CCIV.—Metallic Hydroxy-acid Complexes. Part II. Cuprimalates. Their Formation, Properties, and Composition.

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ALTHOUGH comparatively little work has been carried out on the complex compounds of malic acid and cupric hydroxide, there is a fairly extensive literature dealing with those formed by other hydroxides—both basic and acidic. A short account of the more important papers is now given.

Glucinum complexes : Rosenheim and Itzig (Ber., 1899, **32**, 3433). Two series are described, monoglucinum-malates, $M_2O,2GIO,2C_4H_4O_4$, and diglucinum-malates, $M_2O,4GIO,(C_4H_3O_3)_2O$.

Arsenic and antimony complexes: Henderson and Prentice (T., 1895, 67, 1030) and Henderson and Barr (T., 1896, 69, 1451). Unstable derivatives of antimoniomalic acid,

 $CO_2H \cdot CH_2 \cdot CH(O \cdot SbO) \cdot CO_2H$,

are described.

Boron complexes: Adam (Compt. rend., 1894, **118**, 1274); Grossmann and Wieneke (Z. physikal. Chem., 1906, **54**, 385). From measurements of optical rotation the latter authors suggest that a complex $NH_4C_4H_5O_5$, HBO₂ exists.

Thorium complexes: Rosenheim, Samter, and Davidsohn (Z. anorg. Chem., 1903, 35, 424). Sodium, ammonium, and potassium thoriomalates are described. Type, Th $O(C_4H_4O_5K)_2$.

Uranium complexes: Itzig (Ber., 1901, 34, 3822) isolated the sodium salt of a complex uranomalic acid,

 $CO_{2}H \cdot CH_{2} \cdot CH(OH) \cdot CO_{2}UrO_{2} \cdot OH.$

Molybdenum and tungsten complexes: Rosenheim and Bertheim (Z. anorg. Chem., 1903, 34, 442) and Rimbach and Neizert (*ibid.*, 1907, 52, 397) studied the conductivity of solutions of these complexes. Gernez (Compt. rend., 1889, 109, 151, 769; 1890, 110, 529, 1365; 111, 792), Itzig (Ber., 1901, 34, 2391), Grossmann and Krämer (Ber., 1903, 36, 1607; Z. anorg. Chem., 1904, 41, 50), and Grossmann and Pötter (Ber., 1904, 37, 85; Z. physikal. Chem., 1906, 56, 577) worked on their optical activity. Henderson, Orr, and

Whitehead (T., 1899, **75**, 542) isolated crystalline compounds belonging to the two series $MoO_2:C_4H_3O_5M$ and $MoO_2(C_4H_4O_5M)_2$.

Cupric complexes: Grossmann and Loeb (Z. Ver. deut. Zuckerind., 1908, 994) studied the effect of varying amounts of cupric sulphate and caustic soda on the rotatory power of malic acid, and came to the conclusion that a complex sodium copper malate was produced. For this compound, they suggested the composition

NaO₂C·C₂H₃(OH)·CO₂Cu·OH.

Pickering (T., 1912, **101**, 174), studying the action of caustic soda on a solution of normal cupric malate, found that one molecule of alkali per atom of copper could be added without thereby precipitating any cupric hydroxide or rendering the solution alkaline, and that the addition of further alkali produced alkalinity. From a very concentrated neutral solution of cupric malate in caustic potash, he obtained a fine, dark blue, crystalline solid which, after drying at 100°, contained 26.12 per cent. of copper and 16.76 per cent. of potassium (Calc. for $C_8H_8O_{11}Cu_2K_2$, Cu = 26.19; K = 16.11per cent.).

Following the methods adopted in the analogous work on the cupritartrates and the cuprilactates, the author wished to investigate the reaction between caustic soda and the normal and acid malates of copper. Difficulties were encountered in the preparation of the latter salts, and it was not until a somewhat detailed study of the ternary system malic acid-cupric hydroxide-water had been made that it became possible to prepare them at will.

A rather curious transformation occurs when the crystalline trihydrate of normal cupric malate is heated at 100°. It loses all three molecules of water of crystallisation, its colour meanwhile deepening to a bright lavender blue. Now the trihydrate has a colour very similar to that of ordinary copper sulphate, which, as is well known, loses its blue colour when dehydrated, and therefore it seemed probable that some deep-seated change must occur during the dehydration of the malate. This conclusion receives support from the fact that, in marked contrast with the normal cupric salts of organic acids, the product of dehydration is extremely soluble in water. A satisfactory explanation of this phenomenon is that, during dehydration, cupric malate undergoes an intramolecular rearrangement, "cuprimalic acid" being formed according to the equation $CuC_4H_4O_5 \longrightarrow H \cdot CuC_4H_3O_5$.

