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Solution–Solid Phase Equilibrium in the Systems $MgBr_2$–NR_4Br–H_2O at 25°C (R = Me, Et, Bu)

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Abstract—Solubility in the ternary systems $MgBr_2$–NR_4Br–H_2O (R = Me, Et, Bu) at 25°C was determined by the isothermal saturation method. A comparative analysis of phase diagrams was fulfilled. The results obtained were interpreted in the context of competition between hydration and association processes in water-salt systems. The structure of double salts $NMe_4Br\cdot MgBr_2\cdot 6H_2O$ and $NEt_4Br\cdot MgBr_2\cdot 8H_2O$ was determined, and the possibility for predicting compositions of crystallizing double salts on the basis of crystallographic characteristics of ions was analyzed.

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Ternary systems MgX_2–MX–H_2O (M is a singly charged cation of an alkali metal or ammonium) are a traditional subject of studying in the chemistry of water–salt systems. Unique stability of the first hydrate sphere of the magnesium ion (it remains practically constant both on the variation of the second salt component and on temperature increase up to 200°C) makes it possible to analyze systematically the effect of the second component nature on the properties of ternary water–salt solutions with dominating hydration interactions. However, until now ternary systems of this type with such singly charged cations as tetraalkylammonium ions remained practically unstudied. Cations of ternary ammonium bases NR_4^+ in many respects are a prolongation of the series of alkali metals cations, but exhibit some specific properties caused by a special type of interaction between an ion and water, i.e. a hydrophobic hydration. These properties are reflected also in the shapes of solubility isotherms of ternary systems and in the composition and structure of crystallizing compounds [1, 2]. In the absence of strong interactions in a solution (complex formation and hydrolysis) the specificity of the nature of tetraalkylammonium cations should be most pronounced.

When analyzing solubility in ternary systems (Fig. 1), it seems reasonable to consider the following characteristics of solubility isotherms: the shape and expansion of crystallization branches of initial bromides, the presence and composition of complicated compounds. On passing from the bromide of an alkali metal (of cesium, the nearest in size to tetraalkylammonium cations) to tetramethylammonium bromide a very strong weakening of salting-out a salt containing a singly charged cation occurs. The intensity of the salting-out, dmMBr/dmMgBr$_2$ [at $m(MgBr_2)$ 0 mol/kg H_2O], is –1.32 for CsBr and only –0.38 for NMe_4Br, i.e. the salting-out is weakened approximately by a factor of three. This sequence prolongs the series observed also for other alkaline cations [3–5], and can be explained by strengthening the destructing action of singly charged cations on water: large singly charged cations, incapable of forming proper stable hydrate shell, destroy the system of hydrogen bonds in a solution, thus strengthening the dissolving power of a solvent [6].

In the system $MgBr_2$–NEt_4Br–H_2O strong salting-out of tetraethylammonium bromide is observed in the initial section of its crystallization branch. The negative hydrophylic hydration of the NMe_4^+ cation is replaced by the hydrophobic hydration of the NEt_4^+ cation. The increase in the bromide anion concentration, as well as the formation of the magnesium hexaaquo ion $Mg(H_2O)_6^{2+}$ will result in the destructing “local icebergs” formed around the tetraalkylammonium cation [7] and, therefore, in the intensification of the $NR_4^+\cdot Br^-$ association. Accordingly, the threshold concentration of contact ionic pairs, which are precursors of the solid phase formation, will be

