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INVESTIGATION OF DEHYDRATION PROCESS, II.

PROCESSES PRECEDING DEHYDRATION OF ALKALINE EARTH HALIDES

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The dehydration of hydrated calcium and strontium bromides and iodides was studied by thermogravimetry and differential thermal analysis. The melting in the crystallization water was distinguished from the dehydration in a self-generated atmosphere. The results of the TG and DTA curves made simultaneously were verified by measurements with a Du Pont DSC apparatus. This latter investigation was extended to the previously studied chlorides too. Correlations were found between the temperature of melting or of dehydration and the ionic radii of the respective cations and anions.

In our previous papers we have reported studies on the dehydration of some alkaline earth halide hydrates [1, 2]. Our object has been to elucidate the nature of the dehydration of hydrates containing different amounts of water of crystallization, that is, to determine the stoichiometry of the reaction, the number of stable hydrate phases, and the processes preceding, or going on simultaneously with the dehydration. The experimental methods used were adapted to these objectives. From TG and DTA curves taken simultaneously, conclusions were drawn as to the appearance of the different hydrate phases and to the modification of the physical state. It must be emphasized that a clear picture of the processes taking place can be obtained only on the basis of the results of this type of investigation. In order to resolve the different processes, different experimental conditions were applied.

In order to separate different stable hydrate phases, dehydration and rehydration experiments were carried out using a sample holder ensuring a large surface. In this way a dehydration involving the formation of a liquid phase can be distinguished from the further dehydration of the solid hydrate precipitated in the course of incongruent melting. At a sufficiently low heating rate the processes may be separated to an extent similar to that obtained under reduced pressure. This can be seen by comparing our results for $SrCl_2.6H_2O$ ([1], Fig. 2) with those reported by Wendlandt ([3], Fig. 3).

The best way of making a distinction between processes accompanied and not accompanied by weight change (melting, transformation) was found to be the simultaneous recording of TG and DTA curves of the sample under a self-generated atmosphere [2]. At an appropriate heating rate, the melting appears separately, without overlapping the evaporation process, in contrast to the results obtained by Wendlandt ([3], Fig. 2). The increased partial pressure of water enables further hydrate phases to be observed. This is reflected by the comparison of our results obtained with $SrCl_2.6H_2O$ ([2], Fig. 2) with those obtained by Wendlandt in experiments carried out under pressure ([3], Fig. 3). Both experiments suggest the formation of $SrCl_2.0.5H_2O$.

Our investigations have been extended to various calcium and strontium halides. The investigation of processes preceding dehydration was completed by DTA experiments using a sample holder with an airtight cover.

Experimental

Chemicals

$CaCl_2 \cdot 2H_2O$, $CaCl_2 \cdot 6H_2O$, $CaBr_2 \cdot xH_2O$, $CaI_2 \cdot 4H_2O$, $SrCl_2 \cdot 6H_2O$, $SrBr_2 \cdot 6H_2O$, $SrI_2.6H_2O$ (Merck analytical grade reagents).

Methods

Simultaneous TG, DTG and DTA measurements were carried out with a Derivatograph (MOM, Budapest). In some cases platinum crucibles were used as sample holders in some other cases multiplate sample holders with increased surface areas; and further a labyrinth crucible [4] ensuring a self-generated atmosphere.

Measurements were also made with a Du Pont Thermoanalyser 990, using an aluminium sample holder with plastic layer and with an airtight cover in the DSC cell of the apparatus and a chromel-constantan thermoelement. The heating rate was 5°/min.

Results

$CaBr_2$

In the literature [5] various hydrates of $CaBr_2$ are described, with 6, 4, 3, 2, 1.5, 1 and 0.5 molecules of water of crystallization, but only the existence of the hexahydrate is considered as certain. The preparation we used had a composition $CaBr_2.4H_2O$. According to the literature, $CaBr_2.6H_2O$ dissolves in its water of crystallization at 34° and transforms into $CaBr_2.4H_2O$, which undergoes a transformation at 55°. Amirova et al. [6] reported the melting of $CaBr_2.6H_2O$ at 40° and the escape of 5 molecules of water of crystallization from $CaBr_2.6H_2O$ between 130 and 200° in a single step, then 0.5 and again 0.5 molecules, these leaving separately.

