

direction only (i.e., $u_w > 0$, $v_w = 0$) which implies that $\alpha = 0$. For $\xi > 0$, $\beta < 0$ and $a < 0$. This means that there is a reverse flow in the x direction and the line $\xi = a/\beta$ divides the line into two regions: To the left of this line, the wall shear is to the left and to the right of it, the same shear is to the right. The value of c^* ($c^* < 0$) for which $s_w'' = 0$ depends on the parameters ω , f_w , and g_w . Some of the features of this case are shown schematically in figure 2.

Now we consider the surface shear lines in the region $-1 \leq c < c^*$. As in earlier cases, $u_w > 0$, $v_w = 0$, hence $\alpha = 0$. Also for $\xi < 0$, $\beta > 0$ and $a < 0$. Thus it reduces to the case I ($c > 0$) described earlier. Also, the direction of the shear lines is the same as that for $c > 0$. This is due to the reverse flow in y component of the velocity which occurs at $c \approx -0.5$ independent of the wall which is moving in the x direction. Thus it can be concluded that for both nodal and saddle point flows ($-1 \leq c \leq 1$), the line $\xi = a/\beta$ is a locus of surface shear lines dividing the flow into "upstream" and "downstream" regions and is analogous to a three-dimensional separation line without the other manifestations of separation.

CONCLUSIONS

Here, we have extended the analysis of Libby for the steady three-dimensional stagnation-point flow over a moving wall for incompressible fluid to compressible fluid case with mass transfer. The effect of compressibility and mass transfer on the flow field

is found to be significant. Also the three-dimensional analog of two-dimensional separation is shown.

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POLAROGRAPHIC STUDY OF MIXED LIGAND COMPLEXES OF COPPER WITH SOME CARBOXYLIC ACIDS AND PROPYLENEDIAMINE

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ABSTRACT

Equilibrium studies on the formation of the ternary complexes with homo donors of the type $CuXY$, where X is propylenediamine and Y succinic, maleic or malonic acid, has been studied by polarography. The overall formation constants have been evaluated at 25°C and at an ionic strength of 1.0 M (KNO_3) using Schaap and McMasters' method. The mixed ligand stabilisation constant, clearly indicates the preferred formation of copper (II) mixed ligand complexes with nitrogen donors over oxygen donors. The other driving forces leading to the favoured formation of mixed ligand complexes are also discussed. The stability constants of complex species are reported.

INTRODUCTION

MIXED-Ligand Complexes of metal ions have been extensively studied in recent years since

these play an important role in biological process¹⁻³ Ternary complexes of various metal ions involving aminoacids, diamines and carboxylic acids have been studied by pH metric technique⁴⁻⁶ Research

workers⁷⁻¹⁰ have studied recently the behaviour of mixed complexes of copper with some aminoacids, carboxylic acids and diamines by polarographic technique, using Schaap and McMasters¹¹ method. The present investigation deals with the study of mixed ligand complexes formed by Cu(II) with (i) propylenediamine-succinate, (ii) propylenediamine-maleate and (iii) propylenediamine-malonate systems.

THEORY

Since the coordination number of copper (II) is unlikely to exceed four, only the mixed species of the type Cu XY can be formed with bidentate ligands.

The DeFord and Hume¹² expression for $F_0(X)$ may be extended to give a new function $F_{00}(X, Y)$ given by

$$F_{00}(X, Y) = \text{Antilog} \left[\frac{0.4343 nF}{RT} \Delta E_{1/2} + \log \frac{I_M}{I_C} \right]$$

The symbols have their usual meanings. The function F_{00} can also be expressed as

$$F_{00}(X, Y) = A + B[X] + C[X]^2$$

where $A = 1 + \beta_{01}[Y] + \beta_{02}[Y]^2$;
 $B = \beta_{10} + \beta_{11}[Y]$;
 and $C = \beta_{20}$

Here X and Y represent variable and fixed ligands respectively.

