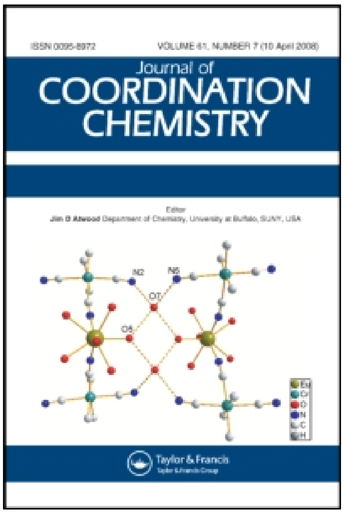

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POTENTIOMETRIC INVESTIGATION OF THE COPPER(II)-GLUCONATE SYSTEM IN ACID SOLUTION

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Complex formation between copper(II) and gluconate ions (L^-) has been investigated potentiometrically in aqueous acid solutions in the range $3.5 < -\log[H^+] < 6.5$ at 25° and in 1 M $NaClO_4$, by employing copper amalgam and glass electrodes. In the range $3.5 < -\log[H^+] < 4.5$ experimental data are entirely explained by assuming the formation of the mononuclear complexes CuL^+ and CuL_2, while in less acidic solutions the deprotonated mononuclear complexes $CuH_{-1}L$, $CuH_{-2}L^-$, $CuH_{-1}L_2^-$ are also formed and evidence is given for the existence of the polynuclear deprotonated complex $Cu_2H_{-3}L$. The formation constants of the various species have been calculated.

INTRODUCTION

Gluconate ion is an interesting polyhydroxy ligand; several studies have been carried out in this laboratory to investigate the equilibria between gluconate ions and metallic cations in aqueous solution. Complex formation with lead(II),[1] cadmium(II)[2] and calcium(II)[3] has already been studied by potentiometric method. For all these cations the results obtained in acid solution have been explained by assuming the formation of two mononuclear complexes ML^+ and ML_2 between the metal M^{2+} and the gluconate ion L^-, which binds only through the carboxylic group.

In order to check the behaviour of gluconate ion towards a transition element, for which the participation in complex formation of the alcoholic groups of the ligand could be postulated even in acid solution, we decided to investigate the copper(II)-gluconate system. A few papers have been published on the complex formation between copper(II) and gluconate ions in acid solution, mainly at unstated conditions of temperature and ionic strength. According to polarographic measurements carried out by Zolotukhin *et al.*,[4] no complex is formed below pH 3, the complex [†]$CuH_{-1}L_2^-$ forms at pH 4-5 while at pH 6-9 the complex $CuH_{-2}L^-$ predominates. Panda and Patnaik,[5] using potentiometric method with glass electrodes, found different complexes at different pH ranges. At pH 3.75 the species CuL^+ is present ($\log \beta_{1,0,1} = 1.60$ by assuming $\log \beta_{0,1,1} = 3.48$), which at higher pH deprotonates to $CuH_{-1}L$ ($\log \beta_{1,-1,1} = -3.20$) and to $CuH_{-2}L^-$ ($\log \beta_{1,-2,1} = -9.91$). Evidence for the existence of dimeric species was found only in strongly alkaline solution by Pecsok and Juvet[6] by means of polarographic, spectrophotometric and potentiometric measurements, and by Toy and Smith[7] by electron spin resonance. Therefore the copper(II)-gluconate system in acid solution is not yet fully explained, as some disagreement is observed between the results of the different authors.

To investigate this system in acqueous acid solution, potentiometric measurements were made in 1 M $NaClO_4$ at 25° by measuring the Cu^{2+} concentration with a copper

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[†] L^- = gluconate ion ($C_6H_{11}O_7^-$), B = total concentration of copper(II), b = free concentration of copper(II), A = total concentration of gluconate ions, a = free concentration of gluconate ions, H = analytical excess of hydrogen ions, h = free concentration of hydrogen ions, $\beta_{q,p,r}$ = formation constant of the complex $Cu_qH_pL_r$, defined by $\beta_{q,p,r} = [Cu_qH_pL_r]\, b^{-q}h^{-p}a^{-r}$ where $q > 1$, $p \geq 0$, $r > 1$ and electric charges are omitted.

amalgam electrode and the hydrogen ion concentration with a glass electrode. Measurements up to $-\log h < 6.5$ could be performed, as in a less acidic range the copper amalgam electrode is no longer Nernstian. As preliminary measurements showed a different experimental trend with varying hydrogen ion concentration, the data obtained at $-\log h < 4.5$ will be treated separately from those at higher $-\log h$ values.

