THERMODYNAMIC PROPERTIES OF MOLTEN MAGNESIUM CHLORIDE HYDRATES IN PRESENCE OF POTASSIUM CHLORIDE

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ABSTRACT

Vapour pressure measurements had been performed in the ternary system \( x\text{KCl} + (1-x)(\text{MgCl}_2 + R \text{H}_2\text{O}) \) up to a maximum temperature of 523 K. The investigated compositions varied between \( 0 \leq x \leq 0.3 \) and \( 4.6 \leq R \leq 6.0 \). From the experimental vapour pressures water activities, enthalpies of evaporation, and partial molar excess entropies of water were calculated. The present results confirm the appearance of direct cation-anion contacts within the concentration range of molten hydrates due to \( \text{H}_2\text{O} \leftrightarrow \text{Cl}^- \) exchange reactions in the first coordination sphere of \( \text{Mg}^{2+} \).

1. Introduction

Molten salt hydrates represent a class of liquids interconnecting features of aqueous solutions and molten salts. Recently, we proposed to define the concentration range of molten hydrates more generally as a range, which is characterized by a quantitative predominance of ion-water contact interactions /1,2/. A peculiar transition behaviour in the concentration dependence of thermodynamic properties is observed within this range. The sharpness of this transition is related to the strength of ion-water and cation-anion interactions. Its position on the concentration scale corresponds to the average hydration number of the strongest hydrating ion.

In this respect, \( \text{MgCl}_2 \) can be considered as a model substance, consisting of a strongly hydrating cation with almost no tendency to associate with the anion in aqueous solutions /3,4/. In agreement with the primary hydration number of \( \text{Mg}^{2+} \), at a molar \( \text{H}_2\text{O}/\text{MgCl}_2 \) ratio \( R \approx 6 \), distinct changes in the partial molar quantities of water were revealed from vapour pressure measurements in the binary system \( \text{MgCl}_2-\text{H}_2\text{O} /2,5,6/ \).

On the other hand, the properties of the anhydrous molten mixtures \( \text{MgCl}_2-\text{ACl} \) (\( \text{A}=\text{K}, \text{Rb}, \text{Cs} \)) are governed by the formation of tetrahedrally coordinated chlorocomplexes of magnesium /7,8/.

There arises the question, whether chlorocomplex formation becomes important in the range of molten hydrates of \( \text{MgCl}_2 \). A ligand exchange \( \text{H}_2\text{O} \leftrightarrow \text{Cl}^- \) at the \( \text{Mg}^{2+} \) ions should be reflected in a relative increase of the water activity. Thus, in this work the influence of \( \text{KCl} \) on the vapour pressure of molten...
magnesium chloride hydrates has been investigated for molar \( H_2O/MgCl_2 \) ratios between six and four. Tab. 1 gives a summary of the compositions, which are covered by our measurements.

2. Experimental

The preparation and analysis of magnesium chloride hydrates have been described previously /9/. Reagent grade KCl (VEB Jenapharm Laborchemie Apolda) was recrystallized and dried to constant weight at 473 K. Aliquots of magnesium chloride, potassium chloride and water were weighed directly into the teflon vessel of the autoclave to give a sample of the desired bulk composition.

A detailed description of the apparatus for vapour pressure measurements and the procedure used is given in /9/.

In this study some improvements were introduced increasing the accuracy of the experiments. Two-wire circuits of the Pt-100 resistance thermometers were replaced by four-wire arrangements and all measurements of voltage were performed in both current directions to compensate thermoelectric effects. The samples were homogeneously melted before evacuating the apparatus. Likewise, for the correction of slight shifts in bulk composition (< 0.5 per cent) the quantity of water vapour, exhausted during the evacuation, was weighed after freezing-out at liquid nitrogen temperature.

For all compositions given in Tab. 1 a vapour pressure polytherm was determined with temperature steps of about 12 K until a maximum temperature of 523 K. The experiments were started at a temperature about 10 K above the crystallization temperature according the phase diagram of D'ANS and SYPIENA /10/.

In order to ensure a temperature interval of at least 50 K the maximum concentration of KCl was limited to 30 mol-% related to the anhydrous salt mixture.

