ELSEVIER

Thermochimica Acta 296 (1997) 135–139

thermochimica acta

Nonisothermal dehydration kinetics of sodium-light lanthanoid double sulfate monohydrates

Önder Kolcu, B. Zümreoğlu-Karan*

Department of Chemistry, Hacettepe University, Beytepe Campus, 06532 Ankara, Turkey

Received 20 December 1995; received in revised form 8 August 1996; accepted 12 December 1996

Abstract

Dehydration kinetics of sodium-light lanthanoid double sulfate monohydrates has been evaluated by applying two methods of different categories for the analysis of dynamic TG data. The Coats–Redfern integral and Achar differential methods gave similar results. The possible mechanism was found to be diffusion controlled. The apparent dehydration activation energies are in the range of ≈100–180 kJ mol^{-1} and show an upward trend from La to Sm with the decreasing ionic radius of the Ln^{3+} ion. The double salt structure with the smallest Ln^{3+} ion is the most kinetically stable but the most thermodynamically unstable one towards the dehydration process. © 1997 Elsevier Science B.V.

Keywords: Nonisothermal kinetics; Dehydration; Mechanism; Lanthanoid double sulfates

1. Introduction

In a recent work [1], we have described the thermal properties of sodium-light lanthanoid double sulfate monohydrates over a wide temperature range. The decomposition of the double salts having the formula of $\text{MLn(SO}_4)_2\cdot\text{H}_2\text{O}$, where M is sodium and Ln is lanthanum, cesium, neodymium and samarium, was found to follow a complex pattern after the dehydration step. In this article we report on the analyses of dynamic TG data to derive the kinetic parameters and the mechanism for the dehydration stage.

The advantages of evaluating reaction kinetics by dynamic methods are that, they demand less time than the isothermal methods and a number of methods of data evaluation are available. The mathematical accuracy of the methods using thermogravimetric data has been shown to be satisfactory for the computation of kinetic data [2]. On the other hand, due to the kinetic compensation effect, the methods of kinetic analysis which attempt to describe all the kinetic parameters from a single experimental TA curve are somewhat problematic since they show dependence on experimental conditions [3].

We assume, in the following study, that the kinetic parameters do not change with the heating rate and sample size. Similar studies with a single heating rate and sample size were carried out by earlier workers particularly for dehydration reactions [4–6]. The purpose of this work is to determine the dehydration mechanism of the Na–Ln double sulfate monohydrates and to use the estimated kinetic parameters for comparison within a given set of samples without any physical significance. We have selected the following methods representative of different categories

---

*Corresponding author: Fax: (312) 235 2596 e-mail: bkaran@e-ti.cc.hun.edu.tr.

PII S0040-6031(97)00004-X

and applied several mechanistic equations to treat the thermal data. We have not considered the difference-differential method employing the Freeman–Carroll equation [7] because this method strongly depends on the sample mass and heating rate [8].

1.1. The integral method using the Coats–Redfern equation [9]

This method is applied to TG data assuming the orders of reaction of 0, 1/2, 2/3, 3/4 and 1, justified for most solid state decompositions [10]. The linearity of each case is compared to obtain the correct order. The Coats–Redfern equation is:

$$\log[f(\alpha)/T^2] = \log\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{2.3RT}$$

and, assuming $(2RT/E)\ll 1$, leads to

$$\log[f(\alpha)/T^2] = \log\left[\frac{AR}{\beta E}\right] - \frac{E}{2.3RT}$$

In the above equation $f(\alpha)$ is the integral mechanism function, A is the pre-exponential constant and β is the constant heating rate. log $[AR/\beta E]$ is nearly constant and and by plotting log $[f(\alpha)/T^2]$ vs $1/T$, the slope equals $(-E/2.3)$ and the intercept equals log $[AR/\beta E]$ for a correctly chosen value of n.

The $f(\alpha)$ functions, applied to the Coats–Redfern equation, are listed in Table 1, corresponding to the mechanisms more commonly used [11].