In solution, measurements of copper-ion concentration and of the apparent molecular weight show that an equilibrium is quickly established between these two isomerides, the normal malate largely preponderating. Nevertheless, there is always present a sufficient concentration of hydrogen- and of cuprimalate-ions to give to the

solution some very characteristic properties not possessed by the copper salts of the simpler fatty acids. For instance, the solution is strongly acid to litmus and will remain so until one molecule of caustic soda per atom of copper has been added. This action is simply one of neutralisation: NaOH + $\text{H}\cdot\text{CuC}_4\text{H}_3\text{O}_5 \longrightarrow \text{H}_2\text{O} + \text{NaCuC}_4\text{H}_3\text{O}_5$. As the added alkali reacts with the small quantity of the acid which is present initially, some of the normal cupric malate changes into the acid in an endeavour to maintain the equilibrium between them. When sufficient alkali has been added, no cupric malate only.

A solution of acid cupric malate, $Cu(C_4H_5O_5)_2$, behaves towards alkalis like a mixture of malic acid and normal cupric malate. On neutralisation, a mixture of the sodium salts of malic and cuprimalic acids is formed.

Several of the cuprimalates have been isolated in a fairly pure, crystalline form. The alkali-metal salts are very soluble in water and their solutions exhibit no tendency to deposit copper hydroxide. Thus they are much more stable than the corresponding cuprilactates and of about the same degree of stability as the cupritartrates. Barium, silver, mercurous, and lead cuprimalates are much less soluble than the alkali-metal salts and are easily prepared by double decomposition. One of the most interesting compounds in this series is cupric cuprimalate, $Cu(CuC_4H_3O_5)_2$ or $Cu_3(C_4H_3O_5)_2$, first described by Liebig (Annalen, 1838, **26**, 137), which has been regarded as a basic cupric malate up to the present time.

The degree of stability of the cuprimalates may be judged from the value of the copper-ion concentration in N/20-solutions of the sodium and ammonium salts. This is of the order of 10⁻⁴, about 1/100 of its value in a solution of cupric malate containing the same quantity of copper per litre. Molecular-weight determinations which have been made in solutions of various cuprimalates indicate that association occurs fairly generally. In more dilute solutions, the associated molecules break down to a certain extent.

EXPERIMENTAL.

A. The Ternary System Malic Acid-Cupric Hydroxide-Water.

Several compounds belonging to this system have been mentioned in the literature (Liebig, *loc. cit.*; Pickering, *loc. cit.*; T., 1913, **103**, 1355; Hagan, Annalen, 1841, **38**, 257; Traube, Z. Kryst. Min., 1898, **31**, 162; Luck, Annalen, 1845, **54**, 117).

In the present work, only three of these salts—Liebig's salt, Hagan's acid malate dihydrate, and Pickering's crystalline normal malate—have been obtained from solution, but it is not claimed that

the work on the system is at all complete. Another compound, of the composition $2Cu(OH)_2, C_4H_6O_5$, is described in a subsequent section (D), but its field is not shown in the diagrams. In describing the relationships between these compounds, it will be expedient to consider briefly the form of the isotherms of the ternary system at 15° and at 50°. No solubilities have been measured, so the diagrams are purely qualitative. Nevertheless, they do show why it is that, at the ordinary temperature, neither the normal nor the acid cupric malate can be purified by recrystallisation, a fact which was, at first, rather perplexing.

Fig. 1 shows the form of the isotherm at 15° . *a*, *b*, and *c* represent the three solid phases $Cu_3(C_4H_3O_5)_2,7H_2O$, $CuC_4H_4O_5,3H_2O$, and $Cu(C_4H_5O_5)_2,2H_2O$, respectively. The solubilities of Liebig's salt



and of the normal malate have been grossly exaggerated in the figures.

Like many other hydroxy-compounds, these salts crystallise very slowly even from highly supersaturated solutions. Sometimes a week will elapse before the normal salt begins to crystallise, and "seeding" does not hasten matters. A further complication arises from the fact that a fungus growth sometimes forms on the surface of a solution exposed to the air.

A solution of the acid malate may be represented by some point, d, on the line joining c and A. Evaporation will bring its composition back along the same line to a point e where crystallisation will result in the formation of the normal salt. Thus the acid salt cannot be recrystallised from its own solution. Neither can the normal salt, as a glance at Fig. 1 will show.

Fig. 2 shows the general features of the 50° isotherm. As the temperature rises, the solubility of the normal salt increases very

rapidly, and at the temperature of this isotherm it occupies no stable region. Thus, at this temperature, the acid malate will begin to crystallise from its own solution, and, once started, this process will continue at a lower temperature where it is not so soluble, although, of course, the crystals are then metastable.

