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IDENTIFICATION OF THE LOW-TEMPERATURE PHASE TRANSITION OF SOME SOLID CADMIUM CRYSTALLOHYDRATES

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ABSTRACT

The cadmium crystallohydrates $CdBr_2 \cdot 4H_2O$ and $3\ CdSO_4 \cdot 8H_2O$ were investigated in regard to phase and structural changes appearing in the dehydration process. Besides phase changes corresponding to transition to a crystallohydrate of lower hydration degree, the low-temperature phase transition of these samples at about 310 K was especially followed. This phase transition was identified as the congruent melting of these crystallohydrates.

The results obtained by IR spectroscopy were compared to those of thermal analysis (DSC, TG). It was shown that in certain cases, where by thermal analysis it was not possible to register this type of crystallohydrate phase transition, IR spectroscopy could be applied.

INTRODUCTION

By the methods of IR spectroscopy and thermal analysis the phase and structural changes in the cadmium crystallohydrates $CdBr_2 \cdot 4H_2O$ and $3CdSO_4 \cdot 8H_2O$, occurring during the dehydration process, were followed. It was shown that these crystallohydrates, beside the usual phase transitions at higher temperatures corresponding to the transition of the crystallohydrate to a lower hydration degree, also have a low-temperature phase transition at about 310 K. At that temperature, part of the crystalline water leaves the crystalline lattice of the crystallohydrate, but remains in the system, hydrates ions of the crystalline lattice and is detected as a liquid phase in the solid. On the basis of characteristic bands in IR spectra at about 1585 and 1630 cm^{-1} this low-temperature phase transition was identified and by the ratio of the intensities of the characteristic bands the dehydration $\rightleftharpoons$ solvation process was followed. The results obtained by the method of IR spectroscopy were correlated with the results of thermal analysis.

EXPERIMENTAL

The IR spectra of the samples were recorded on a Perkin-Elmer 457 spectrophotometer in the region from 4000 to 250 cm^{-1}. The fluorolube and

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nujol mull technique was used. Spectra at higher temperatures, up to 473 K, were recorded in an adapted variable-temperature cell (model VLT-2) manufactured by RIIC, London. The samples were from Merck of p.a. purity. Recrystallization of the samples was performed from bidistilled water and deuterated forms were prepared by double recrystallization from D_2O (99% D_2O).

The DSC and TG curves were recorded on a DuPont 1090 thermal analysis system. The heating rate was 20° $\min^{-1}$ for DSC measurements in order to obtain optimum peak resolution, and 10° $\min^{-1}$ for thermogravimetric measurements. TG measurements were performed in a stream of nitrogen. Hermetic-coated alumina pans were applied in DSC measurements. The peak areas in DSC curves were calculated by the program Interactive DSC V1.1.

RESULTS AND DISCUSSION

The IR spectra of $CdBr_2 \cdot 4H_2O$ in the spectral region 4000–250 cm^{-1} (Fig. 1a and b) show that this ionic salt has no other bands except those characteristic of water in the regions 3600–3400 and 1630–1585 cm^{-1}. The IR spectrum of $3CdSO_4 \cdot 8H_2O$ is considerably more complex (Fig. 1c and d). The appearance of bands characteristic of ν_1 and ν_2 vibrations for the SO_4^{2-} ion, which are otherwise inactive in IR spectra, and the multiple splitting of bands characteristic of ν_3 and ν_4 vibrations, indicate that in the case of solid $3CdSO_4 \cdot 8H_2O$ the formation of a sulphato complex [1–3] takes place (Fig. 1c and d, Table 1). This implies that the T_d symmetry of the SO_4^{2-} ion has been disturbed and that distortion of the sulphate ion in the lattice has taken place. These results suggest that the symmetry of the SO_4^{2-} ion is lowered to C_{2v}. The SO_4^{2-} group in this complex is concluded to be a bridging bidentate [1–3].

