513. *Stability Constants of Copper*(II) *Chloride Complexes.*

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A cation-exchange resin in the H^+-form has been used in an investigation of solutions containing copper(II) chloride complexes. Values have been obtained for the stability constants, $\beta_j = [CuCl_j^{(2-j)+}]/[Cu^{2+}][Cl^-]^j$ ($j = 1, 2,$ 3, and 4), which are valid for 20° and ionic strength 0·691M maintained with perchloric acid.

THIS paper reports the application of the cation-exchange resin Amberlite IR-120 to a study of copper(II) chloride complexes. Values for the individual stability constants, defined by

$$\beta_j = [CuCl_j^{(2-j)+}]/[Cu^{2+}][Cl^-]^j \ (j = 1, 2, 3, \text{ and } 4),$$

have been obtained. Since appreciable concentrations of chloride are required for the formation of the four successive $CuCl_j^{(2-j)+}$ species in significant quantities in aqueous solution, the ionic strength of the solutions studied has been held constant at the quite high value of 0·691M by the use of perchloric acid. The tacit assumption has been made that ion association between ClO_4^- and Cu^{2+} is negligible. Since the ionic strength of the solutions has been such that interionic-attraction theories cannot be rigorously applied, the evaluation of " true " or " thermodynamic " stability constants has been precluded. However, the values obtained for β_j should be collatable with those obtained by us for chloride complexes of zinc [1] and manganese(II).[2]

The experimental procedure in the present investigation differed from those in our other studies in that distribution of the metal between resin and solution was determined spectrophotometrically rather than by radiochemical assay. In deriving the stability constants from the experimental data the methods of Fronaeus [3] and of Carleson and Irving [4] were adopted in the main. The notation and equations used for the calculations are described in previous papers.[1,2]

EXPERIMENTAL

Pure analytical reagents were used. A stock solution of copper(II) was made by dissolving a small, known weight, of purified copper perchlorate in perchloric acid. Tests for traces of chloride in the solution, which contained 0·001 g. of copper per ml., were carried out periodically and were always negative. Stock solutions of hydrochloric and perchloric acid were also prepared. All solutions were adjusted to 0·691M.

The cation-exchange resin Amberlite IR-120 (30—60 mesh) was transformed into the H^+-form, oven-dried for 36 hr. at 40°, and stored in a closed bottle to ensure that the water content should remain constant. The exchange capacity was 3·86 milliequiv. per g. of dried resin.

Fixed volumes, v (10 ml.), of solutions of copper complexes, made up from different volumes of the stock solutions of copper(II), hydrochloric acid, and perchloric acid, were shaken with portions (m, 0·75 g.) of the resin in 25-ml. Pyrex conical flasks fitted with ground-in stoppers and immersed in a thermostat-bath at 20°. Shaking for 48 hr. ensured attainment of equilibrium.

The copper concentrations of the resin phases $(C_M)_R$ and the aqueous phases (C_M) at equilibrium were determined from spectrophotometric analyses of aliquot parts (5 ml.) of solutions before addition of ion-exchanger and after equilibrium had been obtained. Each aliquot part was transferred to a 25-ml. volumetric flask. 0·5% Ammonium acetate solution (1 ml.) was added, followed by 3 drops of aqueous ammonia (d 0·880) and 1 drop of 0·01% Neutral Red solution. The mixture was titrated with 10% sodium hydroxide solution until

[1] Short and Morris, *J. Inorg. Nuclear Chem.*, 1961, **18**, 192.
[2] Morris and Short, *J.*, 1961 5148.
[3] Fronaeus, *Acta Chem. Scand.*, 1951, **5**, 859; 1952, **6**, 1200; *Svensk Kem. Tidskr.*, 1953, **65**, 19.
[4] Carleson and Irving, *J.*, 1954, 4390.

the colour of the indicator had just changed from red to yellow. At this point di-(N'-cyclo-hexylidene)oxaldihydrazide solution (1 ml.) (0·1 g. in 20 ml. of warm ethanol and 20 ml. of water) was introduced, and the 25-ml. volumetric flask was filled to the mark with water. Ten minutes after development of the blue colour the absorbance of the solution was measured at 595 mμ against a control, in cells 4 cm. thick. A Unicam S.P. 600 spectrophotometer was used for the absorption measurements and the blue phototube was employed.

A reference curve was constructed in a similar manner by using solutions prepared from the stock copper(II) solution and containing 2·5, 5, 7·5, 10, and 12·5 × 10⁻⁶ g. of copper. The graph of concentration of copper against absorbance was rectilinear and Beer's law was obeyed over the whole range. (It should be noted that dilute copper–hydrazone solutions are not stable and after some time their colour diminishes.[5] However, experiments showed that 7·5 min. after the addition of the colorimetric reagent to copper solutions the absorption of the complex reached a maximum and remained constant for 30 min. thereafter.)

