STUDIES ON QUATERNARY MIXED-LIGAND COMPLEXES OF SOME TRANSITION METALS

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ABSTRACT

Potentiometric evidences have been cited for the formation of 1 : 1 : 1 : 1 quaternary complexes of the type MABC [where M(II) = Cu(II), Ni(II) and Zn(II), A = nitrilotriacetic acid (NTA), B = oxalic acid (OX) and C = ethylenediamine (en) or 1,2-propanediamine (pn)]. Formation constants and free energies of formation have also been evaluated at 25 ± 1° C.

INTRODUCTION

THE ternary complexes[1-5] of transition metals have been extensively studied by using various physico-chemical techniques, but much less work has been undertaken on the quaternary systems[6-10] involving these metal ions. It was therefore considered of interest to undertake potentiometric studies on some of these systems: M(II)-NTA-OX-en/pn [where M(II) = Cu(II), Ni(II), Zn(II); NTA = nitrilotriacetic acid, OX = oxalic acid, en = ethylenediamine, pn = 1,2-propanediamine]; the results are presented in this paper.

MATERIALS AND METHODS

All the chemicals used were either of (A.R., BDH) or (G.R., Merck) grade. Stock solutions of metal nitrates were prepared in double distilled water and standardised by usual methods[11]. The solutions of diamine dihydrochlorides and oxalic acid were prepared by direct weighing. NTA was used as its mono-potassium salt. The detailed experimental procedure has been described in our earlier communication[12].

The dissociation constants of the ligands were calculated by the method of Chaberek and Martell[13]. Formation constants for the simultaneous addition of primary (NTA) and secondary (OX) ligand to the metal ion were evaluated by the method of Ramamoorthy and Santappa[14], and those for the addition of tertiary ligand en/pn to the intermediate ternary species: M(II)-NTA-OX by the Thompson and Loraas method[15].

RESULTS AND DISCUSSION

Representative curves for the systems Cu(II)-NTA-OX-en/pn are given in Figs. 1 and 2. Curves for the other systems: Ni(II)/Zn(II)-NTA-OX-en/pn, being identical in nature, are omitted. Curves *a*, *b* and *c* depicting inflections at $m = 1$, 2 and 1, represent the titrations of diamine-dihydrochlorides (en/pn), oxalic acid and mono-potassium salt of NTA respectively.

Curves *e* and *f* exhibiting the titrations of the systems: *1 : 1* Cu(II)-OX, 1 : 1 Cu(II)-en/pn respectively, exhibit two inflections at $m = 2$ and $m = 3$, which may be correlated to the formation of 1 : 1 binary complexes and their subsequent disproportionation as is evident by the formation of heterogeneous phase ($CuO \cdot H_2O$). In the case of *1 : 1* Cu(II)-NTA (curve *d*) a single inflection, however, indicates the formation of hydrolysis resistant 1 : 1 Cu(II)-NTA species.

Curves *g* and *h* representing the titrations of 1 : 1 : 1 Cu(II)-NTA-en/pn, 1 : 1 : 1, Cu(II)-OX-en/pn exhibit

