

Electrochemical reduction of copper(II) galacturonate

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MS received 18 February 1982

Abstract. The complexes formed in the interaction between copper(II) and α - and β -galacturonic acid, in the pH range 2.5-11.0, have been investigated by means of d.c. polarography and cyclic voltammetry. With α -galacturonic acid, no complex is formed with copper up to pH 6. Between pH 6 and about 9.5, a complex is formed in solution. Above pH 9.5, the complex appears to break up releasing the ligand. In the case of β -galacturonic acid, no complex is formed until pH 3.5, and persists in solution up to a pH of about 9.5. A second complex forms above pH 6.9 and co-exists with the first complex up to pH 9.5. The complexes formed with both forms of galacturonic acid were studied and the stability constant of the copper α -galacturonate determined.

Keywords. Electrochemical studies ; polarography ; cyclic voltammetry ; stability constant ; copper(II) α - and β -galacturonate.

1. Introduction

As a result of investigations on the method of uptake of copper by certain types of bacteria (Payne *et al* 1981) in which the metallic species was found to be bound to uronic acids, it was necessary to investigate the interaction of copper(II) with galacturonic acid over a wide pH range. In a recent report (Payne and Magee 1982), the authors have presented results for the reaction of copper(II) with glucuronic acid. In the present paper, a similar study for copper(II) and galacturonic acid is reported.

2. Experimental

Polarographic and cyclic voltammetric studies were carried out on the AMEL 471-Multipolarograph System and the Princeton Applied Research (PAR) 170 Electrochemistry System. Results were plotted on a Hewlett-Packard 7040 A X-Y Recorder. pH was recorded on an ET1572 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 studies, the hanging mercury drop electrode (HMDE) was used.

All polarographic and cyclic voltammetric data were obtained at $25 \pm 0.02^\circ \text{C}$, solutions being deoxygenated with pre-dried oxygen-free nitrogen. Optical rotation measurements on galacturonic acid were carried out using a Perkin-Elmer 141 Polarimeter. Galacturonic acid exists in the α - and β -form, with the following properties :

α -galacturonic acid	Mpt 159°C	Optical rotation $+107 \rightarrow 51.9^\circ (\text{H}_2\text{O})$
β -galacturonic acid	Mpt $164\text{--}166^\circ \text{C}$	Optical rotation $+31.1 \rightarrow 56.7^\circ$

Galacturonic acid (Sigma) which was mainly in the α -form was purified to give the pure α -form of the acid using the method of Isbell and Frush (1943). Similarly, the β -form was obtained in a pure state. The purity of both forms were checked by optical rotation measurements and by means of the melting points. From the β -form, sodium galacturonate was prepared by direct titration of the β -galacturonic acid with sodium hydroxide. However, α -galacturonic acid was used as the acid without conversion to the sodium salt, as it has been shown (Isbell and Frush 1943) that sodium galacturonate consists of the β -D-galacturonic acid.

Copper nitrate was used as the source of Cu(II) ions. Stock solutions of copper nitrate were standardised with EDTA using a potentiometric end-point determination.

All results were obtained at an ionic strength of 0.74 M NaClO_4 . pH values were checked before and after recording the voltammograms.

3. Results and discussions

3.1. Studies on α -galacturonic acid

3.1a *Polarographic investigations—the effect of pH on $E_{1/2}$ values* : To 30 ml of 0.276 M α -galacturonic acid and 1 ml of a $2 \times 10^{-2} \text{ M}$ solution of copper nitrate in a polarographic cell was added 9.0 ml of 2.822 M NaClO_4 solution. The pH was varied over the range 2.5–11.0. In each case polarograms were recorded in the potential range $+0.2$ to -0.7 volt.

Up to pH 6, a single wave (wave I) was obtained, which was clearly indicative of the reduction of free Cu(II) ions in a 2-electron reduction step (figure 1a). At pH 6, a second wave (wave II) began to appear following wave I, with $E_{1/2} \cong -0.145 \text{ V}$ (figure 1b). As the pH was increased, wave I decreased in size, while wave II continued to increase. By pH 8.0, the free Cu(II) wave had disappeared, but wave II persisted up to a pH of about 9.5 (figure 1c). Over the pH range, the $E_{1/2}$ of wave II varied from -0.145 to -0.197 volt. Above pH 9.5, wave II began to disappear rapidly due to the growth of a wave which was suspected to be a ligand wave (figure 1d). Investigations carried out on the ligand alone and in the presence of Cu(II) at pH 10.00 confirmed the presence of a large ligand wave.

