

Solubility and Ionic Processes in the $\text{CuX}_2\text{--MX--H}_2\text{O}$ ($\text{X}^- = \text{Cl}^-, \text{Br}^-$; $\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{NH}_4^+, \text{Cs}^+$) Systems

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Summary. Solubility isotherms in the $\text{CuBr}_2\text{--MBr--H}_2\text{O}$ ($\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{Cs}^+$) systems at 298.15 K were measured. The results together with other available literature data for copper chloride and bromide systems were treated by hydration analysis, and comparative discussion of ionic processes taking place in the respective saturated solutions was performed.

Keywords. Alkali metal halides; Association; Copper halides; Hydration; Solubility.

Introduction

In concentrated solutions of electrolytes hydration, hydrolysis, association of different order, and complex formation can be accepted as the main ionic processes. As a rule, these ionic processes can be understood to be competitive. Systems of rising complexity have been studied from this point of view and an attempt to discuss the ionic processes in multicomponent salt systems in relation to the composition and structure of compounds crystallizing from the solution of that systems has been made earlier [1].

In $\text{MgCl}_2\text{--MCl--H}_2\text{O}$ ($\text{M} = \text{Li} - \text{Cs}, \text{NH}_4$) systems hydration of the components and association of alkali metal chlorides may be supposed as the main processes, complexing and hydrolysis being virtually absent. Under these assumptions, the properties of the solutions as well as the processes of formation of double salts have been discussed as a function of the nature of the univalent cation [2]. As a next step, the investigation of the systems $\text{CuCl}_2\text{--MCl--H}_2\text{O}$ [3] made it possible to involve the role of complexing. In the present work, the bromide systems are involved to gain information on the role of the anion in the respective

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Dedicated to Prof. Dr. Heinz Gamsjäger on the occasion of his 70th birthday

processes. For this purpose, the solubility diagrams in the $\text{CuBr}_2 - \text{MBr} - \text{H}_2\text{O}$ ($M = \text{Li, Na, Cs}$) were measured at 25°C .

Recently, a method for the computational analysis of solubility isotherms in ternary systems termed ‘‘hydration analysis’’ has been developed [4] to yield information about ionic processes in saturated electrolyte solutions on the basis of a computational analysis of the solubility isotherms and tested on systems consisting mainly of halogenides and sulfates. The most important value used during hydration analysis in these systems can be defined by Eq. (1), where $(w_0^{\text{B}})_{\text{changed}} = w_0^{\text{B}} - [(n_1^{\text{B}})^{1/2} \cdot w_{0,1}^{\text{A}}/n_1^{\text{A}}] \cdot (n_1^{\text{B}} + 2n_2^{\text{B}})^{1/2}$, when $M^{\text{I}}X$ is the saturating solid phase and $(w_0^{\text{B}})_{\text{changed}} = w_0^{\text{B}} - [(n_1^{\text{B}})^{1/3} \cdot w_{0,1}^{\text{A}}/(2^{2/3} \cdot n_1^{\text{A}})] \cdot (2n_1^{\text{B}} + n_2^{\text{B}})^{2/3}$, for $M^{\text{II}}X_2$ as the saturating solid phase.

$$P = (w_0^{\text{B}})_{\text{changed}}/(M_r)_{\text{H}_2\text{O}} \cdot (n_0^{\text{B}} + n_1^{\text{B}} + n_2^{\text{B}}) \quad (1)$$

Here, the superscripts ‘‘A’’ and ‘‘B’’ refer to the binary and ternary saturated solution of the component, respectively, subscripts ‘‘1’’ and ‘‘2’’ indicate the saturating solid phase and the non-saturating component. The subscript ‘‘0’’ is used for water. $(M_r)_{\text{H}_2\text{O}}$ denotes the relative molecular weight of water, n_i is the number of mols of the i -th component in 100 g of solution specified by the superscript, and $w_{0,1}^{\text{A}}$ is the mass% of water in the binary saturated solution of the respective saturating solid phase. The parameter P is equal to the amount of water that attains different properties in the three-component saturated solution compared to a saturated binary solution [4]. For the sake of clarity, this parameter is usually expressed relative to one mole of the non-saturating component, *i.e.* P/x_1 . Discussion of the results obtained with hydration analysis in families of related systems can yield interesting information, which can help substantially in understanding the questions under consideration. The method has been applied to systems with magnesium chloride recently [5]. In this paper, the application of the method to the systems with copper halides was performed. Among these systems, only the system $\text{CuCl}_2 - \text{NaCl} - \text{H}_2\text{O}$ has been discussed in this way earlier [6], being used as the model system for the application of hydration analysis to systems with complexation. At the same time, the data of different authors were analysed critically.

