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Solution–Solid Phase Equilibrium in the Systems Copper(II) Halide–Aprotic Organic Solvent–Water

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Abstract—In the study of the solution–solid phase equilibrium in CuX_2–S–H_2O system (X = Cl, Br, S = dimethyl sulfoxide, *N*,*N*-dimethylformamide, tetrahydrofuran, 1,4-dioxane) at 25ºC we established the effect of the solvent properties and the type of the halide ligand (dielectric premeability, donor number, hydrophobicity) on the solubility of the solid phase in binary and ternary systems, the length of the fields of crystallization of the compounds and the structure of the water–organic solvates.

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Nonaqueous solvents and their mixtures with water are widely used in chemistry and chemical technology. As known, the choice of a suitable solvent for a particular reaction can significantly influence the reaction route and yield, and sometimes allows the initiation of processes that cannot occur in the other conditions [1–3]. This is the reason for the active study of interactions in multicomponent systems containing nonaqueous and mixed solvents. However, while the problem of the solvent competition for a site in the solvation shell of an ion in liquid phase has been studied extensively, the investigations of the solvent effect on the solution–solid phase equilibrium and the studies of solubility in such systems have practically not been performed. Here we report on a study of the influence of nature and properties of halide ligands and organic solvents on the solubility of copper(II) halides in binary and ternary salt systems, the length of the fields of crystallization of the compounds, and the structure of water–organic solvates.

In the case of ionic compounds the most important property that determines the solubility is assumed to be the dielectric permittivity: the higher dielectric constant, the better solubility of the compound, and, on the contrary, at the lower dielectric constant of the solvent the solute association increases and thus its solubility diminishes [4, 5]. This pattern is typical for most of the studied solvents: the solubility decreases in the series dimethyl sulfoxide > tetrahydrofuran > dioxane (Table 1). However, the consideration of the dielectric constant as the main parameter determining the solubility in these systems cannot be accepted as a valid approach. Thus, the concentration of saturated solutions of copper halides in DMSO is slightly higher than in THF, although these solvents are very different by their permittivity. DMF also is out of this series: solubility in the CuX_2–DMF systems is much higher than in the others. This probably is caused by the specificity of the molecular structure of these solvents. The low solubility of copper salts in DMSO is largely due to the fact that the sulfur atoms in the DMSO molecules coordinated to the copper ion are shielded by methyl groups and thus are unable to coordinate the free solvent molecules with the formation of the subsequent solvation shell. In addition, DMSO is a strongly associated solvent (the degree of association is up to 90%) [6], therefore additional energy is required for dissolution. As for DMF, the coordinated molecules of this solvent are capable of bonding the outer-sphere molecules through the formyl hydrogen atom, leading to the formation of a unified polymer structure in the solution. The coordination to metal ion further promotes this interaction, because the positive charge on the formyl hydrogen atom in this case increases [7].

Similar trends also govern the copper dihalides solubility in ternary water–organic systems (Figs. 1–5). Minimum solubility is observed in the system CuX_2–1,4-dioxane–H_2O, which is due to a sharp decrease in the dielectric permittivity with increasing mole fraction

Table 1. Main properties of organic solvents used and the solubility of copper dihalides in binary systems

Solvent	ε	*DN*, kcal mol^{-1}	Solubility of CuX_2, mol per 100 mol of solvent	
			$CuCl_2$	$CuBr_2$
DMF	37.8	24.0	9.64	20.40
DMSO	46.4	29.8	0.78	1.96
THF	7.6	20.0	0.50	1.11
1,4-Dioxane	2.2	14.8	0.03	0.23

of the organic component [8]. Very high solubility (up to 25 mol per 100 mol of solvent) is observed in the system CuX_2–DMF–H_2O, probably due to the above-noted ability of coordinated DMF molecules to form bonds with outer-sphere solvent molecules (DMF or H_2O) through formyl hydrogen.

