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SUMMARY

The copper II thiocyanate complex is used as indicator for the determination of the stability constants of some copper anion association complexes in solution. Based upon the K values obtained, the various anions examined are arranged according to their complexing power. The agreement between the K values of the copper II-citrate complex using the direct and indirect methods is established.

INTRODUCTION

Copper II can be determined colorimetrically by its reaction with thiocyanate which yields an orange-brown colour. The rate of colour development, its intensity and stoichiometry of the complex formed in solution depends on some factors including the order of addition of reagents, the concentration of foreign ions present, the ionic strength and temperature(1).

Generally, the values of the formation constants of the Cu^{2+} -anion complexes were found to depend largely on the nature and concentration of the other ions present in solution. McConell and Davidson(2) reported the equilibrium constant of the 1:1 copper chloro-complex. Matheson(3) determined the equilibrium constant of the Cu^{2+} -SO_4 complexes.

The present article is devoted to an investigation of the behaviour of the Cu^{2+} -CN^- complex in the presence of various anions in an attempt to evaluate the formation constants of the Cu^{2+} -complexes liable to be formed with such anions.

EXPERIMENTAL

The copper II-solution:

Standard Cu^{2+} -solution was prepared by dissolving a known weight of BDH electrolytic copper wire in the least quantity of perchloric acid (Merck pro-Analyse). The solution was evaporated on a water bath to get rid of excess $HC1O_4$, then diluted with redistilled water in a calibrated measuring flask of appropriate volume.

The Cu^{2+} -concentration of the resulting solution was further checked colorimetrically by the sodium diethyl dithiocarbamate method(4). The acidity was also determined by direct titration with a standard Na_2CO_3 solution using methyl orange as indicator. The final stock solution was 10^{-2}M with respect to Cu^{2+} and 003 N with respect to $HC1O_4$.

Preparation of solution for spectrophotometric measurement:

A volume of 2 ml of the 10^{-2}M stock copper II perchlorate solution was placed in a 10 ml calibrated measureming flask followed by the necessary quantity of the anion solution added as the sodium salt and 1.0 ml of 2×10^{-2} M NH_4CNS. This condition was chosen to ensure the formation of 1:1 $(Cu\text{-}CNS)^+$ complex only. If it happens that higher order complexes would be formed their concentration would be too low that it can be neglected without appreciable error. Finally, the calculated amount of $NaC1O_4$ and $HC1O_4$ necessary, to adjust the ionic strength and acidity were added and the reaction mixture was completed to the mark with redistilled water.

Apparatus and light absorption measurement:

Light absorption measurements were carried out on a Unicam SP 700 U.V. -spectrophotometer using 1.0 cm matched silica cells. The absorbance of the reaction solution was directly measured at a wavelength of 357-1 nm which corresponds to maximum absorption of the Cu^{2+} -CNS^- complex formed under prevailing experimental conditions. The absorbance values recorded were compared with those obtained with similar solutions deprived of the additive anion.

RESULTS AND DISCUSSION

The determination of the stability constants of the Cu^{2+} -anion association complexes were carried out at a constant ionic strength of

0.056, the acidity was mostly maintained at 0.006 M $HClO_4$. All measurements were carried out at 20 ∓ 0.5°C.

If the equilibrium reaction leading to the formation of the copper II-anion complex can be formulated as follows.

$$Cu^{2+} + X^{n-} \rightleftarrows (CuX)^{(+2-n)}$$

then the formation constant can be expressed by the relation

$$K_f = \frac{[(CuX)^{(+2-n)}]}{[Cu^{2+}]\,[X^{n-}]} \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad 1$$

If one takes x as the concentration of the ion pair, a and b as the analytical concentration of Cu^{2+} and X^-, respectively then

$$K_f = \frac{x}{(a-x)\,(b-x)} \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad 2$$

If A and A≠ represent the absorbance of the Cu^{2+} solution in absence and presence of the complexing anion then

$$A - A_{\neq} = x\,l\,(\varepsilon - \varepsilon_{\neq}) = x \triangle \varepsilon\, l \quad \dots\dots\dots\dots \quad 3$$

for which ε and $\varepsilon_{\neq}$ are the molar extinction coefficients of the copper thiocyanate solutions in absence and presence of the additive anion.

