X-Ray Diffraction Studies on Ternary $MgCl_2–KCl–H_2O$ and $MgCl_2–CsCl–H_2O$ Solutions Saturated with the Corresponding Double Salts

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X-ray scattering measurements have been done on aqueous $MgCl_2–KCl$ and $MgCl_2–CsCl$ solutions saturated with their double salts of $MgCl_2 \cdot KCl \cdot 6\,H_2O$ and $MgCl_2 \cdot KCl \cdot 6\,H_2O$, respectively, at 293 K. The Mg^{2+} ion was found to be coordinated with six water molecules at an Mg–O distance of 209 and 208 pm, respectively, whereas K^+ and Cs^+ ions were surrounded by both water molecules and chloride ions in the first coordination sphere. The interatomic distance between the alkali cation and the chloride ion was 320 pm and 339 pm for K^+ and Cs^+, respectively, and the coordination numbers of K^+ and Cs^+ with respect to Cl^- were 2.4 and 2.0, respectively. The alkali metal–H_2O distance and the hydration number of the cation were 277 pm and 3.7, respectively, for K^+ and 315 pm and 4.7, respectively, for Cs^+. The structures of the solutions are discussed in connection with the nucleation processes of the salts from the aqueous solutions.

1. Introduction

A number of X-ray diffraction studies on aqueous solutions of electrolytes have been carried out so far, and the structures of most of the hydrated single-atom cations and anions in solution have been determined by the method. Few investigations however, have dealt with the hydration of two cations and a common anion in relatively concentrated solutions, where the number of water molecules may not be sufficient to fully hydrate both cations and the common anion.

The nucleation process of crystals is still unknown even for single component systems. In case of double salts, the process may be more complicated. However, the double salt system may sometimes be convenient to obtain some suggestions for the nucleation process of crystals because we may see the role of each ion at nucleation.

For such an expectation, we analyzed the structures of $MgCl_2–KCl–H_2O$ and $MgCl_2–CsCl–H_2O$ solutions saturated with the corresponding $MgCl_2 \cdot KCl \cdot 6\,H_2O$ and $MgCl_2 \cdot CsCl \cdot 6\,H_2O$ double salts at 293 K.

The structures of $MgCl_2 \cdot XCl \cdot 6\,H_2O$ crystals have been determined by X-ray diffraction for $X^+ = K^+$ [1], Rb^+ [2], Cs^+ [3], and NH_4^+ [4]. From the $MgCl_2–XCl$ aqueous solution, precipitates of XCl, $MgCl_2 \cdot 6\,H_2O$ or $MgCl_2 \cdot XCl \cdot 6\,H_2O$ are formed depending on the composition [5–8]. The concentration range for the formation of $MgCl_2 \cdot 6H_2O$ crystals is extremely narrow, a small amount of XCl promoting the formation of the double salt having six water molecules. On the other hand, the range of the formation of XCl crystals is rather wide, and the addition of a small amount of $MgCl_2$ in the solution does not significantly induce the formation of the corresponding double salt. Therefore, it seems that the existence of XCl in a saturated $MgCl_2$ solution may be more important than that of $MgCl_2$ in a saturated XCl solution for the formation of the double salt.

The Mg^{2+} ion has a larger hydration energy than an X^+ ion, and the ion-pair formation between Mg^{2+} and Cl^- is less favorable than that between X^+ and Cl^- in water. This fact is supported by the crystal structure of the $MgCl_2 \cdot XCl \cdot 6\,H_2O$ double salts in which all water molecules belong to the Mg^{2+} ion and the alkali cation is surrounded only by chloride ions.

Ion-pair formation between alkali metal and halide ions has been studied by many workers by molecular dynamics and Monte Carlo simulations [9–13] and

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by X-ray [14–16] and neutron diffraction [17, 18] methods. However few studies have been carried out for mixed MCl+XCl and M(II)Cl_2+XCl systems in water. The degree of the formation of ion pairs is rather small and the ligand number (the number of ligands coordinated to an ion) of alkali metal ions with respect to chloride ions usually much less than unity. However, it is obvious that the ligand number of the alkali metal ions should increase upon the addition of $MgCl_2$ in an XCl solution because the concentration of chloride ions increases. Some water molecules may still remain in the first coordination shell of the alkali metal ions, however. Formation of the $[XCl_y]^{(1-y)+}$ ($y>1$) complex may be favorable for the formation of a double salt having the composition $MgCl_2 \cdot XCl \cdot n\,H_2O$. However, no information has been presented for structures of such ion pairs having an excess amount of anions around the alkali metal ions.

