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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Comparative Analysis of the Solubility in the Systems $CuBr_2$–NR_4Br–H_2O at 25°C

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Abstract—The solubility in the $CuBr_2$–NR_4Br–H_2O (R = Me, Et, *n*-Bu) ternary systems at 25°C was determined by the isothermal saturation method. Comparative analysis of the phase equilibria diagrams was done. The results obtained were interpreted in terms of the competition of two processes, association of tetraalkylammonium salts and copper(II) complex formation in water-salt systems.

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Reciprocal interaction of components in heterogeneous water-salt systems and its manifestation in the solution-solid phase equilibria is a central problem in modern solution chemistry. Revealing for new general trends in the variation of the solubility of substances with their chemical nature, finding new routes of liquid-phase synthesis of compounds with predictabled properties, and development of methods for the enrichment of polymetallic concentrates make urgent the study in this area.

In this work we present results obtained in studying the solution–solid phase equilibria in the $CuBr_2$–NR_4Br–H_2O (R = Me, Et, *n*-Bu) ternary systems.

A systematic study of properties of the systems containing tetraalkylammonium and copper salts is topical. Tetra-alkylammonium salts are used in extraction systems [1, 2] and as phase-transfer catalysts [3]. Application of the above substances in the given areas arises from their good solubility in water and, owing to the presence of lyophilic alkyl radicals, also in nonpolar organic solvents. Therefore, depending on the conditions, a tetraalkylammonium cation with a counter ion can leave the water and pass into the organic phase and vice versa. Copper(II) compounds, pure or in combination with the compounds of copper(I) and alkali metal salts, are effective catalytic systems for a large number of organic reactions [4–8]. It seems promising to combine a copper(II) cation and tetraalkylammonium ions in the same system or substance.

The solubility was studied by the method of isothermal saturation. Sets of solutions were prepared by successive dilution of the initial solutions. As initial solutions were used saturated solutions of $CuBr_2$ and NR_4Br. To them, a third component was added at a step of 0.2–1 mol kg^{-1} H_2O. The solutions were placed into an air thermostat and kept there at 25.0 ± 0.1°C for 1 day at constant agitation (magnetic stirrer). Since the solutions formed in the $CuBr_2$–NBu_4Br–H_2O system with a tetraalkylammonium bromide concentration more than 15 mol kg^{-1} H_2O are viscous, the keeping time was 3 days.

The concentrations of copper(II) and bromide ions were determined by titration (with Trilon B and mercury titrants, respectively). The concentration of tetraalkylammonium bromide was calculated as difference. The relative error of the analysis did not exceed 0.5%. The composition of solid phase was determined by the Skreinemakers' method. Experimental data on the solubility isotherms are given in Tables 1–3 and plotted in Fig. 1.

Noteworthy that the solubility in the binary systems strongly increases in the order NMe_4Br < NEt_4Br < NBu_4Br (6.24 mol kg^{-1} H_2O for tetraalkylammonium bromide, 16.79 mol kg^{-1} H_2O for tetraethylammonium, and 20.40 mol kg^{-1} H_2O for tetrabutylammonium). Precursors of the solid phase in the systems under study are electroneutral particles, contact ion pairs $(NR_4^+Br^-)$, and the condition, at which a solid phase is formed, is a certain threshold value of their concentration in the solution [9]. In its turn, the formation of ion pairs is