EXPERIMENTAL

Material and Analysis

Sodium perchlorate, perchloric acid, sodium gluconate, sodium hydroxide, copper perchlorate and copper amalgam (2% by weight) were prepared and analysed as previously described.[1,8] The purity of the chemicals used was checked by differential pulse polarography on a concentrated solution of each reagent, employing an AMEL 471 multipolarograph. Nitrogen, used to avoid oxidation of the amalgam and the carbonation of the working solutions, was purified as previously described.[1]

Apparatus

All measurements were performed in a thermostated system at 25.00 ± 0.05° in a thermostated room. A cell arrangement similar to that of Forsling, Hietanen and Sillén[9] was employed, with an Ag/AgCl reference electrode prepared as described by Brown.[10] A Radiometer G202B glass electrode, previously calibrated against a hydrogen electrode, was used with a Radiometer PHM64 research pH meter. The potential of the copper amalgam electrode was measured by a Leeds and Northrup K5 potentiometer equipped with a Kipp and Zonen galvanometer.

Method of Investigation

Test solutions were made 1 M in Na^+ by adding $NaClO_4$ in order to minimize the variations of the activity coefficients. The hydrogen ion and copper(II) concentrations were respectively determined from the e.m.f. of the following cells:

$$(-)\mathrm{Ag/AgCl}/\begin{matrix}0.99\ \mathrm{M\ NaClO_4}\\ 0.01\ \mathrm{M\ NaCl}\end{matrix}/1\ \mathrm{M\ NaClO_4}/\mathrm{Solution}\ T/\mathrm{Glass\ electrode}\ (+)$$

$$(-)\mathrm{Cu(Hg)}/\mathrm{Solution}\ T/1\ \mathrm{M\ NaClO_4}/\begin{matrix}0.99\ \mathrm{M\ NaClO_4}\\ 0.01\ \mathrm{M\ NaCl}\end{matrix}/\mathrm{AgCl/Ag}\ (+)$$

The solution T had the general composition: B M in Cu(II), H M in H^+, A M in L^-, $[Na^+] = 1$ M, $[ClO_4^-] = (1 + 2B + H - A)$ M. In the course of each series of measurements, B was kept constant whereas h was gradually decreased. Measurements at B ranging from 0.5 to 5 mM in the range $3.5 < -\log h < 6.5$ were performed. In this concentration range the hydrolytic equilibria of Cu^{2+} are negligible according to Berecki-Biedermann.[11]

The measurements were made in a different way according to the $-\log h$ range investigated; in the more acidic range ($-\log h < 4.5$) A was gradually increased, while in the less acid solution A was kept constant (25-50-100 mM) and h gradually decreased by adding standard NaOH solution. The liquid junction potential E_j was a linear function of h according to the equation $E_j = -j\,h$, where $j = 45$ mV M^{-1}. The E_j values were determined by means of successive approximations.

RESULTS

In order to explain the experimental data in terms of complex formation between copper(II) and gluconate ions, for each experimental point the function $\eta = \log B/b$ was calculated. The free ligand concentration was obtained from the equation of the material balance of A, by using the value $\log \beta_{0,1,1} = 3.48 \pm 0.06$ previously determined under the same experimental conditions.[1]

Measurements at $3.5 \leqslant -\log h \leqslant 4.5$

Measurements at $B = 0.5$, 1.0, 2.0 and 5.0 mM were made for $A \leqslant 50$ mM. By plotting η *vs* $-\log a$, it results that for all the B values the experimental points fall on the same curve within experimental error; η is thus dependent only on a and polynuclear and deprotonated complexes are not present. Therefore the following equation can be written,

$$\eta = \log\left(1 + \sum_r \beta_{1,0,r} a^r\right) \qquad (1)$$

where $r \geqslant 1$ and a "curve fitting" method[12] may be employed to determine the nature of the mononuclear complexes and their stability constants. A good agreement was obtained between the experimental data and the normalized curve relevant to the formation of the complexes $\mathrm{Cu}L^+$ and $\mathrm{Cu}L_2$. In the case of the best fit, the following values were obtained: $\log \beta_{1,0,1} = 2.15 \pm 0.10$ and $\log \beta_{1,0,2} = 3.60 \pm 0.08$. These results were confirmed by the agreement between the experimental points and the theoretical curve calculated with the proposed $\beta_{1,0,r}$ values.

