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Mixed Metal & Polynuclear Complexes in Ti (IV)-Cu(II)-Tartrate System

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A systematic study of Ti-Cu-Tart system with complementary tristimulus colorimetry, Job's and molar ratio methods reveals the formation of $Ti_2CuTart$, TiCuTart, $TiCu_2Tart$, Ti_2Tart and Cu_2Tart complexes. The maximum *p*H up to which the mixed metal complexes remain in solution increases with decrease of Ti(IV) and increase of Cu(II) in the complex. $TiCu_2Tart$ and Cu_2Tart exhibit a tendency to add on hydroxyl groups with increase of *p*H above 7.

MIXED metal complexes (mmc) are relatively less investigated than the mixed ligand ones. Amongst the ligands favouring the formation of mmc, hydroxy carboxylic acids[1-5] are receiving greater attention in the last decade and a half. The metal ions studied are mostly di- and trivalent, except for a mention of tetravalent thorium[6]. This paper describes the spectrophotometric study of mixed metal tartrates (mmt) and polynuclear tartrates involving Ti(IV), Cu(II) and tartrate (Tart).

Materials and Methods

Copper solution (0·2*M*) was prepared by dissolving $CuSO_4.5H_2O$ (BDH, Analar) in acidified water. Titanium solution, other reagents and instruments used were the same as described earlier[7].

As complex formation is slow, the *p*H of the mixed solutions were initially adjusted to the desired value and readjusted after leaving the solutions overnight. (During complexation a decrease of *p*H of about a unit was observed.) The volumes were made up and the absorbance values measured with 5 cm cells.

Complementary tristimulus colorimetric (CTSC) analysis[1] of systems was carried out, dividing the spectra into three regions, viz. 600-750 nm ($u = \Sigma A_{mm}$), 775-925 nm (v) and 950-1100 nm (w). Variation of $Q_u \left(= \frac{u}{u+v+w}\right)$, as a function of *p*H is presented, as the other two are indicating the same transformations.

Results and Discussion

Mixed metal tartrates — Cu(II)Tart system has been studied in the *p*H range of 4·0-9·0 by several workers[1,8]. Formation of 1:1 and 1:2 as well as polynuclear complexes, with and without associated hydroxyls are reported. In the present studies, mixtures of equimolar Ti and Cu ($4{\cdot}0\times10^{-3}M$) with Tart ($2{\cdot}0\times10^{-2}M$) at *p*H 8·0 indicated the formation of mmt on keeping them warm for 6 hr. The blue colour of cupric tartrate complexes changes to green. As the molarity of Tart was reduced to that of Ti, mmt formation was observed at a lower *p*H (6·0) and temperature (28°). However, it takes a few hours to come to equilibrium as mentioned earlier. Then spectra of mixtures of equimolar solutions (Cu-Tart and Ti-Cu-Tart) at *p*H values of 3·0 to 10·0 were scanned against corresponding Tart blanks. Those at *p*H 9·0 are given in Fig. 1 (curves 1 and 2).

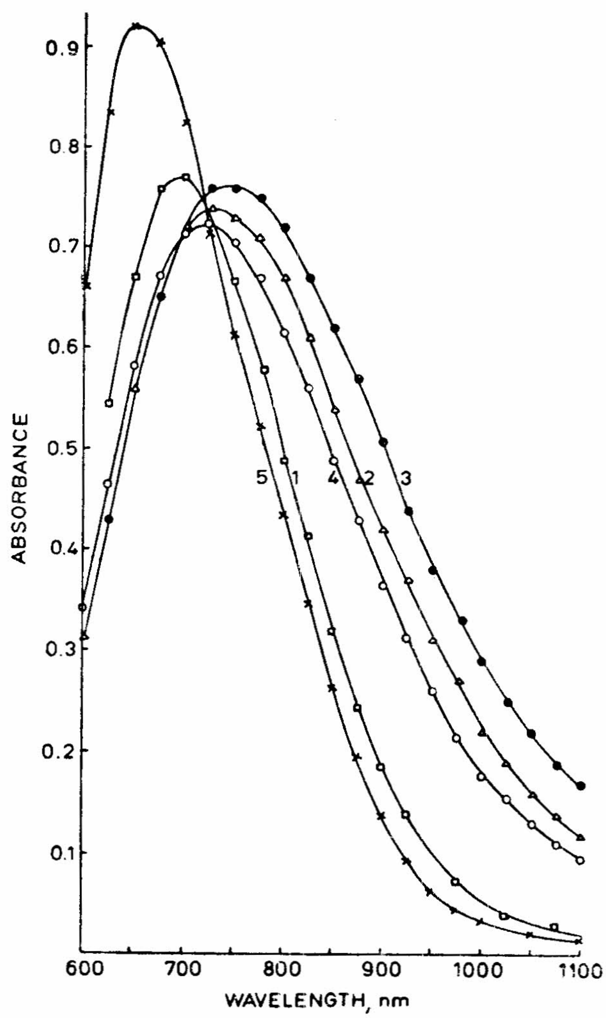

Fig. 1 — Absorption spectra [$C_{Cu} = 4{\cdot}0\times10^{-3}M$; *p*H = 9·0]

