

Formation Constants of $Cu(II)$, $Zn(II)$ and $Cd(II)$ Complexes with $N-N'$ -Dibenzenesulphonyl-*l*-cystine

By

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With 6 figures

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Summary

A potentiometric study on the complex formation of $Cu(II)$, $Zn(II)$ and $Cd(II)$ with the ligand $N-N'$ -dibenzenesulphonyl-*l*-cystine (DBSC, RH_4) in 1:1 aqueous dioxane at a constant ionic strength ($\mu = 0.50$) at $30 \pm 0.5^\circ$ has indicated the formation of a 1:1 complex $M(RH_2)^0$ where $M = Cu(II)$, $Zn(II)$ and $Cd(II)$. The formation constants (K) have been determined by applying the Bjerrum-Calvin titration technique. The $\log K$ values have been computed by a graphical method and found to be 3.30, 2.04 and 1.54 respectively. The stability order is $Cu(II) > Zn(II) > Cd(II)$. The $Cu(II)$ complex $Cu(RH_2)^0$ undergoes two steps of acid dissociation for which pk_2 and pk_1 values have been found to be 4.59 and 6.21 respectively. The two acid dissociation constants (k_2^* and k_1^*) of the ligand RH_4 have also been determined and pk_2^* and pk_1^* values have been found to be 4.02 and 4.70 respectively.

Introduction

The use of the sulphonamido ($-SO_2NH-$) group as complexing agent was introduced by BILLMAN *et al.*¹. Latter on GHOSH *et al.*²⁻⁵ have

¹ J. H. BILLMAN *et al.*, Analytic. Chem. **32** (1960) 1342; **34** (1962) 3408; **36** (1964) 3552.

² N. N. GHOSH and M. N. MAZUMDER, J. Indian chem. Soc. **40** (1963) 945; **44** (1967) 115.

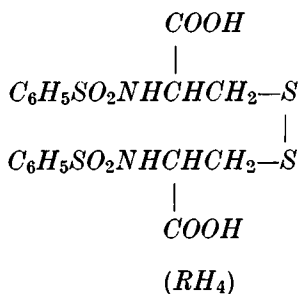
³ N. N. GHOSH and M. DASGUPTA, J. Indian chem. Soc. **43** (1966) 545; **44** (1967) 567; **48** (1971) 15; Z. anorg. chem. Soc. **375** (1970) 315; Sci. and Cult. [Calcutta] **35** (1969) 110.

⁴ N. N. GHOSH and A. BHATTACHARYA, J. Indian chem. Soc. **46** (1969) 1040; **48** (1971) 689, 889; **49** (1972) 1053; Sci. and Cult. [Calcutta] **35** (1969) 270.

⁵ N. N. GHOSH and G. N. MUKHOPADHYAY, J. Indian chem. Soc. **48** (1971) 273; **49** (1972) 1125.

studied a large number of sulphonyl derivatives of the amino acids as chelating agents. Some of the sulphonamido ligands^{6,7} are found to be useful analytical reagents.

The ligand *N-N'*-dibzenesulphonyl-*L*-cystine (DBSC, RH_4) is a dicarboxylic acid containing two sulphonamido ($-SO_2NH-$) groups, as a result it behaves as a tetradentate ligand.



The present communication describes the potentiometric determination of the two acid dissociation constants of DBSC, the formation constants of its *Cu*(II), *Zn*(II) and *Cd*(II) complexes and also the acid dissociation constants of the *Cu*(II) complex $\text{Cu}(\text{RH}_2)^0$ in 1:1 aqueous dioxane, at a constant ionic strength ($\mu = 0.50$) at room temperature $30 \pm 0.5^\circ$ following the Bjerrum-Calvin *pH* titration technique^{8,9}.

Experimental

Materials

The ligand DBSC was prepared and purified by the usual procedure¹⁰. All other reagents were either of A.R. quality or properly purified and their solutions were prepared with double distilled CO_2 -free water and purified dioxane.

