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CALCIUM CHLORIDE HEXAHYDRATE–AMMONIUM CHLORIDE BINARY SOLUTIONS: A DSC STUDY

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ABSTRACT

Experimental results of DSC analyses of binary mixtures of calcium chloride hexahydrate and ammonium chloride are presented and analysed. Evidence for the formation of a mixed compound $CaCl_2 \cdot 2NH_4Cl \cdot 2H_2O$ is given.

INTRODUCTION

The possible use of renewable energies, e.g. direct solar energy, for domestic applications at room temperatures, justifies abundant research work being done on storage materials and devices (good examples have been recently reviewed in refs. 1 and 2). One of the simplest solutions to the storage problem uses the latent heat evolved during the phase change, which is related to a solid–liquid or solid–solid equilibrium at constant temperature and pressure, of certain materials.

Among the phase-change materials (MCP) adopted for applications at room temperatures, e.g. in buildings, greenhouses, etc., calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) appears to be one of the most reliable. Many studies have been devoted to overcoming the main handling difficulties linked to precipitation of the solid phase out of the liquid, and segregation correlated to a slightly non-congruent phase diagram. These problems are quite common for salt hydrates and are not so easy to solve. For $CaCl_2 \cdot 6H_2O$, several different successful solutions have been proposed however [3–5].

The thermophysical properties of pure $CaCl_2 \cdot 6H_2O$ ($\theta_m = 29.4°C$, $\Delta H_m = 220$ kJ kg^{-1}) are lowered for stabilized technical materials modified by the addition of KCl [5] or diatomites [4] ($\theta_m \cong 28°C$, $\Delta H_m \cong 200$ kJ kg^{-1}). Such melting temperatures θ_m are not well suited to some practical applications, for which a domain of 18–25°C is required. Since there are no workable pure salt hydrates in this melting range, our research strategy has been oriented towards synthetizing multi-component mixtures with suitable

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melting temperatures, high latent heats of melting, and with compositions that remain unaltered after thousands of melting–freezing cycles.

Most of the successful mixtures realized have been pseudo-binary mixtures of $CaCl \cdot 6H_2O$ and NH_4Cl.

MATERIALS AND EXPERIMENTAL METHODS

Numerous solubility diagrams involving NH_4Cl in various hydrated solutions have been reported (see e.g. ref. 6), but none of them involves NH_4Cl and $CaCl_2$ in H_2O.

In Fig. 1 solubility curves at 20 °C for $KCl–CaCl_2–H_2O$ [7], $KNO_3–CaCl_2–H_2O$ [8], and some preliminary results which were determined in our laboratory for the $NH_4Cl–CaCl_2–H_2O$ system are given.

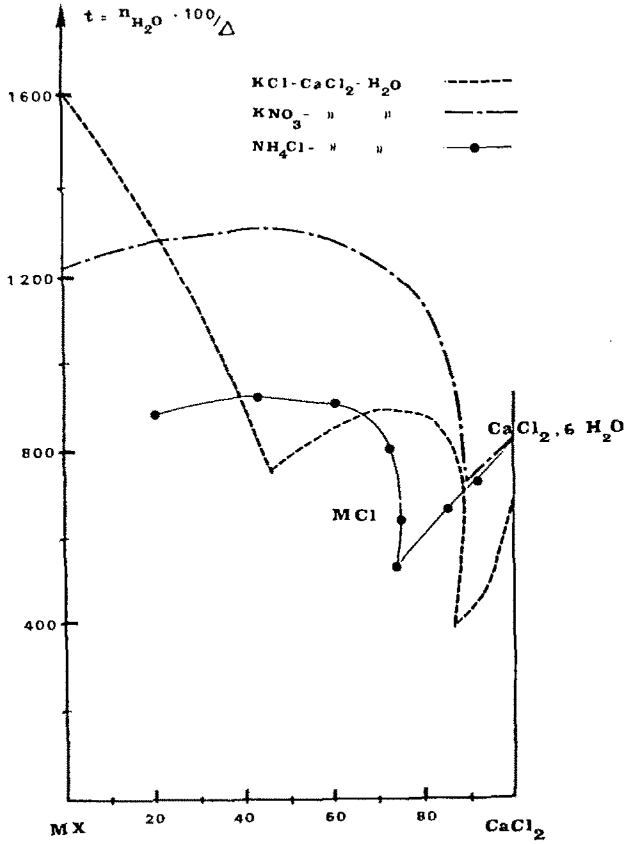

Fig. 1. Phase diagrams of various aqueous salts systems $MX–CaCl_2–H_2O$.

