ON THE DETERMINATION OF E_f° FROM POLAROGRAPHIC DATA

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Received October 16, 1967

(Communicated by Dr. K. S. G. Doss, F.A.SC.)

1. INTRODUCTION

A KNOWLEDGE of the formal potential, E_f°, of a redox system is essential for the evaluation of standard rate constant, k_s, of the electrode process. The direct determination of E_f° is often difficult. Koryta (1962), Matsuda and Ayabe (1956), Tanaka and Tamamushi (1963) and Hale and Parsons (1962) have evolved methods for the calculation of E_f' from a pure cathodic or anodic wave. The quantity E_f' is related to E_f° by the relation

$$E_f' = E_f^\circ - \frac{RT}{nF} \ln \sqrt{\frac{D_O}{D_R}} \qquad (1)$$

where D_O and D_R are the diffusion coefficients of oxidant and reductant and the other terms have their usual significance. If $D_O = D_R$ then $E_f' = E_f^\circ$. In so far the assumption $D_O = D_R$ is valid, these methods lead to the determination of E_f°. In the present communication an attempt is made to compare the three methods.

2. A SURVEY OF THE METHODS

Koryta's method is based on the assumption that even though irreversibility may set in at potentials more negative to E_f°, the wave approximates to a reversible behaviour at potentials positive to E_f°, *i.e.*, at the foot of the wave. Hence the $i - E$ relationship at the foot of the wave may be taken as being given by:

$$E = E_{\frac{1}{2}} - \frac{RT}{nF} \ln \left(\frac{\bar{i}}{\bar{i}_d - \bar{i}}\right) \qquad (2)$$

where $\bar{i}$ and $\bar{i}_d$ represent respectively the mean current and mean diffusion current. E_f' is obtained by plotting E *vs.* log $(\bar{i}/\bar{i}_d - \bar{i})$, drawing tangent,

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with a slope equal to $-2{\cdot}303\,RT/nF$ to the portion of the curve that corresponds to the foot of the wave and taking the potential corresponding to the point of intersection with the potential axis as E_f'. Matsuda and Ayabe's (1956) procedure is similar to that of Koryta.

The method due to Tanaka and Tamamushi (1963) is also based on the assumption that the conditions at the foot of a wave approximates to that of a reversible wave even though the rest of the wave may display an irreversible character. They used the formulation given by Gellings (1962, 1963) and showed that the limiting value of

$$\left[E - \frac{RT}{nF}\, ln\left(\frac{i_d - i}{i}\right)\right]$$

as $i \rightarrow 0$ gives E_f'. The actual method comprises in plotting

$$\left[E - \frac{RT}{nF}\, ln\left(\frac{i_d - i}{i}\right)\right]$$

against $\bar{i}$ and extraploting the curve to $i = 0$ to get E_f'.

Even though the above authors have suggested the use of mean currents for the plots, the methods must be equally valid for maximum instantaneous currents.

The approach of Hale and Parsons (1962) to the problem of determination of E_f° from polarograms is quite different. The current—potential relationship for a pure cathodic wave is given by (Randles, 1959)

$$\frac{i}{i_d} = \frac{F(\chi)}{1 + \exp.\left[\frac{nF(E - E_f')}{RT}\right]} \tag{3}$$

where i and i_d refer, respectively, to the maximum instantaneous current and diffusion current at the end of a drop and the parameter χ is defined by

$$\chi = \sqrt{\frac{12t}{7D_o}}\, k_f\left[1 + \exp.\left(\frac{nF(E - E_f')}{RT}\right)\right] \tag{4}$$

and

$$k_f = k_s \exp.\left[-\frac{\alpha nF(E - E_f')}{RT}\right] \tag{5}$$

where α is the transfer coefficient and k_f is the forward rate constant and t is the drop time. When $E = E_f'$ equation (3) reduces to

$$\frac{i}{i_d} = \frac{F(\chi)}{2}. \tag{6}$$

The problem of finding E_f' therefore simplifies to that of locating the potential at which the condition defined by (6) is satisfied. To do this Hale and Parsons suggested a graphical procedure. Where $k_s \leqslant 5 \times 10^{-4}$ cm.sec.$^{-1}$ equation (3) simplifies to $(i/i_d) = F(\chi)$, thereby permitting the evaluation of χ near the top of the wave with the help of $F(\chi)$ values tabulated by Koutecky (1953). Assuming that α is independent of potential, χ values for the lower portions of the wave is obtained by the extrapolation of E *vs.* log χ plot. Using the values of χ thus obtained the curves log χ *vs.* $\log(i/i_d)$ and $\log(\chi/2)$ *vs.* $\log\left(F(\chi)/2\right)$ are plotted on the same graph. The point of intersection then satisfies the condition expressed in equation (6). The value of E corresponding to the i/i_d at the point of intersection is equal to E_f'.

3. Comparison of the Three Methods

With the help of the polarograms obtained for the reduction of 10^{-3} M Zn^{++} in $0\cdot5$ M $Na_2SO_4 + 0\cdot001$ M H_2SO_4 supporting electrolyte in the presence of varying concentration of *n*-butanol, the E_f' was calculated by the three methods. The results are set in Table I.