The value of v/m in all the distribution experiments was kept constant at $1·333 \times 10^{-2}$ l./g., thus keeping constant the volume decrease of the solutions caused by the swelling of the resin. The swelling factor, δ, was determined by shaking v ml. of standard halogen acid with m g. of resin and determining the change in the hydrogen-ion concentration after equilibration. The value was always 0·96. The distribution ratio $\phi = (C_M)_R/C_M$ was calculated from the expression $\phi = 1·333 \times 10^{-2} [(C_M'/C_M) - \delta]$, where C_M' is the copper concentration of the solution before addition of the ion-exchanger and C_M is the concentration after equilibration.

RESULTS

The distribution of copper between resin and solution was determined at three different values of C_M' and magnitudes of ϕ at a constant load, $(C_M)_R = 1·70 \times 10^{-6}$ mole/g., were obtained by extrapolation. Only a slight variation of ϕ with $(C_M)_R$ was observed, as shown in Table 1.

TABLE 1.

$10^4 C_M'$ (moles/l.) [Cl⁻] (moles/l.)	1·1805		1·574		2·361	
	$10^6(C_M)_R$ (moles/g.)	$10^3\phi$ (l./g.)	$10^6(C_M)_R$ (moles/g.)	$10^3\phi$ (l./g.)	$10^6(C_M)_R$ (moles/g.)	$10^3\phi$ (l./g.)
0	1·3234	67·60	1·7691	68·55	2·6640	70·41
0·018	1·3202	66·60	1·7627	67·16	2·6600	69·85
0·036	1·3158	65·21	1·7592	66·18	2·6500	68·18
0·072	1·3097	63·43	1·7510	64·27	2·6367	66·01
0·108	1·3049	62·06	1·7436	62·70	2·6211	63·68
0·144	1·3000	60·74	1·7360	61·12	2·6119	62·36
0·180	1·2828	58·84	1·7321	59·48	2·5988	60·58
0·216	1·2879	57·63	1·7277	58·00	2·5850	58·74
0·252	1·2815	56·08	1·7087	56·58	2·5727	57·24
0·288	1·2751	54·59	1·7072	55·26	2·5690	56·75
0·360	1·2638	52·14	1·6890	52·60	2·5400	53·43
0·396	1·2560	50·58	1·6777	51·00	2·5263	52·01
0·468	1·2460	48·61	1·6642	48·91	2·4973	49·13
0·504	1·2390	47·30	1·6523	47·36	2·4860	48·04
0·540	1·2307	45·89	1·6477	46·65	2·4668	46·44
0·576	1·2203	44·15	1·6304	44·57	2·4478	44·74
0·612	1·2126	42·94	1·6219	43·43	2·4313	43·42

Values of [Cl⁻] have been taken as $C_{Cl} \approx C_{Cl}'/\delta$.

In Table 2 the results for the functions used in evaluating stability constants and valid for $(C_M)_R = 1·70 \times 10^{-6}$ mole/g. are given. The quantities $\phi°_1$ and $f°$ were determined by graphical extrapolation as illustrated in Fig. 1.

An approximate value for β_1 was obtained from the slope of a plot of $\Delta f/[Cl⁻]$ against $\Delta\phi_1/[Cl⁻]$ at high values of $\Delta\phi_1/[Cl⁻]$. Iterative plots of $(\beta_1\Delta\phi_1/[Cl⁻] - \Delta f/[Cl⁻])$ against [Cl⁻] were then made, with different values for β_1 around the approximate value, until a straight line was obtained (see Fig. 2). The value for β_1 which yielded this rectilinear plot was taken as the correct magnitude for this stability constant. The constant β_4 was obtained from the slope of

⁵ Jacobsen, Langmyhr, and Selmer-Olsen, *Analyt. Chim. Acta,* 1961, **24**, 579.

the straight line, and β_3 was evaluated from the intercept on the $(\beta_1\Delta\phi_1/[Cl^-] - \Delta f/[Cl^-])$ axis. The value of β_2 was obtained from the relations $\phi^\circ_1 = \beta_1 - l'_1$ and $f^\circ = \beta_1(\beta_1 - l'_1) - \beta_2$. This mathematical procedure ensured that all the experimental results were used towards the derivation of each stability constant.

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TABLE 2.

$(C_M)_R = 1.70 \times 10^{-6}$ mole/g. of resin.