	Curve 1	2	3	4	5
$C_{Ti}\times10^3M$	—	4·0	8·0	2·0	—
$C_{Tart}\times10^3M$	4·0	4·0	4·0	2·0	2·0

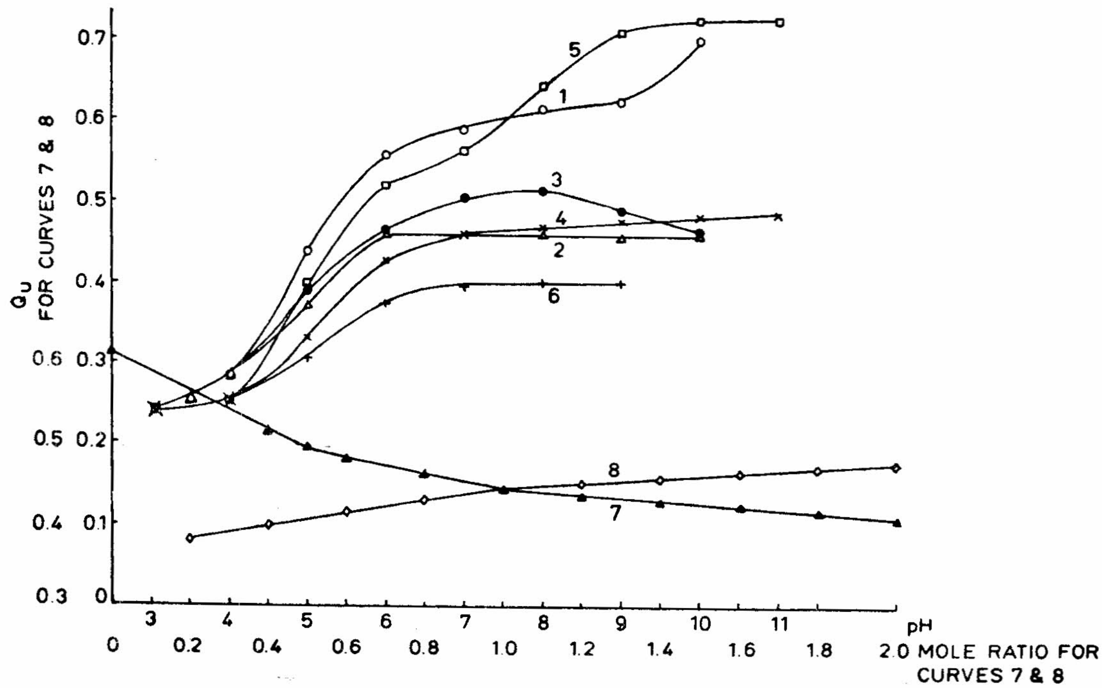

Fig. 2 — CTSC curves [curves 1, 2, 4 and 5: same concentrations as in Fig. 1]

Curve	$C_{Cu} \times 10^3 M$	$C_{Ti} \times 10^3 M$	$C_{Tart} \times 10^3 M$
3	4·0	4·0	10·0
6	2·0	4·0	2·0
7	4·0	Varying	4·0
8	Varying	4·0	4·0

The CTSC analysis showed the divergence of the curve of the ternary mixture (curve 2, Fig. 2) from that of the binary one (curve 1). The mmt appears to start forming around *p*H 4 and is complete in the *p*H range 6-10. At higher *p*H, precipitation occurs. From a comparison of a similar curve (curve 3) of a ternary mixture with a higher concentration of Tart ($= 2\frac{1}{2} \times C_M$) it is inferred that initially mmt and binary Cu-Tart complex form simultaneously up to *p*H 8·0 and that the binary complex thereafter transforms into mmt.