Results and Discussion

The results of the measurement of solubility isotherms in the $\text{CuBr}_2 - \text{MBr} - \text{H}_2\text{O}$ ($M = \text{Li, Na, Cs}$) systems are summarized in Table 1. In Figs. 1 and 2 all available

Table 1. Solubility in the $\text{CuBr}_2 - \text{MBr} - \text{H}_2\text{O}$ ($M = \text{Li, Na, Cs}$) at 25°C

M	[CuBr ₂]		[MBr]		[H ₂ O] mass%	Solid phase
	mass%	mol · kg ⁻¹	mass%	mol · kg ⁻¹		
Li	55.8	5.65	0	0.00	4.20	CuBr ₂
Li	40.48	3.76	11.26	2.69	48.26	’’
Li	39.25	3.77	14.2	3.51	46.55	’’
Li	33.32	3.16	19.46	4.74	47.22	’’

(continued)

Table 1 (continued)

<i>M</i>	[CuBr ₂]		[MBr]		[H ₂ O]	Solid phase
	mass%	mol · kg ⁻¹	mass%	mol · kg ⁻¹	mass%	
Li	25.88	2.44	26.69	6.48	47.43	''
Li	20.2	1.92	32.66	7.98	47.14	''
Li	17.38	1.70	36.8	9.25	45.82	''
Li	17.3	1.77	39.04	0.29	43.66	''
Li	14.41	1.59	45.1	12.82	40.49	''
Li	13.84	1.55	46.13	13.27	40.03	''
Li	14.12	1.64	47.31	14.12	38.57	CuBr ₂ + 2 LiBr · CuBr ₂ · 2 H ₂ O
Li	12.03	1.37	48.78	14.33	39.19	2 LiBr · CuBr ₂ · 2 H ₂ O
Li	10.91	1.24	49.65	14.49	39.44	''
Li	7.68	0.89	53.86	16.12	38.46	LiBr · 2 H ₂ O + 2 LiBr · CuBr ₂ · 2 H ₂ O
Li	2.55	0.29	58.63	17.39	38.82	LiBr · 2 H ₂ O
Li	1.22	0.14	59.16	17.19	39.62	''
Li	0	0	60.88	17.92	39.12	''
Na	55.8	5.65	0	0.00	44.20	CuBr ₂
Na	52.2	5.28	3.13	0.68	44.45	''
Na	46.77	4.82	9.79	2.19	43.44	''
Na	43.24	4.53	13.98	3.18	42.78	''
Na	38.21	4.05	19.6	4.51	42.19	''
Na	31.11	3.51	29.16	7.13	39.73	''
Na	29.99	3.52	31.88	8.13	38.13	CuBr ₂ + NaBr · 2 H ₂ O
Na	29.99	3.52	31.87	8.12	38.14	''
Na	25.57	2.82	33.84	8.10	40.59	NaBr · 2 H ₂ O
Na	17.65	1.76	37.46	8.11	44.89	''
Na	12.72	1.2	39.84	8.16	47.44	''
Na	4.32	0.38	44.78	8.55	50.90	''
Na	1.03	0.09	47.56	8.99	51.41	''
Na	0.0	0	48.58	9.18	51.42	''
Cs	55.8	5.65	0	0.00	44.20	CuBr ₂
Cs	54.05	6.05	5.98	0.70	39.97	''
Cs	53.2	6.22	8.52	1.05	38.28	CuBr ₂ + CsCuBr ₃
Cs	47.73	4.80	7.76	0.82	44.51	CsCuBr ₃
Cs	43.25	4.01	8.34	0.81	48.41	''
Cs	30.46	2.28	9.80	0.77	59.74	''
Cs	29.24	2.19	10.96	0.86	59.80	''
Cs	24.93	1.86	15.15	1.19	59.92	''
Cs	17.17	1.35	25.76	2.12	57.07	''
Cs	14.77	1.21	30.10	2.62	55.13	''
Cs	14.72	1.23	31.91	2.80	53.37	CsCuBr ₃ + Cs ₂ CuBr ₄
Cs	12.05	1.03	35.37	3.16	52.58	Cs ₂ CuBr ₄
Cs	9.36	0.80	38.59	3.48	52.05	''
Cs	4.94	0.46	56.52	4.50	38.54	''
Cs	4.45	0.45	50.73	5.33	44.82	''
Cs	3.89	0.40	52.47	5.65	43.64	''
Cs	3.75	0.41	54.33	6.09	41.92	Cs ₂ CuBr ₄ + CsBr
Cs	2.99	0.31	54.22	5.95	42.79	CsBr
Cs	0	0	55.23	5.54	44.77	''