Table 1. Solubility in the $CuBr_2$–NMe_4Br–H_2O system at 25°C

Concentation of components in liquid phase				Composition of solid phase
wt %		mol kg^{-1} H_2O		
NMe_4Br	$CuBr_2$	NMe_4Br	$CuBr_2$	
0.00	56.41	0.00	5.79	$CuBr_2$
1.31	56.23	0.10	5.96	"
2.48	57.09	0.40	6.30	"
3.32	56.88	0.54	6.40	$CuBr_2$+ $(NMe_4)_2CuBr_4$
3.41	56.18	0.53	6.22	$(NMe_4)_2CuBr_4$
3.84	46.32	0.49	4.15	"
5.54	40.64	0.66	3.37	"
9.04	34.43	1.03	2.72	"
15.66	25.27	1.73	1.92	"
20.13	21.72	2.25	1.67	"
25.02	17.70	2.83	1.38	"
26.91	17.11	3.12	1.37	"
29.07	14.56	3.36	1.16	"
33.54	11.73	3.97	0.96	"
36.52	9.64	4.40	0.80	"
41.11	6.92	5.13	0.59	"
45.63	4.89	5.98	0.44	"
45.92	4.71	6.03	0.43	"
46.83	4.60	6.25	0.42	$(NMe_4)_2CuBr_4$+ +NMe_4Br
46.56	3.42	6.05	0.30	NMe_4Br
46.71	2.21	5.93	0.19	"
46.83	1.87	5.92	0.17	"
47.62	0.88	6.00	0.08	"
47.90	0.71	6.05	0.06	"
49.03	0.00	6.24	0.00	"

Table 2. Solubility in the $CuBr_2$–NEt_4Br–H_2O system at 25°C

Concentation of components in liquid phase				Composition of solid phase
wt %		mol kg^{-1} H_2O		
NEt_4Br	$CuBr_2$	NEt_4Br	$CuBr_2$	
0.00	56.41	0 0.10	5.79	$CuBr_2$
1.02	52.52	0.30	4.95	$CuBr_2$+ NEt_4CuBr_3
3.34	42.76	0.50	3.60	NEt_4CuBr_3
5.66	40.32	0.70	3.30	"
8.14	36.54	1.30	2.90	"
15.03	29.02	1.40	2.30	"
16.55	26.71	2.00	2.10	"
23.05	22.08	2.35	1.80	NEt_4CuBr_3+ $(NEt_4)_2CuBr_4$
26.32	20.43	2.50	1.71	$(NEt_4)_2CuBr_4$
27.87	17.91	2.70	1.50	"
30.53	16.06	3.10	1.40	"
4.08	14.11	3.40	1.20	"
36.49	12.11	3.80	1.10	"
40.02	10.34	3.90	0.90	"
40.91	9.32	5.00	0.80	"
49.11	4.33	6.00	0.40	"
54.38	2.48	6.09	0.30	"
58.49	1.21	9.60	0.13	"
66.32	0.92	10.80	0.12	"
69.21	0.41	11.30	0.06	"
70.21	0.42	14.41	0.06	$(NEt_4)_2CuBr_4$+ NEt_4Br
75.04	0.17	16.79	0.03	NEt_4Br
77.93	0.00		0.00	"

determined by the ion-ion and ion-water interactions. For all the particles considered here, the ion-ion interaction is predominant, whereas the second type of the interaction, negligible.

The radius of the NM_4^+ ion (2.16 Å) is close to the radius of Cs^+ cation (1.69 Å) and, as consequence, the association constants of their bromides in aqueous solutions are also close (1.26 and 1.0, respectively [10]). The same is true for solubilities of the above compounds (5.65 mol CsBr kg^{-1} H_2O and 6.24 mol NMe_4Br kg^{-1} H_2O).

On passing to tetraethylammonium bromide, the cation radius increases (r = 2.79 Å), whereas the ion-ion association becomes weaker. This is due to the specificity of the interaction of a given cation with water. At this size of the cation the zone of the destructurezed water disappears [11] and a specific (hydrophobic) type of the hydration occurs revealed. This involves the interaction between the water molecules and the solute not accompanied by charge transfer and formation of chemical bonds [12]. Owing to the hydrophobic interaction of tetraethylammonium ion with the solute, the hydrogen bonds between water molecules surrounding tetraethylammonium cation become stronger, thus impeding formation of contact ion pairs. Both the above factors (strengthening of hydrogen bonds and weakening of ion-ion attraction in the presence of large cation) determine the larger solubility of tetraethylammonium bromide in comparison with NMe_4Br.

