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**KINETIC STUDY OF DEHYDRATION  
OF CALCIUM OXALATE TRIHYDRATE**

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*The dehydration of calcium oxalate trihydrate was studied by using DSC method. The dehydration proceeds in two steps where the first two molecules of water dehydrate around 100 °C and consequently the last molecule of water dehydrates at a temperature around 200 °C. The kinetic analysis was done and the apparent activation energy, pre-exponential factor and kinetic exponents of autocatalytical model were evaluated for both effects.*

## **Introduction**

Calcium oxalate  $\text{CaC}_2\text{O}_4$  forms three hydrates, stable and naturally occurring monohydrate (COM) and both metastable, dihydrate (COD) and trihydrate (COT) [1,2]. Calcium oxalates were up to now frequently studied as chemicals involved in formation of urinary calculi [3,4], main attention is paid to finding the factors

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and conditions giving support to calcium oxalate and consequently kidney stone formation [5,6]. The most frequently published data on calcium oxalate describe the crystal growth (conditions and kinetics) [7-10] and dissolution of hydrates [11-14]. The crystallization of COM has been the subject of physico-chemical and biological analyses [15,16]. Recently a nephron fluid dynamics model has been proposed [17] that integrates crystallization kinetics, crystal size distribution and allows predicting of the nucleation and growth rates of COM.

Thermal decomposition studies of oxalates are not so frequently published except for data on COM [18-20]. The dehydration of stable COM was studied many times by thermoanalytical methods (thermogravimetry TG, differential scanning calorimetry DSC, differential thermal analysis DTA) and this process was often used to test several methods of kinetic analysis [21-23]. Metastable COT is not mentioned so often, but the work by Skrtic *et al.* [24] describes kinetics of spontaneous precipitation of COT and Gardner [25] published data for nucleation and crystal growth of COT. Nishikawa *et al.* [26] synthesized single crystal of COT from dimethyl oxalate in the aqueous solution of calcium chloride (pH = 3 and 3 °C) and studied it by thermal analysis and single crystal X-ray structure analysis. The activation energies for the two step dehydration reactions were calculated to be 87.9 kJ mol<sup>-1</sup> (for -2 H<sub>2</sub>O dehydration) and 105.3 kJ mol<sup>-1</sup> (for -H<sub>2</sub>O dehydration). The dehydration of COT to the thermodynamically stable monohydrate form has also been studied in aqueous solutions at various supersaturations in the temperature range of 25-40 °C [27]. It has been found that the solid state nucleation and growth of COM takes place after the macroscopic growth and agglomeration of the trihydrate crystals occurs. The concluding processes probably involve solution growth and ageing of the newly formed monohydrate crystals and the overall dehydration process has an approximate activation energy of 188 kJ mol<sup>-1</sup> [27].

This paper focuses on the DSC study of dehydration of COT and kinetic analysis of obtained effects. The authors' main effort is to complete the kinetic information about calcium oxalate hydrates.

## Kinetic Analysis

The measured heat flow  $\Phi$  can be described by the kinetic equation [28]

$$\Phi = \Delta H A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

where  $\Delta H$  is the enthalpy of the process;  $A$  is the pre-exponential factor;  $E$  is the apparent activation energy;  $R$  is the gas constant and  $T$  is temperature. The function  $f(\alpha)$  is an analytical expression of the kinetic model where  $\alpha$  is a degree of

conversion.

Equation (1) can be rewritten in the logarithmic form [29,30]:

$$\ln \Phi_{\alpha,i} = \ln[\Delta H A f(\alpha)] - \frac{E_{\alpha}}{RT_i} \quad (2)$$

where the subscript  $\alpha$  denotes values related to a given extent of fractional conversion. The basic assumption in kinetic analysis of solid state processes is that the expression of the kinetic model,  $f(\alpha)$ , does not depend on temperature or heating rate. Therefore, the first term in the right hand side of Eq. (2) should be constant and the activation energy  $E_{\alpha}$  can be evaluated from the slope of the plot  $\ln \Phi_{\alpha,i}$  vs.  $1/T_i$  obtained from several experiments carried out at different temperatures or heating rates. The linearity of this plot is an important test of the validity of Eq. (1). This method can be applied to both, isothermal and non-isothermal data, and it enables the determination of the activation energy as a function of  $\alpha$ . The  $E_{\alpha}$  vs.  $\alpha$  plot, obtained in this way, may reveal complexity of the solid state process [30]. Usually, the deviations up to about 10 % may occur due to experimental uncertainties or due to numerical data treatment. However, if there is a pronounced variation in  $E_{\alpha}$  in dependence on  $\alpha$ , then simple Eq. (1) has probably a limited validity.

