Monatshefte für Chemie 106, 1337—1347 (1975)

o-Aminophenol and 8-Hydroxyquinoline as Ligands of Cu(II) in 1 M-Na(ClO$_4$) at 25 °C*

By

Emilio Bottari and **Giancarlo Goretti**

Istituto di Chimica Analitica, Cittá Universitaria, Roma, Italia

With 5 Figures

(Received May 17, 1975)

The complex formation between Cu(II) and 8-hydroxyquinolinat (Ox) was studied with the liquid—liquid distribution method, between $1M$-Na(ClO$_4$) and CHCl$_3$ at 25 °C. The experimental data were explained by the equilibria:

$$\begin{array}{ll} Cu^{2+} + Ox \rightleftharpoons CuOx & \log \beta_1 = 12.38 \pm 0.13 \\ Cu^{2+} + 2\,Ox \rightleftharpoons CuOx_2 & \log \beta_2 = 23.80 \pm 0.10 \\ CuOx_{2\,aq} \rightleftharpoons CuOx_{2\,org} & \log \lambda = 2.06 \pm 0.08 \end{array}$$

The equilibria between Cu(II) and o-aminophenolate (AF) were studied potentiometrically with a glass electrode at 25 °C and in $1M$-Na(ClO$_4$). The experimental data were explained by the equilibria:

$$\begin{array}{ll} Cu^{2+} + AF \rightleftharpoons CuAF & \log \beta_1 = 8.08 \pm 0.08 \\ Cu^{2+} + 2\,AF \rightleftharpoons CuAF_2 & \log \beta_2 = 14.60 \pm 0.06 \end{array}$$

The protonation constants of AF and the distribution constants between CHCl$_3$—H$_2$O and (C$_2$H$_5$)$_2$O—H$_2$O were also determined.

Symbols

B	total concentration of Cu(II)
B_{aq}	total concentration of Cu(II) in the aqueous phase
b	concentration of free Cu^{2+}
H	analytical excess of H$^+$
h	concentration of free H$^+$
A	total concentration of ligand
a	concentration of free ligand
q	B_{org}/B_{aq}, distribution ratio between organic and aqueous phases

Ox and AF indicate 8-hydroxyquinolinate and o-aminophenolate, resp.. L indicates a ligand. Charges are omitted.

---

* This work was supported by C.N.R., the Research Council of Italy.

λ_B $[\mathrm{Cu}Ox_2]_{\mathrm{org}}/[\mathrm{Cu}Ox_2]_{\mathrm{aq}}$, distribution constant
λ_A $[\mathrm{H}AF]_{\mathrm{org}}/[\mathrm{H}AF]_{\mathrm{aq}}$, distribution constant
K_n stability constant of the species $[H_nL] = K_n\, h\, [H_{n-1}L]$
β_n stability constant of the species $\mathrm{Cu}L_n$, defined by the equation: $[\mathrm{Cu}L_n] = \beta_n\, b\, a^n$.

The complex formation between Cu(II) and 8-hydroxyquinoline had been previously studied, because of slight solubility of $\mathrm{Cu}Ox_2$ in water, almost always in mixtures of water — dioxan or water — ethanol[1]. Investigations in water had been carried out for low concentrations of reagents and at a very low ionic strength.

Näsänen and *Penttinen*[2] explained the spectrophotometric data obtained at 20 °C and ionic strength → 0, by the equilibrium:

$$\mathrm{Cu}^{2+} + Ox \rightleftharpoons \mathrm{Cu}Ox \qquad \log \beta = 12.56$$

Albert[3], from potentiometric data obtained by means of a glass electrode at 20 °C and ionic strength 0.01, claimed the existence of the equilibria:

$$\mathrm{Cu}^{2+} + Ox \rightleftharpoons \mathrm{Cu}Ox \qquad \log \beta_1 = 12.2$$
$$\mathrm{Cu}^{2+} + 2\,Ox \rightleftharpoons \mathrm{Cu}Ox_2 \qquad \log \beta_2 = 23.3$$

Recently *Fresco* and *Freiser*[4], from distribution measurements at 25 °C and 0.1 ionic strength, obtained the value $\log \lambda = 3.48 \pm 0.06$ for the distribution constant of $\mathrm{Cu}Ox_2$ between $\mathrm{CHCl_3}$ and $\mathrm{H_2O}$.