The unexpectedly high solubility of copper dihalides was found in the case of a mixed solvent containing tetrahydrofuran. While the solubility in the corresponding binary system lies between dimethyl sulfoxide and 1,4-dioxane, which correlates with the dielectric constant of the solvent, such correlation does not occur in mixed solutions, and the solubility in ternary systems CuX_2–THF–H_2O is higher than in the binary subsystem. This fact indicates the important role of some additional factors, the most important one among which, in our opinion, is the organic solvent hydrophobicity. At low concentrations of THF the copper ions are solvated mainly by this solvent due to its greater donor number compared with water (20.0 and 18.0, respectively). At low concentrations of water its molecules are strongly associated with the molecules of THF by hydrogen bonding [9], but the majority of organic molecules are free and are capable of solvating the copper ions. Thus, we can assume that in the entire concentration range the copper ions are solvated predominantly by the THF molecules, which, in turn, have hydrophobic properties. The presence of complex particles in the hydrophobic solution leads to a sharp strengthening of the hydrogen bonds and creation of a "layer" of water molecules, preventing aggregation of complex particles to form a solid phase.

Comparing solubility isotherms of the systems containing the same organic solvent but different halide ligands allowed us to trace the influence of the nature of the latter on copper salts solubility. According to the experimental data, the solubility of copper dibromide in binary systems CuX_2–S (S = DMSO, DMF) is approximately twice higher than the solubility of $CuCl_2$ in the similar system. This fact seems especially unusual, given that in these systems $CuBr_2$ binds three solvent molecules ($CuBr_2 \cdot 3DMF$, $CuBr_2 \cdot 3DMSO$), whereas copper dichloride only two: it is well known [10] that the greater the number of solvent molecules in a solvate, the lower should be its solubility. Most likely, the observed phenomenon is primarily due to the different structure of the individual crystal solvates formed in these systems. The data of XRD analysis [11] indicate that the chloride compounds have polymer structure with the chloride bridges, while the structure of the crystal solvates formed by copper dibromide has an *island* motif. As is known [12], the dissolution of substances having a polymeric structure requires a much higher energy than the same process with the products of *island* structure. As a consequence, the solubility of copper dichloride in DMSO and DMF is much lower than the solubility of copper dibromide in the same solvents.

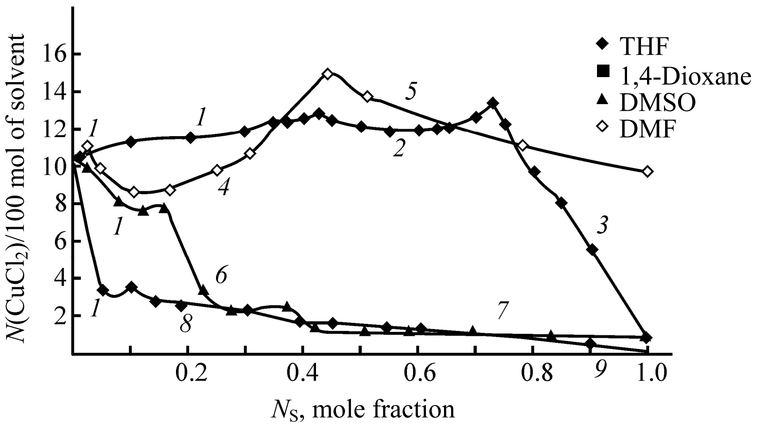

Fig. 1. Solubility isotherms in the system $CuCl_2$–H_2O–S at 25°C.