Very simple way how to test the applicability of commonly used model is calculation of function  $y(\alpha)$  and  $z(\alpha)$  [31]. In non-isothermal conditions the functions are defined as [30]

$$y(\alpha) = \Phi \exp\left(\frac{E}{RT}\right) \quad (3)$$

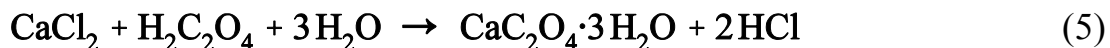
$$z(\alpha) = \Phi T^2 \quad (4)$$

These functions are normalized within the  $\langle 0, 1 \rangle$  range and they exhibit maxima at  $\alpha_M$  and  $\alpha_p^{\infty}$ , respectively. The exact values of these maxima or their relation as well as the shape of the curves  $y(\alpha)$  and  $z(\alpha)$  suggest a suitable kinetic model as is described in papers [30,32]. As the  $y(\alpha)$  and  $z(\alpha)$  functions are invariable with respect to temperature or heating rate, being quite sensitive to subtle changes in the kinetic model  $f(\alpha)$ , they can be conveniently employed as suitable tools for the kinetic model determination [30].

In this work, first the applicability of commonly used models for description of dehydration of calcium oxalate trihydrate is tested and then the parameters are calculated.

## Experimental

The calcium oxalate trihydrate was prepared by mixing solution of calcium chloride and oxalic acid according the equation



The condition of precipitation (mainly temperature, pH and ionic strength) influences the numbers of formed hydrates. The amount of 1.5 l of calcium chloride solution with the concentration of  $0.02 \text{ mol dm}^{-3}$  and pH 1.3 (pH modify by HCl) was kept at temperature  $12 \text{ }^\circ\text{C}$ . Then the solution was mixed with propeller stirrer and 45 ml of oxalic acid solution with the concentration of  $0.5 \text{ mol dm}^{-3}$  was added from dropper during 10 min. The mixture was continuously mixed another 30 min. and the temperature was kept at  $12 \text{ }^\circ\text{C}$ . Then the solution was filtered ( $0.22 \text{ }\mu\text{m}$  filter) and, the solid face was washed with cold distilled water, ethanol and finally with ether. The calcium oxalate trihydrate (COT) is formed under these conditions as was confirmed by X-ray diffraction. The prepared COT was stored at the temperature of  $-6 \text{ }^\circ\text{C}$  before the calorimetric experiments.

The dehydration of calcium oxalate trihydrate was studied in solid state by using differential scanning calorimeter (DSC Pyris 1). The temperature of instrument was calibrated using melting of Hg, Ga, In, Sn, Pb and Zn, and the enthalpy was calibrated using melting of In. The sample (amount approx. 5 mg) was put into the standard aluminium pan whose cover had a little hole (to eliminate water evaporated from the sample); the empty pan was used as a reference. The calcium oxalate trihydrate was measured in the temperature range from 30 to  $280 \text{ }^\circ\text{C}$ , and the heating rates 5, 7, 10, 15, 20 and  $25 \text{ K min}^{-1}$  were applied.

## Results and Discussion

The dehydration of the calcium oxalate trihydrate proceeds in two steps observed as two endothermic peaks on DSC curve — at the temperature about  $90\text{-}150 \text{ }^\circ\text{C}$  two molecules of water are lost, and the last molecule of water is lost at the temperature about  $155\text{-}240 \text{ }^\circ\text{C}$  depending on the heating rate used for the measurement. The amount of dehydrated water in each step was confirmed by thermogravimetry using a TG/DTA Jupiter STA 449 instrument.

The first dehydration effect is in the temperature range around  $100 \text{ }^\circ\text{C}$  where some moisture from the sample can evaporate too. The verification of this presumption was done when the COT sample was kept 2 days in a silica gel desiccator at the temperature of  $-6 \text{ }^\circ\text{C}$  (in following text this sample is referred to as predried) and consequently measured by TG. The selected conditions of drying should be sufficient to eliminate excessive moisture from COT as is described in

Ref. [26]. The theoretical mass change for the first dehydration of 2 molecules of water is 19.8 % and for the second dehydration of the last molecule of water is 9.9 % with regard to original mass of COT. The thermogravimetric results were the same for predried sample and sample without any treatment. The mass change obtained by TG was 19.0 % for the first effect and 10.2 % for the second effect which is close to the theory and confirmed that any evaporation of the moisture did not significantly influence the dehydration of 2 molecules of water proceeding around the temperature of 100 °C.

