Electrochemical studies on copper(II) glucuronate

R PAYNE and R J MAGEE*

Department of Inorganic and Analytical Chemistry, La Trobe University, Bundoora,
Melbourne, Victoria, Australia 3083

Abstract. The complexes formed in the interaction of the copper(II) ion with
glucuronic acid over the pH range 4·0-11·0 were investigated using d.c. polaro-
graphy, cyclic voltammetry and chronoamperometry. It was found that below
about pH 6·1 no complex forms, while in the pH range of approximately 6·2-7·4
and again 7·5-9·8 stable complexes were formed in solution. At high pH values,
the complexes appear to break up. The complex formed in the pH range 6·2-7·4
was studied and stability constants determined by two different methods.

Keywords. Electrochemical investigation; polarography, cyclic voltammetry;
stability constants; copper(II) glucuronate.

1. Introduction

In investigations on the uptake of copper by certain bacteria (Payne *et al* 1981)
a copper complex of glucuronic acid was isolated and the structure compared
with that of model compounds. As a result of these investigations, it became
necessary to investigate the interaction of copper(II) ions with glucuronic acid
over a wide pH range. This study was carried out using electrochemical techniques.
While a number of reports have appeared (Biswas *et al* 1978 ; Rajan and Martell
1967) on the polyhydroxy acids and their complexes with Cu(II), particularly
citric and tartaric acids, little work has been reported on the copper complexes
of the uronic acids in general and glucuronic acid in particular. Makridou
et al 1977 have studied the formation of complexes of the types MA and MA'
between different metal ions, including Cu(II), and glucuronic acid and galacturonic
acid by a potentiometric method. They determined stability constants and
concluded that the metal complexes of galacturonic acid are more stable than
those of glucuronic acid.

In the present paper, the results of a study on the formation of complexes
between the Cu(II) ion and glucuronic acid, using polarography methods, are
presented.

2. Experimental

The polarographic, cyclic voltammetric and chronoamperometric studies were
carried out on the AMEL 471-Multipolarograph System and the Princeton Applied

---

*To whom all correspondence should be made.

Research (PAR) 170 Electrochemistry System. Results were plotted on a Hewlett-Packard 7040A $X-Y$ Recorder. pH was recorded on an ETI572 Digital pH meter. The polarographic cell had a three electrode configuration consisting of a saturated calomel reference electrode and a platinum counter electrode. For the d.c. polarographic measurements a glass capillary dropping electrode (DME) was used : for the cyclic voltammetric and chronoamperometric measurements the hanging mercury drop electrode (HMDE) was used. Experiments were also carried out using a glassy carbon electrode. All polarographic and cyclic voltammetric data were obtained at $25 \pm 0 \cdot 02^\circ$ C, solutions being deoxygenated with pre-dried, oxygen-free nitrogen.

Sodium glucuronate was either prepared by direct titration of the acid with sodium hydroxide solution or was purchased directly (Sigma Chemicals). In both cases, the product was recrystallised. Copper nitrate was used as the source of Cu(II) ions. Stock solutions of copper nitrate were standardized by titration with EDTA using a potentiometric end-point determination. All results were obtained at an ionic strength of $0 \cdot 74$ M (NaClO$_4$). pH values were checked before and after recording voltammograms.

3. Results and discussion

3.1. *Polarographic investigations*

$3 \cdot 1$a *Effect on $E_{1/2}$ of variation in pH* : With the polarographic cell containing $6 \cdot 25 \times 10^{-3}$ mol dm^{-3} Cu^{2+}, a ligand concentration of $0 \cdot 237$ mol dm^{-3} and $0 \cdot 5$ mol dm^{-3} of NaClO$_4$, the pH was varied over the range $4 \cdot 0$–$9 \cdot 8$. In each case, polarograms were obtained in the potential range $+0 \cdot 2$ to $-0 \cdot 700$ volt. In the range pH $4 \cdot 0$ to about $6 \cdot 3$ or $6 \cdot 4$, one wave (wave I) was obtained with an $E_{1/2}$ value around $-0 \cdot 02$ to $-0 \cdot 03$ volt and was clearly indicative of Cu(II) in a 2-electron reduction step. Around pH $6 \cdot 4$, a second wave (wave II) began to appear in addition to and following wave I. As the pH was increased, wave II increased steadily in height, while wave I decreased in height. Maximum development of wave II appears to be around pH $7 \cdot 4$. At this pH, a very small residual first wave (wave I) at $E_{1/2} \cong -0 \cdot 036$ volt still persisted with wave II showing an $E_{1/2}$ around $-0 \cdot 14$ volt. However, beyond pH $7 \cdot 4$, the residual first wave disappeared and a third wave (wave III) now began to develop more negative than wave II ($E_{1/2} \cong -0 \cdot 36$ volt). Both wave II and wave III existed together up to about $9 \cdot 8$: however, wave II gradually decreased in height, while wave III increased in height with increasing pH. At high pH values, waves II and III disappeared and a new wave (wave IV) with $E_{1/2}$ around $+0 \cdot 102$ developed. Examples of the development of the waves mentioned above are shown in figure 1 (a), (b), (c), (d).

