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Organic Solvent Effect on the Solution–Solid Phase Equilibria in the Systems $CuCl_2$–L–H_2O (L = DMSO, DMF, Acetonitrile) at 25°C

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Abstract—A solution–solid equilibrium in ternary water-organic systems $CuCl_2$–L–H_2O (L = dimethyl sulfoxide, *N,N*-dimethyl formamide, and acetonitrile) at 25°C was studied. The expansion of crystallization branches of individual solvates $CuCl_2 \cdot x$L varies in parallel to the donor power of organic solvents. The existence of the mixed crystal-solvates $CuCl_2 \cdot 2H_2O \cdot 2(CH_3)_2SO$, $CuCl_2 \cdot 2H_2O \cdot 2(CH_3)_2NCHO$, $CuCl_2 \cdot H_2O \cdot (CH_3)_2NCHO$, $CuCl_2 \cdot 2H_2O \cdot CH_3CN$, and $CuCl_2 \cdot 3H_2O \cdot 2CH_3CN$ in the studied systems was proved. Various donor power of oxygen-containing solvents determines the composition of the first coordination sphere of the copper ion in the specified compounds: the coordination of the both solvents in the mixed crystal-solvates with DMF and the absence of water in the nearest environment of the copper(II) ions in the $CuCl_2 \cdot 2H_2O \cdot 2(CH_3)_2SO$ compound.

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This work is a prolongation of studying interrelation between composition and structure of copper halides in solution and in solid phase. Earlier we have fulfilled the systematic experimental study of the solution–solid phase equilibrium in ternary aqueous systems containing a copper halide and an alkali metal halide [1, 2]. The domination of acido complex formation involving copper is responsible for the essential similarity of solubility isotherms in these systems. The difference in the phase equilibrium diagrams was assigned to the variation of contributions of alkaline halides and of hydration. In the present work we present the data on the effect of a competing solvation on the phase equilibria in the systems with mixed water-organic solvents: $CuCl_2$–L–H_2O (L is dimethyl sulfoxide, *N,N*-dimethyl formamide, and acetonitrile). Multicomponent systems containing copper(II) halides, water, and an organic solvent are used in liquid chromatography as corrosion inhibitors, and also for obtaining ultrafiltration membranes [3–4].

Phase equilibria in the systems $CuCl_2$–H_2O–DMF and $CuCl_2$–H_2O–DMSO were already studied earlier [5–6]. Water-enriched fields were considered, but the data for organic solvent concentrations higher than 55 wt % of DMF and 75 wt % of DMSO were absent from these works. From our point of view, the authors of [5–6] have chosen not optimal procedures for the analysis of solvating organic solvent, namely, permanganatometry for DMSO and Kjeldahl's method for DMF. In the first case an excess of permanganate ions is determined by the reaction with HI, but the copper ion will oxidize iodide ion as well. The Kjeldahl method gives underestimated data in the case of DMF [7] (about 90% of a theoretical value). All this has caused expediency of carrying out a new study of phase diagrams in the specified systems, the solubility isotherm for $CuCl_2$–H_2O–CH_3CN system being obtained for the first time.

The data obtained have allowed us to compare solubilities in the systems $CuCl_2$–L–H_2O (L = DMSO, DMF, CH_3CN) at 25°C. The solubility of copper dichloride in the binary systems $CuCl_2$–L and $CuCl_2$–H_2O, the length of crystallization branches of individual $CuCl_2 \cdot x$L solvates, and the existence of mixed $CuCl_2 \cdot xH_2O \cdot y$L crystal-solvates in a bottom phase were considered.

According to the generally accepted ideas, the solubility is determined by both the whole combination of solvent–solute interactions and the lattice energy of

Solubility of copper dichloride (mole fractions) in DMSO, DMF, CH_3CN, and H_2O; characteristics of solvents (D_N, kcal mol^{-1} is donor number of a solvent, bp, °C is boiling point at atmospheric pressure)

Solvent	$N(CuCl_2)$	D_N, kcal mol^{-1}	bp, °C
H_2O	0.095	18	100
DMF	0.076	26.6	153
DMSO	0.010	28.9	189
CH_3CN	0.009	14.1	81.6

a solid phase. An examination of the published data has shown an essential similarity in structures of all individual solvates, which represent polymeric compounds with bridging chloride ions, the copper ion coordination number in all cases being six. This similarity allows us to neglect specific structural features of solid compounds and to connect differences in $CuCl_2$ solubility in the binary systems under study with the processes occurring in a solution.

