L.—*Contribution to the Physical Chemistry of Complex Salts. Part I. Transport Numbers of Copper Salicylate.*

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DURING the course of work on the derivatives of copper salicylate [$Cu(HSal)_2$, where H_2Sal = salicylic acid] it seemed desirable to determine its transport number in aqueous solution, with the object of throwing some light on its constitution, for on Werner's theory, the constitution of a complex salt is primarily an expression of its mode of ionisation.

Since hydrogen sulphide readily precipitates copper sulphide from an acid solution * of the salicylate, the latter presumably

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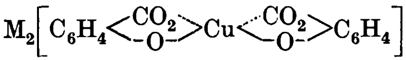
* If hydrogen sulphide is passed into a neutral solution of the compound containing no other electrolyte, a colloidal solution of copper sulphide is obtained, just as in the well-known method of preparing mercuric sulphide sols from mercuric cyanide.

dissociates, to some extent at any rate, as a normal salt with formation of copper and salicylate ions. On the other hand, addition of alkali causes only very slow and partial precipitation of copper hydroxide; from these alkaline solutions, compounds of the type M_2CuSal_2 ($M = Na, K$, or NH_4) can be isolated (Ley and Erler, *Z. anorg. Chem.*, 1908, **56**, 404), and transport-number determinations—qualitative only, owing to the slow decomposition of the compound—show that copper is here part of the negative ion. Since salicylic acid contains the well-known chelate group, $-C(OH){=}\overset{|}{C}{-}\overset{|}{C}{=}O$, which is characteristic of a number of important complex-forming molecules (*e.g.*, acetylacetone), it is probable that the constitution of these compounds is represented by the formula



$$M_2\left[C_6H_4{<}\substack{CO_2\\ O}{>}Cu{<}\substack{CO_2\\ O}{>}C_6H_4\right]$$

(Weinland, "Komplex-verbindungen," 1919, p. 193) and that copper salicylate itself is present in solution largely as the corresponding acid, $H_2(CuSal_2)$.

Titration with alkali, the end-point being determined by means of the conductivity (since the deep colour of the solutions prohibits the use of indicators), gave sharply defined V-shaped curves indicating that the compound is a monobasic acid. The evidence is thus in favour of copper salicylate being a complex acid; the precipitation of copper sulphide by hydrogen sulphide merely proves the existence of traces of copper ions in solution.

EXPERIMENTAL.

Copper salicylate was prepared from copper sulphate and sodium salicylate, washed, recrystallised from water until free from sulphate, and air-dried. Temperatures above 60° were avoided on account of the ready decomposition.

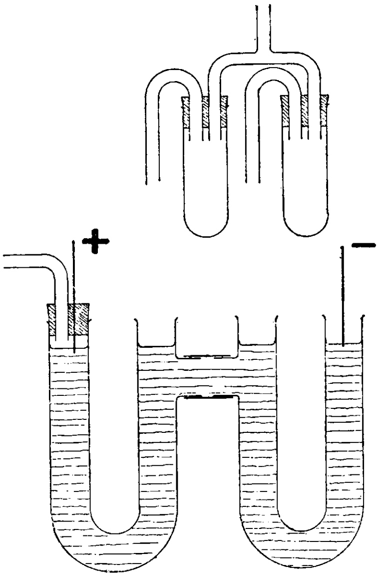
Preliminary experiments showed that the solubility of copper salicylate at 25° is 10·19 g. (0·0302 g.-mol.) per litre of solution : transport-number determinations are thus restricted to somewhat dilute solutions and the highest accuracy is unattainable.

The cell (Fig. 1), of 160 c.c. capacity, constructed throughout from tubing of the same diameter, was made in two pieces and connected by rubber tubing. It was kept in a thermostat at 25·0° ± 0·2°. A current of 10—15 milliamps. was passed between the two platinum electrodes for 1—3 hours; a precipitate (which appears to be the compound CuSal, salicylic acid acting as a dibasic acid) separated at the cathode, causing a rapid increase in the resistance with consequent fall of current; to obviate this, the cathode was lowered slightly every 10 minutes, thus exposing a fresh surface to the solution. This precipitate caused a stirring of the cathode liquid and also precluded its analysis; the transport numbers are therefore based on analysis of the anode portions only.