Apparatus

Measurements of *pH* values were made with a Cambridge-Portable-Type *pH*-Meter with a glass electrode of 1–13 *pH* range in conjunction with a saturated calomel electrode connected to the cell by means of an agar-2M NaNO_3 bridge.

⁶ N. N. GHOSH and M. N. MAZUMDER, *J. Indian chem. Soc.* **41** (1964) 287.

⁷ N. N. GHOSH and A. BHATTACHARYA, *Bull. chem. Soc. Japan* **44** (1971) 407.

⁸ J. BJERRUM, "Metal Amine Formation in Aqueous Solutions", P. Haase, Copenhagen 1941.

⁹ M. CALVIN and K. W. WILSON, *J. Amer. chem. Soc.* **67** (1945) 2003.

¹⁰ J. S. FRUTON and H. T. CLERK, *J. biol. Chem.* **106** (1934) 667.

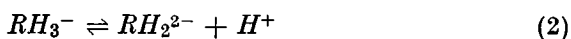
Procedure

The experimental procedure for the determination of the acid dissociation constants of DBSC and the formation constants of its *M* (II) complexes (*M* = *Cu*, *Zn* and *Cd*) consists of a potentiometric titration of 0.02 M solutions of DBSC containing a known amount of *HClO*₄ in 1:1 aqueous dioxane in absence of *M*²⁺ ions and also in presence of *M*²⁺ ions 0.01 M or 0.0075 M, with a 0.1996 M solution of *NaOH* also in 1:1 aqueous dioxane. The ionic strength of the medium was maintained constant ($\mu = 0.50$) throughout by adding a requisite amount of *NaClO*₄. The final acid concentration was determined by a graphical method. For this purpose a known amount of *HClO*₄ was potentiometrically titrated with a standard solution of *NaOH* under identical conditions as stated earlier. The *pH* values at various stages of the titration were plotted against negative logarithm of the acid concentrations. The final acid concentrations were extrapolated from the corresponding *pH* values assuming the behaviour of strong acids in mixed solvents being the same as in the aqueous media¹¹.

Results and discussion

a) The acid dissociation constants of the ligand DBSC

The stepwise acid dissociation of the ligand DBSC (*RH*₄) may be represented as stated below



of which the primary and secondary dissociation constants *k*₂^{*} and *k*₁^{*} respectively are given by

$$k_2^* = \frac{[RH_3^-][H^+]}{[RH_4]} \tag{3}$$

and

$$k_1^* = \frac{[RH_2^{2-}][H^+]}{[RH_3^-]} \tag{4}$$

The values of *p**k*₂^{*} and *p**k*₁^{*} were evaluated graphically employing the relation

$$\frac{(2 - \bar{n}_H)[H^+]^2}{\bar{n}_H} = \frac{k_2^*(\bar{n}_H - 1)[H^+]}{\bar{n}_H} + k_1^* k_2^*, \tag{5}$$

¹¹ N. N. GHOSH and M. N. MAZUMDER, *J. Indian chem. Soc.* **44** (1967) 559.

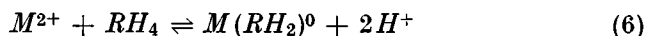
Table 1. Acid dissociation constants of the ligand RH_4 and the formation constants of its $M(II)$ -chelates

Species	pk_2^*	pk_1^*	$\log K$	pk_2	pk_1
RH_4	4.02	4.70
$Cu(RH_2)^0$	3.34 (3.30)	4.59	6.21
$Zn(RH_2)^0$	2.04
$Cd(RH_2)^0$	1.54

where \bar{n}_H is the average number of protons bound to the ligand ion RH_2^{2-} .

b) Formation constants of $M(RH_2)^0$ [$M = Cu(II)$, $Zn(II)$ and $Cd(II)$]