3.2. Wave II

3.2a. *Variation of limiting current with height of Hg column* : The effect of height of the Hg column on the limiting current of wave II was examined. Limiting currents were found to be proportional to \sqrt{h} , indicating diffusion control.

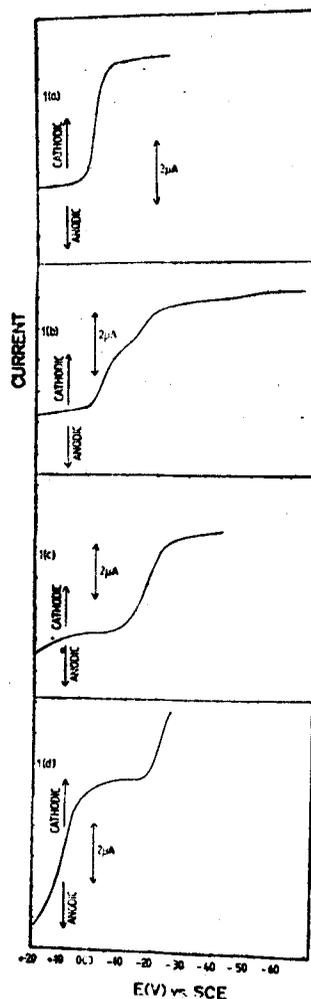


Figure 1. D.C. polarograms at DME at varying pH values of Cu^{II} -galacturonate (a) complexation, 0.635 M NaClO_4 . $T = 25.0^\circ \text{C}$, $h = 62.0 \text{ cm}$; 0.008% Triton X-100 added. (a) $\text{pH} = 4.51$; (b) $\text{pH} = 6.46$; (c) $\text{pH} = 8.92$; (d) $\text{pH} = 9.92$.

3.2b. *Log plot analysis*: Using the same conditions as above ($\text{pH} 8.9$), a log plot analysis was applied to wave II. The plot of E vs $\log(i/i_d - i)$ gave a straight line with a slope of -31 mV , which gives a value of $n = 2$ for the number of electrons involved in the reduction.

3.2c. $E_{1/2}$ vs $\log C(X)$: With the pH at 8.2 , the effect of change in concentration of ligand on $E_{1/2}$ was examined. A linear plot was obtained over the concentration range 0.0 to 0.276 M in α -galacturonic acid. The copper concentration was held at $5 \times 10^{-4} \text{ M}$. The linear plot indicates the presence of a single complex formed at this pH , i.e. for wave II. From the relationship

$$\Delta E_{1/2} = \frac{0.0591}{n} \log \beta - \frac{0.0591}{n} p \log C(X)$$

the values of p (number of ligands coordinated to the metal ion) and $\log \beta$ (the stability constant) were determined using the slope and intercept, respectively, of the straight line plot. $\log \beta_1$ was calculated to be 1.83, which compares favourably with the value obtained by Makridou *et al* (1977) ($\log \beta_1 = 1.81$) by a potentiometric method and confirms (Makridou *et al* 1977) that the copper complex formed with α -galacturonic acid is more stable than that formed with β -glucuronic acid.

The value of p was calculated to be approximately 2 (1.95).

3.2d. $E_{1/2}$ vs pH: In the region at which wave II forms, the pH was varied from pH 6.0 to 11.0. At each pH, the $E_{1/2}$ value was determined and a plot of $E_{1/2}$ vs pH obtained. The plot was curved but consisted of two distinct linear portions. The first over the pH range of 6.0 to approximately 9.0; the second at pH values greater than pH 9.0. The two straight lines were analysed using the relationship

$$E_{1/2} = E^\circ - \frac{0.0591}{n} m \text{ pH} + \frac{0.0591}{n} \log \left(\frac{f_o C_o}{f_r C_r} \right).$$

From the slopes of the two plots, each of which is equal to $(-0.0591/n)m$, where m = number of hydrogen ions involved, m was calculated. For the pH region 6-9, i.e., the region in which the complex represented by wave II forms, m was found to be equal to 2. For the region pH > 9, i.e., the region in which the complex breaks up releasing the ligand, m was found to be equal to 1.

