Temperature Dependence of A. C. Polarographic Waves

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There are few published data on the temperature dependence of a. c. polarographic waves. The most extensive study is that of Bauer and Goodwin(1) who reported the temperature coefficients of the peak heights for the reduction of a number of metal ions and compared these values with the values for the corresponding d. c. polarographic step heights. These temperature coefficients were expressed as a percentage. Randles and Somerton(2) have reported the activation energies of electron transfer reactions involving several inorganic depolarizers. These results were obtained from faradaic impedance measurements.

Vlček(3) has proposed that the temperature dependence of d. c. polarographic step heights be expressed in terms of an activation energy obtained from an Arrhenius type plot. The values obtained should be independent of the temperature range used and activation energies have a deeper physical meaning than temperature coefficients expressed as a percentage. For a diffusion controlled limiting current, this value expresses the activation energy of diffusion. At low frequencies and high values of the electron transfer rate constant, the a. c. polarographic current is determined by mass transfer terms, and hence if this mass transfer is a diffusion process, it should be possible to obtain a value for the activation energy of diffusion from the a. c. polarographic wave height. If the mass transfer is not a diffusion process (e. g. involves a coupled chemical reaction) then this fact should be detectable from the form of Arrhenius plot obtained. Electrode processes, where the rate of electron transfer is slow enough to affect the a. c. polarographic current at low frequencies, should also show a different form of Arrhenius plot. Thus it should be possible, from the temperature dependence of the peak height, to obtain some useful information about the nature of the electrode process.

At low frequencies and high values of the electron transfer rate constant and for mass transfer by diffusion, the faradaic admittance at the peak of an a. c. polarographic wave, Y, is given by:(4)

$$Y=\frac{n^2F^2AC^0(\omega D)^{1/2}}{4RT} \qquad (1)$$

where C^0 is the concentration of depolarizer in the bulk of the solution, ω the angular

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1) H. H. Bauer and P. B. Goodwin, *Aust. J. Chem.*, **14**, 460 (1961).

2) J. E. B. Randles and K. W. Somerton, *Trans. Faraday Soc.*, **48**, 937, 951 (1952).

3) A. A. Vlček, *Coll. Czech. Chem. Comm.*, **24**, 3538 (1959).

4) H. H. Baure, *J. Electroanal. Chem.*, **3**, 150 (1962).

frequency, D the diffussion coefficient of the depolarizer, and $n, F, A, \boldsymbol{R}$, and T have their usual meanings. Assuming that all quantities in Eq. 1 except D and T are independent of temperature, and that the temperature dependence of D may be written :[3]

$$D=D_0 \exp\left(\frac{-Q_\mathrm{D}}{\boldsymbol{R}T}\right) \tag{2}$$

where D_0 is a constant and Q_D is the activation energy of diffusion, the temperature dependence of the faradaic admittance may be written :

$$YT=\alpha \exp\left(\frac{-1/2\, Q_\mathrm{D}}{\boldsymbol{R}T}\right) \tag{3*}$$

where α is a constant made up of the temperature independent terms. A plot of log YT against $1/T$ should yield a straight line of slope $-Q_\mathrm{D}/4.61\,\boldsymbol{R}$ for cases where the above conditions are valid. The activation energy determined in this way should be comparable with that determined from the d. c. polarographic limiting current. According to Vlček[3] the values of Q_D usually fall in the range 4—6 kcal. mol^{-1}.

Table I shows some results obtained for systems of several types. For systems numbers 1 and 2 the electrode process is known to be reversible,[5] and the values of Q_D obtained from a. c. and d. c. polarography are comparable and of the expected order of magnitude. In system number 3 an irreversible chemical reaction follows the reversible electron transfer reaction[5] viz.

$$\mathrm{EuY^{2-} + Ca^{2+} \rightarrow Eu^{2+} + CaY^{2-}}$$

where Y represents ethylenediaminetetraacetic acid (EDTA). Although the d. c. limiting current is diffusion controlled, the height of the a. c. wave is affected by the rate of the chemical reaction.[5] Consequently, the value of Q_D obtained from d. c. polarography is comparable with that obtained for system number 2, whilst a linear plot is not obtained for the a. c. case. Figure 1 shows the difference in the Arrhenius plots from the a. c. polarograms in presence and absence calcium chloride.

