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Solubility of Cuprous Chloride in Various Soluble Aqueous Chlorides

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Smoothed tables of the solubility of CuCl in aqueous HCl and aqueous NaCl from 0.01 to 6.0 M and from 0 to 100 °C are presented. Similar tables are given, for 25 °C only, for mixtures of HCl and NaCl, and for solutions in aqueous KCl, NH_4Cl, $CuCl_2$, and $FeCl_2$. The procedures and parameters necessary for calculation of the solubility at other concentrations and temperatures are given. Simple methods for handling solubility in complex mixtures and in cases where experimental information is scant are discussed.

Table I. Equilibrium Constants and Heats of Reaction[a]

complex formed	K_{298}	ΔH, cal/mol
$CuCl_2^-$	0.0604	6669
$CuCl_3^{2-}$	0.0128	3450
$Cu_2Cl_4^{2-}$	8.24×10^{-4}	6700
$Cu_3Cl_6^{3-}$	3.41×10^{-5}	0.0
combined^{2-}	0.0144	4010

[a] Note that the values given for the higher complexes are somewhat different from those in ref *2*. The values for $Cu_2Cl_4^{2-}$ and $Cu_3Cl_6^{3-}$ are hard to separate; the values above give somewhat better representation of the limited data available at 0 and 100 °C.

Table II. Equations Used for Calculation of Activity Coefficients[a]

$$\ln \gamma_N = (z_N)^2 f^\gamma + 2\sum_a M_a[B_{Na} + (\Sigma Mz)C_{Na}] + \sum_c\sum_a M_c M_a[(z_N)^2 B'_{ca} + z_N C_{ca}]$$

$$\ln \gamma_X = (z_X)^2 f^\gamma + 2\sum_c M_c[B_{cX} + (\Sigma Mz)C_{cX}] + \sum_c\sum_a M_c M_a[(z_X)^2 B'_{ca} - z_X C_{ca}]$$

with

$$f^\gamma = -A_\phi\left[\frac{I^{1/2}}{1 + 1.2I^{1/2}} + \frac{2}{1.2}\ln(1 + 1.2I^{1/2})\right]$$

$$B_{NX} = \beta^{(0)}{}_{NX} + (2\beta^{(1)}{}_{NX}/\alpha^2 I)\{1 - [1 + \alpha I^{1/2}] \times \exp(-\alpha I^{1/2})\}$$

$$B'_{NX} = (2\beta^{(1)}{}_{NX}/\alpha^2 I^2)\{-1 + [1 + \alpha I^{1/2} + (1/2)\alpha^2 I] \exp(-\alpha I^{1/2})\}$$

$$(\Sigma Mz) = \sum_c M_c z_c$$

$$\alpha = 2.0$$

[a] (1) For 2-2 and higher valence type electrolytes an additional parameter $\beta^{(2)}$ must be added. (2) For mixtures, terms of the form $\Sigma_i\Sigma_j M_i M_j \psi_{Nij}$ should be added to the expressions for $\ln \gamma$ to account for interactions between three different ions. These terms have been omitted for simplicity in the present treatment. (3) *M* represents mol/L throughout. (See ref *4* for details on both of the above matters.)

Introduction

The substantial solubility of cuprous chloride (Cu^ICl) in various aqueous chlorides arises almost entirely from the formation of chloro complexes such as $CuCl_2^-$, $CuCl_3^{2-}$, etc. Calculation of its solubility requires knowledge of the equilibrium constants for formation of the important complexes and a set of virial parameters adequate to represent the activity coefficients of the ions present in the solutions. In previous work (*1*, *2*) I have evaluated the equilibrium constants at 25 °C for the formation of $CuCl_2^-$, $CuCl_3^{2-}$, $Cu_2Cl_4^{2-}$, and triply charged complexes (represented as $Cu_3Cl_6^{3-}$), from CuCl(s), the corresponding heats of formation, and sets of virial parameters suitable for calculation of the activity coefficients of the complex species in a number of aqueous chlorides. The principal purpose of this paper is to present tables of solubility of CuCl as a function of concentration and temperature (0-100 °C) in various aqueous media and the parameters necessary for calculation of the solubility under other conditions. In addition methods are discussed for approximate correlations of solubilities in cases where data are not sufficient for detailed analysis.

Procedure for Calculation of Solubilities

The formation of a given complex species is represented by an equation such as

$$m\text{CuCl(s)} + n\text{Cl}^- = (\text{Cu}_m\text{Cl}_{m+n})^{n-} \qquad (1)$$

