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ENTHALPIES OF DEHYDRATIONS OF OXALATE, SULFATE AND CHLORIDE HYDRATES BY TRANSPIRATION METHOD AND DSC

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Abstract

Transpiration method was used to measure the equilibrium water vapor pressures of the dehydration of the respective hydrates, such as oxalates, sulfates, chlorides and acetate, and the enthalpies of dehydrations (ΔH^0_{Tr}) of these hydrates were obtained. The heats of dehydrations ($\Delta H^0_{\mathrm{DSC}}$) were also determined by TG-DSC method. From the comparison with ΔH^0_{Tr} of $\Delta H^0_{\mathrm{DSC}}$, the relation of $\Delta H^0_{\mathrm{DSC}}/\Delta H^0_{\mathrm{Tr}}=R$ (=dehydration molar number determined by TG-DSC peak/stoichiometric dehydration molar number) was yielded. From these results, the following relations were found:

$$\Delta H^0_{\mathrm{DSC}}\ \text{(corrected)}=\Delta H^0_{\mathrm{DSC}}/R=\Delta H^0_{\mathrm{Tr}}$$

Keywords: crystal salt hydrate, dehydration, enthalpy of dehydration, equilibrium water vapor pressure, heat of dehydration, TG-DSC, transpiration method

Introduction

Many crystal salt hydrates are well known as a type of $M_aX_b{\cdot}nH_2O$. These hydrates lose crystalline water by a type of dissociation reaction, i.e., dehydration reaction. Dissociation gives occurrence to water vapor and a new solid phase. On the basis of many thermoanalytical studies on the dehydration processes [1–5], the water vapor equilibria over many salt hydrate systems were thermochemically studied [6, 7]. Although DSC study on the dehydration reaction ought to clarify principally the accurate heat of dehydration, it is not so easy to obtain the accurate and thermodynamically reasonable values due to the difficulty for the attainment of the solid–gas equilibrium condition in the DSC cell. Essentially, the agreement of DSC values, and van't Hoff enthalpy values is expected. Moreover, the thermochemical literature contains remarkably little information about the comparison with DSC values of van't Hoff enthalpy values for the dehydration reactions [8, 9].

In these circumstances, the purpose of this study was to confirm any reproducible relation between DSC values and transpiration values for the dehydration reac-

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tions. The heat of dehydration using TG-DSC measurement was compared with van't Hoff enthalpy of dehydration using transpiration measurement for sixteen dehydration reactions.

The sixteen dehydration reactions examined can be written as 1–16.

$MgC_2O_4 \cdot 2H_2O = MgC_2O_4 + 2H_2O$ 1

$SrC_2O_4 \cdot H_2O = SrC_2O_4 + H_2O$ 2

$BaC_2O_4 \cdot H_2O = BaC_2O_4 \cdot 0.5H_2O + 0.5H_2O$ 3

$MnC_2O_4 \cdot 2H_2O = MnC_2O_4 + 2H_2O$ 4

$NiC_2O_4 \cdot 2H_2O = NiC_2O_4 + 2H_2O$ 5

$ZnC_2O_4 \cdot 2H_2O = ZnC_2O_4 + 2H_2O$ 6

$K_2C_2O_4 \cdot H_2O = K_2C_2O_4 + H_2O$ 7

$Li_2SO_4 \cdot H_2O = Li_2SO_4 + H_2O$ 8

$FeSO_4 \cdot 4H_2O = FeSO_4 \cdot H_2O + 3H_2O$ 9

$NiSO_4 \cdot 4H_2O = NiSO_4 \cdot H_2O + 3H_2O$ 10

$CoSO_4 \cdot 6H_2O = CoSO_4 \cdot H_2O + 5H_2O$ 11

$CoSO_4 \cdot H_2O = CoSO_4 + H_2O$ 12

$ZnSO_4 \cdot H_2O = ZnSO_4 + H_2O$ 13

$FeCl_2 \cdot 2H_2O = FeCl_2 \cdot H_2O + H_2O$ 14

$BaCl_2 \cdot H_2O = BaCl_2 + H_2O$ 15

$Zn(CH_3COO)_2 \cdot 2H_2O = Zn(CH_3COO)_2 + 2H_2O$ 16

Experimental

TG-DSC measurements: TG-DSC measurements were carried out by using Thermoplus TG-DSC of Rigaku Co. Ten mg of sample (200–250 mesh) were weighed accurately in a platinum open pan type crucible (*d* 5.0×*h* 2.5 mm). An optimum heating rate which showed clearly the separation of DSC peak and TG curve for each dehydration stage was selected from those of 1, 2, 5, 10°C min^{-1}. The calibration of DSC was carried out by using the melting points of In, Sn, Pb and Al. The sample crucible was kept in dry nitrogen flow (1.5 ml s^{-1}) atmosphere.

