Voltammetric Studies on Micro-, Ultramicro- and Ultramicro-array Electrodes - Part II Measurement of Standard Heterogeneous Electron Transfer Rate Constant

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Heterogeneous electron transfer rate constant k^o was evaluated for ferrocene - ferrocenium redox process using micro (r=600 μm, Pt, Au Graphite paste), submicro (r=100, 75 μm, Pt), ultramicro array electrode (8 Au electrode of r = 10 μm each). The effect of concentration of electrolyte (0.1M, 0.01M, 0.001M TBAP) on k^o was investigated. The relevance and importance of the finding of Wightman *et. al.* regarding the measurement of fast electron transfer kinetics are highlighted.

Electron transfer reactions are of fundamental importance in chemistry, biology and chemical technological - industrial processes. The metal industry, energy production and storage, are based directly or indirectly upon the heterogeneous electron transfer rates.

Heterogeneous electron transfer studies give insight into the mechanism of one of the most fundamental pathways in chemistry. The solvent dynamics, the (solvent) re-organization and inner organization energies are investigated through the measurements of the heterogeneous electron transfer rate constants [1]. For the measurement of the standard heterogeneous electron transfer rate constant k^o, the techniques generally used are voltammetry and impedance based methods [2]. In particular, voltammetry has been used extensively. Based upon the theory of stationary electrode polorography, Nicholson [3], Gileadi [4] and Kochi [5] proposed methods for the determination of k^o and these have been used by many workers. The peak separation method of Nicholson [3] for voltammetry at stationary microelectrode has been most popular [2]. However, there are experimental problems arising from the solution resistance and capacitance current. Besides, it was claimed by several workers that the use of micro size electrode in conjunction with the peak separation method, (which is essentially based upon inherent quasi-reversible case) give lower k^o values [6].

With the introduction of electrodes of micrometer dimension (submicro and ultramicro electrodes) and high speed voltammetry, several workers [6] made use of

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high speed voltammetry at ultramicro electrode to evaluate k^o. They claimed that faster kinetics - inaccessible to conventional voltammetric methods at a micro electrode and scan rate 100 mV/sec - can be studied by this technique [6 c]. Wightman *et.al.* used ferrocene as substrate. This compound has been studied by many workers and k^o calculated ranged over almost 2 orders of magnitude [7]. Wightman reported k^o for ferrocene - ferrocenium redox process as 3.1 ± 1.0 cm/sec at gold and 0.95 ± 0.44 cm/sec at platinum electrodes.

Heterogeneous electron transfer can be affected by the electrode surface (surface catalysed electron transfer) [8], the viscosity of the medium, the diffusion coefficient of the substrate in that medium and the double layer structure [9].

In the present study, electrodes of different dimension - micro (r=600 μm) down to ultramicro (r=10 μm) - made of various materials (platinum, gold, graphite paste) were used to evaluate k^o for ferrocene-ferrocenium couple in tetra n-butyl ammonium perchlorate of concentration ranging from 0.1 M to 0.00 M. Scan rate used were 100 V/sec down to 0.02 V/sec. An ultramicro array electrode was also used in this study.

EXPERIMENTAL

The fabrication of electrodes, recording of volammograms, purification of chemicals etc. have already been described [11].

Evaluation of k^o

For the evaluation of k^o on micro electrodes (r = 600 μm) Nicholson's peak separation (ΔE_p) method was used. The contribution from the resistance of solution ($(\Delta E_p)_{res}$ = 21R) was accounted and corrected ΔE_p are used to evaluate Ψ from which k^o was obtained from the expression:

$$\Psi = k^o/(aD_o)^{1/2} \quad \ldots (1)$$

where D_o = diffusion coefficient of ferrocene (taken as 2.53×10^{-5} cm^2/sec [11]),
$a = nfv/(RT)$, v being the scan rate.

For the evaluation of k^o on ultramicro electrode, two methods were employed;
(i) the method of Oldham - Zoski - Bond (O-Z-B) [6 a]

$$1 - \exp[nF(E_{1/2} - E_h)/RT] = 2D_o/k^o a \quad \ldots (2)$$

O-Z-B equation

where E_h is the reversible half wave potential given by

$$E_h = E^o + (RT/nF) \ln (D_R/D_o) \quad \ldots (3)$$

and $E_{1/2}$ is the experimental half wave potential of a nearly reversible steady state voltammogram. Using E_h = 0.400 V, RT/F = 25.69 mV at T = 25°C, k^o was calculated from experimental $E_{1/2}$ at ultramicro electrodes.

