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Effect of the Oxidation State of Copper on the Solution–Solid Phase Equilibria in $CuCl_x$–MCl–H_2O Systems

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Abstract—The effect of the oxidation state of the metal on the solubility was analyzed using the example of $CuCl_x$–MCl–H_2O (x = 1, 2; M = Li–Cs, NH_4) ternary systems. The prevalence of acido complex formation is responsible for an essential similarity of the solubility isotherms: the presence of crystallization branches of complex salts and salting-in (or weak salting-out) of copper(I) and (II) chlorides, that increases in the order LiCl < NaCl < KCl < CsCl. The different stability of copper(I) and (II) chloride complexes results in that the chemical individuality of alkali metal cations is differently reflected in the shape of the solubility isotherms: The stronger complex formation in copper(I) systems results in leveling of this effect and the weaker complex formation with copper(II), in its differentiation.

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An essential effect heterovalent metals exert on solubility in multicomponent water–salt systems seems to be obvious and doubtless. However, at present there is little systematic work on this problem. One of reasons for this situation is the limited number of metals having both oxidized and reduced forms capable of existing in solution as aqua cations or complex compounds with the same ligands under the same conditions. Copper(I, II), mercury(I, II), iron(II, III), cerium(III, IV), and some other can be mentioned as such pairs. Among these pairs, of special interest are ternary water–salt systems containing copper(I) and copper(II). Halide complexes of both copper(I) and copper(II) are sufficiently stable in aqueous solutions in respect to redox processes. Furthermore, multicomponent systems based on copper (I) and (II) halides are of considerable practical importance: They are used as sensitizing agents for photochromic glasses, sorbents for certain gases (ethylene and carbon monoxide), catalysts for certain industrially important organic reactions, such as Sandmeyer reaction, oxychlorination of acetylene, and decomposition of diazo compounds.

In the this paper we consider the effect of the oxidation state of a heterovalent metal (copper) on the solubility in $CuCl_x$–MCl–H_2O multicomponent systems at 25°C ($M^+ = Li^+ - Cs^+$, NH_4^+). Earlier we performed a systematic experimental study of solid–solution equilibria in multicomponent chloride systems containing copper(I) [1–3] and revealed an effect of alkali metal chlorides on solubility. The results obtained and published data for analogous systems containing copper(II) [4–7] made possible comparative analysis to reveal main regularities in the effect of the oxidation state of copper and the nature of alkali metal cation on the solubility.

Properties of ternary water–salt systems containing Cu(I) and Cu(II) halides result from a combination of hydration, association, and acido complex formation processes. The difference in the electronic structures of Cu(I) and Cu(II) results in the fact that the hydration, capacity for complex formation, number of forms, and properties of solid compounds appear to be essentially different for mono- and divalent copper. Hence the solubilities of Cu(I) and Cu(II) chlorides even in a binary aqueous solution (s_0) differ more than three orders of magnitude [8]: 5.69 and 1.1×10^{-3} mol kg^{-1} H_2O for $CuCl_2$ and CuCl, respectively.

We explain this difference by the structural difference of these salts, caused by the different electronic structures of copper. The Cu^+ ion of d^{10} configuration features a tetrahedral configuration of ligands with equal metal–ligand bond lengths and energies (black jack-like structure). Such a diamond-like and highly symmetric crystal lattice is one of the strongest. All compounds with such a lattice are very strong and poorly soluble (zinc and lead sulfides, etc.). As for Cu^{2+}, the Jahn–Teller effect that is strongly pronounced in the d^9 configuration, manifests itself, in particular, in unequal equatorial and axial metal–ligand bond lengths and, as a consequence, in the formation of a layered lattice. This lattice is rather weak, and, as a result, Cu(II) chloride is poorer soluble than Cu(I) chloride.

Comparison of the hydration energies of Cu^{n+} ions (–611.7 and –2132.7 kJ mol^{-1} for Cu^+ and Cu^{2+}, respectively [9]) and stability constants of chloride complexes (according to [10], β_2 is 1.1×10^6 for $CuCl_2^-$ and 26.2 for $CuCl_2^{(0)}$, respectively) allows us to conclude that acido complex formation prevails with Cu(I)-containing systems, whereas in the case of Cu(II) hydration interactions make an essential contribution to solution properties. Then we can expect that changing from one alkaline metal to another in Cu(I) systems will produce rather small quantitative changes, whereas in the case of Cu(II) the shapes of solubility isotherms may change quantitatively. In fact, comparison of the solubility isotherms in $CuCl_n$–MCl–H_2O systems (Fig. 1) shows that the solubility isotherms are essentially similar in the case of copper monochloride owing to the domination of acido complex formation processes, and are appreciably different in the case of copper dichloride.

