esters were polymerized with benzoyl peroxide as initiator. The first two esters were readily converted to gels, whereas the last two showed relatively little tendency to polymerize. Copolymerization of the esters with vinyl acetate over the range of from one to forty per cent. hendecenoate yielded insoluble copolymers which ranged in physical appearance from hard, glass-like resins to soft, crumbly gels.

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Cation Complexes of Compounds Containing Carbon–Carbon Double Bonds. II. The Solubility of Cuprous Chloride in Aqueous Maleic Acid Solutions[1]

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Data have been reported previously[2] which illustrate that the solubility of cuprous chloride in aqueous maleic acid solutions varies markedly with the hydrogen ion concentration of the medium. These data were interpreted on the assumption that $H_2M \cdot CuCl$ and $HM \cdot CuCl^-$ were the only water soluble complexes formed in appreciable quantities under the experimental conditions used.[3] More recently[1,4] it has been observed that the extent of formation of water soluble cuprous complexes of compounds containing carbon–carbon double bonds generally depends on the chloride ion concentration of the medium. Accordingly additional experiments with maleic acid have been made, the results of which are reported here. These new data indicate that, in addition to the aforementioned complexes, $H_2M \cdot Cu^+$ and $HM \cdot Cu$ may be formed in significant amounts.

Experimental

The Solubility Measurements.—The methods for preparation of the maleic acid–cuprous chloride solutions and the method of analysis for cuprous content have been described in detail previously.[1,2] As reported earlier the solutions of the maleic acid complexes are intensely yellow colored.[2]

Results

The measured solubilities of cuprous chloride in moles per liter (Cu^+_T) in aqueous solutions as influenced by changes in the initial concentrations of maleic acid (H_2M_i), hydrogen ion and chloride ion are given in Table I. The ionic strengths of the solutions were in the neighborhood of 1.0 (runs 1–9) or 0.1 (runs 10–27). No attempt was made to apply activity coefficient corrections to the concentrations of the complexes in the calculation of equilibrium constants as described later.[5]

TABLE I

THE SOLUBILITY OF CUPROUS CHLORIDE IN AQUEOUS SOLUTIONS OF MALEIC ACID AT 25°[a]

Run	Concns., mole/liter (H_2M_i)	(HCl_i)	(H^+)	(H_2M)	(Cl^-), × 10³	(Cu^+_T) × 10³ meas.	calcd.
1	0.202	0	1.03	0.187	7.1	11.8	12.0
2	.101	0	1.02	.094	5.1	7.7	7.7
3	.0503	0	1.02	.045	3.5	4.8	5.0
4	.202	0.100	1.03	.193	94.5	11.0	10.7
5	.101	.100	1.02	.097	94.2	8.0	8.4
6	.0503	.100	1.02	.048	94.0	6.8	7.3
7	.184	.0091	1.03	.174	12.3	9.2	8.6
8	.101	.0100	1.02	.097	11.6	5.3	5.2
9	.0503	.0100	1.02	.048	10.5	3.0	3.0
10	.202	0	0.138	.159	11.0	19.2	18.8
11	.152	0	.129	.117	9.7	16.0	15.8
12	.101	0	.122	.075	7.9	12.8	12.2
13	.0505	0	.113	.036	5.6	8.3	8.1
14	.202	0.100	.133	.166	94.0	14.2	14.4
15	.152	.100	.126	.124	95.0	12.4	12.5
16	.101	.100	.118	.081	94.0	10.9	10.6
17	.202	.0100	.136	.161	16.8	15.8	15.5
18	.101	.0100	.120	.079	14.2	9.6	9.4
		(KCl)					
19	.202	0	.067	.134	13.6	24.0	24.3
20	.101	0	.043	.056	10.4	17.0	17.1
21	.0504	0	.028	.021	7.9	11.8	11.8
22	.202	0.100	.060	.139	96.1	17.6	17.8
23	.152	.100	.051	.098	96.0	15.4	15.9
24	.101	.100	.040	.060	95.3	12.8	13.3
25	.202	.010	.062	.136	19.1	20.2	21.0
26	.152	.010	.053	.096	18.4	17.3	17.7
27	.101	.010	.043	.057	16.5	14.1	13.8

[a] In runs 1–9 μ was adjusted to 1.0 by the addition of perchloric acid before the addition of maleic acid and cuprous chloride. Similarly in runs 10–18 μ was adjusted to 0.10. In runs 19–27 μ was adjusted to 0.100 by the addition of sodium perchlorate.