3. Calculation of the water activity from vapour pressure

For the calculation of the water activities from the measured vapour pressures \( p_w \) Eq. (1) was applied:

\[
\ln a_w(p^w) = \ln\left(p_w/p_w^*\right) + \frac{1}{RT} \int_{p_w^*}^{p_w} (V_w^w - V_w^D) \, dp + \frac{1}{RT} \int_{p_w^*}^{p_w^*} \frac{p_w^*}{p_w} V_w^w \, dp \quad (1)
\]
Eq. (1) yields the water activity $a_w$ at the vapour pressure of pure water $p^*$, at the given temperature, where $V_w$ is the partial molar volume of water, $T$ the absolute temperature and $R$ the general gas constant ($8.3144 \, \text{J} \, \text{mol}^{-1} \, \text{K}^{-1}$). The subscripts have the following meaning: ° standard state; * pure water; liquid phase and; gas phase.

For a satisfactory accuracy in the analytical solution of the first integral of Eq. (1) up to 523 K - our upper limit in the experiments - it was necessary to take into account the third virial coefficient of water steam (Eq. (2)),

$$V_w^* = RT/p_w + B + C \, p_w$$  \hspace{1cm} (2)

where $B$ and $C$ are the second and third virial coefficient, respectively. The numerical values of $B$ and $C$ as a function of temperature were determined by means of multilinear regression of the PVT-data of water steam /II/ from 373 to 573 K. The obtained power series are given by Eq. (3) and (4).

$$B \ [m^3/kg] = a_0 + a_1/T + a_2/T^2 + a_3/T^3 + a_4/T^4 + a_5/T^5$$  \hspace{1cm} (3)

\begin{align*}
a_0 &= -3.14697 \times 10^{-1} \\
a_1 &= 7.63194 \times 10^2 \\
a_2 &= -7.26904 \times 10^5 \\
a_3 &= 3.37919 \times 10^8 \\
a_4 &= 7.71229 \times 10^{10} \\
a_5 &= 6.78403 \times 10^{12}
\end{align*}

$$C \ [m^3/(kg \, \text{bar})] = a_0' + a_1'/T + a_2'/T^2$$  \hspace{1cm} (4)

\begin{align*}
a_0' &= -1.03334 \times 10^{-3} \\
a_1' &= 1.26910 \\
a_2' &= -3.97580 \times 10^2
\end{align*}

At temperatures $\leq$ 523 K Eq. (2) to (4) represent the original data /II/ within error limits of 0.15%.

From Eq. (1) it follows that the partial molar volume of water in the liquid phase has to be included into the calculation. Different approximations were used for this quantity in the literature. The reason has to be seen in a lack of precise and extensive volumetric data of water-salt systems at temperatures above 373 K and high concentrations. At lower concentrations the most reliable approach consists of the use of the molar volume of pure water $V_w^p$ (e.g. /12, 13, 14/).

The relative contribution of the second integral in Eq. (1) increases with rising vapour pressure difference between salt solution and pure water. In the case of a magnesium chloride hexahydrate melt, with its low water activity, it amounts
to only 0.3 per cent at 423 K, but 1.5 per cent at 523 K already. Accordingly, at higher temperatures the necessary attention has to be directed to the partial molar volume of water to allow an exact calculation of the water activity from vapour pressure data.

For molten hydrates, containing strongly hydrated cations as Mg$^{2+}$, a vigorous decrease of the partial molar volume of water should be expected. AKSMANOVIĆ and KREY /15/ reported an equation for the density of MgCl$_2$-H$_2$O, which we used to calculate the partial molar volume of water. A general plot is given in Fig. 1. With rising temperature, the influence of the salt concentration on $V'_w$ increases, but its maximum variation remains smaller than 10%. At the end of the compiled concentration range (45 wt% = 8.6 mol MgCl$_2$/kg H$_2$O) the uncertainty in the density derivative with respect to composition increases. Consequently, the crossing-point at about 9 mol MgCl$_2$/kgH$_2$O is not significant. In the ternary system KCl-MgCl$_2$-H$_2$O, the partial molar volume of water was considered as to be not influenced by the added KCl.

4. Results and discussion

The experimental results are summarized in Tab. 2. The molalities in column 1 and 2 are corrected for the amount of water in the vapour phase.