When considering ion-solvent interactions three basic components are usually marked out: breaking solvent-solvent bonds, coordination of solvent molecules to the ion (short-range solvation), interaction of solvent molecules of the first solvate shell with solvent outside it (long-range solvation). Strengthening the first-type interactions should reduce solubility, whereas strengthening the interactions of the second and the third types should increase it. Boiling points can serve as characteristics of the intensity of intermolecular interactions in the solvents under consideration. It increases in the series $CH_3CN \rightarrow H_2O \rightarrow$ DMF $\rightarrow$ DMSO, reaching a maximum in the case of dimethyl sulfoxide characterized by a strong dipole-dipole interaction between antiparallel oriented S=O groups. The criterion of ion-solvent interaction strength can be solvent donor number. The donor number (D_N) is the enthalpy of the interaction of one mole of $SbCl_5$ with 1 mole of a solvent under study in 1 l of 1,2-dichloroethane. It characterizes the ability of a solvent to be coordinated by metal ions [8–9]. In the series of the solvents under consideration the donor number decreases in the sequence D_N(DMSO) > D_N(DMF) > $D_N(H_2O)$ > $D_N(CH_3CN)$ (see the table). The competition of the specified oppositely directed effects is the reason which determines the nonmonotonous character of the variation of the copper dichloride solubility depending on the donor number: $N(CuCl_2)(CH_3CN) < N(CuCl_2)$(DMSO) < $N(CuCl_2)$(DMF) < $N(CuCl_2)(H_2O)$, where $N(CuCl_2)$ is a mole fraction of the salt in a saturated solution. The additional factor reducing solubility is weakening of the interaction between solvent molecules of the first and second solvate shells in presence of voluminous substituents at a positive pole of a dipole (DMSO and DMF).

Crystallization fields of pure $CuCl_2 \cdot x$L solvates in the solubility isotherms of $CuCl_2$–L–H_2O (L = DMSO, DMF, CH_3CN) (Figs. 1–3) vary in parallel to donor numbers of organic solvents.

	$CuCl_2 \cdot 2$DMSO	$CuCl_2 \cdot 2$DMF	$CuCl_2 \cdot 1.5CH_3CN$
ΔN(L)	0.628	0.558	0.411
D_N(L), kcal mol^{-1}	28.9	26.6	14.1

An increase in donor power of solvent molecules determines the domination of solvation over hydration and the rise of the extent of the individual $CuCl_2 \cdot x$L solvate crystallization field. The greater is the donor number of a solvent, the longer is the crystallization branch of the corresponding organic solvate in the solubility isotherm. A rather long expansion of the crystallization branch of the pure $CuCl_2 \cdot 1.5CH_3CN$ solvate, despite of much lower donor number of acetonitrile compared to DMSO and DMF, can be connected with another type of a donor atom (nitrogen instead of oxygen).

Crystallization branches of the mixed water-organic solvates of copper dichloride are also present in the solubility isotherms of the systems $CuCl_2$–L–H_2O (Figs. 1–3). The compositions of these solvates were determined analytically.

$CuCl_2$–DMSO–H_2O	$CuCl_2 \cdot 2H_2O \cdot 2$DMSO
$CuCl_2$–DMF–H_2O	$CuCl_2 \cdot 2H_2O \cdot$DMF, $CuCl_2 \cdot H_2O \cdot$DMF
$CuCl_2$–CH_3CN–H_2O	$CuCl_2 \cdot 2H_2O \cdot CH_3CN$, $CuCl_2 \cdot 3H_2O \cdot 2CH_3CN$

In the earlier works [5–6] only one of the specified mixed solvates, $CuCl_2 \cdot H_2O \cdot$DMF, was detected, apparently, owing to proximity of figurative points of the compositions of two mixed solvates in the system with dimethyl formamide and $CuCl_2 \cdot 2H_2O \cdot 2$DMSO and $CuCl_2 \cdot 2$DMSO solvates, respectively. The use of Schreinemakers' method without engaging additional methods of identification of crystal compounds could lead to the above-mentioned error.