We can distinguish three main aspects reflecting the effect of the oxidation state of copper and of the nature of alkaline cation M^+ on the solubility: trends in relative concentrations of salt components, length of copper chloride crystallization branches, and type of crystallizing solid compounds.

The solubility of copper(I) and copper(II) chlorides was found to change in a radically different way with addition of alkali metal chlorides. The formation of stable chloride complexes of CuCl sharply enhanced the solubility of the sparingly soluble salt; the branch of CuCl crystallization in all the systems represents a strong salting-in branch. As for Cu(II)-containing systems, addition of the strongly hydrated lithium ion essentially enhance the degree of water binding in the solution and, consequently, in salting-out of $CuCl_2 \cdot 2H_2O$ (with sodium, similar while weaker effects are observed). The enhancement of acido complex formation in the presence of potassium and cesium cations that cause water and solution destructuring results in appearance of a salting-in branch in these systems, but this effect is weaker than in the case of CuCl. Similar effect is observed with the crystallization branches of alkaline metal chlorides.

The changes in the solubility of copper halides in comparison with the binary solution is illustrated by the following data.

MCl	LiCl	NaCl	KCl	CsCl	NH_4Cl
s_{eut}/s_0(CuCl) 6360	5020	4070	600	9770	
s_{eut}/s_0($CuCl_2 \cdot 2H_2O$)	0.42	0.92	1.12	1.01	1.03

Here s_0 is the solubility in the binary solution, and s_{eut}, solubility in the copper chloride/complex salt eutonic point.

In our opinion, the different effects of the nature of alkali metal M^+ on the solubility of copper mono- and dichlorides are determined by two main factors: action of M^+ on the water and solution structures and ionic association of MCl chlorides.

For the quantitative characteristic of the effect of M^+ on solubility we used the value dm_1/dm_2 that relates to the intensity of salting-in (salting-out) of salt components. Variation of this characteristic along the crystallization branches of CuCl, $CuCl_2$, and alkali metal chlorides is given in Fig. 2. Our results show that the variation of this characteristic with alkaline metal is much more essential for $CuCl_2$-containing systems. Thus, the stronger acido complex formation of monovalent copper levels off the effect of alkaline metal cation, whereas with divalent copper, vice versa, differentiation takes place as a result of the stronger influence of hydration and association of alkali metal chlorides. As a result, the sign of $dm(CuCl_2)/dm$(MCl) changes, i.e. salting-out of copper dichloride gives way to its salting-in, and the dm_1/dm_2 values change stronger when sodium and potassium ions are substituted for lithium cation.

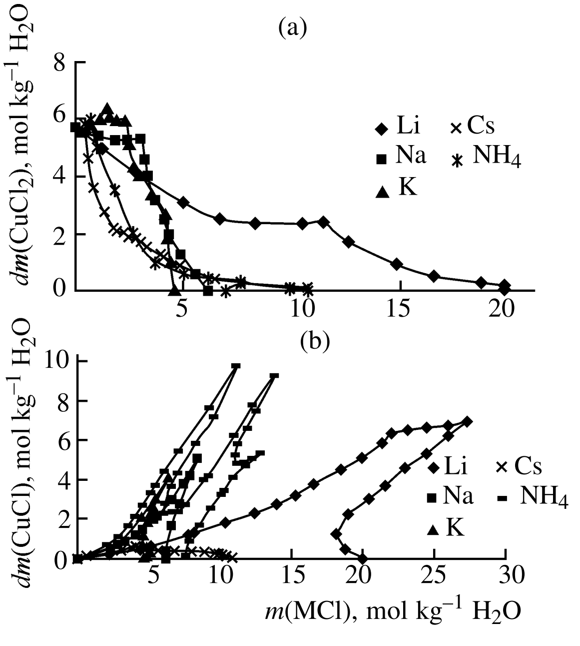

Fig. 1. Solubility isotherms in (a) $CuCl_2$–MCl–H_2O and (b) CuCl–MCl–H_2O systems at 25°C.

