

## Short Communications

### Solubility Equilibria of Copper(II)Aspartate Tetrahydrate

YI-CHANG LIANG,\* ÅKE OLIN and GUNNAR WIKMARK

Department of Analytical Chemistry, University of Uppsala, P.O.B. 531, S-751 21 Uppsala, Sweden

A moderately soluble phase is formed in the copper(II)–aspartic acid system. It was prepared from copper(II)oxide and L-aspartic acid by Lifshitz and Schoutedden,<sup>1</sup> who assigned the formula  $\text{CuA}\cdot 4\text{H}_2\text{O}$  to the air-dried compound. The aspartate(2-) ion is denoted by A. The compound can also be obtained by mixing solutions of  $\text{Cu}^{2+}$  and hydrogen aspartate ion ( $\text{HA}^-$ ) as described by Kirson and Barsily.<sup>2</sup> According to their analytical results, it contains 3 mol water of crystallization. They also observed a strong dependence of the solubility on pH. The optimal pH for the formation of the crystals is about 4. The easily soluble compounds  $\text{Cu}(\text{HA})_2\cdot 0.5\text{H}_2\text{O}$  and  $\text{K}_2\text{CuA}_2\cdot \text{H}_2\text{O}$  have also been prepared from solutions of Cu(II) and aspartic acid of the appropriate compositions.<sup>3</sup>

The complex formation between copper(II) and aspartic acid in aqueous solution has been extensively studied,<sup>4</sup> but the formation of a precipitate has seldom been reported.<sup>5</sup> Obviously the solid has a narrow range of existence when the components are present in moderate concentrations ( $1\text{--}5\cdot 10^{-3}$  M). A slow rate of precipitation may also contribute to the fact that the formation of copper aspartate is seldom observed. In the present work the solubility equilibria of the title compound have been determined, which will permit a more complete description of the important copper(II)–aspartic acid system.

*Method of investigation.* Solutions of the general composition  $0.25$  M  $\text{Na}^+$ ,  $H$   $\text{H}^+$ ,  $A$  hydrogen aspartate,  $(0.25$  M  $+H-A)$   $\text{NO}_3^-$  have been equilibrated with  $\text{CuA}\cdot 4\text{H}_2\text{O}(\text{s})$ .  $H$  is the total (analytical) hydrogen ion concentration with  $\text{HA}^-$  and  $\text{H}_2\text{O}$  as reference levels. Hydrogen aspartate, rather than the aspartate ion, has been chosen as component since it will be a predominant species in the aspartic acid–aspartate system at the pH used in this investigation. The total concentration of this system is denoted by  $A$ . Since the water activity is constant, the solid phase will often be written  $\text{CuA}(\text{s})$  to simplify formulas. In the equilibrium solution the total concentration of Cu(II),  $B$ , and the free hydrogen concentration,  $h$ , were determined.

*Chemicals and analysis.*  $\text{CuA}\cdot 4\text{H}_2\text{O}$  was prepared by neutralizing a mixture of  $\text{Cu}^{2+}$  (0.012 M) and  $\text{H}_2\text{A}$  (0.018 M) with sodium hydroxide at  $75^\circ\text{C}$ . 0.8 mol of  $\text{OH}^-$  were added per mol of  $\text{H}_2\text{A}$ . On cooling to room temperature needle-shaped, blue crystals were formed, which were kept in contact with the mother liquor for one week before filtration. Analysis of the air-dried material yielded  $\text{Cu}-\text{A}-\text{H}_2\text{O}=1:1:4$ .

Sodium nitrate (Merck *p.a.*) and aspartic acid (Fluka), D and L forms, were recrystallized from water and dried at  $105^\circ\text{C}$  before use. Nitric acid (Merck *p.a.*) was standardized against  $\text{KHCO}_3$ . Copper nitrate standard solutions were prepared from recrystallized  $\text{Cu}(\text{NO}_3)_2$  (Merck *p.a.*) and analyzed by electrogravimetry.

