# Thermochemical Studies on Metal Complexes

## III. The Complex Formation between Copper(II) Ions and Acetate Ions in Aqueous Solution at 25°C
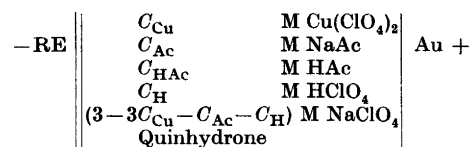
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The complex formation between copper(II) ions and acetate ions has been investigated previously, particularly by Fronæus,[1,2] who has made an exhaustive investigation with several methods using the ionic strength 1.00 M, sodium perchlorate as neutral salt, and a temperature of 20.0°C. From a comparison of reported stability constants of the lead(II) acetate system made by Gobom,[3] it is obvious that the ionic strength influences the stability in the range 1—3 M. To get results more comparable with some earlier measurements,[4] the copper(II) acetate system has been studied by a potentiometric titration method in an aqueous sodium perchlorate medium of ionic strength 3.00 M and a temperature of 25.0°C.

*Experimental. Chemicals. Copper(II) perchlorate* was prepared by dissolving CuO (Baker, *p.a.*) in excess of *ca.* 70 % $HClO_4$ (Baker, *p.a.*), and then evaporated with the acid until no chloride could be found. The stock solution was analysed by electrolysis, and the measuring solutions by EDTA using murexid as indicator. *Sodium perchlorate* was prepared as described earlier.[4] *The ligand stock solution* was a buffer prepared from concentrated HAc (Merck, *p.a.*) and carbonate-free NaOH Titrisol (Merck, *p.a.*) and analysed by potentiometric titrations with base and acid, respectively. From this stock solution the titration solutions were mixed with pipettes.

*Procedure.* The investigation was performed by the ligand measurement method, a quinhydrone electrode being used to determine the hydrogen ion concentration $[H^+]$ in the complex solutions. The starting solutions, consisting of 20.00 ml of $C_{Cu}$ M $Cu(ClO_4)_2$, $C_H$ M $HClO_4$ and $(3-3C_{Cu}-C_H)$ M $NaClO_4$, were titrated

with acetate buffers containing $C_{Cu}$ M $Cu(ClO_4)_2$, 1.000 M NaAc, 1.000 M HAc and $(2-3\ C_{Cu})$ M $NaClO_4$. In this way $C_{Cu}$ is constant during each titration. In similar titration series with $C_{Cu} = 0$, the emf $E'$ was determined and $[H^+]'$ calculated, from which $K_C$ for the acetic acid was derived. The emf $E$ of the following cell

$$-RE \left\| \begin{array}{ll} C_{Cu} & M\ Cu(ClO_4)_2 \\ C_{Ac} & M\ NaAc \\ C_{HAc} & M\ HAc \\ C_H & M\ HClO_4 \\ (3-3C_{Cu}-C_{Ac}-C_H) & M\ NaClO_4 \\ \multicolumn{2}{c}{Quinhydrone} \end{array} \right| Au\ + $$

was determined by means of a Radiometer PHM 4 valve potentiometer. The reference electrode consisted of Ag,AgCl in 2.988 M $NaClO_4$, 0.012 M NaCl and *ca.* $10^{-5}$ M $AgNO_3$, and the salt bridge of 3.00 M $NaClO_4$. The whole cell was thermostated to 25.0°C. The titration solution was added from an all glass syringe with an accuracy of $\pm 0.002$ ml, and every series was repeated at least once. The potentials were stable within one minute and reproducible in general within 0.1 mV. A stream of oxygen-free nitrogen, washed in 3.00 M $NaClO_4$, was led through the solution in the titration vessel, and gave good stirring.

*Calculations.* The methods of calculation have been elaborated by Fronæus.[1] From the given concentrations and the measured values of $[H^+]$ and $[H^+]'$ it is possible to calculate the free ligand concentration $[Ac^-]$ and the ligand number $\bar{n}$. By plotting $\bar{n}/[Ac^-]$ versus $[Ac^-]$ we get $X([Ac^-])\ (=1 + \sum \beta_j\ [Ac^-]^j)$ from a graphical integration. Then the stability constants $\beta_j$ can be computed from the known pairs of $X([Ac^-])-[Ac^-]$ using a graphical method or a least squares procedure. The two methods gave, within the errors, the same constants. The experimental data are shown in Table 1.

*Results.* The stability constants for the copper(II) acetate complexes at ionic strength 3.00 M and at 25.0°C computed by a least squares procedure, presuming 4 complex species, and given with their errors calculated as the standard deviation, were:

$$\begin{array}{llll} \beta_1 = & 74.9 \pm & 0.3 & M^{-1} & (47 \pm & 1) \\ \beta_2 = & 1310 \pm & 12 & M^{-2} & (450 \pm & 50) \\ \beta_3 = & 3829 \pm & 96 & M^{-3} & (1150 \pm & 150) \\ \beta_4 = & 2119 \pm & 186 & M^{-4} & (750 \pm & 200) \end{array}$$

Calculations with 3 complexes gave a poor agreement with the experimental data

*Table 1.* Corresponding values of $C_{Ac}$, $E_A$, [Ac⁻], $\bar{n}$ and $\bar{n}/$[Ac⁻] for the copper(II) acetate system at ionic strength 3.00 M and temperature 25.0°C. ($E_A = E - E'$).