As we are primarily, in this paper, interested in the phase transition tied to the state of crystalline water in the investigated crystallohydrates, we paid special attention to the stretching (at about 3500 cm^{-1}) and bending (at about 1630 cm^{-1}) vibrations of water in the spectra. The IR spectra, especially the spectra of partially deuterated samples (Fig. 1b and d), show that the bands of water, both in the region of stretching and bending vibrations, are complex ones. The complexity of these bands in the samples of $CdBr_2 \cdot 4H_2O$ and $3CdSO_4 \cdot 8H_2O$ indicate the existence of several ways in which the molecules of crystalline water are bonded. These data for $CdBr_2 \cdot 4H_2O$ are in agreement with those obtained by X-ray analysis [4], which indicates that there are two ways of bonding four water molecules in the $CdBr_2 \cdot 4H_2O$ crystal. Two of the four water molecules are coordinated with cadmium, while two are not. The positions of bands characteristic for water in the region of stretching and bending vibrations are close both for

TABLE 1

Observed frequencies (cm^{-1}) and band assignments of $CdBr_2 \cdot 4H_2O$, $3CdSO_4 \cdot 8H_2O$ and their deuterated derivatives

$CdBr_2 \cdot 4H_2O$	$CdBr_2 \cdot 4D_2O$	$3CdSO_4 \cdot 8H_2O$	$3CdSO_4 \cdot 8D_2O$	Assignment
3627 s	2630 s	3630 s	2705 w	H ··· OH (D ··· OD), stretch, type O(2) [a]
3537 s	2530 s	3590 w	2650 w	H ··· OH (D ··· OD), stretch, type O(1) [a]
3460 s,b a2380 m	3400 s,b	2290 m	H_2O, (D_2O) stretch	
		2300 m		
1620 m	1195 s	1630 m	(1203)	H ··· OH (D ··· OD), bend, type O(1) [a], H_2O, (D_2O) bend
	1170 m			
1583 s	1155 m	1585 m	(1155)	H ··· OH (D ··· OD), bend, type O(2) [a]
		1305 w		
		1205 sh		
		1173 sh		$\nu_3 SO_4^{2-}$
		1150 m		
		1120 s		
		977 w		$\nu_1 SO_4^{2-}$ [b]
		630 sh		$\nu_4 SO_4^{2-}$
		620 s		
		475 w		$\nu_2 SO_4^{2-}$ [b]
		350 sh		ν M–O
		290 s		ν M–O

s, strong; m, medium; w, weak; sh, shoulder; b, broad.

[a] Dealing to the crystallographic assignment of water molecules in $CdBr_2 \cdot 4H_2O$.

[b] Infrared inactive.

$CdBr_2 \cdot 4H_2O$ and $3CdSO_4 \cdot 8H_2O$ (Fig. 1, Table 1), which also indicates the similar bonding of water in $3CdSO_4 \cdot 8H_2O$ crystallohydrate. Of particular interest is the appearance of a band at about 1585 cm^{-1} (1155 cm^{-1} for deuterated forms) in both samples (Fig. 1) as well as its similar behaviour in the process of dehydration.