The results of our experiments with hydrates of different water content are summarized in Fig. 1. In the case of the hydrate containing less than 2 molecules of water (curve a), water begins to leave at 120° and dehydration proceeds in two steps. Dehydration is not preceded by melting. Hydrates containing more than 2 molecules of water of crystallization are characterized by endothermic processes not accompanied by weight change (curve b and c). There is a weight increase at the beginning of the curve if a large-surface-area sample holder without lid is

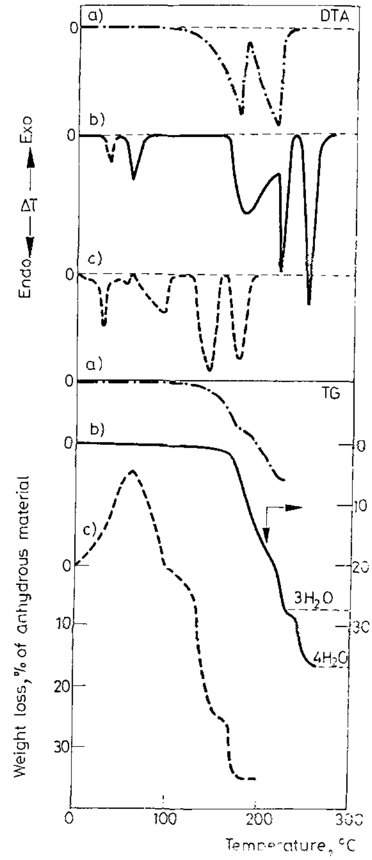

Fig. 1. TG and DTA curves of $CaBr_2.xH_2O$ taken with a Derivatograph. Sample weight: about 200 mg, heating rate: 1°/min. Curve a: $x \sim 2$, crucible. Curve b: $x \sim 4$, labyrinth type crucible; dotted curve: DTA curve of sample with $x > 4$. Curve c: $x \sim 4$, multiplate sample holder

used (curve c). This curve exhibits the melting peak of the hexahydrate ([5], 34°), indicating that there is also hexahydrate present on the surface of the hygroscopic substance. After the escape of the water taken up at lower temperatures 3 molecules and 1 molecule of water leave separately in two steps. TG curves taken in the labyrinth crucible (curve be) showed the presence of nearly stoichiometric $CaBr_2.4H_2O$. According to this the melting peak of the hexahydrate does not appear at 34°, except when the salt was allowed to take up some humidity from the air (dotted line of DTA curve b). In the curve of $CaBr_2.4H_2O$ an endothermic peak appears at 60°. This peak may be due to a process involving the formation of a liquid phase. This is probable from the shape of the DTA curve characteristic for evaporation at around 160°, in parallel with the weight loss, and is confirmed by the fact that the boiling point of the aqueous solution corresponding to $CaBr_2.4H_2O$ is ca. 150°. The last molecule of water escapes separately. In the curve obtained when the closed sample holder is used (Fig. 2) the peak of melting appears at 32.5°, and that of another endothermic transformation at 51 – 52°. The nature of this transformation is not known. Peak temperatures were reproducible within 1°.