The ligand DBSC (RH_4) is biprotic tetradentate at the early stages of the titration and at the latter stages a tetraprotic one. The formation of complexes with M^{2+} ions in the early stages may be represented as



for which the formation constant is

$$K = \frac{[M(RH_2)^0]}{[M^{2+}][RH_2^{2-}]} \quad (7)$$

It is assumed that the acid dissociation of the complex $M(RH_2)^0$ is negligible when the formation of complex takes place and at any stage of this titration the following relations will hold after the attainment of equilibrium,

$$M = M_0 + M_1 \quad (8)$$

$$R = R_4 + R_3 + R_2 + M_1, \quad (9)$$

and as the solution is electrically neutral

$$2M_0 + P + H^+ = 2M + F + OH^- + R_3 + 2R_2, \quad (10)$$

where M , R , F and P are the initial concentrations of M^{2+} ion, the ligand RH_4 , free $HClO_4$ and alkali respectively and M_0 , M_1 , R_4 , R_3 , R_2 , H^+ and OH^- are the equilibrium concentrations of free M^{2+} ion, the complex $M(RH_2)^0$, RH_4 , RH_3^- , RH_2^{2-} , acid and alkali respectively.

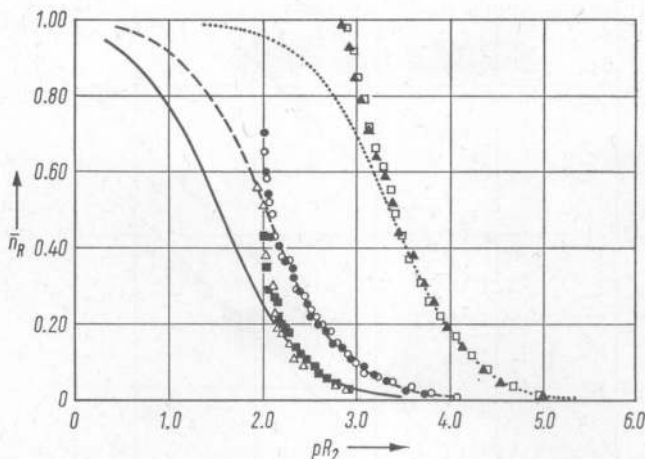


Fig. 1. Formation curves of $M(RH_2)_0$ chelates. $Cu(II)$ 0.01 M, \square ; 0.0075 M, \blacktriangle ; calculated curve employing $\log K = 3.34$,; $Zn(II)$ 0.01 M, \circ ; 0.0075 M, \bullet ; calculated curve employing $\log K = 2.04$, - - - -; $Cd(II)$ 0.01 M, \blacksquare ; 0.0075 M, \blacktriangle ; calculated curve employing $\log K = 1.54$, —————

The formation function \bar{n}_R is given by the relation

$$\bar{n}_R = \frac{1}{M} [R - (R_4 + R_3 + R_2)].$$

One may now deduce from equations (3), (4), (8), (9) and (10)

$$\bar{n}_R = \frac{1}{M} \left[R - \frac{(2R - P + F - H^+ + OH^-)}{\left(\frac{2[H^+]^2}{k_1^* k_2^*} + \frac{[H^+]}{k_1^*} \right)} \cdot \left(\frac{[H^+]^2}{k_1^* k_2^*} + \frac{[H^+]}{k_1^*} + 1 \right) \right] \quad (11)$$

and

$$pR_2 = \log \left(\frac{2[H^+]^2}{k_1^* k_2^*} + \frac{[H^+]}{k_1^*} \right) - \log (2R - P + F - H^+ + OH^-) \quad (12)$$

The formation curves (Fig. 1) were obtained on plotting \bar{n}_R against pR_2 . From this plot the $\log K$ values were found by curve fitting¹² and also from a linear plot (Fig. 2) employing the equation

$$pR_2 = \log \frac{1 - \bar{n}_R}{\bar{n}_R} + \log K \quad (13)$$

which may be deduced from the relation

$$\bar{n}_R = \frac{KR_2}{1 + KR_2}.$$

¹² F. J. C. ROSSOTTI and H. ROSSOTTI, "The Determination of Stability Constants", McGraw Hill, London 1961.