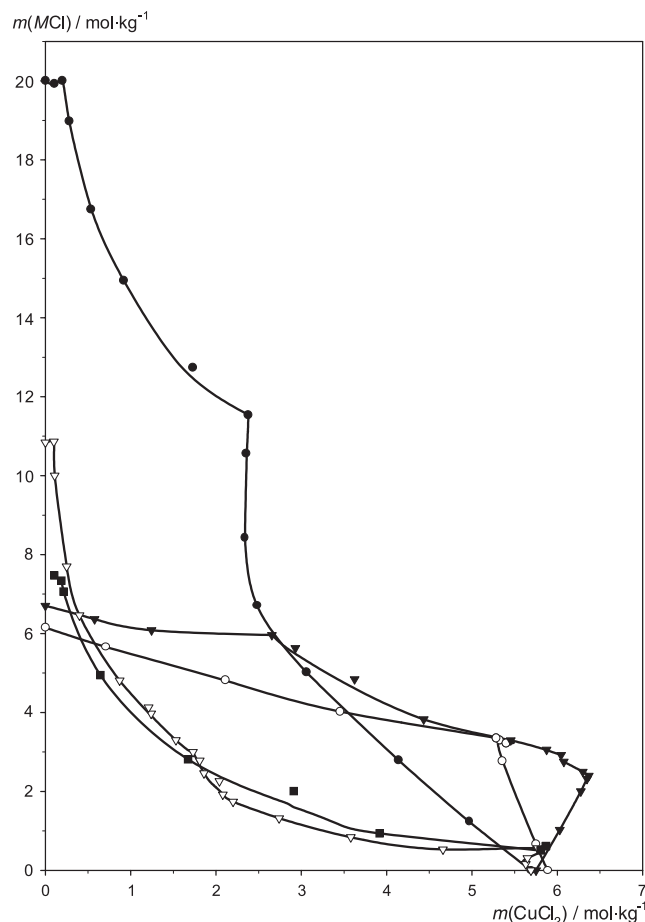


Fig. 1. Solubility isotherms in the $\text{CuCl}_2 - \text{MCl} - \text{H}_2\text{O}$ ($M = \text{Li, Na, K, NH}_4, \text{Cs}$) systems at 25°C ($\bullet \dots M = \text{Li}$, $\circ \dots M = \text{Na}$, $\nabla \dots M = \text{K}$, $\blacktriangledown \dots M = \text{NH}_4$, $\blacksquare \dots M = \text{Cs}$; all experimental data are taken from Ref. [3])

solubility isotherms in the $\text{CuX}_2 - \text{MX} - \text{H}_2\text{O}$ ($X = \text{Cl, Br}$; $M = \text{Li, Na, K, NH}_4, \text{Cs}$) systems at 25°C are depicted. The data for the systems with KBr were taken from our previous measurements [7], the data for the systems with NH_4 were taken from literature [8, 11].

Several systems related to this topic were studied also by *Tepavicharova et al.* [9]. Their solubility curves, however, are not suitable for a treatment with hydration analysis, because a small amount of HBr was added to some phase complexes to prevent hydrolysis [10]. In such a case, the presence of acid would lead to elevated values of the parameter P , overcharging all other effects.

Beside of the differences in the quality and numbers of crystallizing solid phases, the systems depicted in Figs. 1 and 2 differ mutually also in the shape of the individual crystallization branches. Conventionally, these facts have been described only in the terms of “salting-in” or “salting-out” of the component. We wanted to apply the hydration analysis to these systems to obtain more detailed information about the ionic processes in the respective saturated solutions. The important data of the respective crystallization branches are summarized in Table 2.

