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STUDY OF THE NATURE OF THE CRYSTALLIZATION WATER IN SOME MAGNESIUM HYDRATES BY THERMAL METHODS

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Abstract

The nature of the crystallization water in $MgSO_4 \cdot 7H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O$ has been studied with the nonisothermal methods of thermogravimetry (TG), derived thermogravimetry (DTG) and differential thermal analysis (DTA).

Analysis of the characteristic thermogravimetric data (T_M, W_∞) and the kinetic parameters (n, E_a), together with the DTA results, with $CuSO_4 \cdot 5H_2O$ as control sample, provided evidence of the existence of coordinated water and of the nature of the anions in these hydrates.

The results are confirmed by the observation of a real compensation effect. For the compensation effect, the following equation is proposed: $\ln A = 0.220\ E - 0.8$

Structures explaining the presence of the coordinated water and the nature of the anions in these hydrates are also proposed.

Keywords: crystallization water, DSC, kinetics, magnesium hydrates, TG–DTG–DTA

Introduction

Earlier studies of the crystalline structure of hydrates led to the conclusion that several types of crystallization water exist, depending on the role played in the compound: constitution water, coordination water, anionic water, current water and zeolitic water [1a].

With regard to the advantages of nonisothermal methods (TG, DTG, DTA and DSC) in the separation and characterization of decomposition processes, with the possibility of elucidation of the reaction mechanism, in the present paper these methods have been used to establish the type of crystallization water in the magnesium hydrates $MgSO_4 \cdot 7H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O$, with $CuSO_4 \cdot 5H_2O$ as control sample.

Although the literature on this field provides information on the nonisothermal thermogravimetric behaviour of some of these hydrates [2–9], and on the evolution of the kinetic parameters by known thermal methods [10–15] the

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combination of such procedures to establish the nature of crystallization water is less frequent.

Experimental

Results were obtained with the above thermal methods on two types of equipments:

I. A Paulik-Paulik-Erdey (MOM Budapest) derivatograph, which simultaneously records T, TG, DTG and DTA curves. The recording conditions were constant: sample mass ~20 mg, heating rate 12 deg·min^{-1}, maximum temperature 600°C, DTG and DTA sensitivity 1/10, reference material Al_2O_3 calcined at 1000°C, ambient atmosphere.

II. A TGA-2910 thermogravimetric balance (DuPont, Canada), which permits simultaneous recording of TG and DTG curves under nonisothermal conditions in a flow of N_2 at 30 mL·min^{-1}. The main parameters employed were: mass of sample between 30–60 mg, maximum temperature 600°C, heating rate 10 deg·min^{-1}.

The DSC curve of $CuSO_4 \cdot 5H_2O$ was recorded on a DSC-2950 apparatus (DuPont, Canada) in atmospheric air, at a heating rate of 10 deg·min^{-1}, in the temperature interval 27–400°C, with a sample mass of 31 mg.

The A. R. hydrates analysed were supplied by Merck: $CuSO_4 \cdot 5H_2O$ (M=249.68 g·mol); $MgSO_4 \cdot 7H_2O$ (M=246.48 g·mol); $Mg(NO_3)_2 \cdot 6H_2O$ (M=256.41 g·mol); $MgCl_2 \cdot 6H_2O$ (M=203.31 g·mol).

Results and discussion

Figures 1 and 2 depict DTG curves for the studied hydrates, obtained with the above-mentioned equipment. The features depend on the number of molecules of crystallization water and also on the recording conditions, two distinct stages being seen, in accordance with the literature data [2–7].