The analytical figures are now given upon which the evidence for the existence of those compounds is based and some of the properties of the salts are discussed.

Liebig's salt forms small, green crystals which are only very slightly soluble in water. It is readily soluble in acids and in ammonia, to which it imparts an extremely intense colour. Attempts to induce crystallisation in this solution proved futile. The analysis of a sample dried to constant weight at 100° confirmed the composition which Liebig adopted [Found : Cu = 34.96; C = 17.55; H = 3.04. Calc. for $Cu(CuC_4H_3O_5)_{2,}5H_2O$, Cu = 35.14; C = 17.69; H = 2.97 per cent.].

Acid cupric malate crystallises in well-formed, pale blue plates which are much more soluble than Liebig's salt. They retain their water of crystallisation at 105°. Analysis pointed to the composition $Cu(C_4H_5O_5)_{2,2}H_2O$ (Found : Cu = 17.35; C = 26.04; H = 4.27. Calc., Cu = 17.39; C = 26.25; H = 3.87 per cent.).

Normal cupric malate crystallises in beautiful clusters of long, deep blue needles. It is difficult to estimate the solubility of this salt, but it must be fairly low. It dissolves so slowly at the ordinary temperature that before the solution becomes saturated Liebig's salt will separate out. At higher temperatures, it dissolves with great rapidity and its solubility is high. Analysis showed it to be the trihydrate; figures for three different samples are quoted [Found: Cu = 25.49 (I), 25.47 (II), 25.47 (III); C = 19.58 (I), 19.46(II); H = 4.15 (I), 4.12 (II); $H_2O = 21.21$ (II), 21.65 (III). $CuC_4H_4O_5, 3H_2O$ requires Cu = 25.47; C = 19.22; H = 4.04; $H_2O = 21.65$ per cent.]. Water was estimated by heating the substance to constant weight at 110° ; at 120° , it begins slowly to decompose. The same dehydration occurs slowly over phosphoric oxide in a vacuum desiccator (Found : $H_2O = 19.2$ per cent.).

A remarkable change occurs during the dehydration. The colour deepens and the product of dehydration is extremely soluble in water. At first it was thought that the apparent differences in solubility between this compound and the hydrate might be due to the extreme slowness with which the latter dissolves. But it was found that the anhydrous lavender-blue substance was very soluble in a solution from which the hydrate was crystallising. This seems to indicate that some profound change accompanies dehydration, and from the colour and high solubility

of the anhydrous compound it is very probable that it is one of the typical complexes which contain copper in the negative radicle. A large series of complex salts of an acid of the same composition as this substance has now been isolated, and therefore, in view of its seemingly complex nature, it is only reasonable to regard it as the acid itself. Thus, in the sequel, it will be called *cuprimalic acid*, $\mathbf{H}\cdot\mathbf{CuC_4H_3O_5}$.

B. The Reaction between Alkalis and Normal Cupric Malate.

Either hydrated cupric malate or the isomeric cuprimalic acid may be used. The action of alkali on either, whether in solution or in the solid state, leads to the same products. The reaction is essentially one of neutralisation, any normal cupric malate present first changing into the acid and then undergoing neutralisation according to the equations $CuC_4H_4O_5 \rightleftharpoons H \cdot CuC_4H_3O_5$ and $H \cdot CuC_4H_3O_5 +$ NaOH \rightarrow NaCuC₄H₃O₅ + H₂O. The solution remains acid right up to the point of neutralisation and its colour deepens considerably during the addition of the alkali. Further addition of alkali renders the solution alkaline to litmus or phenolphthalein and there is an immediate precipitation of copper hydroxide. large excess of dilute alkali throws most of the copper out of solution, but sufficient always remains to give to it a violet-blue colour. Very concentrated solutions of caustic soda may retain quite a lot of copper in solution, and, on standing, some crystals are deposited; these have not yet been analysed.

It may be demonstrated by Masson's electrolytic method (*Phil. Trans.*, 1899, **192**, [A], 331) that the copper of the neutralised solution is mainly present in the negative ion. Some indication is given, too, of a blue kation, which moves away from the anode compartment. This is presumably the copper-ion, and experiments which are described in a later section show that there is present a definite, although low, concentration of copper-ions. There is a precipitation of copper hydroxide around the cathode, due, no doubt, to the interaction between the neutral salt and the caustic soda which is liberated there.