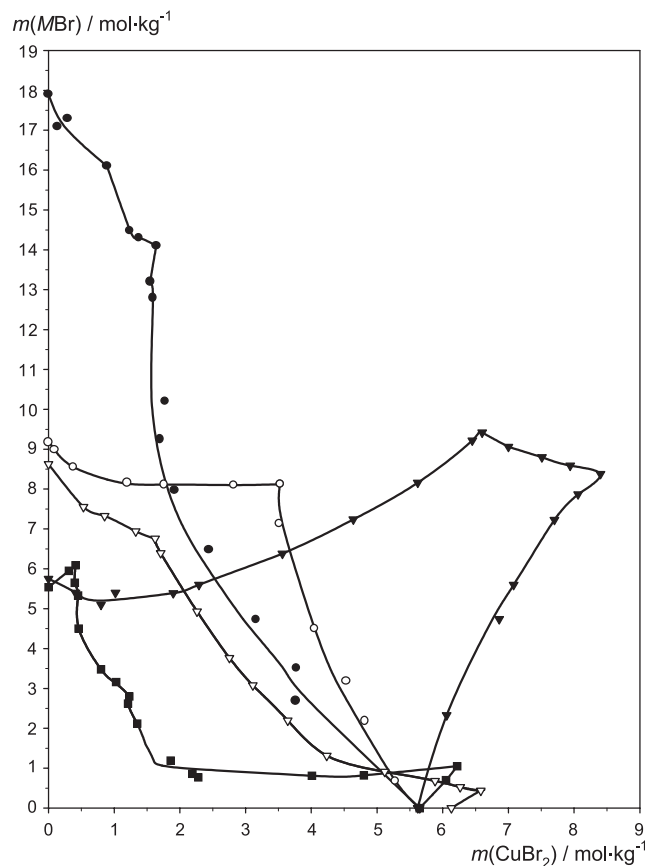


Fig. 2. Solubility isotherms in the $\text{CuBr}_2 - \text{MBr} - \text{H}_2\text{O}$ ($M = \text{Li}, \text{Na}, \text{K}, \text{NH}_4, \text{Cs}$) systems at 25°C ($\bullet \dots M = \text{Li}$, $\circ \dots M = \text{Na}$, $\nabla \dots M = \text{K}$ (Ref. [7]), $\blacktriangledown \dots M = \text{NH}_4$ (Ref. [8, 11]), $\blacksquare \dots M = \text{Cs}$)

The conditions of applicability of the method for a given crystallization branch have been discussed in detail in Ref. [5]. The main one is, that the crystallization branch has to be “long enough” and to contain a sufficient number of experimental points. For the purpose of this work, we define the molality of the component present in the liquid phase only $m^E > 1$ and $n > 3$ as the condition for applicability of the method. When taking this condition into account, the following material are to our disposal: 1) Solubility of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in solutions of alkali metal chlorides (Fig. 3). For the sake of a discussion of hydrolysis, which must be opened as the result of the analysis of all systems, also the hydration analysis of solubility of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in solutions of CsCl is involved in Fig. 3, in spite of $m^E = 0.55 \text{ mol} \cdot \text{kg}^{-1}$. 2) Solubility of NaCl and KCl in solutions of CuCl_2 (Fig. 4). 3) Solubility of CuBr_2 in solutions of LiBr , NaBr , and KBr (Fig. 5). 4) Solubility of $\text{NaBr} \cdot 2\text{H}_2\text{O}$, KBr , and NH_4Br in solutions of CuBr_2 (Fig. 6).

On the solubility branches of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in solutions of LiCl , NaCl , and KCl (Fig. 3a–c), the hydration of the alkali metal ions and the complex formation due to the excess of chloride ion brought about by the alkali metal chloride take place simultaneously. In the system with lithium, hydration of the lithium ion is strong. Therefore positive values of the parameter P/x_1 result as long as the amount of

Table 2. Summary of material available for the $\text{CuX}_2 - \text{MX} - \text{H}_2\text{O}$ ($X = \text{Cl, Br}$; $M = \text{Li, Na, K, NH}_4, \text{Cs}$) systems at 25°C