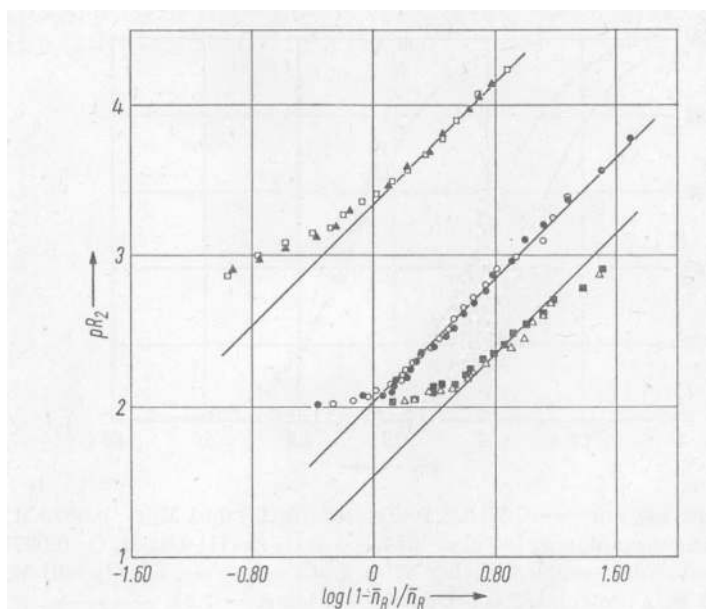
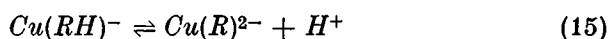
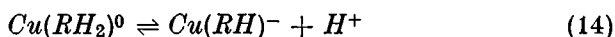


Fig. 2. Linear plot of the equation for $\log K$ values. $Cu(II)$ 0.01 M, \square ; 0.0075 M, \blacktriangle ; $Zn(II)$ 0.01 M, \circ ; 0.0075 M, \bullet ; $Cd(II)$ 0.01 M, \blacksquare ; 0.0075 M, \triangle

The deviations of the formation curves from the calculated ones obtained by employing the determined values of $\log K$, in the region beyond $\bar{n}_R \approx 0.50$ in the case of $Cu(II)$, $\bar{n}_R \approx 0.50$ in the case of $Zn(II)$ and $\bar{n}_R \approx 0.25$ in the case of $Cd(II)$ are presumed to be due to the overlapping of the step of the acid dissociation of the complex $M(RH_2)^0$ in the case of $Cu(II)$ and to precipitation in the cases of $Zn(II)$ and $Cd(II)$, as oxides. The values of $\log K$ found are recorded in Table 1. From the results it is apparent that the stability order is $Cu(II) > Zn(II) > Cd(II)$.

c) Acid dissociation of the complex $Cu(RH_2)^0$

When $\bar{n}_R \approx 1$, the acid dissociation of the complex $Cu(RH_2)^0$ begins through two successive steps as represented below,



for which the primary and secondary acid dissociation constants k_2 and k_1 are given by

