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THERMAL INVESTIGATIONS OF NITRATE-HYDRATES AND DEUTERATES OF Ca^{2+}, Cd^{2+} AND Mg^{2+}

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Abstract

DTA and DSC were used to study the thermal behaviour of $Ca(NO_3)_2 \cdot 4H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and their deuterated analogues. Evidence was found concerning the process of melting of the initial hydrates and deuterates, followed by a one-stage dehydration of the melt to yield the respective anhydrous salt.

T_m, ΔH^o_m, ΔS^o_m and ΔH^o_{deh} were determined and the ΔH^o_f values for the investigated hydrates were calculated from the ΔH^o_{deh} data.

Keywords: Ca^{2+}, Cd^{2+} and Mg^{2+} nitrate-hydrates and deuterates, kinetics

Introduction

Publications on the thermal dehydration and decomposition of $Mg(NO_3)_2 \cdot 6H_2O$ reveal the existence of an abundance of data, but these are rather contradictory. Some authors [1] consider that only five of the six water molecules are readily released in the dehydration process, the sixth being released during formation of decomposition of the product. It has been demonstrated in [2] that magnesium oxide is obtained in the thermal decomposition. The data in [3, 4] show that at 145°C $Mg(NO_3)_2 \cdot 6H_2O$ passes into $Mg(NO_3)_2 \cdot 2H_2O$, which is dehydrated at 230–280°C and undergoes decomposition at 410–435°C. Similar results are presented in [5]. Information on the formation of basic magnesium nitrate is to be found in [6].

The thermal decomposition of $Ca(NO_3)_2 \cdot 4H_2O$ was examined in [7], while the enthalpy of melting of the hydrate, determined by DSC, is discussed in [8]. No calorimetric data have been published on the remaining nitrate-hydrates or their deuterated analogues.

In view of the existing publications, the aim of the present investigation was to study the calorimetric behaviour of $Mg(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$ and their deuterated analogues by DTA and DSC, with determination of the changes in the enthalpies of the phase transitions observed.

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Experimental

The ordinary hydrates were prepared by crystallization from saturated solutions at appropriate temperatures in accordance with the solubility curves; $Mg(NO_3)_2 \cdot 6D_2O$ was obtained by severalfold crystallization from heavy water in a desiccator ($CaCl_2$); and $M(NO_3)_2 \cdot 4H_2O$ ($M^{2+}=Ca^{2+}$, Cd^{2+}) was obtained by crystallization of $M(NO_3)_2$ in a gas phase.

The DTA and TG curves were taken with a Paulik-Paulik-Erdey MOM OD-102 derivatograph at a heating rate of 5 deg·min^{-1} in air up to 600°C, while the DSC curves were taken with DSC-4 Perkin Elmer equipment at the same rate, in aluminium crucibles for volatile samples (1 mg) up to 300°C. The compositions of the starting compounds were determined by methods of quantitative analysis: Ca^{2+}, Cd^{2+} and Mg^{2+} complexometrically [9]; NO_3^- spectrophotometrically with Perkin Elmer 323 equipment; and the hydrate water by Fisher's method [10] and thermogravimetrically.

Results and discussion

The DSC curves of the investigated compounds and their deuterates are shown in Figs 1–3. The endo effects observed were identified on the basis of the information obtained from the curves, in combination with the data published on the thermal behaviour of the investigated compounds [11] and with the derivatograms taken by us (Fig. 4). The characters of these phase transitions, together with their corresponding temperatures and the respective changes in the enthalpies, are presented in Table 1.