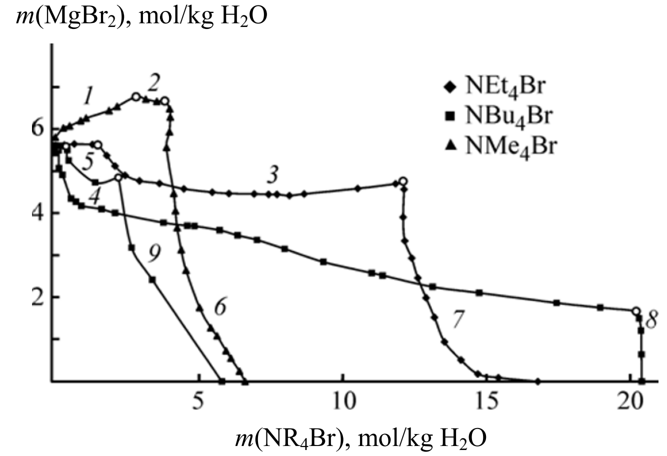

Fig. 1. Solubility isotherms in the systems $MgBr_2$–NR_4Br–H_2O (R = Me, Et, Bu) and $MgBr_2$–CsBr–H_2O [5], at 25°C: (*1*) $MgBr_2 \cdot 6H_2O$, (*2*) $NMe_4Br \cdot MgBr_2 \cdot 6H_2O$, (*3*) $NEt_4Br \cdot MgBr_2 \cdot 8H_2O$, (*4*) $4NBu_4Br \cdot MgBr_2 \cdot 6H_2O$, (*5*) $CsBr \cdot MgBr_2 \cdot 6H_2O$, (*6*) NMe_4Br, (*7*) NEt_4Br, (*8*) NBu_4Br, and (*9*) CsBr.

reached at a lower salt concentration. On passing to tetrabutylammonium bromide, the cation–cation association becomes a dominating process [8] in concentrated solutions of this salt, and the addition of the second salt component practically stops to affect the solubility.

The crystallization field of magnesium bromide decreases on passing from the system $MgBr_2$–NMe_4Br–H_2O to $MgBr_2$–NBu_4Br–H_2O (Fig. 1). If tetraalkylammonium cations are considered as a prolongation of the alkali metals series, it is necessary to note that the expansion of magnesium bromide crystallization branches increases on passing from the system containing potassium bromide to the system with cesium bromide [3–5] and reaches the greatest value in the system containing tetramethylammonium bromide. The salting-out of $MgBr_2$ increases also in the same order when the second salt component is added. Probably it is connected with increasing solubility of double salts owing to a decrease in the crystal lattice energy [5].

In ternary water–salt systems containing bromides of alkali metals and magnesium, a series of double salts is formed, the majority of which belong to carnallite-like compounds. At present the question of conditions for the formation of such salts remains debatable to some extent. In [9] the crystallographic criterion: factor of tolerance was proposed, which is calculated by formula (1).

$$t = \frac{r_A + r_C}{\sqrt{2}(r_B + r_C)}. \tag{1}$$

Here t is the factor of tolerance, r_A is a radius of the hexaaquo cation $Mg(H_2O)_6^{2+}$, r_B is a radius of a singly charged cation, and r_C is a radius of an anion.

For salts ABC_3 with a perovskite-like structure (such structure is observed for the majority of carnallite-like salts [10]) the t value should lie within the limits from 0.8 up to 1. We have calculated the factor of tolerance t for known and hypothetical salts $MBr \cdot MgBr_2 \cdot 6H_2O$. The results are given below.

M^+	Na^+	K^+	NH_4^+	Rb^+	Cs^+	NMe_4^+	NEt_4^+	NPr_4^+	NBu_4^+
t	1.15	1.02	1.00	0.99	0.94	0.83	0.72	0.65	0.59

It follows from the above values of the factors of tolerance that only the system containing tetramethylammonium bromide among the systems $MgBr_2$–NR_4Br–H_2O (R = Me, Et, Bu) should form carnallite-like double salts. In fact, in this system the double salt analogous in composition to other $MBr \cdot MgBr_2 \cdot 6H_2O$ salts, namely $NMe_4Br \cdot MgBr_2 \cdot 6H_2O$ (**I**) is crystallized.

