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THE PHASE DIAGRAM OF MAGNESIUM BROMIDE AND CHLORIDE HEXAHYDRATE MIXTURES

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ABSTRACT

The liquidus of the phase diagram of $MgCl_2 \cdot 6\ H_2O + MgBr_2 \cdot 6\ H_2O$ mixtures was determined, and a continuous series of mixed crystals was found to be formed on freezing. The freezing point of $MgBr_2 \cdot 6\ H_2O$ was confirmed to be 164.4±0.3°C, but on repeated melting–freezing cycles this value decreased, due to loss of water. An approximate value of the specific heat of fusion of $MgBr_2 \cdot 6\ H_2O$, of 150 J g^{-1}, was determined.

INTRODUCTION

Thermal energy can be stored in salt hydrates, utilizing their latent heat of fusion. Heat storage densities (*HSD*) of above 200 MJ m^{-3} can be readily attained with a minimal temperature swing (say 5 degrees either side of the melting point) [1,2]. For applications below 100°C, the storage of thermal energy as sensible heat in water (with a large temperature swing) naturally competes with its storage in phase change materials such as salt hydrates. However, if thermal energy is to be stored at moderate temperatures above 100°C, storage in water is practically excluded, and salt hydrates may become the materials of choice. This results from the favorable heat storage density possible with them [2]

$$HSD \approx 9\nu(M/\text{kg mol}^{-1})^{-1}\ \text{MJ m}^{-3} \tag{1}$$

where ν is the number of particles (ions and water molecules) into which the salt can dissociate, and M is the molar mass. Mean molar masses per particle, M/ν, of $\leqslant 0.04$ kg mol^{-1} are required for the attainment of reasonable *HSD*s. Salts of the light metals are, therefore, indicated according to this criterion [2]. Other criteria, such as availability, low cost, non-toxicity, etc. [1], point to salts of magnesium as candidates, since its nitrate, chloride and bromide have reported melting points of 364, 390, and 445 K, respectively.

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Mixtures of these magnesium salts may have advantages over the pure salts, in that they may permit a choice of the melting temperature according to requirements. An important aspect in the choice of salts as thermal energy storage phase change materials is the thermal stability and the reproducibility of the heat storage density attainable over many fusion–freezing cycles, and a minimal undercooling temperature lag on freezing. These aspects of the magnesium salts have not been studied sufficiently, and the present study is a step in a comprehensive program to this effect.

The behavior of magnesium bromide hexahydrate on melting has not been studied as extensively as that of the corresponding chloride. In fact, even the value of the melting point is controversial: Mylius and Funk [3] report $t_m = 164°C$, which is confirmed by Menschutkin [4], but this value is in conflict with $t_m = 151.5–155°C$ reported by Panfilov [5] and $t_m = 172.4°C$ reported by Getman [6].

The melting behavior of mixtures of magnesium bromide and chloride hexahydrates has not been studied so far. On the other hand, there are reports that mixed crystals are formed when these salts crystallize from aqueous solutions containing magnesium, chloride, and bromide ions. Boecke [7,8] reported a continuous series of mixed crystals to be formed, which was later confirmed by Jaenecke [9]. According to the latter author, the bromide is somewhat enriched in the crystals from bromide-rich solutions and in the solution from chloride-rich solutions.

In the present study the melting behavior of magnesium bromide hexahydrate is reported, as well as the phase diagram of the magnesium bromide–chloride hexahydrate system.

EXPERIMENTAL

Materials

Magnesium bromide, chloride, and nitrate hexahydrates (BDH) were kept for several days above 70 wt% sulfuric acid, in order to fix the composition of the hexahydrate exactly. This was confirmed on the one hand by a Karl–Fischer titration of the water content, and on the other by the magnesium content (titration with EDTA) and the halide content (argentometry). The results for the halides were 5.99 to 6.07 mol H_2O per 1 mol $MgBr_2$ and 6.15 to 6.18 mol H_2O per 1 mol $MgCl_2$. Drying over 97 wt% sulfuric acid did not produce drier salts.

Cooling curves

A sample of 10–15 g salt or salt mixture was placed in a glass test tube open to the atmosphere and melted carefully in a liquid paraffin bath. A narrower glass tube, closed at the bottom and having little glass bumps fused to it, acted as a manual stirrer and as a protective sheath for the temperature probe, a few drops of paraffin oil in it providing the thermal contact. The temperature probe was that of a Hewlett-Packard quartz thermometer (model 2801), and temperatures were read to 0.01°C after integration periods of 10 s.