Saturating solid	Not saturating component	m^E $\text{mol} \cdot \text{kg}^{-1}$	Number of points	Neighbour solid
$\text{LiCl} \cdot \text{H}_2\text{O}$	CuCl_2	0.11	2	$\text{LiCl} \cdot \text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$
NaCl	"	5.40	6	$\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$
KCl	"	2.64	3	$2 \text{KCl} \cdot \text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$
NH_4Cl	"	0.15	2	$2 \text{NH}_4\text{Cl} \cdot \text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$
CsCl	"	0.10	1	$2 \text{CsCl} \cdot \text{CuCl}_2$
$\text{LiBr} \cdot 2 \text{H}_2\text{O}$	CuBr_2	0.89	3	$2 \text{LiBr} \cdot \text{CuBr}_2 \cdot 2 \text{H}_2\text{O}$
$\text{NaBr} \cdot 2\text{H}_2\text{O}$	"	3.52	5	CuBr_2
KBr	"	6.60	10	$\text{KBr} \cdot \text{CuBr}_2$
NH_4Br	"	1.62	5	$2 \text{NH}_4\text{Br} \cdot \text{CuBr}_2 \cdot 2 \text{H}_2\text{O}$
CsBr	"	0.31	2	$2 \text{CsBr} \cdot \text{CuBr}_2$
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	LiCl	11.54	7	$\text{LiCl} \cdot \text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$
"	NaCl	3.30	6	NaCl
"	KCl	3.62	4	$\text{KCl} \cdot \text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$
"	NH_4Cl	1.02	2	$2 \text{NH}_4\text{Cl} \cdot \text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$
"	CsCl	0.56	3	$\text{CsCl} \cdot \text{CuCl}_2$
CuBr_2	LiBr	14.12	10	$2 \text{LiBr} \cdot \text{CuBr}_2 \cdot 2 \text{H}_2\text{O}$
"	NaBr	8.12	6	$\text{NaBr}_2 \cdot 2 \text{H}_2\text{O}$
"	KBr	8.38	7	$\text{KBr} \cdot \text{CuBr}_2$
"	NH_4Br	0.44	1	$2 \text{NH}_4\text{Br} \cdot \text{CuBr}_2 \cdot 2 \text{H}_2\text{O}$
"	CsBr	1.05	2	$\text{CsBr} \cdot \text{CuBr}_2$

water is sufficient by height (in this case, about six mol of water per mol of ions present). After that, the values of P/x_1 become increasingly lower as there is not enough water for complete hydration of the species present, and association and complexation is the main phenomenon. A similar competition between hydration and complexation yields a set of negative values of P/x_1 close to -1.5 in the case of sodium and close to -6.7 in the case of potassium. These absolute values $[(P/x_1)_{\text{Na}^+} > (P/x_1)_{\text{K}^+}]$ as well as the fact that those values grow slowly in the case of sodium with a rising concentration of NaCl yield the idea of consecutive complex formation in the system $\text{Cu}^{2+} - \text{Cl}^-$, afflicted by bonding of deliberated water to the hydration spheres of sodium ions and less disturbed in the case of potassium.

The same situation observed from the side of saturated solutions of alkali metal halides is seen in Fig. 4. The formation of chloro-complexes is caused by addition of copper chloride into saturated solutions of $M\text{Cl}$. In the case of sodium, the water deliberated during the formation of complex ions is incorporated partially in the hydration spheres of sodium ions. Therefore, the absolute value of P/x_1 is larger in the case of $M = \text{K}$ than in the case of the $M = \text{Na}$ system.

The hydration analysis of solubility of CuBr_2 in solutions of LiBr , NaBr , and KBr (Fig. 5) yields results similar to those in chloride systems with only one difference. In the region of small concentration of alkali metal chloride a "tail" of elevated values of P/x_1 appears. Such a phenomenon can be put into relation with the hydrolysis of copper ions. If we take the classical reaction