On passing to tetrabutylammonium bromide, all the above factors impeding formation of precursors of the solid phase are revealed even stronger. In addition, at larger concentrations of the salt a cation-cation association occurs. The latter becomes possible owing to

Table 3. Solubility in the $CuBr_2$–NBu_4Br–H_2O system at 25°C

Concentation of components in liquid phase				Composition of solid phase
wt %		mol kg^{-1} H_2O		
NBu_4Br	$CuBr_2$	NBu_4Br	$CuBr_2$	
0.00	56.41	0.00	5.79	$CuBr_2$
2.63	45.84	0.16	3.97	$CuBr_2$+ NBu_4CuBr_3
2.11	38.32	0.11	2.78	NBu_4CuBr_3
2.28	36.83	0.10	2.70	"
0.54	32.17	0.04	2.14	"
1.73	26.88	0.05	1.69	"
1.62	24.32	0.07	1.47	"
3.24	21.43	0.11	1.27	"
2.83	20.89	0.13	1.23	"
1.08	21.08	0.14	1.21	NBu_4CuBr_3+ (NBu4)2$CuBr_4$
1.32	20.52	0.15	1.17	$(NBu_4)_2CuBr_4$
4.36	17.03	0.17	0.97	"
13.72	8.88	0.55	0.51	"
14.29	9.43	0.58	0.55	"
16.63	8.18	0.69	0.49	"
25.82	5.03	1.16	0.32	"
33.78	2.79	1.66	0.20	"
45.43	1.32	2.60	0.11	"
56.02	1.27	4.01	0.14	"
67.88	2.64	7.67	0.42	"
69.89	3.32	8.01	0.55	"
76.32	5.23	12.80	1.26	"
77.91	6.64	15.61	1.91	"
78.48	7.06	16.93	2.20	"
79.72	7.91	19.96	2.85	$(NBu_4)_2CuBr_4$+ NBu_4Br
81.76	5.19	19.54	1.79	NBu_4Br
82.79	3.83	19.10	1.27	"
86.91	0.00	20.40	0	"

a large radius of the cation, small density of the surface charge, and large length of the hydrophobic chains. The various methods, such as the measurement of electrode potentials [13] and nuclear magnetic relaxation rate [14], were used to demonstrate presence of the strong cation-cation interaction in the NBu_4Br solution and the formation of the cationic associates and, probably, micelles, in them. The formation of such associates decreases the concentration of free tetrabutylammonium ions thus impeding formation of contact cation-anion pairs. All the above is responsible for the attainment of the threshold concentration of the precursors of the solid phase at large concentrations of NBu_4Br and, as a consequence, determines the increase in the solubility

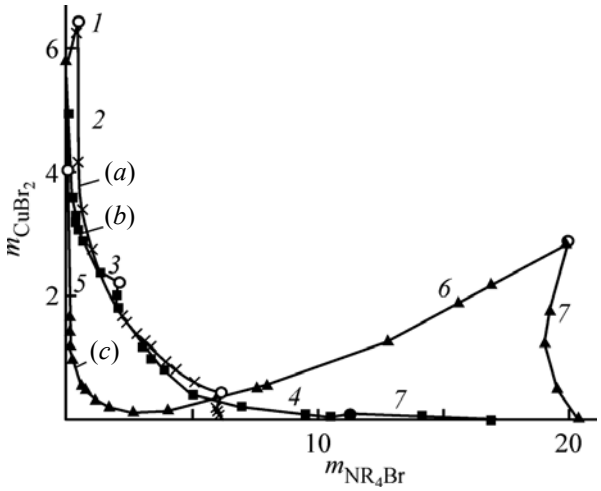

Fig. 1. Solubility isotherms of the systems $CuBr_2$–NR_4Br–H_2O (R = (*a*) Me, (*b*) Et, and (*c*) *n*-Bu at 25°C. (m_{CuBr_2}, m_{NR_4Br}) Solubility (mol kg^{-1} H_2O); the same for Fig. 2. Crystallization branch: (*1*) $CuBr_2$, (*2*) $(NMe_4)_2CuBr_4$, (3) NEt_4CuBr_3, (*4*) $(NEt_4)_2CuBr_4$, (*5*) NBu_4CuBr_3, (*6*) $(NBu_4)_2CuBr_4$, and (*7*) NR_4Br. (Circles) Eutonic points.

in the ternary systems in comparison with the binary systems containing lower members of the series of tetraethylammonium bromides.

In studying the solution-solid phase equilibria in the ternary systems it is appropriate to make comparison of the single crystallization branches, which correspond to constant composition of the bottom phase, rather than to analyze the solubility isotherm as a whole.