$$k_2 = \frac{[Cu(RH)^-][H^+]}{[Cu(RH_2)^0]} \quad (16)$$

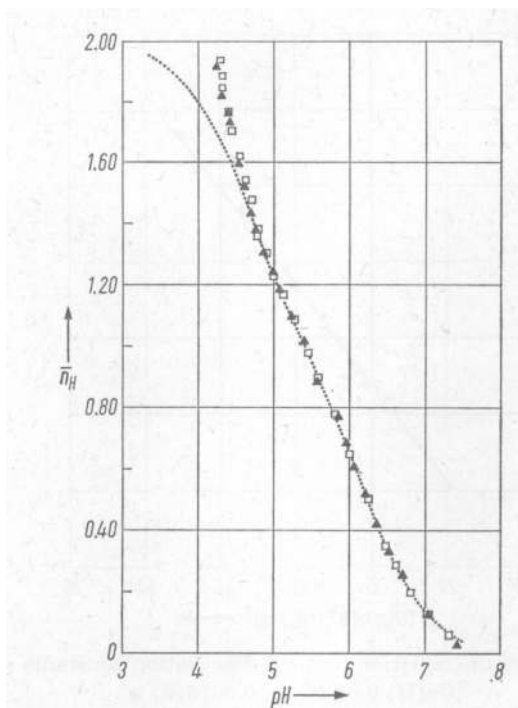


Fig.3. Acid dissociation curve of $Cu(RH_2)^0$. Cu 0.01 M, \square ; 0.0075 M, \blacktriangle ; calculated curve employing $pK_2 = 4.59$ and $pK_1 = 6.21$,

and

$$k_1 = \frac{[Cu(R)^{2-}][H^+]}{[Cu(RH)^-]} \quad (17)$$

Now at any stage of the titration the following relations will hold after the attainment of equilibrium,

$$M = M_1 + M_1' + M_1'' \quad (18)$$

$$R = R_4 + R_3 + R_2 + M \quad (19)$$

and as the solution is electrically neutral,

$$P + H^+ = 2M + F + OH^- + M_1' + 2M_1'' + R_3 + 2R_2, \quad (20)$$

where M_1' and M_1'' are the equilibrium concentrations of $Cu(RH)^-$ and $Cu(R)^{2-}$ ions respectively, the other notations have their meanings already stated.

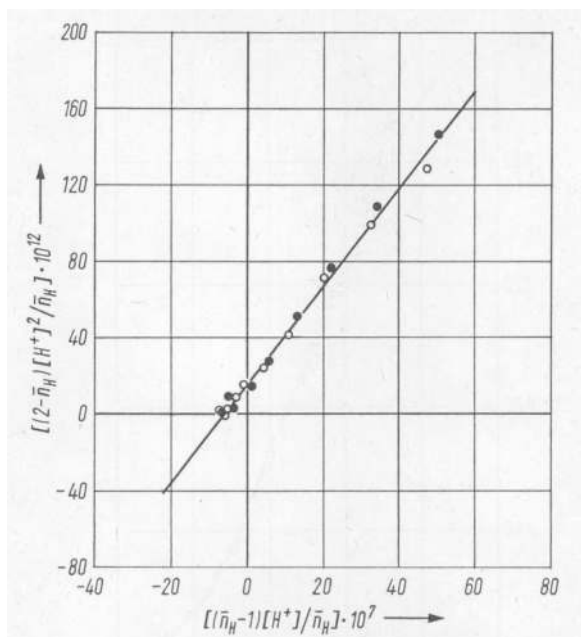


Fig. 4. Linear plot of the equation for acid dissociation constants of $Cu(RH_2)^0$. $Cu(II)$ 0.01 M, O; 0.0075 M, ●

The average number of protons (\bar{n}_H) bound to the complex $Cu(R)^{2-}$ ion is given by the relation

$$\bar{n}_H = \frac{1}{M} (2M_1 + M_1'). \quad (21)$$

One may now deduce from equations (3), (4), (18), (19), (20) and (21)

$$\bar{n}_H = 4 - \frac{1}{M} \left[(P - F + H^+ - OH^-) - \frac{(R - M) \left(2 + \frac{[H^+]}{k_1^*} \right)}{\left(\frac{[H^+]^2}{k_1^* k_2^*} + \frac{[H^+]}{k_1^*} + 1 \right)} \right] \quad (22)$$

\bar{n}_H values were plotted against pH (Fig. 3), the successive dissociation constants k_2 and k_1 were found from a linear plot (Fig. 4) employing the relation

$$\frac{(2 - \bar{n}_H)[H^+]^2}{\bar{n}_H} = \frac{k_2(\bar{n}_H - 1)[H^+]}{\bar{n}_H} + k_1 k_2 \quad (23)$$

which may be deduced from the equations (16), (17), (18) and (21). The values of pk_2 and pk_1 are recorded in Table 1.