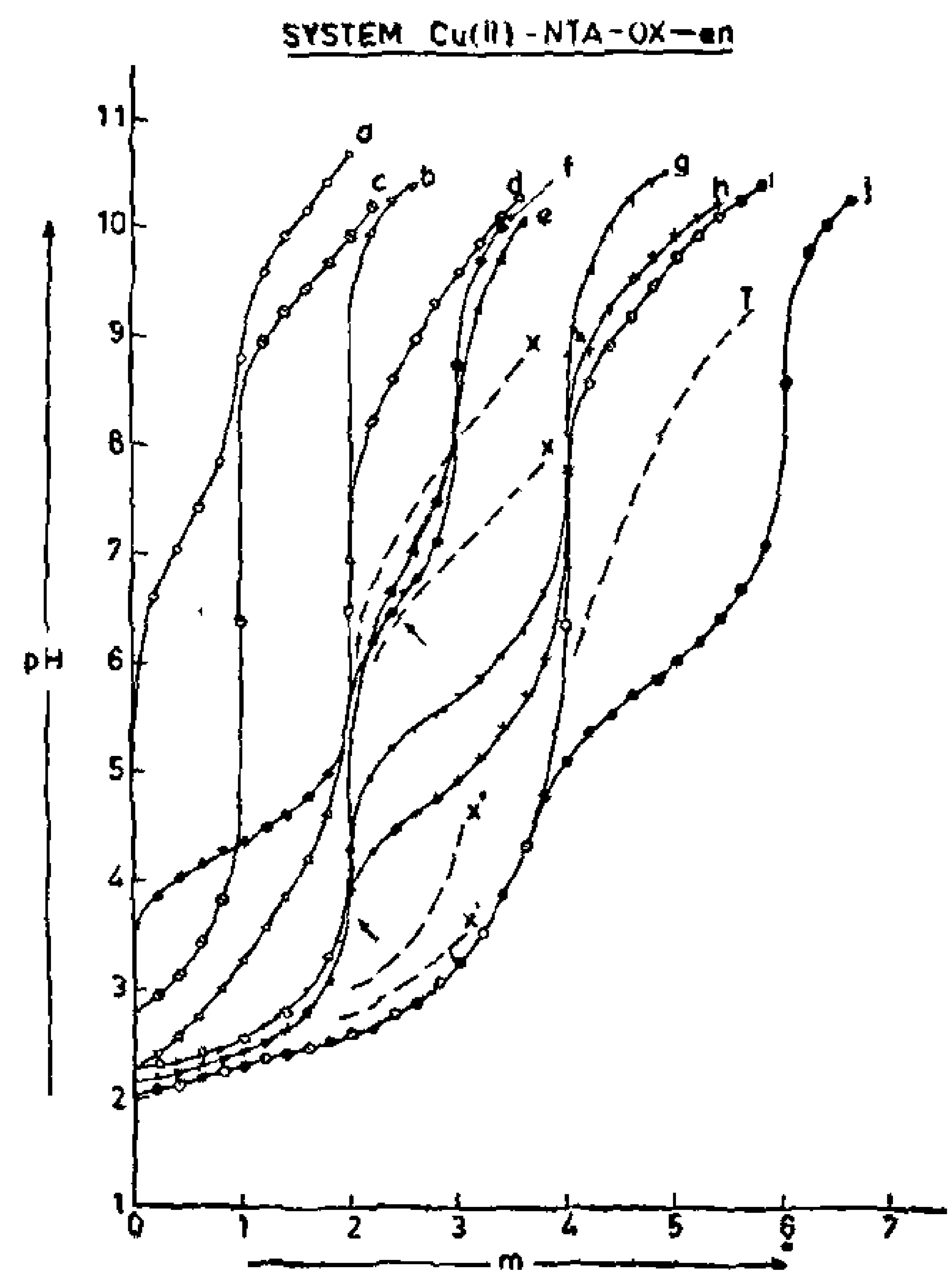

FIG. 1. Curves a = en/pn, b = OX, c = KNTA, d = 1 : 1 Cu(II)-NTA, e = 1 : 1 Cu(II) OX, f = 1 : 1 Cu(II)- en/pn, g = 1 : 1 : 1 Cu(II)-NTA-en/pn. h = 1 : 1 : 1 Cu(II)-OX en/pn, i = 1 : 1 : 1 Cu(II)-NTA-OX, j = 1 : 1 : 1 : 1 Cu(II)-NTA-OX-en/pn. → appearance of turbidity.
Composite curves* drawn by adding horizontal distances of the respective curves shown in parenthesis:
*X = (curves d & a; e & a), X' = (curves d & b), X'' = (curves e & c), T = (curves i & a).

TABLE I
Formation constants and free energies of formation

Quaternary system	Log K^{M}_{MAB}	Log K^{MAB}_{MABC}	Overall formation constant	Overall $\Delta G°$ Kcal/mol/deg.
Cu(II)-NTA-OX-en	$8 \cdot 93 \pm 0 \cdot 21$	$7 \cdot 46 \pm 0 \cdot 09$	16·39	−22·19
Ni(II)-NTA-OX-en	$9 \cdot 19 \pm 0 \cdot 12$	$6 \cdot 04 \pm 0 \cdot 13$	15·23	−20·62
Zn(II)-NTA-OX-en	$9 \cdot 38 \pm 0 \cdot 15$	$4 \cdot 70 \pm 0 \cdot 18$	14·08	−19·06
Cu(II)-NTA-OX-pn	$8 \cdot 93 \pm 0 \cdot 21$	$5 \cdot 75 \pm 0 \cdot 11$	14·68	−19·87
Ni(II)-NTA-OX-pn	$9 \cdot 19 \pm 0 \cdot 12$	$4 \cdot 77 \pm 0 \cdot 16$	13·96	−18·90
Zn(II)-NTA-OX-pn	$9 \cdot 38 \pm 0 \cdot 15$	$4 \cdot 41 \pm 0 \cdot 17$	13·79	−18·67