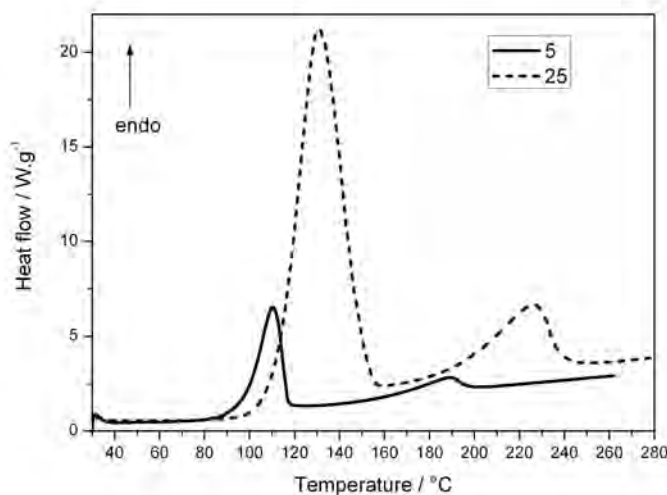


Fig. 1 DSC scan of COT obtained at the heating rates 5 and 25 K min<sup>-1</sup>

As seen from DSC scans (Fig. 1) both the dehydration effects shift to higher temperature with increasing heating rate. The quantity of the shift with the heating rate correlate with the activation energy  $E$  of observed process and is often used to determine the value of  $E$ . Generally, the first dehydration effect of two molecules of water is well developed with clearly indicated beginning and end of the peak and sharp maximum of the peak. On the other hand, the second peak corresponding to the loss of one water molecule is broad with well defined end but it was difficult to identify the beginning of the effect. Figure 1 clearly shows that the distance between both the effects is shorter with increasing heating rate, which increases the uncertainty of the indication of the beginning of second peak. The area under the DSC peak is used to determine the enthalpy of the process and its value for each experimental conditions is given in Tables I and II. The  $\Delta H$  values for the first peak (691-837 J g<sup>-1</sup>) are higher compared to 521 J g<sup>-1</sup> published by Nishikawa [26] but for the second peak (134-276 J g<sup>-1</sup>) it is comparable with Nishikawa's result 263 J g<sup>-1</sup>. The second peak, i.e., dehydration of one water molecule can be compared with results for calcium oxalate monohydrate, where published  $\Delta H$  value is 495.8 J g<sup>-1</sup> [33] and recalculated this for the weight of COT it is 398 J g<sup>-1</sup> which is higher as compared to our results.

The kinetic analysis of both the dehydration effects was done using the set of DSC data obtained for heating rates from 5 to 25 K min<sup>-1</sup> as is shown in Fig. 2.

Table I Parameters describing COT dehydration of 2 molecules of water around 100 °C measured for different heating rates:  $\Delta H$  enthalpy change,  $\alpha_M$  conversion corresponding to the maximum of  $y(\alpha)$  function,  $\alpha_p^\infty$  conversion corresponding to the maximum of  $z(\alpha)$  function,  $A$  pre-exponential factor,  $m$  and  $n$  parameters of autocatalytical model. The error limits are standard deviations calculated from values given in this table

Heating rate K min <sup>-1</sup>	$\Delta H$ J g <sup>-1</sup>	$\alpha_M$	$\alpha_p^\infty$	$\ln(A/s^{-1})$	$m$	$n$
5	729	0.49	0.53	24.73	0.61	0.63
7	729	0.42	0.56	24.64	0.54	0.74
10	691	0.38	0.53	24.39	0.48	0.79
15	750	0.32	0.50	24.52	0.41	0.88
20	837	0.32	0.45	24.70	0.51	1.06
25	828	0.30	0.45	24.66	0.50	1.16
Average		0.37 ± 0.08	0.50 ± 0.05	24.6 ± 0.1		

Table II Parameters describing COT dehydration of last molecule of water around 200 °C measured for different heating rates:  $\Delta H$  enthalpy change,  $\alpha_M$  conversion corresponding to the maximum of  $y(\alpha)$  function,  $\alpha_p^\infty$  conversion corresponding to the maximum of  $z(\alpha)$  function,  $A$  pre-exponential factor,  $m$  and  $n$  parameters of autocatalytical model. The error limits are standard deviations calculated from values given in this table

