DETERMINATION OF RATE CONSTANTS OF A HOMOGENEOUS OXIDATION-REDUCTION REACTION ASSUMING NON-IDEAL BEHAVIOUR OF THE INDICATOR ELECTRODE*

A. TOCKSTEIN and F. SKOPAL

Department of Physical Chemistry,
Institute of Chemical Technology, 530 00 Pardubice

Received February 1st, 1973

The influence of a nonideal behaviour of the electrode on the dependence of $\tau(1 - n')$ on $\mathfrak{z}$ defined previously[1] was studied and a transformation was proposed to enable its linearization and thus the determination of the homogeneous rate constant of an oxidation-reduction process under consideration. The behaviour of a nonideal electrode was simulated on a computer and the derived theoretical relations were verified on 125 model systems.

In the preceding work[1], we derived theoretical equations and procedures for the determination of the rate constant of a homogeneous oxidation-reduction reaction proceeding in the bulk of a solution on the basis of a complete equation of potential–time curves in the currentless state referred to an ideal electrode (*i.e.*, an electrode on which the rate constants of the electrode reaction are independent of the composition of the reaction mixture). In practice, however, cases are sometimes encountered where one of the reaction components (*e.g.*, a strong oxidation agent such as Ce^{4+} ions, or substances such as nitrogen oxides causing poisoning of the indicator electrode during diazotation) changes the behaviour and properties of the indicator electrode so that existing methods of analysis of the E–t curves cannot be used in the determination of the rate constant.

It is the aim of the present work to generalize the procedures derived previously[1] for the determination of the homogeneous rate constant from a set of E–t curves so that they could be applied to the case of a nonideal electrode.

Nonideal Electrode

We define a nonideal electrode as one on which the rate constants of the electrode process, $\mathscr{R}_i$, and the transfer coefficients, α_i, can change with changing composition of the reaction mixture which influences the properties of the electrode surface (*e.g.*, by the formation or dissolution of oxide films). Every intersection of the line $E =$ $=$ const with individual E–t curves of a family with n' as parameter can therefore

* Part XIV in the series Application of Potential–Time Curves in Reaction Kinetics; Part XIII: This Journal *39*, 1518 (1974).

correspond to different values of $\mathscr{R}_i$ and α_i, which can be accordingly (in the case of a nonideal electrode) considered as functions of n'. It follows that in the equation which describes the dependence of the parameter n' and time t on the line E = const (Eq. ($2b_3$) in ref.[1]) the terms A and D (which were constant for an ideal electrode and for a chosen constant potential, E) must be considered as functions of the parameter n'. It is not possible to conclude directly from the dependence of $t(1 - n')$ on $\ln n'$ found experimentally whether the indicator electrode used in the measurements behaves ideally or not. However, this is possible if the $t(1 - n') - \mathfrak{z}$ dependence is used (for definition of $\mathfrak{z}$ see Eq. ($2e_1$), ref.[1]), especially with such $t(1 - n') - \ln n'$ curves that have an extremum. If the electrode behaves ideally, then the $t(1 - n') - \mathfrak{z}$ dependence has the form of a straight line, where both the descending and rising branches (corresponding to the rising and descending arc of the $t(1 - n') - \ln n'$ curve) fuse together. With a nonideal electrode, a beak-like curve is obtained (Fig. 1) whose rising portion does not coincide with the falling one owing to the variability of the terms A and D with changing n'. The problem is how to determine the rate constant, k_1, of the homogeneous oxidation-reduction reaction from the beak-like curve. Since the dependences of A and D on n' are not known, we shall try to derive them in substance from the deviations between the $t(1 - n') - \mathfrak{z}$ dependences obtained with an ideal and a nonideal electrode.

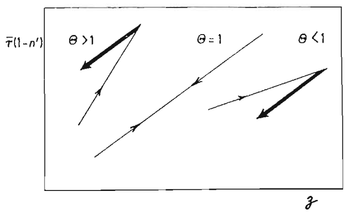


FIG. 1

$\bar{\tau}(1 - n') - \mathfrak{z}$ Curves for a Nonideal and an Ideal Electrode ($\Theta = 1$)

The thick portion of the descending curve has a slope corresponding to the theoretical one.