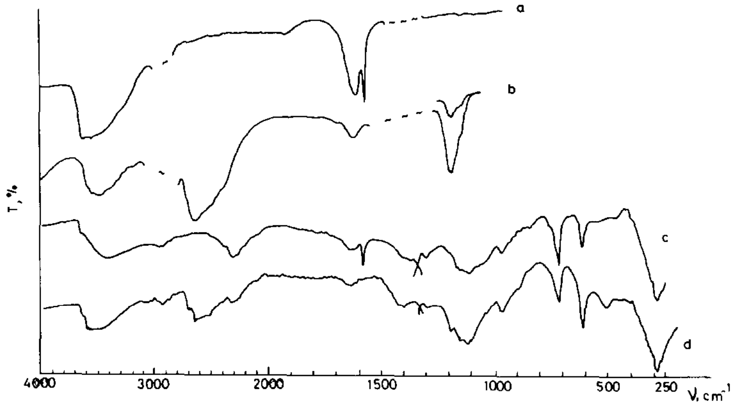
The water band in the region of bending vibrations (at about 1630 and 1585 cm^{-1}) was graphically resolved [5] and the ratio of the areas of the peaks at room temperature indicates the number of water molecules differently bonded in these crystallohydrates (Table 2). For $CdBr_2 \cdot 4H_2O$ that ratio is 1.10 which shows that the two pairs of water molecules are energetically equivalent. However, for $3CdSO_4 \cdot 8H_2O$ that ratio is 0.30, which indicates that the ratio of differently bonded water molecules is 2 : 6 (Table 2). Therefore, it could be expected that two water molecules are coordinated with each Cd^{2+}, i.e., six water molecules are coordinated with three Cd^{2+} ions (band at about 1630 cm^{-1}). The remaining two water molecules are not coordinated with cadmium ions (band at about 1585 cm^{-1}), but interact by means of hydrogen bonding with SO_4^{2-} groups and thus reduce the repulsive forces between the neighbouring SO_4^{2-} ions from adjacent chains and increase crystal cohesion.

During sample heating the intensity of these bands changes (Fig. 2). With regard to intensity, first the band at about 1585 cm^{-1} weakens and the intensity of the band at about 1630 cm^{-1} increases (Fig. 2), which also leads to a change in the area ratio of these bands (Table 2). At 309 K for $CdBr_2 \cdot 4H_2O$ and 316 K for $3CdSO_4 \cdot 8H_2O$ the band at about 1585 cm^{-1} completely disappears and only the band at 1620, i.e., 1600 cm^{-1}, remains in the spectrum. Therefore, a part of the crystalline water resulting in a band at about 1585 cm^{-1}, for both samples, transforms into the state of liquid water (1620 and 1600 cm^{-1}), but does not leave the system below 361 and 384 K for $CdBr_2 \cdot 4H_2O$ and $3CdSO_4 \cdot 8H_2O$, respectively. This water solvates the ions of the crystalline lattice and thus forms a liquid phase in the solid. The

TABLE 2

The area ratio of water bands at about 1585 and 1630 cm^{-1} at various temperatures

Sample	Temperature of spectra recording (K)	Band area ratio P_{1585}/P_{1630}
$CdBr_2 \cdot 4H_2O$ (recrystallized)	300	1.10
	305	0.40
	309	0.00
$3CdSO_4 \cdot 8H_2O$ (recrystallized)	298	0.30
	308	0.13
	316	0.00



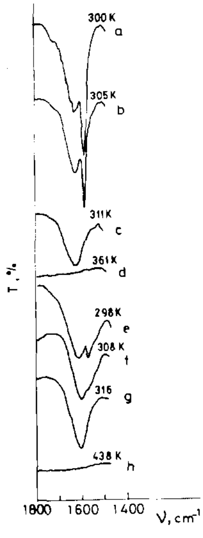


Fig. 1. IR spectra of $CdBr_2 \cdot 4H_2O$ (a), $3CdSO_4 \cdot 8H_2O$ (c) and their deuterated forms (b) and (d), respectively.

Fig. 2. Water bands in the bending vibration region at various temperatures in the spectra; $CdBr_2 \cdot 4H_2O$ (a–d) and $3CdSO_4 \cdot 8H_2O$ (e–h).

area of the band at 1620 cm^{-1} in the IR spectrum of cadmium bromide during further heating (above 309 K) continuously decreases to complete sample dehydration at 361 K. At that temperature the band disappears from the spectrum. However, in cadmium sulphate spectra the intensity of this band does not change up to 384 K, only to start decreasing above this temperature. Therefore, the dehydration process of cadmium bromide takes place continuously, while cadmium sulphate loses water by evaporation above 384 K. In the temperature interval 313–384 K the monohydrate $CdSO_4 \cdot H_2O$ is stable. The sample is completely dehydrated at 438 K.