Therefore, in the present study we aimed at determining the structures of Mg^{2+} and K^+ or Cs^+ ions in the chloride aqueous solutions to provide information on the crystal formation of the double salts.

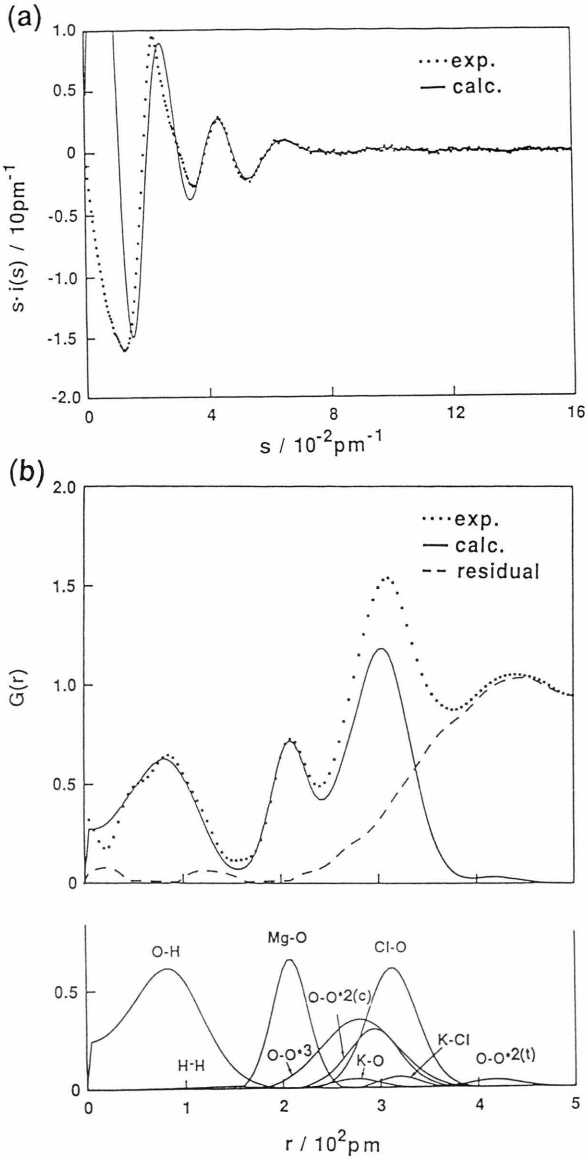

Fig. 1. (a) Structure function of the $MgCl_2$–KCl–H_2O solution: experimental (·····) and calculated (——). (b) The residual $G(r)$ curve (– – –) obtained after subtraction of the calculated $G(r)$ curves (——) from the observed $G(r)$ curve (·····) for the $MgCl_2$–KCl–H_2O solution. *2(c), *2(t) and *3 are defined in Table 2.

Table 1. Concentrations (mol/l) and densities (g/cm^3) of $MgCl_2$–KCl–H_2O (A) and $MgCl_2$–CsCl–H_2O (B) solutions.

Solution	$[K^+]$	$[Cs^+]$	$[Mg^{2+}]$	$[Cl^-]$	$[H_2O]$	*d*
A	0.652	–	3.826	8.304	47.961	1.28
B	–	1.185	3.715	8.615	49.126	1.40

2. Experimental

The $MgCl_2$–KCl–H_2O and $MgCl_2$–CsCl–H_2O solutions were prepared from commercially available magnesium chloride (>99.9%), potassium chloride (>99.5%) and caesium chloride (>99.9%). The saturated solutions were prepared by mixing the $MgCl_2$ and KCl or CsCl aqueous solutions of known concentrations calculated from the phase diagram [5, 7]. The solutions were adjusted to have almost the same concentration of $MgCl_2$. Concentrations of the cations were determined by using liquid chromatography. Densities of the solutions were measured by a densitometer at 293 K. Data of the sample solutions are summarized in Table 1.

