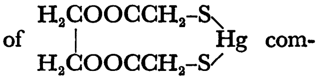
Polarographic Behavior of Glycol Dimercaptoacetate

R. S Saxena and S. K. Bhatia

Department of Chemistry, Malaviya Regional Engineering College, Jaipur, India

(Received November 20, 1973)

Polarographic behaviour of glycol dimercaptoacetate has been studied in 25% ethanol at d.m.e. in the pH range 1.56—11.56 in presence of 0.1 M KNO_3. In the acidic media, the current-voltage curves consist of three waves; a prewave due to the adsorption of anodic reaction product at the mercury drop surface, main anodic wave due to the electroxidation of –SH groups and a third wave at more positive potential due to the insoluble film formation on the electrode surface whose solubility depends on pH of the solution. In the alkaline media only two waves, a prewave and the main anodic wave, are observed. The effects of various factors such as different buffer, Hg-pressure, temperature, ethanol and depolarizer concentrations on the wave characteristics have been investigated. The electrode reaction is irreversible at higher pH but in acid media it is reversible and diffusion controlled involving a two electron transfer process, with the formation of  $\begin{matrix} H_2COOCCH_2\text{-}S\diagdown \\ | \qquad\qquad\quad Hg \\ H_2COOCCH_2\text{-}S\diagup \end{matrix}$ complex. The overall dissociation constant (pK) of the sulphydryl groups has been found to be 8.20 at 20 °C. At pH 4.80, the maximum number of moles adsorbed on unit area is 6.83×10^{-10} mol/cm^2 *i.e.* 4.12×10^{14} molecule/cm^2. Adsorption coefficient and molar adsorption energy are calculated to be 1.445×10^4 and 31.2 kcal/gm mol respectively. The respective values of kinetic parameters, *viz.* transfer coefficient (α) and formal rate constant ($K^\circ_{\text{f,h}}$) for the irreversible wave at pH 11.56 are 0.76 and 2.6×10^{-9} cm/s.

Thiols are very useful from biological, pharmaceutical and analytical points of view and hence the importance of this groups of compounds has considerably grown during the past few years. Whereas the electrochemical behavior of some monothiols has already been reported by Saxena and co-workers,[1–3)] this communication describes the polarographic behavior of glycol dimercaptoacetate in presence of different buffers, *viz.* Clark-Lub's, B. R., acetate and various concentration of ethanol. There is, however, no reference in the literature on the present work.

Experimental

Glycol dimercaptoacetate (referred to herein as GDA) was obtained from Evan's Chemetics, Inc., New York and all chemical used were of Anal-R (BDH) quality. A manual polarograph, with scalamp galvanometer and SCE as reference electrode, was used for recording the polarograms. The $m^{2/3}t^{1/6}$ value for the capillary was 0.7543 mg$^{2/3}$ s$^{-1/2}$ in 25% ethanol and 0.1 M KNO_3 at -0.3 V *vs.* SCE with $h_{\text{eff}}=47.95$ cm. Polarograms were recorded in an inert atmosphere of nitrogen at a temperature 20±0.1 °C.

Results and Discussion

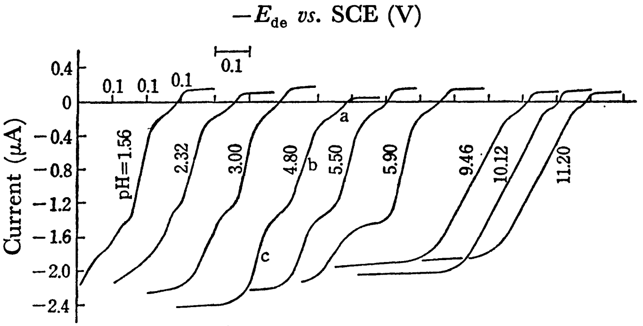


Fig. 1. Polarograms for 1.0 mM GDA at different pH values using G–L buffers.