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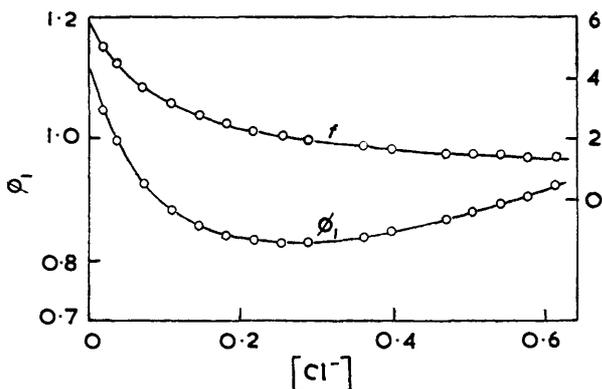| [Cl⁻] (moles/l.)	$10^3\phi$ (l./g.)	ϕ_1 (moles/l.)⁻¹	f (moles/l.)⁻²	$\Delta\phi_1/[Cl^-]$ (moles/l.)⁻²	$\Delta f/[Cl^-]$ (moles/l.)⁻³
0	68·42	(1·117)	(5·80)	—	—
0·018	67·15	1·047	5·040	−3·87	−42·22
0·036	66·05	0·9950	4·501	−3·39	−36·09
0·072	64·15	0·9252	3·698	−2·664	−29·19
0·108	62·47	0·8827	3·155	−2·169	−24·49
0·144	60·91	0·8560	2·770	−1·810	−21·04
0·180	59·44	0·8399	2·478	−1·539	−18·46
0·216	58·00	0·8318	2·250	−1·320	−16·44
0·252	56·61	0·8279	2·072	−1·147	−14·794
0·288	55·24	0·8285	1·927	−1·002	−13·45
0·360	52·58	0·8368	1·713	−0·778	−11·35
0·396	51·25	0·8460	1·629	−0·684	−10·532
0·468	48·70	0·8652	1·500	−0·538	−9·19
0·504	47·44	0·8775	1·455	−0·4752	−8·62
0·540	46·20	0·8907	1·414	−0·4191	−8·12
0·576	45·00	0·9035	1·380	−0·3707	−7·674
0·612	43·72	0·9232	1·348	−0·3167	−7·275

FIG. 1. Evaluation of ϕ°_1 and f° for the copper(II)–chloride system.

FIG. 2. Evaluation of β_1, β_3, and β_4 for the copper(II)–chloride system.

$X = \beta_1\Delta\phi_1/[Cl^-] - \Delta f/[Cl^-]$ ($\beta_1 = 9.60$).
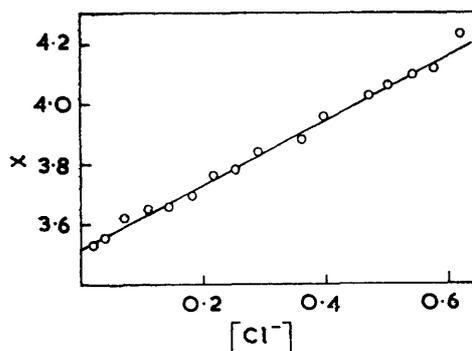
This treatment has been based on the presumption that no polynuclear complexes of copper were formed, either in the resin or in solution. This appears to be a reasonable conclusion since only low metal-ion concentrations were employed and the solutions were of quite high acidity.

Table 3 summarises values derived in the present work for the overall stability constants β_j

TABLE 3.

Stability constants for Cu^{II}–Cl complexes valid for 20° and 0·691M-perchloric acid

β_1	β_2	β_3	β_4	K_1	K_2	K_3	K_4
9·60 ± 0·5	4·92 ± 0·5	3·52 ± 0·3	1·0 ± 0·5	9·6	0·51	0·72	0·28

and for the step-constants $K_j = \beta_j/\beta_{j-1}$. It is difficult to make any quantitative comparisons between these results and those of other workers [6] because of differences in experimental conditions. In the studies involving added perchlorate it has been assumed that the tendency for copper(II) to associate with perchlorate ions is negligibly small. A recent article [7] has indicated that perchlorate can be co-ordinated to copper(II) in anhydrous nitrobenzene but no such effect has been noted in aqueous solution.

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[6] Bjerrum, Schwarzenbach, and Sillen, " Stability Constants, Part II, Inorganic Ligands," *Chemical Soc. Special Publ.* No. 11, 1958; Trémillon, *Bull. Soc. chim. France*, 1958, 1483; Reed, D.Phil. Thesis, Oxford.

[7] Barker, Harris, and McKenzie, *Proc. Chem. Soc.*, 1961, 335.