Heating rate K min <sup>-1</sup>	$\Delta H$ J g <sup>-1</sup>	$\alpha_M$	$\alpha_p^\infty$	$\ln(A/s^{-1})$	$m$	$n$
5	729	0.49	0.53	24.73	0.61	0.63
7	729	0.42	0.56	24.64	0.54	0.74
10	691	0.38	0.53	24.39	0.48	0.79
15	750	0.32	0.50	24.52	0.41	0.88
20	837	0.32	0.45	24.70	0.51	40694
25	828	0.30	0.45	24.66	0.50	1.16
Average		0.37±0.08	0.50±0.05	24.6±0.1		

The first and the most important step in kinetic analysis of DSC data is to determine the apparent activation energy. The second step of kinetic analysis consists in determination of the appropriate kinetic model and its parameters. This was done by using the functions  $y(\alpha)$ ,  $z(\alpha)$  [31] and the values of conversion corresponding to their maximum.

As described in previous part of introduction — kinetic analysis, the method of determination of effective activation energy  $E$  applicable to both isothermal and non-isothermal experiments is the isoconversional method. The advantage of this method is that we can check if there is any systematic change of the value of  $E$  with conversion and thus if there is any complex nature of observed process. The isoconversional method [29] is valid within the  $\langle 0.2, 0.8 \rangle$  range of conversion and

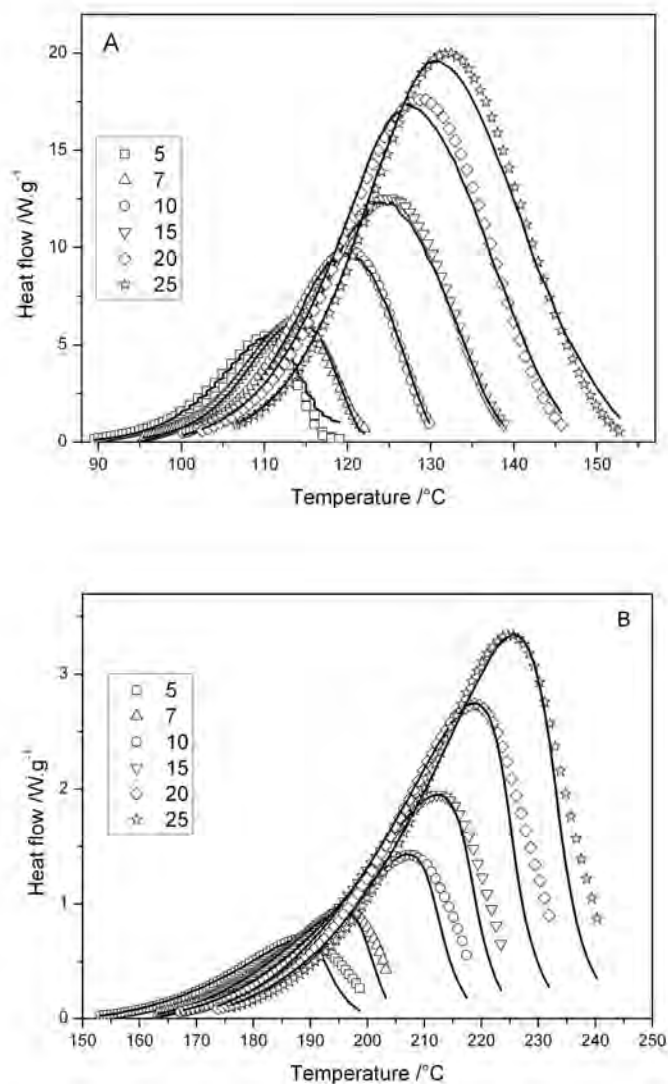


Fig. 2 The non-isothermal data of dehydration of A) 2 molecules of water and B) last molecule of water from COT for different heating rates. The theoretical dependences (lines) are calculated for parameters summarized in Tables I and II

the results for both the dehydration effects are illustrated in Fig. 3. The results for dehydration of 2 molecules of water show strong dependence of  $E$  on conversion so that the average value of  $E$  necessary for following kinetic analysis was not calculated. The other frequently used method of  $E$  determination based on the shift of the temperature corresponding to the maximum of observed peak  $T_p$  with the heating rate  $\beta$  is according to Kissinger [34]. Using Kissinger method, the slope of the  $\ln(\beta/T_p^2)$  dependence on  $1/T_p$  is equal to the  $-E/R$ . Applying the Kissinger method to data of dehydration of COT, we obtained the apparent activation energy for the first peak  $89 \pm 4 \text{ kJ mol}^{-1}$  and for the second peak  $79 \pm 4 \text{ kJ mol}^{-1}$ . The value of  $E$  can be compared with results published by Nishikawa *et al.* [26] (as described in Introduction, it is  $87.9 \text{ kJ mol}^{-1}$  for the first peak and  $105.3 \text{ kJ mol}^{-1}$  for thesecond peak) —  $E$  for the first peak is close to published results but for the

