A NEW METHOD OF ANALYSIS OF POLAROGRAPHIC WAVES

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A method of analysis of polarographic waves of simple electrode processes is proposed. The quasi-reversible half-wave potential, $E_{1/2}^r$, is involved in the determination of thermodynamic and kinetic parameters of electrode processes. This potential is determined very easily and with great precision. In order to facilitate the use of the method proposed, we have developed a computer program for Windows.

Keywords: Quasi-reversible wave; Polarography; Electrochemistry; Kinetics; Thermodynamics; Mercury electrodes; Charge transfer coefficient; Standard rate constant; Half-wave potential.

Polarography is one of the most widely used electrochemical techniques for both thermodynamic and kinetic studies and especially for the determination of coordination equilibria. In general, its application is very straightforward and reliable in those studies in which reduction at the dropping mercury electrode (DME) proceeds as a reversible, ($k^o > 1 \times 10^{-2}$ cm/s) or irreversible process ($k^o < 5 \times 10^{-4}$ cm/s). For the extraordinarily frequent cases in which the reduction takes place as a quasi-reversible process, $5 \times 10^{-4} < k^o < 1 \times 10^{-2}$ cm/s, the determination is more complicated and less accurate. In the present work we report on a new method for the analysis of polarographic waves (and for which have developed a computer program for Windows) that has been verified experimentally by studying reduction of the Zn^{2+} ion at ionic strength of 1 M $NaClO_4$ and at 25 °C.

THEORY

The analysis of polarographic waves has traditionally been made by logarithmic analysis of the function $[(i_d - i)/i]$ *vs* E^{1-5}. For over 25 years, the analysis of quasi-reversible polarographic waves has been carried out by the

graphical method proposed by Ruzić and co-workers[6]. It is based on the equation

$$\frac{i_d - i}{i} = e^{\frac{nF}{RT}\left(E - E_{1/2}^r\right)} + e^{\frac{\alpha nF}{RT}\left(E - E_{1/2}^i\right)},$$ (1)

derived from that obtained by Matsuda and Ayabe[7–9].

Our method is based on the determination of the quasi-reversible half-wave potential, $E_{1/2}^c$. By definition, we thus named the potential at which the relation $i = i_d/2$ is fulfilled. Its value can be readily obtained from the point at which the plot of the function log $[(i_d - i)/i]$ *vs* E intersects the axis of the abscissae, since at that potential the value of this function is zero. In order to achieve maximum precision, we resorted to polynomial adjustment

$$\ln [(i_d - i)/i] = A + BE + CE^2 + ... + ZE^n$$ (2)

finding the potential $E_{1/2}^c$ when

$$0 = A + B(E_{1/2}^c) + C(E_{1/2}^c)^2 + ... + Z(E_{1/2}^c)^n .$$ (3)

In order to relate this potential to Eq. (*1*), we multiply the two terms on the second right-hand side in order by $e^{\frac{nF}{RT}\left(E_{1/2}^r - E_{1/2}^c\right)}$ and $e^{\frac{\alpha nF}{RT}\left(E_{1/2}^c - E_{1/2}^c\right)}$:

$$\frac{i_d - i}{i} = e^{\frac{nF}{RT}\left(E - E_{1/2}^r\right)} e^{\frac{nF}{RT}\left(E_{1/2}^c - E_{1/2}^c\right)} + e^{\frac{\alpha nF}{RT}\left(E - E_{1/2}^i\right)} e^{\frac{\alpha nF}{RT}\left(E_{1/2}^c - E_{1/2}^c\right)},$$ (4)

or use

$$\varphi_{(i)} = R\, e^{\frac{nF}{RT}\left(E - E_{1/2}^c\right)} + I\, e^{\frac{\alpha nF}{RT}\left(E - E_{1/2}^c\right)},$$ (5)

where

$$\varphi_{(i)} = \frac{i_d - i}{i}$$ (6)

$$R = e^{\frac{nF}{RT}\left(E_{1/2}^c - E_{1/2}^r\right)}$$ (7)

$$I = e^{\frac{\alpha nF}{RT}\left(E_{1/2}^c - E_{1/2}^i\right)}. \tag{8}$$

R and *I* are constant for a certain polarogram since the parameters on which they depend are likewise constant.