The temperature dependence of the vapour pressure can be described by means of relation (5),

$$\ln p_w = A_0 + A_1/T$$

where $p_w$ is the vapour pressure in kPa. The numerical values of $A_0$ and $A_1$ together with the standard deviation obtained from a linear regression are listed in Tab. 3.

Column 6 of Tab. 2 contains the water activities $a_w^{\text{corr}}$, recalculated to constant compositions of the sample and rounded molar ratios H$_2$O/MgCl$_2$. For the temperature dependence of the water activity at constant composition, relation (6) was applied

$$\ln a_w^{\text{corr}} = A_0' + A_1'/T$$

The coefficients $A_0'$ and $A_1'$ are reported in Tab. 4.

Fig. 2 exhibits a graphical representation of the results at a molar H$_2$O/MgCl$_2$ ratio R=6.0. The logarithm of the water activity $a_w^{\text{corr}}$ was plotted against the reciprocal absolute temperature, 1/T. The four polythermal data sets given in Fig. 2a scatter within ±1.1 per cent around the regression line. This value
can be considered as the reproducibility of our vapour pressure measurements. In Fig. 2b, the regression function from the present work (Fig. 2a) is plotted together with previous data /9, 16/. The comparison between the two figures points out the higher accuracy of the recent data.

Fig. 2 reveals also an unexpected result. Within the experimental uncertainty the water activity of a magnesium chloride hexahydrate melt is not changed after addition of anhydrous potassium chloride. The experimental results at lower water contents are shown in Fig. 3. Filled circles and their regression lines (drawn as continuous lines) refer to a KCl content of $x = 0.3$, whereas the dashed lines represent the water activities in the binary system MgCl$_2$·H$_2$O at the same molar (H$_2$O/MgCl$_2$) ratio $R$.

At $R < 6$ an increase of the water activity becomes evident after addition of KCl. In Fig. 4 the effect of composition variation is presented in form of isothermal plots. At a temperature of 473 K the relative increase of the water activity referred to the corresponding pure magnesium chloride hydrate melt is plotted. Fig. 4a demonstrates the effect of the addition of 30 mol-% KCl in regard to the molar H$_2$O/MgCl$_2$ ratio, whereas in Fig. 4b the variation of the water activity in regard to the KCl content is given for constant $R = 4.6$.

The most distinct effect was found at the lowest water content (Fig. 4a) and after addition of the largest amount of KCl (Fig. 4b). In spite of the higher total salt content the water activity is increased by 14.5 per cent. This result is in contrast to the common behaviour of aqueous solutions, where the vapour pressure decreases with growing total salt concentration.

Returning to the question formulated in the introduction, from our results it can be stated that in molten magnesium chloride hydrates ligand exchange processes H$_2$O$\leftrightarrow$Cl$^-$ become important. At $R < 6$ the release of water from the coordination sphere of Mg$^{2+}$ ions reaches such an extent that the water activity is not only relatively increased, but absolutely.

Equations of type (1) can be formulated to describe the coordination competition between H$_2$O and Cl$^-$

$$[\text{Mg(H}_2\text{O)}]_{6-n}\text{Cl}_n\]^{2-n} + n\text{Cl}^- \rightleftharpoons [\text{Mg(H}_2\text{O)}]_{6-n}\text{Cl}_{n+m}\]^{2-n-m} + m\text{H}_2\text{O} \quad (1)$$

This agrees with a recent raman spectroscopic investigation /17/, which proves the existence of direct cation-anion contacts in melts of magnesium chloride hydrates.
A displacement of equilibrium (I) to the right-hand side enhances the water activity and should become large as the total ratio of $\text{Cl}^-/\text{H}_2\text{O}$ in the melt is changed. Tab.5 gives the variation of this ratio in comparison to pure magnesium chloride hydrate melt $\Delta$. With decreasing $R$ we find increasing values of $\Delta$, which explains the enlargement of the effect observed in this direction. At the instance of molten magnesium chloride hexahydrate, the water activity increasing effect by reaction (I) is just compensated by the simultaneous increase in total salt content. At still lower molar ratios $\text{H}_2\text{O}/\text{MgCl}_2$ reaction (I) produces an absolute enhancement of vapour pressure.