Molar ratio method was applied at *p*H 9·0 taking constant Ti-Tart and Cu-Tart and varying Cu and Ti concentrations respectively (curves 1 and 2, Fig. 3). Curve 1 exhibits a break at Cu/Ti = 0·5, and curve 2 at Ti/Cu of 0·5 and 1·0. In both the cases, precipitation occurs when the ratio exceeds 2·0. This reveals the formation of strong complexes with compositions of 2:1, 1:1 and 1:2 with respect to the metal ions. To know the *p*H range in which the first and third of these mmts are forming, mixtures of Ti, Cu and Tart in 2:1:1 and 1:2:1 molar ratios were prepared at different *p*H values and their spectra scanned against Tart blank. Those at *p*H 9 are included in Fig. 1 (curves 3 and 4). The CTSC plots are included in Fig. 2 (curves 6 and 4). These mmts also start forming around *p*H 4. Formation of the one with excess titanium appears to be complete by *p*H 7, with no further change up to *p*H 9. Above this *p*H, precipitation occurs. Formation of mmt with excess Cu(II) is nearly complete by *p*H 7 but there appears to be a further change up to *p*H 11. Above this *p*H, precipitation occurs.

The compositions of mmts with respect to titanium and copper at *p*H 9 were further elucidated by applying the continuous variation (c.v.) method in different ways. In one case concentrations of Ti and Cu were continuously varied, keeping that of Tart constant. The curve obtained at 1000 nm is given in Fig. 4 (curve 1). Since the breaks in molar ratio method indicate a high degree of formation of complexes, the compositions of the three mmts with respect to the metal ions are inferred from the X_{max} values as well as breaks in the c.v. curves to be 2:1, 1:1 and 1:2. These are in agreement with the compositions obtained by molar ratio method. The same compositions can be inferred from the curves at other wavelengths. In the other method, concentrations of titanium and copper were continuously varied, keeping that of Tart as a constant multiple of C_{Cu}. Curve 2 (Fig. 4) exhibits an X_{max} around 0·55 with a break around 0·3. Solutions beyond 0·67 were turbid. This can be taken as further support to the three compositions arrived at earlier as the degree of formation of complexes is high. If a single highly dissociating mmt were to form predominantly X_{max} is expected at 0·33 and 0·25 for 1:1:1 and 1:2:1 complexes respectively[9].

The composition with respect to tartrate in the three cases is inferred indirectly to be one mole per mole of mmt from the minimum amount required to form the complexes, as has been done earlier by Petit-Ramel *et al.*[4].

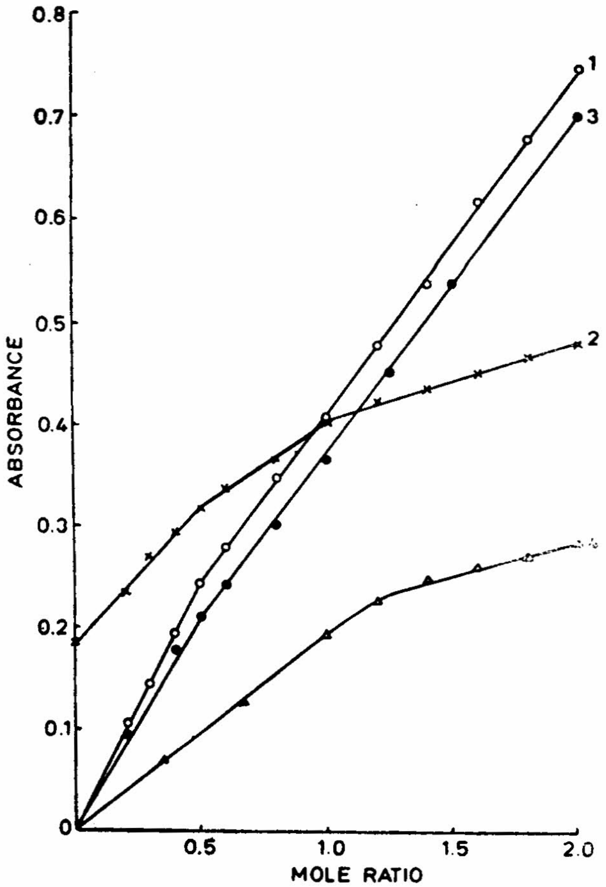

Fig. 3 — Molar ratio method [$C_{Tart} = 4{\cdot}0 \times 10^{-3} M$; $\lambda = 900$ nm]

Curve	$C_{Cu} \times 10^3 M$	$C_{Ti} \times 10^3 M$	*p*H
1	Varying	4·0	9·0
2	4·0	Varying	9·0
3	Varying	4·0	7·0
4	Varying	—	9·0