The copper content of the equilibrium solutions were determined by differential pulse polarography after acidification of the sample with  $\text{HNO}_3$ . The method of standard additions was employed for the quantification.

*Apparatus and experimental details.* The experiments were carried out as solubility titrations in the apparatus described by Olin and Wikmark.<sup>6</sup> The start solution had the composition  $A=0.005$  M and  $H=0.001$  M. The titrant was a 0.005 M solution of  $\text{H}_2\text{A}$ . The equilibration was followed by a copper-selective electrode (Radiometer F3000 Selectrode) and a glass electrode (Ingold 10201). A Metrohm 437 Ag/AgCl electrode was used as reference electrode with ionic medium in the salt bridge. The electrodes were

\* On leave from the Central-South Institute of Mining and Metallurgy, Changsa, Hunan, People's Republic of China.

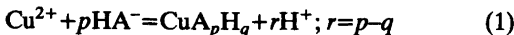
standardized with solutions of known  $\text{Cu}^{2+}$  concentrations in the ionic medium. Potentials were measured to  $\pm 0.1$  mV. The copper selective electrode was well suited for monitoring the changes in the free copper concentration but not for accurate determination of this concentration, as described previously.<sup>6</sup> The time for equilibration was 1–2 h. When stable electrode potentials indicated that equilibrium had been reached, two samples were withdrawn with a time interval of about 30 min. No significant difference in solubility (within 2 %) was observed between the two samples indicating that equilibrium had been reached. This was further confirmed by another experiment in which the equilibration was allowed to proceed for an additional 24 h. No increase (<0.2 %) in the copper(II) concentration was observed.

The polarographic determination of copper(II) was made with a home-built automated voltammetric instrumentation.<sup>7</sup>

All experiments have been performed in a thermostated room at  $25 \pm 0.3$  °C.

**Results and Calculations.** The complexation of  $\text{Cu}^{2+}$  by aspartic acid leads to the formation of the complexes  $\text{CuA}$ ,  $\text{CuA}_2$ ,  $\text{CuAH}$ ,  $\text{CuA}_2\text{H}$ , and  $\text{CuA}_2\text{H}_2$ .<sup>8</sup> The intrinsic solubility of  $\text{CuA}(\text{s})$  is fairly high ( $5 \cdot 10^{-4}$  M), which leads to large solubilities at pH values above or below the solubility minimum. These properties of the  $\text{Cu}(\text{II})$ –aspartic acid system make it difficult to determine the stability constants of the complexes and the solubility product of  $\text{CuA}(\text{s})$  simultaneously. In the following we shall therefore assume that the stability constants of the various aspartatocopper(II) complexes as well as the protonation constants of the hydrogen aspartate ion are known.<sup>8</sup>

The complexation equilibria will be written



$$\beta_{pq} = \frac{[\text{CuA}_p\text{H}_q]h^r}{b \cdot a^p} \quad (2)$$

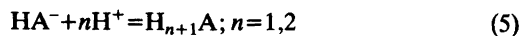
where  $b$  is the free concentration of  $\text{Cu}(\text{II})$ ,  $[\text{Cu}^{2+}]$ , and  $a$  is the concentration of  $\text{HA}^-$ . The solubility of  $\text{CuA}(\text{s})$  is governed by



and the solubility product equals

$$k_s^* = b a/h \quad (4)$$

The protonation constants of the hydrogen aspartate ion are defined by



$$\beta_n^{\text{H}} = \frac{[\text{H}_{n+1}\text{A}]}{a h^n} \quad (6)$$

The mass balance relations are

$$A_t = A_o + S = a + \sum_n \beta_n^{\text{H}} a h^n + \sum_{p,q} p \beta_{pq} b a^p h^{-r} \quad (7)$$

$$B = S = b + \sum_{p,q} \beta_{pq} b a^p h^{-r} \quad (8)$$

$S$  is the solubility of  $\text{CuA}(\text{s})$ ,  $A_o$  the total concentration of aspartic acid in the start solution and  $A_t$  the corresponding quantity in the equilibrium solution.