C. The Reaction between Alkalis and Acid Cupric Malate.

Three molecules of caustic soda per atom of copper are necessary to neutralise a solution of acid cupric malate, and about one extra molecule may be subsequently added before the precipitation of copper hydroxide commences. At first sight, this appears to be an entirely different reaction from that of alkali on the normal malate. But it has been shown that the same sodium and barium salts may

be thrown out of either solution and it has been established that the reaction may be represented by the equation

 $3NaOH + Cu(C_4H_5O_5)_2 \longrightarrow Na_2C_4H_4O_5 + NaCuC_4H_3O_5 + 3H_2O.$ The acid malate, therefore, behaves as an equimolecular mixture of the normal malate and malic acid, the former requiring one and the latter two molecules of caustic soda for neutralisation. The free sodium malate produced during the reaction evidently opposes the precipitation of copper hydroxide formed by the reaction

 $H_2O + NaOH + (CuC_4H_3O_5)Na \longrightarrow Na_2C_4H_4O_5 + Cu(OH)_2$, and so it is possible to add some alkali after the point of neutralisation is reached without thereby precipitating any copper hydroxide. The alkaline solution thus produced is of the intense violet-blue colour characteristic of all alkaline cupric solutions and, like Fehling's solution, is able to oxidise glucose. (The neutral compounds never oxidise glucose and are of a paler colour.)

D. Salts of Cuprimalic Acid.

The production of sodium cuprimalate by the interaction between solutions of copper malate and caustic soda has already been described. Potassium and ammonium malates may be similarly prepared. The majority of the other cuprimalates are fairly soluble in water, and so it is not usually possible to prepare them by double decomposition. A few of the heavy metals do form comparatively insoluble salts in this way: barium, silver, lead, copper, and mercury (Hg[•]). Some of the others, for example, manganese, tin, and ferric iron, although their salts do not yield a precipitate with sodium cuprimalate, decolorise the solution, presumably by replacing, or partly replacing, the copper in the complex. An account of some of these cuprimalates follows.

Sodium Cuprimalate.—On the addition of absolute alcohol to a solution of sodium cuprimalate prepared as above, a separation into two liquid phases occurs. From the lower of these, which contains most of the complex, the water may be removed by repeatedly washing it with absolute alcohol until finally it crystallises. It is not necessary to start with pure crystalline cupric malate. Instead, cupric carbonate or hydroxide may be dissolved in the right amount of malic acid solution, and the mixture neutralised by caustic soda. Often, however, the tricupric malate of Liebig will crystallise out before the alkali can be added, and the preparation is then lost.

Better crystals may be obtained by adding alcohol or acetone to the point of an incipient cloudiness and keeping the solution for a week: at the end of this time, nearly all of the copper will have been deposited in the form of fine, deep blue crystals. Before analysis, the crystals were purified by recrystallisation and air-dried. The

figures point to a composition $NaCuC_4H_3O_5, 4H_2O$ (Found : Cu =21.75, 21.68; Na = $\overline{7.63}$, 7.65; C = 16.59; H = 3.83. Calc., Na = 7.94; C = 16.57; H = 3.82Cu = 21.94:per cent.). Sodium was estimated as carbonate after ignition in an electric furnace at 650°. Copper was estimated either electrolytically after ignition, or its percentage was deduced from the weight of the residue from ignition (which consists of a mixture of sodium carbonate and cupric oxide) and the found sodium content. Carbon and hydrogen were estimated by combustion, the former in the presence of lead and potassium chromates, which, when fused, prevent the retention of carbon dioxide by sodium. The salt loses all four molecules of water at 120° (Found : $H_2O = 23.7$. Calc., $H_0O =$ 24.85 per cent.), and begins to decompose at 130°.

Another method may be adopted for the production of the alkali metal cuprimalates. As much copper hydroxide as possible is dissolved in a solution of the desired alkali metal acid malate, when the following reaction takes place—

$$Cu(OH)_2 + MHC_4H_4O_5 \rightarrow MCuC_4H_3O_5 + 2H_2O.$$

Ammonium Cuprimalate.-It has been mentioned that the attempt to prepare sodium cuprimalate is sometimes thwarted by the precipitation of Liebig's salt during the preparation of a solution of the normal cupric malate. If the ammonium salt be desired, this precipitate is not fatal to the preparation, for it may be dissolved in an excess of ammonia. On removal of the excess of ammonia by heating on a water-bath, a pure solution of ammonium cuprimalate remains. Pure crystals separate out from such a solution to which sufficient acetone has been added to produce a slight cloudiness. Before analysis, the bright blue crystals were purified by recrystallisation, and, as they were deliquescent, were rapidly dried by acetone and ether (Found : Cu = 23.16, 23.10; N = 4.90, 4.81;C = 17.21; H = 5.72. $NH_4CuC_4H_3O_5, 4H_2O$ requires Cu = 22.33; N = 4.92; C = 16.86; H = 5.30 per cent.). Nitrogen was estimated as ammonia liberated by boiling the compound with alkali. All four molecules of water were lost at 110° (Found : $H_2O = 24.96$. Calc., $H_2O = 25.31$ per cent.).