THEORETICAL

If we plot the quantity $t(1 - n')$ against $\mathfrak{z}$, we transform in this way the dependence

$$ak_1tz_1(1 - n') = \ln \frac{(1 - n')\,n' + D(E, n')\,n'}{A(E, n')\,(1 - n') + D(E, n')\,n'} \qquad (1a_1)$$

on introducing the independent variable

$$\mathfrak{z} = \ln \frac{(1 - n')\,n' + \overline{D}(E)\,n'}{\overline{A}(E)\,(1 - n') + n'\overline{D}(E)}\,, \qquad (1a_2)$$

where the constants $\bar{A}$ and $\bar{D}$ are found from the extremum and zero coordinate according to Eq. $(2c_1)$ or $(2b_3)$ of ref.[1] as in the case of an ideal electrode. The form of this transformed dependence, *i.e.* its deviations from the straight line with a slope $1/ak_1z_1$ valid for an ideal electrode, can be analysed most easily by differentiation. *E.g.*, if a function $y = f(x)$ is to be transformed on replacing the variable x by $g(x)$, then its slope $\mathrm{d}y/\mathrm{d}g(x)$ will be given by

$$\mathrm{d}y/\mathrm{d}g(x) = (\mathrm{d}f(x)/\mathrm{d}x)\, \mathrm{d}x/\mathrm{d}g(x)\,; \tag{1b_1}$$

in our case the slope of the $\bar{\tau}(1 - n') - \mathfrak{z}$ dependence is given by

$$\frac{\mathrm{d}[\bar{\tau}(1 - n')]}{\mathrm{d}\mathfrak{z}} = \frac{[\bar{A}(1 - n') + \bar{D}n']\,(1 - n' + \bar{D})}{\bar{A}(1 - n')^2 - \bar{D}n'^2 + \bar{A}\bar{D}}\,.$$

$$\cdot\frac{A(1 - n')^2 - Dn'^2 + AD + (1 - n')\,[(\mathrm{d}D/\mathrm{d}\ln n')\,(A - n') - (\mathrm{d}A/\mathrm{d}\ln n')\,(1 - n' + D)]}{[A(1 - n') + Dn']\,(1 - n' + D)} \tag{1b_2}$$

whence it is seen that

$$\lim_{n' \to 1} \frac{\mathrm{d}\bar{\tau}(1 - n')}{\mathrm{d}\mathfrak{z}} = \frac{A - 1}{\bar{A} - 1}\frac{\bar{D}}{D}\,, \quad \lim_{n' \to 0} \frac{\mathrm{d}\tau(1 - n')}{\mathrm{d}\mathfrak{z}} = 1 - \frac{\mathrm{d}\ln[A/(1 + D)]}{\mathrm{d}\ln n'} \tag{1c_{1,2}}$$

so that the slope at the end of the descending portion of the beak-shaped $t(1 - n') - \mathfrak{z}$ curve is given by Eq. $(1c_1)$, whereas at the beginning of the rising portion by $(1c_2)$.

With families of E–t curves well developed in the region below the equivalence point, the dependence of $t(1 - n')$ on $\ln n'$ with an extremum has a value of the parameter D practically equal to $\exp[(E - E_{02})\, z_2 F/RT]$, although the parameter A changes with n' since the term $A \exp[(E_{eq} - E)(z_1 + z_2)\, F/RT]$ does not exceed several hundredths. Consequently, D can be considered independent of n', and in Eq. $(1c_1)$ it is possible to set $D \approx \bar{D}$. Since furthermore $A(n') \ll 1$, the slope of the final portion* of the $t(1 - n') - \mathfrak{z}$ curve is the same as with an ideal electrode. The dependence of the parameter A on n', important mainly for the rising portion of the $t(1 - n') - \mathfrak{z}$ curve, can be determined for a nonideal electrode as a first approximation from the position of the extremum and width of the beak: For the ratio, Θ, of the slopes of the final descending and initial rising portion of the beak-like curve we have according to $(1c_{1,2})$ (since $D + 1 \approx \text{const}$)

$$\Theta = 1 - d\ln A/\mathrm{d}\ln n'\,, \tag{1d_1}$$

* We shall denote as final that part of the $t(1 - n') - \mathfrak{z}$ curve which corresponds to $n' > n'_{ex}$. The condition $n' < n'_{ex}$ corresponds to the initial portion, which is rising.