Very few quantitative results are available for the system copper(II)—o-aminophenol and for the o-aminophenolate protonation[1]. All the data of reference[1] were obtained at 20 °C, extrapolating the ionic strength to zero.

The aim of this paper is to study both systems in a wide concentration range at 25 °C and in $1M$-Na($\mathrm{ClO_4}$), in order to obtain the stability constants for both systems and the protonation constants for the o-aminophenolate, unknown under these experimental conditions. Furthermore the values of the distribution constants of $\mathrm{Cu}Ox_2$ between $\mathrm{CHCl_3}$—$\mathrm{H_2O}$ and o-aminophenol between $\mathrm{CHCl_3}$—$\mathrm{H_2O}$ and $(\mathrm{C_2H_5})_2\mathrm{O}$—$\mathrm{H_2O}$ are given.

Experimental

Chemical and Analysis

$\mathrm{NaClO_4}$, $\mathrm{Cu(ClO_4)_2}$, $\mathrm{HClO_4}$, NaOH were prepared and analysed as previously described[5].

8-Hydroxyquinoline (Merck p.a.) and o-aminophenol (C. Erba) were purified by sublimation. $\mathrm{CHCl_3}$ and $(\mathrm{C_2H_5})_2\mathrm{O}$ were C. Erba pure reagents.

Nitrogen from cylinders was purified as previously described[6] and was bubbled through the solutions during the potentiometric measurements.

Apparatus

The atomic absorption apparatus was an Optica "Densatomic".

The e.m.f. measurements were carried out by means of an apparatus similar to that previously described[6].

Method of Investigation and Results

1. Copper(II)—8-Hydroxyquinoline

The complex formation between copper(II) and 8-hydroxyquinolinate (*Ox*) was studied by means of liquid—liquid distribution at 25 °C and 1*M*-$NaClO_4$.

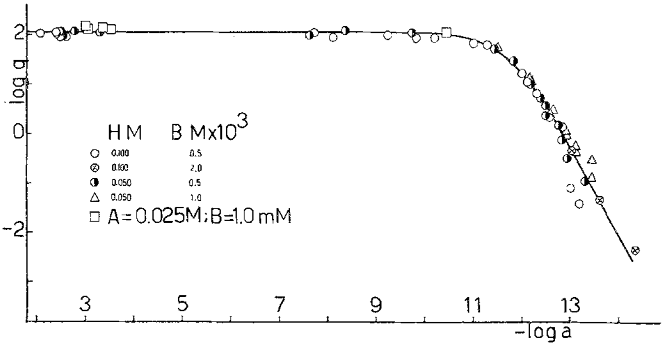

Fig. 1. Experimental data for the system Cu(II)—8-hydroxyquinoline. The curve is the normalized one of eqn. (4) in the position of best fit

The aqueous phase was always made 1*M* in Na^+ by adding an excess of $NaClO_4$. In this way the activity coefficients of the reagents could be assumed constant and concentrations could replace activities in all calculations. Thus the aqueous phase had the following general composition: B *M*- in Cu(II); H_1 *M* in H^+; 1.0*M* in Na^+; $(1 + 2B + H)M$ in ClO_4^-.

A volume v_{aq} was equilibrated with a volume v_{org} of $CHCl_3$ H_2 *M* in H*Ox*, previously saturated by water.

The H_1 and H_2 values were selected in order to have:

$$\frac{H_1 v_{aq} + H_2 v_{org}}{v_{aq} + v_{org}} = H\,M$$

When $v_{aq} = v_{org}$, four hours were sufficient to obtain the equilibrium, while if $v_{aq} = 2\,v_{org}$, 12 hours were necessary.

After obtaining the equilibrium, the phases were separated; the $-\log h$ value of the aqueous phase was potentiometrically measured, and B_{aq} was determined by means of atomic absorption. At high B, B_{aq} was obtained by means of calibration straight lines, while at low Cu(II) concentrations, B_{aq} was determined by means of the addition method. In this way, by taking in account the B value, the data $\log q$ ($-\log h$) could be obtained.