Because the stability constant of copper bromo-complexes (K_1 = 0.97 [10]) is close to the association constant of tetraethylammonium bromide (K=1.26 [10]) at $K_{sa\ t} > K_{non\text{-}sat,}$ the calculations [15,16] predict salting-out (salting-in) branch in the solubility isotherm. Indeed, on addition of minor amounts of $CuBr_2$ to the NMe_4Br saturated solution the salting-out of NMe_4Br was observed at the Cu^{2+} concentrations up to 0.1 mol kg^{-1} H_2O. As was mentioned above, the contact ion pairs are precursors of the solid phase and at larger concentration of bromide ions their threshold concentration is attained at lesser concentration of NMe_4Br. On further increase in the $CuBr_2$ concentration, the salting-out of tetraethylammonium is changed to salting-in. This is because at larger concentrations of $CuBr_{2,}$ a Cu^{2+} ion competes with tetraethylammonium ions for the bromide ion in the ion-cation association.

In the system $CuBr_2$–NEt_4Br–H_2O, the crystallization branch of NEt_4Br shows the sharp and strong salting-out. The strong structure-breaking effect exerted by bromo

cuprate complexes on the water causes hydrogen bonds to break not only in the structure of pure water but also in the water clusters formed around NEt_4^+ cations. As a result, the NEt_4^+–Br association increases and the threshold concentration of precursors of the solid phase is attained at lesser concentrations.

In the system $CuBr_2$–NBu_4Br–H_2O, the solubility of tetrabutylammonium bromide depends only slightly on the copper bromide concentration over the entire crystallization branch (the decrease in the NBu_4Br concentration in a saturated ternary solution, in comparison with binary solution, does not exceed 6%). This suggests that in the solution at least two processes proceed exerting the opposite effects on the solubility. In a tetrabutylammonium bromide saturated solution, some of the NBu_4^+ cations are in the form of cation-cation associates possessing hydrophobic properties. The increase in the total concentration of the ions in the solution in the presence of copper(II) bromide showed break the hydration shells of such associates, thus making interaction of bromide anions and tetrabutylammonium cations stronger. This will cause concentration of the precursors of the solid phase to increase and tetrabutylammonium bromide to salt-out. On the contrary, the introduction of copper(II) ion, which forms complexes with bromide ions, stabilizes cation associates and increases the solubility of tetrabutylammonium bromide. Thus, the effects exerted by two processes on the NBu_4Br solubility on the branch of its crystallization compensate each other.

The effect of tetraalkylammonium bromides on the solubility of copper(II) bromide is also determined by competition of two processes. These are formation of copper(II) acido complexes and NR_4^+–Br– association. The stronger association of tetramethylammonium bromide decreases the concentration of free bromide ions in the solution, which results in the left-side shift of the equilibrium

$$Cu(H_2O)_5Br^+_{aq} + Br^-_{aq} \leftrightarrows Cu(H_2O)_4Br^2_{aq} + H_2O_{aq}.$$

Correspondingly, the threshold concentration of the electroneutral dibromocomplexes is attained at larger concentrations of copper(II) bromide; the uniform salting-in of this salt is observed. The same situation was also found in the previously studied system $CuBr_2$–$CsBr$–H_2O [18], where the constant of the cesium bromide association (1.07) is also larger than the stability constant of copper(II) bromocomplexes.

In the system $CuBr_2$–NEt_4Br–H_2O, sharp and very strong salting-out is observed in the crystallization branch of $CuBr_2$. The introduction of NEt_4Br into a copper(II) bromide saturated solution sharply decreases the $CuBr_2$ concentration by approximately 1 mol kg^{-1} H_2O. The concentration of NEt_4Br at the eutonic point is 0.10 mol kg^{-1} H_2O. Because the NEt_4^+–Br^- association is weak, the tetraethylammonium ion cannot compete with copper(II) cation in formation of associates with bromide ion and therefore, tetraethylammonium bromide simply serves as anion donor. In this case, the equilibrium of the complex formation shifts to the right, and the concentration of the copper ions necessary to attain the threshold concentration of dibromocomplexes decreases correspondingly. The same tendency is also retained for the system $CuBr_2$–NBu_4Br–H_2O, where the tetraalkylammonium bromide association is even weaker: with minor amounts of tetrabutylammonium bromide added to the saturated solution, the $CuBr_2$ concentration is decreased by about 2 mol kg^{-1} H_2O.