representing a differential equation for $A(n')$ at the beginning of the rising portion of the $t(1 - n') - \mathfrak{z}$ curve. On integrating we obtain

$$(1 - \Theta) \ln n' = \ln A + \text{const} \quad \text{or} \quad A = \beta n'^{(1-\Theta)} . \qquad (1d_2)$$

In practice, the whole rising portion of the $t(1 - n') - \mathfrak{z}$ curve has often the same slope – it is practically linear – so that Eq. $(1d_1)$ and hence also $(1d_2)$ can be used in the whole region of the rising portion of the beak-like curve.

Thus, the A–n' dependence is defined (D is approximately independent of n') and we can rewrite Eq. $(1a_1)$ in the form

$$a_1 k_1 t z_1 (1 - n') = \ln \frac{(1 - n' + D)\, n'}{n'^{(1-\Theta)}(1 - n')\, \beta/D + n'} - \ln D , \qquad (1d_3)$$

where β/D is determined from the position of the extremum on the $t(1 - n') - \ln n'$ curve:

$$\beta/D = (n'_{\text{ex}})^{(1+\Theta)}/\{(1 - n'_{\text{ex}})^2\, \Theta + D\,.\,[\Theta + n'_{\text{ex}}(1 - \Theta)]\} . \qquad (1d_4)$$

Linearization of the $t(1 - n') - \mathfrak{z}$ Curve for Nonideal Electrode

Provided that the quantity Θ was determined from the ratio of the slopes of the descending and rising portions of the $t(1 - n') - \mathfrak{z}$ curve, the value of n'_{ex} from the dependence of $t(1 - n')$ on $\ln n'$, and the ratio of β/D from Eq. $(1d_4)$, the whole beak-like curve can be linearized by plotting $t(1 - n')$ against the quantity

$$\mathfrak{z}(\text{nonid}) \equiv \ln \frac{(1 - n')\, n'}{[n'^{(1+\Theta)}_{\text{ex}}/(1 - n'_{\text{ex}})^2\, \Theta]_{\text{ex}}\, (1 - n')\, n'^{(1-\Theta)} + n'} . \qquad (2a_1)$$

As a first approximation, we neglect D against $1 - n'$ in the numerator of Eq. $(4d_3)$ and $D[\Theta + n'_{\text{ex}}(1 - \Theta)]$ against $(1 - n'_{\text{ex}})^2\, \Theta$ in the denominator of $(1d_4)$.

Note: The dependence of A on n', Eq. $(1d_2)$, comprises also the case of an ideal electrode, namely for $\Theta = 1$. The course of the beak-like $t(1 - n') - \mathfrak{z}$ curve for typical values of Θ is shown schematically in Fig. 1.

Simulation of Nonideal Electrode Behaviour

To check the suitability of the somewhat approximative relations for linearization of the $t(1 - n') - \mathfrak{z}$ curves for nonideal electrodes, a nonideal electrode was simulated by assuming a second-order reduction-oxidation homogeneous reaction with rate constants, $\mathscr{R}_1$ and $\mathscr{R}_2$, of the electrode processes depending on the parameter n' as follows:

$$\mathscr{R}_1 = \mathscr{R}_1 n' + (1 - n')\,\mathscr{R}_1'', \quad \mathscr{R}_2 = \mathscr{R}_2 n' + (1 - n')\,\mathscr{R}_2''. \tag{3}$$

This means that the rate constants change continuously from their initial values $\mathscr{R}_1''$ and $\mathscr{R}_2''$ (before the beginning of the measurement) with increasing n' by increasing additions of the Ox_2 form until they attain their final values, $\mathscr{R}_1'$ and $\mathscr{R}_2'$, for $n' = 1$ (at the equivalence).