Drop calorimeter

Preliminary experiments utilized a makeshift drop calorimeter, consisting of a Dewar vessel, the quartz thermometer probe, a resistance heater, a magnetic stirring bar and an external magnetic stirrer, and an electrical calibration circuit. The calorimetric fluid was paraffin oil, and samples were dropped into the calorimeter from an external heating vessel. Samples heated to just below and just above the melting point were used for the determination of the heat of fusion.

RESULTS AND DISCUSSION

Pure salts

The cooling curve method was used for the determination of the freezing points of magnesium nitrate, chloride, and bromide hexahydrates. The following values were found

$Mg(NO_3)_2 \cdot 6\ H_2O$ $t_m = 89.7 \pm 0.7°C$; lit.: 89.2 [10], 89.7 [11]
$MgCl_2 \cdot 6\ H_2O$ $t_m = 116.0 \pm 0.2°C$; lit.: 116 [12], 117.2 [13]
$MgBr_2 \cdot 6\ H_2O$ $t_m = 164.4 \pm 0.3°C$; lit.: ~ 153 [5], 164 [3,4], 172.4 [6]

Whereas the nitrate showed undercooling of about 11 K on freezing the undercooling in the cases of the chloride and bromide was only 1.0 and 0.5 K, respectively. In the case of the nitrate melting occurred at the upper limit of the range quoted, freezing at the lower limit. For the halides no temperature lag between melting and freezing was noted, and the limits reflect the reproducibility obtained with independent samples.

Bromide–chloride mixtures

Eighteen mixtures of $MgBr_2 \cdot 6\ H_2O$ and $MgCl_2 \cdot 6\ H_2O$ were prepared by weight, covering the whole composition range, and cooling curves were taken. Duplicates were measured for a few compositions, with very good agreement.

The reproducibility of the freezing point was tested not only on duplicate samples, but some of the samples were remelted and allowed to cool again. The case of the sample with $x_{Br} = 0.771$ is shown in Fig. 1, where it is noted that practically the same freezing temperature t_m is obtained. This behavior contrasts with that of the pure bromide salt, where loss of water causes a steady fall of the freezing temperature (see below). The phase diagram is presented in Fig. 2. Only one break in the cooling curve was noted for bromide mole fractions (i.e., $x_{Br} = n_{Br}/(n_{Br} + n_{Cl})$ in the mixed salt) < 0.2 and > 0.7, but within these limits a less well marked second break was noted, 0.5–4.0 K below the freezing point. A slight decrease in the freezing point is noted when bromide ions start to replace the chloride ions of $MgCl_2 \cdot 6\ H_2O$, a very shallow minimum is noted at $t_m = 115°C$, and the freezing point of the pure chloride is regained at $x_{Br} = 0.22$. On the other hand, when chloride ions start to replace the bromide ions in $MgBr_2 \cdot 6\ H_2O$, the freezing point falls steadily (linearly down to $x_{Br} = 0.55$). No eutectic point is seen in the curve, nor indications of limited solid solubility. Thus, a continuous series of mixed crystals is formed on freezing.

The liquidus curve can be described (within ± 0.5°C) by the following expression

$$t_m = 164.4 - 69.4(1 - x_{Br}) + 21.0(1 - x_{Br})^2 °C \tag{2}$$

The complete solid solubility of $MgCl_2 \cdot 6\ H_2O$ and $MgBr_2 \cdot 6\ H_2O$ obtained both on freezing mixed melts as found in the present study and on crystallization from mixed aqueous solutions [7–9] is a natural consequence of the great similarity of their crystal structures [14,15]. The bimolecular monoclinic unit cells have practically the same angles $\beta = 93.78°$ for the chloride and 93.42° for the bromide, and the dimensions a, b, and c of latter