In this method, other functions have been calculated from the following equations:

$$F_{10}(X, Y) = \frac{F_{00}[X, Y] - A}{[X]} = B + C[X]$$

$$\text{and } F_{20}[X, Y] = \frac{F_{10}[X, Y] - B}{[X]} = C$$

The intercepts of plots of $F_{10}(X, Y)$ vs $[X]$ extrapolated to $[X] = 0$ give respective values of A , B and C . The mixed stability constant β_{11} for the Cu XY can be evaluated by the knowledge of B .

MATERIALS AND EXPERIMENTAL DETAILS

Propylenediamine and potassium salts of succinic, maleic and malonic acids were used as complexing agents. All the chemicals used were of A.R. grade. The ionic strengths of all the solutions were maintained at

1.0 M by adding the required amount of potassium nitrate. pH of the solution was maintained at the required value by adding nitric acid solution or carbon dioxide free potassium hydroxide. The solutions were deaerated with pure nitrogen. Capillary characteristics for the open circuits were $m = 1.89$ mgm per sec and $t = 3.5$ sec. The polarograms were taken using H type of cell and a manual polarograph.

The acid dissociation constants of the ligands used were determined under the present experimental conditions by the method of Albert and Serjeant¹³. The pK_2 values were 5.44, 6.26, 5.69 and 9.78 respectively for succinic acid, maleic acid, malonic acid and propylenediamine. These values are in good agreement with literature values¹⁴.