A θ–θ diffractometer (JEOL, Tokyo, Japan) was used with MoKα radiation ($\lambda=71.07$ pm) for the measurement. The range of the scattering angle (2θ) was 2–140°, which corresponds to an s range of 0.003 to 0.16 pm^{-1} ($s=4\pi \sin\theta/\lambda$). At angles below 1° the measured intensities were linearly extrapolated to zero at $\theta=0°$. 40000 counts at each data point were accumulated in the whole scan range. Details of measurements and data collections were described elsewhere [19]. Corrections for absorption, polarization,

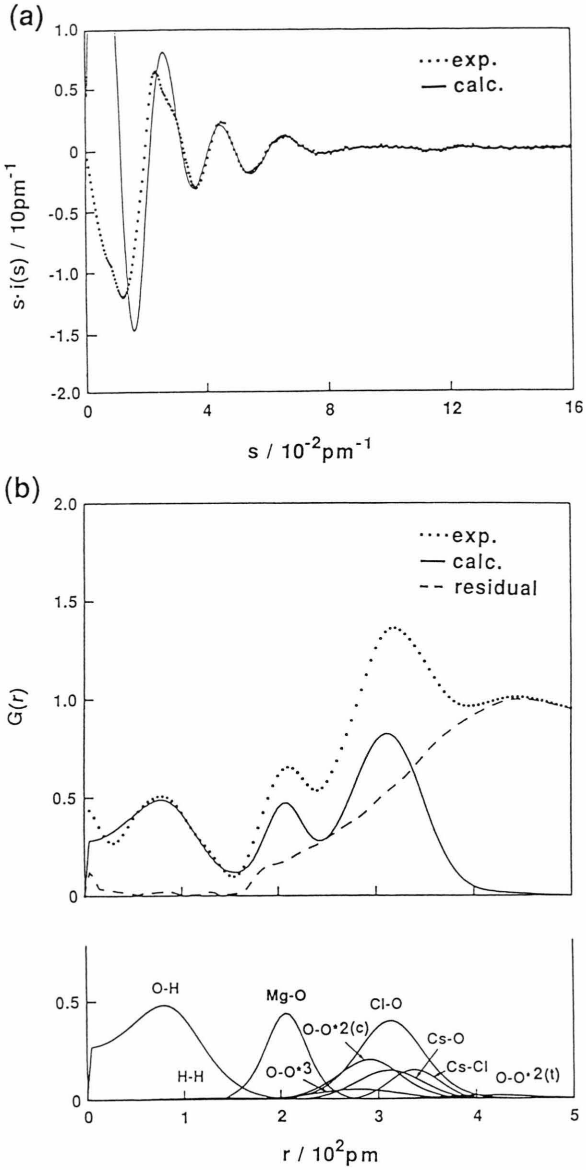

Fig. 2. Figure, corresponding to Fig. 1, for the $MgCl_2$–CsCl–H_2O solution.

double scattering and incoherent scattering, and subsequent scaling of the corrected scattering intensities to electron units were carried out as previously described [19, 20].

The structure function $i(s)$ was obtained by subtracting the independent scattering intensities from all atoms in the sample solutions from the scaled intensities $I(s)$:

$$i(s) = I(s) - \sum x_i\, f_i(s)^2\,, \tag{1}$$

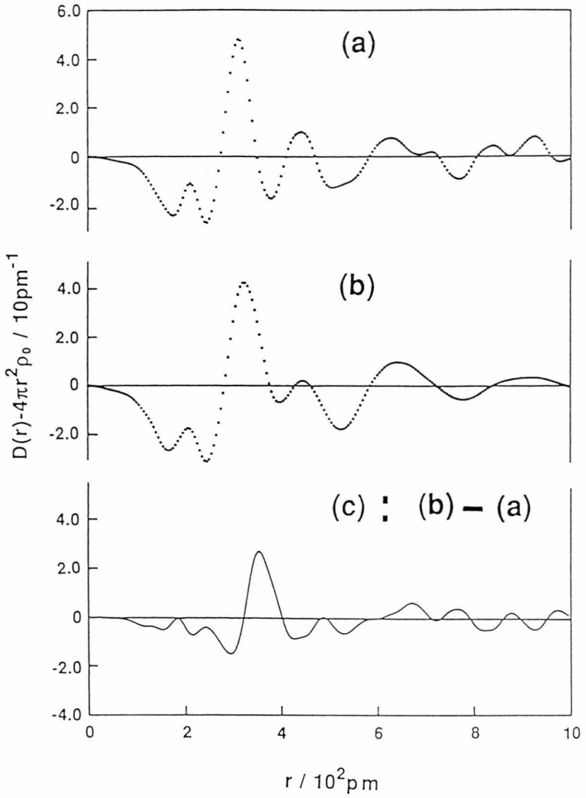

Fig. 3. The radial distribution functions in the form of $D(r) - 4\pi r^2 \varrho_0$ of the $MgCl_2$–KCl–H_2O (a) and $MgCl_2$–CsCl–H_2O (b) solutions. The difference between the radial distribution functions of (a) and (b) is shown as (c).

where x_i is the number of the i-th atom in the stoichiometric volume V containing one Mg atom and $f_i(s)$ is the coherent scattering factor corrected for the real and imaginary parts of the anomalous dispersion. The coherent and incoherent scattering factors of neutral atoms were taken from the International Tables [21]. The structure functions multiplied by s of the sample solutions are shown in Figs. 1a and 2a for the $MgCl_2$–KCl–H_2O and $MgCl_2$–CsCl–H_2O solutions, respectively.

The radial distribution function (RDF), $D(r)$, and the correlation function, $G(r)$, are calculated by the Fourier transform of the structure function:

$$D(r) = 4\pi r^2 \varrho_0 + \frac{2r}{\pi} \int_0^{s_{\max}} s\, i(s)\, M(s) \sin(sr)\, \mathrm{d}s\,, \tag{2}$$

$$G(r) = D(r)/4\pi r^2 \varrho_0$$

$$= 1 + \frac{1}{2\pi^2 r \varrho_0} \int_0^{s_{\max}} s\, i(s)\, M(s) \sin(sr)\, \mathrm{d}s\,, \tag{3}$$

where ϱ_0 denotes the average electron density and $s_{\max}$ the maximum s value attained in the measurement. A modification function $M(s)$ was introduced in the form

$$M(s) = [f_1(0)^2/f_1(s)^2]\exp(-100\,s^2)\,. \tag{4}$$

The $G(r)$ curves of the $MgCl_2$–KCl–H_2O and $MgCl_2$–CsCl–H_2O solutions are shown in Figs. 1 b and 2 b, respectively. The $D(r)$ curves are shown in Figs. 3 a and 3 b. The synthetic structure function based on a model is obtained by

$$i(s)_{\text{syn}} = \sum\sum x_i\, n_{ij}\, f_i\, f_j \frac{\sin(s r_{ij})}{s r_{ij}} \exp(-b_{ij} s^2)\,. \tag{5}$$

Equation (5) includes the interatomic distance, r_{ij}, the temperature factor, b_{ij}, and the number of interactions,. n_{ij}, for atom pairs i–j. All the calculations were carried out by means of the program KURVLR [22].

3. Results

3.1. $G(r)$ and RDFs

The $G(r)$ curve of the $MgCl_2$–KCl aqueous solution is shown in Fig. 1 b. The RDF in the form $D(r)-4\pi r^2\varrho_0$ of the solution is given in Figure 3 a.

The $G(r)$ curves in Figs. 1 b and 2 b have peaks at about 90, 200, 310 and 450 pm. The first peak around 90 pm is certainly due to the O–H bonds in the water molecule. The second peak at 200 pm is ascribable to the Mg–O interactions in the first coordination sphere of Mg^{2+}, which agrees well with the literature values obtained from aqueous solutions of $MgCl_2$ (Mg–O = 200–212 pm) [23–27], from crystal of $MgCl_2 \cdot 6\,H_2O$ (Mg–O = 205.7 and 206.2 pm) [28] and the $MgCl_2 \cdot XCl \cdot 6\,H_2O$ double salts (Mg–O = 202.8–205.6 pm for $MgCl_2 \cdot KCl \cdot 6\,H_2O$ [1] and 200.1–214.1 pm for $MgCl_2 \cdot CsCl \cdot 6\,H_2O$ [3]). The third and broad peak appearing around 310 pm contains many contributions, and the most pronounced one among them may be K–O and Cl–O interactions. Contributions from H_2O–H_2O interactions within the first coordination sphere of Mg^{2+} [23–27] and in the bulk water [23] are also involved in the peak. The K^+–Cl^- distance in the ion pair may appear in the region as expected from their ionic radii. The fourth peak contains long range interactions which will not be discussed in the present study.