A = Nitrilotriacetic acid, B = Oxalic acid, C = Ethylenediamine or 1,2-propanediamine.

inflections at $m = 2$ and $m = 4$. Overlapping of the curve g with d and curve h with curve e upto $m = 2$ indicate respectively, the initial formation of 1 : 1

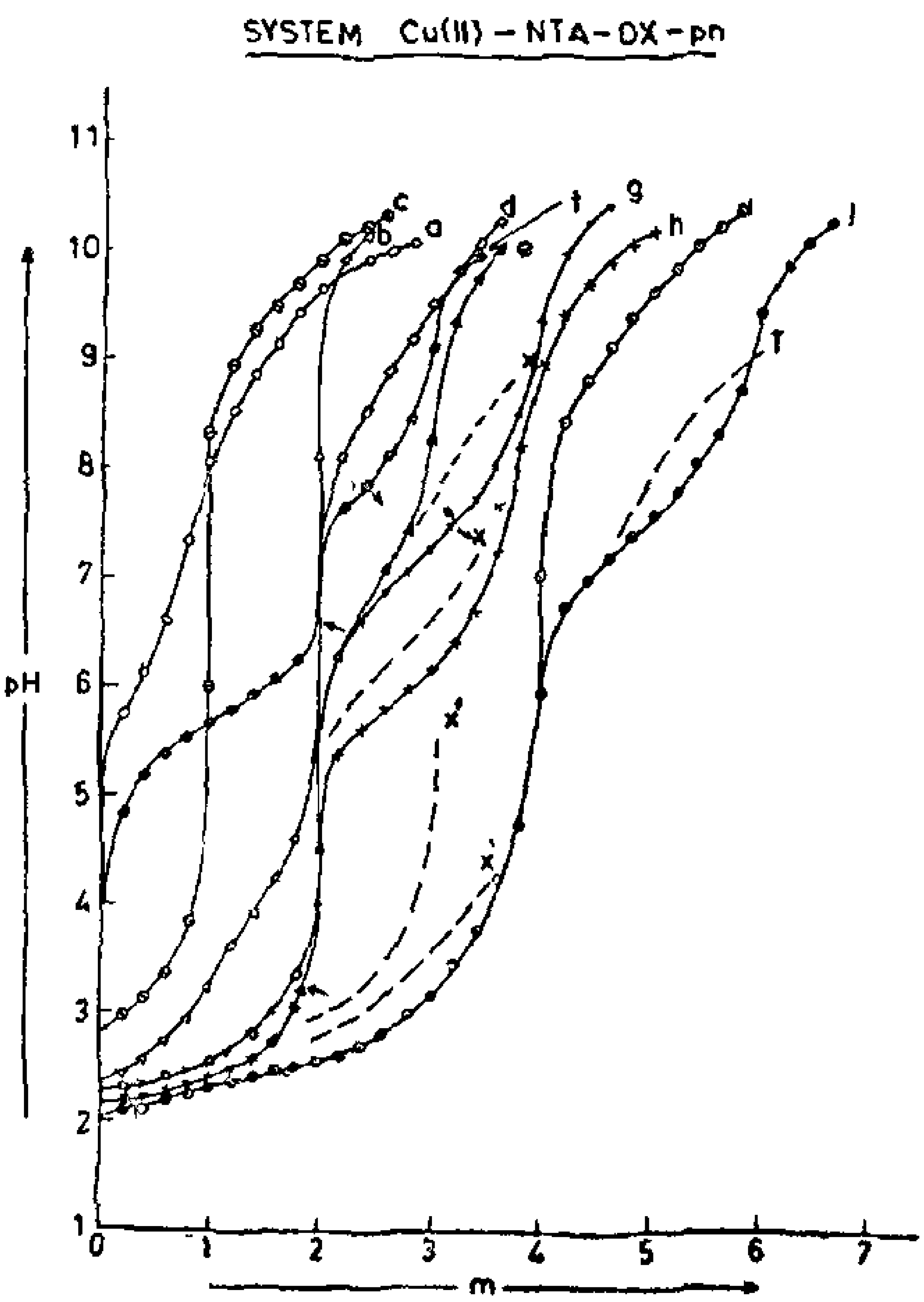

FIG. 2. Curves a = en/pn, b = OX, c = KNTA, d = 1 : 1 Cu(II)-NTA, e = 1 : 1 Cu(II)-OX, f = 1 : 1 Cu(II)-en/pn, g = 1 : 1 : 1 Cu(II)-NTA-en/pn, h = 1 : 1 : 1 Cu(II) OX-en/pn, i = 1 : 1 : 1 Cu(II)-NTA-OX, j = 1 : 1 : 1 : 1 Cu(II)-NTA-OX en/pn. → appearance of turbidity.