On the basis of this model concept, sets of E–t curves were calculated from Eq. (*1a*) in ref.[1] for $E_{01} = 0$, $E_{02} = 400$ mV, $\lambda_i = 0.01$ and for combinations of $\mathscr{R}_i', \mathscr{R}_i''$ and α_i values given in Table I. The obtained families of theoretical curves were intersected with straight lines, $E = 50$, 100, 200 and 300 mV, the dependences of $\tau(1 - n')$ on $\log n'$ plotted and linearized by replacing the variable $\log n'$ by $\bar{\mathfrak{z}}$ ($\bar{\mathfrak{z}} = \mathfrak{z} \log e$ when decadic logarithms are used). Further the dependences of A on n' were calculated for the model Eq. (*3*) for the chosen potentials and combinations of $\mathscr{R}_i', \mathscr{R}_i''$ and α_i and plotted in bilogarithmic coordinates. The obtained curves are of the type shown in Fig. 2.

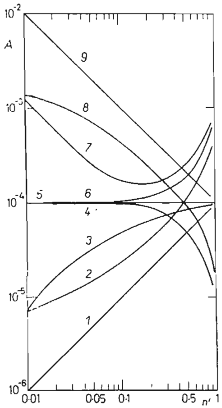


FIG. 2

Various Types of A–n' Dependences

Mapping of the set of all combinations of $\mathscr{R}$ and α on the shown curve types is not unique; these curves can correspond, *e.g.*, to the combinations denoted in Table I by dashed lines with the corresponding curve numbers. The curves are shifted along the ordinate to save space.

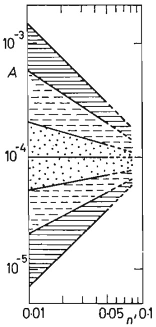


FIG. 3

Slope Field of the log A–log n' Dependences

Shown are the courses of secants of the log A–log n' curves passing through points $n' = 0.01$ and $n' = 0.05$. These courses correspond (beginning from the bottom) to the following values of Θ for the beak-like $\bar{\tau}(1 - n') - \mathfrak{z}$ curves: 0, 0·64, 0·85, 1·0, 1·3, 1·7, and 2·0.

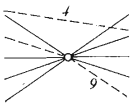
The following conclusions followed from the geometric form of these dependences by comparison with the $\bar{\tau}(1 - n') - \bar{\mathfrak{z}}$ curves: A characteristic beak-like curve was formed at such combinations of $\mathscr{R}'_i$, $\mathscr{R}''_i$ and α_i for which the slope of the log A – log n' curve between the points $n' = 0.01$ and 0.05 was either larger than 0·36 (*i.e.* for $\Theta < 0.64$ according to Eq. $(1d_1)$) or smaller than $-0.7(\Theta > 1.7)$ – *cf.* shaded area in Fig. 3. For the secant slope equal to one, only the descending portion of the $\bar{\tau}(1 - n')$ – log n' dependence was obtained. As long as the slope of the secant

TABLE I

Combinations of Parameters $\mathscr{R}$ and α (For the meaning of dashed lines see Text at Fig. 2)

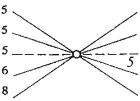
$\alpha_1 = 0.01$, $\alpha_2 = 0.01$

$\mathscr{R}'_1$	$\mathscr{R}''_1$	$\mathscr{R}'_2$	$\mathscr{R}''_2$
10^{-10}	10^{-7}	10^{-4}	1
10^{-8}	10^{-7}	10^{-1}	1
10^{-7}	10^{-7}	1	1
10^{-7}	10^{-8}	1	10^{-1}
10^{-7}	10^{-10}	1	10^{-4}