To prove the individual nature and to detect singularities in the structure of crystallizing copper(II)

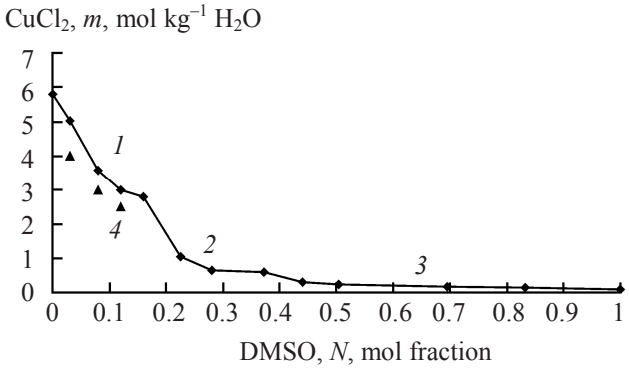

Fig. 1. Solubility isotherm of the system $CuCl_2$–DMSO–H_2O at 25°C. (*1*) $CuCl_2·2H_2O$, (*2*) $CuCl_2·2H_2O·2DMSO$, (*3*) $CuCl_2·2DMSO$, and (*4*) published data [5].

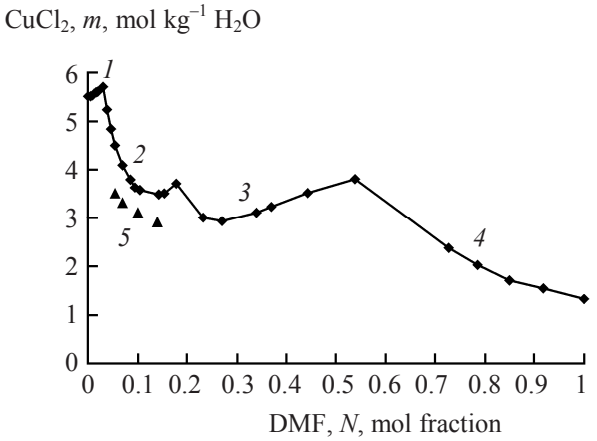

Fig. 2. Solubility isotherm of the system $CuCl_2$–DMF–H_2O at 25°C. (*1*) $CuCl_2·2H_2O$, (*2*) $CuCl_2·2H_2O·DMF$, (*3*) $CuCl_2·H_2O$ DMF, (*4*) $CuCl_2·2DMF$, and (*5*) published data [6].

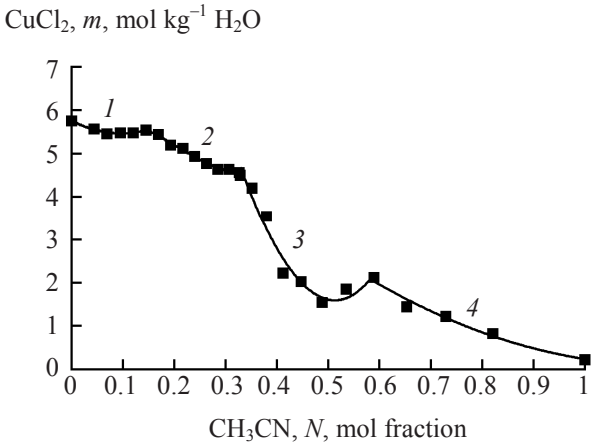

Fig. 3. Solubility isotherm of the system $CuCl_2$–CH_3CN–H_2O at 25°C. (*1*) $CuCl_2·2H_2O$, (*2*) $CuCl_2·2H_2O·CH_3CN$, (*3*) $CuCl_2·3H_2O·2CH_3CN$, and (*4*) $CuCl_2·1.5CH_3CN$.

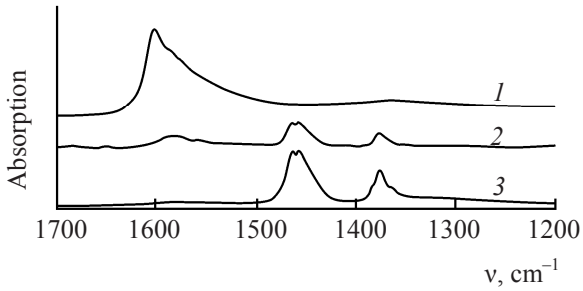

Fig. 4. IR spectra of compounds crystallizing in the $CuCl_2$–DMSO–H_2O system. (*1*) $CuCl_2·2H_2O$, (*2*) $CuCl_2·2DMSO·2H_2O$, and (*3*) $CuCl_2·2DMSO$.

mixed solvates, we have recorded IR spectra of the solid phase in the range of 400–4000 cm^{-1}. Their analysis has confirmed the individual nature of the crystallizing substances and has allowed us to trace the competition of oxygen-containing solvents for a position in the first coordination sphere of copper ions. We can assume that two limiting types of structures of mixed crystal-solvates exist: either the both solvents enter into the first coordination sphere of the metal ion, or one of them is in hollows of the formed structure. The size of DMSO molecules and its high coordination power make improbable its arrangement in hollows of the structure; the copper ion is immediately solvated by DMSO molecules in the first coordination sphere. This assumption is confirmed by the presence of a band at 455 cm^{-1} assigned to Cu–O (DMSO) stretching vibration in the IR spectrum [10]. As to water molecules, judging from the position of the bending vibration band of water (~1580 cm^{-1}, Fig. 4) and from the absence of the Cu–O(H_2O) stretching vibration band near 406 cm^{-1}, water is absent from the first coordination sphere of the copper ion, being in hollows of the formed structure (Figs. 4 and 5).