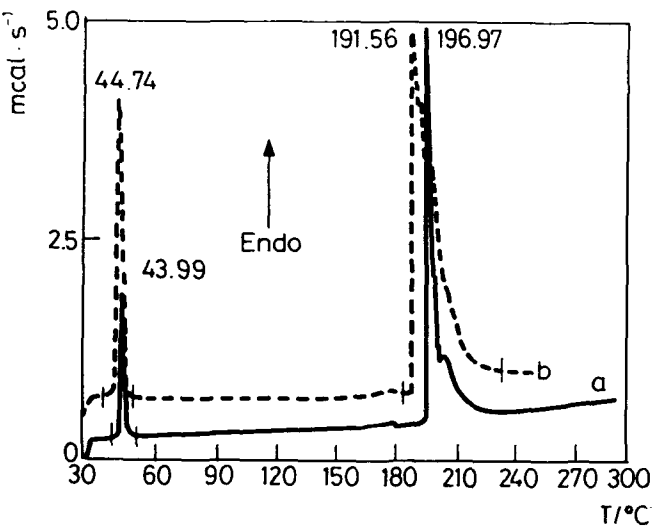

Fig. 1 DSC curves of $Ca(NO_3)_2 \cdot 4H_2O$ (a) and $Ca(NO_3)_2 \cdot 4D_2O$ (b)

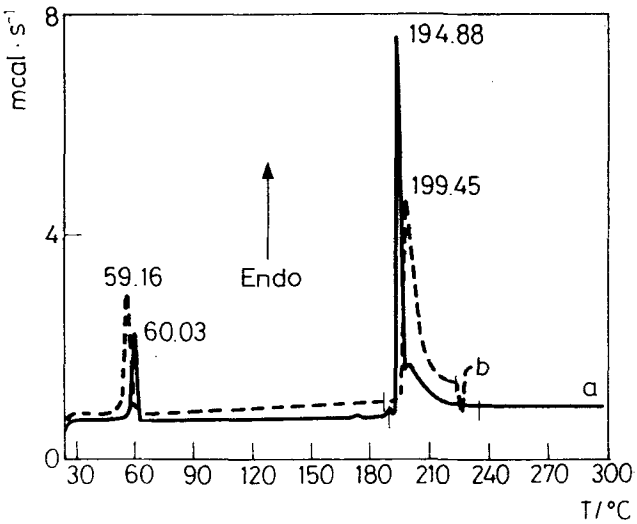

Fig. 2 DSC curves of $Cd(NO_3)_2 \cdot 4H_2O$ (a) and $Cd(NO_3)_2 \cdot 4D_2O$ (b)

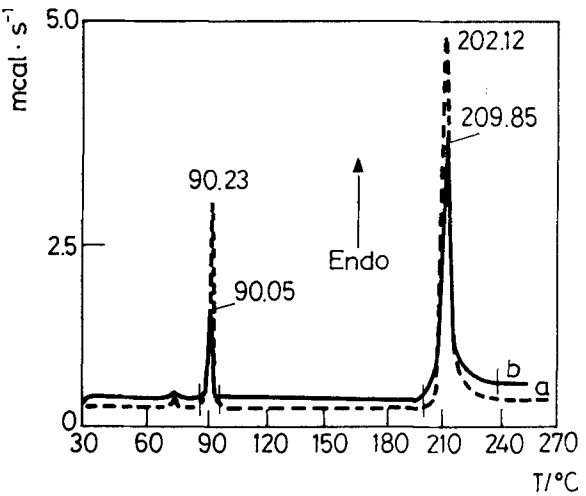

Fig. 3 DSC curves of $Mg(NO_3)_2 \cdot 6H_2O$ (a) and $Mg(NO_3)_2 \cdot 6D_2O$ (b)

The melting temperatures (T_m) of the investigated hydrates and deuterates are taken from the DSC curves (Table 1). However, there are contradictions in the data published on the T_m of $Mg(NO_3)_2 \cdot 6H_2O$, with some authors reporting congruent melting [6], and others incongruent melting [5]. The value obtained for the melting temperature of $Mg(NO_3)_2 \cdot 6H_2O$ is 90.3°C, in good agreement with the literature datum, 89°C [12]. The data on T_m of $M(NO_3)_2 \cdot 6H_2O$ ($M^{2+} = Ca^{2+}$,

Cd^{2+}) are also in good agreement with those in other published sources, which were determined by other methods. Determinations were also made of the T_m of the respective deuterates, for which there are no published data. DSC was used to record ΔH° for melting (ΔH°_m) (Table 1), while ΔH°_m and T_m were used to calculate the respective ΔS°_m, as shown in Table 2.