RESULTS AND DISCUSSION

(a) The Binary Systems

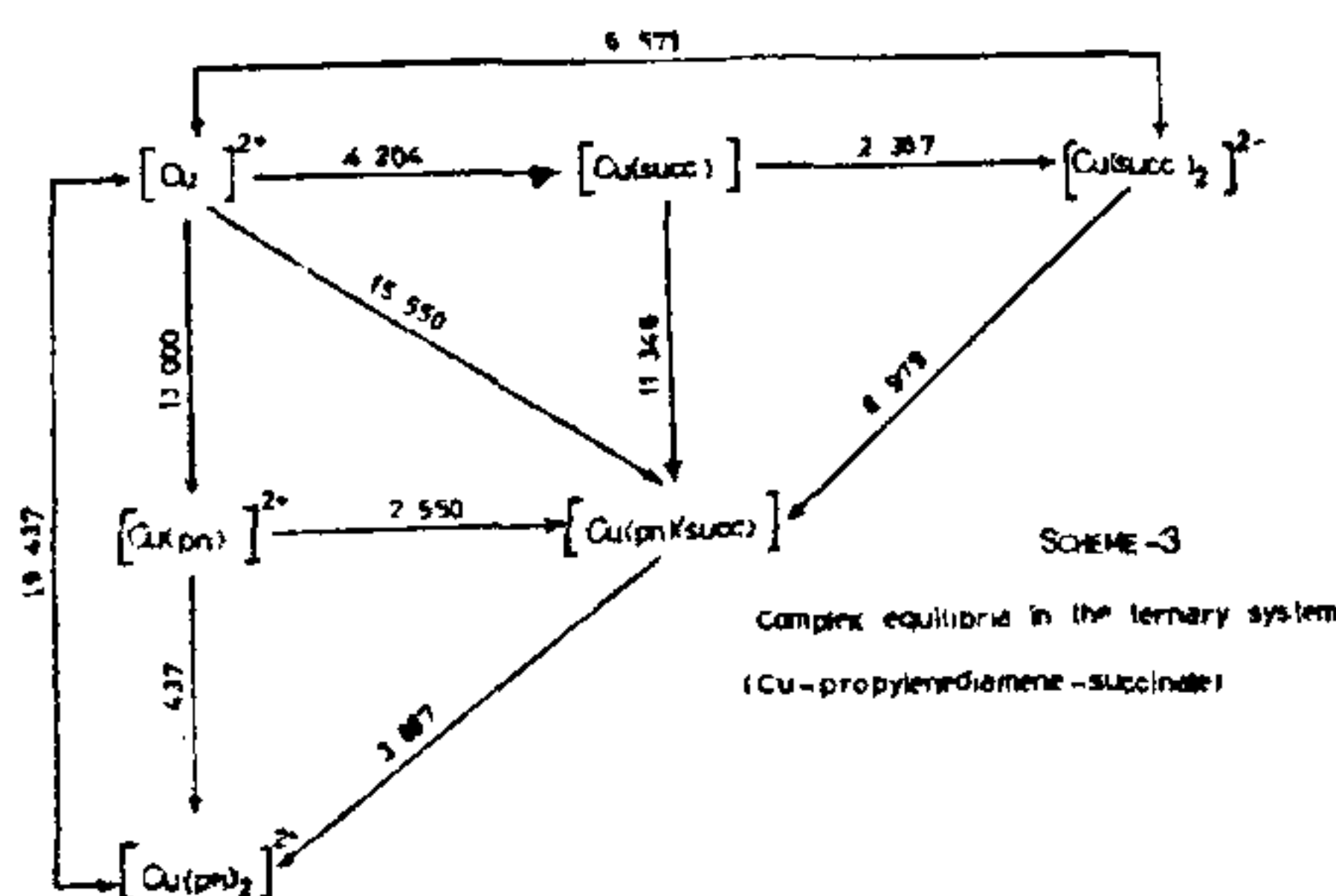
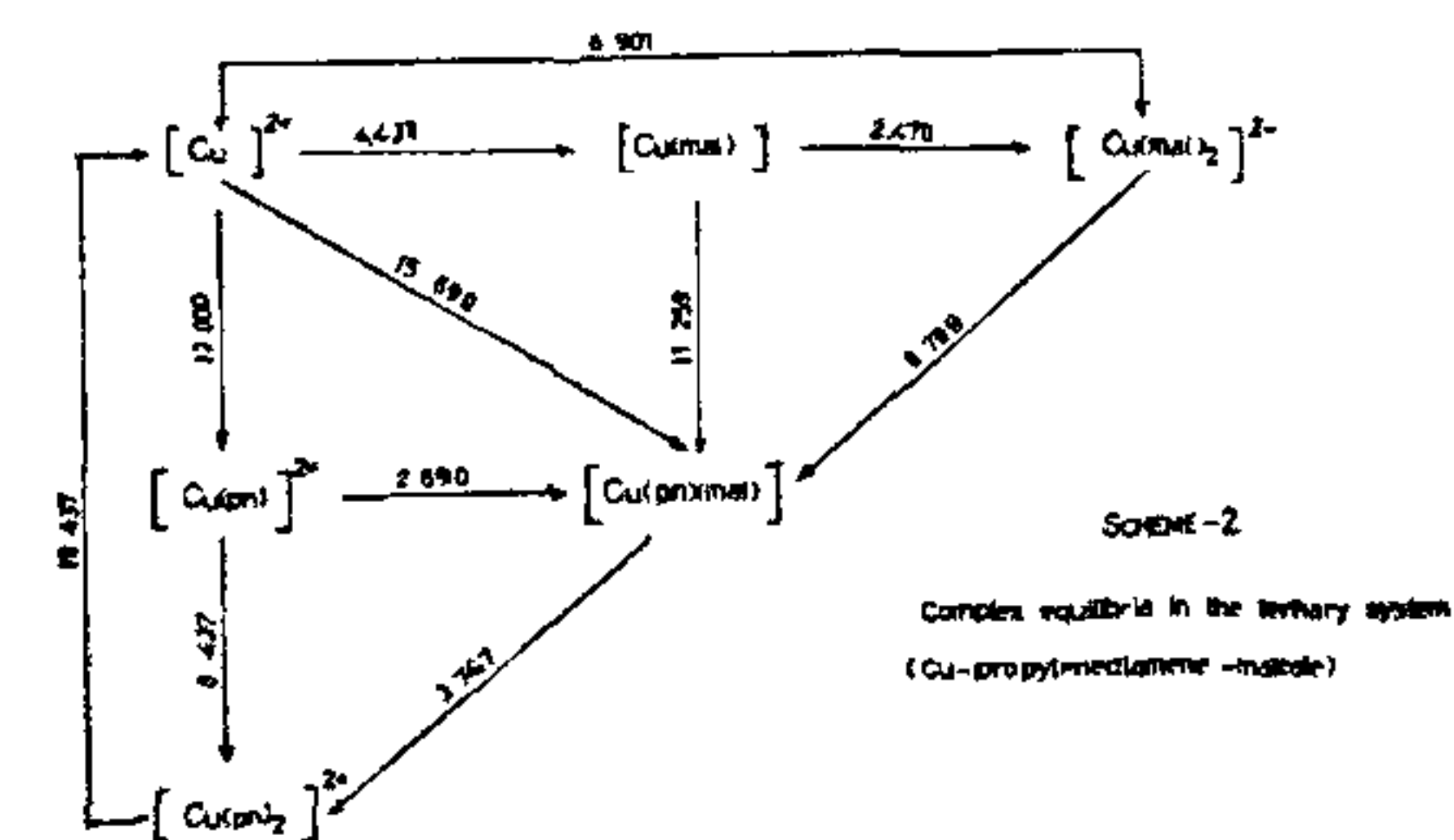
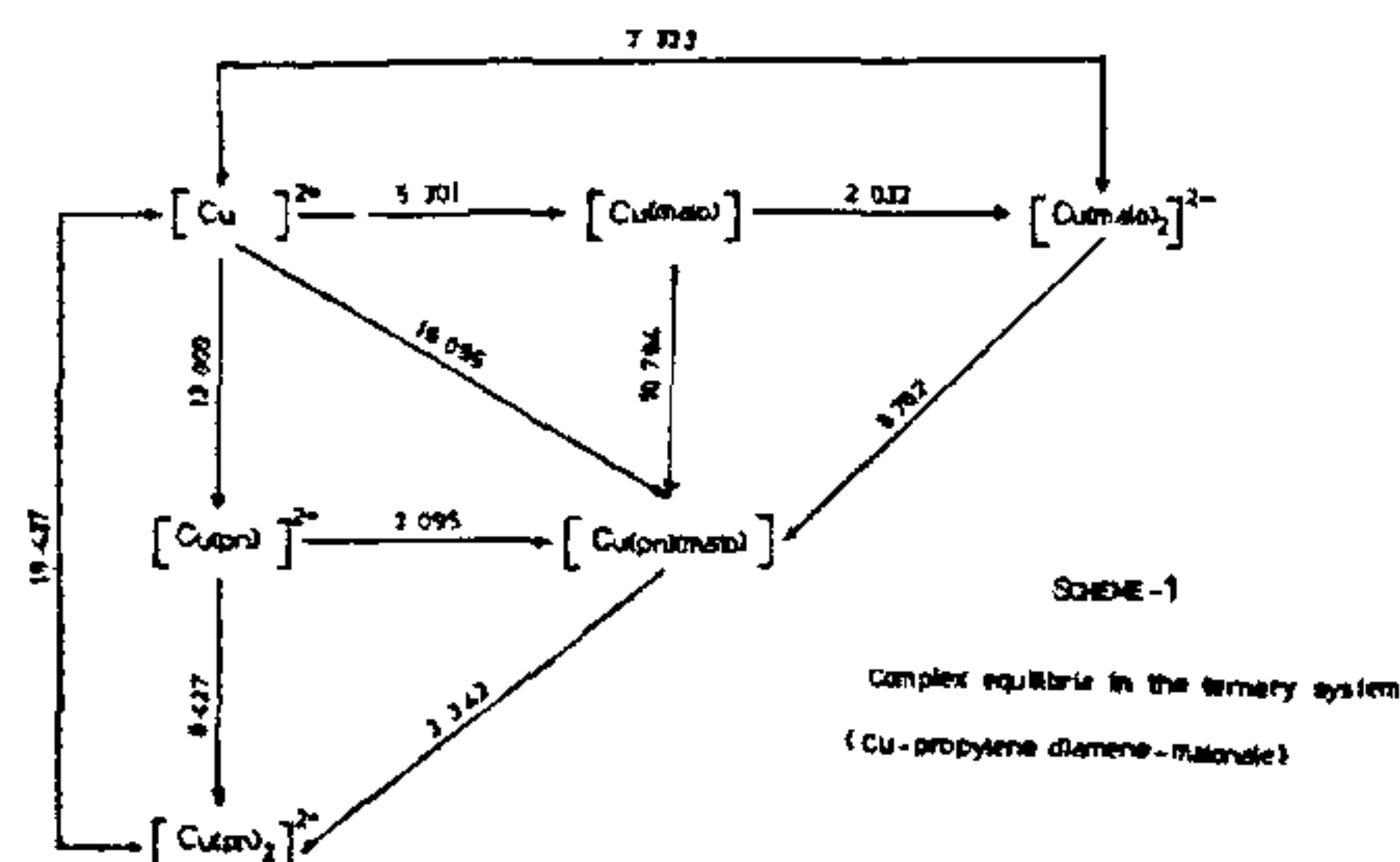
The reduction of Cu(II) was found to be diffusion-controlled in each case as indicated by the linear plots of i_d vs $h_{\text{eff}}^{1/2}$ passing through the origin. The plots of $\log i/i_d - i$ vs $h_{\text{eff}}^{1/2}$ were linear with a slope of 31 ± 2 mV indicating a reversible wave. The concentrations of 'free' ligand ions were calculated from pH data, pK value and the total amount of ligand present. The overall formation constant of simple complexes have been evaluated by DeFord and Hume¹² method.