The libration of coordinated water according to (I) is also clearly reflected in the molar enthalpy of evaporation $\Delta V_{\text{H}_2\text{O}}$ as well as in the partial molar excess entropy of water $\Delta S_{\text{ex}}$. For the calculation of these quantities Eq.(7) and (8) were used, respectively.

$$
\Delta V_{\text{H}_2\text{O}} = T(V''-V') \frac{dp_w}{dT} \tag{7}
$$

$$
\Delta S_{\text{ex}} = -R(\ln a_{\text{corr}}^w - \ln x_w) - RT \ln a_{\text{corr}}^w \frac{dP}{dT} \tag{8}
$$

where $x_w$ is the mole fraction of water on an ionized basis. The needed vapour pressures and water activities as well as their temperature dependencies were derived from Eq.(5) and (6), respectively.

In Fig.5 both $\Delta V_{\text{H}_2\text{O}}$ and $\Delta S_{\text{ex}}$ are plotted against the KCl content at a $\text{H}_2\text{O}/\text{MgCl}_2$ ratio, $R = 4.6$ and 473 K.

The deviation of the points at $x = 0.15$ (run 8) from the general tendency exposes the sensitivity of these quantities to relative small errors in the activity data. In preparation of run 8 obviously rest gas was not removed completely from the reference system resulting in a slightly larger slope in the temperature dependence of the water activity.

With increasing KCl concentration the absolute values of $\Delta V_{\text{H}_2\text{O}}$ as well as of $\Delta S_{\text{ex}}$ decreases, which is adequate to a decrease of the ion-water interactions.

The present results confirm our general view of the concentration range of molten hydrates as to be characterized by dominant ion-water contacts and the appearance of direct cation-anion contacts due to coordination competition.
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Tab. 1: Bulk compositions of the investigated samples in the system \([x \text{KCl} + (1-x)(\text{MgCl}_2 + R \text{H}_2\text{O})]\)

| R  | x = 0.05 | 0.10 | 0.15 | 0.20 | 0.25 | 0.30 |
|----|----------|------|------|------|------|------|
| 6.0| *        |      |      |      |      |      |
| 5.5|          | *    |      |      |      |      |
| 5.0|          |      | *    |      |      |      |
| 4.6| *        | *    | *    | *    | *    | *    |
### Table 2: Experimental vapour pressures $p_w$ and water activities $a_w$