(ii) Safford - Weaver (S-W) diagrams in conjunction with S-W's eqs. [6 b].

The S - W equation is

$$\Delta E_k = \Delta E_p - \Delta E_{rev} \quad .... (4)$$

ΔE_k = additional peak separation due to finite electrode kinetics, ΔE_p is observed peak separation and ΔE_{rev} is the reversible value obtained when k^o approaches infinity and

$$\Delta E_{res} = \Delta E_p' - \Delta E_k - \Delta E_{rev} \quad .... (5)$$

where $\Delta E_p'$ is the total cathodic - anodic peak separation obtained in the presence of both finite kinetics and solution resistance effects, ΔE_{res} is the peak separation component "attributable" to solution resistance effects [6 b].

ΔE_{rev} is taken as 59 mV at 25°C. Diagrams given by S - W may then be used for the calcutation of k^o.

RESULTS AND DISCUSSION

Standard heterogeneous electron transfer rate constant k^o of ferrocene was obtained on micro - (Au, Pt, Graphite Paste all r =600 μm), sub/ultra micro (Pt, r = 100, 65 μm; Graphite Paste, r = 50 μm; Au, r = 10 μm) and ultramicro array electrodes. Ferrocene is a standard redox (ferrocene / ferrocenium) substrate and is proposed as a standard for studying heterogeneous electron transfer rate constant k^o. However, the reported k^o values vary by a factor of 100 (by two orders of magnitude) [6 c].

Table 1

The Values of k^o Under Different Conditions

Electrode (μm)	[TBAP] M	Scan Rate V/sec	Method	k^o cm/sec
Au(10)	0.1	-	O-Z-B	0.10±0.01
G.P.(50)	0.1	-	O-Z-B	0.20±0.01
Pt(100,75)	0.1	10	S-W	0.10±0.02
G.P.(50)	0.1	10	S-W	0.05±0.01
Pt(100,75)	0.01*	10	S-W	0.03±0.01
G.P.(50)	0.01*	10	S-W	0.04±0.02
Au array (8x10 mm)	0.01 to 2	100 to 2	S-W	0.05±0.02
Pt,Au,G.P (600)	0.1	100 to 0.02	ΔE_p	0.08±0.07
	0.01	2 to 0.02	ΔE_p	0.02±0.01
	0.001*	0.1 - 0.02	ΔE_p	<0.01

* k^o could not be obtained at lower concentration of TBAP at this electrode

Heterogeneous electron transfer is affected by various factors (electrode material, double layer structure etc). In the present study, factors which have been taken into consideratiion are

(i) material and nature of electrode,
(ii) the supporting electrolyte concentration,
(iii) the scan rate and
(iv) the size of the electrode.

The results are collected in the Table I.

From the Table it is clear that

(i) there is hardly any scan rate effect,
(ii) there is hardly any effect of electrode size (k^o values are 0.08 cm/sec. for micro - to 0.11 cm/sec. for ultramicro electrode),
(iii) there is a perceptible concentration effect but
(iv) there is significant effect of electrode morphology (k^o on G.P. is a high - 0.50 cm/sec).

The G.P. electrode does not possess a polished smooth surface. The higher value of k^o could be due to the rough surface of electrode - the fractal surface of solid electrode could lead to different - probably higher - values of k^o. The result of Wightman *et.al.* [6.c] (3.1 ± 1.0 cm/sec. at Au and 0.95 ± 0.44 cm/sec. at Pt electrodes) may be indicative of the difference in fractal surface of the two electrodes or the two electrodes behaved fractal towards ferrocene. Evans [1.b] has forewarned about the effect of the preparation of electrode on k^o and also pointed out the possible large double layer effect. Wightman *et.al.* have used 0.6M TBAP - a high concentration of electrolyte. Compton *et.al.* [8] have suggested about the contribution of the surface catalysis towards k^o.

The importance of Wightman's work [6.c] lies in the measurement of relatively large values of k^o. True, there are many factors which influence k^o (e.g. viscosity of the medium, diffusion constant of the electroactive species under study, the electrode surface etc.); no matter what is the reason for the large k^o, it can be measured only by high speed voltammetry at ultramicro electrodes. Their suggestion to re-evaluate some previous measurements are worthwhile to pursue. It is best that some previous studies on the evaluation of k^o be re-examined on mercury ultramicro electrode [12] (this will eliminate the fractal effect) and under varying conditions of concentration of electrolyte, viscosity etc.

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