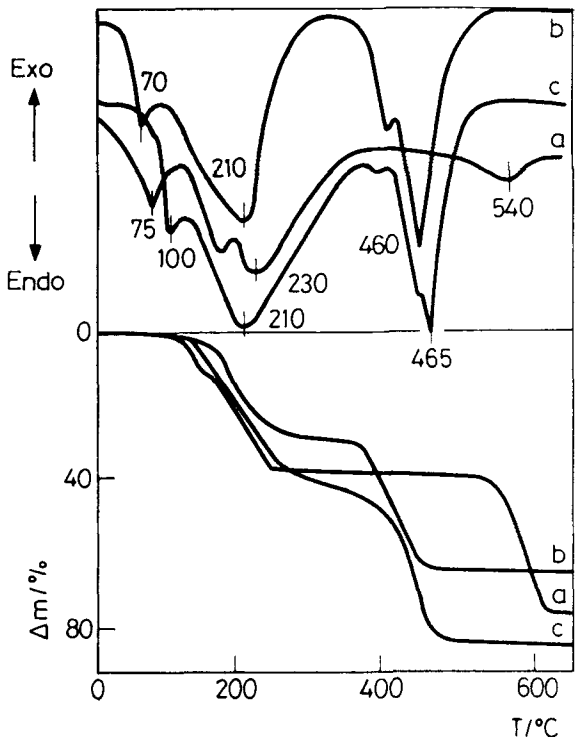

Fig. 4 DTA and TG curves of $Ca(NO_3)_2 \cdot 4H_2O$ (a), $Cd(NO_3)_2 \cdot 4H_2O$ (b) $Mg(NO_3)_2 \cdot 6H_2O$ (c)

When compared, these data show that there is a correlation between T_m or ΔH°_m and the crystal-chemical radius of M^{2+} ($r_{Ca^{2+}} = 104$ pm, $r_{Cd^{2+}} = 99$ pm, $r_{Mg^{2+}} = 74$ pm). Such a correlation is manifested in increase in T_m and ΔH°_m and a decrease in $r_{M^{2+}}$, and this displays the role of the electrostatic factor in the thermal stability of the hydrates considered. Hence, the type of the coordination polyhedron around M^{2+} has no significant effect on this thermal stability. The isotopic effect with respect to T_m is significant with regard to its value and is not unidirectional. This was anticipated since it has been observed for several other hydrates [15], moreover, the particular compounds examined are not heterogeneous.

The second endo effect in the DSC curves corresponds to the dehydration process, which proceeds until the anhydrous salt is obtained. The latter is