Ammonium cuprimalate also forms in large, sphericular aggregates of bright, needle-shaped crystals from a very concentrated aqueous solution. Usually it is contaminated with a little of Liebig's salt when allowed to form in this way.

Potassium Cuprimalate.—This salt cannot be induced to crystallise by adding alcohol or acetone to its aqueous solution. Like the potassium salt of many other complex cupri-acids, it passes into an emulsion instead. As a general rule, however, the potassium

salts are less soluble than the corresponding sodium salts and they may often be crystallised from a concentrated aqueous solution. Potassium cuprimalate readily crystallises, but, like the ammonium salt, it is usually contaminated with crystals of Liebig's salt. After drying at 100°, one sample, not so badly contaminated as most others, contained 28.0 per cent. of copper and 14.8 per cent. of potassium (KCuC₄H₃O₅ requires Cu = 27.2; K = 16.7 per cent.).

Barium Cuprimalate.-This be may prepared as a pale blue, granular precipitate by double decomposition between solutions of barium chloride and sodium cuprimalate. Although sparingly soluble in cold, it is much more soluble in hot water and may be purified by recrystallisation. For analysis, a sample was recrystallised twice and air-dried. (The exact estimation of the water of crystallisation was unimportant, since the object of the work was to examine the constitution of the compounds rather than their individual characteristics. Accordingly, it was unnecessary to take any elaborate precautions in drying the compounds.) Analysis indicated a composition Ba(CuC4H3O5)2,7H2O, but it is possible that the number of water molecules may be one more or less than 7 (Found : Ba = 20.35, 20.90; Cu = 19.32; C = 14.67; H = 3.33; $H_{2}O = 17.6$. Calc., Ba = 21.06; Cu = 19.48; C = 14.71; H = 10.483.10; $H_{2}O = 19.3$ per cent.). Barium was estimated as sulphate, first on the pure salt, and again after ignition. Copper was estimated electrolytically after ignition. In the estimation of carbon, admixture with lead and potassium chromates prevented the retention of carbon as barium carbonate. Water was estimated by heating the salt to constant weight at 120°; at 130°, decomposition proceeds slowly.

Silver Cuprimalate.-This salt may be prepared by double decomposition between solutions of sodium or ammonium cuprimalate and silver nitrate. It forms pale blue granules which are soluble in excess of the cuprimalate and darken when exposed to light. For this reason the salt was prepared in artificial light; it then proved to be perfectly stable when kept for some months in a darkened place.

In the analysis, silver was estimated as chloride after the compound had been ignited, and copper electrolytically after removal of the silver. It is not possible to estimate satisfactorily the amount of water of crystallisation, for the compound is decomposed by heat before all the water is expelled. The figures showed it to be a dihydrate (Found : Ag = 33.0; Cu = 17.9; C = 14.2; H = 1.9. $AgCuC_4H_3O_5, 2H_2O$ requires Ag = 31.9; Cu = 18.8; C = 14.2; H = 2.1 per cent.).

Lead Cuprimalate.—This compound, which may be formed by double decomposition between solutions of sodium cuprimalate and lead acetate, resembles the silver salt in appearance and, like it, is soluble in excess of sodium cuprimalate. It is not sufficiently soluble in water to enable it to be purified by recrystallisation, and for analysis the precipitate was merely washed with hot water and then air-dried. The lead content is considerably higher and the copper content is much lower than the amounts that would correspond with the formation of a simple cuprimalate. It is suggested that the lead has partly replaced the copper of the complex ion (Found : Pb = 41.8; Cu = 11.7; C = 12.2; H = 1.7 per cent. for which the ratio Pb : Cu : C : H = 1.00 : 0.92 : 5.05 : 8.4. If a simple cuprimalate had been formed, the ratio would have been 1:2:8:x).

It is of interest to note that Masson and Steele, in their work on the cuprotartrates (T., 1899, 75, 725), found a similar high lead content: they ascribed it to adsorption effects.

Cupric Cuprimalate.—As was pointed out earlier, Liebig's tricupric malate is the copper salt of cuprimalic aid. Its low solubility dominates the chemistry of the cuprimalates, giving to them an instability which somewhat overshadows their great stability in another respect, namely, that, like the α -cupritartrates, their solutions have no tendency to deposit copper hydroxide. It is easily seen why this salt so readily forms in solutions of normal cupric malate or any of the soluble cuprimalates. As has been already emphasised, a solution of normal cupric malate changes partly into the isomeric cuprimalicacid, so that both cupric (Cu") and cuprimalic (CuC₄H₃O₅)' ions will be present. Both of these ions are also present in a solution of sodium or ammonium cuprimalate. In either case, if the concentration be sufficiently high, the solubility product of cupric cuprimalate, a very insoluble salt, may be exceeded and then precipitation results.