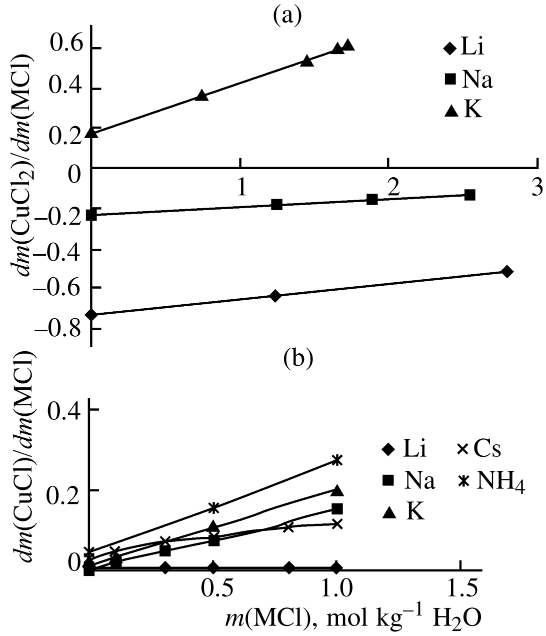

Fig. 2. Variation of the solubility of copper(I) and (II) chlorides along their crystallization branches in (a) $CuCl_2–MCl–H_2O$ and (b) $CuCl–MCl–H_2O$ systems.

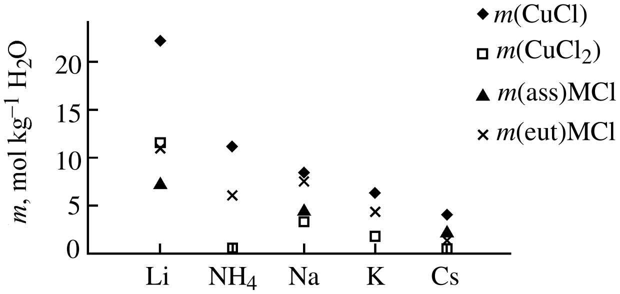

Fig. 3. Correlation between the position of eutonic points and the concentration boundaries of regions with prevailing MCl association.

Similar effect is also observed for the crystallization branch of alkali metal chlorides.

The competition of acido complex formation and association should also affect significantly the length of the crystallization branches of copper(I) and (II) chlorides. In CuCl-containing systems, the necessity of essential structural rearrangements in the solution before crystallization of complex compounds and the above-mentioned high strength of the black jack-like CuCl lattice are responsible for a considerable length of CuCl crystallization branches. As for $CuCl_2$-containing systems, precipitation of complex solid compounds begins much earlier, i.e. the necessary concentration of solid phase precursors is reached at fairly low concentrations of alkali metal chlorides. The specificity of alkali metal cation reveals itself through competition for chloride ions between copper(I) and copper(II) ions (formation of polynuclear acido complexes) and alkali metal cations (ionic association). Note a clear correlation between the position of eutonic points, on the one hand, and the concentrations of the beginning of prevalence of ion-ion association in binary MCl solutions, on the other [6] (Fig. 3). Furthermore, it is seen from the available solubility isotherms that in the systems containing copper(I) the lengths of the crystallization branches differ more considerable than in the systems containing copper(II), and the influence of association of alkali metal chlorides on the length of the crystallization branches of copper(I) and (II) chlorides in the case of monovalent copper is stronger. Probably, this is connected with the fact that with Cu(I) much higher concentrations of alkali metal chlorides are attainable than with Cu(II).

The nature of alkali metal cation M^+ and the oxidation state of copper also affect the type of solid compounds crystallizing in the systems. In ternary water–salt systems of copper(I) and copper (II) halides, three main types of complex salts can crystallize [4]: conjugated crystal hydrates; complex salts formed by acido complex formation of chloride ions with the central copper cation and outer-sphere coordination of M^+; and binary salts formed by coordination of ion pairs.

In the $CuCl_2–MCl–H_2O$ systems, where the MCl association constants (0.1–0.9 for KCl–CsCl [11]) and the stability constant of $CuCl^+$ (8.2 [10]) are quite comparable, the specificity of alkali metal rather strongly affects formation of complex copper salts. As a result, all the three types of solid compounds crystallize in these systems [4]: $LiCuCl_3 \cdot 2H_2O$; $KCuCl_3 \cdot 2H_2O$, $K_2CuCl_4 \cdot 2H_2O$; $(NH_4)_2CuCl_42 \cdot H_2O$; and $CsCuCl_3$, Cs_2CuCl_4.

The M–Cl bond length ($r_{M–Cl}$) in first- and second-type complex compounds will be larger compared to pure MCl salt, and in third-type compounds (dipole coordination) $r_{M–Cl}$ should remain practically invariable. Actually, X-ray diffraction data provide evidence for these suggestions (see table). As for the Cu–Cl bond, in first- and third-type compounds it should be weakened and in second-type compounds, strengthened. The Raman spectra of the compounds, measured on a Renishaw System-l00 spectrometer equipped with a Leica-DMLM microscope, diode laser (wavelength 780 nm, power 25 mW), and a Peltier-cooled CCD detector, gave evidence for this conclusion. The bands of Cu–Cl stretching vibrations of second-type complex salts are shifted to the high-frequency region, and those of first- and third-type complex salts, to the low-frequency region as compared to copper dichloride.