The standard deviation (σ) was also calculated using the relation¹³

$$\sigma = \pm \left[\frac{\sum (\bar{n}_{\text{expt}} - \bar{n}_{\text{calc}})^2}{\text{Number of observations}} \right]^{1/2}.$$

¹³ H. IRVING and H. S. ROSSOTTI, J. chem. Soc. [London] 1953, 3397.

The values of (σ) obtained in the case of *Cu*(II) in the region $0 < \bar{n}_R < 0.50$ is ± 0.015 , in the case of *Zn*(II) in the region $0 < \bar{n}_R < 0.50$ is ± 0.018 , in the case of *Cd*(II) in the region $0 < \bar{n}_R < 0.25$ is ± 0.014 and in the case of acid dissociation of $Cu(RH_2)^0$ is ± 0.013 in the region $0 < \bar{n}_H < 1.45$. The higher values of (σ) beyond the regions stated above in the case of *Zn*(II) and *Cd*(II) are due to the commencement of precipitation of oxides, while in case of the formation of the *Cu*(II) complex and the acid dissociation of $Cu(RH_2)^0$ are probably due to the simultaneous occurrence of the processes represented by the equations (6), (14) and (15).

d) Refinement of the formation constant of $Cu(RH_2)^0$ considering its formation and acid dissociation simultaneously

The validity of the assumptions made above can be proved if one considers the formation of $Cu(RH_2)^0$ and its acid dissociation to occur simultaneously, particularly in the region beyond $\bar{n}_R \geq 0.50$. If reactions (6), (14) and (15) run side by side, the following relations will hold after the attainment of equilibrium,

$$M = M_0 + M_1 + M_1' + M_1'' \tag{24}$$

$$R = R_4 + R_3 + R_2 + M_1 + M_1' + M_1'' \tag{25}$$

and as the solution is electrically neutral

$$2M_0 + P + H^+ = 2M + F + OH^- + R_3 + 2R_2 + M_1' + 2M_1'' \tag{26}$$

where the notations have their usual significances as stated earlier. One may now obtain from the equations (3), (4), (16), (17), (24), (25) and (26)

$$R_2 = \frac{\left\{ \frac{R \left(2 + \frac{3k_2}{[H^+]} + \frac{4k_1 k_2}{[H^+]^2} \right)}{\left(1 + \frac{k_2}{[H^+]} + \frac{k_1 k_2}{[H^+]^2} \right)} - (P - F + H^+ - OH^-) \right\}}{\left\{ \frac{\left(1 + \frac{[H^+]}{k_1^*} + \frac{[H^+]^2}{k_1^* k_2^*} \right) \left(2 + \frac{3k_2}{[H^+]} + \frac{4k_1 k_2}{[H^+]^2} \right)}{\left(1 + \frac{k_2}{[H^+]} + \frac{k_1 k_2}{[H^+]^2} \right)} - \left(2 + \frac{[H^+]}{k_1^*} \right) \right\}} \tag{27}$$