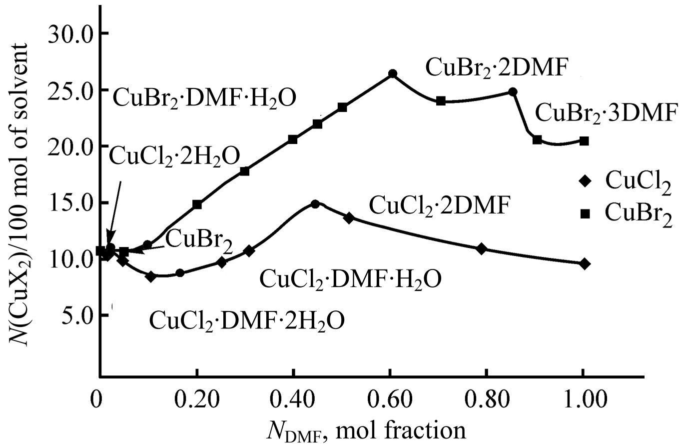

Fig. 2. Solubility isotherms in the system CuX_2–H_2O–DMF at 25°C.

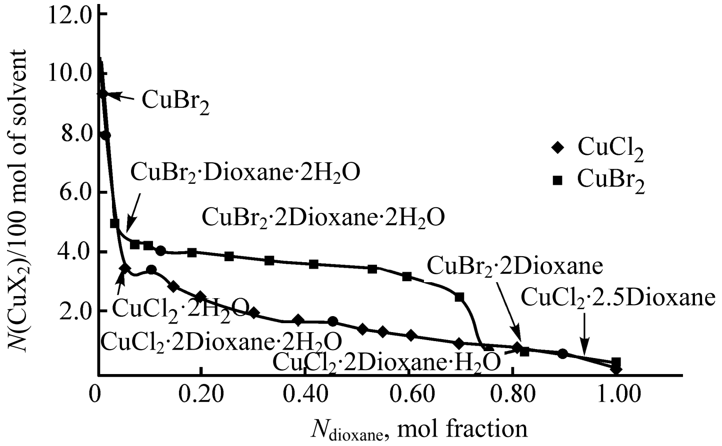

Fig. 3. Solubility isotherms in the system CuX_2–H_2O–1,4-dioxane at 25°C.

It is worth noting that in the ternary system $CuBr_2$–H_2O–S (S = DMSO, DMF) also individual crystal solvates are formed containing two molecules of the solvent and having a polymer structure, but the latter is less strong than the polymer structure of the same composition though containing chloride anion. Thus, in the case of solvate $CuBr_2·2DMSO$ the polymerization occurs through the bromide bridges, which because of the lower σ-donor ability of the bromide ligand is much weaker than in the structure of $CuCl_2·2DMSO$.

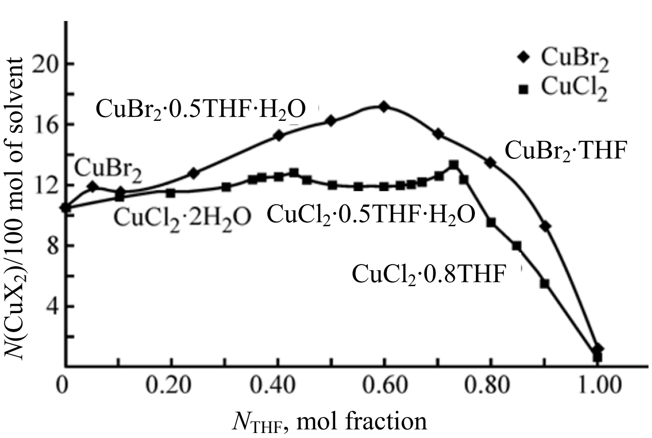

Fig. 4. Solubility isotherms in the system CuX_2–H_2O–THF at 25°C.

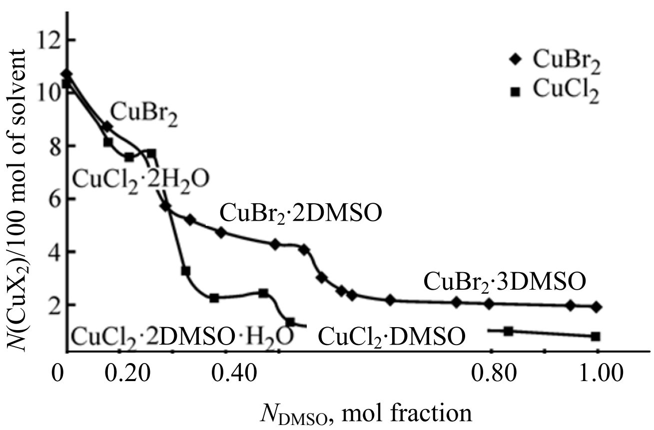

Fig. 5. Solubility isotherms in the system CuX_2–H_2O–DMSO at 25°C.