The equilibrium constant for the *i*th complex is then

$$K_i = \frac{a_i}{(a_{\text{Cl}^-})^{n_i}} = \frac{c_i}{(c_{\text{Cl}^-})^{n_i}}\,\frac{\gamma_i}{(\gamma_{\text{Cl}^-})^{n_i}} \qquad (2)$$

so that the concentration (c_i) of the complex can be calculated from that of Cl^-, provided that the necessary K_i and the activity coefficients are known. Table I gives values of the equilibrium constants at 25 °C and the corresponding heats of reaction for the complex species considered hereafter (*1*, *2*). Activity coefficients can be calculated by using the virial model developed by Pitzer and co-workers (*3*, *4*), in which the second virial coefficient *B* for a given ion pair depends on both ionic strength and ionic concentrations, while the third virial coefficient *C* is independent of both. The necessary equations are represented by eq 12-15 of Pitzer and Kim (*4*), with three modifications. First, molarity (*M*, mol/L) has been used in place of molality (*m*, mol/(1000 g of solvent)) throughout. (See discussion in ref *1*.) Second, only the principal terms in the equations have been found necessary to represent the solubility data. Finally, the

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Table III. Parameters Used to Correlate Solubilities

ion pair	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C	ref
Full Set of Parameters					
H^+-Cl^-	0.1775	0.2945		0.0012	*3*
H^+-$CuCl_2^-$	0.2072	0.3215		0.0107	*1*
H^+-$CuCl_3^{2-}$	0.2746	1.587		0.0254	*1*
H^+-$Cu_2Cl_4^{2-}$	0.3666	1.774		0.0076	*1*
H^+-$Cu_3Cl_6^{3-}$	0.4498	4.567		0.0218	*1*
Na^+-Cl^-	0.0765	0.2664		0.00127	*3*
Na^+-$CuCl_2^-$	0.0837	0.1595		0.0098	*2*
Na^+-$CuCl_3^{2-}$	0.0896	1.178		0.0329	*2*
Na^+-$Cu_2Cl_4^-$	−0.0169	0.6372		0.0154	*2*
Na^+-$Cu_3Cl_6^{3-}$	0.1577	3.4014		0.0209	*2*
K^+-Cl^-	0.0484	0.2112		−0.00084	*2*
K^+-$CuCl_2^-$	0.2837	0.4180		0.0098	*2*
K^+-$CuCl_3^{2-}$	0.0480	0.9540		0.0114	*2*
K^+-$Cu_2Cl_4^{2-}$	−0.1719	−0.7000		0.0076	*2*
K^+-$Cu_3Cl_6^{3-}$	−0.1123	2.133		0.0219	*2*
Three-Parameter Set					
H^+-$CuCl_2^-$	0.2097	0.3556		0.0107	*2*
H^+-$CuCl_3^{2-}$	0.2749	1.588		0.0254	*2*
H^+-$Cu_3Cl_6^{3-}$	0.4473	4.559		0.0215	*2*
Na^+-$CuCl_2^-$	0.0747	0.2052		0.0107	*2*
Na^+-$CuCl_3^{2-}$	0.0619	0.9999		0.0254	*2*
Na^+-$Cu_3Cl_6^{3-}$	0.1294	3.119		0.0215	*2*
K^+-$CuCl_2^-$	0.3221	0.4635		0.0107	*2*
K^+-$CuCl_3^{2-}$	−0.0503	0.4495		0.0254	*2*
K^+-$Cu_3Cl_6^{3-}$	−0.1821	1.921		0.0215	*2*
NH_4^+-Cl^-	0.0522	0.1918		0.0045	*3*
NH_4^+-$CuCl_2^-$	−0.1422	0.0545		0.0107	*2*
NH_4^+-$CuCl_3^{2-}$	−0.0677	0.2610		0.0254	*2*
NH_4^+-$Cu_3Cl_6^{3-}$	−0.1775	1.893		0.0215	*2*
Cu^{2+}-Cl^-	0.3080	1.376		−0.06065	*3*
Cu^{2+}-$CuCl_2^-$	0.4589	1.757		−0.0372	this work
Cu^{2+}-$CuCl_3^{2-}$	0.0192	7.699	−20.79	−0.0396	this work
Cu^{2+}-$Cu_3Cl_6^{3-}$	0.9515	9.252	−10.57	−0.1708	this work
Fe^{2+}-Cl^-	0.3359	1.5323		−0.01291	*3*
Fe^{2+}-$CuCl_2^-$	0.5489	1.6713		−0.00071	this work
Fe^{2+}-$CuCl_3^{2-}$	0.3880	4.274	−4.82	0.0323	this work
Fe^{2+}-$Cu_3Cl_6^{3-}$	0.9329	7.466	−3.20	−0.01229	this work

equations have been rewritten for calculation of individual ion activity coefficients (rather than mean ion activity coefficients) for convenience in dealing with solutions containing more than a single cation. The equations in the form used and to the order of approximation used are given in Table II. The theoretical single-ion activity coefficients cannot be validated experimentally. However, they appear only as ratios, which should be in no substantial error. When only one cation is present, the results are identical with those using the equations for mean ion activity coefficients.

The parameters $\beta^{(0)}$, $\beta^{(1)}$, and C for the various chlorides were taken from the literature. The corresponding parameters for ion pairs involving the complex species were obtained by optimizing the prediction of available solubilities in either this or previous work (*1*, *2*). The parameters pertinent to the solubilities reported in this paper are listed in Table III, along with their sources.