The law of mass action also affords an explanation of why it is that this compound is soluble in malic acid. The following equations will serve to make the point clear.

$$\begin{array}{c} \operatorname{Cu}(\operatorname{CuC}_4\operatorname{H}_3\operatorname{O}_5)_2 \rightleftharpoons \operatorname{Cu}(\operatorname{CuC}_4\operatorname{H}_3\operatorname{O}_5)_2 \rightleftharpoons \operatorname{Cu}^* + 2\operatorname{CuC}_4\operatorname{H}_3\operatorname{O}_5' \quad (1) \\ \text{(solid)} \quad (\text{dissolved}) \end{array}$$

 $H_2 C_4 H_4 O_5 \implies C_4 H_4 O_5'' + 2H'$. (2)

$$Cu'' + C_4 H_4 O_5'' \rightleftharpoons Cu C_4 H_4 O_5 \dots \dots (3)$$

 $2H' + 2CuC_4H_3O_5' \implies 2HCuC_4H_3O_5 \dots \dots (4)$

If to a saturated solution of Liebig's salt, which will contain a certain concentration of both cupric and cuprimalic-ions (1), malic

acid be added (2), there will be formed a quantity both of cupric malate and of cuprimalic acid (equations 3 and 4). One of these reactions will reduce the concentration of the cupric-ion and the other that of the cuprimalic-ion, and accordingly more of the solid will dissolve in an endeavour to maintain its solubility product constant.

Accepting this view of the nature of Liebig's salt, one would expect it to form by double decomposition between solutions of cupric sulphate and sodium cuprimalate according to the equation $CuSO_4 + 2NaCuC_4H_3O_5 \longrightarrow Na_2SO_4 + Cu(CuC_4H_3O_5)_2$. When solutions were mixed in the proportions required by this equation, there was no immediate precipitate, but on boilling, or on keeping the solution for some time, bluish-green crystals were deposited. These resembled Liebig's salt in appearance and, like it, were soluble in excess of cuprimalate. But analysis of a sample dried at 100° showed it to be a basic salt containing more copper than Liebig's salt. A second sample was obtained using ammonium instead of sodium cuprimalate; the analyses of the two samples are marked I and II, respectively [Found : Cu = 40.75 (I), 40.69 (II); C = 15.60 (I), 15.24 (II); H = 2.8 (I), 2.4 (II).

 $Cu(CuC_4H_3O_5)_2, CuO, 5H_2O$

requires Cu = 40.85; C = 15.43; H = 2.6 per cent.].

Cuprimalic Acid.—It has been contended that cuprimalic acid is formed in the solid state by the dehydration of a hydrate of normal cupric malate. An attempt was made to prepare it in solution by the action of sulphuric acid on a suspension of barium cuprimalate, care being taken that there was no excess of the mineral acid. A deep blue solution was obtained which was acid to litmus. The solution could be neutralised by alkalis and then gave a precipitate of the original cuprimalate with a solution of barium chloride. The solution was in every way identical with one of the lavender-blue acid itself or with one of normal cupric malate. All three deposit crystals of Liebig's salt on standing; this enriches the solution in malic acid, and after a time, the normal malate will separate out too.

E. Molecular Weights.

The cryoscopic method was used. The freezing points of the aqueous solutions were probably correct to within 0.005°. This figure corresponds with an error of about 15 units in the more dilute solutions used. In the table, a = gram-atom of copper per litre, $\Delta =$ depression of freezing point, and m = apparent molecular weight.

$\begin{array}{l} \text{Ammonium} \\ \text{cuprimalate.} \\ M = 212 \cdot 6. \end{array}$		Sodium cuprimalate. $M = 217 \cdot 6.$			Cuprimalic acid. $M = 195 \cdot 6.$			
a.	Δ.	m.	a.	Δ.	m.	a.	Δ.	m.
0.0500	0.120°	167	0.05	0·108°	188	0.05	0∙069°	264
0.0875	0.170	203	0.10	0.218	187	0.10	0.119	306
0.262	0.498	206	0.20	0.390	208	0.20	0.185	394
0.392	0.770	202	0.50	0.932	218	0.20	0.382	477
						(0.10)	(0.111)	(328)

The values obtained for the two salts point to a partial association among the cuprimalate-ions. Were no such association to occur, ionisation of these salts would certainly give rise to much lower values of the apparent molecular weights. Association is much more advanced in concentrated than in dilute solutions; N/20solutions show a considerably lower value than N/2-solutions.

