GLASS ELECTRODE STUDIES: SOME CUPRIC HYDROXY-ACID COMPLEXES.

BY CHARLES MORTON.

Received 28*th October*, 1931.

It is commonly supposed that in Fehling's solution the copper is present as a complex anion, and attempts have been made by Masson and Steele,[1] Pickering,[2] and Packer and Wark,[3] to isolate the blue complex by fractional precipitation with alcohol from neutralised solutions of cupric tartrate. Similar analytical methods have been used by Pickering [4] and Wark [5] in the investigation of the supposed cupricitrates, cuprimalates, etc. The identity of these salts has recently been denied by Dumanski and Chalisew.[6] In an attempt to confirm their existence by a physical method, E. E. Wark and I. W. Wark,[7] overlooking the fact that the normal electrode potential of copper is positive with respect to hydrogen, sought to follow the course of the neutralisation of various cupric hydroxy-acid salts by means of the hydrogen electrode. It is clear from their published curves that the potentials which the authors observed—potentials which, as measured against the saturated calomel electrode, reversed at neutrality—were not those of the hydrogen electrode.

In the present work, the neutralisation curves of a number of cupric hydroxy-acid salts have been determined by means of the glass electrode. The ballistic system of measurement recently described by the author [8] was employed, a condenser of 0·5 microfarad capacity being used with a constant charging period of thirty seconds. Measurements were also made by means of a Dolezalek electrometer having a maximum sensitivity of about 1000 mm. per volt at 1 metre. A preliminary titration of 100 c.c. of the universal buffer solution of Prideaux and Ward [9] with 0·2 *N*. sodium hydroxide solution was carried out, and a calibration curve constructed from which the p_H value corresponding to a given electrometer deflection could be read directly.* The calibration serves to eliminate errors due to non-linearity both of the E.M.F.-p_H relationship of the glass and of the potential-deflection relationship of the electrometer. The method gives results equal in accuracy to those obtained by a null potentiometric method, and is more convenient when an electrometer of long period is used.

The neutralisation curves are shown in Figs. 1 and 2. In each case, to 10 c.c. of 0·1 *M*. cupric sulphate solution, excess of the sodium salt

---

[1] Masson and Steele, *J.C.S.*, **75**, 725, 1899.
[2] Pickering, *ibid.*, **99**, 169, 1911.
[3] Packer and Wark, *ibid.*, **119**, 1348, 1921.
[4] Pickering, *ibid.*, **97**, 1837, 1910; **99**, 1347, 1911; **101**, 174, 1912.
[5] Wark, *ibid.*, **123**, 1815, 1826, 1923; 1753, 1927.
[6] Dumanski and Chalisew, *Kolloid Z.*, **47**, 121, 1929.
[7] E. E. Wark and I. W. Wark, *J.C.S.*, 2474, 1930.
[8] Morton, *J. Sci. Inst.*, **7**, 187, 1930.
[9] Prideaux and Ward, *J.C.S.*, **125**, 426, 1924.

* A more convenient universal buffer mixture for this purpose has recently been described by Britton and Robinson, *J.C.S.*, 1456, 1931.

of the hydroxy-acid was added, and the reaction mixture was diluted so that the solution was approximately 0·01 *M.* with respect to copper. The titrations were carried out with 0·1 *N.* sodium hydroxide solution. The molar ratio of hydroxy-acid anion to copper in the reaction mixtures varied from 5 : 1 for the less stable solutions to 1 : 1 for the more stable salts. In the titration of the tartrate, citrate, malate, and salicylate solutions (Fig. 1) two inflections appeared in the course of each neutralisation curve. The first, which was reached when 1·0 (citrate, malate, salicylate) or 1·25 (tartrate) equivalents of alkali had been added, presumably marks the completion of the process of complex formation: the second occurred in all cases when the theoretical amount (2 equivalents) of strong base required for complete alkaline decomposition had been added. On back-titrating the strongly alkaline solutions with 0·1 *N.* hydrochloric acid the inflections reappeared in the reverse order.