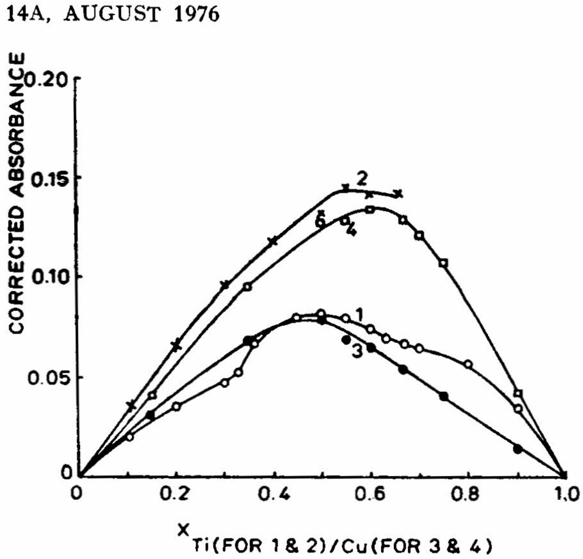

Fig. 4 — Job's method

Curve	$C_{Cu}+C_{Ti}$ $\times 10^3 M$	$C_{Cu}+C_{Tart}$ $\times 10^3 M$	C_{Tart} $\times 10^3 M$	*p*H	λ nm
1	4·0	—	4·0	9·0	1000
2	8·0	—	$=C_{Cu}$	9·0	1000
3	—	4·0	—	4·8	900
4	—	4·0	—	4·8	725

To know more about the transformations observed in the CTSC plot with excess copper (curve 4, Fig. 2), molar ratio method was applied at *p*H 7 also, adding copper to Ti-Tart (1:1) mixture (curve 3, Fig. 3). This curve runs almost parallel to that obtained at *p*H 9 (curve 1), indicating a break at Cu/Ti of 0·5 and extending to 2·0. This shows that the $Ti.Cu_2.Tart$ formation is nearly complete at *p*H 7 in the CTSC plot. The further transformation beyond *p*H 7 may, therefore, be attributed to a change in the number of hydroxyls associated with the mmt. This may be correlated with the fact that the spectra of the solution at *p*H 7 is identical with that of the solution at *p*H 11 between 750 and 1100 nm and the absorption at lower wavelengths increasing only slightly with *p*H.

To know whether $Ti.Cu_2.Tart$ is forming through Ti.Cu.Tart in the CTSC plot, Coleman *et al.*'s analysis[10] of spectral data was carried out. A_{600}/A_{500} values were plotted against A_j/A_{500}, where *j* varied from 520 to 580 nm. The one at 540 nm is given in Fig. 5 (curve 1). The points corresponding to solutions at *p*H 5-7 fall in one straight line and those corresponding to solutions at *p*H 7·0 to

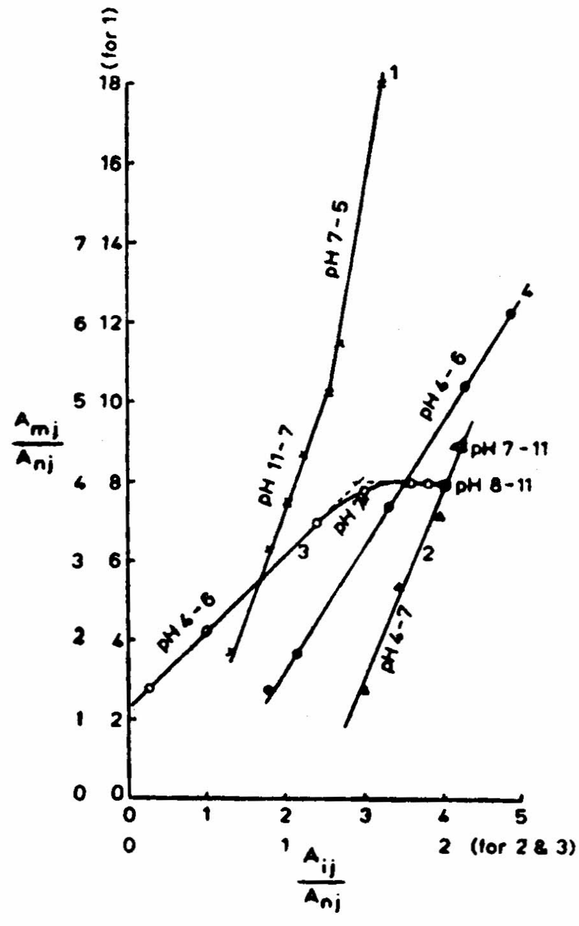

Fig. 5 — Graphical fit for two species [(1) A_{600}/A_{500} vs A_{540}/A_{500}; (2) A_{725}/A_{1000} vs A_{900}/A_{1000}; (3) A_{725}/A_{1000} vs A_{600}/A_{1000}; and (4) A_{725}/A_{1000} vs A_{300}/A_{1000}]