| $m$(MgCl$_2$) | $m$(KCl) | $T$ | $p_w$ | $a_w$ | $a_w^{corr}$ |
|---------------|----------|-----|-------|-------|--------------|
| [mol/kgH$_2$O] | [mol/kgH$_2$O] | [K] | [kPa] |       |              |
|----------------|-------------|-----|-------|-------|--------------|
| 1              | 2           | 3   | 4     | 5     | 6            |
| MgCl$_2$ + 6H$_2$O (run 1) | | | | | |
| 9.253 | 433.60 | 103.6 | 0.1731 | 0.1732 |
| 9.286 | 502.95 | 686.2 | 0.2738 | 0.2756 |
| 9.308 | 524.02 | 1104.7 | 0.3119 | 0.3148 |
| MgCl$_2$ + 6H$_2$O (run 2) | | | | | |
| 9.248 | 402.42 | 33.9 | 0.1315 | 0.1313 |
| 9.250 | 422.83 | 70.9 | 0.1560 | 0.1560 |
| 9.256 | 448.04 | 159.9 | 0.1896 | 0.1899 |
| 9.266 | 473.74 | 333.2 | 0.2283 | 0.2291 |
| 9.283 | 500.04 | 639.7 | 0.2685 | 0.2701 |
| 0.85(MgCl$_2$ + 6H$_2$O) + 0.15KCl (run 3) | | | | | |
| 9.267 | 1.635 | 338.09 | 103.8 | 0.1714 | 0.1722 |
| 9.270 | 1.636 | 446.65 | 153.9 | 0.1884 | 0.1894 |
| 9.274 | 1.637 | 459.09 | 222.3 | 0.2064 | 0.2076 |
| 9.280 | 1.638 | 472.04 | 317.8 | 0.2254 | 0.2269 |
| 9.287 | 1.639 | 484.75 | 441.8 | 0.2446 | 0.2466 |
| 9.297 | 1.641 | 497.44 | 602.0 | 0.2644 | 0.2668 |
| 9.309 | 1.643 | 510.51 | 816.2 | 0.2865 | 0.2895 |
| 9.324 | 1.646 | 523.51 | 1089.6 | 0.3102 | 0.3138 |
| 0.70(MgCl$_2$ + 6H$_2$O) + 0.30KCl (run 4) | | | | | |
| 9.281 | 3.977 | 469.23 | 294.1 | 0.2208 | 0.2224 |
| 9.287 | 3.980 | 481.68 | 407.2 | 0.2391 | 0.2410 |
| 9.294 | 3.983 | 494.26 | 553.3 | 0.2573 | 0.2596 |
| 9.305 | 3.988 | 507.41 | 751.1 | 0.2778 | 0.2806 |
| 9.318 | 3.993 | 520.67 | 1005.3 | 0.2995 | 0.3028 |
| 0.90(MgCl$_2$ + 4.6H$_2$O) + 0.10KCl (run 5) | | | | | |
| 12.099 | 1.345 | 462.35 | 127.6 | 0.1113 | 0.1121 |
| 12.105 | 1.346 | 475.08 | 188.8 | 0.1271 | 0.1281 |
| 12.113 | 1.347 | 487.85 | 272.9 | 0.1461 | 0.1454 |
| 12.138 | 1.349 | 513.76 | 538.6 | 0.1819 | 0.1840 |
| 12.155 | 1.351 | 526.51 | 730.9 | 0.2021 | 0.2048 |
| 12.124 | 1.348 | 500.55 | 387.2 | 0.1630 | 0.1647 |
| 0.70(MgCl$_2$ + 4.6H$_2$O) + 0.30KCl (run 6) | | | | | |
| 12.100 | 5.177 | 458.67 | 123.9 | 0.1167 | 0.1176 |
| 12.105 | 5.179 | 471.72 | 183.9 | 0.1323 | 0.1333 |
| 12.112 | 5.182 | 485.08 | 269.4 | 0.1496 | 0.1509 |
| 12.122 | 5.186 | 497.94 | 379.8 | 0.1672 | 0.1688 |
| 12.133 | 5.191 | 510.80 | 524.7 | 0.1857 | 0.1878 |
| 12.147 | 5.197 | 522.25 | 688.2 | 0.2030 | 0.2055 |
|   |   | 2  | 3  | 4  | 5  | 6  |
|---|---|----|----|----|----|----|
| 0.95(MgCl₂ + 4.6H₂O) + 0.05KCl (run 7) |   |    |    |    |    |    |
| 0.95(MgCl₂ + 4.6H₂O) + 0.05KCl (run 7) |   |    |    |    |    |    |
| 0.85(MgCl₂ + 4.6H₂O) + 0.15KCl (run 8) |   |    |    |    |    |    |
| 0.80(MgCl₂ + 4.6H₂O) + 0.20KCl (run 9) |   |    |    |    |    |    |
| 0.75(MgCl₂ + 4.6H₂O) + 0.25KCl (run 10) |   |    |    |    |    |    |
| 0.70(MgCl₂ + 5.0H₂O) + 0.30KCl (run 11) |   |    |    |    |    |    |
| 0.70(MgCl₂ + 5.5H₂O) + 0.30KCl (run 12) |   |    |    |    |    |    |
Tab. 3: Regression coefficients of Eq. (5)

| run  | $A_0$  | $A_1$ [K] | $\sigma$  |
|------|--------|-----------|-----------|
| 1 and 2 | 18.518 | -6026.5   | 0.014     |
| 3    | 18.395 | -5966.7   | 0.005     |
| 4    | 18.117 | -5833.0   | 0.002     |
| 5    | 19.183 | -6624.3   | 0.007     |
| 6    | 18.918 | -6464.3   | 0.005     |
| 7    | 19.172 | -6630.5   | 0.007     |
| 8    | 19.322 | -6686.0   | 0.005     |
| 9    | 19.027 | -6528.0   | 0.004     |
| 10   | 18.952 | -6485.3   | 0.005     |
| 11   | 18.676 | -6287.4   | 0.003     |
| 12   | 18.357 | -6036.7   | 0.003     |