Particularizing Eq. (*5*) for the potential $E_{1/2}^c$, in which $i = i_d/2$, we get

$$R + I = 1. \tag{9}$$

Multiplying Eq. (*5*) by $e^{-\frac{nF}{RT}\left(E - E_{1/2}^c\right)}$, one finally arrives at

$$\Omega_A = R + I\,\Omega_B\,, \tag{10}$$

where

$$\Omega_A = \varphi(i)\, e^{-\frac{nF}{RT}\left(E - E_{1/2}^c\right)} \tag{11}$$

$$\Omega_B = e^{\frac{(\alpha-1)nF}{RT}\left(E - E_{1/2}^c\right)}. \tag{12}$$

Ω_A is known for each pair (*i*, *E*) of the polarogram under study, while Ω_B is a function moreover of the charge transfer coefficient, which is a priori not known. By means of this mathematical treatment the successful transformation of the Ružić equation (*1*) into Eq. (*10*) was achieved, the latter presenting only two unknown parameters to be determined: α, and *R* or *I* (since, as already shown, $R + I = 1$), and with the added advantage that the analysis of Eq. (*10*) is based upon the potential $E_{1/2}^c$ that can be calculated very easily and accurately.

Determination of the Parameters α, *R, I,* $E_{1/2}^r$, $E_{1/2}^i$ *and* k^o

In accordance with Eq. (*10*), if the value of α were known, it is evident that a plot of Ω_A *vs* Ω_B would give a straight line with intercept *R* and slope *I*, and from the expression of parameters *R* and *I*, the reversible and irreversible half-wave potentials would be obtained. Although the value of the charge transfer coefficient is not known, we know that it ranges between 0 and 1. Thus, if the computer program considers values of α in the given interval in increments of 0.0001 units and for each one of them it carries out

the linear fitting of Ω_A *vs* Ω_B, with statistic weight, the true value of α will evidently be that whose correlation coefficient is closest to one. The goodness of the obtained value of α and that of the analysis of the wave must be verified by checking the convergence of the correlation coefficient and by a good linearity of the plot of Ω_A *vs* Ω_B; also, Eq. (*9*) must be fulfilled. If small experimental errors in the wave give anomalies in the convergence, the program considers the option of determining α by successive approximations. In Fig. 1, the above is illustrated for a simulated wave with $\alpha = 0.35$. The perfect linearity for the said transfer coefficient contrasts with the curves observed for the rest of the values of α considered. The linear fit of the curves is drawn by the dashed line.

At the end of the process of iteration, α, R and I will be obtained, and the use of Eqs (*7*) and (*8*) will allow to calculate the value of potentials $E_{1/2}^r$ and $E_{1/2}^i$, respectively.

The value of the standard rate constant can be easily obtained from the equation

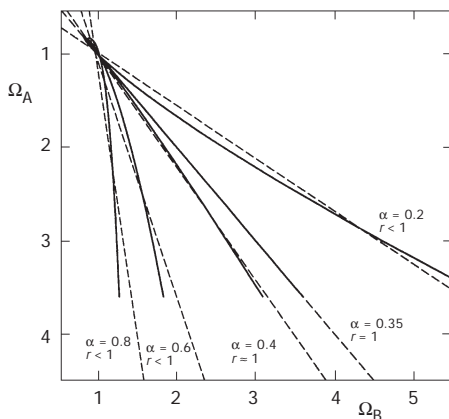$$E_{1/2}^i = E^o + \frac{RT}{\alpha nF} \ln \left\{ 1.35 \frac{k^o}{\sqrt{D_o}} \tau^{1/2} \right\}. \tag{13}$$

Fig. 1

Analysis by linear fitting of the equation $\Omega_A = R + I\Omega_B$, using different values of the α coefficient: 0.2, 0.4, 0.6, and 0.8, for the study of a simulated process with α coefficient equal to 0.35