It is apparent that an increase in the hydrogen ion concentration of the solutions results in a decrease in the solubility of cuprous chloride (*cf.* runs 1, 10 and 19 at constant initial maleic acid concentration). Similarly an increase in chloride ion concentration inhibits the formation of the maleic acid complexes. This effect is not immediately obvious in terms of Cu^+_T values since they include the concentrations of $CuCl_2^-$.

On the basis of these qualitative observations it has been postulated that equations (1)–(7) are sufficient to account for the equilibrium conditions in these solutions, and the solubility data have been used to calculate the val-

(1) For paper I of this series see Keefer and Andrews, THIS JOURNAL, **71**, 1723 (1949).

(2) Andrews and Keefer, *ibid.*, **70**, 3261 (1948).

(3) The terms H_2M and HM^- are used, respectively, to represent maleic acid and acid maleate ion.

(4) Keefer, Andrews and Kepner, *ibid.*, **71**, 2381 (1949).

(5) This seems justifiable since the concentrations are sufficiently high in these solutions so that the electrostatic effects no longer change rapidly with concentration and are small enough so that nonelectrostatic forces are still small. For hydrochloric acid, the two effects compensate almost exactly at these two concentrations. *Cf.* Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 475.

ues of K_3, K_4, K_5 and K_6,[6] which are recorded.

$$(CuCl)_s = Cu^+ + Cl^- \qquad S.P. = 1.85 \times 10^{-7} \quad (1)$$

$$Cu^+ + 2Cl^- = CuCl_2^- \qquad K_2 = 3.51 \times 10^5 \quad (2)$$

$$Cu^+ + H_2M = H_2M{\cdot}Cu^+$$
$$K_3 = (H_2M{\cdot}Cu^+)/(Cu^+)(H_2M) = 1.1^3 \times 10^3 \quad (3)$$

$$Cu^+ + Cl^- + H_2M = H_2M{\cdot}CuCl$$
$$K_4 = (H_2M{\cdot}CuCl)/(Cu^+)(Cl^-)(H_2M) = 9.7 \times 10^4 \quad (4)$$

$$Cu^+ + HM^- = HM{\cdot}Cu$$
$$K_5 = (HM{\cdot}Cu)/(Cu^+)(HM^-) = 2.02 \times 10^4 \quad (5)$$

$$Cu^+ + Cl^- + HM^- = HM{\cdot}CuCl^-$$
$$K_6 = (HM{\cdot}CuCl^-)/(Cu^+)(Cl^-)(HM^-) = 7.6 \times 10^5 \quad (6)$$

$$H_2M = H^+ + HM^-$$
$$K_7 = (H^+)(HM^-)/H_2M = 0.022 \quad (7)$$

In addition the following relationships, (8)–(10), which also apply to equilibrium conditions, were used in evaluating the unknown equilibrium constants (H_2M_i and Cl^-_i represent initial concentrations in the solutions before the addition of cuprous chloride)

$$(Cu^+_T) = (Cu^+) + (CuCl_2^-) + (H_2M{\cdot}CuCl) + (H_2M{\cdot}Cu^+) + (HM.CuCl^-) + (HM{\cdot}Cu) \quad (8)$$

$$(Cu^+_T) + (Cl^-_i) = (Cl^-) + 2(CuCl_2^-) + (H_2M{\cdot}CuCl) + (HM{\cdot}CuCl^-) \quad (9)$$

$$(H_2M_i) = (H_2M) + (HM^-) + (H_2M{\cdot}CuCl) + (H_2M{\cdot}Cu^+) + (HM{\cdot}CuCl^-) + (HM{\cdot}Cu) \quad (10)$$