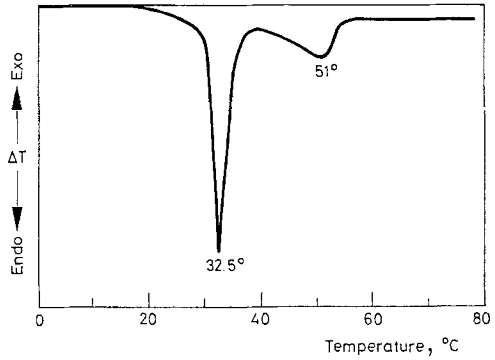

Fig. 2. DTA curve of $CaBr_2.4\ H_2O$ taken by DSC, in a closed sample holder. Sample weight: 5.605 mg; heating rate: 5°/min

CaI_2

In the literature hydrates of CaI_2 are described [5] with 6, 4, 3.5 and 3 molecules of water of crystallization. The hexahydrate melts in its water of crystallization at 42°, and the tetrahydrate begins to decompose at about 65°. The hydrate having 3.5 molecules of water of crystallization melts between 70 and 80°, and the trihydrate just below 100°. The existence of the latter two hydrates is disputed, the trihydrate being observed only in the course of a dehydration process.

We observed three endothermic peaks without weight change on the DTA curves of two preparations containing more than 4 and 5 molecules of water, respectively (Fig. 3). The peak at 40° indicates the presence of the hexahydrate in various amounts on the surface of the hygroscopic salt. The second peak, at about 45°, is very small, and in fact appears only as a break-point in curve *a*. The third peak occurs at a T_m value of about 70°. In the curve for the hydrate containing about 4 molecules of water of crystallization (*b*) the peak at T_m = 70° predominates. The subsequent portion of the curve is not characteristic, since it is connected with the evaporation of the aqueous solution. (In the curve of a hydrate with less water a further peak is observed with a T_m of 190°.) The TG curve reflects that the process takes place in two stages.

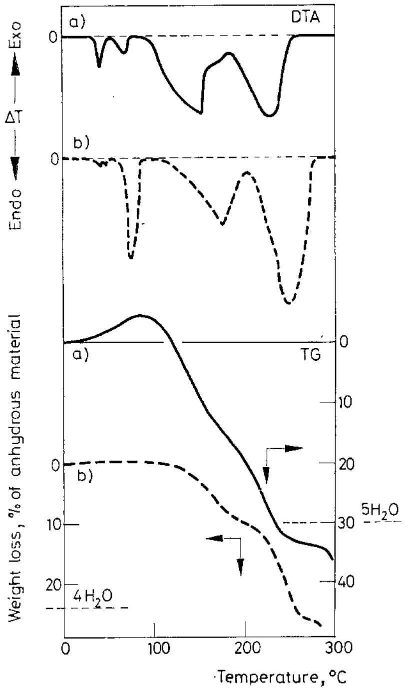

Fig. 3. TG and DTA curves of $CaI_2.xH_2O$ taken with a Derivatograph. Sample weight: about 200 mg, heating rate: 1°/min; curve a: $x > 5$; b: $x > 4$. sample holder: crucible

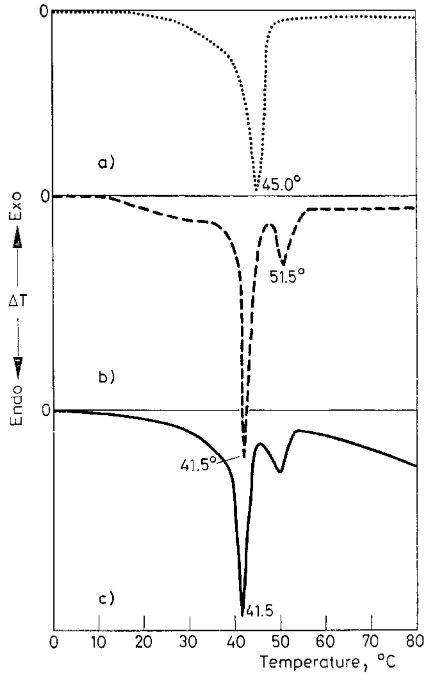

Fig. 4. DTA curve of $CaI_2.5\ H_2O$ taken by DSC. Sample weight: 6.837 mg; heating rate: 5°/min. Curves a and b: in closed sample holder, repeated heating; curve c: in open sample holder

The results of experiments made with samples in the closed sample holder are shown in Fig. 4. On the first heating of the sample (curve *a*) an endothermic peak appeared at 45°, corresponding to the melting of $CaI_2.6H_2O$, and there was no enthalpy change up to 100°. The absence of the endothermic peak at about 75–80°, observed when using the open sample holder, shows that the corresponding process may proceed at a lower partial pressure of water vapour. This peak is lacking from the DTA curve taken in the labyrinth crucible too, which supports the above explanation.