The chosen representation uses the Janecke coordinates, with

$$\Delta = n_{\mathrm{MX}} + n_{\mathrm{CaCl_2}} \qquad t = n_{\mathrm{H_2O}} \times \frac{100}{\Delta} \qquad u = n_{\mathrm{CaCl_2}} \times \frac{100}{\Delta}$$

MX may be KCl, KNO_3 or NH_4Cl; n_{MX} and $n_{\mathrm{CaCl_2}}$ are the number of moles of anhydrous MX and $CaCl_2$, respectively.

As may be seen from Fig. 1, addition of NH_4Cl to $CaCl_2 \cdot 6H_2O$ has a greater influence than addition of KCl. At 20 °C the solubility of NH_4Cl may rise to about 20 mol%. This result may explain the scarce results presented by Meissingset and Gronvold [9] for KCl and/or NH_4Cl mixtures with $CaCl_2 \cdot 6H_2O$, by an adiabatic calorimetry technique. It would appear, however that their solutions were somewhat beyond the solubility limit of NH_4Cl and they did not notice that they were studying subcooled systems.

In the present study the system NH_4Cl–$CaCl_2$–H_2O was carefully examined using the differential scanning calorimetry technique. All the materials were of the highest purity (Fluka). The solutions were prepared by first dissolving the appropriate amount of NH_4Cl in water. This solution was then added to $CaCl_2 \cdot 2H_2O$ in the correct proportion to give the hexahydrate. This first step is quite endothermic. $CaCl_2 \cdot 2H_2O$ was then added and the mixture was stirred vigorously. About 100 g of each sample were prepared and kept in tightly closed polyethylene flasks.

Samples for calorimetric analysis (140–180 mg) were removed from the flasks with a calibrated syringe at 32 °C, transferred to a stainless steel capsule, weighed, and then covered with a sealed cap. They were then put in a freezer and kept for at least half an hour at a temperature of -20 °C, in order to ensure complete and rapid quenching.

For each run, a blank of the empty capsule covered with its cap was tested in the temperature range investigated (10–30 °C).

The calorimeter used was a DSC Setaram 111, which was programmed for C_p measurement within a 0.1 °C rise in temperature. An integrator gave the corresponding value of ΔH. The calorimeter was also programmed to determine the first derivative of C_p with temperature.

In order to obtain precise and reproducible results with these solutions, and moreover to compare our results with observations of cycling of large quantities of the same material in the real environment, we chose a low heating rate, 3–5 °C h^{-1}.

RESULTS AND DISCUSSION

In the range of concentrations explored, $X_{\mathrm{CaCl_2}} = 0.72$–$1$ ($X_{\mathrm{CaCl_2}} = n_{\mathrm{CaCl_2}}/(n_{\mathrm{CaCl_2}} + n_{\mathrm{NH_4Cl}})$, where n is the number of moles, the C_p signal exhibited a continuously varying shape, showing a single peak for $X_{\mathrm{CaCl_2}} = 0.75$ and $X_{\mathrm{CaCl_2}} = 1$, two peaks for $0.75 < X_{\mathrm{CaCl_2}} < 0.875$, three peaks for