With the necessary virial parameters selected, solubilities can be calculated by an iterative procedure. Starting with the nominal ionic strength of the solution and a preliminary estimate of the concentration of uncomplexed chloride ion, a computer program calculates the activity coefficients of eq 2 and then the concentration of each complex species corresponding to these assumptions. Comparison of the total (Cl^-) and the total ionic strength with the values previously assumed generates corrections to each. Successive iterations are carried out until estimated and calculated values agree within some designated precision (in the present case 0.01%). At this point the solubility (total Cu^+ in solution) is calculated. The algorithm used required about 0.05 s of computer time per calculated solubility when only one cation was present and proportionately longer times for mixtures containing two or more cations.

For solutions in HCl, NaCl, and KCl, sufficient precise data were available to permit assignment of virial parameters for all four complex species. For NH_4Cl, $CuCl_2$, and $FeCl_2$, the smaller number of data available were correlated by the "three-parameter" method described previously (*2*), in which the two doubly charged complexes were lumped together. In using these parameters, the heat of solution labeled "combined 2⁻" in Table I should be used. Table III contains the parameters to be used for all of the chlorides, to permit calculations by the three-parameter method for mixtures.

Solubility in Aqueous HCl, NaCl, and Their Mixtures

Calculated values for the solubility of CuCl in aqueous HCl are presented in Table IV. The parameters used represent the data of Hikita et al. (*5*) between 15 and 35 °C with an average deviation of about 1%. They agree with the much less precise data of Morosov et al. (*6*) from 0 to 100 °C with an average deviation of 14%. The calculated solubilities should be correct within about 1% between 10 and 40 °C but could be in error by as much as 10% at 100 °C, especially at the higher concentrations.

Table V gives corresponding results for the solubility of CuCl in aqueous NaCl. These agree with the data of Ahrland and Rawsthorne (25 °C) (*7*) within 1.4% and with the data of Utkina et al. (*8*) (0–95 °C) within an average of 12%.

In view of the substantially different solubility of CuCl in the two media, it is interesting to examine the predictions of the model for its solubility in mixtures of the two soluble chlorides. In the absence of data, these can only be estimates, since in

Table IV. Solubility of CuCl in Aqueous HCl[a]

(HCl), mol/L	solubility at temperature shown, mol/L								
	0 °C	10 °C	20 °C	25 °C	30 °C	40 °C	60 °C	80 °C	100 °C
0.10	0.0022	0.0033	0.0047	0.0058	0.0069	0.0095	0.0166	0.0259	0.0366
0.20	0.0047	0.0070	0.0101	0.0120	0.0142	0.0194	0.0338	0.0520	0.0732
0.30	0.0074	0.0110	0.0157	0.0187	0.0220	0.0298	0.0509	0.0283	0.110
0.50	0.0140	0.0202	0.0285	0.0335	0.0391	0.0526	0.0873	0.132	0.184
0.80	0.0270	0.0378	0.0517	0.0601	0.0694	0.0911	0.147	0.217	0.296
1.00	0.0381	0.0522	0.0704	0.0812	0.0931	0.121	0.190	0.276	0.372
1.50	0.0754	0.0996	0.130	0.147	0.166	0.208	0.312	0.435	0.569
2.00	0.1287	0.165	0.208	0.233	0.259	0.317	0.453	0.608	0.774
2.50	0.200	0.249	0.307	0.339	0.372	0.446	0.612	0.796	0.987
3.00	0.290	0.356	0.426	0.465	0.526	0.594	0.787	0.996	1.209
4.00	0.536	0.625	0.725	0.777	0.831	0.945	1.186	1.44	1.69
5.00	0.875	0.988	1.109	1.172	1.237	1.373	1.65	1.94	2.23
6.00	1.31	1.44	1.58	1.66	1.73	1.89	2.55	2.55	2.88

[a] In this table and in Tables V–VIII, the entries are solubilities calculated by the methods described in the text, using the parameters given in the Tables I–III and IX. In each case, the agreement with available solubility measurements is discussed in the text.

Table V. Solubility of CuCl in Aqueous NaCl[a]

(NaCl), mol/L	solubility at temperature shown, mol/L								
	0 °C	10 °C	20 °C	25 °C	30 °C	40 °C	60 °C	80 °C	100 °C
0.10	0.0023	0.0034	0.0050	0.0060	0.0071	0.0097	0.0169	0.0263	0.0372
0.20	0.0049	0.0073	0.0105	0.0125	0.0148	0.0202	0.0347	0.0536	0.0752
0.30	0.0079	0.0117	0.0167	0.0198	0.0233	0.0315	0.0535	0.0818	0.1140
0.50	0.0155	0.0223	0.0312	0.0367	0.0428	0.0570	0.0942	0.1414	0.1942
0.80	0.0313	0.0435	0.0593	0.0687	0.0791	0.1032	0.1641	0.239	0.321
1.00	0.0452	0.0617	0.0827	0.0950	0.1086	0.1397	0.217	0.310	0.440
1.50	0.0940	0.1233	0.1594	0.1800	0.202	0.252	0.371	0.508	0.650
2.00	0.1658	0.211	0.264	0.294	0.326	0.397	0.557	0.735	0.916
2.50	0.264	0.326	0.398	0.438	0.480	0.571	0.774	0.992	1.209
3.00	0.393	0.472	0.564	0.613	0.666	0.777	1.022	1.278	1.536
4.00	0.761	0.872	0.998	1.066	1.137	1.288	1.611	1.94	2.26
5.00	1.292	1.426	1.579	1.662	1.749	1.933	2.331	2.73	3.11
6.00	1.95	2.10	2.28	2.37	2.47	2.69	3.15	3.61	4.05

[a] See footnote of Table IV.