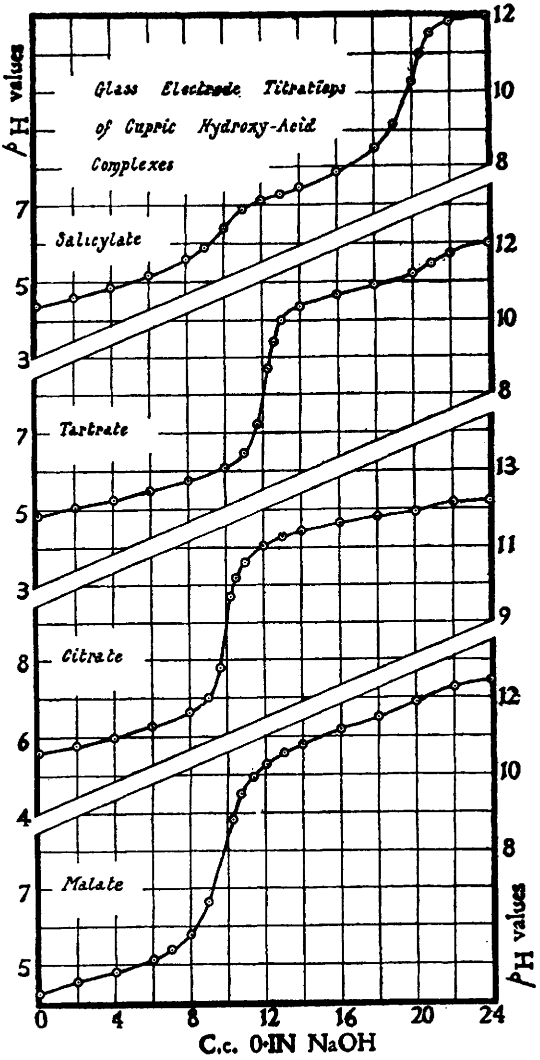

FIG. 1.

The changes in copper-ion concentration during the earlier stages of the neutralisation were followed by means of the copper electrode. The potentials observed showed that the copper-ion concentration diminished at first slowly, but later rapidly as the neutral point was approached. The inflection point in each case coincided with the first inflection point in the corresponding neutralisation curve. There is, in fact, a close parallelism between changes of cuprion and of hydrion concentration. Whether or not a simple relationship exists was not discovered, for at this stage it was learned that Dr. Britton was engaged in similar work, and the experiments were discontinued. A few dialysis experiments were carried out, using Whatmans dialysing shells, and it was found that from the acid solutions the whole of the copper could be removed by dialysis: slightly alkaline solutions, on the other hand, yielded almost colourless diffusates, and the dark blue dialysates flocculated on standing. The transition from electrolytic to colloidal solution or *vice versa* is reversible, and takes place whenever the reaction of the solution is changed.

These results may be interpreted in various ways. If the theory of the formation of complex anions be adopted, it must be supposed that the first inflection corresponds with the formation of the neutral cupritartrate, cupricitrate, etc., and the second with its subsequent decomposition by excess of alkali. The evidence in favour of this view appears to be based solely on the observation of Kahlenberg[10] and Masson and Steele (*loc. cit.*) that, under the influence of a potential gradient, the blue complexes migrate towards the anode. As Britton[11] has pointed out, the cataphoretic behaviour may equally well be due to the colloidal nature of the complex. In agreement with this suggestion, Dumanski and Chalisew found that the blue complex of Fehling's solution, whilst moving from the cathode, was unable to penetrate a collodion sac surrounding the anode. In view of the discovery of heterogeneous equilibria in the solutions, the analytical procedure employed in the precipitation of the supposed cupritartrates, etc., must be regarded with suspicion.