$\sigma = \left[ \sum (\ln p_w(\text{exp}) - \ln p_w(\text{cal})) / (n-2) \right]^{1/2}$

with $n$ = number of experimental points.
Tab. 4: Regression coefficients of Eq. (6)

| run  | \( A_0 \)  | \( A_1 \) [K] | \( \sigma \)  |
|------|------------|---------------|--------------|
| 1 and 2 | 1.7050    | -1504.4   | 0.008 |
| 3    | 1.7346    | -1518.0   | 0.004 |
| 4    | 1.6109    | -1461.7   | 0.002 |
| 5    | 2.7616    | -2287.9   | 0.003 |
| 6    | 2.4465    | -2104.1   | 0.001 |
| 7    | 2.7174    | -2275.1   | 0.002 |
| 8    | 2.8751    | -2338.8   | 0.005 |
| 9    | 2.5789    | -2180.1   | 0.002 |
| 10   | 2.4895    | -2130.5   | 0.001 |
| 11   | 2.1993    | -1925.0   | 0.002 |
| 12   | 1.8503    | -1667.1   | 0.002 |

\( \sigma = \left[ \sum (\ln a^{corr}_{exp} - \ln a^{corr}_{cal}) / (n-2) \right]^{1/2} \)

1) with \( n \) = number of experimental points
Tab. 5: The change of the Cl⁻/H₂O ratio in the system {xKCl + (1-x)(MgCl₂ + R H₂O)} in comparison to the pure magnesium chloride hydrate melt

| R   | x = 0.15 | x = 0.30 |
|-----|---------|---------|
| 6.0 | 0.030   | 0.072   |
| 5.5 | 0.032   | 0.078   |
| 5.0 | 0.035   | 0.086   |
| 4.6 | 0.038   | 0.093   |
Fig. 1: Concentration dependence of the partial molar volume of water $V'_w$ at several temperatures [K] in the system MgCl$_2$·H$_2$O
(473 K = max. compiled temperature; dashed straight line = limit of the compiled concentration range /15/)
Fig. 2a: Experimental results for \( x \text{KCl} + (1-x)(\text{MgCl}_2 + 6.0 \text{H}_2\text{O}) \)

(continuous line refers to the regression line of runs 1 and 2)

Present work: + \( x=0 \) (run 1 and 2)
- \( x=0.15 \) (run 3)
- \( x=0.30 \) (run 4)
Fig. 2b: Experimental results for $[xKCl + (1-x)(MgCl_2 + 6.0 H_2O)]$
(continuous line refers to the regression line of runs 1 and 2)
Previous data: + $x=0$ (from /9/)
• $x=0.10$ (from /16/)
○ $x=0.20$ (from /16/)
Fig. 3: Experimental results for \( x\text{KCl} + (1-x)(\text{MgCl}_2 + R\text{H}_2\text{O}) \)
(filled circles and continuous lines refer to \( x = 0.3 \), whereas dashed lines represent the binary system \( \text{MgCl}_2 + R\text{H}_2\text{O} \) taken from /9/)

\[ \begin{align*}
\ln \alpha_w^\text{corr} & \quad R = 6.0 \\
\quad & \quad R = 5.5 \\
\quad & \quad R = 5.0 \\
\quad & \quad R = 4.6 \\
\end{align*} \]

\[ 1/T \cdot 10^3 \]

[1/K]
Fig. 4: Isothermal representation of the variation of water activity in the system \( \{ x \text{KCl} + (1-x)(\text{MgCl}_2 + R \text{H}_2\text{O}) \} \) at \( T = 473 \text{ K} \)

a) Dependence on the molar ratio \( \text{H}_2\text{O}/\text{MgCl}_2 \) at \( x = 0.3 \) content at \( R = 4.6 \)

\[
\Delta a_W [%] \quad x = 0.3
\]

b) Dependence on the KCl content at \( R = 4.6 \)

\[
\Delta a_W [%] \quad R = 4.6
\]
Fig. 5: Dependence of the molar enthalpy of evaporation $\Delta_{w}H_w$ and the partial molar excess entropy of water $\Delta_{m}S_{w}^{ex}$ on the KCl content in the system $xKCl + (1-x)(MgCl_2 + RH_2O)$ at $R = 4.6$ and $T = 473 K$. 

![Graph showing the dependence of $\Delta_{w}H_w$ and $\Delta_{m}S_{w}^{ex}$ on KCl content.](image-url)