Table VI. Solubility of CuCl in HCl/NaCl Mixtures at 25 °C[a]

(MCl), mol/L	solubility at mole fraction of Na^+ shown, mol/L				
	0	0.25	0.50	0.75	1.00
0.10	0.0058	0.0059	0.0059	0.0059	0.0060
0.20	0.0120	0.0121	0.0123	0.0124	0.0128
0.30	0.0187	0.0189	0.0192	0.0195	0.0198
0.50	0.0335	0.0342	0.0350	0.0358	0.0367
0.80	0.0601	0.0620	0.0641	0.0663	0.0687
1.00	0.0812	0.0842	0.0875	0.0911	0.0950
1.50	0.147	0.159	0.161	0.170	0.180
2.00	0.233	0.245	0.258	0.275	0.294
2.50	0.339	0.357	0.379	0.405	0.438
3.00	0.465	0.490	0.522	0.562	0.613
4.00	0.777	0.823	0.884	0.964	1.066
5.00	1.172	1.255	1.361	1.496	1.66
6.00	1.66	1.80	1.96	2.15	2.37

[a] See footnote of Table IV.

the mixtures calculation of the activity coefficients may require parameters (ψ's) to account for the effect of triple interactions involving the two different cations with each of the anions. However, since such parameters were not required to represent the solubility in mixtures of HCl and NaCl with the corresponding perchlorates (*1*, *2*), and since the third virial coefficients for HCl and NaCl solutions are not radically different, the omission of the ψ's should not produce serious errors. The results for 25 °C are given in Table VI, for mixtures in which Na^+ is 0%, 25%, 50%, 75% and 100% of the total cation present.

They are displayed graphically in Figure 1, where the solubility relative to that in aqueous HCl is plotted against the mole fraction of NaCl for six different total molarities. It will be seen that the solubility predicted by the model is not a linear function of the mole fraction of NaCl at any but low concentrations. However, the maximum deviation from linearity is at most 2-3% when the solubility changes by as much as 45%.

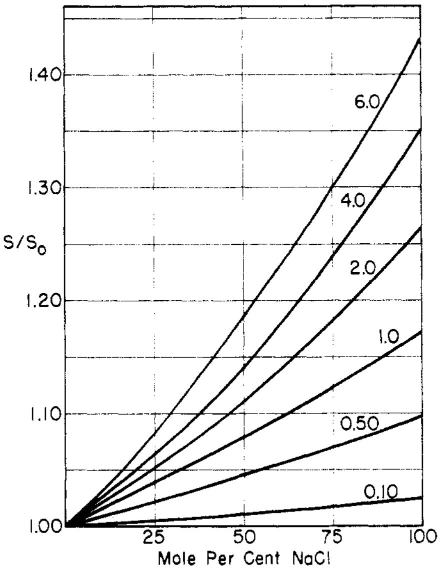

Figure 1. Solubility (s) at 25 °C of CuCl in mixtures of aqueous HCl and NaCl relative to that in pure aqueous HCl(s_0) as a function of the mole percent of NaCl in the mixed solvent. Each curve is labeled with the total molarity of the HCl-NaCl mixture.

Table VII. Solubility of CuCl in Aqueous KCl and Aqueous NH_4Cl at 25 °C[a]

(M_{MCl}), mol/L	solubility, mol/L	
	in KCl	in NH_4Cl
0.10	0.0055	0.0061
0.20	0.0110	0.0131
0.30	0.0167	0.0213
0.50	0.0300	0.0418
0.80	0.0581	0.0850
1.00	0.0852	0.1232
1.50	0.195	0.253
2.00	0.383	0.435
2.50	0.659	0.671
3.00	(1.951)	1.78

[a] See footnote of Table IV.

Solubility in Aqueous KCl and NH_4Cl

The available data on solubility of CuCl in aqueous KCl and aqueous NH_4Cl are scant and of limited precision, so that the virial coefficients necessary for calculation of the solubilities over extended ranges of concentration and temperature are rather tentative. The virial coefficients derived from literature data are given in Table III. The solubilities predicted at 25 °C are given in Table VII for molarities up to 4.0. The parameters used for KCl predict the data of Bronsted (*9*) at 22 °C within an average deviation of 4% in the range 1.4-3.9 M. (The Bronsted data below 1 M KCl are inexplicably low and cannot be reconciled with solubilities of CuCl in other aqueous media.) Those used for NH_4Cl predict the (quite rough) data of Morosov (*6*) within about 8% for 0 and 25 °C and within 10-20% at higher temperatures. At low concentrations the solubilities are nearly the same as for aqueous HCl and aqueous NaCl but become substantially higher at high concentrations in both cases. For both KCl (*9*) and NH_4Cl (*6*) there is evidence for a double salt as the stable solid phase at concentrations higher than those listed in Table VII.