Table 2. Length of the solvate crystallization field of copper dihalides in organic solvents

Compound	ΔN, mol fraction	DN, kcal mol^{-1}
$CuCl_2 \cdot 2DMSO$	0.63	
$CuCl_2 \cdot 2DMF$	0.45	
$CuCl_2 \cdot 0.8THF$	0.27	
$CuCl_2 \cdot 2.5Dioxane$	0.10	
$CuBr_2 \cdot n$DMSO (n = 2, 3)	0.86	29.8
$CuBr_2 \cdot n$DMF (n = 2, 3)	0.57	24.0
$CuBr_2 \cdot THF$	0.40	20.0
$CuBr_2 \cdot 2Dioxane$	20.0	14.8

The chains of polyhedra in the structure of $CuBr_2 \cdot 2DMF$ are formed due to the weak interaction of the bromine atoms of the anion $CuBr_4^{2-}$ with the formyl hydrogen of DMF in the $Cu(DMF)_4^{2+}$ moiety. Apparently, this fact generally leads to the higher solubility in these bromide systems comparing to the chloride ones.

Similar situation occurs in the binary and ternary systems containing 1,4-dioxane. The solubility of copper dichloride in this solvent is lower than that of copper dibromide. Furthermore, the number of solvent molecules in the individual crystal solvates is 2.5 and 2, respectively. This fact reflects a strong association of ions in the case of copper chloride. The X-ray structural analysis of mixed crystal solvates formed in the system of CuX_2–1,4-dioxane–H_2O [13] indicates the polymeric structure of the bromide-containing solvates and the absence of the such structure in the solvates formed by $CuCl_2$. The polymerization in the structures of the first type is due to the bridging dioxane molecules. In the case of chloride solvate, the individual polyhedra are linked by weak hydrogen bonds.

These assumptions are fully confirmed at the consideration of the CuX_2–THF system. The solubility of copper bromide in the pure solvent is twice higher than that of chloride (1.11 and 0.50 mol per 100 mol of the solvent, respectively), which again is due to a stronger association of copper ions with chloride anions.

The length of the crystallization fields of individual organic crystal solvates of copper halides clearly correlates with the donor numbers of organic solvent: the higher the donor number of solvent, DN_S, the greater the extent of the crystallization branch of the corresponding organic solvate on the solubility isotherm, ΔN_S (Table 2). As for the effect of the acido ligand on the length of the crystallization fields of the solvates with the same solvent, it decreases with increasing rigidity of the anion, as is seen well in the systems containing dimethyl sulfoxide and dimethylformamide. The copper chloride complexes are harder acids than bromide complexes, so the latter are better solvated with the soft bases, the organic solvents. As a consequence, the length of the crystallization fields of organic solvates of copper dibromide is higher.