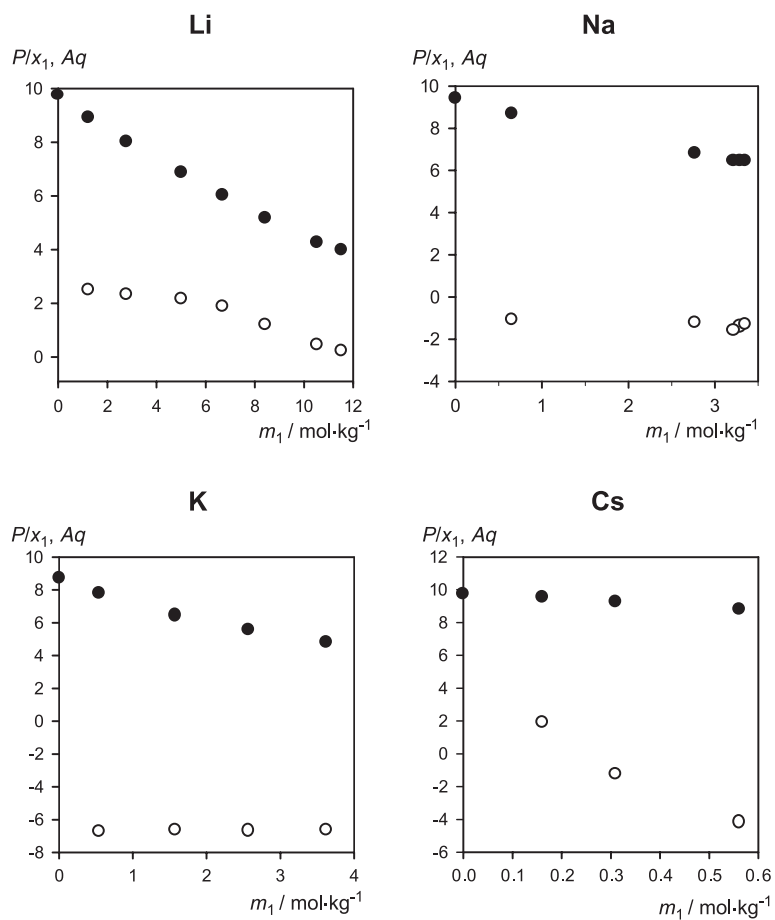


Fig. 3. Hydration analysis of the solubility of $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$ in solutions of alkali metal chlorides ($\bullet \dots Aq$, $\circ \dots P/x_1$)

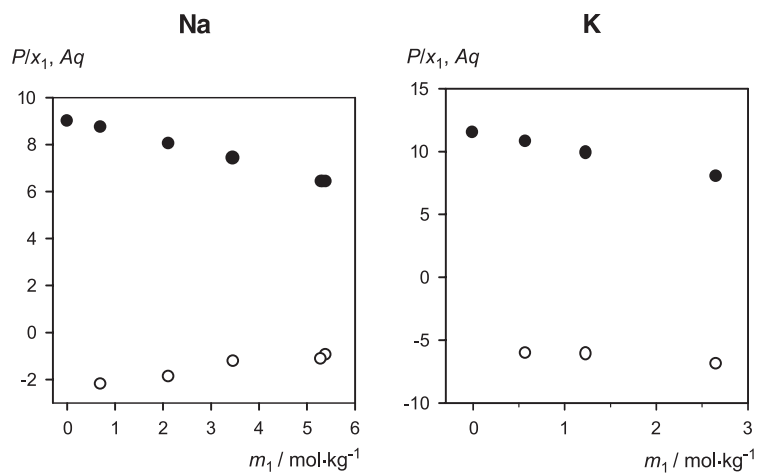


Fig. 4. Hydration analysis of solubility of NaCl and KCl in solutions of CuCl_2 ($\bullet \dots Aq$, $\circ \dots P/x_1$)