In the pH range $4 \cdot 0$–$6 \cdot 3$, the single wave (wave I) present was shown to be due to the reduction of free Cu^{2+} ion (figure 1a) i.e., no complex is formed in acidic solution between Cu^{2+} and glucuronic acid. In the range pH $6 \cdot 4$–$7 \cdot 4$, the first wave is due to reduction of Cu^{2+}, while the second wave (wave II) is indicative of the presence of a copper glucuronate complex (figure 1b). The third wave which appears after pH $7 \cdot 4$ may indicate the presence of a new copper complex which is forming preferentially at the higher pH. Above about pH $9 \cdot 8$, the
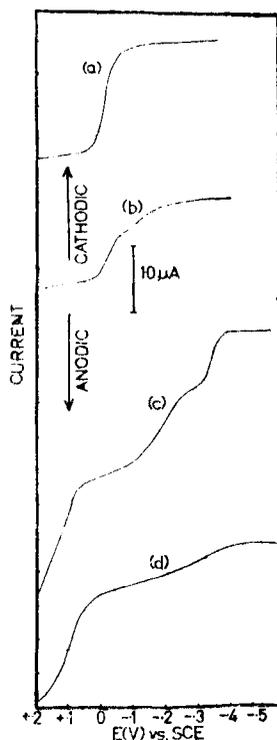
Figure 1. D.C. polarograms at DME at varying pH values of Cu(II) glucuronate complexation in aqueous solution, $0 \cdot 5$ M $NaClO_4$. (a) pH $= 5 \cdot 74$; (b) pH $= 6 \cdot 4$; (c) pH $= 8 \cdot 70$; (d) pH $= 9 \cdot 70$. $T = 25^\circ$ C ; $h = 62 \cdot 0$ cm ; $0 \cdot 004\%$ Triton x-100 added.

appearance of wave IV appears to be indicative of the ligand itself. To check this assumption, polarograms of the ligand were obtained. At pH $11 \cdot 0$, a wave was obtained identical to that obtained for the solution which had the copper complex present (figure 1d). It is concluded that this wave may be due to the reduction of the ligand or a mercury complex formed by the ligand. It would appear then that at high pH values any copper complexes formed at lower pH values break up releasing the ligand.

3.2. *Wave II*

3.2a. *Variation of limiting current with height of Hg column* : Using the same concentration of Cu^{2+}, ligand and $NaClO_4$ as for the investigation of the effect of pH on $E_{1/2}$, the effect of the height of the mercury column on the limiting current of the copper complex formed around pH $7 \cdot 4$ was examined. Limiting currents for wave II were found to be proportional to $\sqrt{h}$ indicating diffusion control under the polarographic conditions.

3.2b. *Log plot analysis* : For the solution containing the copper-glucuronate complex at pH $7 \cdot 4$, a log plot analysis was applied to wave II. The plot of

E vs log $(i/id - i)$ gave a linear plot from which the slope (average of a series of results) was found to be $- 87$ mv, indicating a quasi-reversible reduction. Assuming a value of a not too different from $0 \cdot 5$, gives a value of $n \cong 2$ for the number of electrons involved in the reduction.

3·2c. $E_{1/2}$ *vs* log *C* (*x*): With the pH at 7·4, the effect of change in the concentration of ligand on $E_{1/2}$ was examined. A linear plot was obtained indicating the presence of a single complex at this pH. From the relationship

$$\Delta E_{1/2} = \frac{0 \cdot 0591}{n} \log \beta - \frac{0 \cdot 0591}{n} p \cdot \log (C (x)).$$

the value p (number of ligands coordinated to metal ion) and log β were determined using the slope and intercept of the straight line plot.