Effect of pH. Figure 1 illustrates the polarograms for 1.0 mM glycol dimercaptoacetate in 25% ethanol and 0.1 M KNO_3 at different pH values using Clark-Lub's buffers. In acidic medium, the main anodic wave (b) is associated with a prewave (a) of constant height at more negative potential and a third wave (c) at more positive potential. The third wave (c) disappears in the alkaline media. The wave c is due to the insoluble film formation at the electrode surface whose solubility depends on the pH of the solution.[4)] Analogous behavior with dithiocarbaninocarboxylic acid was reported by Zahradnik.[5,6)] The half-wave potentials of the main wave as well as those of the prewave and the third wave shift towards the more negative potential with increase in pH according to the following equation.[7)]

$$E_{1/2} = \text{Const.} - \frac{2.3pRT}{nF}\text{pH}$$

The point of intersection of two linear portions in the plot of pH *vs.* $-E_{1/2}$ of the main wave (b) corresponds to the overall dissociation constant (pK) of the sulphydryl group[8)] which is found to be 8.20. Slopes of the plots of log $(i_d-i)/i$ *vs.* $-E_{\text{de}}$ indicate that the electrode process is reversible in acidic media and irreversible in alkaline media.

Several polarograms were taken at different pH values using various buffers *viz.* Britton-Robinson, Clark-Lub's, Michaelis Borate, and acetate. It was observed that the nature of the wave is not affected by the constituents in the buffers used.

Effect of Hg-pressure, Temperature GDA and Ethanol Concentration at pH 4.80 (Fig. 2). For 1.0 mM GDA total diffusion current (i_d) of the three waves is proportional to $h_{\text{eff}}^{1/2}$ but that of the prewave (i_1) varies linearly with h_{eff}. While the height of the prewave decreases with increase in temperature that of the main anodic wave increases and it remains almost constant for the third wave. The temperature coefficient of i_d is calculated to be 2.78% per degree. The height of

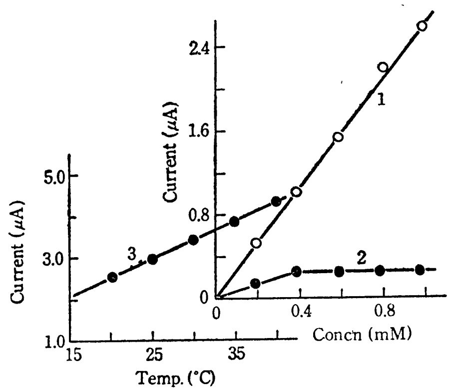


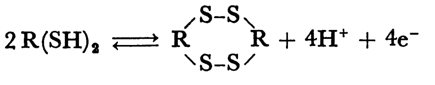
Fig. 2. Curve 1: Plot of i_d *vs.* [GDA], Curve 2: Plot of i_l *vs.* [GDA], Curve 3: Plot of i_d *vs.* Temp.

the prewave, i_1, increases with [GDA] up to 0.4 mM above which it remains almost constant while i_2, i_3, and i_d vary linearly with [GDA] (0.2 to 1 mM). The mean values of diffusion current constant ($I=i_d/\mathrm{cm}^{2/3}\cdot t^{1/6}$) and diffusion coefficient are 3.406 μA/mM/l/mg$^{2/3}$·s$^{-1/2}$ and 6.60×10^{-6} cm^2/s respectively. These observations substantiate the diffusion controlled nature of the waves.

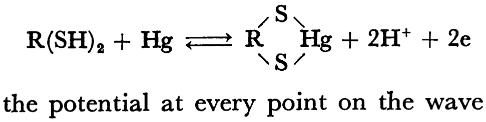
The total diffusion current (i_d) decreases with increase in ethanol percentage passing through a minimum in between 40—50% and then increases but the nature of the main wave remains the same.

Effect of $HgCl_2$ on Main Anodic Wave. Solutions containing GDA and $HgCl_2$ in proportions of 1 : 0, 1 : 0.5, and 1 : 1 were prepared. The insoluble mercury complex was removed by filtration and the filtrates were polarographed under identical conditions. In presence of increasing amounts of $HgCl_2$ the main anodic wave with decreased wave height was obtained; it disappeared completely, when GDA and $HgCl_2$ was present in 1 : 1 ratio. This shows the formation of 1 : 1 complex of GDA with Hg(II).