Several determinations at $H = 0.100$; 0.050*M* and $B = (0.5;\ 1.0;\ 2.0) \times 10^{-3}M$ were performed at 25 °C in a thermostated room, and, suc-

Table 1. *Experimental Data for the System* Cu(II)—*8-hydroxyquinoline*

$H = 0.100M$

$B = 0.5 \times 10^{-3}M$

Series **a**:

log q (— log h, — log a):
1.10 (2.06, 12.11); 1.88 (2.64, 10.99);
1.97 (3.09, 10.20); 1.97 (3.33, 9.81);
1.97 (4.75, 8.09); 1.97 (10.20, 2.62);
1.97 (10.32, 2.50).

series **b**:

log q (— log h, — log a):
— 1.38 (1.57, 13.19); — 1.06 (1.64, 13.01);
0.18 (1.73, 12.83); 0.37 (1.84, 12.59);
0.83 (1.97, 12.30); 1.26 (2.12, 11.99);
1.83 (2.48, 11.27); 1.86 (2.64, 10.99);
*2.01 (3.62, 9.23); *2.07 (4.84, 7.71);
*2.06 (10.12, 2.40).

$B = 2.0 \times 10^{-3}M$

log q (— log h, — log a):
— 2.30 (1.17, 14.34); — 1.39 (1.40, 13.59);
— 0.39 (1.64, 13.03).

$H = 0.050M$

$B = 0.5 \times 10^{-3}M$

series **a**:

log q (— log h, — log a):
— 0.92 (1.70, 13.31); — 0.09 (1.90, 12.82);
0.21 (1.92, 12.76); 0.60 (2.05, 12.48);
0.75 (2.10, 12.38); 1.04 (2.19, 12.20);
1.51 (2.37, 11.82); 1.75 (2.57, 11.42);
*2.08 (3.49, 9.73); *2.10 (4.52, 8.36);
*2.08 (10.36, 2.46).

series **b**:

log q (— log h, — log a):
2.01 (5.22, 7.61); 2.09 (9.51, 3.31);
2.09 (10.05, 2.78); 1.99 (10.25, 2.57);
2.04 (10.42, 2.41); 2.06 (10.09, 2.43);
2.04 (10.45, 2.07).

$B = 1.0 \times 10^{-3}M$

series **a**:

log q (— log h, — log a):
— 0.85 (1.65, 13.43); — 0.33 (1.77, 13.12);
0.02 (1.85, 12.94); 0.54 (1.98, 12.65);
1.09 (2.19, 12.20).

series **b**:

log q (— log h, — log a):
— 0.48 (1.65, 13.44); — 0.21 (1.78, 13.11);
0.10 (1.87, 12.90); 0.44 (2.01, 12.58);
1.19 (2.21, 12.15); 1.87 (2.53, 11.50).

Special series:

$A = 0.025M$; $B = 1.0 \times 10^{-3}M$

log q (— log h, — log a):
2.09 (3.01, 10.43); 2.14 (10.13, 3.49);
2.15 (10.38, 3.35); 2.20 (10.62, 3.02);
2.16 (10.79, 3.03).

---

* $v_{\mathrm{aq}} = 2\, v_{\mathrm{org}}$.

cessively, under the same experimental conditions, another series at $A = 0.025M$ and $B = 1.0 \times 10^{-3}M$ was performed. All the data are collected in table 1 in the form log q (— log h, — log a) and plotted in figure 1 in the form log q (— log a).

The a value was calculated from the material balance of H:

$$H = h + \sum_{n} n\, K_n\, h^n\, a + \lambda_A\, K_1 K_2\, h^2\, a. \tag{1}$$

In eqn. (1) the presence of possible mixed complexes with participation of H^+ was neglected, by taking in account the H and B values ($B \leqslant 0.02\, H$), and also the hydrolytic species of copper(II) were neglected in the b and h range studied, according to *Berecki—Biedermann*[7]. The K_1, K_2 and λ_A values had been previously determined[8], under the same experimental conditions.

