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The Temperature Dependence of the Radio-Frequency Polarographic Wave Height

By Tomihito KAMBARA and Shogo WATARAI

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

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When the radio-frequency polarographic current, i_{RF}, is regarded approximately as the difference between the Fournier current and the ordinary DC polarographic current, i_{DC}, one can elucidate the temperature dependence of i_{RF}. It may be theoretically predicted that the relative temperature coefficient of i_{RF} for the completely-reversible system is less by 0.66% than that of i_{DC}. The plot of log ($i_{RF}\cdot T^2$) against $1/T$, where T is the absolute temperature, gives two straight lines which join each other at a knick, coresponding to the transition from a completly reversible process to a less reversible one. Experiments with thallium(I) and zinc(II) ions in various supporting electrolytes reveal the essential validity of the present theory.

It was reported in our previous study[1] that the AC polarographic peak heights of the zinc ion in various supporting electrolytes, therefore with varying reversibilities, show different temperature dependencies. In the present study the effect of the temperature on the radio-frequency (R-F) polarographic wave heights observed with various redox systems will be investigated.

Theoretical

The R-F polarographic method developed by Barker[2,3] and the theoretical treatment of the Faradaic rectification developed by several authors[4-9] offer many complicated problems. Because of the mathematically-complicated expression for the R-F polarographic process, we will here employ the simplified concept suggested by Yasumori[10] that, during the half-period of R-F modulation, the electrolytic current observed is the Fournier current,[11] while the signal recorded in R-F polarography is the Fournier current minus the ordinary DC polarographic current, i_{DC}, as is illustrated in Fig. 1.

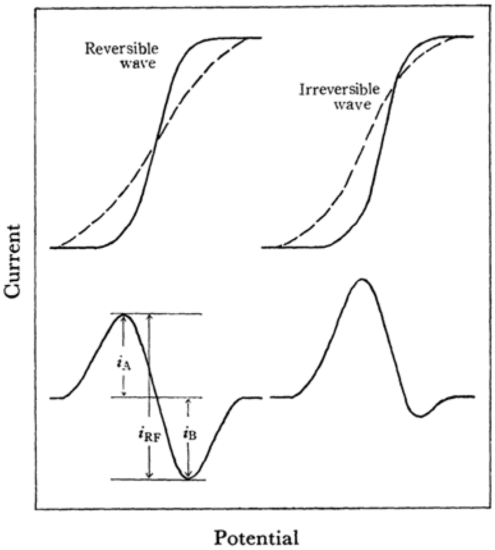

Fig. 1. Relation between the ordinary DC polarographic wave (full line), the Fournier polarogram (dashed line) and the R-F polarogram. (The construction method for evaluating the R-F wave heights, i.e. i_{A}, i_{B} and i_{RF}, are also schematically illustrated.)

Applying the Senda-Tachi[12] theory for the Fournier polarogram, one can derive the following expressions for a reversible system:

$$i_{\mathrm{DC}} = j_0 i_d = \frac{i_d}{2}(1-\tanh x) \tag{1}$$

$$x = \frac{n\boldsymbol{F}(E-E_{1/2})}{2\boldsymbol{R}T} \tag{2}$$

$$i_{\mathrm{F}} = i_{\mathrm{DC}} + \frac{i_d}{4}\left(\frac{n\boldsymbol{F}}{2\boldsymbol{R}T}\right)^2 \frac{\mathrm{d}^2 j_0}{\mathrm{d}x^2}\varDelta E^2 \tag{3}$$

$$\begin{aligned} i_{\mathrm{RF}} = i_{\mathrm{F}} - i_{\mathrm{DC}} &= \frac{i_d}{4}\left(\frac{n\boldsymbol{F}}{2\boldsymbol{R}T}\right)^2 \frac{\mathrm{d}^2 j_0}{\mathrm{d}x^2}\varDelta E^2 \\ &= \frac{i_d}{4}\left(\frac{n\boldsymbol{F}}{2\boldsymbol{R}T}\right)^2 \varDelta E^2 \frac{\sinh x}{\cosh^3 x} \end{aligned} \tag{4}$$

In these equations, i_d is the DC diffusion current and $\varDelta E$ the amplitude of the R-F voltage; the other symbols have their usual meanings.