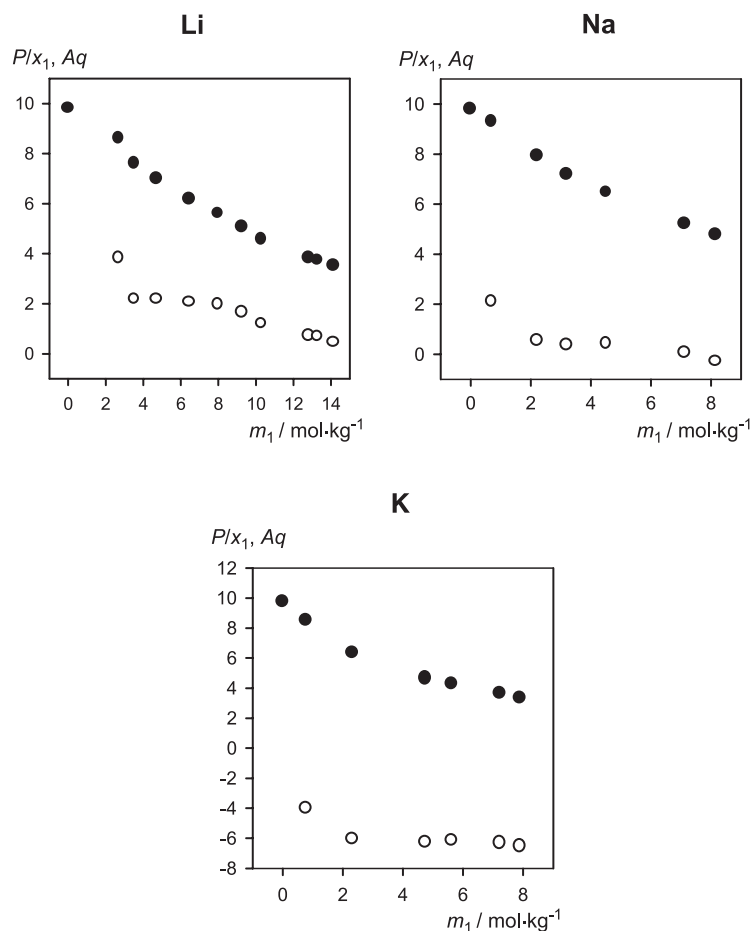


Fig. 5. Hydration analysis of solubility of CuBr_2 in solutions of LiBr, NaBr and KBr ($\bullet \dots Aq$, $\circ \dots P/x_1$)

scheme, $\text{Cu}^{2+} + \text{H}_2\text{O} \rightarrow \text{CuOH}^+ + \text{H}^+$, into account, strong water bonding during formation and/or hydration of the hydroxonium ion is easy to understand. With greatest probability, ions of the general formulae $[\text{Cu}_p(\text{H}_2\text{O})_r(\text{OH})_q \text{Br}_s]^{(q+s-2p)-}$ (with $q \neq 0$) are present in a saturated solution of copper bromide. With highest probability, their concentration is very low, but the big sensitivity of hydration analysis towards hydrogen ions produced during formation of such ions allows to bring evidence of them. The first addition of alkali metal bromide and the first excess of bromide ions shift the equilibrium of the formation of such hydroxo ions to the right. With a bigger excess of bromide ions, the equilibria producing tri- and tetrabromo ions prevail and the situation becomes similar to that observed in chloride systems. In this sense, the results may be considered as supporting the idea, that the complexation of chloride ions is stronger than that of bromide.

However, some hydrolysis of the type just considered is probable even in chloride systems, in spite of the fact that only very slightly elevated values of P/x_1 are observed in the first point of hydration analysis curves in the systems with lithium, sodium, and potassium chloride. The curve of hydration analysis on