1.2. The differential method using the Achar equation [10,12]

This method applies generally to all reaction mechanisms where the rate can be expressed as a function of α. The data are plotted for each of the selected methods and the linearity compared to determine the best model. The Achar equation is:

$$\log\left[\frac{\mathrm{d}(\alpha)/\mathrm{d}T}{g(\alpha)}\right] = \log\frac{A}{\beta} - \frac{E}{2.3RT}$$

The slope and the intercept of the plots of log $[(\mathrm{d}(\alpha)/\mathrm{d}T)/g(\alpha)]$ vs $1/T$ allow the calculation of the activation energy and the pre-exponential constant. The function $g(\alpha)$ is derived from $1/g(\alpha) = \mathrm{d}(f(\alpha))/\mathrm{d}(\alpha)$. The assumed $g(\alpha)$ functions are listed in Table 1.

2. Experimental

The preparation of the compounds and details of thermal analyses were described previously [1]. Samples were run in duplicate with a resultant agreement between runs of about ±2% on the temperature axis and ±1% on the weight axis.

Thermal data (a set of weight and temperature points) were processed in several steps. The values of α and $\mathrm{d}\alpha/\mathrm{d}T$ were calculated for each datum point using a computer programme. By means of the least squares method, the best fit straight line through the points was obtained and E and A determined from this line. The linear correlation coefficient (r) was considered as a quantitative value for the deduction of the most appropriate model that shows the best linearity.

3. Results and discussion

The values of activation energies, pre-exponential terms and orders of reaction obtained by the two methods, are summarized in Table 2. The linear cor-

Table 1
Kinetic functions $f(\alpha)$ and $g(\alpha)$ used for the present analysis

Kinetic model	Integral form, $f(\alpha)$	Differential form, $g(\alpha)$
Order of reaction(n=1)	$-\log(1-\alpha)$	$(1-\alpha)^n$
Order of reaction (n=1)	$[1-(1-\alpha)^{1-n}/(1-n)]$	$(1-\alpha)^n/(1-n)$; $n<1$
D1 one-dimensional diffusion	α^2	$1/2\alpha$
D2 two-dimensional diffusion	$(1-\alpha)\ln(1-\alpha)+\alpha$	$[-\ln(1-\alpha)]^{-1}$
D3 three-dimensional diffusion	$[1-(1-\alpha)^{1/3}]^2$	$-3(1-\alpha)^{2/3}[1-(1-\alpha)]^{-1/2}$
A2 Avrami–Erofeev	$[-\ln(1-\alpha)]^{1/2}$	
A3 Avrami–Erofeev	$[-\ln(1-\alpha)]^{1/3}$	

Table 2
Kinetic parameters from the Coats–Redfern Integral Method (I) and Achar Differential Method (II)