4. Cyclic voltammetry

Cyclic voltammograms were obtained under the same conditions as for the d.c. polarography, pH being varied over the range of 4-10. Figure 2 shows the results obtained. Below pH \approx 6.0, the voltammogram consisted of one cathodic peak (peak I_{pc}) and one anodic peak (peak I_{pa}) (figure 2a). The voltammogram showed clearly that only free Cu(II) ions were present in solution ($E_{pc} = -0.03$ V). Above pH 6 a second cathodic peak began to appear at a more negative potential than the Cu peak (peak II_{pc}). On the anodic sweep at this pH the main oxidation peak of copper was still present and no other major peak except the semblance of a peak with E_{pa} around +0.045 V (peak III) (figure 2b). As the pH was increased further, the second peak on the cathodic sweep increased in size with a corresponding reduction of the copper peak, until by about pH 8 it was fully developed ($E_{pc} = -0.205$ V) and the copper peak had disappeared. On the anodic sweep one major peak was present: this did not occur at the same potential as the original copper oxidation peak but, although close was at a more negative potential ($E_{pa} \approx -0.025$ V). The same small peak ($E_{pa} \approx +0.065$ V) as mentioned above still persisted but was more clearly marked (figure 2c). Above pH 9, there were clear indications of the break up of the complex (figure 2d) with a rapid decrease in the major cathodic and anodic peaks obtained at the lower pH values and the rapid increase of a peak with E_{pc} around +0.09 V. This was found to correspond to the free ligand. At first sight, it looked as if the reduction represented by peak II (i.e. wave II in d.c. polarography) was irreversible as there appeared to be no current on the anodic sweep. However, on further investigations during

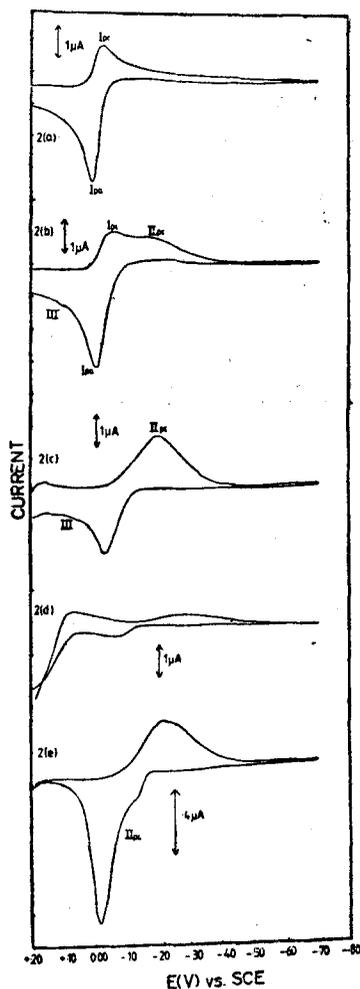


Figure 2. Cyclic voltammograms at HMDE (scan rate -0.020 v/s, $T = 25$ °C), 0.635 M NaClO_4 in the presence of nitrogen at varying pH values. (a) pH = 4.27; (b) pH = 6.81; (c) pH = 8.0; (d) pH = 9.57; (e) pH = 8.0.

which the scan rate was varied, it was found that at very slow scan rates, the major anodic peak at $E_{pa} \cong +0.025$ V had a shoulder ($E_{pa} = -0.138$ V) which disappeared at faster scan rates (figure 2e). It would appear that this anodic peak is the oxidation peak of the main reduction peak (peak II) ΔE_p , averaged over a number of experiments was found to be 83 mV indicating a quasi-reversible reaction in agreement with d.c. polarography. The main anodic peak ($E_{pa} \cong +0.25$ V) was examined more closely. It was found that this peak of sharp symmetry increased in magnitude with increasing scan rate and decreasing concentration while anodic potentials became more negative with increasing scan rate. This peak, therefore, showed the characteristics of an adsorption wave.