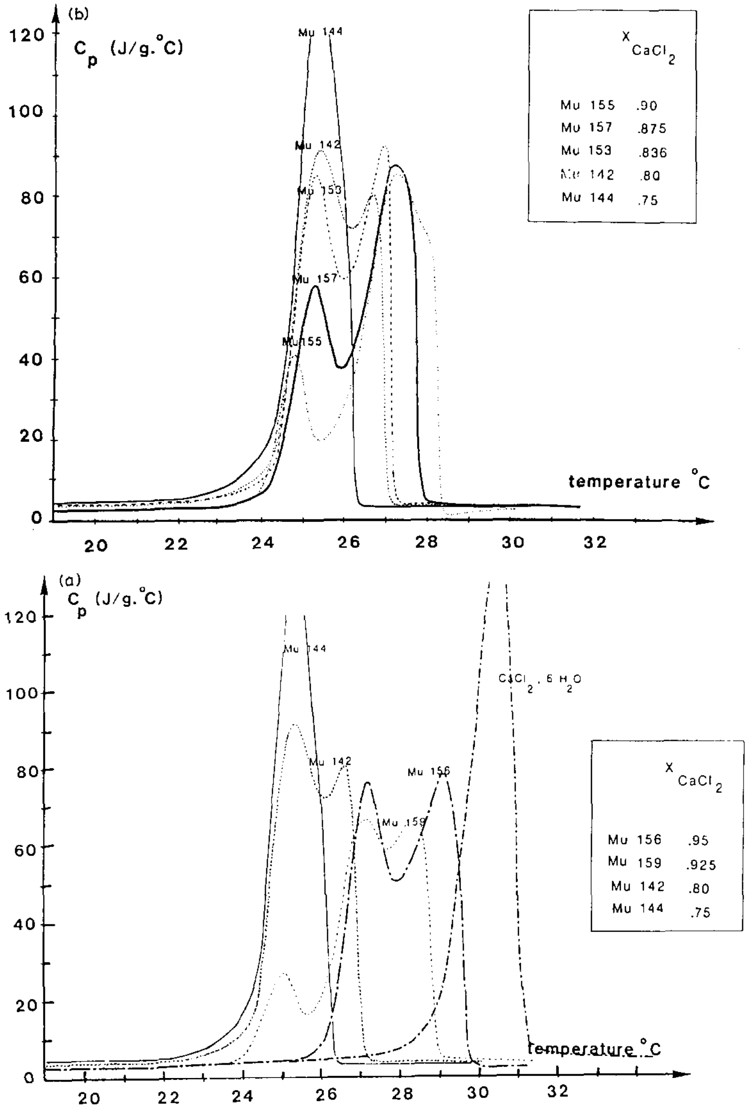

Fig. 2. C_p signals for pseudo-binary $NH_4Cl–CaCl_2 \cdot 6H_2O$ systems.

$0.875 < X_{CaCl_2} < 0.925$, and two peaks again for $0.925 < X_{CaCl_2} < 1$. This is clearly shown in Fig. 2, and reflects a somewhat more complicated situation than expected from the crude phase diagram in Fig. 1. We must take into account these complications when we study the compositions of the solutions in detail and attempt to determine the solid phases in equilibrium with them.

However the presence of the first peak of the C_p curves, corresponding to a constant onset (of melting) temperature of 24.2 °C may be related to a

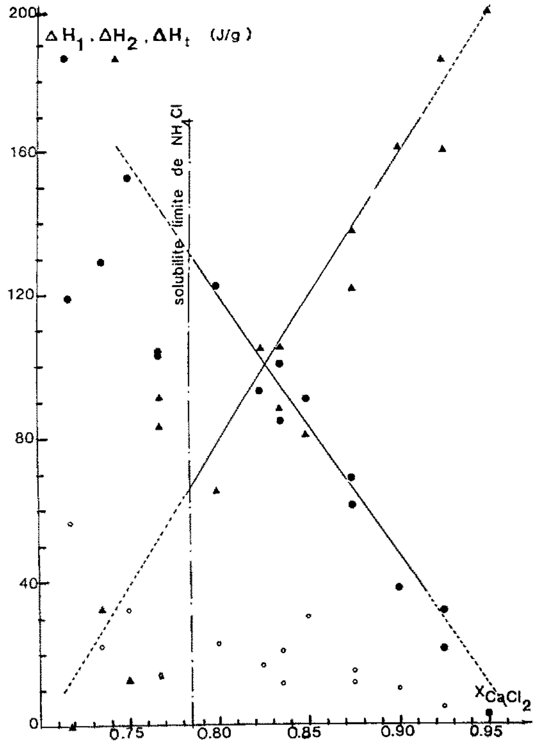

Fig. 3. Peak enthalpy analysis of C_p signals for NH_4Cl–$CaCl_2 \cdot 6H_2O$.

well-defined phase. A close examination of the shape of the C_p versus temperature curve allows us to distinguish between three different domains:

(1) The region from the departure of the base line to the onset temperature θ_1, an area whose importance increases as the solubility limit of NH_4Cl is approached or even surpassed. The behaviour of the solution is like that of hydrated salt with an excess of water, and we call the corresponding enthalpy ΔH_{drag} (sensible heat).

(2) The area from the onset temperature θ_1 to the temperature denoted θ_2, in which we observe the melting of phase 1, with related latent enthalpy ΔH_1.

(3) The area from θ_2 to θ_3, in which we have the melting of phase 2, related to the enthalpy change ΔH_2 (see e.g. the Mu 142 curve), corresponding to the total enthalpy change from θ_2 to the final temperature, including the two last peaks of the C_p curves if they are present.

