# A Study of the Polarographic Behaviour of N,N'-Ethylenebis-[2-(o-hydroxyphenyl)] glycine in the Presence of Iron Ions

KNUT HENNING SCHRØDER

Kjemisk Institutt, Norges Lærerhøgskole, Trondheim, Norway

The system iron-N,N'-ethylenebis[2-(o-hydroxyphenyl)]-glycine has been studied polarographically up to pH = 12. The ferric complex yields a wave due to reversible reduction at pH above 9. In this case the half-wave potentials are constant, independent of pH and concentrations of ligand and metal ions, and are equal to −0.630 V *vs.* S.C.E. The stability constant of the ferrous complex has been obtained. The reductions are always diffusion controlled. Diffusion current constants are reported. The reversibility in solutions with pH below 9 is discussed.

In the last few years there has been a growing interest in different sequestering agents, among them the reagent N,N'-ethylenebis[2-(o-hydroxyphenyl)]-glycine (EHPG) with the formula:
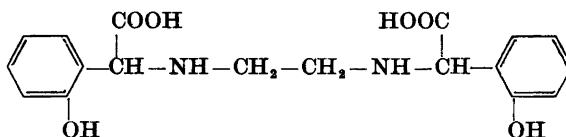
As the stability of the ferric complex is very high, ferric hydroxide does not precipitate even in strong alkaline solutions, and this fact has been utilized in agriculture for correcting the mineral deficiency in plants grown in alkaline soils.[1] The ferric chelate, which has a red colour suitable for spectrophotometric determinations, has also become important in analytical chemistry.[2-4] The chelating tendencies of EHPG towards different metal ions, among them trivalent iron, have been studied by Frost and co-workers.[5] From pH-titration data they estimate the logarithmic stability constant of the ferric complex to be > 30. The present author, using spectrophotometric measurements in acid solutions, has determined this constant to be 33.86.[6]

Systematic polarographic investigations of the complexing properties of EHPG have not previously been performed. Sympson and Caldwell [7] have worked out a procedure for polarographic determination of manganese by means

of the manganese(III)-EHPG complex, and Hoyle and West [8,9] recommend polarography for the analysis of complexones in mixture, by use of the different copper and cadmium chelates. The present paper reports a polarographic study of the complexes of iron and EHPG.

EXPERIMENTAL

Apparatus and technique. The polarograms were recorded with the polarograph Radiometer PO4 (Copenhagen, Denmark). The half wave potentials were obtained by means of manual plots; $\log[i/(i_d - i)]$ *vs.* E was plotted, and the half wave potentials were taken to be the potential with zero log-plot. The potentials were measured at zero current by means of a Vernier d.c. potentiometer and a Multiflex galvanometer.

The conventional type of dropping mercury electrode was used. The capillary characteristics, measured in open circuit at a mercury height of 50 cm, were $m = 2.96$ mg/sec, and $t = 2.79$ sec. An external saturated calomel electrode (S.C.E.) served as reference electrode, and was connected to the cell with an agar-KCl bridge. The total a.c. resistance of the cell, agar bridge and reference electrode was measured to 900 Ω. The temperature of the solutions was kept within $\pm 0.1°C$, and all the experiments except the temperature studies were performed at 25.0°C. Dissolved air was removed from the solutions by bubbling oxygen-free nitrogen through the cell for 5 min and passing it over the solution during the electrolyses.

For the reversibility studies a Krizik P-576 polaroscope (Prague, Czechoslovakia) was used.

Materials. Purum N,N'-ethylenebis[2-(o-hydroxyphenyl)]glycine was obtained from Fluka A. G., Switzerland. Stock solutions were made by dissolving a known amount of the reagent in distilled water. Stock solutions of ferric iron were made by dissolving metallic iron in perchloric acid and oxidizing it to the trivalent state by means of nitric acid prior to diluting. The remaining chemicals were of reagent grade.

RESULTS

Frost *et al.* [5] could not obtain meaningful titration curves from the Fe(II)-EHPG complex because of irreversible oxidation of the metal ions in the presence of the ligand. These results would seem to predict that the ferric complex is reduced irreversibly at the dropping mercury electrode, but the results below partially contradict this prediction.