There is no evidence from figure 1 for polynuclear and mixed complexes in the range $2 \leqslant -\log a \leqslant 14$. Furthermore, from the trend of experimental points, the formation of $\mathrm{Cu}L_n$ complexes (with $n > 2$) can be excluded, either because the slope of the curve is $\leqslant 2$, or because the log q values do not decrease even if $-\log a \simeq 2$.

Consequently the function q can be expressed as:

$$\log q = \log (\lambda_B\, \beta_2\, a^2) - \log (1 + \beta_1\, a + \beta_2\, a^2). \tag{2}$$

The eqn. (2), in the following form:

$$\log q = \log \lambda_B - \log (1 + \beta_1 \beta_2^{-1}\, a^{-1} + \beta_2^{-1}\, a^{-2}) \tag{3}$$

can be normalized in the form:

$$y = \log (1 + \alpha\, u^{-1} + u^{-2}) \tag{4}$$

where $\log q - y = \log \lambda_B$; $u^{-1} = a^{-1}/\sqrt{\beta_2}$; $\alpha = \beta_1/\sqrt{\beta_2}$.

By comparing a family of curves of eqn. (4) with the experimental data, in the position of best fit, the values

$$\log \lambda_B = 2.06 \pm 0.08;\ \log \beta_1 = 12.38 \pm 0.13;\ \log \beta_2 = 23.80 \pm 0.10$$

were obtained. Experimental points agree very well with the theoretical curve (Fig. 1).

2. *Copper(II)—o-aminophenol*

The study of the Cu(II)-o-aminophenol system requires the knowledge of the free concentration of o-aminophenolate, a, and therefore it was necessary to determine the K_1 and K_2 values for the ligand at 25 °C and $1M$-NaClO$_4$. These values were determined potentiometrically. Also the distribution coefficient of o-aminophenol could be obtained potentiometrically, by means of a two phase titration method, as described below.

2a. *Protonation constants of AF*

Potentiometric measurements were carried out by measuring, at 25 °C, the e.m.f. of the cell:

$$(-)\ R.E.\ /\ 1.0M\text{-NaClO}_4\ //\ \text{Solution } S\ /\ G.E.\ (+) \tag{A}$$

where *R.E.* = Ag, AgCl/0.01M-NaCl, 0.99M-NaClO$_4$ and
G.E. = Glass electrode.

In order to minimize the variations of the activity coefficients, all solutions were made 1.0M in Na^+, by adding $NaClO_4$. Thus the general composition of the solutions S was:

A M in L; H M in H^+; 1.0M in Na^+; $(1 + H - A)M$ in ClO_4^-

and so the concentrations could replace the activities in all the calculations. The e.m.f. (in mV) of the cell (A) at 25 °C can be written:

$$E_A = E_A^\circ + 59.15 \log h + E_j. \tag{5}$$

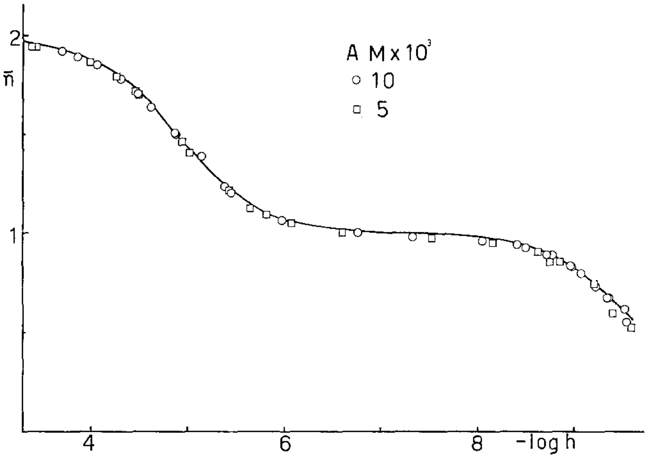

Fig. 2. Protonation function of o-aminophenolate. The curve is the normalized one of eqn. (7) in the position of best fit

E_A° and E_j were determined in the first part of each titration ($E_j = -56\,h$), where $H = h$; successively AF was added and the obtained solution was titrated by OH^- standard solution, keeping A constant.