The value obtained for p was approximately 2 (1·85). For the stability constant determination (log β), a standard pH titration method was also carried out for comparison with the polarographic method and the copper complexes of glutamic acid were also determined by both methods. The basis of the pH titration method, as given by Albert and Sargent (1971) is that the average number of ligands bound by one atom of the metal is defined as

$$\bar{n} = \frac{\text{moles of bound ligand}}{\text{total moles of Cu}^{2+}} = \frac{[\text{Cu (gluc)}^+] + 2 [\text{Cu (gluc)}_2]}{[\text{Cu}^{2+}] + [\text{Cu (gluc)}^+] + [\text{Cu (gluc)}_2]} .$$

This may be re-written in terms of stability constants as

$$\bar{n} = \frac{K_1 (\text{gluc}^-) + 2K_1 K_2 (\text{gluc}^-)^2}{1 + K_1 (\text{gluc}^-) + K_1 K_2 (\text{gluc}^-)^2} = \frac{\beta_1 (\text{gluc}^-) + 2\beta_2 (\text{gluc}^-)^2}{1 + \beta_1 (\text{gluc}^-) + \beta_2 (\text{gluc}^-)^2} .$$

On re-arranging we get

$$\frac{\bar{n}}{(1 - \bar{n}) (\text{gluc}^-)} = \beta_1 + \frac{(2 - \bar{n}) (\text{gluc}^-)}{(1 - \bar{n})} \beta_2.$$

A plot of $\bar{n}/(1 - \bar{n}) (\text{gluc}^-)$ *vs* $(2 - \bar{n}) (\text{gluc}^-)/(1 - \bar{n})$ should give a straight line of intercept β_1 and slope β_2.

In the present work, a computer was used to determine the stability constants instead of using the graphical plot. Results are shown in table 1.

Table 1. Stability constants of Cu(II) glucuronate and glutamate.

Complex	Method			Literature values
	Polarography	pH titration		
Cu glucuronate	log β_1 ..	1·01	1·48	
	log β_2 4·100	4·103	..	Makridou *et al* 1977
Cu glutamate	log β_1 ..	8·314	8·20	
	log β_2 14·600	14·921	15·1	Shah *et al* 1980

Table 2. Effect of pH on $E_{1/2}$ value of wave II.

pH	$E_{1/2}$	pH	$E_{1/2}$
6·3	..	7·05	−0·147
6·5	−0·094	7·15	−0·150
6·7	−0·136	7·25	−0·154
6·85	−0·141	7·5	−0·161
6·95	−0·143	8.1	

3.2d. $E_{1/2}$ *vs pH* : For wave II, the pH was varied from the value at which the wave first appeared until its disappearance at the higher pH. For each pH the $E_{1/2}$ value was determined. The variation of $E_{1/2}$ with pH is shown in table 2. From the plot of $E_{1/2}$ *vs* pH a straight line resulted. Now,

$$E_{1/2} = E^0 - \frac{0 \cdot 0591}{n} m \, \text{pH} + \frac{0 \cdot 0591}{n} \log \left(\frac{f_0 C_0}{f_r C_r} \right).$$

Thus, from the slope of the plot which is equal to $- 0 \cdot 591/n \cdot m$, m = number of hydrogen ions involved may be determined. The average of a number of experiments gave a value of $m \cong 2$.

3.3. *Wave III*

As indicated earlier, this wave which appears above pH 7·5 may possibly be the result of the formation of a second complex. Attempts were made to apply the same sort of tests to it as applied to wave II. However, difficulties were always experienced in deciding the point at which the wave began as it followed so closely on wave II. Log plot analyses indicated a value between 1 and 2 electrons for the number of electrons involved in the reduction and there was evidence for considerable irreversibility.

4. Cyclic voltammetry

Cyclic voltammograms were obtained at varying pH values, under the same conditions as used for the d.c. polarographic studies discussed above. Figure 2 (a), (b), (c) shows the results obtained. Below pH $\cong$ 6·1, a voltammogram with one cathodic peak and one anodic peak (figure 2a) was obtained. This voltammogram showed clearly that only free Cu^{2+} ions were present in the solution. Above pH 6·3 a second cathodic peak appeared and by pH 7·4 this was the only cathodic peak ; the first wave due to Cu^{2+} had disappeared. Figure 2b shows the voltammogram at pH 7·4. The cathodic peak at E_p approximately − 0·14 volt corresponds to reduction of the same copper complex observed in the polarographic study at this pH. The anodic peak (I_{p_a}) corresponds to the main reduction wave (I_{p_a}) and indicates a quasi-reversible electrode reaction, in agreement with the polarographic findings. A second small anodic peak (II_{p_a})
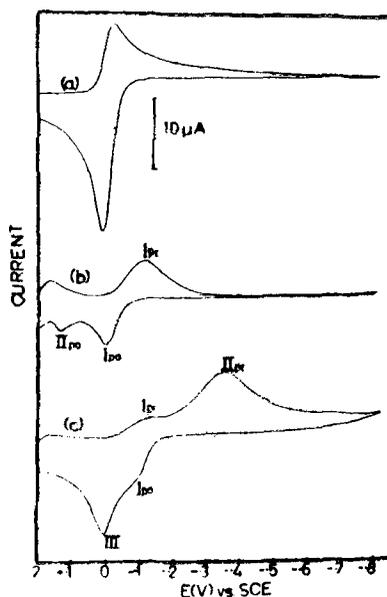
Figure 2. Cyclic voltammograms at HMDE (scan rate — 20 mV/sec, $T = 25°C$) in aq. solution, 0·5 M $NaClO_4$ in presence of nitrogen at varying pH values. (a) pH = 5·74 ; (b) pH = 7·40 ; (c) pH = 8·70.