The thermochemical behaviour of cadmium bromide and cadmium sulphate crystallohydrates is presented in Figs. 3 and 4. The DSC curve of $CdBr_2 \cdot 4H_2O$ (Fig. 3) shows two endothermic effects in the temperature region up to 373 K of which only the second one at 362.3 K is followed by mass loss (TG curve, Fig. 3). This thermal effect corresponds to the dehydration process of four water molecules which takes place stepwise (Fig. 3, Table 3). The low-temperature phase transition at 317.2 K was not followed by any mass loss. It is seen from the DSC curve that the first and second thermal effects partially overlap. The graphical peak resolution was performed, assuming that the contour of the DSC line is of the Lorentzian line-shape [6], in order to calculate the corresponding enthalpy changes. The enthalpy of dehydration is $\Delta H_{362.3} = 28.69$ kJ mol^{-1}. The enthalpy of the low-temperature phase transition was calculated per mole of $CdBr_2 \cdot 4H_2O$

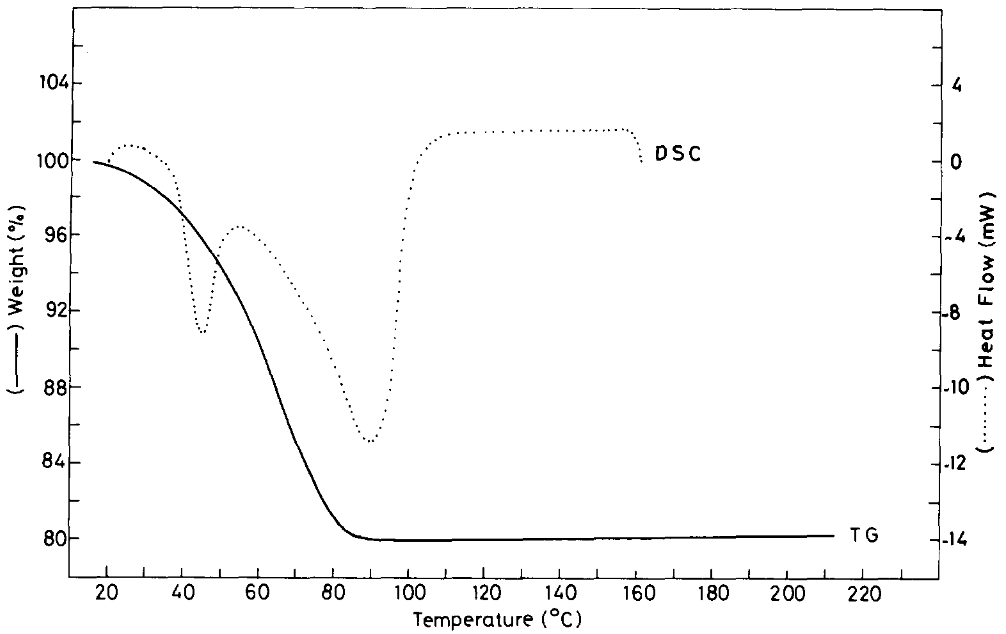


Fig. 3. DSC and TGA curves of $CdBr_2 \cdot 4H_2O$.

and was attributed to congruent crystallohydrate melting, $\Delta H_{317.2} = 27.15$ kJ mol^{-1}. This low-temperature phase transition was also noted in the IR spectra which was discussed above.

The DSC curve of $3CdSO_4 \cdot 8H_2O$ shows two well-resolved endothermic peaks, the first at 396.8 K and the second at 490.4 K, which are both followed by a mass loss (TG curve, Fig. 4). On the DSC curve of this sample a change in the baseline at about 440 K is also noted, upon passing through the first endothermic peak. The mass loss at 396.8 K calculated to the number of water molecules indicates that five molecules leave in the first process and the monohydrate forms (Table 3). Monohydrate formation is also evident from the baseline change in the DSC curve. The dehydration of

TABLE 3

Thermochemical data for crystallohydrates of cadmium

Sample	Phase transition temperature (K)	Number of dehydrated water molecules	ΔH (kJ mol^{-1})
$CdBr_2 \cdot 4H_2O$	317.2	–	27.15
(recrystallized)	362.3	$4H_2O$	28.69
$3CdSO_4 \cdot 8H_2O$	396.8	$5H_2O$	45.8
(recrystallized)	490.4	$3H_2O$	50.1