In the second part of the titration, from the e.m.f. measurements and the knowledge of E_A° and E_j, h could be calculated for each experimental point, and from the analytical A and H values, the function:

$$\bar{n} = \frac{H - h}{A} = \frac{K_1 h + 2 K_1 K_2 h^2}{1 + K_1 h + K_1 K_2 h^2} \tag{6}$$

could be obtained.

The experimental data are plotted in the form $\bar{n}$ ($-\log h$) in figure 2.

In order to obtain the K_1 and K_2 values, the method of the normalized curves was employed[9]. The experimental points were compared with a family of curves of equation:

$$\bar{n} = \frac{R u + 2 u^2}{1 + R u + u^2} \tag{7}$$

where $u = h \sqrt{K_1 K_2}$ and $R = K_1/\sqrt{K_1 K_2}$.

In the position of best fit the values

$$\log K_1 = 9.67 \pm 0.08 \text{ and } \log K_1K_2 = 14.56 \pm 0.08$$

were obtained. As it can be seen from figure 2, experimental points and theoretical curve agree very well.

2b. Distribution coefficient of o-aminophenol

It was convenient to determine potentiometrically the distribution coefficient as described below, because, this compound is easily oxidizable in solution. To this purpose, a two phase titration method, employed by *Rydberg*[10] and by *Dyrssen*[11], was performed.

A known quantity of o-aminophenol, dissolved in measured volumes of aqueous and organic phases, was titrated by a NaOH standard solution, by measuring the e.m.f. of a cell similar to A.

In this case the solution S had the general composition:

$$A\,M \text{ in } L;\ H\,M \text{ in } \mathrm{H}^+;\ 1.0M \text{ in } \mathrm{Na}^+;\ (1 + H - A)M \text{ in } \mathrm{ClO_4}^-;$$

at known v_{aq} and v_{org} values.

From the λ_A definition and as the AF^- concentration can be neglected for $-\log h \leqslant 6$, it can be written:

$$\log \frac{[\mathrm{H}\,AF]_{\mathrm{org}}}{[\mathrm{H_2}\,AF^+]} = \log Y = \log \lambda_A - \log h - \log K_2 \tag{8}$$

By plotting $\log Y$ vs. $-\log h$, a straight line with slope 1 is obtained. At $\log Y = 0$,

$$\log \lambda_A = \log K_2 + \log h. \tag{9}$$

By introducing in eqn. (9) the known $\log K_2$ value, $\log \lambda_A$ can be calculated. The $[\mathrm{H_2}AF^+]$ and $[\mathrm{H}AF]_{\mathrm{org}}$ values, necessary to calculate $\log Y$ [s. eqn. (8)], could be obtained from the electroneutrality law:

$$[\mathrm{H_2}AF^+] = [\mathrm{ClO_4}^-] + [\mathrm{OH}^-] - [\mathrm{H}^+] - [\mathrm{Na}^+] + [AF^-] \tag{10}$$

and from the material balance:

$$A_{\mathrm{tot}} = A_{\mathrm{aq}}\,v_{\mathrm{aq}} + A_{\mathrm{org}}\,v_{\mathrm{org}} = v_{\mathrm{aq}}\,([\mathrm{H_2}AF^+] + [\mathrm{H}AF] + [AF^-]) + {} + [\mathrm{H}AF]_{\mathrm{org}}\,v_{\mathrm{org}} \tag{11}$$

In the range $-\log h \geqslant 8.5$, $[\mathrm{H_2}AF^+]$ can be neglected, consequently:

$$\log \frac{[\mathrm{H}\,AF]_{\mathrm{org}}}{a} = \log Y' = \log \lambda_A + \log K_1 + \log h \tag{12}$$

As described above, also in this case the a and $[\mathrm{H}AF]_{\mathrm{org}}$ values could be calculated from eqns. (10) and (11), resp.

A straight line with slope 1 is obtained by plotting $\log Y'$ vs. $-\log h$; at $\log Y' = 0$, the value

$$\log \lambda_A = -\log h - \log K_1 \tag{13}$$

can be calculated.

From the straight lines reported in figures 3 and 4, the values

$$\log \lambda_A = -0.47 \text{ and } \log \lambda_A = 0.58$$

were obtained for $\mathrm{CHCl_3}$ and $(\mathrm{C_2H_5})_2\mathrm{O}$, resp.