The same argument can be raised for the $MgCl_2$–CsCl–H_2O system, whose $G(r)$ and $D(r)-4\pi r^2\varrho_0$ curves are shown in Figs. 2 b and 3 b, respectively. The Cs–O and Cs–Cl interactions may be included in the third peak appearing about 310 pm in the curves.

The contributions of the various interactions to the third peaks can not easily be resolved. However, the ambiguities can be partly avoided by taking the difference between two $D(r)-4\pi r^2\varrho_0$ curves [14, 15], because the contribution of Cs–Cl, which is expected to be at about 350 pm from the sum of the ionic radii [23], can be distinguished from the other shorter range interactions in the curve as seen in Figure 3 c.

3.2. *Models and Least-Squares Fitting*

In order to determine the values of the structural parameters, the experimental structure functions were compared with theoretical ones calculated from the models employed by the use of (4). A non-linear least-squares fitting procedure was employed, in which the function

$$U = \sum_{s_{\min}}^{s_{\max}} w(s)\,[i_{\text{exp}}(s) - i_{\text{syn}}(s)]^2 \tag{5}$$

was minimized with respect to variables r_{ij}, b_{ij} and n_{ij} by using the program NLPLSQ [29]. Here, $s_{\min}$ and $s_{\max}$ are the lower and upper limits of s, respectively, used in the calculations, and $w(s) = s^2$ is the weighting function.

The following models were tentatively adopted for the solutions:

a) The hydration of Mg^{2+} is defined by the first neighbor Mg–O distance and the corresponding temperature factor. The coordination shell is assumed to have six water molecules around the Mg^{2+} ion according to the results previously obtained [23–27]. The H_2O–H_2O interactions within the coordination shell were also taken into account in terms of the temperature factor with fixing the number of interactions. The interatomic distances were calculated from the Mg–O distance by assuming regular octahedral geometry.

b) The structures of the first coordination shells of K^+, Cs^+ and Cl^- were taken into account, which were described in terms of interatomic distances, r_{ij}, temperature factor, b_{ij}, and the number of water molecules in the coordination shells, n_{ij}, for ion-water and cation-anion interactions. The above parameters were allowed to vary independently. The H_2O–H_2O interactions in the first hydration shells of K^+, Cs^+ and Cl^- were not taken into account because these weakly hydrated ions should have hydration shells in which the water molecules are rather randomly situated, and in such concentrated solutions it is hardly possible that such ions form some rigid polyhedral structure with water molecules. Furthermore, even if these ions would have a regular polyhedral hydration shell, the H_2O-H_2O interactions with the hydration shell would appear at least beyond 400 pm. In that region, however, many other second neighbor interactions should overlap, and thus it is very difficult to obtain a definite reliable conclusion for the intermolecular interactions.

c) Contact K^+-Cl^- and Cs^+-Cl^- ion-pairs are tentatively assumed and characterized by the interatomic distance, the temperature factor and the number of interactions.

d) First neighbour H_2O-H_2O interactions in the bulk water, which should be present in aqueous solutions, were introduced.

The s range used was 0.001–0.16 pm^{-1} for both solutions. The final results are summarized in Table 2. Figures 1 and 2 show that the theoretical curves satisfactorily reproduce the experimental results over the range $s \geqq 0.03$ pm^{-1}.

Table 2. Parameter values used for the model calculations on the $MgCl_2-KCl-H_2O$ (A) and $MgCl_2-CsCl-H_2O$ (B) solutions *1.