Method	Kinetic Model		$NaLa(SO_4)\cdot H_2O$			$NaCe(SO_4)\cdot H_2O$			$NaNd(SO_4)\cdot H_2O$			$NaSm(SO_4)\cdot H_2O$		
			E^a	A	r	E^a	A	r	E^a	A	r	E^a	A	r
I	Order	$n=0$	48.0	1.15×10^{1}	0.986	53.9	7.85×10^{1}	0.996	54.7	1.02×10^{2}	0.996	86.4	2.98×10^{5}	0.981
		$n=1/2$	52.7	1.17×10^{1}	0.997	60.2	2.28×10^{2}	0.991	60.3	2.44×10^{2}	0.993	90.5	4.68×10^{5}	0.985
		$n=2/3$	55.5	3.06×10^{1}	0.997	61.9	2.39×10^{2}	0.987	62.5	2.97×10^{2}	0.991	93.2	6.65×10^{5}	0.984
		$n=3/4$	56.1	2.70×10^{1}	0.975	63.5	2.76×10^{2}	0.988	64.9	4.28×10^{2}	0.992	92.4	3.92×10^{5}	0.986
		$n=1$	59.0	1.18×10^{2}	0.972	64.5	1.24×10^{3}	0.984	67.0	1.55×10^{3}	0.988	95.4	1.80×10^{6}	0.988
	D1		104.0	2.18×10^{6}	**0.989**	116.0	9.10×10^{7}	**0.996**	119.4	2.37×10^{8}	**0.996**	180.7	7.64×10^{14}	**0.982**
	D2		110.7	6.46×10^{6}	0.985	123.9	3.85×10^{8}	0.994	127.1	9.62×10^{8}	0.995	186.3	1.73×10^{15}	0.985
	D3		118.6	1.13×10^{6}	0.978	132.1	7.84×10^{8}	0.990	137.4	4.48×10^{9}	0.993	194.5	3.30×10^{15}	0.985
	A2		25.2	2.80×10^{-2}	0.960	29.1	1.04×10^{-1}	0.978	30.3	1.48×10^{-1}	0.988	43.9	5.27	0.985
	A3		14.4	1.45×10^{-3}	0.963	166	3.31×10^{-3}	0.973	17.6	4.61×10^{-3}	0.984	26.2	5.12×10^{-2}	0.981
II	Order	$n=0$	68.2	3.98×10^{6}	0.993	62.9	2.27×10^{6}	0.980	57.1	6.28×10^{5}	0.992	62.0	2.25×10^{6}	0.990
		$n=1/2$	80.6	9.37×10^{7}	0.986	76.8	8.54×10^{7}	0.961	71.5	1.76×10^{7}	0.983	71.1	2.44×10^{7}	0.995
		$n=2/3$	84.9	2.73×10^{8}	0.983	81.7	3.04×10^{8}	0.956	75.7	8.27×10^{7}	0.981	74.2	5.64×10^{7}	0.996
		$n=3/4$	88.2	7.11×10^{8}	0.941	73.5	3.60×10^{7}	0.930	77.5	1.29×10^{8}	0.978	76.0	8.56×10^{7}	0.995
		$n=1$	92.7	2.02×10^{9}	0.976	91.0	3.38×10^{9}	0.947	85.0	9.28×10^{8}	0.972	80.5	2.96×10^{8}	0.995
	D1		124.3	1.39×10^{12}	**0.993**	125.3	5.30×10^{12}	**0.991**	120.5	1.98×10^{12}	**0.996**	156.3	1.10×10^{16}	**0.991**
	D2		136.2	1.44×10^{13}	0.989	137.7	6.79×10^{12}	0.984	133.6	3.03×10^{13}	0.994	165.0	5.40×10^{16}	0.994
	D3		148.3	1.13×10^{6}	0.983	168.1	7.84×10^{8}	0.927	148.2	4.48×10^{9}	0.989	174.3	3.30×10^{15}	0.997

^{a}kd mol^{-1}

Table 3
Kinetic parameters calculated for the dehydration of $NaLn(SO_4)_2 \cdot H_2O$ using the D1 kinetic model

$NaLn(SO_4)_2 \cdot H_2O$	Method I			Method II			Dehydration peak temp.(°C) [a]	Effective ionic radius of Ln^3(pm) [b]
	E	*A*	*r*	*E*	*A*	*r*		
$NaLa(SO_4)_2 \cdot H_2O$	104.0	2.18×10^6	0.989	124.3	1.39×10^{12}	0.993	259+279	135.6
$NaCe(SO_4)_2 \cdot H_2O$	116.0	9.10×10^7	0.996	125.3	5.30×10^{12}	0.991	271	133.6
$NaNd(SO_4)_2 \cdot H_2O$	119.4	2.37×10^8	0.996	120.5	1.98×10^{12}	0.996	265	130.3
$NaSm(SO_4)_2 \cdot H_2O$	180.7	7.64×10^{14}	0.982	156.3	1.10×10^{16}	0.991	250	127.2
		av	0.991		av.	0.993		

[a] DTG data [1]
[b] For nine coordination [from R.D. Shannon, Acta Crystallogr. Sect. A, 32 (1969) 751]

relation coefficients for the four compounds are approximately the same from the Coats–Redfern and Achar methods and $r \approx 1$ for diffusion type models. D1 kinetic model gave a perfect straight line with the highest *r* value. In diffusion controlled reactions D1 denotes a one-dimensional diffusion process. Other adapted kinetic models yielded relatively lower values. Thus, the probable mechanism for the loss of water from the double salt structure is that of diffusion controlled. The vapor pressure at the interface of the solid reactant and product is controlled by the diffusion of the water molecules.