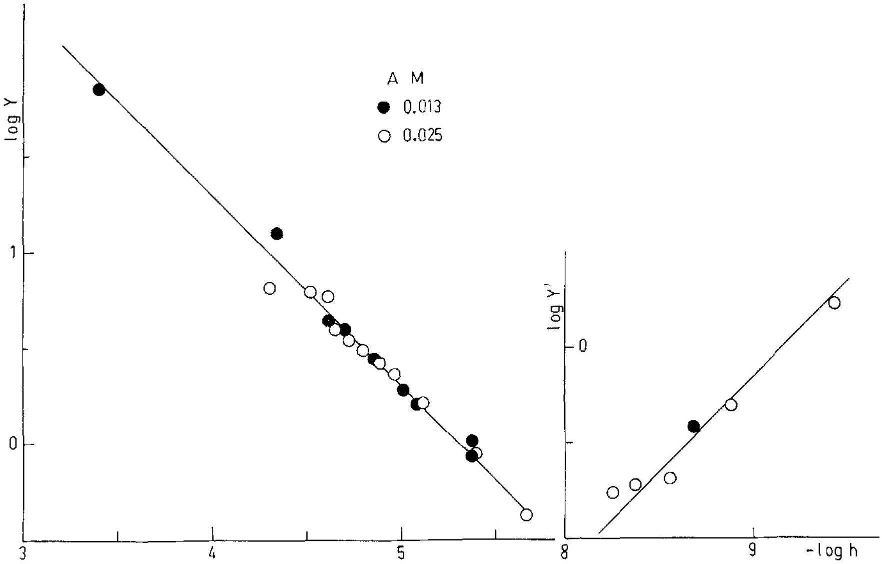

Fig. 3. Plot of the two phase titration of o-aminophenol between $CHCl_3$ and H_2O

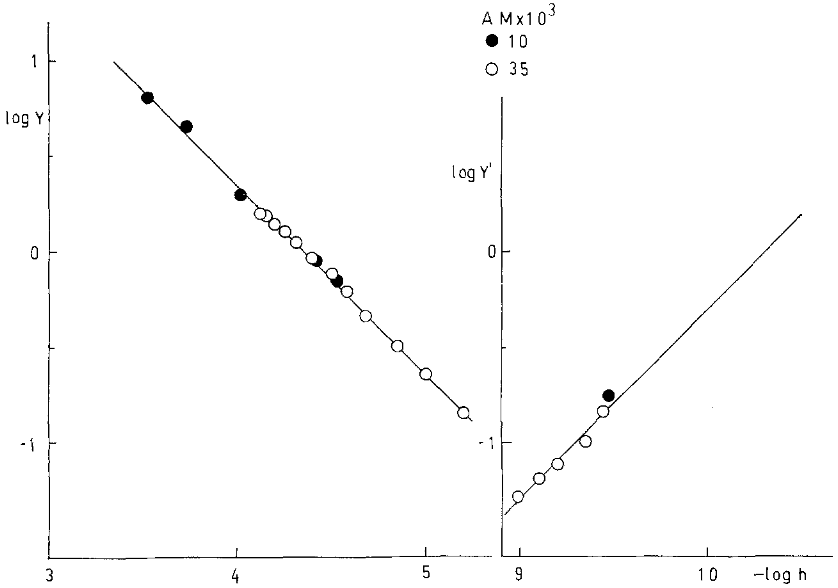

Fig. 4. Plot of the two phase titration of o-aminophenol between $(C_2H_5)_2O$ and H_2O

2c. Complex formation between Cu(II) *and* AF

This system was investigated potentiometrically, by measuring the e.m.f. of a cell similar to (A), where the solution S had the general composition:

$B\,M$ in Cu(II); $H\,M$ in H^+; $A\,M$ in L, $1.0M$ in Na^+; $(1 + 2B + \mathrm{H} - A)M$ in $\mathrm{ClO_4}^-$.