The examination of the IR spectra of the mixed crystal-solvates crystallizing in the $CuCl_2$–DMF–H_2O system (Fig. 5) has allowed us to conclude that the both solvents enter in the first coordination sphere of the metal ion. This is proved by the low-frequency shift and splitting of the C=O band of dimethyl formamide (1675 cm^{-1} in pure DMF, 1660–1640 cm^{-1} in the complex), the frequency of bending vibrations, and a high resolution of water stretching vibrations. In the region of Cu–O stretching vibrations two bands are

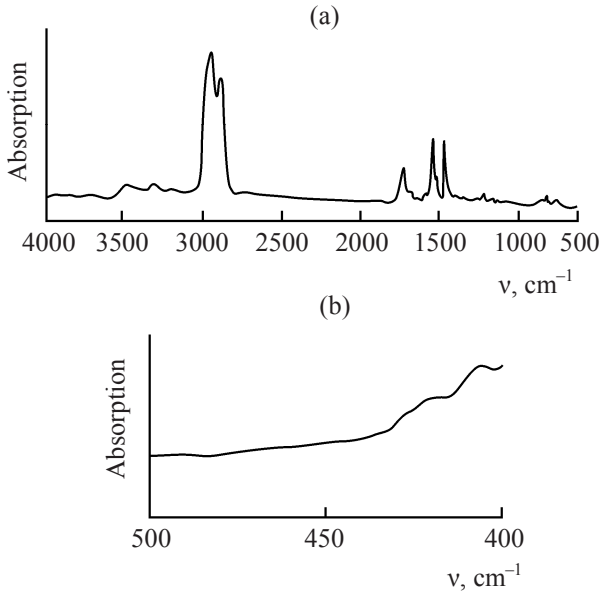

Fig. 5. IR spectrum of $CuCl_2 \cdot 2H_2O \cdot DMF$ solvate crystallizing in $CuCl_2$–DMF–H_2O system: (a) region of 500–4000 and (b) region of 400–500 cm^{-1}.

also observed: 405 and 419 cm^{-1} [Cu–OH_2 and Cu–$OCHN(CH_3)_2$, respectively].

Thus, the length of crystallization branches of copper dichloride individual solvates with organic solvents varies in parallel to the solvent donor number. In the ternary water–organic systems $CuCl_2$–L–H_2O mixed crystal-solvates of copper dichloride are formed. Their structure correlates with solvent donor power: in the compounds $CuCl_2 \cdot xH_2O \cdot y$DMF and $CuCl_2 \cdot xH_2O \cdot yCH_3CN$ the both solvents are present in the first coordination sphere of the copper(II) ion, whereas in the compound $CuCl_2 \cdot 2H_2O \cdot 2$DMSO water is completely superseded from the nearest environment of copper by DMSO molecules.

EXPERIMENTAL

In this work we have obtained solubility isotherms of the $CuCl_2$–H_2O–DMF, $CuCl_2$–H_2O–DMSO, and $CuCl_2$–H_2O–CH_3CN systems at 25°C, and determine the compositions of mixed copper(II) solvates crystallizing therein. The study of solubility was carried out by the isothermal saturation method, solutions being temperature-controlled at 25±0.1°C for a day with permanent stirring. The composition of solutions and solid phases was analyzed by trilonometry [11], the accuracy of the analysis was ±0.5%. The fraction of an organic component was set by the preparation of a system (in all samples the amount of a bottom phase was minimal and did not affect the solvent composition). For some compositions of the systems liquid phases were analyzed by chromatography. We determined the weight fraction of copper dichloride (% $CuCl_2$) in bottom phases and, using chromatography, the organic solvent fraction in mixed solvates $CuCl_2 \cdot xH_2O \cdot y$L.

The IR spectra of finely ground crystalline compounds, suspended in liquid paraffin and placed between polyethylene windows, were taken on a Perkin–Elmer BXII instrument. In the course of recording IR spectra of copper solid compounds the spectra of polyethylene and of water vapors in air were subtracted from the experimental spectra, and the spectra were also normalized, smoothed, and subjected to deconvolution using the Grams32 program.

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