Transpiration measurement: The equilibrium water vapor pressures were measured by using the transpiration method [10, 11]. The experimental apparatus and reaction tube were described previously [12, 13]. The transpiration method is one of the dynamic methods for the determination of vapor pressure and is a very reliable transportation technique [14].

At a given temperature, the transpiration experiments were realised at a variety of flow rates of dry nitrogen carrier gas. In these experiments, a saturated water vapor composition in the carrier gas was obtained over the sample so that the composition would be independent of changes in the carrier gas flow rate.

In this condition, the partial pressures of water vapor would be identical with the dissociation pressures that the water vapor would establish over the sample in an evacuated vessel at the same temperature [10, 11]. The exit carrier gas containing water vapor passed to magnesium perchlorate absorber for analysis.

Hydrates: Reagent grade hydrates (Kanto Chem. Co) were used. Four sulfate hydrates i.e., $FeSO_4·4H_2O$, $NiSO_4·4H_2O$, $CoSO_4·6H_2O$ and $CoSO_4·H_2O$ were prepared by the dehydrations of highly hydrated salts in the appropriate isothermal heating system until the proper mass loss was observed, respectively. The hydrate stage of each hydrate sample was confirmed by both the X-ray analysis and TG-DTA (or TG-DSC).

Results and discussion

Heats of dehydrations (ΔH^0_{DSC}) of the above mentioned sixteen reactions were estimated from each DSC peak area computed by standard procedure in DSC apparatus, respectively. In practice, although it was very difficult to identify the DSC baseline properly except for some cases in the sixteen dehydration reactions, the DSC peak area was defined between point A and point B as typically shown in Fig. 1. The estimated ΔH^0_{DSC} values for the sixteen dehydration reactions were summarized in Table 1.

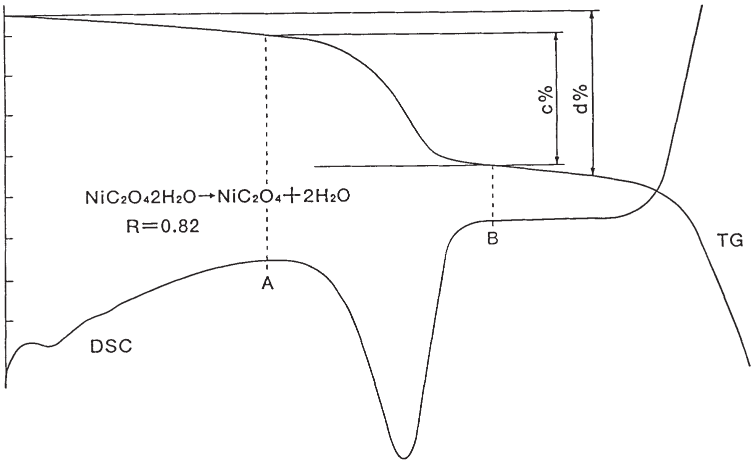

Fig. 1 TG-DSC curves for the determination of dehydration fraction *R* at DSC peak area between A and B

Van't Hoff enthalpies for dehydration reactions were also measured by the transpiration method. In the plots of partial pressure of water vapor *vs*. carrier gas flow rate at each temperature, there was a relatively wide plateau range of gas flow for which the sample is in equilibrium with the gas flow, as shown by an example of $Li_2SO_4{\cdot}H_2O$ system in Fig. 2. From a micro gravimetric analysis of the water vapor in nitrogen stream using magnesium perchlorate absorber, the partial pressure of water vapor in equilibrium gas was calculated on the basis of ideal gas law for each of the dehydration reaction. As an example, van't Hoff plot for $LiSO_4{\cdot}H_2O$ (Table 1) yielded the following equation for 1 mole of water vapor from the least square fits of the plots

$$\log P_{H_2O}=\log K_p=8.03-\frac{3567.26}{T} \tag{1}$$

$$\Delta G^0= 66300-154.8T\ (\mathrm{J\ mol^{-1}}) \tag{2}$$

Van't Hoff enthalpies for the sixteen dehydration reactions (ΔH^0_{Tr}) are also shown in Table 1.