Table I

E_f' data for the reduction of Zn^{++} in $0\cdot5$ M $Na_2SO_4 + 0\cdot001$ M H_2SO_4 medium with and without the addition of n-*butanol*

S. No.	Concentration of *n*-butanol added in millimoles per litre	Standard rate constant k_s	E_f' value based on Koryta method	E_f' value based on Tanaka and Tamamushi method	E_f' value based on Hale and Parsons method
1	nil	$5\cdot5\times10^{-4}$ cm. sec.$^{-1}$	$-1\cdot439$ T	$-1\cdot436$ V	$-1\cdot430$ V
2	84	$3\cdot5\times10^{-4}$ cm. sec.$^{-1}$	..	$-1\cdot443$ V	$-1\cdot434$ V
3	252	$0\cdot2\times10^{-4}$ cm. sec.$^{-1}$	..	..	$-1\cdot440$ V

The voltages reported are those measured with Hg/Hg_2SO_4, $0\cdot5$ M Na_2SO_4 reference electrode.

From Table I the following conclusions are evident:

(i) The values given by the three methods agree.

(ii) The addition of *n*-butanol does not change the value of E_f', showing that the additive does not form a complex with Zn^{++}. Incidentally it may be pointed out that this may be employed as a method for finding out the presence of any chemical reaction between the depolariser and the inhibitor.

(iii) Addition of *n*-butanol lowers the value of rate constant, k_s and makes it difficult to evaluate E_f' by the methods of Koryta and Tanaka and Tamamushi.

4. LIMITS OF VALIDITY OF THE THREE METHODS

Tanaka and Tamamushi have mentioned that their method is useful for systems with $k_s \geqslant 10^{-3}$ cm. sec.$^{-1}$ No explicit statement regarding the limit of applicability has been made by Koryta. Hale and Parsons have pointed out that the upper limit for their method is $k_s \leqslant 5 \times 10^{-4}$ cm. sec.$^{-1}$ To find out the range of k_s values within which each method is valid, theoretical polarograms were constructed for the case $D_R = D_O = 10^{-5}$ cm.^{2} sec.$^{-1}$, $\alpha = 0 \cdot 5$, $n = 1$ and $n = 2$, $T = 298°$ K, $t = 4$ secs., $E_f' = 0$ and $k_s = 10^{-2}$, 10^{-3}, 10^{-4} and 10^{-5} cm. sec.$^{-1}$ Using these the

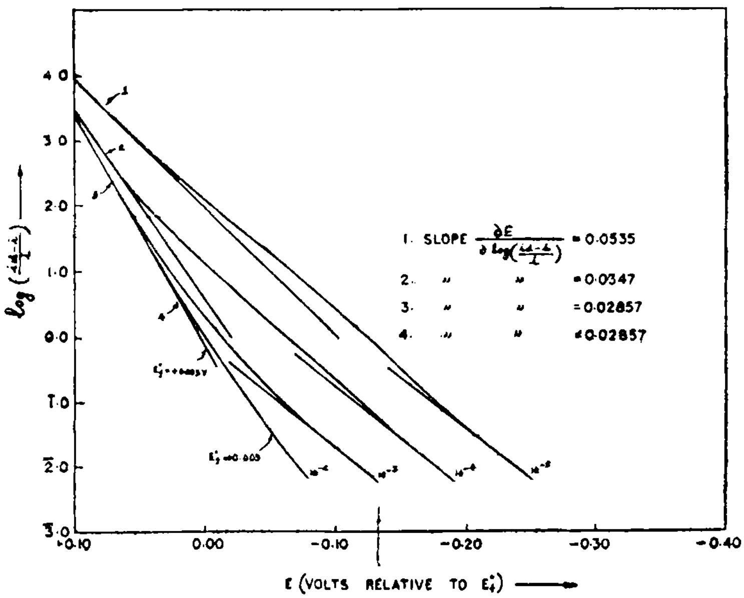

FIG. 1. Koryta method: E *vs.* $\log(i_d - i/i)$ plot for various k_s values. The numbers on the curves denote k_s values in cm. sec.$^{-1}$.

characteristic plots were made. Figs. 1 to 3 show the typical plot for the case $n = 2$.