Solubility of CuCl in Aqueous $CuCl_2$ and $FeCl_2$

Data on the solubility of CuCl in aqueous solutions of divalent metals are available only for $CuCl_2$ (*10*) and for $FeCl_2$ (*11*). In

Table VIII. Solubility at 25 °C of CuCl in Aqueous $CuCl_2$ and $FeCl_2$[a]

(MCl_2), mol/L	solubility, mol/L	
	in $CuCl_2$	in $FeCl_2$
0.05	0.0067	0.0059
0.10	0.0149	0.0122
0.15	0.0236	0.0190
0.25	0.0416	0.0340
0.40	0.0690	0.0595
0.50	0.0876	0.0786
0.75	0.136	0.134
1.00	0.190	0.200
1.25	0.250	0.277
1.50	0.317	0.364
2.00	0.463	0.566
2.50	0.610	0.792
3.00	0.729	1.032

[a] See footnote of Table IV.

each case they are reported for only one temperature, and the number of data points are not sufficient for unambiguous evaluation of the necessary virial parameters. However, examination of the reported solubilities indicated that they followed the same pattern as for aqueous HCl, although lower for a given total chloride concentration (substantially lower for $CuCl_2$). The ambiguity in selection of parameters was removed by imposing the additional requirement that the relative proportions of singly, doubly, and triply charged complexes should match (as well as possible) that for solutions in aqueous HCl of the same total chloride concentrations. The resulting parameters are given in Table III. They represented the data on $CuCl_2$ (*10*) within 4% and those on $FeCl_2$ (*11*) within 1.5%. Smoothed values of the solubilities are given for 25 °C in Table VIII for molarities up to 3.0 M.

Comparison with Table IV illustrates the fact that, for a given total chloride concentration, the solubilities are nearly the same as for aqueous HCl at low concentrations but are substantially lower at high chloride concentrations. In the case of $FeCl_2$, this effect is primarily due to the high ionic strengths involved. The additional decrease in solubility in the $CuCl_2$ solutions almost certainly results from the fact that Cu^{2+} itself forms complexes with Cl^-, reducing the chloride concentration available to Cu^+.

Solubility of CuCl in More Complex Mixtures

In practical situations, dissolved CuCl may be found in solutions containing two or more cations and also anions other than chloride. For example, in the CYMET process for extraction of copper from its ores, CuCl is crystallized from a mixture containing sustantial amounts of Cu^{2+}, Fe^{2+}, Fe^{3+}, H^+, and SO_4^{2-}, along with minor concentrations of Zn^{2+} and Na^+. At a given temperature, the solubility of the CuCl depends on the concentrations of all of these ions as well as that of Cl^-. Solubility data on solutions containing a wide range of concentration of Cu^{2+}, Fe^{2+}, and Cl^-, with or without Na^+ and SO_4^{2-}, were available for four temperatures between 40 and 100 °C. (I thank the Cyprus Metallurgical Products Corp. for making these data available for analysis.) The test data revealed a number of interesting features. For a given chloride ion content, the solubility was enhanced by the presence of Na^+ or by substitution of Fe^{2+} for Cu^{2+}, with the Na^+ more effective. These effects are as would be expected from the solubility of CuCl in the separate aqueous chlorides. Similarly, increasing the chloride ion content by addition of NaCl increased the solubility substantially. Increasing chloride ion content by addition of $FeCl_2$ produced a more modest effect for low concentrations of Cu^{2+} (less than 2.0 M) and actually produced a *decrease* in solubility for a solution with (Cu^{2+}) originally over 2.5 M. The most striking result was the fact that addition of Cl^- in the form of $CuCl_2$ produced in most cases a decrease in solubility, and at best only a very slight increase, for solutions with low Fe^{2+} content. These latter effects could not be anticipated by the behavior of CuCl in aqueous solutions of the individual chlorides. Replacement of chloride by sulfate produced reductions in solubility as would be expected.

As could be anticipated from the general observations above, the simplified theoretical model did not fit the observations when only the parameters employed for the separate aqueous systems were used. At 40 °C, for example, predictions ranged from 24% low to 170% high, on the average 19% high, with a root mean square (rms) deviation of 46%. In order to obtain an approximate fit, it was necessary to introduce sizable interaction coefficients $\psi_{MM'X}$ or $\psi_{MXX'}$ to account for simultaneous interaction of two positive ions with a single negative ion or vice versa. To obtain rms deviation of 13% for all of the data, it was necessary to select values for 8 (of 45 possible) ψ's and to alter the heats of solution of CuCl to form $CuCl_3^{2-}$ and $Cu_3Cl_6^{3-}$ substantially from the values which were suitable for solutions in aqueous HCl and aqueous NaCl. No attempt was made to make further improvement, since evaluation of all possible ψ's would require substantially more data points than were available.