The figures enclosed in brackets were obtained using a solution of normal cupric malate instead of the acid. Their nearness to the corresponding values for cuprimalic acid indicates that these compounds yield identical solutions, a conclusion which is thoroughly confirmed by the measurements of the concentrations of the copperion which are described in the next section. In concentrated solutions especially, there is a high degree of association. Tower (J. Amer. Chem. Soc., 1902, **24**, 1012) observed similar high molecular weights in solutions of nickel and cobalt malates, and correspondingly low conductivities.

F. Copper-ion Concentrations.

The method of making the measurements has been described in the preceding paper (p. 1815). The temperature used throughout was 18° .

Normal Cupric Malate.—Table I shows the values obtained for solutions containing various concentrations of cupric malate. α represents the degree of dissociation of cupric malate into copperions.

TABLE I.

Grmatom Cu per litre.	Single electrode potential diff. (volt).	Copper-ion conc. $\times 10^2$.	α per cent.
0.05	0.552	1.4	28
0.10	0.552	1.4	14
0.20	0.555	1.7	8.5
0.25	0.551	1.3	$5 \cdot 2$

It was impossible to obtain figures for higher concentrations than those recorded, because Liebig's salt was too readily deposited, or for lower concentrations, because the conductivity became so low that accurate measurements could not be made.

Ionisation increases so much with dilution that 1/4M- and 1/20Msolutions contain practically the same copper-ion concentration. The figures support the conclusion that in concentrated solutions associated molecules are numerous and that these loose combinations break down in more dilute solutions.

Sodium and Ammonium Cuprimulates.—Table II shows the effect of dilution on the copper-ion concentration of sodium cuprimulate.

TABLE II.

Sodium cuprimalate.

Gmatom Cu per litre	0.05	0.10	0.20	0.50
Single electrode pot. diff	0.486	0.483	0.476	0.473
Copper-ion conc. $\times 10^5$	$7 \cdot 3$	$5 \cdot 7$	$3 \cdot 3$	$2 \cdot 6$

It will be seen that whilst the concentration has increased tenfold the number of copper-ions has actually decreased threefold. These figures support the view, previously expressed, that association is more advanced in concentrated than in dilute solutions.

The single electrode potential difference in a solution of the ammonium salt containing 0.05 gram-atom of copper per litre is 0.491 volt, corresponding to a copper-ion concentration of 1.08×10^{-4} .

Cuprimalic Acid.—The copper-ion concentration of a solution of sodium or ammonium cuprimalate containing 0.05 gram-atom of copper per litre is of the order 10^{-4} . That for a solution of normal cupric malate containing the same amount of copper per litre is 1.5×10^{-2} , and an identical value was obtained for a solution of cuprimalic acid of equal concentration. Hence, it is concluded that these two isomerides yield identical solutions, and, further, that in the equilibrium mixture the malate must predominate.

Influence of Alkali on the Copper-ion Concentration of Copper Malate.—Table III shows the effect produced on the copper-ion concentration by the addition of sodium hydroxide to a solution of normal cupric malate. All solutions contained 0.05 gram of copper per litre, unless otherwise indicated.

TABLE III.

	Single			Single	
\mathbf{Ratio}	electrode		Ratio	electrode	
NaOH :	pot. diff.	Copper-	NaOH :	pot. diff.	Copper-
CuC ₄ H ₄ O ₅ .	(volt).	ion conc.	CuC4H4O5.	(volt).	ion conc.
0	0.554	$1{\cdot}6 imes10^{-2}$	(a) 1.00	0.490	$9.8 imes 10^{-5}$
0.25	0.537	$6\cdot8 imes10^{-3}$	(b) 1·03	0.456	$6.6 imes 10^{-6}$
0.50	0.526	$1.7 imes10^{-3}$	(c) 1·25	0.386	$2\cdot 5 imes 10^{-8}$
0.75	0.519	$1{\cdot}0 imes10$ –8	(d) 2.00	0.365	$4.8 imes 10^{-9}$
0.92	0.203	1.3×10^{-4}	• •		

(a) This solution was prepared from pure sodium cuprimalate. (b) Slightly alkaline. (c) Alkaline. Contained 0.75 gram-atom of copper per litre. (d) Alkaline. Practically all the copper had been precipitated as hydroxide, but sufficient remained in solution to give a slight precipitate with hydrogen sulphide.

As caustic soda is added to the solution of cupric malate, the concentration of the copper-ion falls from 10^{-2} to 10^{-4} during neutralisation. As soon as the solution becomes alkaline there is a further marked fall in the cuprion content. Further, since no great quantity of copper remained in the solution marked (d), it will be seen that the reaction

 $H_2O + NaCuC_4H_3O_5 + NaOH \rightarrow Cu(OH)_2 + Na_2C_4H_4O_5$ occurs almost quantitatively.