From Figs. 1 and 2 it is seen that for systems having $k_s < 10^{-3}$ cm. sec.$^{-1}$ the slope of E *vs.* $\log(i_d - i/i)$ significantly departs from the value 0·03 and the Tanaka and Tamamushi plot is asymptotic to the

$$\left[E - \frac{RT}{nF} \ln\left(\frac{i_d - i}{i}\right)\right]$$

axis thereby making extrapolation to $i \to 0$ impossible. Thus the methods of Koryta and Tanaka and Tammaushi are useful for system with $k_s \geqslant 10^{-3}$ cm. sec.$^{-1}$

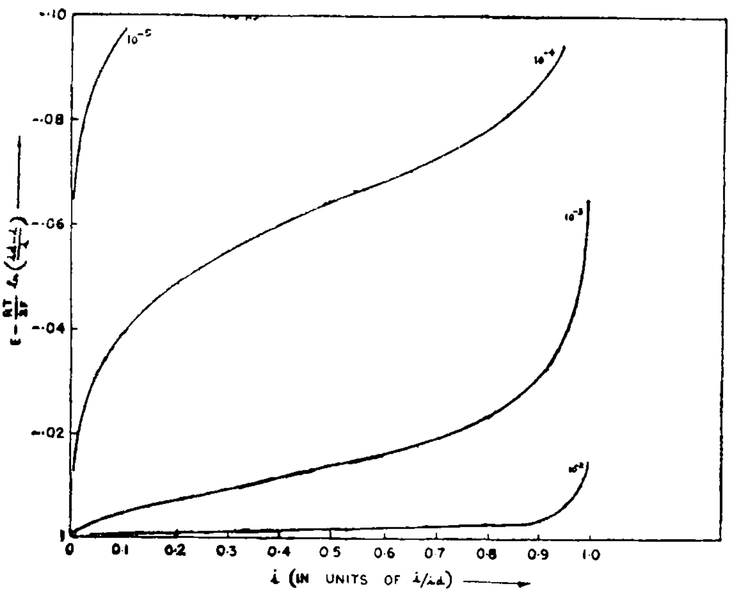

FIG. 2. Tanaka and Tamamushi method: $E - (RT/nF) \ln(i_d - i/i)$ *vs.* i plot for various k_s values. The number on the curves denote k_s values in cm.sec.$^{-1}$.

In the method due to Hale and Parsons (Fig. 3) the point of intersection shifts to lower values of i/i_d as k_s decreases. For a system with $k_s = 10^{-5}$ cm. sec.,$^{-1}$ the i/i_d value at the point of intersection is about 0·01. Determination of i/i_d value less than 0·01 cannot be carried out with accuracy due to practical difficulties. Hence the E_f' of systems having k_s less than 10^{-5} cm.sec.$^{-1}$ cannot be found by applying Hale and Parsons method. There is an upper limit to this method. The assumption that at the top of the wave $i/i_d = F(X)$ is valid to within 5% error in the case of systems with $k_s \leqslant 10^{-3}$ cm. sec.$^{-1}$ Therefore, in the case of systems with k_s greater than 10^{-3} cm. sec.$^{-1}$ it is not possible to determine X from the polarogram and hence the method is not applicable.

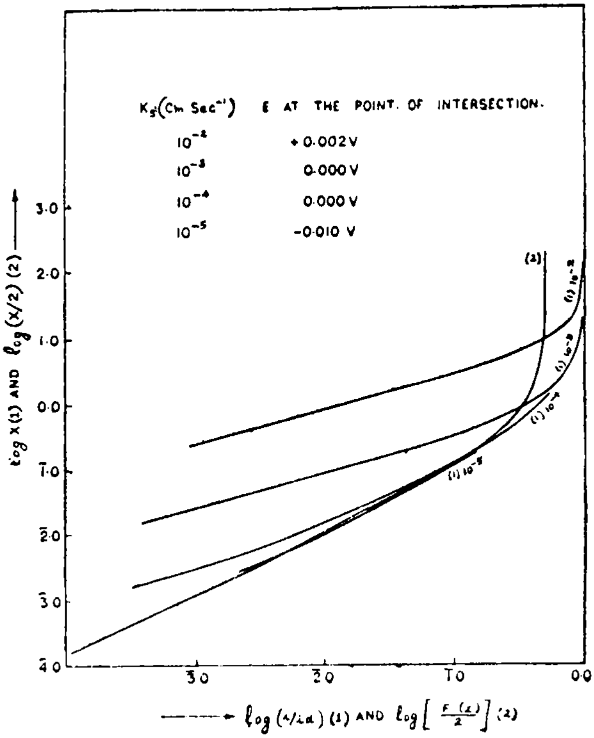

FIG. 3. Hale and Parsons method.

The above limits are applicable to electrode processes invovling one electron too. For the one-electron process the lower limit of k_s value below which the methods fail is higher than that for a two-electron process.

5. CONCLUSIONS

Hale and Parsons method is complementaıy to those of Koryta (1962), Matsuda and Ayabe (1956) and Tanaka and Tamamushi (1963). These methods make it possible to determine E_f', for systems with k_s value from 10^{-5} to ∞. At present there appears to be no method for the determination of E_f' for systems with k_s less than 10^{-5} cm. sec.$^{-1}$, using a purely cathodic and anodic wave. However, E_f' of such totally irreversible systems can be found (Randles, 1962) if it is possible to obtain a compositive wave.

6. Acknowledgements

The authors are grateful to Prof. M. V. C. Sastri for his interest and encouragement. It is a pleasure to acknowledge the stimulating discussion one of us (S.R.R.) had with Dr. S. Satyanarayana, I.I.T., Bombay-76, which was responsible for starting this work. One of us (S.R.R.) is thankful to C.S.I.R. for granting leave of absence.

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