Experimental data

Preliminary investigations proved that the reagent was not reduced at the dropping mercury electrode prior to the reduction of the supporting electrolyte. However, an increase of the residual current was observed for potentials exceeding -1.2 V; this may result from air oxidation products, like quinones, as Underwood reported.[3]

pH-Studies. Polarograms of the ferric complexes were recorded from solutions with different pH values. Sodium perchlorate was used as a supporting electrolyte with addition of sodium hydroxide or perchloric acid to obtain the proper pH and ionic strength of 0.1. Some of the typical results are shown in Table 1. It was found that the slope of the log-plots rapidly decreases with an increase of pH. This could indicate increasing reversibility of the reduction of the ferric compound as the pH is raised to higher values.

Table 1. Half-wave potentials and log slopes from solutions with different pH values. 5.00×10^{-4} M Fe^{3+}, 5.00×10^{-3} M EHPG; NaOH, $HClO_4$ and $NaClO_4$ added to proper pH and ionic strength $= 0.1$; 25°C.

pH	$-E_{1/2}$	$\log[i/(i_d - i)]$ (mV)
4.50	0.479	145
6.60	0.595	83
9.25	0.641	65
11.45	0.643	61

The shift of half-wave potentials at different pH values was studied with other solutions containing different supporting electrolytes. A typical pH plot is shown in Fig. 1. It is seen that the half-wave potential is shifted to more
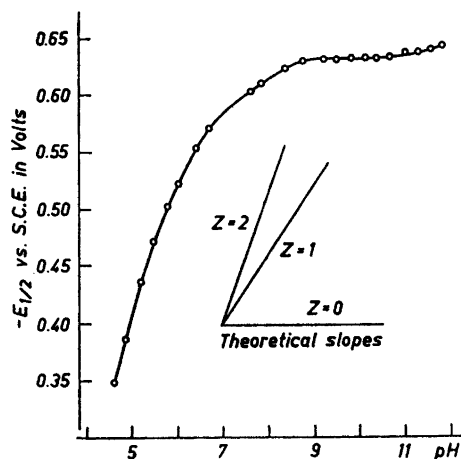

Fig. 1. Plots of half-wave potentials of 2×10^{-4} M Fe^{3+} in 2×10^{-3} M EHPG with 0.1 M NH_4Ac (HAc or NH_3 added to proper pH). Z is the number of protons involved in the reduction process.

negative potentials with increasing pH, and that the slope of the pH-curve reaches zero near pH $= 9.0$. The log-slopes would indicate reversible processes at all pH values. The same results were obtained with polarograms recorded from solutions containing other supporting electrolytes, though the shape of the pH curve and the log-slopes of the polarograms were quite different in some electrolytes at pH below 9.0. To examine the dependence on pH of the polarographic reductions in the pH-range below 9, experiments were performed with different quantities of supporting buffer at the same pH. A typical experimental series at pH 4.75 is recorded in Table 2. As shown, the reversibility of the reduction process seems to increase with added acetate buffer. Similar results were obtained at other pH values below 9 when buffers were added.

Table 2. Half-wave potentials and log slopes from solutions with different supporting electrolytes pH = 4.75; 5.00×10^{-4} M Fe^{3+}, 5.00×10^{-3} M EHPG; 25°C.

supporting electrolyte	$-E_{1/2}$	$\log[i/(i_d - i)]$ (mV)
a	0.496	135
b	0.343	72
c	0.314	63

a 0.1 M $NaClO_4$ + $HClO_4$
b 0.1 M $NaClO_4$ + $HClO_4$ + 0.1 M NaAc/HAc buffer
c 0.1 M $NaClO_4$ + $HClO_4$ + 0.5 M NaAc/HAc buffer

As seen from Table 2 the half-wave potential is shifted to more positive values with increasing concentration of acetate ions.

Polarograms were recorded with a constant concentration of ferric iron and different quantities of complexing agent. The pH was kept constant by means of buffer solutions. The dependence of the half-wave potentials on the EHPG concentration is indicated in Table 3. As shown in the table, the potential is independent of pH in most alkaline solutions, but seems to be shifted to more positive values with decreasing concentrations of the ligand in neutral or acid solutions.

Table 3. The dependence of half-wave potentials with the concentration of EHPG. 5.00×10^{-4} M Fe^{3+}.

EHPG	$-E_{1/2}$	Buffer and pH
1.00×10^{-2}	0.635	
7.50×10^{-3}	0.634	
5.00×10^{-3}	0.634	pH = 9.30 with
2.50×10^{-3}	0.636	0.1 M NH_4Cl/NH_3 buffer
1.00×10^{-3}	0.638	
1.00×10^{-2}	0.587	
7.50×10^{-3}	0.584	
5.00×10^{-3}	0.585	pH = 6.55 with
2.50×10^{-3}	0.580	0.1 M KH_2PO_4/K_2HPO_4 buffer
1.00×10^{-3}	0.569	
1.00×10^{-2}	*	
7.50×10^{-3}	*	
5.00×10^{-3}	0.337	pH = 4.75 with
2.50×10^{-3}	0.315	0.1 M NaAc/HAc buffer
1.00×10^{-3}	0.288	

* precipitation of EHPG.