EXPERIMENTAL

The TAST polarographic curves were obtained with a PDC1212 potentiostatic system (INELECSA). An Ag|AgCl|NaCl(sat.), Metrohm EA427 electrode and a platinum electrode were employed as the reference and auxiliary electrodes, respectively. The temperature was always 25 ± 0.05 °C and the drop time was variable between 0.3 and 4 s. The ionic strength was maintained constant at 1.0 M by addition of sodium perchlorate. pH of the solutions was 3.0 and was measured with a Radiometer digital pH-meter (model pHM84) and a GK240lC combined electrode. The concentration of Zn^{2+} was 2.14×10^{-4} M. Zinc nitrate was Merck product of p.a. quality, as well as sodium hydroxide and perchloric acid used to adjust the pH.

We have recorded 2 polarograms for each of the nine drop life-times used. All the waves exhibit a quasi-reversible behaviour. Figure 2 shows the dependence log $[(i_d - i)/i]$ *vs* E.

RESULTS AND DISCUSSION

Table I shows the different parameters obtained using the Ružić method (computer software TTORL, INELECSA) and the new method proposed.

Reversible Half-Wave Potential, $E_{1/2}^{r}$

The reversible half-wave potential is independent of the drop life-time used for the Zn(II) solution. As a consequence, the mean of all the values will allow us to verify the precision with which the said magnitude is measured by both methods. It is obtained
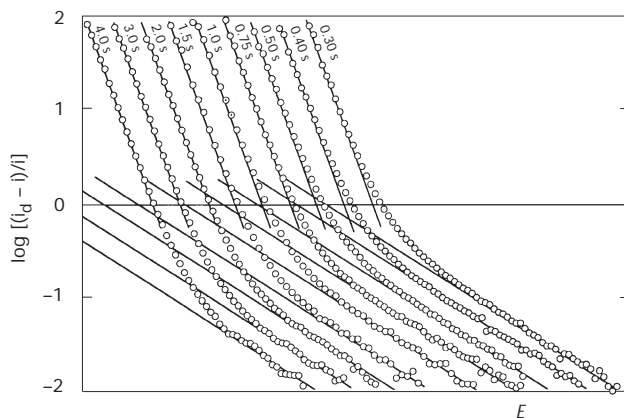

F<small>IG.</small> 2
Tomeš plot for each drop time-life ($C_{Zn^{2+}} = 2.14 \times 10^{-4}$ M; $I = 1.0$ M (NaClO$_4$); $T = 25$ °C; pH 3.0; $\tau = 0.30, 0.40, 0.50, 0.75, 1.0, 1.5, 2.0, 3.0,$ and 4.0 s)

TABLE I
Parameters obtained by the analysis of the quasi-reversible waves of the system: $C_{Zn^{2+}} = 2.14 \times 10^{-4}$ M, I = 1.0 M (NaClO$_4$), T = 25 °C, pH 3.0