It is generally known that, under nonisothermal thermogravimetric conditions, $CuSO_4 \cdot 5H_2O$ loses its 5 water molecules in two very distinct stages, according to the following mechanism [2–5]:

$$CuSO_4 \cdot 5H_2O \xrightarrow{45-189^\circ C} CuSO_4 \cdot H_2O + 4H_2O$$

$$CuSO_4 \cdot H_2O \xrightarrow{225-298^\circ C} CuSO_4 + H_2O$$

which leads to the conclusion, supported by the results of other methods [1b], that four water molecules are coordinated, while the last is more strongly bound in the anion. Consequently, $CuSO_4 \cdot 5H_2O$ can be written as

$$[Cu(H_2O)_4]^{2+}(SO_4 \cdot H_2O)^{2-}.$$

Fig. 1 DTG curves of hydrates 1–4, recorded on apparatus I

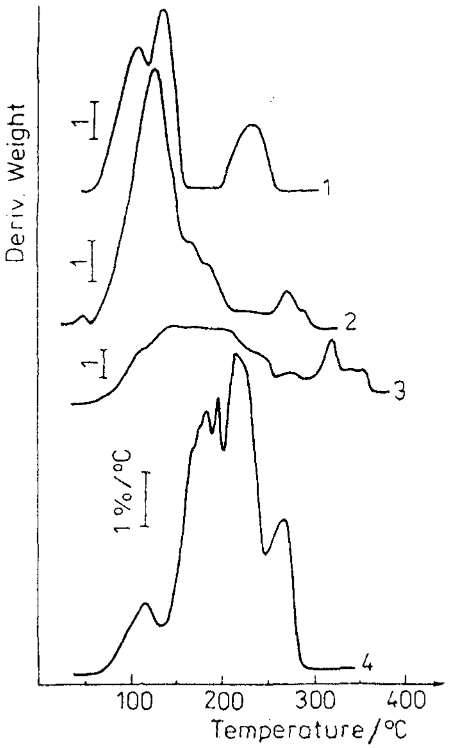


Fig. 2 DTG curves of hydrates 1–4, recorded on apparatus II

With $CuSO_4 \cdot 5H_2O$ as reference, separate analysis has been carried out on the thermogravimetric values obtained from the TG and DTG curves, and also the activation energy and reaction order calculated by the Freeman-Carroll [16] and Coats-Redfern [17] methods by means of our own computer programs [18a]. The data obtained are listed in Table 1.

Comparison of the mass losses $W_{\infty \text{ theoretical}}$ and $W_{\infty \text{ experimental}}$ indicates that, in the first stage, over the temperature range 20–280°C, hydrates 2, 3 and 4 lose 6, 5 and 5 water molecules, respectively, both in the ambient and in the inert atmosphere. Further, the average activation energies are very similar, suggesting the same nature of the binding of the molecules of crystallization water, which are probably of coordination type for hydrates 1–4, since $CuSO_4 \cdot 5H_2O$ loses its coordination water over the same interval of temperature.

In the second stage, over the temperature interval 206–368°C, $CuSO_4 \cdot 5H_2O$ loses the final one water molecule, as confirmed by the agreement between the theoretical and experimental W_∞ values and by the fact that the activation energies are equal for hydrates 1 and 2, suggesting that the same type of bond is broken, as in the following mechanism [1b]:

$$Cu^{2+}(SO_4 \cdot H_2O)^{2-} \longrightarrow CuSO_4 + H_2O$$

$$Mg^{2+}(SO_4 \cdot H_2O)^{2-} \longrightarrow MgSO_4 + H_2O$$

For hydrates 3 and 4, although the temperature range is approximately the same, the activation energy is different. Comparison of hydrates 2, 3 and 4 suggests that it depends on the nature of the anion, once the cation is the same. It is concluded that for hydrates 3 and 4 the mechanism is:

$$Mg^{2+}((NO_3)_2 \cdot H_2O)^{2-} \longrightarrow Mg(NO_3)_2 + H_2O$$

$$Mg^{2+}(Cl_2 \cdot H_2O)^{2-} \longrightarrow MgCl_2 + H_2O$$

All these observations agree with the DTA data presented in Table 2.

The enthalpies of the two stages were calculated [18b, 19] from the thermal effects, DSC analysis of $CuSO_4 \cdot 5H_2O$ (Fig. 3) being taken as reference.