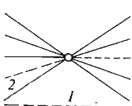
$\alpha_1 = 0.99$, $\alpha_2 = 0.99$

$\mathscr{R}'_1$	$\mathscr{R}''_1$	$\mathscr{R}'_2$	$\mathscr{R}''_2$
10^{-8}	10^{-5}	10^{-4}	1
10^{-6}	10^{-5}	10^{-1}	1
10^{-5}	10^{-5}	1	1
10^{-5}	10^{-6}	1	10^{-1}
10^{-5}	10^{-8}	1	10^{-4}



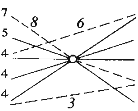
$\alpha_1 = 0.01$, $\alpha_2 = 0.99$

$\mathscr{R}'_1$	$\mathscr{R}''_1$	$\mathscr{R}'_1$	$\mathscr{R}''_2$
10^{-10}	10^{-7}	10^{-4}	1
10^{-8}	10^{-7}	10^{-1}	1
10^{-7}	10^{-7}	1	1
10^{-7}	10^{-8}	1	10^{-1}
10^{-7}	10^{-10}	1	10^{-4}



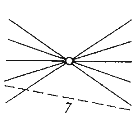
$\alpha_1 = 0.99$, $\alpha_2 = 0.01$

$\mathscr{R}'_1$	$\mathscr{R}''_1$	$\mathscr{R}'_2$	$\mathscr{R}''_2$
10^{-7}	10^{-7}	10^{-4}	1
10^{-5}	10^{-5}	10^{-1}	1
10^{-4}	10^{-4}	1	1
10^{-4}	10^{-4}	1	10^{-1}
10^{-4}	10^{-4}	1	10^{-4}



$\alpha_1 = 0.5$, $\alpha_2 = 0.5$

$\mathscr{R}'_1$	$\mathscr{R}''_1$	$\mathscr{R}'_2$	$\mathscr{R}''_2$
10^{-8}	10^{-5}	10^{-4}	1
10^{-6}	10^{-5}	10^{-1}	1
10^{-5}	10^{-5}	1	1
10^{-5}	10^{-6}	1	10^{-1}
10^{-5}	10^{-8}	1	10^{-4}



between the points $n' = 0{\cdot}01$ and $0{\cdot}05$ was in the interval from $-0{\cdot}3$ to $-0{\cdot}7$ $(1{\cdot}3 \leqq \Theta \leqq 1{\cdot}7)$ or from $0{\cdot}15$ to $0{\cdot}36$ $(0{\cdot}64 \leqq \Theta \leqq 0{\cdot}85)$, the beak-like curves were less well-developed (*cf.* dashed area in Fig. 3). If the slope was in the interval from $-0{\cdot}3$ to $0{\cdot}15$ $(0{\cdot}85 \leqq \Theta \leqq 1{\cdot}3)$ (*cf.* dotted area in Fig. 3), the dependence of $\bar{\tau}(1 - n')$ on $\bar{\mathfrak{z}}$ was practically always linear with a slope other than would correspond to the rate constant (up to 100% deviation).

It follows that the slope of the secant of the $\log A - \log n'$ curve for small values of n' (*e.g.* $0{\cdot}01 \leqq n' \leqq 0{\cdot}05$) can serve as a criterion for the formation of a beak-like $\bar{\tau}(1 - n') - \bar{\mathfrak{z}}$ curve. The remaining course of this dependence (*i.e.* for $n' > 0{\cdot}05$) is essentially without significance. Hence, if the values of $\mathscr{R}_i$ change with n' in any way (generally differing from Eq. (*3*)), provided that the slope of the $\log A - \log n'$ dependence remains in the range corresponding to the formation of well developed beak-like $\bar{\tau}(1 - n') - \bar{\mathfrak{z}}$ curves (Fig. 3), the value of Θ can be reliably determined from the width of the beak and the curve can be linearized by plotting $\bar{\tau}(1 - n')$ against $\mathfrak{z}$(nonid) according to Eq. (*2a*$_1$). (If decadic logarithms are used, $\mathfrak{z}$(nonid) is replaced by $\bar{\mathfrak{z}}$(nonid) = $\mathfrak{z}$(nonid) log e.) The slope of this straight line gives the rate constant of the reduction-oxidation reaction followed with a nonideal electrode. The model E–$\bar{\tau}$ curves for a nonideal electrode calculated for comparison substantiated the theoretical prediction that the slope of the descending part of the beak-like curve (in that portion which is practically linear) is equal to the theoretical slope