The small anodic peak which appears constantly in the voltammograms above pH 6 until the complex breaks up, was thought to be due to oxidation of a mercury

complex of the ligand or the ligand itself. On examination of the free ligand a peak was obtained at the same potential.

5. Studies on β -galacturonic acid

5.1. Polarographic investigations—the effect of pH on $E_{1/2}$ values

To 30 ml of 0.1309 M sodium galacturonate and 1 ml of a 2×10^{-2} M solution of copper nitrate in a polarographic cell was added 9.0 ml of 0.635 M NaClO_4 solution. The pH was varied over the range 2.5–11.0. In each case, polarograms were recorded in the potential range +0.2 to –0.700 volt.

In the pH range 2.5–3.5, a single wave (wave I) was obtained with $E_{1/2}$ around –0.03 volt. This wave was clearly indicative of free Cu(II) in a 2-electron reduction step. Above pH 3.5, a second wave (wave II) (figure 3a) appeared

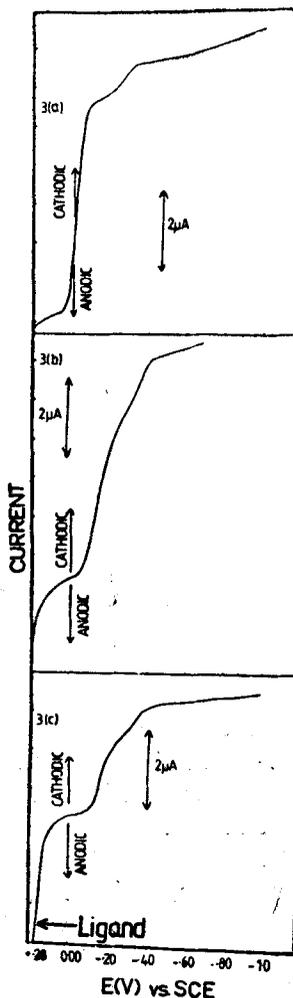


Figure 3. D.C. polarograms at DME at varying pH values of the complexation between Cu^{2+} and (β) galacturonate, 0.635 M NaClO_4 . $T = 25^\circ \text{C}$; $h = 62.0$ cm; 0.008% Triton X-100 added. (a) pH = 5.29; (b) pH = 7.00; (c) pH = 8.60.

following wave I and persisted up to pH values around 9. Above pH 6, wave I began to decrease, while a third wave (wave III) began to appear at pH values greater than 6.9 between wave I and wave II (figure 3b). Waves II and III existed together up to pH values greater than about 9. Both disappeared together at pH values greater than 9.5, being replaced by a single wave which was found to be due to the reduction of the ligand (figure 3c). Wave I never completely disappeared until, like waves I and III, it was replaced by the ligand wave. The polarography of the copper β -galacturonate was never as clear as that of the copper α -galacturonate: the waves tended to run into each other, making measurements difficult. $E_{1/2}$ values for the three waves varied as follows over the pH range studied—wave I -0.026 to -0.04 volt; wave II -0.292 to -0.311 volt; wave III -0.123 to -0.140 volt. It is presumed that waves II and III represent the formation of copper complexes of the β -galacturonic acid.

5. 1a. *Wave II*: The effect of height of the Hg column on the limiting current was examined and indicated diffusion control under the polarographic conditions. From a log-plot analysis, the number of electrons involved in the reaction was found to be 2, while the slope indicated a reversible reduction. Because of proximity of the waves it was not possible to determine unequivocally the effect of concentration of ligand on $E_{1/2}$.

6. Cyclic voltammetry

Cyclic voltammograms were obtained at varying pH values under the same conditions as used for the d.c. polarographic studies.

Below pH 3.5, the voltammogram showed only one peak, clearly indicating the presence of free Cu(II) ions (figure 4a). Above about pH 3.5 a second peak (peak II_c) appears existing alongside peak I due to the Cr(II) (figure 4b). Both peaks exist up to a pH greater than 5, when a third peak (peak III) begins to develop, initially as a shoulder on peak I (figure 4c).^{*} By pH 7.5–8.0 the free Cu(II) disappears leaving peaks II and III. Above pH around 9, peaks II and III decrease and are ultimately replaced by a ligand peak. At all stages of its development, peak III was small and broad, making measurements impossible.