The data in Table 2 demonstrate that the enthalpy in the first stage depends on the number of molecules of coordination water, this depending only on the nature of the cation (hydrates 1 and 2), the values being 733.8 and 1524.0, respectively; the values found for hydrates 3 and 4 are quite close (1349.0 and 1337.8 J/g) when the same number of water molecules are eliminated, the cation being the same.

In the second stage, involving the elimination of the last water molecule, the enthalpies for hydrates 1 and 2 are equal (223.4 J/g), whereas those for hy-

Table 1 Characteristic thermogravimetric values

			Weighed	Stage I						Stage II						
No.	Hydrate	A_p^*	amount/	T_i/	T_f/	No. molec.	$W_{\infty t}$	$W_{\infty exp}$	E/ kJ·mol^{-1}	T_i/	T_m/	T_f/	No. molec.	$W_{\infty t}$	$W_{\infty exp}$	E/ kJ·mol^{-1}
			mg	°C		H_2O	mg			°C			H_2O	mg		
1.	$CuSO_4\cdot$	air I	18.80	45	189	4	6.4	6.30	162.52	225	255	298	1	1.71	1.70	242.49
	$5H_2O$	N_2 II	55.017	56	166	4	15.864	15.67		206.6	243.9	273.8	1	7.93	7.33	
2.	$MgSO_4\cdot$	air I	19.10	20	212	6	8.4	8.30	168.58	212	260	310	1	1.40	1.40	253.19
	$7H_2O$	N_2 II	32.879	21	212.5	6	14.4	14.04		212.5	270	300	1	2.40	2.12	
3.	$Mg(NO_3)_2\cdot$	air I	19.40	40	255	5	6.81	6.90	98.50	255	315	368	1	1.36	1.80	193.77
	$6H_2O$	N_2 II	60.688	50	280	5	21.29	24.20		280	315.6	368	1	4.26	4.49	
4.	$MgCl_2\cdot$	air I	20.00	30	254	5	8.85	8.90	130.90	254	276	355	1	1.77	1.70	372.00
	$6H_2O$	N_2 II	51.138	50	244	5	22.63	21.78		244	264	285.3	1	4.53	4.36	

T_i – initial temperature; T_m – temperature corresponding to the maximum speed rate; T_f – final temperature; E – activation energy; $W_{\infty t}$ – theoretical weight loss; $W_{\infty exp}$ – experimental weight loss; A^* – type of installation

Table 2 Characteristic values for DTA

No.	Hydrate	A_p^*	Stage I T_i/	Stage I T_m/	Stage I T_f/	Stage I No. molec. H_2O	Stage I ΔH/ $kJ \cdot g^{-1}$	Stage II T_i/	Stage II T_m/	Stage II T_f/	Stage II No. molec. H_2O	Stage II ΔH/ $kJ \cdot g^{-1}$	Thermal nature of the process
			°C	°C	°C			°C	°C	°C			
1.	$CuSO_4 \cdot 5H_2O$	DSC	56.88	–	161.79	4	733.8	210.57	243.4	285.67	1	223.40	endo
		DTA	75.00	–	170.00			233.00	258.0	295.00			
2.	$MgSO_4 \cdot 7H_2O$	DTA	30.00	–	208.00	6	1524.04	208.00	263.0	290.00	1	223.78	endo
3.	$Mg(NO_3)_2 \cdot 6H_2O$	DTA	60.00	–	228.00	5	1349.06	270.00	305.0	330.00	1	134.04	endo
4.	$MgCl_2 \cdot 6H_2O$	DTA	60.00	–	255.00	5	1337.77	255.00	270.0	310.00	1	259.144	endo

ΔH – variation of enthalpy (kJ/g); T_i – initial temperature of the DTA peak (°C); T_m – temperature at the maximum DTA peak (°C); T_f – final temperature of the DTA peak (°C); A_p^* – type of installation