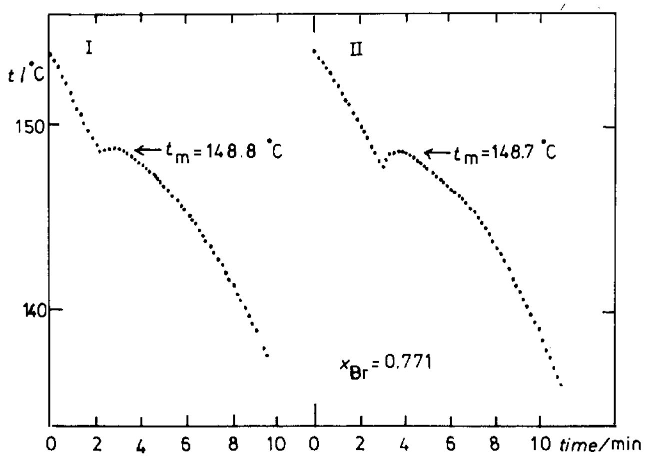

Fig. 1. Cooling curves for $Mg(Cl, Br)_2 \cdot 6\ H_2O$ at $x_{Br} = 0.771$, for the first and second cycles on the same sample.

are larger by only 4.38, 3.19, and 2.34%, respectively, than those of the former.

The continuously varying melting points between those of magnesium chloride hexahydrate (116°C) and magnesium bromide hexahydrate (164°C) on varying the composition of the mixed salts between $x_{\mathrm{Br}} = 0.2$ and $x_{\mathrm{Br}} = 1.0$ permit the construction of a thermal energy storage system at any desired temperature in between. The presence of some chloride in the bromide, and the consequent lowering of t_{m}, seem to stabilize the salt against incongruent melting and loss of water, since the freezing point of the mixed melt is stable on melting-freezing recycling.

Behavior on melting-freezing cycles

Magnesium nitrate hexahydrate showed excellent reproducibility of the melting and freezing temperatures on repeated cycling (four cycles were tested on several samples). The relatively large undercooling noted above could be reduced to insignificance when boiling chips or a little sand were added, the melting and freezing temperatures being unaffected.

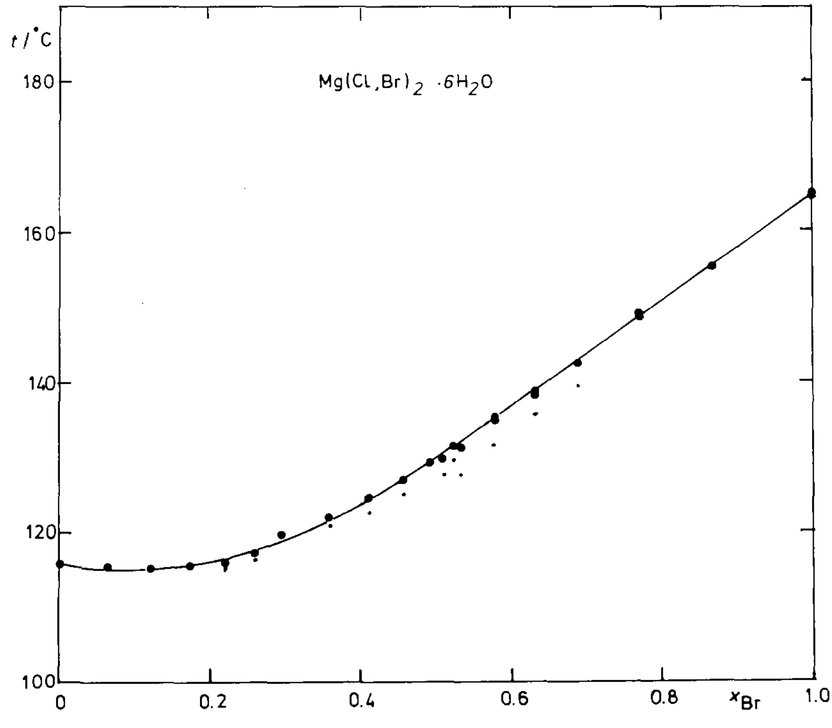

Fig. 2. Liquidus curve of the phase diagram of Mg(Cl, Br)$_2$·6 H$_2$O. The dots below the curve correspond to a second (less distinct) break in the cooling curve for a given composition. The liquidus curve is drawn according to eqn. (2).

Magnesium bromide hexahydrate could also be melted and frozen repeatedly (four cycles were tested on several samples). In all cases a water-clear melt was obtained, and no acidic vapors were given off from melts held for some time a few K above the melting point. The cooled salt dissolved completely in water. These observations confirm those of Amirova et al. [16] on magnesium bromide, and similar ones of Cantor [12] on the chloride.