Influence of Potassium Chloride on the Copper-ion Concentration of Normal Cupric Malate.—It is of interest to compare the above results with those obtained on addition of potassium chloride to a solution of normal cupric malate (Table IV).

TABLE IV.

	Single			Single	
Ratio	electrode	~	Ratio	electrode	~
KCI:	pot. diff.	Copper-	KU:	pot. diff.	Copper-
$CuC_4H_4O_5$.	(volt).	ion conc.	$CuC_4H_4O_5$.	(volt).	ion conc.
0	0.552	$1{\cdot}4$ $ imes$ 10^{-2}	2.00	0.499	$2{\cdot}0 imes10$ $^{-4}$
0.50	0.531	$2{\cdot}6 imes10^{-3}$	4.00	0.483	$5.8 imes10^{-5}$
1.00	0.515	$7\cdot3 imes10$ -4			

At first, potassium chloride is almost as effective as caustic soda in reducing the copper-ion concentration. In greater amounts, it has not nearly so much influence. It is probable that some complex formation is responsible for this reduction in the concentration of copper-ions. The figures show clearly why it was so essential to prevent diffusion into the electrode vessel while the potential difference measurements were in progress.

Other Measurements.—For comparative purposes it is interesting to tabulate some of these results along with those obtained for a few other compounds. Sodium α -cupritartrate was described in an earlier paper (Packer and Wark, T., 1921, **119**, 1348). All solutions contained 1/20 gram-atom of copper per litre and all measurements were made at 18°.

TABLE V.

	Single electrode	
Compound.	pot. diff. (volt).	Copper-ion conc.
Sodium cuprimalate (NaCuC ₄ H ₃ O ₅)	0.486	$7\cdot3$ $ imes$ 10^{-5}
Ammonium cuprimalate $(NH_4CuC_4H_3O_5)$	0.491	$1{\cdot}08 imes10$ $^{-4}$
Cuprimalic acid (HCuC ₄ H ₃ O ₅)	0.553	$1.5~ imes~10^{-2}$
Normal cupric malate $(CuC_4H_4O_5)$	0.553	$1.5~ imes 10^{-2}$
Sodium α -cupritartrate (Na ₃ Cu ₄ C ₁₂ H ₉ O ₁₉)	0.458	$9.3 imes 10^{-6}$
Acid cupric malate $(Cu[C_4H_5O_5]_2)$	0.550	$1{\cdot}2~ imes~10^{-2}$

Summary.

(1) The system copper hydroxide-malic acid-water has been partly investigated at 15° and at 50°, and the following compounds have been described. An acid cupric malate, $Cu(C_4H_5O_5)_{2,2}H_2O$; a normal cupric malate, $CuC_4H_4O_5,3H_2O$; and tricupric malate or cupric cuprimalate, $Cu_3(C_4H_3O_5)_{2,7}H_2O$.

(2) It has been shown that the dehydration of normal cupric malate is accompanied by the formation of an isomeride, cuprimalic acid, $HCuC_4H_3O_5$.

(3) The following salts of cuprimalic acid have been isolated : sodium, $NaCuC_4H_3O_5, 4H_2O$; ammonium, $NH_4CuC_4H_3O_5, 4H_2O$; barium, $Ba(CuC_4H_3O_5)_2, 7H_2O$; silver, $AgCuC_4H_3O_5, 2H_2O$; potassium; lead; cupric cuprimalate, $Cu(CuC_4H_3O_5)_2, 7H_2O$, mentioned in (1) above, and a basic cupric cuprimalate,

 $Cu(CuC_4H_3O_5)_2, CuO, 5H_2O.$

(4) Measurements of molecular weight in aqueous solutions of sodium and ammonium cuprimalates, of cuprimalic acid, and of normal cupric malate indicate a partial association in concentrated solutions.

(5) The concentration of the copper-ion in solutions of some of these compounds has been measured. The value in solutions of sodium and ammonium cuprimalates is of the order 10^{-4} when the total copper-ion content is 0.05 gram-atom per litre. Cuprimalic acid and normal cupric malate yield identical solutions in which the value is 1.5×10^{-2} ; this solution contains an equilibrium mixture of the two, the normal malate predominating.

The constitution of the cuprimalates will be considered in a later communication.

The author has much pleasure in expressing his thanks to Professor Donnan for his kind advice and assistance, and to the Royal Commissioners of the Exhibition of 1851 for a scholarship which has enabled him to carry out the work.

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[Received, June 4th, 1923.]