Table 2. *Experimental Data for the System Copper(II)—o-aminophenate*

$A = 1.0 \times 10^{-3}M$; $B = 0.5 \times 10^{-3}M$

$\bar{n}$ (—log h, —log a): 0.235 (4.58, 8.63); 0.300 (4.68, 8.48); 0.367 (4.78, 8.34);
0.439 (4.87, 8.22); 0.512 (4.97, 8.09); 0.588 (5.08, 7.96);
0.669 (5.19, 7.83); 0.714 (5.25, 7.77); 0.744 (5.32, 7.65);
0.826 (5.39, 7.63); 0.852 (5.47, 7.54); 0.903 (5.56, 7.46);
0.955 (5.66, 7.36); 0.990 (5.72, 7.31); 1.03 (5.79, 7.24);
1.06 (5.87, 7.18); 1.10 (5.94, 7.12); 1.13 (5.99, 7.07);
1.15 (6.05, 7.02); 1.18 (6.11, 6.97); 1.22 (6.20, 6.90);
1.31 (6.38, 6.77); 1.38 (6.53, 6.66).

$A = 1.0 \times 10^{-3}M$; $B = 0.25 \times 10^{-3}M$

$\bar{n}$ (—log h, —log a): 0.442 (4.82, 8.24); 0.550 (4.94, 8.08); 0.646 (5.06, 7.91);
0.838 (5.35, 7.56); 0.961 (5.54, 7.35); 1.12 (5.77, 7.12);
1.33 (6.06, 6.83); 1.51 (6.25, 6.67).

$A = 0.5 \times 10^{-3}M$; $B = 0.50 \times 10^{-3}M$

$\bar{n}$ (—log h, —log a): 0.062 (4.29, 9.41); 0.104 (4.18, 9.09); 0.164 (4.65, 8.84);
0.237 (4.80, 8.64); 0.318 (4.95, 8.48); 0.407 (5.11, 8.31);
0.510 (5.29, 8.16).

$A = 0.5 \times 10^{-3}M$; $B = 1.00 \times 10^{-3}M$

$\bar{n}$ (—log h, —log a): 0.044 (4.01, 9.89); 0.024 (4.21, 9.55); 0.050 (4.38, 9.27);
0.084 (4.53, 9.05); 0.124 (4.65, 8.92); 0.163 (4.77, 8.74);
0.209 (4.89, 8.63); 0.258 (5.02, 8.53); 0.295 (5.09, 8.51);
0.313 (5.16, 8.47); 0.342 (5.25, 8.43); 0.373 (5.34, 8.41).

Titrations at $B = (0.25,\ 0.50,\ 1.0) \times 10^{-3}M$ were performed; at $B > 1.0 \times 10^{-3}M$ precipitation took place.

The a value could be calculated by taking in account the material balance of H and the mass action law:

$$a = \frac{H - h}{K_1 h + 2\,K_1 K_2 h^2} \qquad (14)$$

In eqn. (14) the hydrolized species of copper(II) and the mixed complexes were neglected.

From the knowledge of B, A, h and a, the function:

$$\bar{n} = \frac{A - a - K_1 ha - K_1 K_2 h^2 a}{B} = \frac{\sum\limits_n n\,\beta_n a^n}{1 + \sum\limits_n \beta_n a^n} \qquad (15)$$

could be calculated.

The data $\bar{n}$ ($-\log h$, $-\log a$) are collected in table 2 and they are plotted in the form $\bar{n}$ ($-\log a$) in figure 5. From figure 5, it can be seen that $\bar{n}$ is independent of B, consequently the validity of eqn. (14) and the absence of polynuclear complexes are confirmed.

The experimental data were superimposed to a family of normalized curves, with equation

$$\bar{n} = \frac{R u + 2 u^2}{1 + Ru + u^2} \tag{16}$$

where $u = a\sqrt{\beta_2}$ and $R = \beta_1/\sqrt{\beta_2}$.