Studies with a constant concentration of EHPG and different concentrations of ferric iron showed that the half-wave potentials and the shape of the polarograms were independent of the concentration of the metal ions. The limiting current was always directly proportional to the concentration of metal ions in the solution.

An increase of the height of the mercury reservoir increased all the polarographic waves, irrespective of pH and metal ion and ligand concentrations. The wave height was proportional to the square root of the mercury height (studied in the range from 35 to 65 cm) when this had been corrected for "back pressure". This indicates the processes to be diffusion controlled.

The measurements reported above were repeated at least two more temperatures. Only small temperature coefficients of half-wave potentials and diffusion currents were observed.

DISCUSSION

As seen in Fig. 1, the half-wave potential for the reduction of the complex is independent of pH at pH values above 9. This indicates that protons are not involved in the reaction. Table 3 shows that the electrode reaction is essentially independent of the concentration of the ligand. It may therefore by concluded that the elctrode reaction is:

$$FeX^- + e^- \rightleftharpoons FeX^{2-} \tag{1}$$

There is no evidence of formation of polynuclear complexes as the half-wave potentials are independent of the concentration of metal ions. In the reversible electrode process above, the following equation for the polarographic reduction is valid:

$$(E_{\frac{1}{2}})_c = (E_{\frac{1}{2}})_s - 0.0591 \log (K_{ox}/K_{red}) \tag{2}$$

(A term with diffusion coefficient ratio of the reduced and oxidized complexes is omitted, as this has no significance in this case. From diffusion current constants reported below, this ratio is found to be only 1.19.)

In eqn. (2), $(E_{\frac{1}{2}})_c$ and $(E_{\frac{1}{2}})_s$ are the half-wave potentials of the iron-EHPG system (1) and of the aqua ferric-ferrous system, respectively. K_{ox} and K_{red} are the stability constants of the ferric and ferrous complexes respectively. As no amalgam is formed, $(E_{\frac{1}{2}})_s$ may be identified with the formal potential of the aqua ferric-ferrous couple at 25°C, taken to be 0.771 V vs. N.H.E., or 0.529 V vs. S.C.E. This leads to a value for the ratio K_{ox}/K_{red} of $10^{19.60}$. By means of the reported value [6] of $K_{ox} = 10^{33.86}$, the stability constant K_{red} is:

$$K_{red} = \frac{[FeX^{2-}]}{[Fe^{2+}][X^{4-}]} = 10^{14.26} \tag{3}$$

The very high stability of the ferric complex as compared with the ferrous complex explains the impossibility of isolating the ferrous complex in studies of its properties as reported by Frost et al.[5] In order to eliminate the possibility that oxidation from a ferrous to a ferric complex could be due to traces of oxygen impurities in the nitrogen gas used, these researchers repeated the titration in an atmosphere of hydrogen in the presence of a suspended palladium catalyst, but the titration curves remained essentially unchanged, and it was concluded
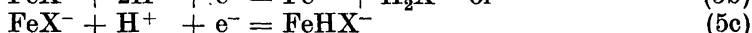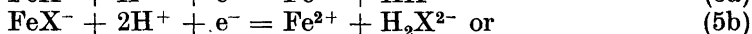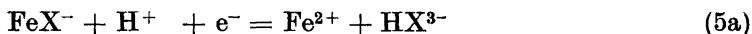
that the oxidation of the divalent metal apparently occurs through the decomposition of some of the ligand or of the solvent. The present author investigated the shape of polarograms recorded from alkaline solutions of the ferric complex after reduction at -1.0 V (S.C.E.) by means of a potentiostat. The electrodes were inserted directly into the polarographic cell, and stirring during the electrolysis was done with nitrogen-bubbling; the working cathode was a platinum-wire. An external Ag/KCl working anode was used, connected to the polarographic cell by means of an agar/KCl bridge. The reduction to the ferrous complex was complete after $1^1/_2$ h, as determined from the fact that the polarograms were completely anodic. Reversibility was further proved by the exact coincidence of the anodic and cathodic half-wave potentials. Polarograms were recorded after 4 h with almost complete absence of cathodic current, and this should indicate that the ferrous complex is a stable compound in aqueous solutions. However, its very great affinity to air oxygen makes direct studies of the compound very difficult. The diffusion current constants were measured to 1.33 and 1.22 for the anodic and cathodic waves in 0.1 M NH_3-NH_4Cl buffer with 5.0×10^{-4} M Fe^{3+} and 5.0×10^{-3} M EHPG. The currents were measured at -0.40 V and -0.80 V, respectively.