τ, s	$-E^r_{1/2}$, mV		$-E^I_{1/2}$, mV		α		$k^o \times 10^3$, cm/s		%R/%I/%(R + I)
	Rz[a]	N[b]	Rz	N	Rz	N	Rz	N	N
0.30	962.2	962.3	928.8	933.0	0.22	0.23	6.48	6.20	49.6/50.4/100.0
	961.9	962.1	934.7	933.8	0.24	0.24	5.85	6.28	50.5/50.0/100.5
0.40	961.7	962.3	928.1	926.5	0.24	0.24	5.68	6.23	54.8/44.3/99.1
	962.0	962.6	921.1	926.9	0.22	0.23	6.40	5.99	55.1/46.0/101.1
0.50	963.0	962.9	902.7	920.1	0.20	0.24	7.84	6.28	58.4/39.5/97.9
	962.0	962.2	920.4	918.9	0.24	0.24	5.79	6.42	59.0/39.2/98.2
0.75	962.1	962.8	906.9	908.0	0.23	0.23	5.96	6.13	65.5/34.0/99.5
	962.5	962.7	900.0	906.7	0.22	0.23	6.71	6.28	65.3/33.3/98.6
1.0	962.5	962.9	902.6	901.3	0.24	0.23	5.56	5.99	70.6/30.6/101.2
	962.5	963.0	890.0	894.7	0.20	0.23	6.89	6.74	72.3/27.3/99.6
1.5	962.7	962.9	887.8	879.4	0.23	0.23	5.85	7.24	76.5/21.1/97.6
	962.9	962.7	881.0	884.4	0.21	0.22	6.57	6.20	76.1/24.0/100.1
2.0	963.5	962.9	847.3	873.2	0.18	0.21	10.1	6.04	79.2/22.0/101.2
	963.1	962.0	867.6	879.8	0.21	0.23	7.15	6.22	79.2/21.8/101.1
3.0	963.0	963.1	875.1	876.7	0.24	0.23	5.14	6.43	80.0/16.9/96.9
	962.8	962.4	867.7	866.6	0.24	0.24	5.83	5.77	83.0/19.3/102.3
4.0	962.7	962.3	860.2	859.0	0.23	0.23	5.74	6.38	84.8/15.2/100.0
	963.0	962.2	836.1	857.4	0.20	0.23	8.68	6.57	84.0/14.7/98.7

[a] Ruzić method; [b] new method.

$$(E_{1/2}^r)_{Rz} = -962.5 \pm 0.10 \text{ mV} \qquad (E_{1/2}^r)_N = -962.6 \pm 0.07 \text{ mV}.$$

As can be observed, the half-wave potential results coincide extraordinarily, the new method possesses a slightly higher degree of accuracy.

Charge Transfer Coefficient, α

An examination of Table I confirms the good constancy of the values of α, obtained by both methods. They have been plotted in Fig. 3, where the greater precision of the new method in the calculation of α can be clearly observed. This precision is shown in the mean values obtained for α:

$$(\alpha)_{Rz} = 0.22 \pm 0.004 \qquad (\alpha)_N = 0.23 \pm 0.002 .$$

Irreversible Half-Wave Potential, $E_{1/2}^i$

As is already known, the irreversible half-wave potential depend on the drop life-time and its determination is, in general, rather more imprecise
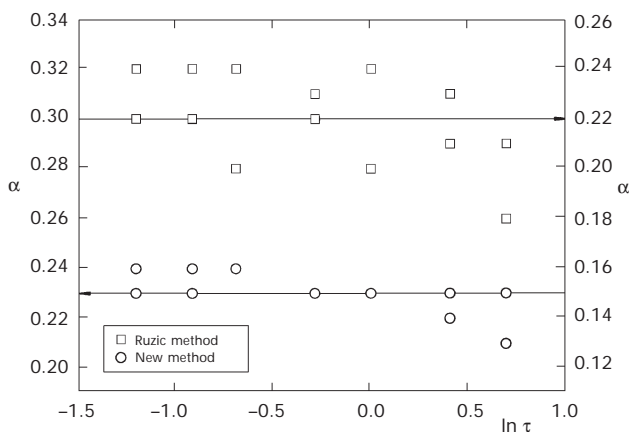

FIG. 3

Plot of the charge transfer coefficient *vs* ln τ, by the new method (○) and the Ružić method (□) ($C_{Zn^{2+}} = 2.14 \times 10^{-4}$ M; $I = 1.0$ M (NaClO$_4$); $T = 25$ °C; pH 3.0; $\tau = 0.30, 0.40, 0.50, 0.75, 1.0, 1.5, 2.0, 3.0,$ and 4.0 s)