The basic crystallographic parameters of salt **I**: orthorhombic crystal system, space group $P2_12_12_1$, a 7.7445(2) Å, b 9.4562(4) Å, c 22.5197(8) Å, V 1649.2(1) Å^3, Z 4, d_x 1.797 g cm^{-3}, $R1$ 0.0519 ($wR2$ 0.0733, 5290 reflexes) (Tables 1 and 2). The structure of this compound can be presented as an island structure. Practically regular isolated octahedra with magnesium atoms $\{Mg(H_2O)_6\}$ [distances Mg–O 2.034(4)–2.090(3) Å, angles OMgO 84.08(16)°–95.23(16)°] and tetrahedral tetramethylammonium cations [distances C–N 1.481(6)–1.491(6) Å, angles CNC 108.4(3)°–110.1(4)°] alternate with isolated bromide anions. All bromine atoms interact with water molecules of magnesium polyhedrons by means of numerous weak hydrogen bonds O–H···Br (Fig. 2).

In the system $MgBr_2$–NEt_4Br–H_2O the double salt $NEt_4Br \cdot MgBr_2 \cdot 8H_2O$ (**II**) is crystallized. The basic structural characteristics of compound **II** crystals: triclinic system, space group P-1, a 7.2679(3) E, b 12.0063(5) Å, c 13.5779(7) Å, 81.647(4), 82.061(4), 74.862(4), V 1125.33(9) Å^3, Z 2, d_x 1.589 g cm^{-3}, R_1 0.0364 (wR_2 0.0736, 3612 reflects). The formation of such double salts in MX–MX_2–H_2O systems was not reported earlier in the literature [10]. The compounds $LiCl \cdot MgCl_2 \cdot 7H_2O$ [11] and $LiBr \cdot 2MgBr_2 \cdot 16H_2O$ [12] appear to be the closest case, but in these compounds

Table 1. Coordinates (×10^4) and thermal parameters (Å^2×10^3) of basis atoms in the structure of compounds **I** and **II**

Atom	*x*	*y*	*z*	U_{eq}
		Compound **I**		
Br^1	5654(1)	13544(1)	425(1)	40(1)
Br^2	10582(1)	7943(1)	1254(1)	52(1)
Br^3	15324(1)	5809(1)	2273(1)	72(1)
Mg	19571(2)	8060(2)	3298(1)	31(1)
O^1	2535(4)	14093(4)	1357(2)	54(1)
O^2	8442(4)	8549(4)	2480(1)	56(1)
O^3	9418(5)	12510(4)	902(2)	58(1)
O^4	18293(5)	6154(4)	3298(2)	59(1)
O^5	19081(5)	4924(4)	1681(2)	68(1)
O^6	11648(5)	7201(6)	2831(2)	91(2)
N	5612(5)	9060(4)	556(2)	33(1)
C^1	5700(7)	9673(5)	1165(2)	55(1)
C^2	7115(6)	9549(6)	196(3)	50(2)
C^3	4001(6)	9544(5)	260(2)	50(2)
C^4	5615(7)	7496(4)	593(3)	55(1)
		Compound **II**		
Br^1	4898(1)	13511(1)	7308(1)	42(1)
Br^2	6079(1)	12774(1)	3628(1)	43(1)
Br^3	10968(1)	12374(1)	983(1)	53(1)
Mg^1	5000	15000	0	34(1)
Mg^2	10000	15000	5000	28(1)
O^1	7837(4)	14217(3)	–403(3)	56(1)
O^2	5169(5)	14354(4)	1479(3)	60(1)
O^3	5628(4)	16522(3)	229(3)	53(1)
O^4	2759(4)	14120(3)	5245(2)	48(1)
O^5	8939(4)	14498(3)	6441(2)	45(1)
O^6	9529(4)	13551(3)	4519(3)	47(1)
O^7	9735(5)	14936(4)	1940(2)	53(1)
O^8	12125(5)	12033(3)	3391(3)	64(1)
N	8874(4)	9250(2)	2568(2)	28(1)
C^{1A}	7786(6)	8570(4)	3323(3)	44(1)
C^{1B}	6394(7)	9249(5)	4094(4)	61(2)
C^{2A}	7539(6)	10155(4)	1959(3)	40(1)
C^{2B}	6276(7)	9719(5)	1379(4)	66(2)
C^{3A}	10192(6)	8396(4)	1934(3)	39(1)
C^{3B}	11422(6)	8900(5)	1077(4)	56(1)
C^{4A}	9946(6)	9879(4)	3057(3)	37(1)
C^{4B}	11289(7)	9157(5)	3789(4)	61(2)