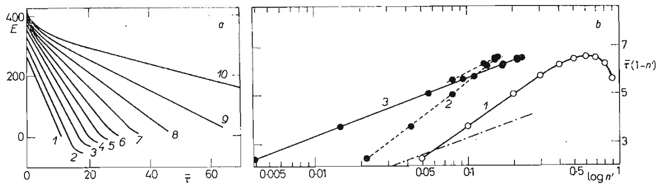


FIG. 4

Theoretical Set of $E - \bar{\tau}$ Curves for Nonideal Electrode (*a*) and Linearization of the Beak-Like $\bar{\tau}(1 - n') - \bar{\mathfrak{z}}$ Curve (*b*)

The curve set was calculated on the basis of the model Eq. (*3*) for the following parameter values: $\mathscr{R}'_1 = 10^{-8}$, $\mathscr{R}''_1 = 10^{-7}$, $\mathscr{R}'_2 = 1$, $\mathscr{R}''_2 = 10^{-4}$, $\alpha_1 = \alpha_2 = 0{\cdot}01$. The value of n' was changed from 0·05 for curve *1* to 0·1 and further at 0·1 steps up to 0·9 for curve *10*. The dependence of $\bar{\tau}(1 - n')$ on $\log n'$ (curve *1*) was plotted for the intersecting line $E = 200$ mV, the extremum is at $n' = 0{\cdot}6$. The corresponding dependence of $\bar{\tau}(1 - n')$ on $\bar{\mathfrak{z}}$ (curve *2*) shows a beak; its linearization using the dependence of $\bar{\tau}(1 - n')$ on $\bar{\mathfrak{z}}$ (nonid) leads to curve *3* whose slope is in accord with the theoretical denoted by broken line. The logarithmic scale on the abscissa is the same for $\log n'$, $\bar{\mathfrak{z}}$ and $\bar{\mathfrak{z}}$ (nonid). The ratio of the slopes of both branches $\Theta = 2$.

corresponding to chosen values of the rate constant and concentration, *i.e.* $1/\log e$ if the $\bar{\tau}(1 - n') - \bar{\mathfrak{z}}$ coordinates are used.

If a characteristic beak-like $\tau(1 - n') - \mathfrak{z}$ curve is not obtained, such a curve can simulate a straight line and thus an ideal electrode behaviour. Its slope would then lead to an increased value of the rate constant. Since the parameter A for a nonideal electrode depends on n' and E, it is possible to obtain different $\bar{\tau}(1 - n') - \mathfrak{z}$ curves by choosing different $E =$ const lines. If these curves simulate straight lines, their slopes are different. With an ideal electrode, all $\bar{\tau}(1 - n') - \mathfrak{z}$ curves would be straight lines with an identical slope. If the pseudo-linear $t(1 - n')$ $- \mathfrak{z}$ dependences are met in practice, it is best to choose other $E =$ const lines to obtain a well-developed beak.

Of the 125 theoretical sets of E–t curves calculated on the basis of the model Eq. (*3*), one was chosen for illustration, transformed in $\bar{\tau}(1 - n') - \log n'$ coordinates and linearized with the aid of the quantity $\bar{\mathfrak{z}}$(nonid) (Fig. 4). It is seen that the proposed method indeed gives correct values of the rate constant of a homogeneous oxidation-reduction reaction with the use of a nonideal electrode. The method proved well in practical measurements as will be shown in subsequent communications.

REFERENCES

1. Tockstein A., Skopal F.: This Journal *39*, 1518 (1974).

Translated by K. Micka.