(b) Mixed (Ternary) Systems

The copper-pn-malo., copper-pn-mal. and copper-pn-succ. systems were studied by keeping the concentration of the weaker ligand ($Y = \text{malonate or maleate or succinate}$) constant (0.20 M) and by varying the concentration of stronger ligand ($X = \text{pn}$) in each case.

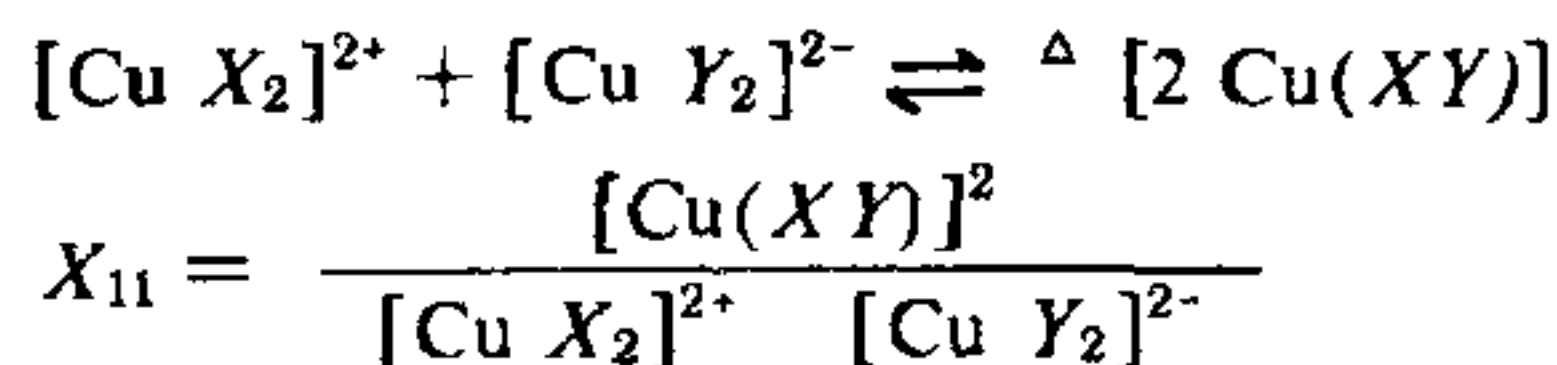
Copper-pn-malo, Copper-pn-mal and Copper-pn-succ. systems were studied at pH 7.7, 8.5 and 8.2 respectively, because at these pH it is much easier to hold the concentration of malonate (malo), maleate (mal) or succinate (succ) constant and to vary the concentration of pn. The corresponding binary systems were also studied under identical pH values and experimental conditions. The equilibrium concentration of stronger ligand (pn) was determined from pH of the solution and determined pK value.