The evolution of the different enthalpies with temperatures is shown in Fig. 3. Within errors estimated to be ± 10 J g^{-1}, we observe a linear decrease of ΔH_1 and a corresponding linear increase of ΔH_2 with increasing X_{CaCl_2}, while a slight decrease of ΔH_{drag} is noticed. The total enthalpy change ΔH_{tot} $(\Delta H_{drag} + \Delta H_1 + \Delta H_2)$, is slightly different from the latent

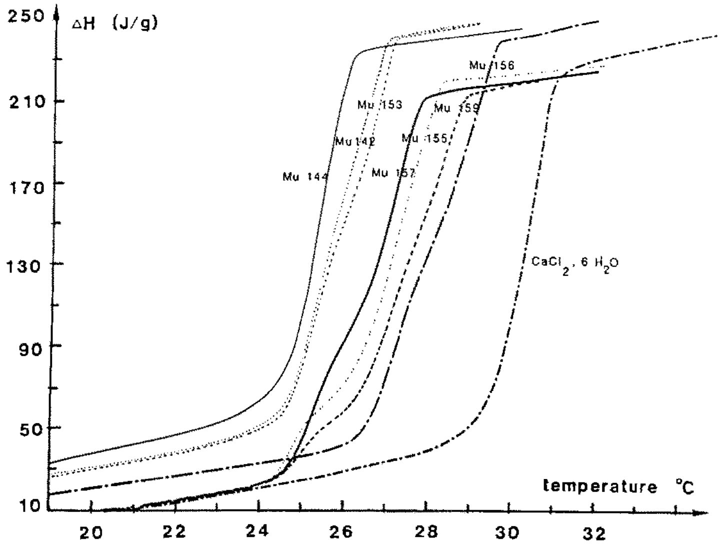

Fig. 4. Enthalpy content vs. temperature for $NH_4Cl–CaCl_2 \cdot 6H_2O$ solutions $72 \leqslant X_{CaCl_2} \leqslant 1$.

heat effect ($\Delta H_1 + \Delta H_2$) but on the whole may be estimated to be constant and equal to 200 J g^{-1}.

The variation of latent heat of melting for the $NH_4Cl–CaCl_2 \cdot 6H_2O$ solutions is illustrated in Fig. 4. The sensible heat part is more pronounced for high NH_4Cl content, where the melting interval is shifted towards lower temperatures.

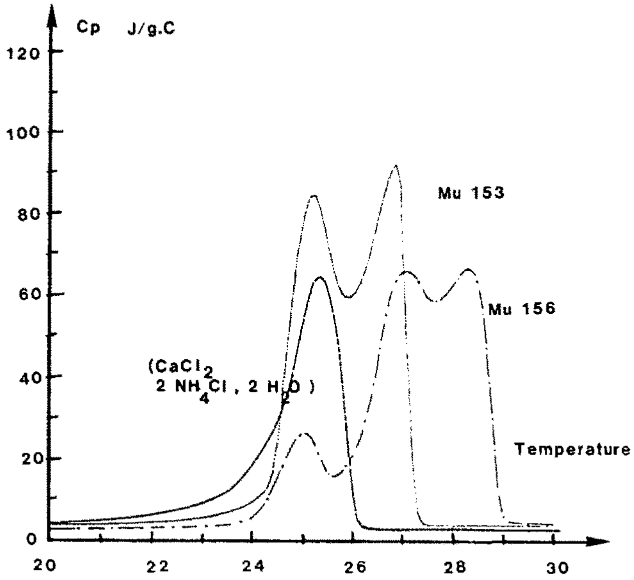

Fig. 5. C_p vs. temperature for synthetic compound ($CaCl_2 \cdot 2NH_4Cl \cdot 2H_2O$) compared to the Mu 153 and Mu 156 mixtures.

These solutions are not stable upon cycling, but they may possibly be suitably modified by adding diatomites, as for pure $CaCl_2 \cdot 6H_2O$ [4], and be used as precursors for multi-component systems as described elsewhere [10,11].

We tried to isolate the compound precipitating out from the solutions with $X_{NH_4Cl} > 0.25$. As a first estimate this was concluded to be the mixed compound $CaCl_2 \cdot 2NH_4Cl \cdot 2H_2O$. Such a compound was synthesized from an aqueous solution containing 1 mole of $CaCl_2$ per 2 moles of NH_4Cl, by evaporation of excess water.

A calorimetric run on the crystals obtained gave the results shown in Fig. 5. As can be seen, the superposition of this peak ($\theta_m = 24.2°C$) over the first peak observed for all our mixtures, is evident. This observation would help to establish the nature of solid phases in equilibrium with the liquid phase, and evolutions on the phase diagrams even with multi-component systems. An X-ray investigation is currently being undertaken.

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