for which there is no corresponding cathodic wave was found and is thought to be due to oxidation of the ligand or a mercury complex of free ligand. Accordingly, cyclic voltammograms were obtained for the free ligand. As expected, a peak was obtained exactly at the same peak potential as the anodic peak in figure 2b, confirming that this peak is caused by oxidation of the ligand.

The data for peak I_{p_a} at different scan rates is shown in table 3. Figure 2c shows the cyclic voltammogram at pH 8·5 of the copper-glucuronic acid system. Two cathodic peaks are present, the first, very small one at $E_p \cong -0·14$ (I_{p_c}) representing a residual part of the complex which forms between pH 6·1 and 7·4. The second cathodic peak with E_p around $-0·4$ (II_{p_c}) is the major peak in the voltammogram and represents the complex which forms at pH values greater than 7·4. The absence of a corresponding anodic peak for the cathodic peak II_{p_c} indicates that the electrode reaction is irreversible. For the small cathodic peak, I_{p_c}, a corresponding anodic peak is discernible (I_{p_a}) as a shoulder on a larger anodic peak (III_{p_a}). This again indicated the quasi-reversible nature of the electrode reaction of this complex. The large anodic peak (III_{p_a}) found in the voltammograms is of interest. There appears to be no corresponding cathodic peak at any scan rate. Initially it was supposed that it was due to oxidation of free ligand or a mercury complex of the ligand. However, experiments carried out with the free ligand indicated that it was not a ligand peak. On further investigation, it was found that this peak of sharp symmetry increased in magnitude with increasing scan rate and decreasing concentration, thus showing characteristics of adsorption waves. Further, anodic potentials became more negative with increasing scan rate.

Table 3. Effect of voltage scan rate on wave II.

Scan rate V sec^{-1}	E_{pc} vs SCE 0·005 V	E_{pa}	ΔE_p (mV)	I_{pc}	I_{pa}	$\dfrac{I_{pa}}{I_{pc}}$
0·002	−0·144	−0·064	80	0·425	0·689	1·62
0·005	−0·148	−0·064	84	0·453	0·709	1·57
0·01	−0·156	0·068	88	0·709	0·709	1·00
0·02	−0·154	−0·062	92	0·866	0·778	0·898
0·05	−0·158	−0·065	93	0·900	0·720	0·800
0·10	−0·160	−0·066	94	1·024	0·787	0·762
0·20	−0·180	−0·060	118	1·732	1·339	0·760

5. Chronoamperometery

Chronoamperograms were recorded for the complex formed around pH 7·4 by applying a voltage on the plateau of wave II to the HMDE. The derived "current *versus* time$^{-1/2}$ plot" was a straight line. This linear i versus $t^{-1/2}$ plot shows that the electrode reaction responsible for wave II is diffusion controlled and that there is no preceding chemical reaction coupled with the electron transfer process.

References

Albert A and Sargeant E P 1971 *The determination of ionisation constants* (London : Chapman and Hall)

Biswas S P, Krishnamoorthy T S and Venkateswarlu Ch 1978 *Indian J. Chem.* A16 972

Makridou C, Cromer–Morin M and Scharff J P 1977 *Bull. Soc. Chim. Fr.* 1–2 Part 1 59

Payne R, Magee R J, Sarode R and Rao C N R 1981 *Inorg. Nucl. Chem. Lett.* 17 125

Rajan K S and Martell A E 1967 *J. Inorg. Nucl. Chem.* 29 463

Shah S K, Suyan K M and Gupta C M 1980 *Talanta* 27 455