than that of reversible half-wave potential. These facts can be clearly verified in Table I. In Fig. 4, the potentials have been plotted against $RT \ln \tau/\alpha nF$, in both cases obtaining a good linear dependence, predicted by Eq. (*13*). The slope determined is 0.51 for the two straight lines, very close to the
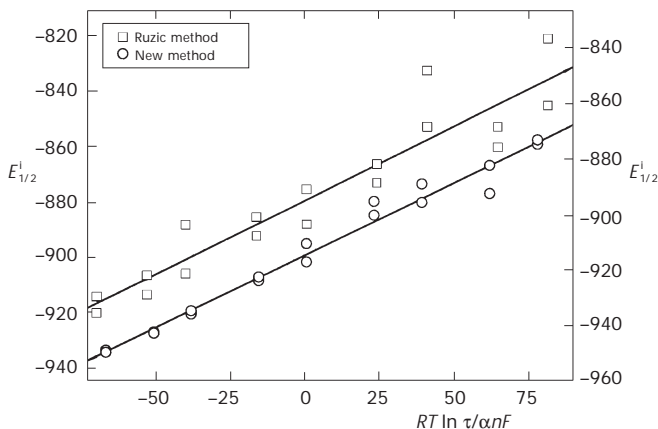

Fɪɢ. 4
Plot of the irreversible half-wave potential *vs* $RT \ln \tau/\alpha nF$, by the new method (○) and the Ruzić method (□) ($C_{Zn^{2+}} = 2.14 \times 10^{-4}$ ᴍ; $I = 1.0$ ᴍ (NaClO$_4$); $T = 25$ °C; pH 3.0; $\tau = 0.30, 0.40, 0.50, 0.75, 1.0, 1.5, 2.0, 3.0,$ and 4.0 s)
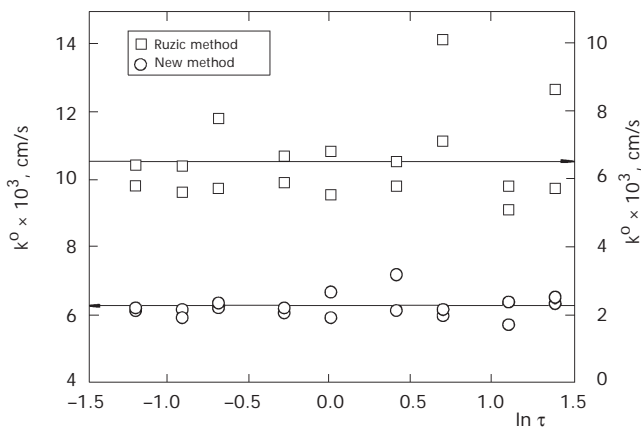

Fɪɢ. 5
Plot of the standard rate constant *vs* $\ln \tau$, by the new method (○) and the Ruzić method (□) ($C_{Zn^{2+}} = 2.14 \times 10^{-4}$ ᴍ; $I = 1.0$ ᴍ (NaClO$_4$); $T = 25$ °C; pH 3.0; $\tau = 0.30, 0.40, 0.50, 0.75, 1.0, 1.5, 2.0, 3.0,$ and 4.0 s)

theoretical value of 0.50. The greater precision of the values of $E_{1/2}^i$ determined by our method can likewise be concluded.

Standard Rate Constant, k^o

The acceptable coincidence can be verified in Table I between the values of the rate constants determined by both methods. As was concluded in the determination of the half-wave potentials and α, the precision of the rate constant values (Fig. 5) is markedly better in the method proposed by us:

$$(k^o)_{Rz} = (6.57 \pm 1.24) \times 10^{-3} \text{ cm/s} \qquad (k^o)_N = (6.30 \pm 0.32) \times 10^{-3} \text{ cm/s} .$$

The values obtained are in good agreement with reported values by other authors[10–14] although higher than the typical data obtained in the same experimental conditions: $k^o \cong 3.5 \times 10^{-3}$ cm/s.

SYMBOLS

D_o	diffusion coefficient of oxidised species
E^o	standard redox potential
$E_{1/2}^c$	quasi-reversible half-wave potential
$E_{1/2}^i$	irreversible half-wave potential
$E_{1/2}^r$	reversible half-wave potential
F	Faraday constant
i	instantaneous dc polarographic current at end of drop life
i_d	instantaneous dc polarographic diffusion current at end of drop life
k^o	standard rate constant
n	total number of electrons transferred in the electrochemical reaction
R	gas constant
T	absolute temperature
α	charge transfer coefficient
τ	drop life-time

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