Table 1 Comparison with ΔH^0_{Tr} and ΔH^0_{DSC}

No.	Hydrate	ΔH^0_{Tr} kJ mol^{-1}	ΔH^0_{DSC} kJ mol^{-1}	$\Delta H^0_{DSC}/\Delta H^0_{Tr}$	*R*	$\Delta H^0_{DSC}c$/ kJ mol^{-1}
1	$MgC_2O_4{\cdot}2H_2O$	110.5	100.1	0.91	0.90	111.2
2	$SrC_2O_4{\cdot}H_2O$	49.8	47.8	0.96	0.91	52.4
3	$BaC_2O_4{\cdot}2H_2O$	23.0	20.9	0.91	0.90	23.1
4	$MnC_2O_4{\cdot}2H_2O$	103.5	97.2	0.94	0.92	105.6
5	$NiC_2O_4{\cdot}2H_2O$	118.6	98.5	0.83	0.82	119.6
6	$ZnC_2O_4{\cdot}2H_2O$	127.2	99.3	0.78	0.81	123.3
7	$K_2C_2O_4{\cdot}H_2O$	72.1	69.2	0.96	0.95	72.6
8	$Li_2SO_4{\cdot}H_2O$	66.3	58.6	0.88	0.92	63.4
9	$FeSO_4{\cdot}4H_2O$	112.8	93.1	0.83	0.82	113.6
10	$NiSO_4{\cdot}4H_2O$	145.0	118.4	0.82	0.81	146.7
11	$CoSO_4{\cdot}6H_2O$	228.4	217.3	0.95	0.96	227.3
12	$CoSO_4{\cdot}H_2O$	89.2	64.2	0.72	0.71	91.1
13	$ZnSO_4{\cdot}H_2O$	77.5	71.6	0.92	0.92	77.0
14	$FeCl_2{\cdot}2H_2O$	58.6	49.9	0.85	0.88	56.6
15	$BaCl_2{\cdot}H_2O$	74.9	59.4	0.79	0.79	75.0
16	$Zn(CH_3COO)_2{\cdot}2H_2O$	83.3	97.7	1.17	1.01	96.4

The thermochemical data in the Table show that the relation of $\Delta H^0_{Tr}>\Delta H^0_{DSC}$ is yielded except for the dehydration of $Zn(CH_3COO)_2{\cdot}2H_2O$ system.

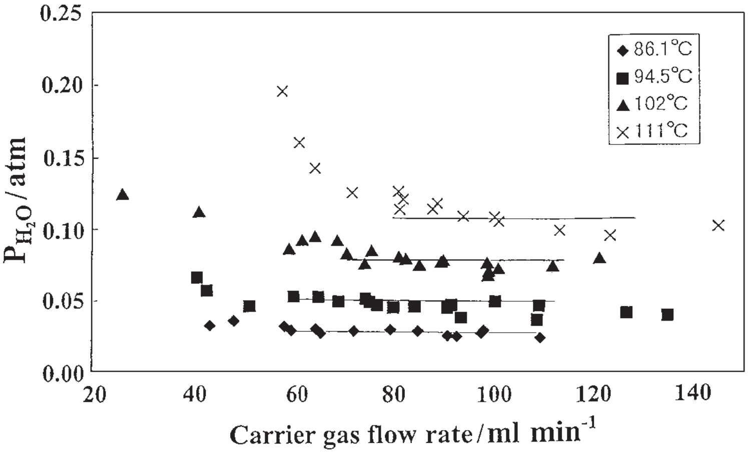

Fig. 2 Dependence of water vapor pressure on carrier gas flow rate in the dehydration reaction of $Li_2SO_4{\cdot}H_2O$ system