There is little to choose between the Methods I and II for the D1 model (Table 3). The apparent activation energies are in the range of $\approx$100–180 kJ mol^{-1}, showing an upward trend from lanthanum to samarium, if one neglects the disagreement for the neodymium case. No such uniform trend was observed in the pre-exponential terms and it is difficult to interpret the *A* values qualitatively as for most solid state reactions. The variation in the activation energies is accompanied by a decrease in the radii of Ln^{+3} ions. Our previous work [1] has shown that dehydration proceeds as a single step thermal process except for the lanthanum salt for which the existence of a shoulder on the DTG peak suggests fractional dehydration occurring upon removal of one mole of water. Nevertheless, it is possible to assume the same mechanism for these isostructural compounds and the results reflect the effect of decreasing ionic radii on the kinetic stability of the compounds. It is reasonable to explain the increase in the dehydration activation energies from La^{3+} to Sm^{3+} considering the increasing cation solvation energies. A stronger interaction is expected between the water molecule and the smaller Ln^{3+} ion in the activated complex. Vibrational studies of the compounds also confirm the strong coordinate bonding of water to the rare earth ion by the absence of a broad band in the O–H stretching region [1]. On the other hand, the downward trend in the dehydration peak temperatures on moving from La to Sm can be attributed to thermodynamic stability. It appears that the smaller Ln^{3+} ions build up relatively unstable crystal lattices due to the polarizing power of the cation. This results in the greater degree of diffusibility of water molecules into the structure, higher vapor pressures at the interface and hence increasing tendencies of dehydration.

4. Conclusions

Our work on the dehydration kinetics of the sodium-light lanthanoid double sulfate monohydrates reveals the following characteristics:

1. The mechanism of dehydration is diffusion controlled and D1 kinetic model gives the best linearity.
2. The linear correlation coefficients calculated for the D1 kinetic model using the Achar differential method and the Coats–Redfern integral method are approximately equal and close to unity.
3. The apparent activation energies range from $\approx$100–180 kJ mol^{-1} from La to Sm. The double salt structure with the smallest Ln^{3+} ion is the most kinetically stable as having the highest activation energy but the most thermodynamically unstable one dehydrating at the lowest temperature.

References

[1] Ö. Kolcu and B. Zümreoğlu-Karan, Thermochim. Acta, 240 (1994) 185.
[2] D.W. Johnson Jr. and P.K. Gallagher, J. Phys. Chem., 76 (1972) 1474.
[3] J. Malek, Thermochim.Acta, 200 (1992) 257.
[4] A. Venkataraman, N.V. Sasty and A. Ray, J. Phys. Chem. Solids, 53 (1992) 681.
[5] B. Kowalczyk, P. Bragiel and M. Czerwinski, Thermochim. Acta, 243 (1994) 35.
[6] K. Krishnan and K.N. Ninan, Thermochim. Acta, 89 (1985) 295.
[7] E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
[8] T. Hatakeyama and F.X. Quinn, Thermal Analysis, John Wiley and Sons, Chichester (1994) p. 68.
[9] A.W. Coats and J.P. Redfern, Nature, 201 (1964) 68.
[10] J.H. Sharp and S.A. Wentworth, Anal. Chem., 41 (1969) 2060.
[11] M.E. Brown, Introduction to Thermal Analysis, Chapman and Hall, London (1988) p. 127.
[12] N.N.B. Achar, G.W. Brindley and J.H. Sharp, Proc. Int. Clay Conf., Jerusalem, 1 (1966) 67.