CCCXXV.—*Metallic Hydroxy-acid Complexes. Part V. Neutral α-Cupritartrates.*

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DUMANSKI and CHALISEW (*Kolloid Z.*, 1929, **47**, 121) deny the existence of the α-cupritartrates described by Packer and Wark (J., 1921, **119**, 1348). They further question the existence of many similar compounds described by other workers in this field, particularly the compounds from alkaline solutions, contending that these supposed compounds are merely colloidal suspensions of copper hydroxide in neutral or alkaline tartrate solutions.

While we are of the opinion that the earlier work of Pickering

(J., 1911, **99**, 169; and subsequent papers) proves conclusively that the constituents of such alkaline solutions are prone to hydrolysis, giving colloidal solutions of copper hydroxide, we consider that there is abundant evidence that the neutral α-cupritartrates are stable compounds substantially free from hydrolysis. Dumanski and Chalisew admit the existence of compounds of the tartar emetic type, but do not consider that copper-bearing solutions contain similar complexes. This is in contradistinction to the views expressed in an earlier communication (I. W. W., J., 1924, **125**, 2004), where a similarity of type is pointed out.

These same authors state that they have followed the method of preparation of Packer and Wark (*loc. cit.*) for sodium α-cupritartrate, but that on washing this compound with 36% alcohol they effected a change in composition, indicated in the following table taken from their paper.

	Na.	Cu.	Tartrate.	H_2O.	Mols. Cu/Na.
Salt prepared after Packer and Wark	7·11	25·9	31·12	18·20	1·33
	7·05	25·95	31·27	11·20	—
Washed many times by decantation with 36% alcohol	10·7	26·11	41·90	20·40	0·9
	10·74	26·18	42·12	20·50	—
By recrystallisation with sufficient alcohol	11·64	25·8	42·4	—	0·81
	11·72	25·8	42·3	—	—

We have followed the same procedure in attempting to confirm their work, but can find no change in composition on washing with alcohol. A preparation of the original salt, designated Sample I, was washed with 36% alcohol, and washing was stopped while a portion remained undissolved (Sample II). On addition of alcohol to the washings, Sample III crystallised. The analyses of these three samples, together with the results of Packer and Wark, are set out in the following table.

Analysed by	Na.	Cu.	C.	H.	H_2O.	Tartrate.
Packer and Wark	7·10	25·63	14·71	3·30	20·34	—
	6·98	25·73	14·73	3·39	—	—
Wark and Wark :						
Sample I	6·8	25·6	—	—	—	—
,, II	6·9	25·6	—	—	—	—
,, III	7·0	26·5	—	—	—	—
Calc. for $Na_3Cu_4C_{12}H_9O_{19},11H_2O$	7·05	25·99	14·73	3·19	20·25	46·03

In addition to the sodium salt of α-cupritartaric acid there have been prepared and analysed the potassium, silver, and lead salts (Masson and Steele, J., 1899, **75**, 725) and the ammonium and barium salts (Packer and Wark, *loc. cit.*). There cannot, therefore, be any doubt as to the identity of the series.

Dumanski and Chalisew further question the accepted view of the reaction between sodium hydroxide and copper tartrate, although the equation

$$5NaOH + 4CuC_4H_4O_6 \longrightarrow Na_2C_4H_4O_6 + Na_3Cu_4C_{12}H_9O_{19} + 4H_2O$$

appears to be the only one which will fit the analytical data—including their own analysis cited above. They state that the point of solution of copper tartrate in sodium hydroxide does not always coincide with the ratio 5/4, varying in fact from 1·35 in *N*/10-sodium hydroxide to 1·18 in 2*N*-sodium hydroxide. In repeating their work, we found that if the titration was carried out slowly, *N*/10-alkali gave the ratio Na/Cu = 1·17 for complete solution; that *N*/2-alkali gave 1·22 at room temperature and only 1·15 at 35°; that 2*N*-alkali gave 1·22 at room temperature; that the apparent ratio varied also with the rapidity of titration, and, in short, that the process resembled an ordinary solubility phenomenon rather than a chemical action. This, in fact, it is, in so far as the sodium tartrate formed by the reaction—and to a less extent, the water itself—is a solvent for copper tartrate.* At the point of complete solubility the solution may remain acid to litmus (compare Dumanski and Chalisew), but when the ratio Na/Cu reaches 5/4, alkalinity towards phenolphthalein develops; this is illustrated in the following table:

$NaOH/CuC_4H_4O_6$, for complete solubility.	$NaOH/CuC_4H_4O_6$, for development of alkalinity.	Conc. of NaOH and temp.
1·17	1·22	*N*/10 at ?
1·22	1·24	*N*/2 at 18°
1·15	1·24	*N*/2 at 35
1·22	1·27	2*N* at 18

Following the method of an earlier paper (I. W. W., J., 1923, **123**, 1823), Dumanksi and Chalisew, adding 2*M*-sodium tartrate to prevent hydrolysis of the complex formed, found that the ratio NaOH/Cu for complete solution was unity. They interpreted this result in terms of the equation

$$2CuC_4H_4O_6 + 2NaOH \longrightarrow Na_2C_4H_4O_6 + CuC_4H_4O_6,Cu(OH)_2.$$

In making this deduction the solubility of copper tartrate in sodium tartrate has been lost sight of. It can be shown experimentally that copper tartrate is completely soluble in sufficient sodium tartrate, 100 c.c. of a 1·5*N*-solution of the latter dissolving 1 g. of the former. Such a solution, however, still required $5NaOH/4CuC_4H_4O_6$ to render it alkaline to phenolphthalein. The variations

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* This solubility is itself probably due to a chemical reaction (*loc. cit.*), but the compound formed is less stable than the α-cupritartrate whose formation continues as sodium hydroxide is added.

in ratio observed by Dumanski and Chalisew are therefore due to solubility and not to any variations in the primary chemical action.

The end-point in the titration against sodium hydroxide is difficult to determine. Lack of sharpness has resulted in the variations in col. 2 of the above table. In order to determine the position of this end-point with greater certainty, we carried out a potentiometric titration, successively increasing amounts of sodium hydroxide being added to the solid tartrate. Before each measurement, the unchanged copper tartrate was removed from the solution by

FIG. 1.

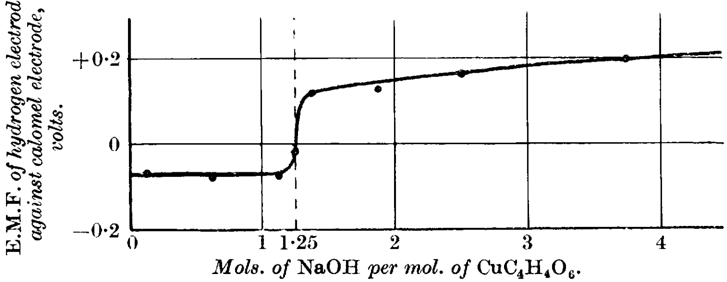
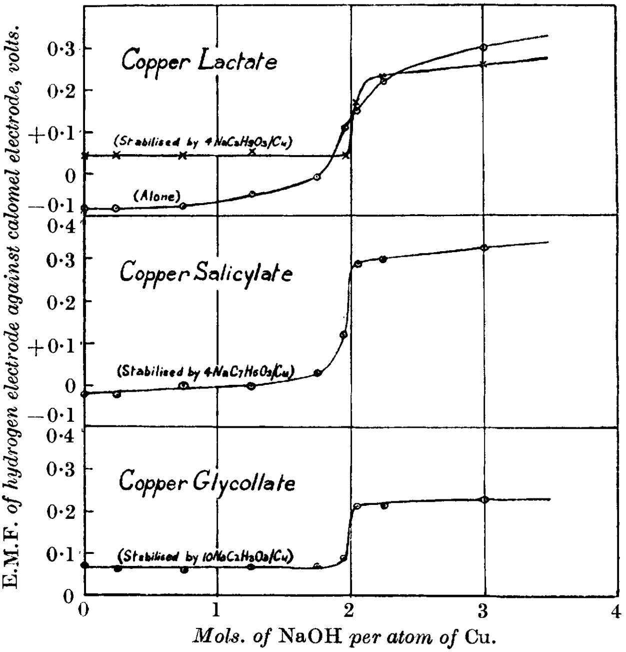


FIG. 2.



filtration. The saturated calomel electrode, which was used for reference, was connected with the hydrogen electrode through a saturated potassium chloride bridge. Results are plotted in Fig. 1. A sharp break occurs at an NaOH/Cu ratio very close to 5/4. This curve should be compared with similar ones (Fig. 2) which we obtained for copper salts of salicylic, lactic, and glycollic acids. It has been shown (J., 1927, 1753) that 1 mol. of each of these salts reacts with 2 mols. of alkali to give the sodium salt of the corresponding complex acid. The curves show that the potentiometric method gives a trustworthy indication of complex formation, and by analogy, the case for the tartrate is strengthened.

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