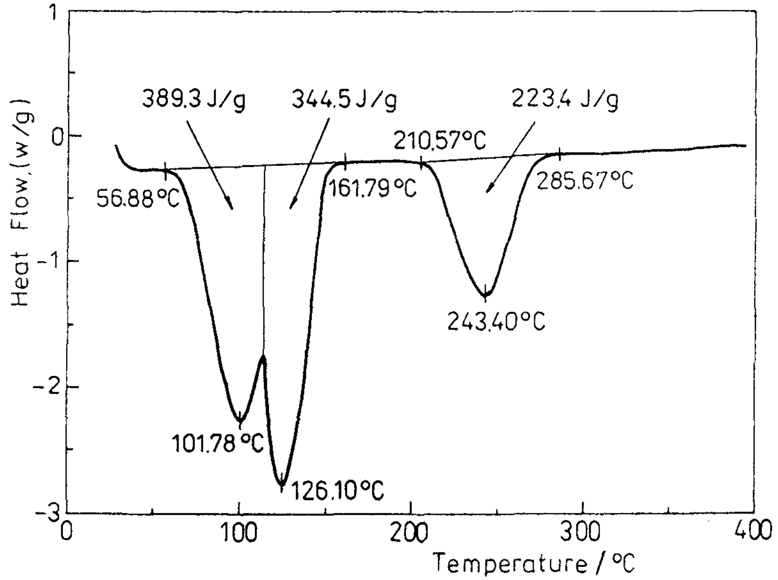


Fig. 3 DSC curve of $CuSO_4 \cdot 5H_2O$

drates 3 and 4 are different (134.0 and 259.1 J/g). The data are plotted in Fig. 4, which confirms the dependence of the enthalpy on the nature of the anion.

The real compensation effect observed in the second stage for hydrates 2, 3 and 4 and the absence of the compensation effect for hydrates 1 and 2 support our conclusions.

Table 3 lists the kinetic and compensation parameters introduced by Nikolaev [20, 21] and Gorbachev [22, 23] for the second stage, as calculated from the thermoanalytical curves plotted under the same conditions (apparatus I) and over the same domain of temperature within which $n=1$, as determined from the rate of the chemical reaction [24, 25].

It is to be observed that the compensation parameter a is constant, which indicates that the same type of linkage [26] is involved, i.e. the loss of crystallization water [27], while parameter S_p is the same for hydrates 1 and 2, as evidence that the same bond is involved, independently of the nature of the cation.

For hydrates 2, 3 and 4, the variation in the compensation parameter S_p shows that the bond to be broken depends only on the nature of the anion, the cation being the same.

The graph illustrating the compensation effect in Fig. 5 confirms via the Nikolaev and Gorbachev method the results derived from the TG, DTG and DTA data.