On cooling, two exothermic effects can be observed and on repeated heating (curve *b*) a further endothermic process takes place at 51°. The curve was found to be reproducible. The endothermic peak at 51° may correspond to the dissolution of a hydrate with a lower water content which is formed only during the first cooling process.

$CaCl_2.6H_2O$ and $CaCl_2.4H_2O$

These hydrates were studied earlier in an open crucible under a self-generated gas atmosphere [2]. The curves taken in the closed sample holder are shown in Fig. 5. The peak temperatures are the same as those obtained with the labyrinth crucible.

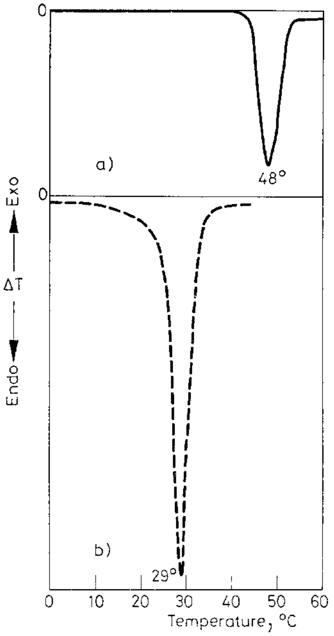

Fig. 5. Curve a: DTA curve of $CaCl_2.4\ H_2O$, curve b: DTA curve of $CaCl_2.6\ H_2O$, both taken by DSC in closed sample holder. Sample weight: about 6 mg; heating rate: 5°/min

SrI_2

Various hydrates of SrI_2 are described in the literature, with 6, 2 and 1 molecules of water of crystallization [7, 8].

The thermal dehydration of the hexahydrate (Fig. 6) is preceded by an endothermic process without weight change, which is due to the melting of $SrI_2.6H_2O$ in its water of crystallization and formation of $SrI_2.H_2O$ (Fig. 6*b*, *c*). The departure of the last molecule of water can be distinguished clearly in the curves taken in an inert atmosphere, since the decomposition proceeding simultaneously with the dehydration in an air atmosphere is negligible in this case. The advantage of working in a self-generated atmosphere can be seen in curve *c*, as the processes appear in a differentiated form. In the curve of the hydrate with lower water content (*a*) the peak height corresponding to the dissolution in its water of crystallization decreases. On the other hand, another endothermic peak appears at 110–120° which is not accompanied by a weight change. The processes preceding the dehydration can be clearly distinguished in the curves of samples in the closed sample holder (Fig. 7). In the curve of the hexahydrate the sharp melting point (79°) is preceded and overlapped by an endothermic peak. Both peaks are reversible. In the case of the hydrate containing 2.9 molecules of water, a very sharp reversible endothermic peak appears at 110° in addition to the peak mentioned above.