However, the freezing temperature t_m of the magnesium bromide hydrate decreased steadily for each new melting and freezing cycle. These results are shown in Fig. 3. A concurrent decrease in the mass of the samples was also noted. Since no acidic vapors were given off, it is concluded that some water was lost, up to 4% of the total mass in three cycles, corresponding to 0.67 mol of water out of the initial 6.0. Amirova et. al. [16] noted a 0.6% loss of mass on a single melting event, but they did not state the exact initial water content specifically. Their samples were 98.2–98.7% pure [16], the rest could have been extra water. In the case of the chloride, melting has been reported to lead to partial decomposition to $MgCl_2 \cdot 4\ H_2O + 2\ H_2O$, from which the water is then partly lost [17], but this was not confirmed in a later study [17], where congruent freezing was noted. However, in the case of the bromide the $MgBr \cdot 4\ H_2O$, which is apparently formed, is soluble in the molten $MgBr_2 \cdot 6\ H_2O$, and the freezing point is correspondingly depressed.

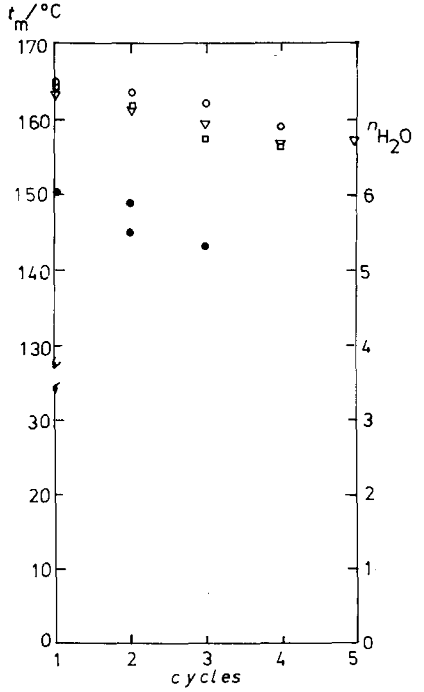

Fig. 3. Changes of the freezing point and water content of $MgBr_2 \cdot 6\ H_2O$ on repeated melting and freezing cycles for three samples. Open symbols, left-hand ordinate; filled symbols, right-hand ordinate.

The heat of freezing of $MgBr_2 \cdot 6\ H_2O$

In a preliminary experiment the heat of freezing of $MgBr_2 \cdot 6\ H_2O$ was determined in a drop calorimeter. A 2.12-g sample of salt heated to just below the melting point (162°C) delivered 411 J to the calorimeter on cooling to 23°C. A 2.28-g sample heated to above the melting point (170°C) delivered 804 J to the calorimeter on cooling to 25°C. The integrated specific heat (of the solid salt) over the stated temperature range is 1.40 J K^{-1} g^{-1} (that of the chloride is 1.55 J K^{-1} g^{-1} as a mean from room temperature to the melting point [18]). The specific heat of the melt is, presumably, somewhat higher (that of the chloride is 2.05 J K^{-1} g^{-1} [18]), but since the salt was heated to only 6°C above the melting point, the uncertainty introduced thereby is small. The resulting division of the total of 804 J into cooling and solidification leaves 342 J for the latter, or a specific latent heat of freezing of 150 J g^{-1}. This corresponds to a molar heat of fusion, ΔH^F, of 44 kJ mol^{-1} (compared with 35 kJ mol^{-1} for the chloride [18]).

The molar entropy of fusion ΔS^F is 100 J K^{-1} mol^{-1}, corresponding to 1.34 R per particle (ions and water molecules) into which the salt may dissociate on melting (R is the gas constant). This is on the low side, since the average [2] for salt hydrates is $(2.0 \pm 0.6)\ R$. However, the heat storage density permitted in magnesium bromide hexahydrate is not so low, since the density of the salt is pretty high, estimated at 1.95 kg dm^{-3} at the melting point [2,15]. Thus $HSD = (150\ kJ\ kg^{-1}) \times (1.95\ kg\ dm^{-3}) = 290$ MJ m^{-3}, which is a good average figure for salt hydrates, and higher than the $HSD = 234$ MJ m^{-8} for the chloride or $HSD = 254$ MJ m^{-3} for the nitrate [2].

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