Measurements at $4.5 \leqslant -\log h \leqslant 6.5$

By plotting η *vs* $-\log h$ for every A value, it results that η depends both on B and h, being a decreasing function of h. Therefore in this acidity range polynuclear and deprotonated complexes are also present, and the following equation can be written,

$$B = b + \sum_q \sum_p \sum_r q\, \beta_{q,p,r} b^q h^p a^r \qquad (2)$$

where $q \geqslant 1$, $p \leqslant 0$ and $r \geqslant 1$. In order to determine q, p, r and $\beta_{q,p,r}$, corrected values of η (η_c) were calculated by subtracting from B the concentrations of $\mathrm{Cu}L^+$ and $\mathrm{Cu}L_2$. First the data relevant to $B = 0.5$ mM were treated, for which the concentrations of polynuclear complexes may be assumed negligible and $a \simeq A$. Thus the function η_c may be expressed as

$$\eta_c = \log\left(1 + \sum_p \sum_r \beta_{1,p,r} h^p a^r\right) \qquad (3)$$

where $p \leqslant 0$ and $r \geqslant 1$. By plotting η_c *vs* $-\log h$, different curves are obtained for each A value. Equation (*3*) can be rearranged to give (*4*)

$$Y = 10^{\eta_c - 1} a^{-1} h = \sum_p \sum_r \beta_{1,p,r} h^{p+1} a^{r-1} \qquad (4)$$

and by plotting Y *vs* h^{-1} parallel straight lines with positive slopes are obtained for each A. Therefore $q = 1, r > 1$ and the permitted p values are -1 and -2, deprotonated mononuclear complexes being present. The hypothesis of the formation of the complexes $CuH_{-1}L$, $CuH_{-1}L_2^-$ and $CuH_{-2}L^-$ is the simplest one consistent with the experimental data. In this case equation (*4*) yields (*5*).

$$Y = \beta_{1,-1,1} + \beta_{1,-1,2}\, a + \beta_{1,-2,1}\, h^{-1} \qquad (5)$$

The intercepts for $h^{-1} = 0$ provides the $\beta_{1,-1,1}$ and $\beta_{1,-1,2}$ values and the slope the value of $\beta_{1,-2,1}$. The following values were obtained: $\log \beta_{1,-1,1} = -3.47 \pm 0.10$, $\log \beta_{1,-2,1} = -8.82 \pm 0.10$ and $\log \beta_{1,-1,2} = -1.64 \pm 0.10$. By using these values, theoretical curves were calculated for $B = 0.5$ mM at each A value and were found in good agreement with the experimental points. A satisfactory agreement can also be obtained for $B = 1$ mM and $A = 50$ and 100 mM, whereas at the highest B values the data cannot be explained in terms of mononuclear complexes only. Actually, by subtracting from B the contribution of all the mononuclear complexes, significant η_c' values are obtained. By plotting these values *vs* $-\log h$, it results that η_c' is a function of B but not of A and parallel curves are obtained with a constant ratio $\Delta \log h / \Delta \log B = 1.5 \pm 0.1$. Thus the simplest hypothesis which can be made is the presence of a complex $Cu_2H_{-3}L$. The quantity $(10^{\eta_c'} - 1)/2bh^{-3}a$ is quite constant for all B and A values and gives the approximate value, $\log \beta_{2,-3,1} = -9.97 \pm 0.3$.

DISCUSSION

In the range $3.5 < -\log h < 6.5$ the following equilibria between copper(II) and gluconate ions are important.

$Cu^{2+} + L^- \rightleftharpoons CuL^+$	$\log \beta_{1,0,1} = 2.15 \pm 0.10$
$Cu^{2+} + 2L^- \rightleftharpoons CuL_2$	$\log \beta_{1,0,2} = 3.60 \pm 0.08$
$Cu^{2+} + L^- \rightleftharpoons CuH_{-1}L + H^+$	$\log \beta_{1,-1,1} = -3.47 \pm 0.10$
$Cu^{2+} + L^- \rightleftharpoons CuH_{-2}L^- + 2H^+$	$\log \beta_{1,-2,1} = -8.82 \pm 0.10$
$Cu^{2+} + 2L^- \rightleftharpoons CuH_{-1}L_2^- + H^+$	$\log \beta_{1,-1,2} = -1.64 \pm 0.10$
$2Cu^{2+} + L^- \rightleftharpoons Cu_2H_{-3}L + 3H^+$	$\log \beta_{2,-3,1} = -9.7 \pm 0.3$