In highly alkaline solutions, the slope of the curve in Fig. 1. increases, which indicates that protons are then involved in the electrode reaction, which probably is:

$$Fe(OH)X^{2-} + H^+ + e^- = FeX^{2-} + H_2O \qquad (4)$$
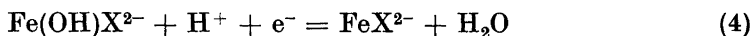
The existence of such a ferric complex has been discussed by Frost et al.[5]

For solutions with pH values below 9, half-wave potentials are strongly dependent on pH, and probably correspond to electrode reactions of the kind:

$$FeX^- + H^+ \quad + e^- = Fe^{2+} + HX^{3-} \qquad (5a)$$
$$FeX^- + 2H^+ + e^- = Fe^{2+} + H_2X^{2-} \text{ or} \qquad (5b)$$
$$FeX^- + H^+ \quad + e^- = FeHX^- \qquad (5c)$$
$$FeX^- + 2H^+ + e^- = FeH_2X \qquad (5d)$$

The slopes at pH values corresponding to these reactions are shown in Table 1. As seen in Table 3, in the case of solutions with low pH, the half-wave potentials of the reaction shift to more negative values with increasing concentrations of the ligand. This indicates the formation of uncomplexed (solvatized) ferrous iron and liberation of (protonized) ligand (reactions 5a and b). The shift of the half-wave potentials to positive values with increasing concentration of acetate ions (Table 2) might be due to a formation of a ferrous acetate complex; also this indicates the electrode reaction to be 5a and b.

Preliminary to the above experiments, the complexes were studied in perchlorate media to avoid complex formation with buffer anions. It was of interest to observe that the reduction was apparently irreversible in neutral and acid perchlorate media. Different authors have discussed the more general rules for the reversibility of the reduction of metal complexes.[10,11] In the case of complexones, it is claimed that irreversibility often occurs when hexadentate complexes are reduced directly to the metallic state or to amalgam. However, reduction from one oxidized state to another may occur reversibly in the case of one electron processes, particularly when the compounds have equal stoi-

chiometric composition, and when there is no change in spin state from one compound to the other. In the present case, the principles above would indicate irreversibility in neutral and acid solutions — as is also apparently shown by the experiments. However, an oscillopolarographic study of the complex in pechlorate media, with curves recorded from various solutions with pH values from 3 to 12, gave in all experiments two exactly coinciding sets of anodic-cathodic incisions. Blanks indicated that the most positive incision pair was due to the ferric-ferrous couple. (The more negative one results from the EHPG.) This indicates reversibility at all pH values. As protons are involved in the reactions in neutral and acid media, the apparent irreversibility in d.c. polarography must be due to a buffer effect, the pH value being different at the mercury surface and in the bulk of the solution. In oscillographic polarography with alternating current, protons liberated in one cycle will react in the next and opposite one. During the reaction no protons are liberated, and reversible processes are therefore observed at all pH values.

REFERENCES

1. Knell, M. and Kroll, H. U. S. Patent 2,921, 847 (1960).
2. Underwood, A. L. *Anal. Chem.* **30** (1958) 44.
3. Underwood, A. L. *Anal. Chem. Acta* **20** (1959) 228.
4. Hill-Cottingham, D. G. *Analyst* **1957** 524.
5. Frost, A. E., Freedman, H. H., Westerback, S. J. and Martell, A. E. *J. Am. Chem. Soc.* **80** (1958) 530.
6. Schrøder, K. H. *Nature. In press.*
7. Sympson, R. F. and Caldwell, V. E. *Chemist-Analyst* **49** (1960) 19.
8. Hoyle, W. and West, T. S. *Talanta* **2** (1959) 158.
9. Hoyle, W. and West, T. S. *Talanta* **3** (1959) 47.
10. Pribil, R. *Komplexone in der chemischen Analyse*, VEB. Deutscher Verlag der Wissenschaften, Berlin 1961, p. 52.
11. Schläfer, H. L. *Komplexbildung in Lösung*, Springer Verlag, Heidelberg 1961, p. 217.