TABLE I. TEMPERATURE DEPENDENCE OF POLAROGRAPHIC WAVES

Frequency : 60 c. p. s.
Amplitude : 15 mV. r. m. s.
Temperature range : 25—65°C

	System studied	Q_D, kcal. mol^{-1}	
		D. C. polarography	A. C. polarography
(1)	1.0×10^{-3}M Cd^{2+} in 0.5M KCl + 0.5M HCl	4.4	4.4
(2)	2.0×10^{-3}M Eu(III)-EDTA in 0.2M ammonia buffer + 1.0×10^{-3}M Ca(II)-EDTA + 2×10^{-4}% Triton X-100	4.0	5.1
(3)	as (2) + 5×10^{-2}M CaCl$_2$	3.7	curve
(4)	1.0×10^{-3}M Zn^{2+} in 1M KCl	3.8	curve

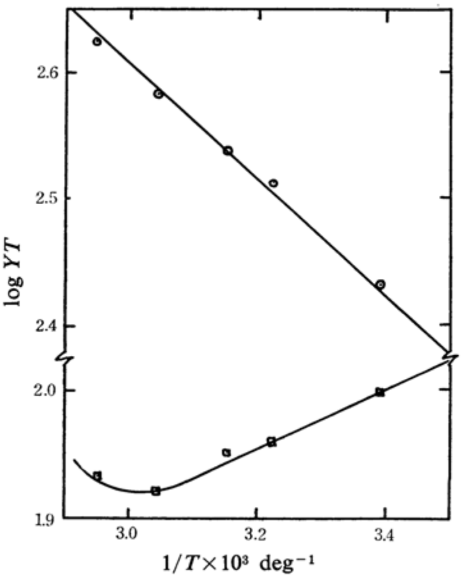

Fig. 1. Temperature dependence of a. c. polarographic wave heights for reduction of Eu(III)-EDTA in absence ⊙ and presence ⊡ of calcium chloride (for conditions see Table I).

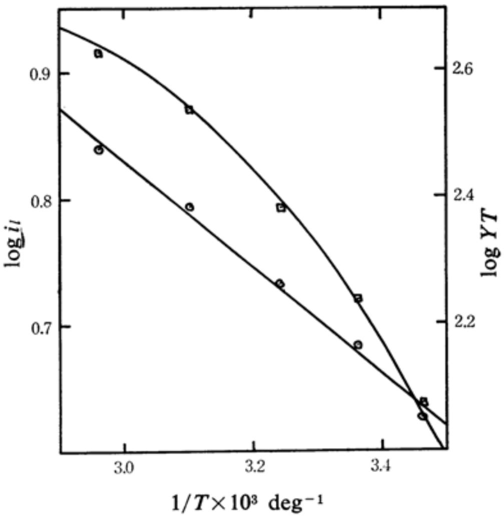

Fig. 2. Temperature dependence of limiting current ⊙, and a. c. polarographic wave height ⊡ for reduction of zinc ions (for conditions see Table I).

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[5] G. H. Aylward and J. W. Hayes, *Anal. Chem.*, **37**, 195 (1965).

* Added in Proof : Since submission of this paper, T. Kambara and K. Kunimatsu in *Review of Polarography*, **13**, 20 (1965) have published a development of Eq. 3 and its application to quasi-reversible systems.

By means of a plot of the logarithm of the rate constant against $1/T$, the activation energy of the chemical reaction has been determined.[5]

System number 4 is a well known quasi-reversible system, and the height of the a.c. wave is influenced by the rate of the electron transfer reaction. Although a linear Arrhenius plot is obtained from the d.c. polarograms, and the value Q_D obtained from the limiting current is in the expected range of magnitude, marked non-linearity is found from a.c. polarograms, see Fig. 2.

Further work in this field should prove useful in the assignment of mechanisms to electrode processes.

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