In the system $CuBr_2$–NMe_4Br–H_2O a complex salt formed of the composition $(NMe_4)_2CuBr_4$. The run of the crystallization branch of the compound $(NMe_4)_2CuBr_4$ resembles the run of crystallization branches of the complex compounds formed in the $CuBr_2$–$CsBr$–H_2O system. The only difference is that in the ternary system containing cesium bromide two complex salts, $CsCuBr_3$ and Cs_2CuBr_4, are formed (Fig. 2). The solubilities in the region of crystallization of complex salts in these two systems are similar.

In both cases, salting-out of the complex salts arises from the strong structure-breaking effect exerted by cesium and tetramethylammonium cations on water and hydration spheres of other ions in the solution. Dehydration of copper cations, bromide ions, and complex $CuBr_n^{2-n}$ particles intensifies acido complex formation and, in the case of $CuBr_4^{2-}$ anion, strengthens the association between complex anion and inner-sphere cation owing to the breaking the hydration shell. The increasing concentration of the associates, precursors of the solid phase, decreases the saturation concentration.

In the system $CuBr_2$–NEt_4Br–H_2O, two complex salts, $(NEt_4)_2CuBr_4$ and NEt_4CuBr_3, are crystallized. The crystallization branches of these complex compounds resemble crystallization branch of $(NMe_4)_2CuBr_4$, but lie a little bit lower (Fig. 1). At the same time, in the system under consideration the low solubility of the

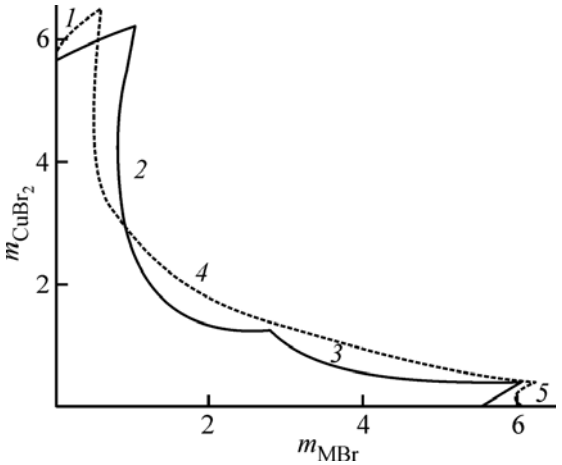

Fig. 2. Solubility isotherms in the $CuBr_2$–MBr–H_2O systems at 25°C. M = Cs [17] (Solid) and M = NMe_4 (dashed). Crystallization branch: (*1*) $CuBr_2$, (*2*) $CsCuBr_3$, (*3*) Cs_2CuBr_4, (*4*) $(NMe_4)_2CuBr_4$, and (*5*) MBr.

complex salt is primarily governed by the specificity of hydration of tetraalkylammonium cation. Hydration of the NEt_{4+} cation possessing large radius and larger length of nonpolar alkyl radical is hydrophobic. Strengthening of the hydrogen bonds between water molecules causes hydration shells of the complex particles to break. As a result, their concentration increases and the complex compound precipitates into the bottom phase.

In the systems $CuBr_2$–NEt_4Br–H_2O and $CuBr_2$–NMe_4Br–H_2O the difference in solubilities of the complex salt is the largest at large concentrations with respect to copper bromide, where a compound NEt_4CuBr_3 crystallizes. In this concentration range the crystallization branch of the complex salt "is pressed to (merges with)" the axis of the copper bromide concentrations. In this region, NEt_4^+ continues to salt-out copper bromide from the solution. Previously, this effect was observed for crystallization branch of $CuBr_2$, only the form of copper(II) in the bottom phase changed.

