CAPSULES
notes and applications from Bioanalytical Systems, Inc.

May 1999

Determination of Heterogeneous Electron Transfer Rate Constant

Key Terms
Cyclic Voltammetry, Heterogeneous electron transfer rate constant, BAS 100 Series

The heterogeneous electron transfer rate constant (k^o) is commonly determined using cyclic voltammetry. For a totally reversible compound, the difference in the potentials between the anodic peak current and cathodic peak curent (ΔEp) is 59/n mV. When the electron transfer reaction is quasi-reversible, the rate of electron transfer is too slow to keep the redox couple in equilibrium as the potential is changed. Thus, ΔEp increases with the scan rate (v) (Figure 1). The increase in ΔEp may be used to determine the rate of heterogeneous electron transfer following the method described by Nicholson (1). Working curves which relate ΔEp to a kinetic parameter (Ψ) have been published (1,2). See Table 1. The rate-constant for a reduction is determined by the following equation:

$$k^o = \Psi \left[D_O \pi \left(\frac{nF}{RT} \right) \right]^{1/2} \left(\frac{D_R}{D_o} \right)^{\alpha/2}$$

The ratio of the diffusion coefficients in many cases is approximately one, and is thus ignored (see below).

This method was used to determine k^o for the reduction of ferricyanide in 1 M KCl, pH 3 at a glassy carbon electrode, The diffusion coefficient for ferricyanide (D_O) is 7.6 x 10^{-6} cm^2 s^{-1} (3) and for ferricyanide (D_R) is 6.3 x 10^{-6} cm^2 s^{-1}. The transfer coefficient (α) used was 0.5. Ignoring the diffusion coefficient ration resulted in 5% increase in the k^o value. This is relatively insignificant in these rate determinations.

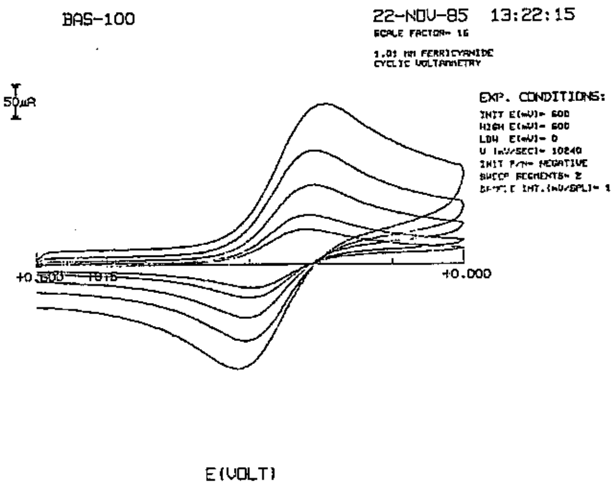

Figure 1. Cyclic votammograms of 1.01 mM ferricyanide in 1.0 M KCl at pH 3 obtained with a glassy carbon electrode, scan rates of 1, 2, 5, 10, and 20 Vs^{-1}.

The results shown in Table 2 are in fairly good agreement with literature values which range from 0.02 to 0.1 cm s^{-1}. The variation in the reported rate-constants may be due to differences in the electrode surfaces or because, in some cases, methods other than cyclic voltammetry were employed.

It is important that iR problems are not present. Resistance effects cause a variation in ΔEp with scan rate similar to that caused by finite kinetics. Thus, the k^o determination will be low. Often measurements are made at two different concentrations to ensure that iR drop is not significant. If a potential loss does occur, the use of iR compensation should be employed to minimize the problem.

Table 1 (From Ref. 2)

ΔEp (mV)	ψ	ΔEp (mV	ψ
60	19.00	95	0.653
61	11.50	100	0.568
62	8.40	105	0.496
63	6.45	110	0.441
64	5.10	115	0.394
65	4.3	120	0.356
66	3.63	125	0.323
67	3.16	130	0.295
68	2.81	135	0.269
69	2.51	140	0.248
70	2.26	145	0.229
75	1.51	150	0.212
80	1.14	160	0.185
85	0.92	170	0.162
90	0.77		

Table 2

v(Vs^{-1})	ΔEp(mV)	ψ	k^{o}(cm s^{-1})
1	76 mV	1.43	0.042
2	82	1.04	0.043
5	96	0.633	0.041
10	102	0.538	0.050
20	122	0.348	0.045
50	152	0.210	0.043
		Average:	0.044

Notes

1. The switching potential should be at least 150 mV past the peak potential.
2. Best results are obtained when ΔEp is between 80 mV and 140 mV.
3. Reproducability of ±20% is good within a laboratory.
4. Values within a factor of 2 between different laboratories are considered to be in good agreement.
5. Too much analog filtering at the output will also cause an increase in ΔEp.
6. It should be clear that the rate will usually vary when different electrode materials are used. This often influences the variation between literature values.
7. Please see Ref. 4 for further information on electrochemical rate measurements.

References

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