In column 7 of Table I the measured values of (Cu^+_T) are compared with the values for (Cu^+_T) calculated using equations (1)–(10). The agreement is good. To facilitate recalculation of the concentrations of the different complexes found, equilibrium concentrations of hydrogen ion, maleic acid and chloride ion are given in columns 4, 5 and 6 of Table I. The concentration of $H_2M{\cdot}CuCl$ varies from 0.4×10^{-3} *M* in run 21 to 3.5×10^{-3} *M* in run 4; that of $H_2M{\cdot}Cu^+$ from 0.1×10^{-3} *M* in run 6 to 5.5×10^{-3} *M* in run 1; that of $HM{\cdot}CuCl^-$ from 0.1×10^{-3} *M* in runs 6 and 9 to 7.1×10^{-3} *M* in run 22; that of HM·Cu from 0.04×10^{-3} *M* in run 6 to 12.7×10^{-3} *M* in run 19; and that of $CuCl_2^-$ from 0.2×10^{-3} *M* in run 3 to 6.3×10^{-3} *M* in run 23.

It is interesting to note that K_5 is twenty times larger than K_3 indicating that the acid maleate ion complexes the cuprous ion to a greater extent than does maleic acid as would be expected. The equilibrium constants for reactions (11)–(14) are also of considerable interest. Both $H_2M{\cdot}CuCl$ and $H_2M{\cdot}Cu^+$ are stronger acids than maleic and $H_2M{\cdot}Cu^+$ is a somewhat stronger acid than $H_2M{\cdot}CuCl$, as one might predict.

$$H_2M{\cdot}CuCl = H_2M{\cdot}Cu^+ + Cl^-$$
$$\frac{(H_2M{\cdot}Cu^+)(Cl^-)}{(H_2M{\cdot}CuCl)} = \frac{K_3}{K_4} = 1.2 \times 10^{-2} \quad (11)$$

$$HM{\cdot}CuCl^- = HM{\cdot}Cu + Cl^-$$
$$\frac{(HM{\cdot}Cu)(Cl^-)}{(HM{\cdot}CuCl^-)} = \frac{K_5}{K_6} = 2.7 \times 10^{-2} \quad (12)$$

$$H_2M{\cdot}CuCl = HM{\cdot}CuCl^- + H^+$$
$$\frac{(HM{\cdot}CuCl^-)(H^+)}{(H_2M{\cdot}CuCl)} = K_6K_7/K_4 = 0.17 \quad (13)$$

$$H_2M{\cdot}Cu^+ = HM{\cdot}Cu + H^+$$
$$\frac{(HM{\cdot}Cu)(H^+)}{(H_2M{\cdot}Cu^+)} = K_5K_7/K_3 = 0.39 \quad (14)$$

Similarly the tendency to dissociate chloride ion is greater for $HM{\cdot}CuCl^-$ than for $H_2M{\cdot}CuCl$. The values for K_3/K_4 and K_5/K_6 are consistent with those obtained for the equilibrium constants for the dissociation of chloride ion from cuprous chloride complexes of other unsaturated acids.[4]

The task of calculating these equilibrium constants as outlined above is a lengthy process. The method however can be duplicated readily by anyone sufficiently interested to repeat the work, and it seems unnecessary to include a detailed description of the calculations in this report. Considering the number of variables to be treated the results obtained are surprisingly good.

Summary

Data are presented for the solubility of cuprous chloride in aqueous maleic acid solutions. The results are explained on the assumption that four water soluble complexes, $H_2M{\cdot}CuCl$, $H_2M{\cdot}Cu^+$, $HM{\cdot}CuCl^-$ and HM·Cu are formed. The relative amounts of the several complexes present in solution at equilibrium are dependent on the hydrogen and chloride ion as well as on the maleic acid concentrations of the original solutions. Equilibrium constants for the reactions to form the complexes are calculated.

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(6) (a) See ref. 1 for the values of equilibrium constants for equations (1) and (2); (b) The value of K_7 is that of Ashton and Partington, *Trans. Faraday Soc.*, **30**, 598 (1934), corrected to ionic strengths 1.0 or 0.1 on the basis of the data available for hydrochloric acid solutions.[5]