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The Solubility of Cuprous Chloride in Aqueous Alcohol Solutions

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An earlier publication[1] described the results of a study of the formation of a water soluble complex of allyl alcohol with cuprous chloride. A few measurements of the solubility of cuprous chloride in dilute hydrochloric acid solutions of allyl alcohol were reported, and the results were interpreted on the assumption that the only important equilibrium established with respect to complex formation was (A represents allyl alcohol)

$$A + CuCl \rightleftharpoons A{\cdot}CuCl$$

A more detailed investigation of the solubility of cuprous chloride in aqueous allyl alcohol indicated that the degree to which complex formation occurs is influenced by the chloride ion concentration of the solution. The results of these measurements are described here and are interpreted on the assumption that both A·CuCl and $A{\cdot}Cu^+$ are present in the aqueous solution at equilibrium.

Experimental

Materials.—Cuprous chloride and allyl alcohol were prepared as described previously.[1] In all solubility measurements the water used was freshly boiled just prior to its use in preparation of solutions.

The Solubility Experiments.—A standard solution of allyl alcohol in water was prepared. Aliquots of this solution and of standard solutions of hydrochloric acid and of perchloric acid or sodium perchlorate solution were added to 125-ml. glass-stoppered erlenmeyer flasks to provide 50 ml. of solutions of the concentrations specified in Table I. In all cases the ionic strength of the solutions was 0.1. Samples of cuprous chloride (0.5 g.) were added to the nitrogen flushed flasks, and the stoppers were sealed in with paraffin. The flasks were shaken for four hours at 25°. It should be noted that the accuracy of the experimental method is greatly diminished because of oxygen inclusion if the stoppers of the flasks are not paraffin-sealed during the shaking period. After the excess solid had settled, aliquots of the solution were withdrawn and analyzed volumetrically for cuprous content by the dichromate procedure using barium diphenylaminesulfonate indicator.[1] All values of Cu^+_T reported in Table I have been corrected for a slight titration blank characteristic of the indicator.[2]

TABLE I

SOLUBILITY OF CUPROUS CHLORIDE IN AQUEOUS ALLYL ALCOHOL SOLUTIONS AT 25°

Ionic strength of solvent = 0.10. $(H^+) = 0.10\ N$ except in 13 and 14 where $(H^+) = 0.010\ N$

Run	$(A_{\text{init.}})$, moles/l.	$(Cl^-_{\text{init.}})$, moles/l.	(Cu^+_T), moles/l.
1	0.0809	0	0.0393
2	.0400	0	.0226
3	.0300	0	.0175
4	.0200	0	.0128
5	.0101	0	.0072
6	.0809	0.00938	.0378
7	.0404	.00938	.0207
8	.0202	.00938	.0117
9	.0101	.00938	.0065
10	.0400	.0938	.0196
11	.0300	.0938	.0160
12	.0200	.0938	.0125
13	.0809	0	.0394
14	.0202	0	.0131

Results

The solubility of cuprous chloride in aqueous solutions of allyl alcohol is given in Table I. By comparing runs 1 and 4 with 13 and 14 it is evident that the solubility of cuprous chloride in the allyl alcohol solution is not affected by changing hydrogen ion concentration from 0.100 to 0.0100 *N*. However when one compares runs at constant allyl alcohol concentration but varying chloride ion concentration (*e. g.*, runs 2, 7 and 10), it is evident that increasing chloride ion concentration causes a decrease in the solubility of cuprous chloride.[3] In order to explain such a result it is probable that in addition to the reaction

$$CuCl + A = A{\cdot}CuCl \qquad K_1 = (A{\cdot}CuCl)/(A) \quad \text{(I)}$$

the following reaction is taking place.

$$CuCl + A = A{\cdot}Cu^+ + Cl^- \qquad K_2 = (A{\cdot}Cu^+)(Cl^-)/(A) \quad \text{(II)}$$

In addition to reactions (I) and (II) some cuprous chloride will dissolve due to the following reactions[4,5]

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

$$CuCl + Cl^- = CuCl_2^- \qquad K_4 = (CuCl_2^-)/(Cl^-) = 0.065 \quad \text{(IV)}$$

A copper balance gives

$$(Cu^+_T) = (Cu^+) + (CuCl_2^-) + (A{\cdot}CuCl) + (A{\cdot}Cu^+) \quad \text{(V)}$$

where Cu^+_T = concentration of soluble cuprous species. Equating chloride ion added to the solution to all ionic species containing chloride ion gives

$$(Cu^+_T) + (Cl^-_{\text{init.}}) = 2(CuCl_2^-) + (Cl^-) + (A{\cdot}CuCl) \quad \text{(VI)}$$

where $(Cl^-_{\text{init.}})$ = concentration of Cl^- in solution before the addition of CuCl. A similar balance for allyl alcohol gives

$$(A_{\text{init.}}) = (A) + (A{\cdot}CuCl) + (A{\cdot}Cu^+) \quad \text{(VII)}$$

where $(A_{\text{init.}})$ = concentration of A in solution before the addition of CuCl. There are six un-

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(1) Kepner and Andrews, *J. Org. Chem.*, **13**, 208 (1948).

(2) Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Company, New York, N. Y., 1943, p. 494.