From equations 2 and 3, the following relation is obtained.

$$K_f = \frac{A - A_{\neq}}{l \triangle \varepsilon\,(a-x)\,(b-x)} \quad \dots\dots\dots\dots\dots\dots \quad 4$$

if the value of x is small compared to a and b then

$$K_f = \frac{A - A_{\neq}}{l \triangle \varepsilon\,(ab)} \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad 5$$

thus the value of the formation constant can be directly determined from the decrease in absorbance of the Cu^{2+} -CNS^- solution on addition of the complexing anion. This can be readily applied in case of weak complexing ligands; but for strong complexing ones where x is not negligible with respect to a or b, plots of $ab / A - A_{\neq}$ as a function of (a+b) were first established to obtain approximate values for $\triangle \varepsilon$ and K. From the values thus calculated and using equation 4, the values of x can be determined hence the correct equilibrium concentrations of Cu^{+2} and X^{n-} are determined, accordingly the correct value of K_f can be obtained.

These facts can be reached by carrying out the following modification of equation 4.

$$1\triangle\ \varepsilon\ K_f = \frac{A—A\#}{ab—x\,(a+b—x)} \quad \dots\dots\dots\dots\dots\dots \quad 6$$

from equation 6 the following relation is obtained

$$\frac{1}{1\triangle\ \varepsilon\ K_f} = \frac{ab}{A\text{-}A\#} + \frac{a+b\text{-}x}{\triangle\ \varepsilon\ 1} \quad \dots\dots\dots\dots\dots \quad 7$$

hence

$$\frac{ab}{A—A\#} = \frac{1}{1\triangle\varepsilon K_f} + \frac{a+b\text{-}x}{\triangle\ \varepsilon\ 1} \quad \dots\dots\dots\dots\dots \quad 8$$

if x is too small with respect to a and b then

$$\frac{ab}{A—A\#} = \frac{1}{1\triangle\varepsilon K_f} + \frac{a+b}{\triangle\ \varepsilon\ 1} \quad \dots\dots\dots\dots\dots \quad 9$$

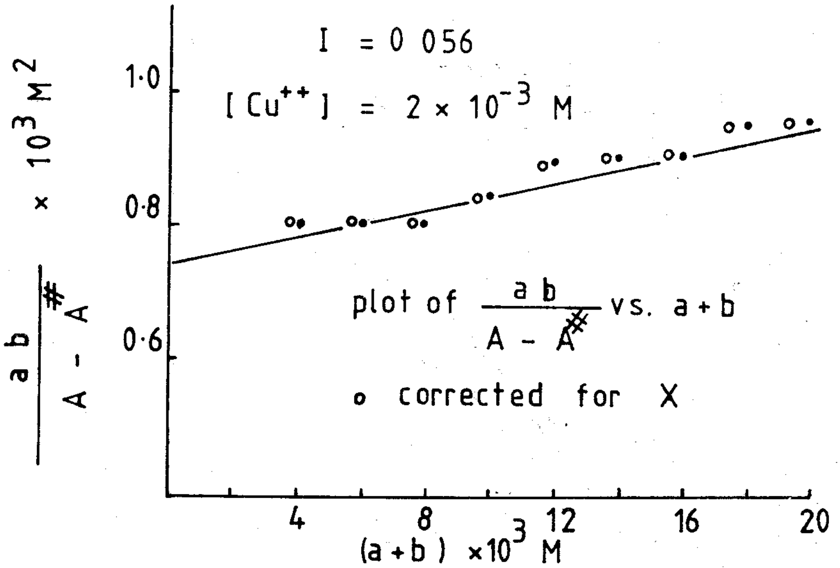
The results for the various anions examined were obtained from either $(ab/A—A\#)$ vs $(a+b)$ or $(ab/A—A\#)$ vs $(a+b—x)$ plots. Representative curves for two anions, Br^- as an example of weak complexing anion and tartrate as strong complexing, are shown in Figs. 1 and 2. The results are in Table 1. The plots are linear relations with slopes equal to $1/1\ \triangle\ \varepsilon$ and intercept at $(ab/A—A\#)$ equals zero amounting to $1/1\ \triangle\ \varepsilon\ K_f$. From these two values K_f can be calculated.

The values of $\triangle\ \varepsilon$ and K_f are depicted in Table II, these results are in agreement with those given in earlier investigations(5). Based on the value of K_f, the anions can be arranged according to the stability of their copper II complexes as follows:

citrate > oxalate > phosphate > tartrate.