Table 1 Data from DSC

Compounds	Reactions	Phase transition T / °C		Dehydration ($1H_2O$)	
		T_{onset}	T_{max}	ΔH / kJ·mol^{-1}	ΔH / kJ·mol^{-1}
$Ca(NO_3)_2{\cdot}4H_2O$	$Ca(NO_3)_2{\cdot}4H_2O_{(s)} \rightarrow Ca(NO_3)_2{\cdot}4H_2O_{(l)}$	42.58	43.99	28.71	
	$Ca(NO_3)_2{\cdot}4H_2O_{(l)} \rightarrow Ca(NO_3)_2 + 4H_2O$	195.79	196.97	199.08	49.77
$Ca(NO_3)_2{\cdot}4D_2O$	$Ca(NO_3)_2{\cdot}4D_2O_{(s)} \rightarrow Ca(NO_3)_2{\cdot}4D_2O_{(l)}$	42.67	44.74	23.20	
	$Ca(NO_3)_2{\cdot}4D_2O_{(l)} \rightarrow Ca(NO_3)_2 + 4D_2O$	190.14	191.56	138.94	34.73
$Cd(NO_3)_2{\cdot}4H_2O$	$Cd(NO_3)_2{\cdot}4H_2O_{(s)} \rightarrow Cd(NO_3)_2{\cdot}4H_2O_{(l)}$	58.33	60.03	37.10	
	$Cd(NO_3)_2{\cdot}4H_2O_{(l)} \rightarrow Cd(NO_3)_2 + 4H_2O$	193.90	194.88	242.24	60.56
$Cd(NO_3)_2{\cdot}4D_2O$	$Cd(NO_3)_2{\cdot}4D_2O_{(s)} \rightarrow Cd(NO_3)_2{\cdot}4D_2O_{(l)}$	56.94	59.16	34.71	
	$Cd(NO_3)_2{\cdot}4D_2O_{(l)} \rightarrow Cd(NO_3)_2 + 4D_2O$	197.46	199.45	161.47	40.25
$Mg(NO_3)_2{\cdot}6H_2O$	$Mg(NO_3)_2{\cdot}6H_2O_{(s)} \rightarrow Mg(NO_3)_2{\cdot}6H_2O_{(l)}$	89.33	90.23	39.21	
	$Mg(NO_3)_2{\cdot}6H_2O_{(l)} \rightarrow Mg(NO_3)_2 + 6H_2O$	200.96	202.12	307.78	51.29
$Mg(NO_3)_2{\cdot}6D_2O$	$Mg(NO_3)_2{\cdot}6D_2O_{(s)} \rightarrow Mg(NO_3)_2{\cdot}6D_2O_{(l)}$	88.83	90.05	39.70	
	$Mg(NO_3)_2{\cdot}6D_2O_{(l)} \rightarrow Mg(NO_3)_2 + 6D_2O$	208.68	209.85	254.75	42.45

proved by the data of the TG curves from the respective derivatograms taken by us (Fig. 4), and by the published data already quoted. The ΔH°_{deh} values recorded, corresponding to the dehydration and calculated per 1 mol hydrate water released from the melt, vary within limits of 49 to 60 kJ·mol^{-1} for the ordinary hydrates and 34 to 42 kJ·mol^{-1} for the deuterates. They correspond fully to the enthalpies of dehydration determined for other types of compounds [13]. The ΔH°_{f} values of the starting hydrates and deuterates were calculated from the data on ΔH°_{deh} according to Hess's law (Table 3).

Table 2 Temperatures (T_m) and entropies of melting (ΔS°_{m}) of $M(NO_3)_2 \cdot 4H_2O$ ($M^{2+} = Ca^{2+}, Cd^{2+}$), $Mg(NO_3)_2 \cdot 6H_2O$ and their deuterated forms

Compounds	T_m / °C		ΔS°_{m} / J·mol^{-1}·deg^{-1}	
	Reported in [12]	Experim. (DSC)	Reported in [12]	Calculated
$Ca(NO_3)_2 \cdot 4H_2O$	42.7	43.9	92.8	90.5
$Ca(NO_3)_2 \cdot 4D_2O$		44.7		117.0
$Cd(NO_3)_2 \cdot 4H_2O$	59.5	60.0	98.3	111.4
$Cd(NO_3)_2 \cdot 4D_2O$		59.1		104.5
$Mg(NO_3)_2 \cdot 6H_2O$	89.0	90.2	113.4	107.9
$Mg(NO_3)_2 \cdot 6D_2O$		90.0		109.4

Table 3 Values ΔH°_{f} of $M(NO_3)_2 \cdot 4H_2O$ ($M^{2+} = Ca^{2+}, Cd^{2+}$), $Mg(NO_3)_2 \cdot 6H_2O$ and their deuterated forms