On the other hand, in all CuCl-containing systems copper(I) acido complexes is the predominant type of interactions, which determines the similarity of the composition and structure of crystallizing solid compounds. Hence we can expect that complex salts formed in these systems belong to one type of compounds, namely, products of acido complex formation of the central cation Cu^+ with chloride ions; M^+ cations in such salts occupy positions in cavities of the resulting structure. We earlier showed [3] that compounds of this type are characterized by elongated M–Cl bonds and shortened central atom–ligand bonds, compared to the corresponding binary compounds. The available data on the structures of potassium, ammonium, and cesium chlorocuprates(I) confirm this assumption on the type of crystallizing compounds (see table). The high-frequency shift of stretching vibration bands, too, points to formation of a stronger copper–chlorine bond compared to CuCl. The Cu–Cl bond in CuCl compounds should be the stronger, the weaker is the polarizing action of the outer-sphere cation M^+ ($Li^+ > NH_4^+ > K^+ > Cs^+$), which is confirmed experimentally.

As seen from the table, copper(I) systems have r_{M-Cl} distances longer and r_{Cu-Cl} shorter than the corresponding binary compounds, which provides evidence for the above assumption. Therefore, the state of the Cu–Cl bond in a compound should be determined by the polarizing action of the outer-sphere cation M^+: $r_{Cu-Cl}(CuCl) > r_{Cu-Cl}(K_2CuCl_3) > r_{Cu-Cl}(Cs_3Cu_2Cl_5)$, which corresponds to X-ray diffraction and IR and Raman spectral data (see table). The stretching frequencies increase in the same order, implying strengthening of the Cu–Cl bond. According to published data [13], the absence of complex solid compounds in the systems $CuCl–NaCl–H_2O$ and $CuCl_2–NaCl–H_2O$ is not a special feature of these system, but is characteristic of the majority of systems containing sodium salts (for example, $MgCl_2–NaCl–H_2O$, $CuBr_2–NaBr–H_2O$, and $CuBr–NaBr–H_2O$).

Lengths of M–Cl and Cu–Cl bonds [12] and frequencies of Cu–Cl stretching vibrations for copper(I) and copper(II) compounds

Complex	r_{M-Cl}, Å		r_{Cu-Cl}, Å	ν(CuCl), cm^{-1}
	compound	MCl		
$CuCl_2 \cdot 2H_2O$			2.30, 2.98	295, 276, 246, 208
$K_2CuCl_4 \cdot 2H_2O$	3.28	3.15	2.29, 2.79	303, 280, 256, 215
$(NH_4)_2CuCl_4 \cdot 2H_2O$	3.40	3.24	2.30, 2.97	315, 272, 244, 222
$CsCuCl_3$	3.59	3.56	2.32, 2.66	293, 254, 234, 218
Cs_2CuCl_4	3.60	3.56	2.23	283, 256
CuCl			2.46	236, 215
$KCuCl_3$	3.27	3.15	2.31	245, 226
$NH_4Cu_2Cl_3$	3.34	3.24	2.34	243, 223
$Cs_3Cu_2Cl_5$	3.69	3.56	2.28	252, 242
$Cs_3CuCl_4 \cdot H_2O$	No data			251, 236

Analysis of the resulting data allowed us to reveal both general regularities and essential differences in $CuCl_x–MCl–H_2O$ ($x = 1, 2$) systems, associated with the electronic structures of copper (I) and copper(II). The prevalence of acido complex formation processes in all the copper chloride systems under consideration is responsible for the following general trends: crystallization of complex salts in all the systems studied (except for NaCl-containing systems); salting-in or weak salting-out of copper chlorides on addition of alkali metal chlorides; and increase in the solubility of copper chlorides in the order LiCl < NaCl < KCl.

At the same time, the different stabilities of acido complexes of mono- and divalent copper and, as a consequence, different contributions of association of alkaline chlorides and hydration interactions result in different shapes of solubility isotherms. In $CuCl_2$-containing systems, both salting-out and salting-in of the components take place, depending on the nature of the M^+ cation. In CuCl-containing systems, salting-in takes place exclusively, the effects of the chemical individuality of M^+ on the intensity of salting-in of CuCl and the nature of crystallizing compounds are leveled, while in the case of copper(II) these effects are differentiated. All chlorocuprates(I) crystallizing in the systems studied are of the same type, whereas chlorocuprates(II) represent three different types of complex salts.

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