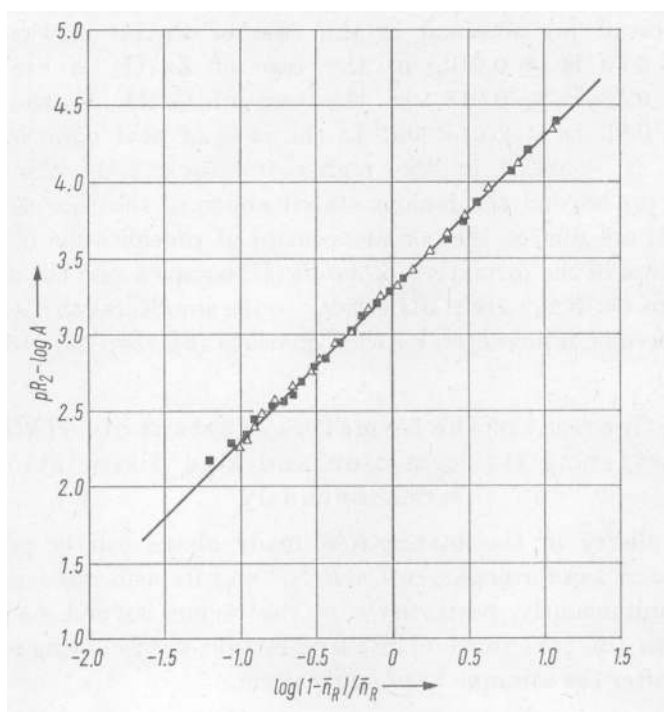


Fig. 5. Linear plot of the equation for refined $\log K$ value of $\text{Cu}(\text{RH}_2)^0$. $\text{Cu}(\text{II})$ 0.01 M, \blacksquare ; 0.0075 M, \blacktriangle

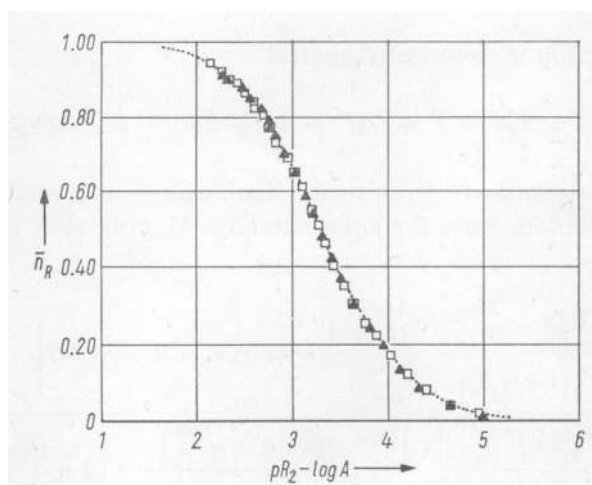


Fig. 6. Formation curve of $\text{Cu}(\text{RH}_2)^0$ with refined values. $\text{Cu}(\text{II})$ 0.01 M, \square ; 0.0075 M, \blacktriangle ; calculated curve employing $\log K = 3.30$, $\cdots\cdots$

In calculating R_2 the experimentally determined values of pk_2 and pk_1 were used. Now \bar{n}_R (expt) may be obtained from the experimental data as,

$$\bar{n}_R = \frac{1}{M} \left\{ R - R_2 \left(\frac{[H^+]^2}{k_1^* k_2^*} + \frac{[H^+]}{k_1^*} + 1 \right) \right\}.$$

By linear plot (Fig. 5) of the equation

$$pR_2 - \log \left(1 + \frac{k_2}{[H^+]} + \frac{k_1 k_2}{[H^+]^2} \right) = \log \frac{1 - \bar{n}_R}{\bar{n}_R} + \log K \quad (28)$$

the refined value of $\log K$ has been obtained and found to be (3.30) which has also been recorded in Table 1. The equation (28) may be deduced from the relation

$$\bar{n}_R = \frac{M_1 + M_1' + M_1''}{M_0 + M_1 + M_1' + M_1''} = \frac{KR_2 \left(1 + \frac{k_2}{[H^+]} + \frac{k_1 k_2}{[H^+]^2} \right)}{1 + KR_2 \left(1 + \frac{k_2}{[H^+]} + \frac{k_1 k_2}{[H^+]^2} \right)} \quad (29)$$

\bar{n}_R (calc) values are obtained with the help of the equation (29) using the refined value of K and the calculated and experimental formation curves have been redrawn (Fig. 6) by plotting the respective \bar{n}_R against $(pR_2 - \log A)$ where $A = \left(1 + \frac{k_2}{[H^+]} + \frac{k_1 k_2}{[H^+]^2} \right)$. Smaller values of $(\sigma) = \pm 0.011$ obtained with these new values even including the whole region ($0 < \bar{n}_R < 1.0$) as well as the shape of the formation curve indicate much more precision.

Acknowledgement

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