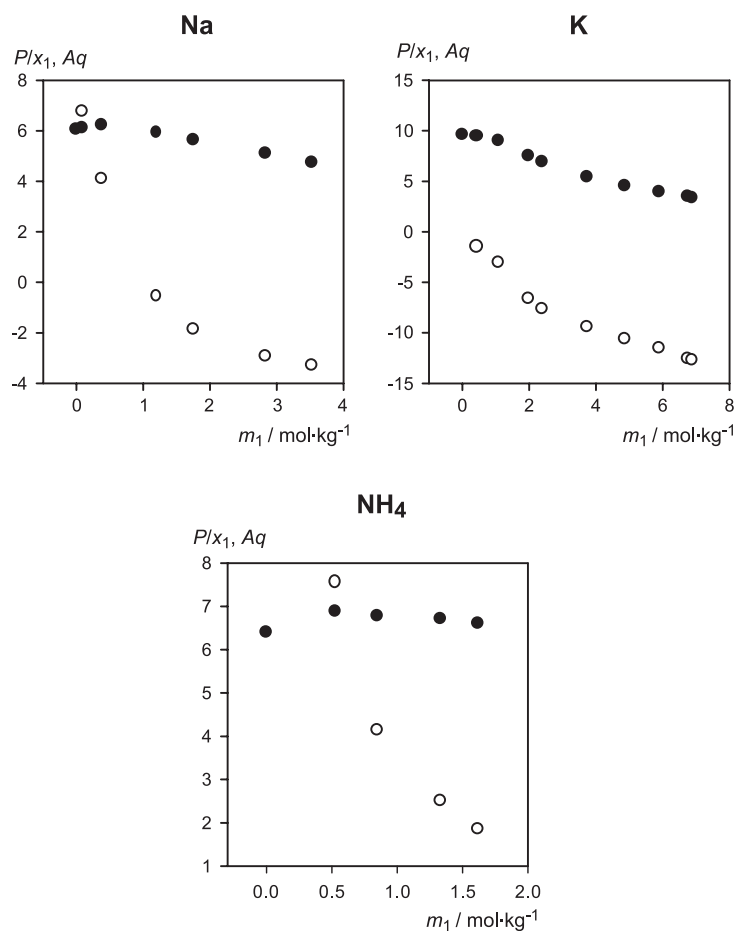


Fig. 6. Hydration analysis of solubility of $\text{NaBr}\cdot 2\text{H}_2\text{O}$, KBr and NH_4Br in solutions of CuBr_2 (●... Aq , ○... P/x_1)

the crystallization branch of copper chloride in solutions of cesium chloride (Fig. 3d) is falling at concentrations up to 0.6 molal CsCl . Such brightening of the “hydrolysis tail” seems to answer to older assuming of reasonable association [3] in solutions of CsCl . The real concentration of chloride ions, which is the decisive factor for the equilibria involving hydrolysis and complexation, is lower in solutions of CsCl and elevated values of P/x_1 are observable.

The hydration analysis of the crystallization branches of $\text{NaBr}\cdot 2\text{H}_2\text{O}$ and KBr in solutions of CuBr_2 (Fig. 6) yields a set of values falling as the concentration of CuBr_2 rises. For the explanation of such a shape of hydration analysis curves we must take into account the fact, that the concentration of copper starts from low values and rises to eutonic concentrations on these crystallization branches. The coexistence of hydrolytic and complexing equilibria seems to prefer the hydrolysis first. Complexation grows stronger as the concentration of copper rises (or, reciprocally, the effect of deliberating water molecules during complexation is more suppressed by bonding water molecules due to hydrolytic equilibria in solutions with low concentration of copper).

Hydrolysis of copper ions has been observed several times already. As far as the authors are aware, no more detailed discussions of these phenomena as well as the comparison on chloride and bromide systems has been performed until now.

As far as the mutual comparison between chloride and bromide systems is concerned as well as more detailed discussions in the series of alkali cations, the situation is more complicated by a different hydration of the equilibrium solid phases (CuCl_2 occurs as dihydrate at 25°C and CuBr_2 as anhydrous self, and an analogous difference is valid between sodium and potassium bromide). The existence of a hydrated equilibrium solid phase may afflict the values of P/x_1 in a substantial way [12].

Conclusions

By definition, hydration analysis yields detailed information about ionic processes taking place in the ternary saturated solutions. In this case, a sufficient amount of comparative material was at our disposal for the first time. The main conclusions which can be made based on the results just presented are:

1. In saturated solutions of copper halides, halide complexes are present without any regard to the fact, if a double salt occurs as neighbouring solid phase or the system is eutonic as in the case of sodium.
2. In the systems under consideration, stronger complexation occurs in chloride systems than in bromide systems.
3. Occurrence of mixed hydroxo complexes of the general formula $[\text{Cu}_p(\text{H}_2\text{O})_r(\text{OH})_q\text{X}_s]^{(q+s-2p)-}$ (with $q \neq 0$) is probable in chloride systems and may be declared as proven in solutions of copper bromide. In saturated solutions of copper halides, hydrolysis producing such ions is supported by a small concentration of alkali metal halides. A reasonable excess of halide ions leads to predominant formation of generally known chloro- and bromo ions. If copper halide is added into saturated solutions of alkali metal halides, the concentration of the copper ion is the most important factor influencing the respective equilibria.

Experimental

Reagent grade chemicals salts recrystallized twice from bidistilled H_2O were used in this study. The phase complexes were equilibrated in a water thermostat for 24 h, the temperature being kept constant within $25 \pm 0.1^\circ\text{C}$. The equilibrium was checked by complexometric determination of copper contents in the saturated solutions. After equilibration the contents of copper in the saturated solutions were determined complexometrically and that of bromide ion argentometrically with potentiometric check of the equivalent point. The content of alkali metal was calculated from the condition of electroneutrality, H_2O was calculated by difference. For the calculations of hydration analysis, an universal computational program named "HYDRAN" was developed in Microsoft Visual Basic Version 5.0 [12]. Solubility diagrams and other graphs were created using the Sigma Plot version 4.01 program.

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