		(A) M = K	(B) M = Cs
M–O	r	277(9)	315(1)
	$10\,b$	17(7)	41(2)
	n	3.7(9)	4.7(3)
M–Cl	r	320(3)	339.1(8)
	$10\,b$	15(3)	26(1)
	n	2.4(3)	2.0(1)
Mg–O	r	209.2(4)	208.1(1)
	$10\,b$	3.5(5)	4.3(5)
	n	6	6
O–O *2 (c)	r	295.9	294.3
	$10\,b$	15(2)	22(2)
	n	12	12
O–O *2 (t)	r	418.4	416.2
	$10\,b$	14(8)	67(15)
	n	3	3
Cl–O	r	314.5(4)	316.4(5)
	$10\,b$	21.4(6)	35.0(9)
	n	6.1(1)	6.0(1)
O–H	r	95.5	95.5
	$10\,b$	10	10
	n	2	2
H–H	r	151.0	151.0
	$10\,b$	28	28
	n	1	1
O–O *3	r	284(1)	282(6)
	$10\,b$	46(3)	54(9)
	n	1.45(7)	0.26(6)

*1 The interatomic distance r (pm), the temperature factor $10b$ (pm^2) and the number of interactions n. The values in parentheses are their standard deviations estimated from the least-squares fits. The parameter values without parentheses were fixed during the calculations.

*2 The O–O interactions within the first hydration shell of Mg^{2+} ((c) and (t) represent cis- and trans-positions, respectively). r is the interatomic distance as estimated from the octahedral geometry assumed around the Mg^{2+}.

*3 The first neighbor O–O interactions in water. The value n is the number of H_2O molecules around one water molecule.

Discussion

As seen in Table 2, the average hydration numbers of K^+, Cs^+ and Cl^- are small in comparison with those in solutions of single electrolytes (n_{ij} has been given as 6 to 8) [10, 11, 14, 17, 18, 23–27, 30–35]. This may be caused by the following two factors: One is due to the strong hydration of the Mg^{2+} ion, leaving an insufficient amount of water molecules in the bulk to fully hydrate the univalent ions, and the other is due to the formation of contact K^+-Cl^- and Cs^+-Cl^- ion-pairs. In the crystals of the XCl simple salts [36], $MgCl_2 \cdot 6\,H_2O$ [28] and $MgCl_2 \cdot XCl \cdot 6\,H_2O$ double salts [1–4], the alkali metal ion X^+ is coordinated with only Cl^- ions and the Mg^{2+} ion is surrounded by only water molecules. The K–O, Cs–O and Cl–O distances obtained in the present study are in good agreement with those of the mean ion-water interatomic distances summarized by Marcus [23]. The K^+-Cl^- distance (320 pm) is also in good agreement with the sum of the ionic radii of K^+ and Cl^- (321 pm = 141 pm (K^+) + 180 pm (Cl^-), [23]). On the other hand, the Cs^+-Cl^- distance (339.1 pm) is somewhat shorter than the sum of the ionic radii of Cs^+ and Cl^- (353 pm = 173 pm (Cs^+) + 180 pm (Cl^-), [23]). The Cs^+-Cl^- distance observed in the $MgCl_2-CsCl$ aqueous solution, however, is very similar to that in the $MgCl_2 \cdot CsCl \cdot 6\,H_2O$ double salt crystal (337.3 pm, [3]). The similarity of the Cs^+-Cl^- distances in the solution and in the $MgCl_2 \cdot CsCl \cdot 6\,H_2O$ double salt crystal suggests that a crystal-like structure around each ion may be formed in the concentrated ternary solution.

In the $CaCl_2-MgCl_2-H_2O$ system at 25 °C [5], which has three solid phases ($CaCl_2 \cdot 6\,H_2O$, $MgCl_2$

$\cdot 6H_2O$ and $CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$), the range of the formation of $MgCl_2 \cdot 6H_2O$ is much wider than that found in the $MgCl_2$–XCl–H_2O systems. The solution X-ray diffraction data of an $MgCl_2$–$CaCl_2$–H_2O solution (Mg:Ca:Cl:$H_2O \approx 1:1:4:24$) reported by Caminiti et al. [37] has shown that all three ions are octahedrally coordinated with six water molecules and that no contact ion-pair is formed between Ca^{2+} or Mg^{2+} and Cl^-, as already found in their single electrolyte solutions. The hydration energy of Ca^{2+} is comparable to that of Mg^{2+} [38], and therefore water molecules can be strongly bound to Ca^{2+}. These facts show that the formation of K^+–Cl^- or Cs^+–Cl^- contact ion-pairs should strongly influence the crystallization of the double salts and thus the phase diagrams of the $MgCl_2 \cdot KCl \cdot 6H_2O$ and $MgCl_2 \cdot CsCl \cdot 6H_2O$ ternary systems.

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