Mechanism of the Electrode Reaction. The electrooxidation of GDA (referred here as $R(SH)_2$) may involve (A) the formation of a disulphide, a four electron transfer Process (1) and (B) the formation of a mercuric-complex, a two electron transfer Process (2)



$$2\mathrm{R(SH)_2} \rightleftharpoons \mathrm{R}\genfrac{}{}{0pt}{}{\diagup\mathrm{S{-}S}\diagdown}{\diagdown\mathrm{S{-}S}\diagup}\mathrm{R} + 4\mathrm{H}^+ + 4e^- \tag{1}$$



$$\mathrm{R(SH)_2} + \mathrm{Hg} \rightleftharpoons \mathrm{R}\genfrac{}{}{0pt}{}{\diagup\mathrm{S}\diagdown}{\diagdown\mathrm{S}\diagup}\mathrm{Hg} + 2\mathrm{H}^+ + 2e \tag{2}$$

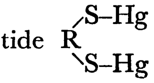
Then the potential at every point on the wave should be given by

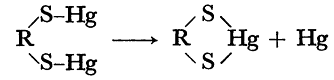
$$E = \text{Const.} - \frac{RT}{4F}\ln\frac{(i_d-i)^2}{i} \quad \text{(for reaction A)} \tag{3}$$

and

$$E = \text{Const.} - \frac{RT}{2F}\ln\frac{i_d-i}{i} \quad \text{(for reaction B)} \tag{4}$$

If the formation of a disulphide is involved (1), then the plot of $-E_{de}$ *vs.* log $(i_d-i)^2/i$ should yield a straight line with slope 0.059/4 V. On the other hand, if Reaction (2) is involved, the plot of $-E_{de}$ *vs.* log i_d-i/i gives a straight line having a slope of 0.059/2 V. It is observed that only the analysis corresponding to Eq. (4) yields a straight line with a slope of 0.031 V close enough to the theoretical slope of 0.029 V. Furthermore, it was found that the $E_{1/2}$ of the main wave was independent of [GDA]. This constancy of $E_{1/2}$ is characteristic of Eq. (4) and not of Eq. (3). This analysis indicates that the anodic reaction of GDA at d.m.e. occurs according to (2) and not to the formation of a disulphide.

If the reaction is reversible, then the mercury in the mercuric–GDA complex should be reversibly reducible at d.m.e. But on the contrary, the preceding experiments on the effect of added $HgCl_2$ show that the final product of the electrode reaction is an insoluble complex of mercury. It may, therefore, be concluded that the anodic wave is due to the formation of mercurous mercaptide  $\mathrm{R}\genfrac{}{}{0pt}{}{\diagup\mathrm{S{-}Hg}}{\diagdown\mathrm{S{-}Hg}}$ (soluble compound) which is unstable and changes into more stable mercuric complex and Hg.



$$\mathrm{R}\genfrac{}{}{0pt}{}{\diagup\mathrm{S{-}Hg}}{\diagdown\mathrm{S{-}Hg}} \longrightarrow \mathrm{R}\genfrac{}{}{0pt}{}{\diagup\mathrm{S}\diagdown}{\diagdown\mathrm{S}\diagup}\mathrm{Hg} + \mathrm{Hg}$$

Adsorption Prewave. A steep depression in *E-t* curve was obtained for 1.0 mM GDA and 0.1 M KNO_3 at pH 4.80 in the potential range where the prewave appeared, showing the strong adsorption of the electrolysis product at d.m.e. A general theoretical treatment of adsorption waves (prewave) at the d.m.e. was first described by Brdicka who gave the expression for the average limiting current of the adsorption wave i_p.[9)]

$$i_p = 0.85nFZm^{2/3}t^{-1/3} \tag{5}$$

in which i_p is expressed in ampere, Z is the maximum number of moles adsorbed per cm^2, m is the rate of mercury flow in g/s, t is the droptime in s, n and F have their usual significance. From Eq. (5), $Z=6.83\times10^{-10}$ mol/cm^2 *i.e.* 4.12×10^{14} molecule/cm^2 which corresponds to an area of 24.29 Å^2 per adsorbed molecule. Adsorption coefficient (ω) and molar adsorption energy (ϕ) are 1.445×10^4 and 31.2 kcal/g·mol, respectively, which are evaluated from the following equations:

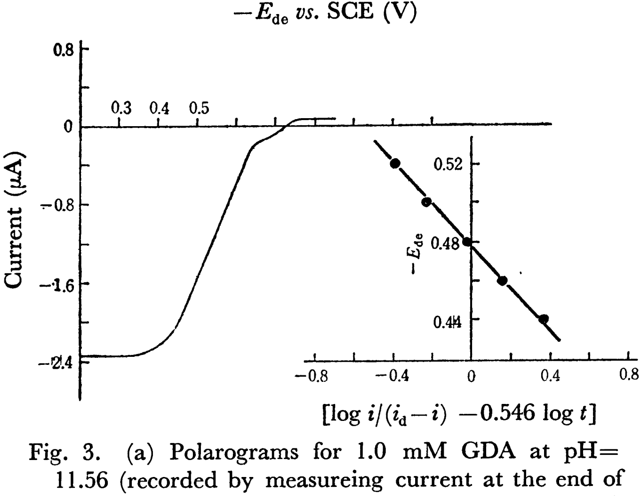


Fig. 3. (a) Polarograms for 1.0 mM GDA at pH= 11.56 (recorded by measureing current at the end of the drop life). (b) Plot of $-E_{de}$ *vs.* [log $i/(i_d-i)$ -0.546 log t]

$$\omega = \frac{2}{C_a} \exp \frac{n\Delta EF}{RT} \tag{6}$$

$$\phi = n\Delta EF + RT \ln \frac{2}{C_a V} \tag{7}$$

Where ΔE stands for the difference in half-wave potentials of the prewave and the main wave at concentration C_a at which adsorption and diffusion currents are equal and V is the molar volume of the particles.

Kinetic Parameters. The values of kinetic parameters are calculated at pH 11.56 from Koutecky's treatment[10] as extended by Meites and Israel.[11] For an irreversible anodic wave it follows:

$$E_{de} = -0.2412 + \frac{0.05915}{(1-\alpha)n} \log \frac{1.349 K^{\circ}_{b,h}}{D_o^{1/2}} + \frac{0.0542}{(1-\alpha)n} \left[\log \frac{i}{i_d - i} - 0.546 \log t \right] \tag{8}$$

and

$$E^{\circ}_{1/2} = -0.2412 + \frac{0.05915}{(1-\alpha)n} \log \frac{1.349 K^{\circ}_{b,h}}{D_o^{1/2}} \tag{9}$$

The plot of $[\log i/(i_d - i) - 0.546 \log t]$ *vs.* $-E_{de}$ yields a straight line (Fig. 3) whose slope is equated to $0.0542/(1-\alpha)n$ and the value of α is found to be 0.76. The intercept ($E^{\circ}_{1/2}$), obtained from the same plot, is substituted in Eq. (9) and the value of $K_{b,h}{}^{\circ}$ is calculated to be 2.6×10^{-9} cm/s.

The authors are thankful to C.S.I.R., New Delhi for the grant of a research fellowship to one of them (S.K.B.) and to Prof. R. M. Advani, Principal, for providing research facilities.

References

1) R. S. Saxena and U. S. Chaturvedi, *Electrochim. Acta*, **16**, 1107 (1971).

2) R. S. Saxena and K. C. Gupta, *J. Indian Chem. Soc.*, **47**, 101 (1970).

3) R. S. Saxena and Pratap Singh, *Z. Naturforsch.*, **24B**, 1520 (1969).

4) O. Grubner, *Chem. Listy*, **47**, 1133 (1953).

5) R. Zahradnik, *ibid.*, **49**, 1002 (1955).

6) R. Zahradnik, and L. Jensovsky, *ibid.*, **48**, 11 (1954).

7) J. Heyrovsky, "Principles of Polarography," Academic Press, New York (1966), p. 257.

8) M. Brezina and P. Zuman, "Polarography in Medicine, Biochemistry and Pharmacy," Interscience Publishers New York (1958), p. 472.

9) J. Herovsky and J. K. Kuta, "Principles of Polarography," Academic Press, New York (1966), p. 291.

10) L. Meites, "Polarographic Techniques," Interscience Publishers, New York (1965), p. 241.

11) L. Meites and Y. Israel, *J. Amer. Chem. Soc.*, **23**, 2903 (1961).