In this study, DSC values of van't Hoff enthalpy were compared with the values of the respective dehydration reactions, and it was found that this DSC peak between A and B does not correspond to 100% dehydration fraction. This DSC peak area shows an equivalent dehydration fraction, which corresponds to c% of TG mass loss between A and B as shown in Fig. 1. The dehydration fraction R at DSC peak area between A and B can be written.

$$R=\frac{N_{AB}}{N_M} \tag{3}$$

$$N_{AB}=\frac{cM}{(100-d)18} \tag{4}$$

where, N_{AB} – dehydration water molar number obtained by TG values between A and B, N_M – stoichiometric dehydration water molar number, c – mass loss% obtained by TG values between A and B, d – total mass loss% obtained by TG stoichiometric values, M – formula mass of product hydrate or unhydrate salt.

The R values of the sixteen dehydration reactions examined are shown in Table 1. It is seen from the table that except for the dehydration of $Zn(CH_3COO)_2{\cdot}2H_2O$, R values show below unity and the values disperse from 0.79 to 0.96.

In our opinion, van't Hoff enthalpies (ΔH^0_{Tr}) are essentially the criterion values. Therefore, disagreements in ΔH^0_{Tr} and ΔH^0_{DSC} values, shown in Table 1, should be caused by some non-equilibria in DSC measurements of dehydration reactions, i.e., solid–gas heterogeneous equilibrium reactions. Further investigation in DSC measurement applicable for the dehydration reaction is required to clarify the attainment of equilibria in the measurement system for the reaction as well as the identification of DSC baseline.

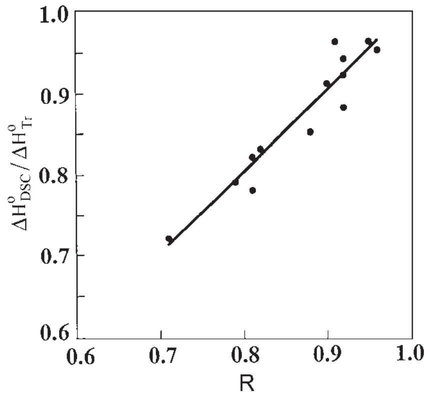

Fig. 3 Plot of $\Delta H^0_{DSC}/\Delta H^0_{Tr}$ *vs*. dehydration fraction R

On the other hand, it should be notified that the value of dehydration fraction R denoted by Eq. (3) was comparable to the ratio of $\Delta H^0_{DSC}/\Delta H^0_{Tr}$ approximately, as shown in Table 1. Figure 3 shows linear relationship between $\Delta H^0_{DSC}/\Delta H^0_{Tr}$ and R exhibiting that the relation of $\Delta H^0_{DSC}/\Delta H^0_{Tr}=R$ may be written formally as ΔH^0_{Tr} is criterion value.

These results lead to the conclusion that the corrected $\Delta H^0_{DSC}c$ value can be estimated by the following relation,

$$\Delta H^0_{DSC}c(\text{corrected}) = \frac{\Delta H^0_{DSC}}{R} = \Delta H^0_{Tr} \qquad (5)$$

$\Delta H^0_{DSC}c$ values agree well with ΔH^0_{Tr} values as shown in Table 1.

Conclusions

From the comparison with van't Hoff enthalpies of the heats of dehydration for the respective oxalate, sulfate, and chloride hydrate systems, the ratio of heat of dehydration (ΔH^0_{DSC}) and van't Hoff enthalpy (ΔH^0_{Tr}) shows below unity for the dehydration reactions. In other words, the relation of $\Delta H^0_{Tr}>\Delta H^0_{DSC}$ is obtained. The precise investigation of the stoichiometric estimation using TG-DSC curves showed that the apparent DSC peak area does not correspond to 100% dehydration fraction. The DSC peak area corrected by the equivalent dehydration fraction gives simply the thermochemical reasonable heat of dehydration in the comparison of van't Hoff enthalpy.

As compared with the process of phase transition or melting, it should be emphasized that an accurate and reliable study of DSC for solid–gas heterogeneous process in dehydration reaction is difficult. In this study, the dehydration fraction of R values show below unity in the fifteen dehydration reactions. Further research is important to confirm this fact in many other dehydration reactions, including the dependence of the experimental results on DSC instruments.

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