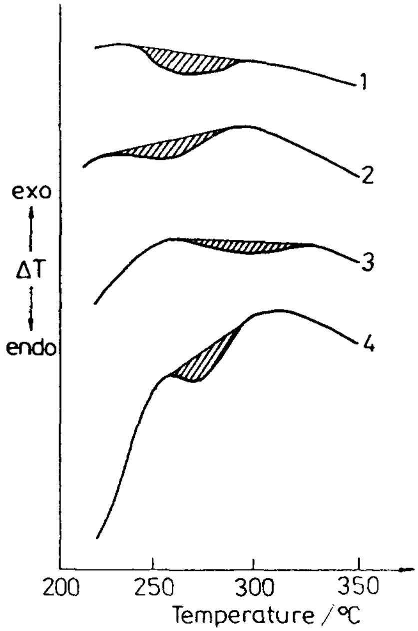


Fig. 4 DTA curves of hydrates 1–4, recorded on apparatus I

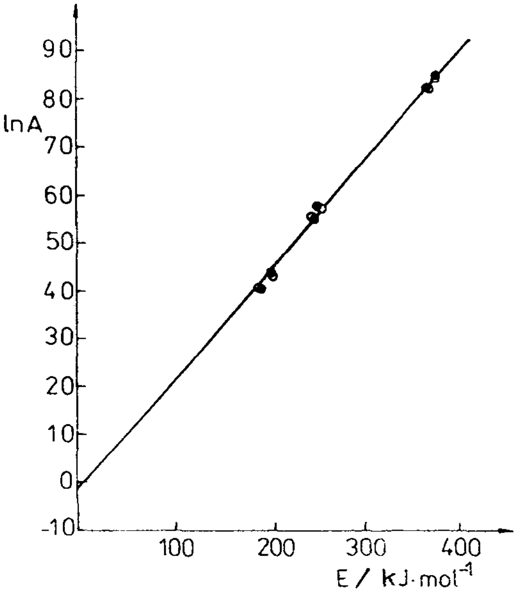


Fig. 5 Compensation effect of the second dehydration for stage hydrates 2–4: • – Nikolaev method; o – Gorbachev method

Table 3 Kinetic and compensating parameters ($dT/dt = 17.46\ K \cdot min^{-1}$)

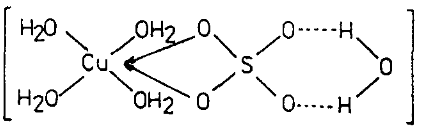
No.	Hydrate	$T_{interval}$/ °C	Stage I				T_{max} / K	$Sp = \frac{E}{\ln A}$	Compensation effect				
			F.C.		C.R.				Nikolaev			Gorbachev	
			n	E	n	E			a	b	$\ln A$	T_{cr}/K	$\ln A$
1.	$CuSO_4 \cdot 5H_2O$	225–298	1.05	242.49	1	239.50	528	4.3424(N) 4.3515(G)	0.2278	0.60245	55.8416	523.395	55.7255*
								4.3428(N) 4.3517(G)		0.59008	55.1484	523.428	55.0349**
2.	$MgSO_4 \cdot 7H_2O$	212–310	0.52	253.19	1	247.69	533	4.3845(N) 4.3838(G)	0.2256	0.6268	57.7464	527.287	57.7549*
								4.3839(N) 4.3843(G)		0.6048	56.4995	527.342	56.4944**
3.	$Mg(NO_3)_2 \cdot 6H_2O$	255–368	1.02	193.77	1	207.85	588	4.8699(N) 4.8872(G)	0.2045	0.1629	39.7888	587.651	39.6603*
								4.8619(N) 4.8639(G)		0.2330	42.7500	585.027	42.7330**
4.	$MgCl_2 \cdot 6H_2O$	254–355	1.06	372.00	1	376.90	549	4.5134(N) 4.5121(G)	0.2190	0.9524	82.4202	542.711	82.4449*
								4.5115(N) 4.5131(G)		0.9655	83.5406	542.829	83.5120**

n – the reaction order; E – the activation energy /kJ·mol^{-1}; a, b, Sp – compensation parameters; T_{cr} – critical temperature /K;
**F.C.* = Freeman-Carroll method; ***C.R.* = Coats-Redfern method

The compensation effect is calculated from the equation

$$\ln A = 0.220\,E + 0.8$$

The results obtained through the application of the thermal methods may be supported on the basis of the following structures for the studied hydrates, according to several literature data [1c, 1d, 29]:



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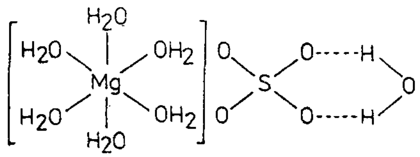

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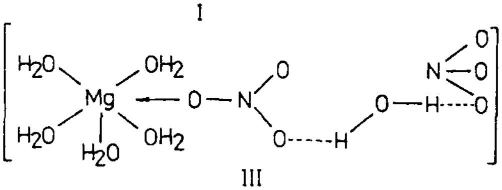

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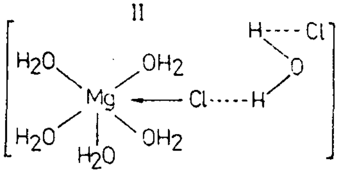

IV

For $CuSO_4 \cdot 5H_2O$, hexacoordination around the Cu^{2+} is achieved by 4 water molecules and 2 oxygen atoms of the SO_4^{2-}. The fifth water molecule is linked with the other 2 oxygen atoms of the SO_4^{2-} through hydrogen-bonds, a 6-membered inorganic cycle being formed [1d] (structure I).