The maximum and minimum in the R-F polarogram are obtained by solving $\mathrm{d}i_{\mathrm{RF}}/\mathrm{d}E = 0$ at:

$$x = \pm\frac{1}{2}\ln(2+\sqrt{3}) = \pm 0.6584 \tag{5}$$

Thus, it is found that:

$$i_{\mathrm{RF}} = k \cdot i_d \cdot T^{-2} \cdot \varDelta E^2 \tag{6}$$

where k is the proportionality factor. On the other hand, one has:

$$i_d \propto D^{1/2} \tag{7}$$

$$D = D_0 \cdot \exp\frac{-\varDelta H_D}{\boldsymbol{R}T} \tag{8}$$

where $\varDelta H_{\mathrm{D}}$ is the activation heat of diffusion.

Hence, it may be seen that:

$$\frac{1}{i_{\mathrm{RF}}}\cdot\frac{\mathrm{d}i_{\mathrm{RF}}}{\mathrm{d}T} = \frac{1}{i_d}\cdot\frac{\mathrm{d}i_d}{\mathrm{d}T} + \frac{2}{T} \tag{9}$$

It is thus expected that, for the completely reversible electrode process the R-F wave height would have a relative temperature coefficient less by 0.66% than that of the ordinary DC step height. Further, the plot of log $(i_{\mathrm{RF}}T^2)$ vs. $1/T$ would give a straight line in the reversible region.

Experimental

A Yanagimoto polarograph, type PF-500, was used; the radio frequency was 455 kC, and the square-wave frequency was 200 c. p. s.

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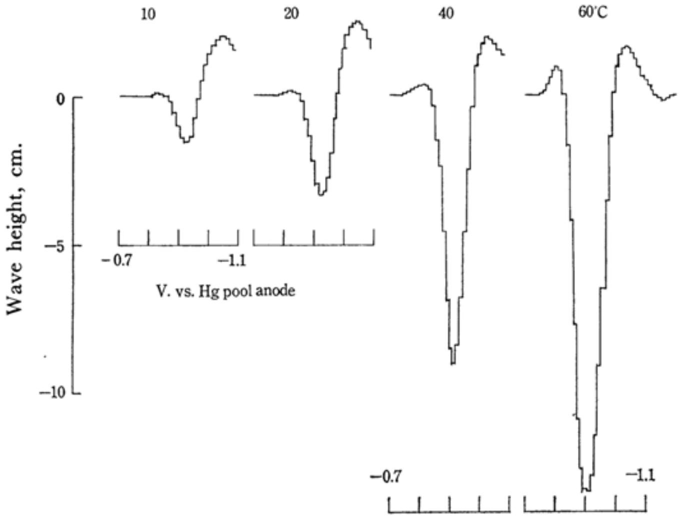

Fig. 2. R-F polarograms of 10^{-4} M Zn^{2+} in 1 M KCl at various temperatures.

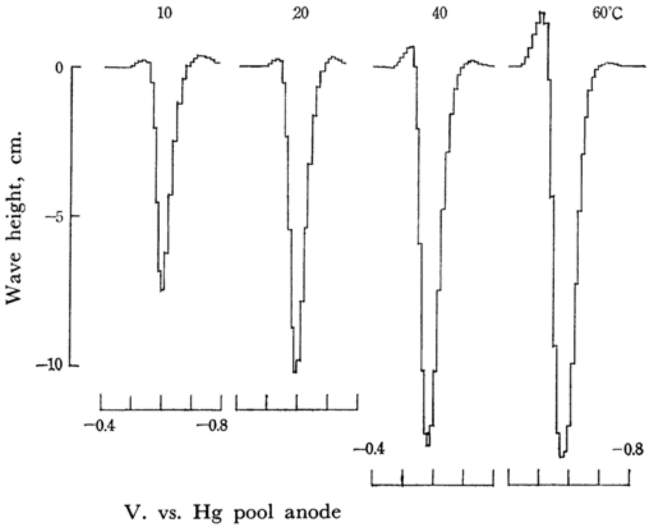

Fig. 3. R-F polarograms of 5×10^{-5} M Zn^{2+} in 1 M KI at various temperatures.

TABLE I. RELATIVE TEMPERATURE COEFFICIENT OF THE R-F POLAROGRAPHIC WAVE HEIGHT IN PERCENT

Absolute temp.	10^{-4} M Zn^{2+} in		5×10^{-5} M Zn^{2+} in	10^{-4} M Tl^{+} in
T°K	1 M KCl	1 M KBr	1 M KI	1 M KCl
283	7.6	6.5	3.9	4.3
293	6.4	5.9	2.1	2.6
303	5.0	4.1	1.2	1.8
313	4.2	1.7	0.6	1.1
323	1.7	0.6	0.5	0.6
333	1.0	0.3	0.3	0.4

The drop time was controlled to about 4 sec. at a constant mercury level, and the low frequency current was gated to a time interval from 2 to 3 sec. for each drop. The R-F voltage was 5 V., and the amplifier and recorder sensitivities were kept to 0.1.