11·0 fall in another straight line, showing that two absorbing species are involved in each of the two transformations. Taking into consideration the results of molar ratio method at *p*H 7 and 9, it is concluded that Ti.Cu_2.Tart directly forms from Cu^{2+} in the *p*H region 4-7 and this mmt changes over to another with the same composition with respect to the three reactants but differing in the number of hydroxyls associated with it in the *p*H region 7-11.

When A_{725}/A_{1000} was plotted against A_{900}/A_{1000} in the above case (curve 2, Fig. 5) points corresponding to *p*H 4-7 fall in a straight line, but those corresponding to *p*H 7 to 11 cluster around. The latter is not due to the formation of the same absorbing species but is due to the superimposable spectra of the two species in the wavelength region of 725-1100 nm. A similar plot (curve 3, Fig. 5) of A_{725}/A_{1000} against A_{600}/A_{1000} brings out the difference in the slopes of the two linear portions. In addition, it clearly shows that the point corresponding to *p*H 7 deviates from either straight line. This may be attributed to the presence of all the three absorbing species, the $TiCu_2Tart$ being the predominant one. On either side, only two absorbing species are involved.

The spectral data of mixtures prepared for molar ratio method at *p*H 9 were subjected to CTSC analysis. Variation of Q_u as a function of Ti/Cu and Cu/Ti ratios are included in Fig. 2 (curves 7 and 8). The one in which Ti was varied shows the transformation of CuTart→$TiCu_2$Tart→TiCuTart→Ti_2Cu Tart, while the other shows TiTart→TiCuTart→$TiCu_2$Tart. The transformation of TiCuTart to $TiCu_2$Tart, when Cu was varied, is clear in the CTSC plot, while it is not in molar ratio method. The formation of Ti_2CuTart is indicated in the molar ratio method but not in the CTSC plot. From this it is apparent that transformations occurring when one reactant is varied can also be studied by the CTSC analysis of the spectral data.

It may be pointed out that the maximum *p*H at which an mmt is stable (without precipitation) increases with decrease of number of moles of titanium and increase of number of moles of copper.

Binary polynuclear complexes — In view of the stability of mmts with one Tart and three metal ions (two of one metal and one of the other), experiments were carried out at *p*H 7 with mixtures of 3:1 and 2:1 of metal to tartrate in the two binary systems. Precipitation was observed in the mixtures with 3:1 ratio, while the others with 2:1 ratio were clear even after 24 hr. Since the binary system with titanium is colourless, further experiments were carried out on Cu-Tart system. Spectra of mixtures of Cu and Tart (2:1) at different *p*H values from 3 to 11 were scanned. With increase of *p*H up to 9, the λ_{max} shifts from 800 to 650 nm and remains steady beyond. With increase in *p*H, the absorbance increases at 600 nm and decreases at 1100 nm. The spectrum at *p*H 9 is shown in Fig. 1 (curve 5). On analysing these data by CTSC (curve 5, Fig. 2), two transformations are observed, one in the *p*H region 4-7 and another between *p*H 7 and 9. To know the composition of the species forming at *p*H 9, molar ratio method was applied, adding varying amounts of Cu to constant Tart. Curve 4 in Fig. 3 at 900 nm reveals the formation of 1:1 and 2:1 complexes depending on the relative amounts of copper. When Job's method was applied around *p*H 5, the formation of similar 1:1 (curve 3, Fig. 4) and 2:1 (curve 4) complexes is revealed. From this, the first transformation in the CTSC plot appears to correspond to the formation of 2:1 complex from metal. The second transformation is ascribed to hydroxylation of the 2:1 complex with increase in *p*H. Further confirmation of the direct formation of 2:1 complex from metal ion in the *p*H region 4-6 was obtained from the Coleman *et al.*'s analysis, (curve 4, Fig. 5), which showed the presence of only two absorbing species.

A comparison of spectra in Fig. 1 indicates that formation of mmt shifts the λ_{max} of the Cu-Tart system to higher values. In the binary Cu-Tart as well as ternary complexes, there is a decrease of λ_{max} with increase of copper content.

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