For $MgSO_4 \cdot 7H_2O$, hexacoordination around the Mg^{2+} is achieved by 6 water molecules, the seventh being linked by 2 oxygen atoms of the SO_4^{2-}, an inorganic cycle similar to that in $CuSO_4 \cdot 5H_2O$ being formed; however, it is more stable as the other 2 oxygen atoms of the SO_4^{2-} are not involved in other linkages (structure II).

In hydrates 3 and 4 (structures III and IV), the coordination number specific for the central ion is obtained through 5 molecules of water, together with 1 oxygen atom from the NO_3^- or with the Cl^-, while the sixth water molecule in the anion is linked through hydrogen-bonds to the 2 oxygen atoms or the 2 Cl^- [1c].

The hydrogen-bonding involving the anion water is stronger in the case of the chloride anion than in the case of oxygen from the nitrate ion. This is probably due to the fact that the nitrate ion forming the hydrogen-bonding is previously involved in the covalent bond to the central method ion.

The difference in the enthalpies of the first stage for hydrates 1 and 2 (structures I and II) may be explained by the involvement of 2 oxygen atoms of the SO_4^{2-} in the coordination to the central ion for the achievement of its specific hexacoordination in the case of hydrate 1, and its non-involvement in hydrate 2.

The enthalpies for the first stage are equal for hydrates 3 and 4, due to the breaking of 6 coordinate linkages, 5 of them with water molecules, and the sixth with the oxygen from the NO_3^- or with the Cl^-.

As concerns the anion water, literature data [29] indicate that the linking energies for the strong hydrogen-bonds vary between 41.8 and 83.6 kJ·mol^{-1}, while those for the weak ones vary between 16.72 and 29.26 kJ·mol^{-1}; with regard to the structures proposed for the hydrates under study, the reaction enthalpies may be estimated from the correlation between them and the linking energy [30].

For hydrates 2, 3 and 4, values in the range 68.7–110.3 kJ·mol^{-1} have been obtained, while when the two hydrogen-bonds involving the molecule of anion water are broken, the theoretical values lie in the range 83.6–167.2 kJ·mol^{-1}, depending on the nature of the electronegative partner involved.

The differences found between the above-mentioned theoretical values and the experimental ones for hydrates 1–4 indicate that, besides the effect produced by the breaking of the hydrogen-bonds, other effects too are manifested (such as that of the cycle of 6 atoms or the effects resulting from the modification of the crystalline network) [31].

* * *

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Zusammenfassung — Mittels nichtisothermer Methoden der Thermogravimetrie (TG), Derivationsthermogravimetrie (DTG) und Differentialthermoanalyse (DTA) wurde die Art des Kristallwassers in den Verbindungen $MgSO_4 \cdot 7H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ und $MgCl_2 \cdot 6H_2O$ untersucht.
Eine Analyse der charakteristischen thermogravimetrischen Angaben (T_M, W_∞) und der kinetischen Parameter (n, E_a) zusammen mit den DTA-Ergebnissen (mit $CuSO_4 \cdot 5H_2O$) als Referenzprobe) lieferten den Beweis für die Existenz koordinierten Wassers und für die Art der Anionen in diesen Hydraten.
Die Ergebnisse wurden durch die Beobachtung eines tatsächlichen Kompensationseffektes bestätigt. Für den Kompensationseffekt wird nachstehende Gleichung empfohlen: $\ln A = 0.220\ E - 0.8$.
Weiterhin wurden Strukturen vorgeschlagen, welche die Gegenwart von koordiniertem Wasser und die Natur der Anionen in diesen Hydraten erklären.