodes of radius 10 $\mu$m each) came out to be of the order of $10^{-4}$ cm$^2$/sec in the scan range 10 to

**Table 1**

**Diffusion Coefficient Calculated using Various Electrodes**

Electrolyte TBAP 0.1 M; Ferrocene 1 mM

| Electrode | Size $\mu$m | Scan range V/sec | eqn | $Dx10^{-5}$ cm$^2$/sec |
|---|---|---|---|---|
| Pt, Au | 600 | 2 to 0.02 | 2 | $2.58\pm0.75$ |
| Pt | 100 | 10 to 2 | 2 | $4.50\pm0.55$ |
| Pt | 100 | 0.5 to 0.02 | 2,3 | 10 |
| Pt | 75 | 100 to 0.02 | 2,3 | 10 |
| G.paste | 50 | 100 to 0.02 | 2,3 | 10 |
| G.paste | 600 | 100 to 0.02 | 2 | $0.65\pm0.05$ |
| UMA | 8x10 | 10 to 2 | 2,3 | 10 |
| UMA | 8x10 | 0.5 to 0.02 | 3 | $3.80\pm2.20$ |
| Au | 10 | 0.5 to 0.02 | 3 | $5.17\pm0.68$ |

concentration of $SO_2$ in solution and the second reduction observed at higher sweep rates.

The surface complex may be $SO_2$-$SO_2^{\cdot-}$ and this complex has been reported in the coulometric reduction of $SO_2$ [5].

The effects of illumination on this second reduction are not studied because of the distorted peaks. Some increase in current is however observed.

## CONCLUSIONS

1. $SO_2^{\cdot-}$ undergoes a one electron reduction to $SO_2^{2-}$ in amide melts at glassy carbon electrodes and can be observed only at very slow sweep rates.

2. The reduction process is more facile under illuminated conditions.

3. At mercury electrodes, surface processes are involved.

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measurement of $i_p$ was possible for the concentration of TBAP lower than 0.001 M at micro-sized electrode. Thus, one cannot correlate this variation meaningfully to Walden's rule.

With submicro- and ultra micro - electrodes ($r \leq 100$ $\mu$m), the diffusion coefficient could be obtained in lower concentration range and was found to be in the range 7.0 - 8.0x$10^{-5}$ $cm^2$/sec. Again this slight variation does not warrent invoking Walden's rule.

The case of ultramicro array electrode is interesting. Diffusion coefficient could be calculated over a wide scan range (100 V/sec to 20 mV/sec) and in the concentration range 0.1 M to 0.0000 M TBAP, using either linear or spherical diffussion expression. The diffusion coefficient, obtained using eq. (2) ranged from 1.00$\pm$0.60 x $10^{-5}$ $cm^2$/sec for 0.01 M TBAP to 3.67$\pm$2.9 x $10^{-5}$ $cm^2$/sec for 0.0000 M TBAP; using eq 3, the D value ranged from 6.14$\pm$3.0 x $10^{-5}$ $cm^2$/sec to 6.42$\pm$2.02 x $10^{-5}$ $cm^2$/sec. It may be noted that the concentration of electrolyte has negligible effect on the diffusion coefficient. The numerical values differ according to the equation used to calculate D (eq. 2 or 3). Comparing the value of D obtained in 0.1 M TBAP with reported values, it may be concluded that though ultra micro array electrode may be used to evaluate D, better result is obtained if the linear diffusion expression (eq. 2) is used for the evaluation of D.

The diffusion coefficient obtained using gold ultramicro electrode (r = 10 $\mu$m) came out to be 8.25$\pm$3.00 x $10^{-5}$ $cm^2$/sec, which is 3.5 times the reported value. It is possible that the geometric and electrochemical areas of the electrodes are not the same.

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