During preliminary experiments, inconsistent results were obtained owing to leakage of electricity through the rubber joint into the bath. To eliminate, or alternatively to detect, this source of error, the joint was waxed and two copper voltameters were used, one connected to the anode and the other to the cathode.

At the end of the experiment, two centre portions—the anode centre and the cathode centre portions, each of about 20 c.c.—were withdrawn simultaneously from the two inner limbs by means of the device shown in the upper part of Fig. 1. Withdrawal of the centre portions left the anode and cathode portions isolated in the two U-tubes. The cell was then disconnected at the rubber joint, and the anode portion removed for analysis. All analyses were by weight, not volume of solution. Copper was estimated by Volhard's method (Classen, "Ausgewählte Methoden der Analytischen Chemie," 1901, I, p. 87), since the electrolytic and iodine–thiosulphate methods fail in the presence of salicylic acid.

Fig. 1.



The results are in Table I: cols. 1, 2, and 3 give, respectively, the initial concentrations and the concentrations of the anode-centre

TABLE I.

Concentrations.			Voltameter.		Anode portion.		
Initial.	Anode-centre.	Cathode-centre.	Anode (g.).	Cathode (g.).	Weight (g.).	Copper (g.).	Transport number or cation.
0·02746	0·02755	0·02672	0·0510	0·0508	55·83	0·06484	0·628
	0·02750	0·02701	0·0532	0·0528	52·56	0·05766	0·633
	0·02732	0·02707	0·0406	0·0410	52·06	0·06386	0·646
0·01823	0·01816	0·01852	0·0341	0·0341	54·89	0·04191	0·630
	0·01834	0·01849	0·0342	0·0347	58·88	0·04621	0·627
0·01399	0·01399	0·01391	0·0214	0·0216	55·03	0·03562	0·613
0·01249	0·01247	0·01241	0·0185	0·0187	53·24	0·03067	0·617
	0·01243	0·01250	0·0154	0·0154	53·10	0·03244	0·623
						Mean	0·626

and the cathode-centre portions, in mols. per 1000 g. of water; cols. 4 and 5 show the increase in weight of the cathodes of the two copper voltameters; in cols. 6 and 7 are the weights and copper contents of the anode portion removed after the experiment, and in col. 8 are the calculated values of the transport number of the cation. No change of transport number with concentration can be detected; deviations from the mean appear to be due entirely to experimental error.

Discussion.

Neither the mobility of the copper nor that of the salicylate ion is known accurately at 25°, but assuming these to be 54 and 36, respectively, the transport number of the cation of copper salicylate should be 0·60 if it ionised as a normal cupric salt; whereas, if copper salicylate were a complex acid, there should be an increase in concentration of copper at the anode. The agreement of experiment with the first hypothesis, and the fact that the transport number does not change with concentration, show that copper salicylate ionises in aqueous solution as a normal salt—an unexpected result in view of the arguments put forward in the introduction.

Further consideration shows that hydrogen-ion concentration must have a considerable effect on the stability of the complex ion, and that the indisputable evidence for copper salicylate being a complex acid applies only to alkaline solutions. Assuming the existence of the complex negative ion $(CuSal_2)''$, this must dissociate to some extent into its components :

$$2H^{\cdot} + (CuSal_2)'' \rightleftharpoons Cu^{\cdot\cdot} + 2HSal'.$$

For the conditions of equilibrium of this reaction

$$[H^{\cdot}]^2[(CuSal_2)'']/[Cu^{\cdot\cdot}][HSal']^2 = K_s$$
$$\text{or } [(CuSal_2)'']/[Cu^{\cdot\cdot}] = K_s[HSal']^2/[H^{\cdot}]^2$$

