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A Note on the Kinetic Parameter Determination at the DME by Koutecký's Method

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In Koutecký's[1,2] method the fundamental equation is

$$\frac{i_l}{i_d} = F(x) - \xi H_c(x) = F'(x) \tag{1}$$

where

$$x = K_f\left(\frac{12t}{7D}\right)^{1/2} \tag{2}$$

and

$$\xi = 50.4D^{1/2}m^{-1/3}t^{1/6} \tag{3}$$

i_l is the maximum instantaneous current of the single drop at the potential E, i_d is the maximum instantaneous current of the single drop in the limiting current region, $F(x)$ is a function related with the current at potential E to the current at infinity and $H_C(x)$ is a correction factor introduced because of the curvature of the drop. Koutecký has given a table of numerical values of $F(x)$ and $H_C(x)$ at particular value of x.

Meites and Israel[3] have extended this into a more mathematical form by using Koutecký's table. They found that $\log x$ varies linearly with $\log F(x)/\{1-F(x)\}$ as

$$\log\lambda = -0.1300 + 0.9163\log\frac{F(x)}{1-F(x)} \tag{4}$$

where for simplicity they have taken $\lambda=(7/12)^{1/2}x$ and they assume that diffusion at the electrode surface is linear. Then in Eq. (1) i_l/i_d is virtually equal to $F(x)$ so Eq. (4) can be written as

$$\log\lambda = -0.1300 + 0.9163\log\frac{i}{i_d-i} \tag{5}$$

Heterogeneous rate constant can be described by

$$K_{fh} = K^\circ_{fh}\exp\left(-\frac{\alpha nFE}{RT}\right) \tag{6}$$

on combining Eqs. (2), (5), and (6) yields

$$E_{d.e.} = \frac{0.05915}{\alpha n}\log\frac{1.349K^\circ_{fh}t^{1/2}}{D^{1/2}} - \frac{0.0542}{\alpha n}\log\frac{i}{i_d-i} \tag{7}$$

which may be written

$$E_{d.e.} = E_{1/2} - \frac{0.0542}{\alpha n}\log\frac{i}{i_d-i} \tag{8}$$

With

$$E_{1/2} = \frac{0.05915}{\alpha n}\log\frac{1.349K^\circ_{fh}t^{1/2}}{D^{1/2}} \tag{9}$$

In these equations both $E_{d.e.}$ and $E_{1/2}$ are referred to N.H.E.

Instead of Eq. (5) we find

$$\log\lambda = 0.0523 + 0.9619\log\frac{i}{i_d-i} \tag{10}$$

On combining Eqs. (2), (6), and (10) we obtain

$$E_{d.e.} = \frac{0.05915}{\alpha n}\log\frac{K^\circ_{fh}t^{1/2}}{1.128\times D^{1/2}} - \frac{0.05690}{\alpha n}\log\frac{i}{i_d-i} \tag{11}$$

which may be written

$$E_{d.e.} = E_{1/2} - \frac{0.05690}{\alpha n}\log\frac{i}{i_d-i} \tag{12}$$

with

$$E_{1/2} = \frac{0.05915}{\alpha n}\log\frac{K^\circ_{fh}t^{1/2}}{1.128\times D^{1/2}} \tag{13}$$

In deriving Eqs. (5) and (10) we have considered that diffusion to the electrode surface is linear, but if we consider spherical diffusion then we have to consider the second factor of Eq. (1) *i.e.* $\xi H_C(x)$. Values of $H_C(x)$ are given in the Koutecký's table and the value of ξ changes with capillary to capillary and also depends on the metal ion, solvent *etc.* In our laboratory[4,5] it has been found that the value of ξ lies between 0.05 to 0.25. Keeping this in view we have taken different values of ξ from 0.0 to 0.3 and calculated the value of $F'(x)$ for different values of ξ. We find that $\log x$ again varies linearly with $\log F'x/\{1-F'(x)\}$

Table 1. Values of ξ, C, and m

ξ	C	m
0.000	0.0523	0.9619
0.025	0.0606	0.9650
0.050	0.0679	0.9646
0.060	0.0711	0.9660
0.070	0.0745	0.9662
0.080	0.0778	0.9664
0.090	0.0815	0.9667
0.100	0.0845	0.9668
0.110	0.0878	0.9669
0.120	0.0912	0.9670
0.125	0.0929	0.9671
0.130	0.0945	0.9672
0.140	0.0979	0.9672
0.150	0.1012	0.9773
0.175	0.1095	0.9674
0.200	0.1179	0.9673
0.225	0.1262	0.9671
0.250	0.1345	0.9667
0.275	0.1430	0.9662
0.300	0.1512	0.9656

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[1] J. Koutecký, *Collect. Czech. Chem. Commun.*, **18**, 597 (1953).

[2] J. Koutecký, and J. Cizek, *ibid.*, **21**, 836 (1956).

[3] L. Meites and Y. Israel, *J. Amer. Chem. Soc.*, **83**, 4903 (1961).

[4] D. S. Jain, Ph. D. Thesis, University of Rajasthan, Jaipur, India (1965).

[5] N. K. Goswami, Ph. D. Thesis, University of Rajasthan, Jaipur, India (1967).

(For all values of ξ)

$$\log\lambda = C + m\log\frac{F'(x)}{1-F'(x)} \tag{14}$$

Different values of C and m at particular value of ξ are given in the Table 1. It is also found that the value of C increases as the value of ξ increases and a linear relation exists between ξ and C which can be represented as

$$C = 0.0523 + 0.3335\xi \tag{15}$$

Value of m also increases with the value of ξ, at lower values of ξ untill 0.1 then onwards becomes constant.

By combining Eqs. (2), (6), and (14) we obtained:

$$E_{\text{d.e.}} = \frac{0.05915}{\alpha n}\log\frac{K^{\circ}_{\text{fh}}t^{1/2}}{(\text{antilog}\, C)D^{1/2}} - \frac{0.05915m}{\alpha n}\log\frac{i}{i_{\text{d}}-i} \tag{16}$$

which may be written

$$E_{\text{d.e.}} = E_{1/2} - \frac{0.05915m}{\alpha n}\log\frac{i}{i_{\text{d}}-i} \tag{17}$$

With

$$E_{1/2} = \frac{0.05915}{\alpha n}\log\frac{K^{\circ}_{\text{fh}}t^{1/2}}{(\text{antilog}\, C)D^{1/2}} \tag{18}$$

In Eqs. (9), (13), and (18) the potentials are referred to normal hydrogen electrode. If the potentials are referred to the standard potential of that couple then the equations will correspond to the standard rate constant.