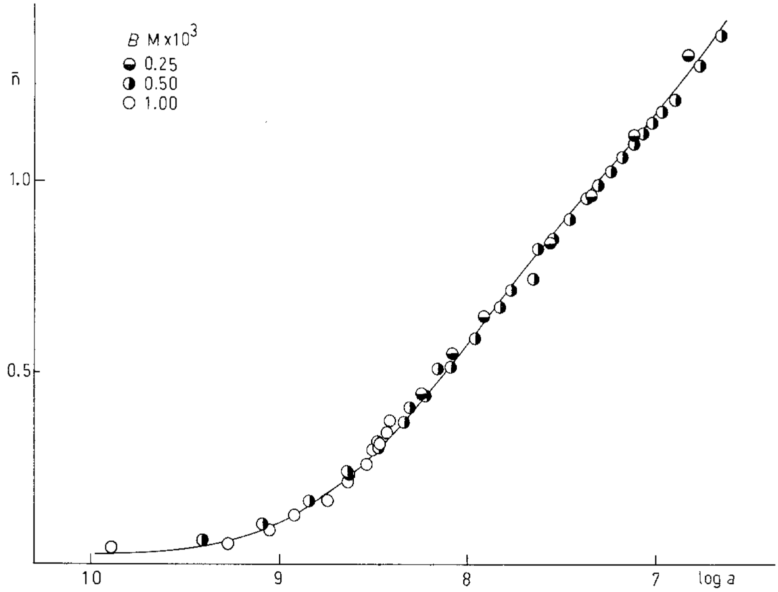

Fig. 5. Experimental data for the system Cu(II)—o-aminophenol. The curve is the normalized one of eqn. (16) in the position of best fit

In the position of best fit, the values:

$$\log \beta_1 = 8.08 \pm 0.08 \text{ and } \log \beta_2 = 14.60 \pm 0.06$$

could be obtained. In figure 5 it can be seen that the theoretic curve and the experimental points agree very well.

Conclusion

The obtained values for the stability constants of the system Cu(II)—*Ox* agree with the values reported by *Näsänen* and *Penttinen*[2], and *Albert*[3], if the difference of ionic strength and temperature is considered. On the contrary, the log λ_B value here obtained, is much lower than that reported by *Fresco* and *Freiser*[4].

The log K_1, log K_2, log β_1 and log β_2 values obtained for *AF* are a little lower than those reported in ref.[1]; this can be attributed to the different experimental conditions.

The main conclusion of the present work is drawn from the different behaviour of 8-hydroxyquinoline and of o-aminophenol.

AF is more soluble than *Ox* in water, while it is less soluble in $CHCl_3$ than in $(C_2H_5)_2O$. This is explainable, if considering that *AF* can give hydrogen bonds with water as well as with ether, but not with $CHCl_3$.

The difference between the investigated compounds can be also pointed out, when considering their behaviour as ligands. Both *Ox* and *AF* form complexes Cu*L* and CuL_2, but their stability constants are very different.

In fact the pyridinic nitrogen, present in *Ox* together with the phenolic OH, gives a planar structure that helps the formation of bonds with copper(II). In addition to it, the higher stability of the complexes formed by *Ox* is explainable by the better overlap of the orbitals of pyridinic nitrogen and Cu(II).

References

[1] *A. E. Martell* and *L. G. Sillén*, Stability Constants, Special Publication No. 17 and Special Publication No. 25, The Chemical Society, London (1964 and 1971).

[2] *R. Näsänen* and *U. Penttinen*, Acta Chem. Scand. **6**, 837 (1952).

[3] *A. Albert*, Biochem. J. **54**, 646 (1953).

[4] *J. Fresco* and *H. Freiser*, Analyt. Chem. **36**, 631 (1964).

[5] *E. Bottari*, *A. Liberti*, and *A. Rufolo*, J. inorg. nucl. Chem. **30**, 2173 (1968).

[6] *E. Bottari* and *A. Rufolo*, Mh. Chem. **99**, 2383 (1968).

[7] *C. Berecki-Biedermann*, Ark. Kemi **9**, 175 (1956).

[8] *E. Bottari*, Mh. Chem. **105**, 187 (1974).

[9] *L. G. Sillén*, Acta Chem. Scand. **10**, 186 (1956).

[10] *J. Rydberg*, Svensk Kem. Tidskr. **65**, 37 (1953).

[11] *D. Dyrssen*, Svensk Kem. Tidskr. **64**, 213 (1952).

Correspondence and reprints:
Dr. E. Bottari
Istituto di Chimica Analitica
Città Universitaria
Roma
Italy