Table 2. Hydrogen interactions in the structure of compounds **I** and **II**

D–H···A	*d*(H···A), Å	*d*(D···A), Å	∠(DHA), deg
	Compound **I**[a]		
$O^1–H^{1a}\cdots Br^1$	2.49	3.242(5)	144
$O^1–H^{1b}\cdots Br^{3\#1}$	2.39	3.399(5)	156
$O^2–H^{2a}\cdots Br^2$	2.39	3.270(5)	157
$O^2–H^{2b}\cdots Br^{3\#2}$	2.70	3.572(5)	145
$O^3–H^{3a}\cdots Br^1$	2.42	3.257(5)	154
$O^3–H^{3b}\cdots Br^{1\#3}$	2.48	3.291(5)	160
$O^4–H^{4a}\cdots Br^2$	2.31	3.315(5)	162
$O^4–H^{4b}\cdots Br^3$	2.41	3.275(5)	143
$O^5–H^{5a}\cdots Br^3$	2.49	3.309(5)	160
$O^5–H^{5b}\cdots Br^{2\#4}$	2.29	3.229(5)	155
$O^6–H^{6a}\cdots Br^3$	2.57	3.379(5)	127
	Compound **II**		
$O^1–H^{1b}\cdots O^{7\#1}$	1.80	2.795(6)	173
$O^5–H^{5a}\cdots O^{7\#2}$	1.93	2.754(6)	180
$O^6–H^{6b}\cdots O^8$	1.73	2.729(6)	176
$O^1–H^{1a}\cdots Br^3$	2.38	3.310(5)	174
$O^2–H^{2b}\cdots Br^{1\#2}$	2.42	3.229(5)	152
$O^3–H^{3a}\cdots Br^{1\#3}$	2.56	3.310(5)	157
$O^3–H^{3b}\cdots Br^{3\#4}$	2.20	3.246(5)	167
$O^4–H^{4a}\cdots Br^1$	2.28	3.288(5)	176
$O^4–H^{4b}\cdots Br^2$	2.31	3.284(5)	156
$O^5–H^{5b}\cdots Br^1$	2.55	3.446(5)	157
$O^6–H^{6a}\cdots Br^2$	2.54	3.318(5)	144
$O^7–H^{7a}\cdots Br^{1\#3}$	2.70	3.490(5)	158
$O^7–H^{7b}\cdots Br^3$	2.59	3.370(5)	162
$O^8–H^{8a}\cdots Br^3$	2.50	3.499(5)	166
$O^8–H^{8b}\cdots Br^2$	2.19	3.290(5)	178

[a] Symmetry transformation used for obtaining equivalent atoms in compound **I**: #1 $x-1, y+1, z$; #2 $x-1, y, z$; #3 $x+1, 2.5-y, -z$; #4 $1+x, y, z$; in compound **II**: #1 $2-x, 3-y, -z$; #2 $2-x, 3-y, 1-z$; #3 $1-x, 3-y, 1-z$; #4 $2-x, 3-y, -z$.