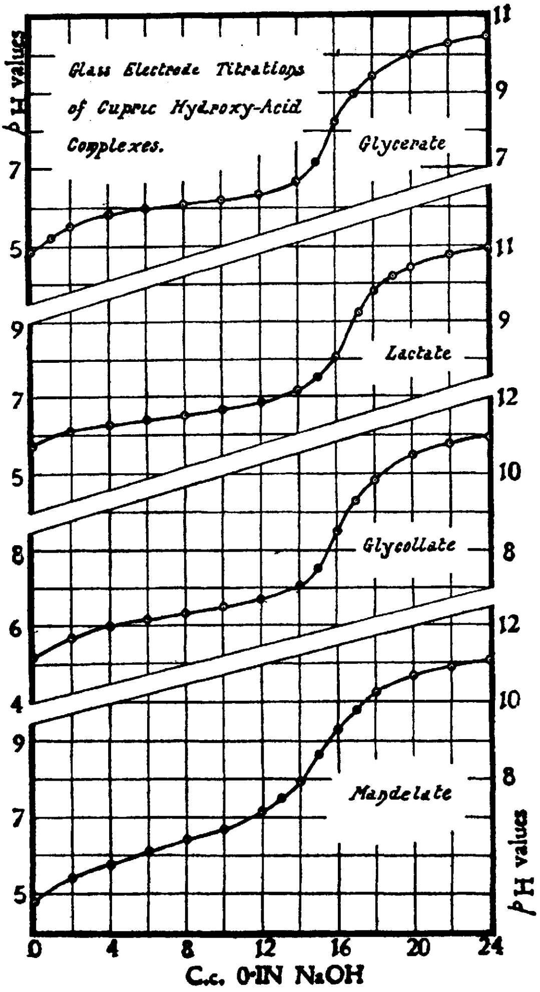

FIG. 2.

In the important paper referred to, Britton, judging by analogy from

---

[10] Kahlenberg, *Z. physik. Chem.*, 17, 586, 1895.
[11] Britton, *J.C.S.*, 269, 1926.

the behaviour of the tartrates of a number of weak inorganic bases, suggested that the complex tartrate of Fehling's solution is essentially basic in nature. This view is in accord with our knowledge of the general physical and chemical properties of the cupric hydroxy-acid complexes. The colour and absorption spectra of the "cupritartrates" (which resemble those of basic copper sols), their amorphous nature, their almost unlimited solubility, and the fact that, in certain cases at any rate, a change in composition can be effected by washing, are accounted for if it be supposed that these precipitates are solid sols of basic copper tartrate in excess of alkali-metal tartrate. Again, the fact that excess of sodium salicylate is necessary to prevent the precipitation of cupric hydroxide from neutralised solutions of cupric salicylate is readily explained on the assumption that the process of neutralisation consists in the reversible formation of basic copper salicylates by progressive alkaline hydrolysis, and that in the absence of excess of one of the products of hydrolysis—the hydroxy-acid anion—alkaline decomposition is complete. Similar considerations account for the ready solubility of cupric tartrate—a sparingly water-soluble salt—in sodium tartrate solution. The essential reaction leading to dissolution of the salt is probably the formation of a neutral soluble basic tartrate by hydrolysis,

$$8CuC_4H_4O_6 + 10H_2O \rightleftharpoons Cu_8(OH)_{10}(C_4H_4O_6)_3 + 5H_2C_4H_4O_6,$$

the function of the sodium tartrate being to remove the liberated acid from the sphere of action in the form of hydrotartrate, and thus to enable the reaction to proceed to completion from left to right. In agreement with this view, it is found that the solution is acid to litmus, and requires for neutralisation 1·25 equivalents of sodium hydroxide per g. atom of copper, regardless of the amount of sodium tartrate present.