Composite curves* drawn by adding horizontal distances of the respective curves shown in parenthesis:

*X = (curves d & a; e & a), X' = (curves d & b), X'' = (curves e & c), T = (curves i & a).

Cu(II)-NTA and 1 : 1 Cu(II)-OX complexes prior to the addition of the secondary ligand en/pn resulting in the formation of ternary species: Cu(II)-NTA-en/pn; Cu(II)-OX-en/pn. The later inflection at $m = 4$ and lowering in pH may be attributed to the formation of ternary species.

A single well-defined inflection at $m = 4$, in the curve i [for 1 : 1 : 1 Cu(II)-NTA-OX] may, however, be ascribed to the simultaneous addition of both the ligands to the metal ion resulting in the formation of 1 : 1 : 1 ternary species.

Curve j representing the systems 1 : 1 : 1 : 1 Cu(II)-NTA-OX-en/pn superimposes the curve i upto $m = 4$, indicating the initial formation of 1 : 1 : 1 Cu(II)-NTA-OX species to which the third ligand en/pn is probably added up forming a soluble quaternary 1 : 1 : 1 : 1 Cu(II)-NTA-OX-en/pn species. Inflection at $m = 6$ and lowering in pH may be ascribed to the formation of such hetero-ligand species.

Non-superimposable nature of the theoretical composite curves[16–17] X and T (in the case of mixed-ligand complex formation by stepwise addition of the ligands involved), X' and X'' (in the case of simultaneous addition of the ligands to the metal ion), drawn by the addition of the horizontal distances of the respective curves as specified in the captions of Figs. 1 and 2, with the experimental curves depicting the respective ternary and quaternary systems, and the non-formation of the heterogeneous phase during the titration lend additional support to the formation of a mixed ligand ternary/quaternary species (Table I).

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SOME OBSERVATIONS ON THE FLOWERING OF BAMBOOS IN MIZORAM

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ABSTRACT

Bambusa tulda, Dendrocalamus longispathus, D. sikkimensis, Melocalamus compactiflorus, Melocanna bambusoides and *Pseudostachyum polymorphum* were observed in flower during 1977–79. The nature and consequences of bamboo flowering are discussed.

INTRODUCTION

ONE of the most puzzling features which has evaded understanding is flowering of certain bamboos after the lapse of several years. Although it is known that bamboos derived originally from the same clump would flower simultaneously, irrespective of where they have been planted, the nature of the factors leading to their 'once flowering' is far from clear. The death of all the clumps with a single act of flowering and fruiting in these monocarpic plants has been attributed to reproductive exhaustion, caused by the movement of reserve food materials from the vegetative parts. It is also likely that developing seeds may be sites of synthesis of certain inhibitors.

The flowering of certain bamboos is accompanied by large scale increase in the population of 'bamboo rats' in Mizoram and other north-eastern hill regions of India. The rats are reported to consume the bamboo seeds and with the exhaustion of this bountiful supply of bamboo food, they attack the standing crops, causing severe devastation resulting in famine.

During a study under the research scheme 'Biology of bamboo rats and their relation to bamboo flowering', supported by the Indian Council of Agricultural Research (1977–79), the authors noted several instances of gregarious as well as sporadic flowering of bamboos in Mizoram. Observations made on the nature and extent of flowering and consequences of flowering have been summarized below. The flowering material and seedlings have been collected and photographed. A detailed account of the biology of certain babmoos is being investigated. A species-wise account follows :

OBSERVATIONS AND DISCUSSION

1. *Bambusa tulda* Roxb. (Mizo name : *Rawthing*)

Flowering in this bamboo has been associated with the 'Thingtam' famine. According to the local people this bamboo flowers gregariously once in 48 years. A survey of the forest records and reports by naturalists indicates that flowering had been observed in 1880 through 1884 and in 1928 through 1929. Recently a few clumps began flowering in 1976 and gregarious flowering occurred and lasted until 1979. Flowering was first observed in the southern parts of Mizoram and it later spread to the northern parts and progressed further into the Assam plains.

The plants stop producing new shoots before the commencement of flowering and shed their leaves completely. The inflorescence is an immense radical leafless panicle, bearing interrupted clusters of fertile long spikelets (1 to 8 cm) (Fig. 1). When the culms are