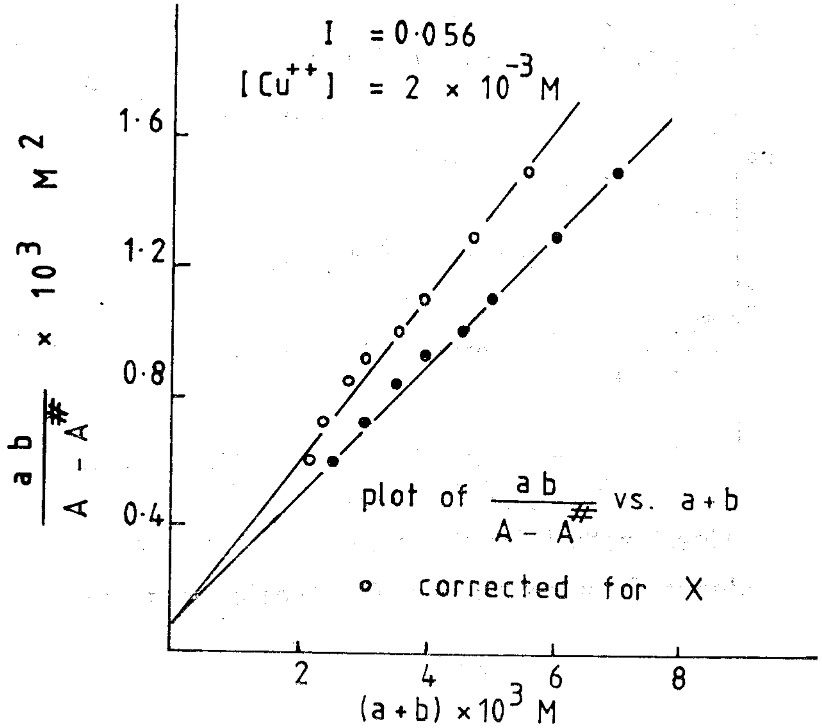
sulphate > fluoride > chloride > bromide.

This order agrees with that predicted by Lewis theory of coordination(6) based on the basicity of the added anion. It seems thus reasonable to expect a certain correlation between the proton affinity of the ligand and the stability of the complexes it forms. This is obvious



Indirect method for the determination of the stability constant of the Cu- bromide complex.

FIG. 1



Indirect method for the determination of the stability constant of the Cu – tartrate complex.

FIG. 2

Table I Results obtained for the Cu^{2+}—Br and Cu^{2+}— tartarte complexes
(Cu^{2+}) (a) $= 2 \times 10^{+3}$ M, $(CNS^{-}) = 2 \times 10^{-3}$ M

Results for Br^{-}				Results for tartrate			
(Br) (b)	$(NaClO_4)$	(A—A±)	$X.10^{-3}$	(tartrate) (b)	$(NaClO_4$	(A—A±)	$X.10^{-3}$
0.002	0.028	0.050	0.05	0.0005	0.0285	0.16	0.33
0.006	0.024	0.15	0.15	0.0010	0.0270	0.27	0.59
0.010	0.020	0.020	0.20	0.0020	0.0240	0.43	0.90
0.014	0.016	0.030	0.30	0.0030	0.0210	0.52	1.09
0.020	0.010	0.040	1.00	0.0050	0.0150	0.62	1.36

Table II Results obtained for Δ and K_f before and after correction for X values with various complexes

Anion	Before correction		After correction			Literature value (K_f)
	DH	K_f	DE	K_f	$\log K_f$	
Bromide	100.0	15.0	—	—	1.18	—
Chloride	40.0	52.1	31.25	72.0	1.86	0.50
Flouride	66.6	83.3	62.50	88.9	1.95	0.70
Sulphate	117.6	1.10×10^2	105.25	1.26×10^2	2.10	0.30
Tartrate	476.0	2.23×10^3	384.00	3.25×10^3	3.51	3.20
Phosphate	416.6	4.80×10^4	322.50	6.20×10^4	4.79	5.20
Oxalote	500.0	600×10^4	400.00	7.50×10^4	4.87	4.50
Citrate	666.6	1.50×10^5	512.80	200×10^5	5.30	6.10

in the case of the three halide anions since the stability of their complexes with Cu^{+2} decreases from F^- to Cl^- or Br^-. The basic strength of the anion can generally be determined from the pKa value of the acid⁽⁷⁾ the data for the three carboxylic acids under investigation are also in-agreement with this expectations.

To ensure the validity of the indirect method for the determination of the stability constants of metal-anion complexes, the results of the thiocyanate method are compared with those of the continuous variation method of Job as modified by Vosburg and Cooper(8) for the Cu^{2+} -citrate complex. The results of the continuous variation method revealed that the stoichiometry of the Cu^{+2} -citrate complex is 1:1 with a formation constant ($\log K_f$) amounting to 5.30 Thus, both the direct and indirect methods gave the same stoichiometry of the complex and concordant K_f values.

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