When eqns. (7) and (8) are combined and the sums are expanded the following equation is obtained

$$A_o = a (1 + \beta_1^{\text{H}} h + \beta_2^{\text{H}} h^2) + S \times \left[ \frac{\beta_{22} a^2 + \beta_{21} a^2 h^{-1} + \beta_{20} a^2 h^{-2} - 1}{\beta_{11} a + \beta_{22} a^2 + \beta_{10} a h^{-1} + \beta_{20} a^2 h^{-2} + \beta_{21} a^2 h^{-1} + 1} \right] \quad (9)$$

From each experimental point  $A_o$ ,  $S$  and  $h$  are known so that  $a$  can be calculated from eqn. (9). Next  $b$  is found from eqn. (8) and  $k_s^*$  calculated from eqn. (4). In these calculations the following values of the stability constants were used ( $n$ ,  $\log \beta_n^{\text{H}}$ ); (1, 3.653); (2, 5.636); ( $p$ ,  $q$ ,  $\log \beta_{pq}$ ); (1, 1, 2.753); (2, 2, 4.32); (1, 0, -0.905); (2, 0, -3.517); (2, 1, 0.65).

The results from a solubility titration with L-aspartic acid,  $\text{L-H}_2\text{A}$ , and  $\text{Cu}(\text{L-A}) \cdot 4\text{H}_2\text{O}$  are collected in Table 1. The value of the solubility product, defined by eqn. (4), obtained with the optically active form of the ligand was  $\text{pk}_s^* = 2.362 \pm 0.006$ .

Studies were also performed with racemic ligand,  $(\text{D-A} + \text{L-A})$ . The solid obtained may be racemic,  $\text{Cu}(\text{D-A}, \text{L-A})(\text{s})$ , or spontaneous resolution may take place with the formation of  $\text{Cu}(\text{D-A})(\text{s})$  and  $\text{Cu}(\text{L-A})(\text{s})$  as separate phases. If stereoselective effects are absent in the formation of the bis-complexes in solution, it is readily shown that the calculation of  $a$  and  $b$  for racemic ligand can be performed in exactly the same way as was done for optically pure ligand. A will then correspond to the sum of the total

**Table 1.** Solubility titration of Cu-aspartate·4H<sub>2</sub>O. A start solution with A<sub>0</sub>=0.005 M and H<sub>0</sub>=0.001 M was titrated with a 0.005 M aspartic acid solution. The notations used in the table are defined in the text. Except for the first point, the data appear in pairs. The first set refers to the results obtained from the sample taken when stable electrode potentials indicate that equilibrium has been reached. The second set refers to a sample withdrawn about 30 min later.

$S \cdot 10^3/M$	$-\log h$	$a \cdot 10^3/M$ eqn. (9)	$b \cdot 10^4/M$ eqn. (8)	$pK_s^*$ <sup>a</sup> eqn. (4)
0.914	4.270	3.872	0.597	2.366
0.924	4.256	3.849	0.625	2.363
0.932	4.253	3.847	0.631	2.359
0.964	4.133	3.630	0.875	2.365
0.967	4.134	3.631	0.877	2.363
1.006	4.036	3.428	1.141	2.371
1.018	4.037	3.429	1.152	2.366
1.073	3.958	3.243	1.449	2.371
1.113	3.959	3.244	1.499	2.354
1.152	3.893	3.079	1.788	2.367
1.150	3.894	3.082	1.780	2.367

<sup>a</sup> Mean  $pK_s^*$  ( $\pm\sigma$ )=2.365 (0.005).