where square brackets indicate concentrations, or, more correctly, activities, which at great dilutions are approximately equal to concentrations. The quantity on the left of the second equation is a measure of the stability of the complex ion; if all the copper is present in the form of a complex ion, its value is infinite; if all is present as simple ions, its value is zero. On combining this with the relation $[HSal'][H^{\cdot}] = K_d[H_2Sal]$, where K_d represents the first ionisation constant of salicylic acid, and with the assumption of equality of positive and negative ions, one obtains the equation :

$$\frac{[(CuSal_2)'']}{[Cu^{\cdot\cdot}]} = \frac{K_sK_d^2(2x - [H^{\cdot}])^2}{[H^{\cdot}]^2(2[H^{\cdot}] + K_d)^2} = \frac{4K_sx^2}{[H^{\cdot}]^2} \text{ (approximately)}$$

where x is the total concentration of copper salicylate in solution, independently of its nature. In neutral and alkaline solution, where $[H^\cdot]$ is not greater than 10^{-7}, no error will be caused by using the simpler approximate expression. The stability of the complex ion depends, therefore, on the total concentration of the compound and on the hydrogen-ion concentration; it should be increased about 10^{12} fold on passing from neutral to $N/10$-alkaline solution.*

It is possible to make a rough estimate of the value of K_s, for in a solution in which the concentration of copper salicylate is $0{\cdot}02M$ and that of sodium hydroxide is $0{\cdot}1N$, copper hydroxide is only precipitated very slowly, which shows that practically all the copper is in the form of complex ion and that the solubility product of copper hydroxide is only just exceeded. Assuming a value of 2×10^{-13} for the solubility product (Immerwahr, *Z. anorg. Chem.*, 1900, **24**, 269), K_s is 6×10^{-15}; in a neutral solution of the same strength (*i.e.*, $0{\cdot}02M$) only one-thousandth of the copper should be present as complex ion. Copper salicylate must therefore undergo a complete change in constitution on passing from neutral to alkaline solution; in other words, it is a "pseudo-acid." The change in colour of its solutions from light blue to dark green, on titration with alkali, will be regarded by many as confirmation of this view.

Similar considerations as to the influence of hydrogen-ion concentration on stability must apply to all complex ions of the type (MX_n), where M is a metal and HX a weak acid, although the equation connecting these factors will depend on the particular complex ion under consideration. It is noticeable that, whilst there are numerous salts containing complex negative ions of this type, the corresponding acids are seldom known; even when they can be prepared, which is only possible with the most stable complex ions, they are unstable compounds.

According to the equation given above, the stability of the complex ion depends on the concentration of the salt; copper salicylate is too insoluble to permit of a study of its transport number over any wide range of concentrations. Preliminary experiments with the very similar, but more soluble, nickel compound, which it is hoped to publish soon, indicate that it resembles the copper compound in dilute solution, and that appreciable quantities of complex ion are present in more concentrated solutions.

It appears to be a corollary of the complete ionisation theory of

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* $[H^\cdot]$ cannot be varied at will without the addition of acid or alkali; if the presence of this is taken into account, solution of six simultaneous equations leads to a more complicated expression, which reduces to the same approximate form when $[H^\cdot]$ is small.

Milner, and of Debye and Hückel, that the terms "pseudo-acid" and "weak acid" are synonymous; it is therefore reasonable to ascribe the behaviour of copper salicylate on titration to the fact that the complex acid, $H_2(CuSal_2)$, is a weak one. With weak dibasic organic acids, the conducto-titrimetric method gives an end-point corresponding to neutralisation of the first hydrogen ion, whilst the second end-point, corresponding to complete neutralisation, is seldom obvious.

Summary.

The transport numbers of copper salicylate in aqueous solution have been determined.

Evidence is presented in favour of the view that copper salicylate is a pseudo-acid, and that, whilst in neutral solution it ionises as a normal copper salt, in alkaline solutions it is present as the salt of a complex cuprisalicylic acid.

A consideration of the ionic equilibria involved indicates that the stability of all complex ions of this type depends to a large extent on the concentration of the hydrogen ions in the solution.

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