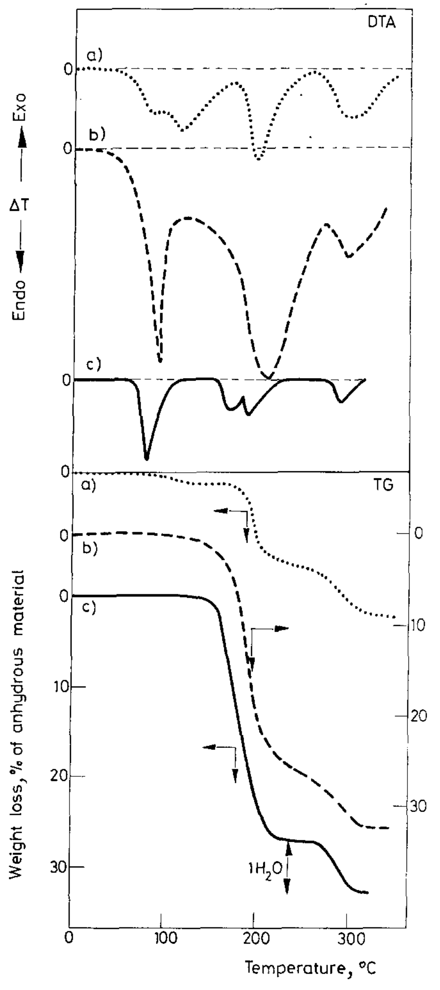

Fig. 6. TG and DTA curves of $SrI_2.xH_2O$ taken with a Derivatograph. Sample weight: about 300 mg; N_2 stream, 20 l/hr. Curves a and b: sample holder: crucible; heating rate: 10°/min. Curve a: $x \sim 2.9$; curve b: $x \sim 6$; curve c: labyrinth crucible, heating rate: 1°/min, $x \sim 6$

The presence of the melting peak of the hexahydrate indicates that the sample is a mixture of the hexahydrate and lower hydrate. The amount of SrI_2 in the system is too great to remain in dissolved form after melting. The dissolution of the lower hydrate presumably occurs at 110°.

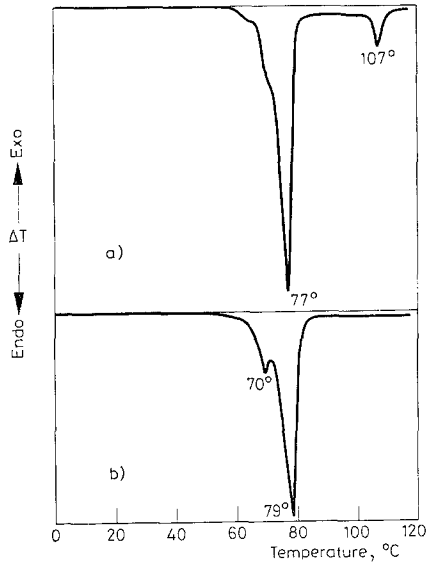

Fig. 7. DTA curve of $SrI_2.xH_2O$ taken by DSC, in closed sample holder; sample weight: about 9 mg, rate of heating: 5°/min. Curve a: $x \sim 2.9$; curve b: $x \sim 6$

$SrCl_2.6H_2O$ *and* $SrBr_2.6H_2O$

The results of experiments with $SrCl_2.6H_2O$ and $SrBr._26H_2O$ in the closed sample holder are given in Table 1. These compounds were earlier studied using open and labyrinth crucibles [2].

Discussion

It is characteristic of calcium and strontium halides that, on heating, the hexahydrate melts in its water of crystallization, with the formation of a lower hydrate. The temperature of melting changes in the same direction as the ionic radius of the anion of the salt (Table 1), with the exception of $SrI_2.6H_2O$. The melting point is also found to change in parallel with the ionic radius of the cation of the salt, if the corresponding compounds of calcium (ionic radius 1.02 Å) and strontium (1.20 Å) are compared. The melting in the water of crystallization is essentially dependent upon the size of the hydrate sheats of the ions composing the salt.