Results

Figures 2 and 3 show some examples of the R-F polarograms recorded. The wave hieghts are plotted against the temperature in Fig. 4; the temperature coefficient is summarized in Table I. In Fig. 5 log ($i_{RF}T^2$) is plotted against the reciprocal of the absolute temperature.

Discussion

The temperature corresponding to the knick in the plot of log ($i_{RF}T^2$) vs. $1/T$ would indicate the transition of the rate-determining step from diffusion to electron-transfer. The transition temperature, as evaluated with AC peak heights

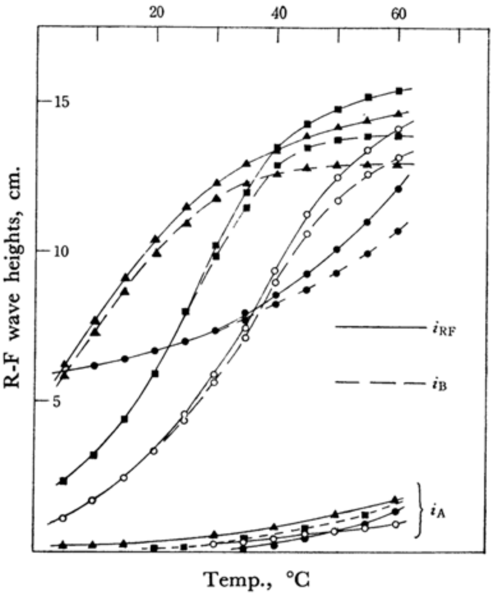

Fig. 4. R-F wave heights plotted against the temperature.

○ Zn^{2+} in KCl; ■ Zn^{2+} in KBr; ▲ Zn^{2+} in KI; ● Tl^+ in KCl (Cf. Fig. 1 and Table I)

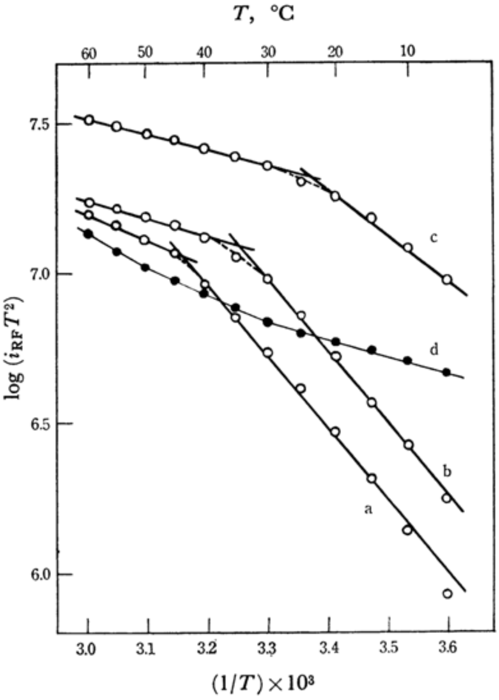

Fig. 5. log ($i_{RF}T^2$) vs. $1/T$.

a Zn^{2+} in KCl; b Zn^{2+} in KBr; c Zn^{2+} in KI; d Tl^+ in KCl. In curve c i_{RF} was doubled for purposes of comparison.

in our previous study,[1] coincides well with that obtained by the present R-F method.

As for the R-F wave height of thallium(I), it may be safe to say that, in the temperature region higher than 35°C, another mechanism plays a role and that the temperature coefficient increases more rapidly than expected with an assumption of complete reversibility.

Summary

On the simplified model that the R-F polarographic current is the difference between the Fournier current and the ordinary DC polarographic current, one can clear up the temperature dependence of the R-F wave height. It has been concluded that, in the reversible case, the temperature coefficient of the R-F wave height is less by 0.66% than that of the DC step height. Further, a new method, in which the logarithm of the product of the R-F wave height and the square of the absolute temperature is plotted against the reciprocal of the absolute temperature, has been introduced and examined. In the reversible region the above plot gives a straight line, the slope of which corresponds to that of log i_{DC} plotted against $1/T$. At lower temperatures the reversibility decreases and the above plot shows a break, indicating the transition from a reversible electrode process to an irreversible one.