(3) Using equations (3) and (4) one can calculate that the solubility of cuprous chloride in water solutions containing excess chloride ion goes through a minimum at a chloride ion concentration of 1.7×10^{-3} *M*. In 0.01 *M* chloride ion solution the solubility of cuprous chloride is greater than that in water and increases rapidly with increasing chloride ion concentration.

(4) Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 170.

(5) Noyes and Chow, THIS JOURNAL, **40**, 739 (1918).

knowns (Cu^+), ($CuCl_2^-$), (A·CuCl), (A·Cu^+), (Cl^-), (A) and five equations (III, IV, V, VI, VII.) By assuming values for K_1 a sixth equation (I) may be obtained. By solution of these six equations the necessary quantities are obtained for the calculation of K_2 by equation II. As a first approximation it was assumed that at ($Cl^-_{init.}$) = 0.1 *M* reaction II was negligible, and values of K_1 were calculated. The value obtained was 0.51. Upon using this value of K_1 to calculate values of K_2 it was found that constant values could not be obtained. By trial it was found that the value of K_1 most compatible with constant values of K_2 was 0.41. Table II gives the calculated concentrations assuming $K_1 = 0.41$.

TABLE II

COMPOSITION OF AQUEOUS SOLUTIONS OF ALLYL ALCOHOL SATURATED WITH CUPROUS CHLORIDE

Run	(A), moles/l.	(A·CuCl), moles/l.	(A·Cu^+), moles/l.	(Cl^-), moles/l.	$K_2 \times 10^2$
1	0.0428	0.0175	0.0205	0.0192	0.92
2	.0180	.0075	.0142	.0133	1.03
3	.0132	.0054	.0114	.0107	0.92
4	.0078	.0032	.0090	.0084	.97
5	.0042	.0017	.0052	.0049	.61
6	.0448	.0184	.0177	.0254	1.00
7	.0213	.0087	.0108	.0190	0.96
8	.0100	.0041	.0066	.0150	.99
9	.0048	.0020	.0037	.0123	.95
10	.0266	.0109	.0028	.0907	.96
11	.0202	.0083	.0019	.0899	.85
12	.0137	.0056	.0011	.0891	.72
13	.0100	.0041	.0066	.0150	.99
14	.0048	.0020	.0037	.0123	.95

The average value for K_2 excluding the results of runs 5, 11 and 12, which seem inconsistent, is 0.97×10^{-2}. The values for K_1 and K_2 may be used to calculate the equilibrium constant K_8 for the ionization of A·CuCl.

$$\text{A·CuCl} = \text{A·Cu}^+ + \text{Cl}^-$$

$$K_8 = \frac{(\text{A·Cu}^+)(\text{Cl}^-)}{(\text{A·CuCl})} = \frac{K_2}{K_1} = 2.4 \times 10^{-2} \quad \text{(VIII)}$$

Since the solubilities were determined for solutions of approximate ionic strengh 0.1, the values for K_2 and K_8 reported above are subject to correction for the activity coefficients of the ionic species involved in the equilibria.[6] Assuming that $\gamma_{\text{A·Cu}}\gamma_{\text{Cl}} = \gamma^2_{\pm\text{HCl}}$ and using the value of $\gamma_{\pm\text{HCl}} = 0.8$ from Harned and Owen[7] at ionic strength = 0.1, the corrected values for K_2 and K_8 are 0.62×10^{-2} and 1.5×10^{-2}, respectively.

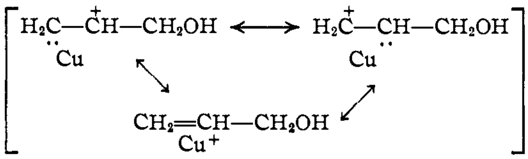
From the distribution experiments described previously[1] the equilibrium constant K_9 for the reaction

$$\text{A} + \text{CuCl}_2^- = \text{A·CuCl} + \text{Cl}^-$$

$$K_9 = \frac{(\text{A·CuCl})(\text{Cl}^-)}{(\text{A})(\text{CuCl}_2^-)} \quad \text{(IX)}$$

was found to be approximately 16. A value of $K_1 = 1.04$ may be calculated by use of this value of K_9 and that for K_4. This value is, however, considerably less reliable than that obtained in the present study because of the limited accuracy of the distribution methods and of certain of the data available in the literature used to calculate K_9.

The resonating type structure proposed for silver ion–olefin complexes[8] seems appropriate to account for the structure of A·Cu^+, as follows



A similar structure in which a chloride ion is coördinated with the copper atom of the complex may be used to designate A·CuCl.

Summary

The influences of changes in the allyl alcohol and chloride ion concentrations on the solubility of cuprous chloride in aqueous allyl alcohol solutions have been studied quantitatively. The data have been used to calculate constants for the equilibria established in these solutions on the assumption that two complexes $CH_2{=}CH{-}CH_2OH{\cdot}CuCl$ and $CH_2{=}CH{-}CH_2OH{\cdot}Cu^+$ are formed.

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[6] Andrews and Keefer, THIS JOURNAL, **70**, 3261 (1948).

[7] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Company, New York, N. Y., 1943.

[8] Winstein and Lucas, THIS JOURNAL, **60**, 836 (1938).