In Table 2 the DTG peak temperatures of the dehydration processes are compared. In this case too there is a correlation between the peak temperature and the ionic radius of the anion. As stated previously in connection with some other compounds, the temperature of dehydration is proportional to the radius of the

Table 1

DTA peak temperatures

Compound (Anion radius Å)		Peak temperature, °C		Literature data	References
		Closed	Open		
		crucible			
$CaCl_2$	6+4	29	*30 [2]	28–30.2	[5]
(1.81)	4+2	48	45 [2]	45.3	[5]
$CaBr_2$	6+4	32.5	30–33	34	[5]
(1.95)	4	51		55	[5]
			*60		
CaI_2	6+4	41.5–45	*40	42	[5]
(2.16)		50–51			
				65	[5]
				95	[7]
$SrCl_2$	6+2	63	*60 (2)	61.6	[10]
(1.81)				65	[9]
$SrBr_2$	6+1	90	*90 (2)	88.6	[8]
(1.95)				91	[9]
SrI_2**	6+2	70	95		
(2.16)		77		79	[9]
	2	107			

* On the basis of measurements with a labyrinth crucible

** Measurement in a stream of N_2

anion. This finding is in accordance with the assumption that anions play a predominant role in the binding of water molecules with negative peripheral charge.

Table 2

Change of peak temperatures as function of the ionic radius

	Anion radius Å	Change in the number of molecules of H_2O		
		2 → 1	1 → 0	
$CaCl_2.2H_2O$	1.81	120°	130°	
$CaBr_2.2H_2O$	1.95	155°	195°	
$CaI_2.2H_2O$	2.16	170°	255°	
		6 → 2	2 → 1	1 → 0
$SrCl_2.6H_2O$	1.81	60°	95°	135°
$SrBr_2.6H_2O$	1.95	95°	135°	200°
		6 → 1		1 → 0
$SrI_2.6H_2O$*	2.16	195°		290°

* On the basis of measurement in a N_2 stream

The melting of calcium bromide hexahydrate is followed by an endothermic transformation, which is ascribed to the transformation of $CaBr_2.4H_2O$.

On cooling, after the melting of calcium iodide hexahydrate, a hydrate with lower water content is formed, which, on repeated heating, produces an endothermic dissolution peak.

The endothermic DTA peak appearing for the lower hydrate of SrI_2 needs clarification. Further studies of this phenomenon are in progress.

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Résumé — Etude de la déshydratation des bromures et iodures de calcium et de strontium hydratés par thermogravimétrie et par analyse thermique différentielle. La fusion dans l'eau de cristallisation a été distinguée de la déshydratation en atmosphère auto-générée. Les résultats des courbes TG et ATD obtenues simultanément ont été vérifiés par des mesures effectuées à l'aide d'un analyseur calorimétrique différentiel (DSC) Du Pont. L'étude a également été étendue aux chlorures précédemment étudiés. On propose des corrélations entre les températures de fusion ou de déshydratation et les rayons ioniques des cations et anions respectifs.

Zusammenfassung — Die Dehydratisierung von Calcium- und Strontium-Bromid- und Jodidhydraten wurde mit den Methoden der Thermogravimetrie und Differentialthermoanalyse verfolgt. Das Schmelzen im Kristallwasser wurde von der Dehydratisierung in der selbsterzeugten Atmosphäre getrennt. Die Ergebnisse der simultan erhaltenen TG- und DTA-Kurven wurden durch Messungen mit einem Du Pont DSC-Gerät bestätigt, wobei die bereits schon untersuchten Chloride mit einbezogen wurden. Korrelationen zwischen den Schmelz- oder Dehydratisierungstemperaturen und den Ionenradien der entsprechenden Kationen und Anionen werden beschrieben.

Резюме — С помощью термогравиметрии и дифференциального термического анализа изучена дегидратация гидратированных бромидов, иодидов кальция и строция. Плавление в кристаллизационной воде было отделено от дегидратации в самогенерируемой атмосфере. Результаты кривых ТГ и ДТА одновременно были проверены измерениями на дифференциальном сканирующем калориметре фирмы Дюпон. Последний метод был также распространен на ранее изученные хлориды. Приведены корреляции между температурой плавления или дегидратацией и ионным радиусом соответствующих катионов и анионов.