$E_{1/2}$ of Cu(II) at ionic strength 1.0 M (KNO_3) was +0.015 volts vs SCE. The shift in $E_{1/2}$ to more negative potential with increase in [pn] was observed in all the cases. This shift is greater in presence of weaker ligand than in its absence. It signifies the formation of mixed ligand complex. The Schaap and McMaster's treatment was applied to the $E_{1/2}$ data and F_{10} functions evaluated.* The calculated values of A are 1.523×10^5 , 3.239×10^5 and 9.0×10^5 for cu-pn-succ., cu-pn-mal. and Cu-pn-malo. systems respectively, whereas the corresponding values of B are 0.072×10^{16} , 0.099×10^{16} and 0.25×10^{16} , while corresponding C_{av} values are 0.177×10^{20} , 0.178×10^{20} and 0.540×10^{20} . Theoretically, $\log C$ must be equal to $\log \beta^{20}$. Our results are almost in conformity with this postulate.



The results of these systems are summarized in schemes 1, 2 and 3 where $\log K$ of the steps are indicated.

The mixed ligand stabilization constant $\log X_{11}$ is calculated from the disproportionation reaction as shown below:



The $\log X_{11}$ value proposed by Sharma and Schubert¹⁵ on statistical grounds is 0.6. The observed values of $\log X_{11}$ greater than 0.6 indicates favoured formation of the mixed ligand complexes over binary complexes. The observed $\log X_{11}$ values are 5.092, 5.042 and 5.420 for cu-pn-succ., cu-pn-mal. and cu-pn-malo. systems respectively.

It is also observed that mixed ligand complexes having one five- and one six-membered ring are more stable than the one having one five- and one seven-membered ring.

Alternatively, the extent to which the ternary complexes are favoured can be inferred from the value of $\Delta \log K$ ($\log K_{MAB} - \log K_{MB}$), where K_{MAB} is the equilibrium constant for the reaction $MA + B \rightleftharpoons MAB$ and K_{MB} the equilibrium constant for $M + B \rightleftharpoons MB$. Sigel¹⁶ has shown when both the ligands are bidentate the statistical value of $\Delta \log K$ is -0.4 for octahedral complexes. According to Sigel¹⁶ the statistical value of $\Delta \log K$ for metal ion like Cu(II) forming distorted octahedral complexes will be still lower. The values for cu-pn-succ., cu-pn-mal. and cu-pn-malo. systems are -1.654, -1.741 and -2.206 respectively.

Many workers¹⁷ have observed that charge neutralisation favours formation of mixed ligand complexes. The results of our investigations are also in agreement with this postulation.

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ANNOUNCEMENT

FIRST ALL INDIA UNIVERSITY YOUTH ACADEMIC WEEK

The First All India University Youth Academic Week will be held during 3-5 April, 1983 at the Birla Institute of Technology and Science, Pilani. The Academic Week will be a unique event where the confluence of the brightest student talent in Engineering, Science, Technology, Economics, Management and many other fields, will take place along with leading academicians and professional experts in the above fields. The Academic Week will also serve as a place where the cream of the students will emerge, providing a unique bonanza, to the major national employer groups to present to the graduating students, professional avenues available.

The following are the areas of interest for papers: Production and Manufacturing systems, Engineering Design and Development, Instrumentation Systems, Micro-processor Systems, Systems Engineering, Computer Systems, Project Management, Research Projects, Management Science based Systems, Environmental Systems, Economic Systems, Operations Research and Statistics Integrated Rural Development, Science Communication and Journalism, Education Research, Science and Society.

Further information may be had from the Coordinator, Academic Week, Students' Union, B.I.T.S., Pilani 333 031.