The difficulties experienced with these mixtures illustrates the hazards involved in treating complex mixtures by using only parameters available from their separate components. The mixtures described above may well represent an especially unfavorable situation, because of the special tendency of Cu^{2+} to form complexes with Cl^-. Such solutions can be treated better by a less detailed pragmatic approach described below.

Estimation of Solubility for Systems with Limited Information

One of the features of the known systems is that the solubility of CuCl follows the same general trends in all of them, even though the observed solubilities may be quite different. Thus, the solubility in a given aqueous medium relative to that in another follows a simple pattern at any given temperature, and a complete table for a given medium can be constructed with reasonable confidence from a table for a reference medium plus a limited number of data points for the new one. For example, the solubility of CuCl in aqueous NH_4Cl (*6*) at 25 °C varies from 2.1 to 2.5 times that in aqueous HCl (Table IV) in the range 2–4 M. A simple linear plot of this ratio enables one to predict the observed points or the points of the detailed treatment (Table VII) within 5–6%. For aqueous KCl, where more data are available (*9*), the solubilities vary from equal (at 1.46 M) to about 1.8 times those of NaCl (Table V). A smooth curve through these ratios permits prediction of the actual solubility or of the results in Table VII (in this concentration range) within 3–5%. In the cases of $CuCl_2$ and $FeCl_2$, the solubility ratio for a given Cl^- concentration changes rapidly with (Cl^-) and can be represented better as $\ln(s/s_{ref})/M$, which is nearly constant. In using estimated solubility ratios to pedict solubility, one should note that this ratio depends somewhat on temperature as well as on concentration (as may be seen by comparing entries in Tables IV and V). Thus, the ratios should not be used for a temperature much different from that where they have been determined.

In dealing with complex mixtures, such as those described in the previous section, the need for evaluation of many interaction coefficients (ψ's) may render detailed treatment impractical. A simple parametric method, preserving the spirit of the detailed calculations, can be used in such cases. It starts with the commonly used approximation that equilibrium quotients depend only on the nominal ionic strength of the solution. The properties of a reference solution are used to obtain a set of effective equilibrium quotients giving the observed concentration for each species as a function of the total chloride ion

Table IX. Equations Used to Fit Solubilities in Complex Mixtures

$$(\mathrm{CuCl_2^-})_{40^\circ\mathrm{C}} = K_{s_2}{}^*(\mathrm{CLN})$$
$$(\mathrm{CuCl_3{}^{2-}})_{40^\circ\mathrm{C}} = K_{s_3}{}^*(\mathrm{CLN})^2$$
$$(\mathrm{Cu_3Cl_6{}^{3-}})_{40^\circ\mathrm{C}} = K_{36}{}^*(\mathrm{CLN})^3$$

with

$$\ln K_{s_2}{}^* = -2.103 - 0.331I - 0.00688I^2$$
$$\ln K_{s_3}{}^* = -3.80 + 0.211I - 0.0564I^2 + 0.001603I^3$$
$$\ln K_{36}{}^* = -8.799 + 0.7400I - 6.6745I^2 + 0.001958I^3$$

and

$$\mathrm{CLN} = (\mathrm{FA})(\mathrm{Cl^-})$$

with

$$\mathrm{FA} = A + B(\mathrm{Cl^-}) + C(\mathrm{Cl^-})^2$$
$$A = 1.000 + 0.0253(\mathrm{Cu^{2+}}) + 0.0168(\mathrm{Fe^{2+}}) + 0.0575(\mathrm{Na^+}) - 0.0100(\mathrm{SO_4{}^{2-}}) + 0.2038(\mathrm{SO_4{}^{2-}})/(\mathrm{Cu^{2+}})$$
$$B = 0.00849 + 0.00656(\mathrm{Cu^{2+}}) - 0.00752(\mathrm{Cu^{2+}})^2 + 0.00147(\mathrm{Fe^{2+}})^2$$
$$C = 0.000290 + 0.000121(\mathrm{Cu^{2+}})^2 - 0.000261(\mathrm{Fe^{2+}})^2$$

Then

$$(\mathrm{soly})_{40^\circ\mathrm{C}} = (\mathrm{CuCl_2^-})_{40^\circ\mathrm{C}} + (\mathrm{CuCl_3{}^{2-}})_{40^\circ\mathrm{C}} + 3(\mathrm{Cu_3Cl_6{}^{3-}})_{40^\circ\mathrm{C}}$$
$$(\mathrm{soly})_T = (\mathrm{soly})_{40^\circ\mathrm{C}}\,e^{\mathrm{DLNS}}$$

with

$$\mathrm{DLNS} = -1000D(T - 313)/(313T)$$
$$D = [-0.9475 + 0.0200(\mathrm{Cu^{2+}}) + 0.294(\mathrm{SO_4{}^{2-}})]/(\mathrm{soly})_{40^\circ\mathrm{C}}$$

concentration. For other solutions, *effective* chloride ion concentrations are determined so as to correctly predict observed solubilities, and those are then represented in terms of the total $\mathrm{Cl^-}$ and simple functions of the concentration of the other ions present. Thereafter, a simple calculation predicts the solubility of CuCl in unknown mixtures containing these ions. The equilibrium quotients contain the effect of the activity coefficients of the reference solution and the depletion of chloride ion due to formation of cuprous complexes in that solution. The parameters for other solutions represent the differences in activity coefficients from the reference solution and further depletion of chloride ion by formation of complexes with other than cuprous ions.