“additional” water molecules enter into the hydrated sphere of the lithium ion. The X-ray structural study has shown that corrugated cationic and anionic layers parallel to *xz* plane alternate in the crystals of compound **II**. Both bromine atoms and free water molecules are involved in the interaction with the

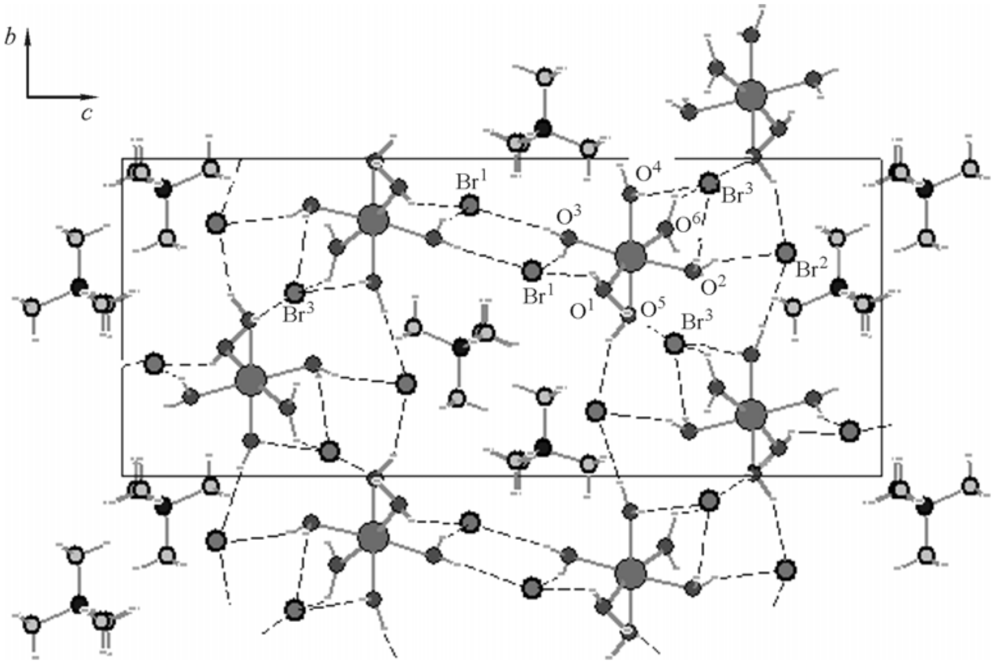

Fig. 2. Structure of the double salt $NMe_4Br{\cdot}MgBr_2{\cdot}6H_2O$.