As is shown in Figure 1, where the distribution curves of the mononuclear complexes are reported, the species CuL^+ and CuL_2 are predominant in the more acidic range where the gluconate behaves as a monodentate ligand binding Cu^{2+} through the carboxylic group only. In less acidic solution the deprotonated species are no longer negligible, (mainly $CuH_{-1}L_2^-$ and $CuH_{-2}L^-$), the alcoholic groups of the ligand being involved in coordination. It is noteworthy that deprotonated complexes *are* formed in acid solution, as the dissociation of the alcoholic groups of gluconate itself may be evidenced only in strongly alkaline solution.[13] Therefore, a transition element as copper(II) noticeably influences the reactivity of the alcoholic groups of the gluconate in acqueous solution, unlike other elements such as lead (II), cadmium(II) and calcium(II) for which only complexes such as ML^+ and ML_2 could be found. The stability of these complexes are compared in Table I. The gluconate binds copper(II) more strongly than calcium(II) and cadmium(II), and a little more strongly than lead(II). It is notable that formation of $CuH_{-2}L^-$ occurs instead of $CuH_{-2}L_2^{2-}$. This could be expected considering the excess of the ligand. For the

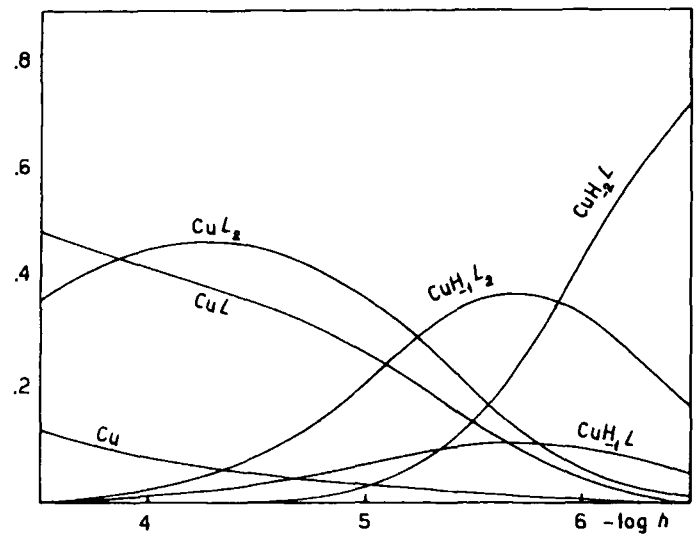

FIGURE 1 Distribution curves of the mononuclear copper(II)-gluconate complexes as a function of −log h at A = 50 mM. In the ordinate the fractions of metal ion present in the different complexes are given. Charges are omitted for simplicity.

complex CuH$_{-2}L^-$, which is predominant at the higher −log h values investigated, a lactonic structure implying the formation of a stable six-membered ring may be proposed.

By comparing our results with those reported in the literature, the formation of the complexes CuL^+, CuH$_{-1}L$, CuH$_{-1}L_2^-$ and CuH$_{-2}L^-$ is confirmed, while the complexes CuL_2 and Cu$_2$H$_{-3}L$ have not been previously reported. However our stability constants differ noticeably from those found by Panda and Patnaik,[5] mostly with respect to the complexes CuL^+ and CuH$_{-2}L^-$, probably because these authors measured only the hydrogen ion concentration. Undoubtedly, the copper(II)-gluconate system is a very complicated one. We believe that the equilibria of mononuclear complexes are now entirely explained, but conditions involving higher metal ion concentrations should be investigated in order to obtain more accurate information on the formation of polynuclear complexes in acid solution. The assumption of Cu$_2$H$_{-3}L$ complex formation must be considered as the simplest hypothesis which is consistent with the reported experimental data.

ACKNOWLEDGEMENT

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TABLE I
Stability constants of gluconate complexes with some cations in acid solution at 25° and in 1 M NaClO$_4$ (for Ca^{2+}, 0.5 M NaCl).

Cation	log $\beta_{1,0,1}$	log $\beta_{1,0,2}$
calcium(II)	1.05	1.88
cadmium(II)	1.15	2.08
lead(II)	2.13	3.35
copper(II)	2.15	3.60

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