Assuming Britton's view of the nature of the cupric hydroxy-acid complexes to be correct, the initial reaction which takes place in the titration of, *e.g.*, the salicylate solution may be expressed thus:—

$$CuSO_4 + C_6H_4OHCOONa + NaOH \rightleftharpoons Cu(OH)(C_6H_4OHCOO) + Na_2SO_4.$$

The inflection which marks the completion of this reaction does not appear in the "hydrogen electrode" titration curve of Wark and Wark. When the theoretical quantity of alkali required for complete decomposition in the sense of the equation,

$$Cu(OH)(C_6H_4OHCOO) + NaOH \rightleftharpoons Cu(OH)_2 + C_6H_4OHCOONa,$$

had been added, a second and more marked inflection appeared in the neutralisation curve. The non-precipitation by excess of alkali is due to the fact that, as demonstrated by dialysis experiments, the product of decomposition is peptised by the hydroxy-acid anion, and passes into colloidal solution.

From the positions of the inflection points in the neutralisation curves of the tartrate, citrate, and malate solutions it may be inferred that the deep blue complexes have the composition,

$$Cu_8(OH)_{10}(C_4H_4O_6)_3,\ Cu_3(OH)_3C_6H_5O_7,$$

and $Cu_2(OH)_2C_4H_4O_5$ respectively. The fact that, in these curves, the second inflection corresponding with the alkaline decomposition of the salts is barely discernible, suggests that these compounds are considerably more stable than the salicylate complex—a conclusion which is borne out by a general study of the properties of the solutions. The alkaline solution obtained in the titration of the salicylate was emerald green (a colour which suggests the presence of a mixed cupric and cuprous oxide sol) and, although stable at air temperature, yielded a copious precipitate of cuprous oxide on boiling. Those obtained in the tartrate, citrate, and malate titrations, on the other hand, were deep blue, and were unchanged on boiling in the absence of reducing sugars.

The behaviour of the glycerate, lactate, glycollate, and mandelate solutions (Fig. 2) in the presence of caustic alkalis differs from that described above, and resembles that of the inorganic cupric salts. In each case the neutralisation curve shows only one inflection: this appeared when about three-fourths of the theoretical amount of alkali required for complete decomposition had been added. A blue basic precipitate appeared in each titration: in the case of the glycerate solution, however, this redissolved in the neighbourhood of the inflection point. Precipitation of the glycollate, lactate, and mandelate solutions by alkali could be prevented by the addition of large excess of the sodium salt of the hydroxy acid. Britton[12] found that, in the titration of copper sulphate with caustic alkalis, an inflection occurred, and precipitation was complete, when three-fourths of the stoichiometric amount of alkali had been added: by means of a subsequent phase rule study[13] it was shown that the precipitate was a definite basic salt, $4CuO, SO_3, 4H_2O$. It seems probable that no stable complexes are formed with glyceric, lactic, glycollic, and mandelic acids, and that the inflection corresponds with the formation of the basic sulphate. The fact that, in the presence of large excess of hydroxy-acid salt, the basic salt is not precipitated, may be attributed to the well-known peptising and protective properties of the hydroxy-acid anion.

Summary.

(1) Electrometric measurements by means of the glass and copper electrodes, indicate that in neutralised solutions of cupric tartrate, citrate, malate, and salicylate, the basic complexes $Cu_8(OH)_{10}(C_4H_4O_6)_3$, $Cu_3(OH)_3C_6H_5O_7$, $Cu_2(OH)_2C_4H_4O_5$, and $Cu(OH)(C_6H_4OHCOO)$ are present respectively. In alkaline solution the complexes are decomposed with the formation of highly basic hydrosols.

(2) There is no electrometric evidence of the formation of stable cupric complexes with glyceric, lactic, glycollic, or mandelic acids: the apparent stability of the cupric salts of these hydroxy-acids in the presence of caustic alkalis is due to the peptising properties of the hydroxy-acid anion.

The author desires to express his indebtedness to Dr. J. C. Crocker for the kind interest he has taken in the work. A grant from the Dixon Fund of the University of London is gratefully acknowledged.

Chelsea Polytechnic.

---

[12] Britton, *J.C.S.*, 2148, 1925.

[13] Britton, *ibid.*, 2796, 1925.