For peak II, the effect of voltage scan rate was examined at a pH 6.9. Results are shown in table 1.

It will be seen that, in agreement with the polarographic data, the reduction is quite reversible at low scan rates.

On the anodic sweep of all the voltammograms, one large anodic wave is present. It is presumed that initially this represents the anodic oxidation of Cu(II) and an adsorption peak. At high pH values, when the copper cathodic peak has disappeared this anodic peak is still present and is an adsorption peak. However, unlike the situation with α -galacturonic acid, it was never possible to separate the adsorption peak and the electroactive peak.

^{*} The broken line represents the same voltammogram as the unbroken line, but on an expanded scale to emphasise the peaks.

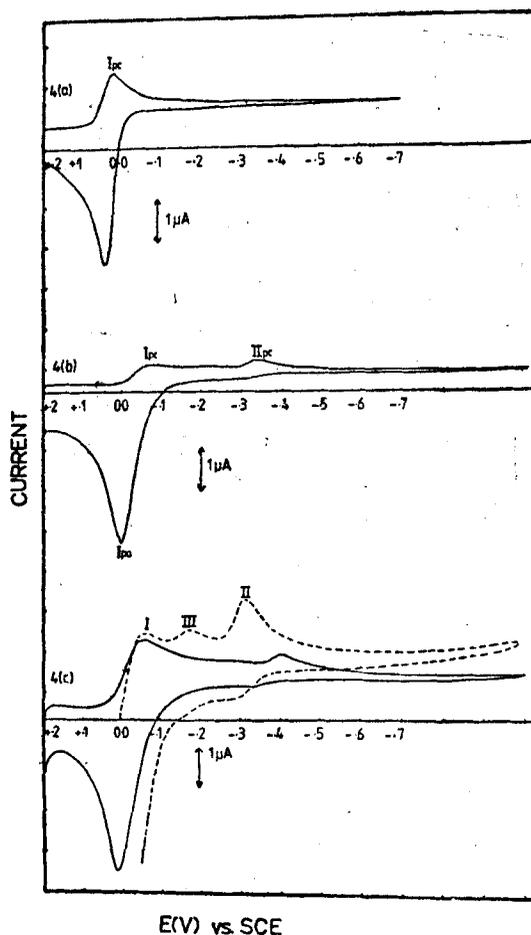


Figure 4. Cyclic voltammograms at HMDE (scan rate -20 mv/sec, $T = 25^\circ\text{C}$ in aq. solution, 0.635 M NaClO_4 in presence of nitrogen at varying pH values. (a) $\text{pH} = 3.0$; (b) $\text{pH} = 4.90$; (c) $\text{pH} = 6.87$.

Table 1. Effect of voltage scan rate on peak II.

Scan rate V sec^{-1}	E_{p_0} vs SCE $\pm 0.005\text{V}$	E_{p_0}	ΔE_p (mV)	I_{p_0} (ma) $\pm 0.05\text{ma}$	I_{p_0}	I_{p_0}/I_{p_0}
0.005	-0.329	-0.299	0.030	0.146	0.124	0.86
0.010	-0.330	-0.298	0.032	0.276	0.228	0.83
0.020	-0.331	-0.281	0.050	0.268	0.197	0.74
0.050	-0.350	-0.287	0.063	0.413	0.285	0.69
0.100	-0.359	-0.293	0.066	0.748	0.512	0.68
0.200	-0.379	-0.299	0.080	1.060	0.710	0.67
0.500	-0.394	-0.305	0.089	1.496	1.024	0.68

Comparison of the results obtained with copper and α -galacturonic acid and copper and β -glucuronic acid (Payne *et al* 1981) shows, especially in the cyclic voltammetric results, a remarkable similarity except for the fact that in the latter case, a third, irreversible peak is obtained above pH 7.4. However, in the case of copper and α -galacturonic acid, voltammograms at pH's > 7.6 do show a weak indication of a peak at $E_{p_0} > 0.3$ volt. This peak, however, never did achieve the magnitude of that for copper and β -glucuronic acid.

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