| $C_{Ac}$ mM | $E_A$ mV | [Ac⁻] mM | $\bar{n}$ | $\dfrac{\bar{n}}{[\text{Ac}^-]}$ M⁻¹ | $E_A$ mV | [Ac⁻] mM | $\bar{n}$ | $\dfrac{\bar{n}}{[\text{Ac}^-]}$ M⁻¹ | $E_A$ mV | [Ac⁻] mM | $\bar{n}$ | $\dfrac{\bar{n}}{[\text{Ac}^-]}$ M⁻¹ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $C_{Cu} = 20.5$ mM $C_H = 0.92$ mM | | | | $C_{Cu} = 41.0$ mM $C_H = 1.97$ mM | | | | $C_{Cu} = 78.0$ mM $C_H = 7.32$ mM | | | |
| 0 | | 0 | | 79 | | 0 | | 76 | | 0 | | 76 |
| 9.95 | 27.0 | 3.79 | 0.257 | 68.0 | 45.0 | 2.08 | 0.146 | 70.1 | 99.0 | 0.39 | 0.035 | 90 |
| 14.85 | 23.9 | 6.20 | 0.379 | 61.0 | 40.5 | 3.49 | 0.231 | 66.2 | | | | |
| 19.71 | 22.1 | 8.72 | 0.493 | 56.5 | 37.7 | 5.01 | 0.312 | 62.3 | 67.9 | 1.93 | 0.138 | 71.5 |
| 24.51 | 20.7 | 11.36 | 0.599 | 52.7 | 35.8 | 6.58 | 0.391 | 59.4 | | | | |
| 29.27 | 19.5 | 14.12 | 0.697 | 49.4 | 34.2 | 8.26 | 0.467 | 56.5 | 59.2 | 3.65 | 0.238 | 65.2 |
| 38.64 | 17.5 | 20.0 | 0.867 | 43.4 | 31.8 | 11.78 | 0.610 | 51.8 | 54.5 | 5.50 | 0.336 | 61.1 |
| 47.8 | 15.8 | 26.3 | 1.005 | 38.2 | 29.7 | 15.6 | 0.741 | 47.5 | 51.5 | 7.41 | 0.429 | 58.0 |
| 65.7 | 13.4 | 39.4 | 1.244 | 31.6 | 26.4 | 24.1 | 0.971 | 40.3 | 47.0 | 11.7 | 0.605 | 51.7 |
| 82.9 | 11.5 | 53.5 | 1.395 | 26.1 | 23.5 | 34.0 | 1.149 | 33.8 | 43.5 | 16.5 | 0.765 | 46.4 |
| 107.6 | 9.7 | 74.4 | 1.580 | 21.2 | 20.5 | 49.2 | 1.383 | 28.1 | 39.4 | 24.7 | 0.979 | 39.6 |
| 131.0 | 8.4 | 95.5 | 1.693 | 17.7 | 18.0 | 66.0 | 1.544 | 23.4 | 35.9 | 34.1 | 1.162 | 34.1 |
| 151.3 | 7.5 | 113.6 | 1.800 | 15.9 | 16.0 | 82.0 | 1.649 | 20.1 | 33.0 | 43.7 | 1.300 | 29.7 |
| 181.1 | 6.5 | 141.1 | 1.917 | 13.6 | 14.2 | 105.1 | 1.815 | 17.3 | 29.8 | 58.6 | 1.494 | 25.5 |
| 207.1 | 5.8 | 165.8 | 1.980 | 11.9 | 12.8 | 126.8 | 1.922 | 15.2 | 27.0 | 74.5 | 1.626 | 21.8 |
| 231.7 | 5.4 | 188.2 | 2.088 | 11.1 | 11.7 | 147.8 | 2.010 | 13.6 | 24.8 | 90.4 | 1.740 | 19.2 |
| 260.2 | 4.9 | 215.5 | 2.146 | 10.0 | 10.6 | 173.2 | 2.088 | 12.1 | 22.6 | 110.2 | 1.854 | 16.8 |
| 286.7 | 4.5 | 241.0 | 2.195 | 9.1 | 9.8 | 196.8 | 2.159 | 11.0 | 20.9 | 129.6 | 1.947 | 15.0 |
| 311.4 | 4.2 | 264.9 | 2.239 | 8.5 | 9.2 | 218.6 | 2.229 | 10.2 | 19.5 | 148.1 | 2.029 | 13.7 |
| 334.4 | 4.0 | 286.8 | 2.293 | 8.0 | 8.7 | 239.4 | 2.285 | 9.5 | 18.4 | 165.9 | 2.097 | 12.6 |
| 429.9 | 3.3 | 378.3 | 2.493 | 6.6 | 7.1 | 327.1 | 2.480 | 7.6 | 14.9 | 243.1 | 2.341 | 9.6 |
| 501.2 | 2.9 | 447.9 | 2.576 | 5.8 | 6.3 | 393.2 | 2.721 | 6.9 | 13.0 | 304.4 | 2.477 | 8.1 |

in the range of high [Ac⁻]. This could possibly depend on medium effects. The values determined by Fronæus[1] at 1.00 M are given within parenthesis. As these were found at 20.0°C, a check of the system at 1.00 M was made at 25.0°C. The results agreed well. ($\beta_1 = 51 \pm 2$, $\beta_2 = 510 \pm 40$). Some of the measurements at 3.00 M were repeated using a glass electrode to determine [H⁺]. The results agreed with the quinhydrone measurements. The dependence of $\bar{n}$ with $C_M$, reported by Fronæus,[1] and indicating polynuclear species, could not be reproduced. The variation in stability found at the change of ionic strength, was not quite so large for the copper(II) acetate system, but of the same order, as for the lead(II) acetate

system, in which the $\beta_1$ value changes from 104 at 1 M to 150 at 2 M and 214 at 3 M.[3]

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