For the tetraethylammonium bromide concentrations above 6.25 mol kg^{-1} H_2O [NMe_4Br concentration at the $(NMe_4)_2CuBr_4$/NMe_4Br eutonic point], the solubility of the complex compound is even smaller. This phenomenon is explained by prevalence of the clathrate-like structure of tetraethylammonium cations surrounded by clustered water molecules at increased concentration of NEt_4Br in the solution. The tetrahedral $CuBr_4^{2-}$ anions are incompatible with this structure and are pushed away into the bottom phase in the form of $(NEt_4)_2CuBr_4$. On going along the crystallization branch of this salt, from NEt_4Br/$(NEt_4)_2CuBr_4$ eutonic point, a very strong salting-out of $(NEt_4)_2CuBr_4$ (from 11 to 6.9 mol NEt_4Br mol kg^{-1} H_2O) is observed at the increase in copper bromide concentration only by 0.1 mol kg^{-1} H_2O. The fact that NEt_4^+ and $CuBr_n^{2-n}$ ions exert absolutely different effects on the water structure (strengthening and breaking, respectively) and the incompatibility of hydration structures determined by them are responsible for the mutual salting-out and, as consequence, the low solubility in the ternary system.

In the ternary system $CuBr_2$–NBu_4Br–H_2O, two compounds, NBu_4CuBr_3 and $(NBu_4)_2CuBr_4$, are also formed. In the crystallization region of tribromocuprate(II) the very strong salting-out of a complex compound is present; its crystallization branch is strongly pressed to the axes. In this system, salting-out is considerably stronger than in the $CuBr_2$–NEt_4Br–H_2O system (Fig. 1). This result is a manifestation of the hydrophobic hydration, which is revealed considerably stronger for NBu_4^+ than for NEt_4^+.

The processes proceeding in the $CuBr_2$–NBu_4Br–H_2O solution in the region under study are similar to those observed in the system containing tetraethylammonium bromide, only hydrophobic interactions and incompatibility of hydrate formations are exhibited given by them to a larger extent.

In the region of the solutions with a tetrabutylammonium bromide concentration above 3 mol kg^{-1} H_2O, salting-out of the complex salt occurs. The salting-out is probably due to the fact that at high concentration the complete hydration clusters with tetrabutylammonium cations cannot be formed owing to the shortage of water molecules and the cation associates, micelles are formed, the number of which increases with NBu_4Br concentration. The micelle formation is impeded by the counter ions (Br^-) present in the solution. The copper(II) cation binds them to form the anion complexes in the solution, thus decreasing the concentration of free bromide ions. A decrease in the concentration of the counter ions intensifies the cation-cation association, and, consequently, sharply decreases the concentration of free NBu_4^+ cations which are necessary for the formation of the complex salt and its sedimentation into the bottom phase. Therefore, the intensification of the cation-cation association is responsible for the salting-in of $(NBu_4)_2CuBr_4$.

It is not quite rightful to perform a detailed comparison of the extent of crystallization branches of the complex compounds (tri- and tetrabromocuprates) in the systems

under consideration. This is because in this case, the crystallochemical and structural features, along with pure chemical ones (such as formation of precursors of the solid phase in saturated solution), can also play an essential role: the corresponding chlorocuprates(II) in the systems containing tetraethyl- and tetrabutylammonium salts have various structures and contain various types of complex anions (tetramer or dimer) [18,19]. Probably, it is just these crystallochemical features that are responsible for the lack of the crystallization branch of tribromocuprate in the $CuBr_2$–NMe_4Br–H_2O system. Noteworthy that the shift of the eutonic point between two complex salts toward considerably smaller tetraalkylammonium bromide concentrations on passing from NEt_4Br to NBu_4Br is in complete agreement with the concept that the complex formation of copper ion increases with size of the outer-sphere tetraalkyammonium cation.

CONCLUSIONS

(1) The study of the systems $CuBr_2$–NR_4Br–H_2O (R – Me, Et, *n*-Bu) showed that the decrease in the associaton of tetraalkylammonium bromides increases the solubility in the NR_4Br–H_2O binary system owing to the decrease in the concentration of contact ion pairs, precursors of the solid phase.

(2) Owing to incompatibility of the hydration structures formed by tetrabromocuprate(II) anions and tetraalkylammonium cations, the solubility of the complex salts is low.

(3) The specific features of the $CuBr_2$–NBu_4Br–H_2O system are due to hydrophobic hydration of cations at low concentration and due to the cation-cation association in concentrated solutions.

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