When this method was applied to solutions in $\mathrm{CuCl_2}$ and $\mathrm{FeCl_2}$, only a single small parameter was required to give the effective chloride concentration as a function of the total chloride concentration and the concentration of the cation sufficiently well to represent the solubilities within a few percent.

The complex mixtures described in the previous section presented special problems. All of the 20 solutions studied contained $\mathrm{Cu^{2+}}$ and $\mathrm{Fe^{2+}}$ in various porportions; about half of them contained $\mathrm{Na^+}$ as well, and in about half of them $\mathrm{SO_4{}^{2-}}$ was substituted for part of the $\mathrm{Cl^-}$. All ionic strengths were high, ranging from 7.7 to 18.0 M. Their precision was estimated at about 5%, although the analyses for individual concentrations were considerably better than this. It was found possible to fit all 80 data points to about 7% (root mean square) by the following procedure: (1) Data for aqueous HCl solutions, extrapolated as necessary, were used to obtain equilibrium quotients $K_{mn}{}^*$ representing the concentrations of $\mathrm{CuCl_2^-}$, $\mathrm{CuCl_3{}^{2-}}$, and $\mathrm{Cu_3Cl_6{}^{3-}}$ in terms of the *total* chloride ion supplied by the acid from low concentrations to 18 M. These were then represented in terms of the ionic strength of the solutions. (2) For the complex mixtures the concentrations of individual species, and thus the solubility, were expressed in terms of the equilibrium quotients and an *effective* chloride concentration, CLN. (3) The effective chloride concentrations at 40 °C were represented as a power series in the initial chloride concentrations whose coefficients depended on the concentrations of other simple ions present. (4) Solubilities at temperatures other than 40 °C were obtained by using an *effective* heat of solution whose value depended somewhat on concentrations of $\mathrm{Cu^{2+}}$ and $\mathrm{SO_4{}^{2-}}$, but mainly on the calculated solubility at 40 °C.

After graphical selection of approximate values of the major parameters needed for items 3 and 4, a computer routine was used to select a set which gave the best fit to the entire 80 points. The final set of parameters is included in the set of equations of Table IX. Note that no cross terms involving two concentrations were needed in either A, B, or C, although the ratio $(\mathrm{SO_4{}^{2-}})/(\mathrm{Cu^{2+}})$ was needed for A. Most linear terms were dropped from B and C because they did not contribute to improvement in the fit.)

The end result, as given in Table IX, was to fit the 80 experimental points in terms of 15 parameters, 12 for CLN and 3 for the temperature dependence. The fit overall was to 6.8% (rms) with nearly two-thirds of the points fitted better than this and almost half to 5% or better (the estimated precision). Table X gives some examples of the representation. The examples chosen span nearly the full range of (a) concentrations of each ion, (b) ionic strength, and (c) solubility of CuCl. Comparisons are shown at 40 °C for all examples, with comparisons at 100 °C for the solutions with lowest and highest solubility. This table gives a somewhat pessimistic view of the quality of fit, since agreement was slightly poorer at the reference temperature (40 °C) than at the higher temperatures. It should be noted that the representation correctly reflects unusual trends in solubility, as in the first four examples, where solubility first increases and then decreases with increasing $(\mathrm{Cl^-})$, or in the third and fifth, where replacement of $\mathrm{Cu^{2+}}$ and $\mathrm{Fe^{2+}}$ by $\mathrm{Na^+}$ results in a substantial increase in solubility. The last two examples in Table X demonstrate its ability to represent the effect of temperature change for solutions giving widely different solubilities.

The number of parameters used in the representation (15) is still small compared with the number of data points fitted (80) and is very small compared with the number required for detailed treatment (27 first-order parameters plus possibly 45 second-order parameters (ψ's)). Moreover, except for the term in $(\mathrm{SO_4{}^{2-}})/(\mathrm{Cu^{2+}})$, the various terms for each ion enter independently, except for the connections implied in their effects on the initial chloride concentrations. Thus, the method should be applicable to other mixtures, including aqueous NaCl, $\mathrm{FeCl_2}$, and $\mathrm{CuCl_2}$ separately. This indeed proves to be true, within limits. In the case of aqueous NaCl, where solubilities at 40

Table X. Observed and Calculated Solubilities of CuCl in Complex Mixtures

$(\mathrm{Cu^{2+}})^a$	$(\mathrm{Fe^{2+}})^a$	$(\mathrm{Na^+})^a$	$(\mathrm{Cl^-})^a$	$(\mathrm{SO_4{}^{2-}})^a$	I^a	temp, °C	solubility, mol/L obsd	solubility, mol/L calcd	error, %
0.772	1.846		5.236		7.85	40	1.102	1.119	1.6
0.819	3.584		8.806		13.21	40	1.795	1.590	−11.4
2.677	2.079		9.512		14.27	40	1.118	0.912	−18.4[b]
2.362	3.638		12.000		18.00	40	0.677	0.718	6.1
2.394	1.828	1.130	9.574		13.80	40	1.606	1.515	−5.6
2.409	1.810	1.391	8.079	0.875	14.92	40	0.961	0.962	0.2
0.866	3.477	1.043	9.729		14.07	40	2.157	1.972	−8.6
						100	2.724	2.512	−7.8
2.425	1.935		6.866	0.927	14.01	40	0.646	0.611	−5.4
						100	1.055	1.034	−2.0

[a] In mol/L. [b] Worst fit of all 80 points.