Compounds	ΔH°_{f} / kJ·mol^{-1}	
	Reported in [14]	Calculated
$Ca(NO_3)_2 \cdot 4H_2O$	-2130.1	-2131.7
$Ca(NO_3)_2 \cdot 4D_2O$	–	-2238.5
$Cd(NO_3)_2 \cdot 4H_2O$	-1648.9	-1630.9
$Cd(NO_3)_2 \cdot 4D_2O$	–	-1702.2
$Mg(NO_3)_2 \cdot 6H_2O$	-2613.3	-2587.7
$Mg(NO_3)_2 \cdot 6D_2O$	–	-2579.7

The calculated values of ΔH°_{f} for the investigated hydrate-nitrates were compared with published data [14] and showed fairly high coincidence (<±1%). This may serve as proof of the reliability of the calculated values of ΔH°_{f} for the corresponding deuterates.

The endo effect observed in the DTA curves (Fig. 4) at T_{max}=540°C for $Ca(NO_3)_2 \cdot 4H_2O$, 460°C for $Cd(NO_3)_2 \cdot 4H_2O$ and 465°C for $Mg(NO_3)_2 \cdot 6H_2O$

corresponds to decomposition of the anhydrous salt to the corresponding oxide, as demonstrated by X-ray phase analysis. The above data correspond with those presented in the literature [11].

Conclusions

The above investigations revealed that the compounds examined undergo phase transitions under the conditions of thermal decomposition, and the enthalpies measured for the phase transitions correspond to the thermodynamically calculated ones.

ΔH_f° and ΔS_m° were calculated for the deuterates, for which there are no published data.

References

1 B. D. Suhomlinskii and I: I. Procenko, Matem/i phys. model. techn. processov, Nor. gornomet. komb., Norilsk, (1977) 173.
2 W. Wendland, Tex. J. Sci., 10 (1958) 392.
3 L. G. Berg, I. Boruhov and M. T. Saibova, Uzb. Khim. Z., 2 (1970) 32.
4 M. T. Saibova and I. Boruhov, Uzb. Khim. Z., 6 (1974) 32.
5 B. M. Nirsha, A. A. Fakeev and A. N. Kniaseva, Neorg. Materiali, 9 (1980) 1597.
6 F. Paulik, J. Paulik, M. Arnold and R. Nauman, J. Thermal Anal., 34 (1988) 627.
7 M. T. Saibova, Uzb. Khim. Z., 6 (1979) 1.
8 M. Laugt, J. D. Sauzade and S. Makhelouf, Calorim. Anal. Therm., 14 (1983) 22.
9 E. Merck, AG, Komplexometrische Bestimmungsmethoden mit Titriplex, Darmstat, 1974, p. 22, 28, 41.
10 Bulgarian State Standard 6730–74.
11 G. Liptay, Atlas of Thermoanalytical curves, Academiai Kiadó, Budapest 1974, p. 137, 146.
12 J. Guinon, Thermochim. Acta, 67 (1983) 167.
13 U. N. Kukushkin, Therm. prevr. koord. soed. v tverdoi phase, Izd. Len. Univ., Leningrad 1981, p. 31.
14 Handbook of Chemistry and Physics, 65 Editions C. R. C Press, Ins. Florida, 1984–1985.
15 M. Maneva, M. Georgiev, D. Nikolova, D. Rusova, V. Koleva, P. Kovandschiev, N. Petrov and G. Liptay, J. Thermal Anal., 36 (1990) 1803.

Zusammenfassung — DTA und DSC wurden zur Untersuchung des thermischen Verhaltens von $Ca(NO_3)_2 \cdot 4H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ und ihrer deuterierten Analoge eingesetzt. Man fand Aussagen bezüglich des Schmelzvorganges der Ausgangshydrate und Deuterate, gefolgt von einer Einschritt-Dehydratation der Schmelze unter Bildung der entsprechenden wasserfreien Salze.

T_m, ΔH_m°, ΔS_m° und ΔH_{deh}° wurden ermittelt und die ΔH_f° Werte für die untersuchten Hydrate wurden anhand der ΔH_{deh}°-Angaben berechnet.