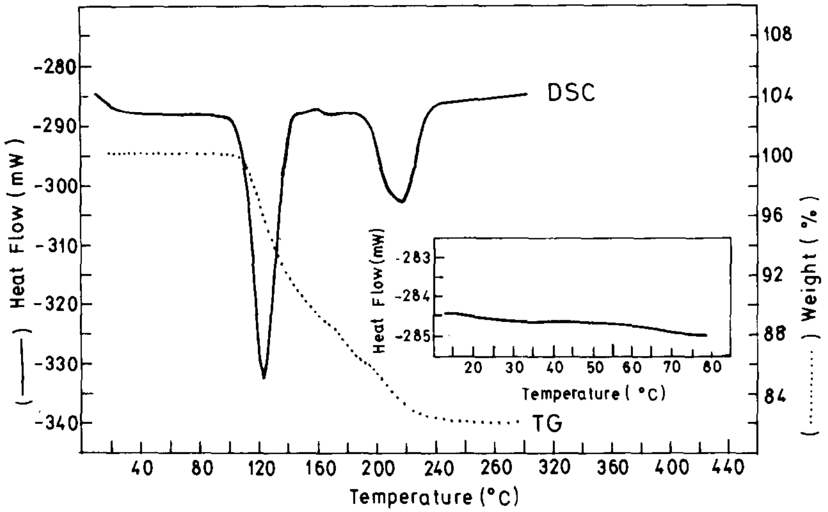


Fig. 4. DSC and TGA curves of $3CdSO_4 \cdot 8H_2O$.

$CdSO_4 \cdot H_2O$ to $CdSO_4$ takes place in a stepwise manner and is given by the second endothermic peak which shows considerable asymmetry. The enthalpies of phase transitions and temperatures are given in Table 3.

The low-temperature phase transition, noted in both crystallohydrates on the basis of IR spectra and other measurements [7], was not followed by any mass loss in the TG curves, which can be expected regarding the determined fact that water leaves the crystalline lattice, but remains in the system and solvates ions. This transition is manifested by an endothermic peak at 317.2 K on the DSC curve only for $CdBr_2 \cdot 4H_2O$, while in the case of $3CdSO_4 \cdot 8H_2O$, the DSC curve in this temperature range shows no thermal effect (Fig. 4). This can be explained by the close values of the enthalpies of the endothermic dehydration process and the exothermic solvation process which are present here.

The processes discussed above can be represented schematically in the following way

$$CdBr_2 \cdot 4H_2O(s) \xrightarrow{317.2} CdBr_2(s) + 4H_2O(l) \qquad (1)$$

$$4H_2O(l) \xrightarrow{362.3} 4H_2O(g)$$

and

$$3CdSO_4 \cdot 8H_2O(s) \xrightarrow{313^*} 3CdSO_4 \cdot H_2O(s) + 5H_2O(l) \qquad (2)$$

$$5H_2O(l) \xrightarrow{396.8} 5H_2O(g)$$

$$CdSO_4 \cdot H_2O(s) \xrightarrow{490.4} CdSO_4(s) + H_2O(g)$$

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* Temperature of the low-phase transition is from the IR spectra.

From the results presented it can also be concluded that IR spectroscopy can be used to detect quadruple points in molten salt systems. In the $CdBr_2 \cdot 4H_2O$ system in the temperature interval 317–363 K the following phases are present: $CdBr_2 \cdot 4H_2O(s)$, $CdBr_2(s)$, $H_2O(l)$ and $H_2O(g)$. For the $3CdSO_4 \cdot 8H_2O$ system in the temperature interval 313–397 K the following phases are present: $3CdSO_4 \cdot 8H_2O(s)$, $CdSO_4 \cdot H_2O(s)$, $H_2O(l)$ and $H_2O(g)$.

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