°C are known (Table V), the single parameter used for (Na^+) represents the solubilities well up to about 1.5 M and within 10–15% at higher concentrations. Similarly, the data of Fedotieff (*10*) for solubility in aqueous $CuCl_2$ at 19 °C and those of Kreman (*11*) for solubility in aqueous $FeCl_2$ at 25 °C can be represented with similar precision for concentrations producing solubilities in the same range as for the complex mixtures, with deviations at higher and lower concentrations. The overall indications are that the parameters given could be applied successfully to any mixture where the concentration of ions falls in the ranges displayed in Table X, and probably to substantially wider ranges. The method itself should be applicable to a much wider range of solutions wherever experimental data are available for determination of the parameters required for other cations or anions.

General Discussion

The results presented in Tables IV and V for aqueous HCl and aqueous NaCl, respectively, should be as precise as any existing solubility data for CuCl in the temperature range 10–40 °C. The equilibrium constants, the heats of solution, and the virial parameters presented in Tables I and III will permit calculation of solubilities at concentrations not listed (up to 6 M) for this same temperature range. At temperatures below 10 °C or above 40 °C, the predictions become much less certain, because of uncertainties in the heats of solution and because of possible temperature dependence of the virial parameters. There is need for data of good precision above 35 °C on at least one system to settle the problem of temperature dependence. In using the parameters for calculation, no attempt should be made to extrapolate them beyond the range for which they were determined (to 6.5 M for HCl and 6.0 M for NaCl). The HCl parameters actually make fair predictions for solubility up to about 9 M but thereafter predict solubility to decrease with chloride concentrations. A more extensive set of parameters will certainly be needed to represent higher concentration ranges.

The data sets used for selection of the parameters for HCl and NaCl (*2*) contained solubilities for solutions in which the corresponding perchlorates were present. These solubilities were represented faithfully by the model, using virial coefficients for the perchlorates (*3*) along with those for the other species present. These solubilities were in general lower than those for the same chloride concentrations without perchlorate, primarily because of the increased ionic strength. It would be expected that the same technique would give reasonable results for solutions containing other "inert" materials, such as HNO_3, $NaNO_3$, etc. Such calculations should be treated with caution, however, since the virial parameters for the perchlorates are much more similar to those for the chlorides than are those for other salts of the same cation.

For prediction involving cations where solubility has not been determined, it would be desirable to correlate the virial parameters for ion pairs involving the complex species with those involving the corresponding chlorides. Inspection of Table III shows that for the monovalent cations the β's for the complex species decrease with those for the chlorides, with one exception. However, there is no obvious functional correlation, except that all β's decrease on going to systems where the solubility of CuCl increases. There is no obvious trend in the third virial coefficients, C.

As demonstrated earlier, it is frequently feasible to predict approximately the solubility of CuCl in a given medium from that in a reference system such as aqueous HCl or aqueous NaCl, given just a few determinations of solubility in the new system. Care should be exercised in doing so, since the dependence of relative solubility on concentration can vary widely, as comparison of the data in Tables IV–VII will demonstrate.

For mixtures in which two or more cations are present in variable concentrations, a very large number of data points may be required to obtain all parameters needed for detailed treatment of the solubility. In such cases a simpler parametric treatment (described above) following the same general lines of approach may well be sufficient for correlation within whatever ranges of concentration are observed.

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Excess Volumes and Isentropic Compressibilities of Binary Mixtures of a Ketone and Acetonitrile

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Excess volumes and isentropic compressibilities have been measured at 303.15 K for the binary systems of acetonitrile with methyl ethyl ketone, diethyl ketone, methyl propyl ketone, cyclopentanone, cyclohexanone, and 2-methylcyclohexanone. Excess volumes have been measured by the dilatometric method, and isentropic compressibilities have been calculated from densities and velocities of sound. The negative excess volumes and deviations in isentropic compressibilities were attributed to complex formation.

Introduction

As a part of studies of thermodynamic properties of binary liquid mixtures, we reported V^E values for mixtures of an alkanol with toluene (*1*), cyclohexylamine (*2*), and acetonitrile (*3*). Now we report the excess volumes and the isentropic compressibilities for the systems of acetonitrile with methyl ethyl ketone (MEK), diethyl ketone (DEK), methyl propyl ketone (MPK), cyclopentanone, cyclohexanone, and 2-methylcyclohexanone. The work has been taken up to study the molecular interactions, keeping in view the results reported by Narayanaswamy et al.

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