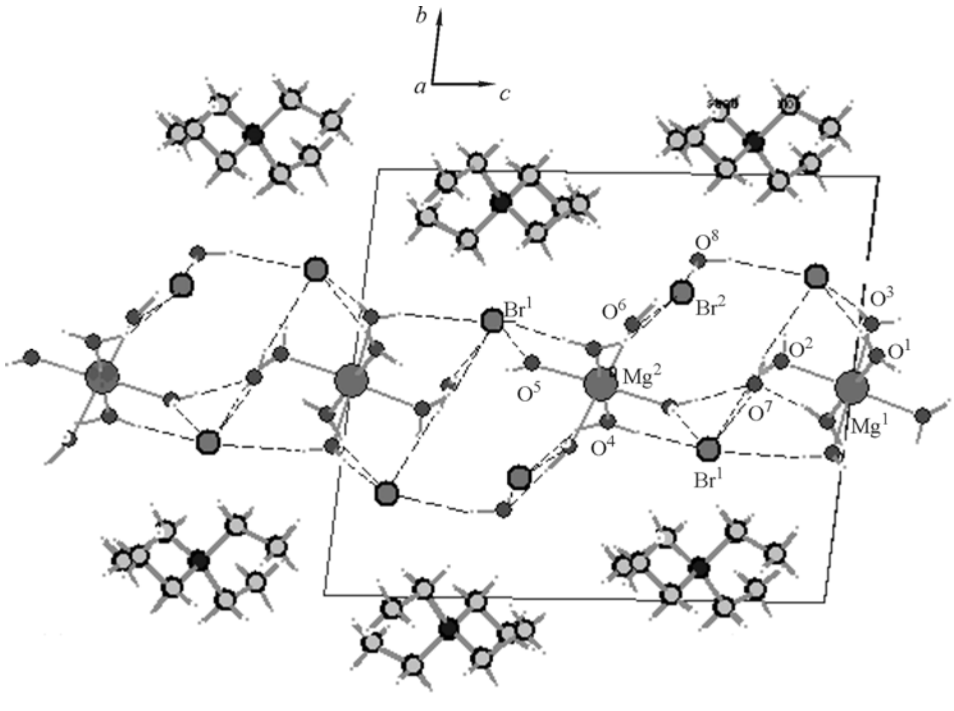

Fig. 3. Structure of the double salt $NEt_4Br{\cdot}MgBr_2{\cdot}8H_2O$.

cationic layer consisting of isolated $\{Mg(H_2O)_6\}$ octahedra [Mg–O distance 2.054(3)–2.070(3) Å, OMgO angles 87.1(2)°–92.9(2)°]. Both of them interact with polyhedrons of magnesium atoms taking positions in various centers of inversion also by means of weak hydrogen bonds O–H···Br and O–H···O (Fig. 3). Another layer is formed by tetraethylammonium cations [C–N distances 1.487(4)–1.491(4), C–C 1.506(4)–1.520(4) Å, CNC angles 106.2(3)°–111.6(3)°, NCC 115.8(3)°–116.6(3)°].

In the system $MgBr_2$–NBu_4Br–H_2O the double salt $4NBu_4Br \cdot MgBr_2 \cdot 6H_2O$, which has no analogs in other MX–MX_2–H_2O systems, also crystallizes. The increase in the tetraalkylammonium cation content in this salt seems to be connected with a strong cation-cation association taking place in saturated solutions and increasing as a result of binding water by strongly hydrated magnesium ions.

Thus, as the factor of tolerance decreases to 0.72 in the series of the systems under consideration, the amount of water molecules in the composition of the crystallizing double salt varies. In this case the size of the hydrated magnesium ion increases, because additional two water molecules are situated within the limits of the second coordination sphere of this cation. As the magnesium cation size increases, the factor of tolerance increases, falling in the required limit. As the factor of tolerance decreases to 0.59 (in the case of the system with tetrabutylammonium bromide), the double salt composition cardinally changes.

EXPERIMENTAL

We studied the solubility by the isothermal saturation method. Solutions were prepared by the method of additions. Saturated solutions of $MgBr_2$ and NR_4Br with solid phases in equilibrium with them were taken as the initial systems. The third component was added to these binary systems in steps of 0.5–1 mol/kg H_2O. The systems were placed in an air thermostat and held at 25.0±0.1°C within a day with permanent stirring by a magnetic stirrer. Because of high viscosity of solutions in the systems $MgBr_2$–NEt_4Br–H_2O and $MgBr_2$–NBu_4Br–H_2O with a concentration of tetraalkylammonium bromide higher than 7 mol/kg H_2O, these systems were held in the thermostat for 3 day with stirring.

Magnesium(II) concentrations in samples were determined by the trilonometry method, and concentrations of bromide anions, by the mercurymetric titration. The concentration of tetraalkylammonium bromide was calculated from the difference. The accuracy of the solubility determination was ±0.02 mol/kg H_2O. The solid phase composition was determined by the Schreinemaker's method. Experimental solubility isotherms are presented in Fig. 1.

Crystals suitable for the single-crystal X-ray diffraction study were grown up by slow evaporation of saturated aqueous solutions at room temperature. The single-crystal X-ray diffraction experiment was carried out on an XCALIBUR autodiffractometer (MoK_α radiation). Structures were solved by direct methods using the SIR-97 program complex [13] and refined in a non-isotropic approximation using the SHELXL complex [14]. Hydrogen atoms of organic anions were arranged in calculated positions. The location of hydrogen atoms in water molecules was determined on the maps of the Fourier difference synthesis. Coordinates of basis atoms and parameters of hydrogen interactions are presented in Tables 1 and 2.

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