The solubility isotherms for all systems under consideration, except for $CuBr_2$–DMSO–H_2O, include the branches of crystallization of the mixed aqueous–organic solvates. Their composition was determined analytically (Figs. 1–5). According to XRD analysis [11, 13] and the data of infrared spectroscopy, these solvates differ by the types of structures, and can be classified according to the following criteria: presence/absence of water in the first coordination sphere of copper ion, polymer/*island* type of structure. Belonging of a mixed solvate to a particular type is determined, in our opinion, by such factors as the ratio of the donor numbers of solvents and the nature of acido ligand, namely, its σ-donor ability. Most likely, just the ratio of the donor numbers of solvents is responsible for the absence of water in the first coordination sphere of the copper atom in compounds crystallizing in the system CuX_2–H_2O–DMSO. A large difference in donor numbers of water and DMSO (18 and 29.8, respectively) contributes to the preferential solvation of copper ion by the DMSO molecules, while water is not coordinated directly to the metal ion in the structure of the solvate $CuCl_2 \cdot 2DMSO \cdot H_2O$ and occupies the channels in the structur. In the system containing copper dibromide the mixed solvates are absent, apparently due to the inability of the bromide ion to form hydrogen bonds, in contrast to the chloride structure. A smaller difference in the donor numbers for the pairs of solvents water–DMF (DN = 24.0), water–THF (DN = 20), and water–1,4-dioxane (DN = 14) allows the appearance of both solvents in the first coordination sphere of the metal ion. For mixed solvates formed in the system of CuX_2–H_2O–DX, this conclusion was confirmed by the XRD analysis on single crystals [13]. The XRD analysis of the $CuBr_2 \cdot DMF \cdot H_2O$ solvate has not been performed, but the similarity of the shape and the position of vibration bands of dimethylformamide in the IR spectrum of individual and mixed solvates, $CuBr_2 \cdot 3DMF$ and

$CuBr_2 \cdot DMF \cdot H_2O$, as well as the presence in the spectrum of the latter of the band ν(OH) at 3500 cm^{-1}, suggests that the first coordination sphere of copper ion includes both these solvents. The comparison of the bands of stretching OH vibrations of water in the IR spectra of $CuBr_2 \cdot DMF \cdot H_2O$ and $CuBr_2 \cdot 2dioxane \cdot 2H_2O$ (3200 cm^{-1}) makes it possible to assert that binding of water in the mixed solvates with DMF is much weaker. This fully agrees with the assumption that the copper–oxygen bond strength is determined by the values of the donor numbers of solvents. Analysis of IR spectra of compounds $CuX_2 \cdot 0.5THF \cdot H_2O$ showed that in the solvate of dichloride the molecules of both the solvents are coordinated to the copper atom [ν_s(OH) = 3155 cm^{-1}; ν_{as}(OH) = 3350 cm^{-1}; ν(COC) = 889 cm^{-1}]. A somewhat different situation is in the case of copper dibromide solvate, $CuBr_2 \cdot 0.5THF \cdot H_2O$: according to the analysis of the IR spectra, the water molecules are coordinated to copper atom, but the band shift is not as significant as in the case of the chloride compound [ν_s(OH) = 3184 cm^{-1}, ν_{as}(OH) = 3363 cm^{-1}]. The band of COC stretching vibrations observed in the pure solvent at 915 cm^{-1} is split into three components: 833, 860 and 917 cm^{-1}. Apparently, the first two are symmetric and asymmetric vibrations of bidentately coordinated THF, so the shift to lower frequencies is significant. The third band belongs to the molecules of THF located in the channels of the structur and are bound by weak hydrogen bonds.

EXPERIMENTAL

The study of solubility was carried out by the methods of isothermal saturation and removal of supersaturation. The values obtained by these two methods were consistent within experimental error. The period of keeping at constant temperature was at least 24 h, with the temperature accuracy within ±0.1ºC. The content of copper(II) ions in solution was analyzed by trilonometry [14], the error of analysis was about ±0.5%. The content of the organic component in the case of DMSO was determined by bichromatometry [15], in the cases of DMF, THF, and 1,4-dioxane, by gas chromatography, the experimental error was 1%. The analysis of the bottom phase composition was carried out similarly.

The IR spectral measurements in the mid-IR region were carried out on a Brucker IFS 55 FT-IR spectrometer equipped with a Varian Golden Gate device (optical crystal is diamond, clamping element is sapphire) with a Globar source and a CdHgTe detector cooled by liquid nitrogen. The spectral resolution was 2 cm^{-1}, number of scans 32. All measurements were performed at room temperature. For processing the IR spectra the Grams32 software was used.

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