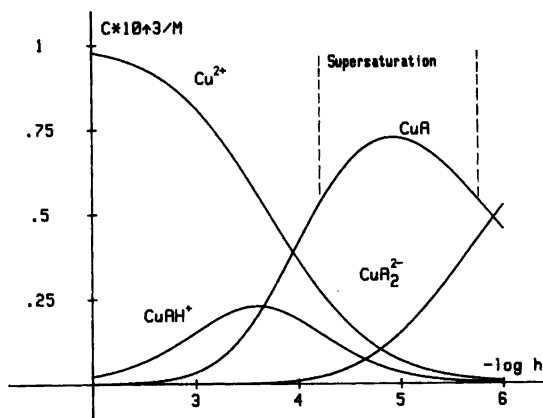
concentrations of D- and L-aspartic acid. From the data we may calculate the concentration quotient  $Q=bah^{-1}$ . When both Cu(D-A)(s) and Cu(L-A)(s) are present as separate phases we expect  $Q=2k_s^*$ . For a racemate with the properties of an ideal mixed crystal we expect  $Q=k_s^*$ . Experimentally,  $pQ=2.036\pm 0.006$  was found. Since  $pK_s^*$  is  $2.362\pm 0.006$ , spontaneous resolution occurs. This was further corroborated by X-ray powder photographs of the solids obtained from optically active and racemic aspartic acid, respectively.

The fact that  $Q$  is somewhat larger than  $2k_s^*$  for crystals prepared from racemic ligand indicates that lattice defects are present and increase the solubility. This could also be the reason why it was more difficult to prepare well-shaped crystals from the racemic form of aspartic acid.

By combining the value of  $k_s^*$  with the formation constant of CuA(aq), ( $\log \beta_{10}=-0.905$ ), the intrinsic solubility of CuA(s), which is equal to the numerical value of the equilibrium constant for the reaction  $CuA(s)=CuA(aq)$ , is found to be  $5.4 \cdot 10^{-4}$  M. In complexation studies the conditions  $A/B=1$  or 2, and  $B=1 \cdot 10^{-3}$  M are often used. With optically pure ligand a broad supersaturation range is then present as shown in Fig. 1.

The solubility of CuA·4H<sub>2</sub>O would conventionally be represented by the reaction scheme  $CuA(s)=Cu^{2+}+A^{2-}$  and the corresponding solu-

bility product,  $k_s=[Cu^{2+}][A^{2-}]$ .  $k_s$  will be estimated by combining  $k_s^*$  with the dissociation constant of HA<sup>-</sup>,  $k_1$ . With  $pK_1=9.61$  determined by the hydrogen electrode in 0.25 M NaCl,<sup>9</sup>  $pK_s=12.0$  is obtained. Since the numerical values of protonation constants do not vary much with



**Fig. 1.** Distribution of copper(II) calculated with the equilibrium constants given in the text for  $B=0.001$  M and  $A=0.002$  M. The species  $CuA_2H$  and  $CuA_2H_2$  have been left out since their concentrations represent at most 3 % of  $B$ . The range where  $CuA \cdot 4H_2O$  is present as solid phase at equilibrium is indicated.

the nature of the inert anion when the total molarity is maintained constant, this estimate is probably very good.

1. Lifshitz, I. and Schouteden, F. L. M. *Rec. Trav. Chim. Pays-Bas* 58 (1939) 411.
2. Kirson, B. and Barsily, I. *Bull. Soc. Chim. France* (1959) 901.
3. Kirschner, S. J. *Am. Chem. Soc.* 78 (1956) 2372.
4. Evans, C. A., Guevremont, R. and Rabenstein, D. L. In Sigel, H., Ed., *Metal Ions in Biological Systems*, Dekker, New York 1979, Vol. 9.
5. Nagypál, I., Gergely, A. and Farkas, E. J. *Inorg. Nucl. Chem.* 36 (1974) 699.
6. Olin, Å. and Wikmark, G. *Anal. Chem.* 55 (1983) 1402.
7. Baecklund, P. and Danielsson, R. *Anal. Chim. Acta* (1983). *In press*; Baecklund, P. and Wikmark, G. *Uppsala University Report UUIC A82/03* (1982).
8. Liang, Y.-C. and Olin, Å. *Acta Chem. Scand. A* 38 (1984) 247.
9. Al-Ani, N. *Private communication*.

Received November 30, 1983.