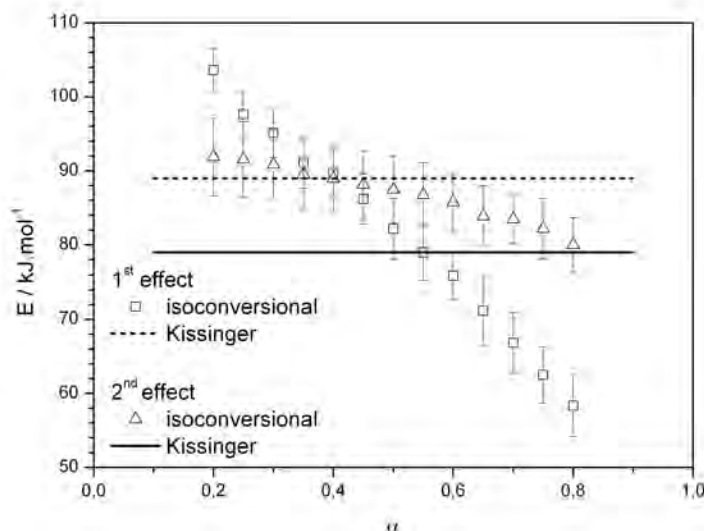


Fig. 3 The conversion dependence of the apparent activation energy determined by isoconversional method for both the dehydration effects — the first effect is dehydration of two molecules of water around the temperature of 100 °C and second is dehydration of the last molecule of water around the temperature of 200 °C. Lines represent value of  $E$  determined by Kissinger method

second peak our result is lower. Again as in the case of  $\Delta H$  value, the second peak — the dehydration of the last water molecule, can be compared with the results obtained for calcium oxalate monohydrate. The DSC measurement of COM under isothermal conditions [21] give the value of  $E$  equal to 82.8 kJ mol<sup>-1</sup> and the thermogravimetry curves [22] gives  $E$  between 97 and 125 kJ mol<sup>-1</sup>. Both these values are not so far from our results for the second peak.

The strong dependence of  $E$  on the conversion determined by isoconversional method could be either the consequence of any complicated character of dehydration which induces a big dependence or some negative influence during DSC experiment. More information about the observed process can be deduced from the conversion dependence of function  $y(\alpha)$  and  $z(\alpha)$ . The values of  $E$  determined by Kissinger method were used for the consecutive kinetic analysis of both the dehydration effects. This eliminates the problem which value of  $E$  determined by isoconversional method should be used when such a big dependence on conversion was obtained.

The experimental data were transformed into the functions  $y(\alpha)$  and  $z(\alpha)$  according to Eqs (3) and (4). The dependence of the functions  $y(\alpha)$  and  $z(\alpha)$  on conversion for both the dehydration effects and different heating rates is shown in Figs 4 and 5. As seen from the figures for dehydration of two molecules of water, the shape mainly of the  $y(\alpha)$  function significantly changes with the heating rate used for DSC measurement. In Table I (first peak) and Table II (second peak), there are summarized the values of conversion corresponding to the maximum of  $y(\alpha)$  and  $z(\alpha)$  functions,  $\alpha_M$  and  $\alpha_p^\infty$ , respectively. These values also show a systematic change with the heating rate used. Thinking about the experimental



conditions and the character of observed process, the big dependence of  $E$  on conversion and the huge change of the shape of functions  $y(\alpha)$  and  $z(\alpha)$  could be a consequence of change of partial water pressure during measurements rather than any complicated character of dehydration. Even if the sample crucible had the hole to eliminate water evaporated from the sample during DSC heating scans, the amount of generated vapour could be significant enough to change the partial pressure condition especially for higher heating rates. The similar effect of change of partial pressure conditions was observed in the case of reversible decomposition of calcium carbonate [35] where the kinetic analysis was done using the equation extended with the part reflecting the partial and equilibrium pressure of  $\text{CO}_2$ .

The values of  $\alpha_M$  and  $\alpha_p^\infty$  (Table I and II) for both the dehydration effects show [32] that the suitable kinetic model describing experimental data is autocatalytical model with parameters  $m$  and  $n$  [28]

$$f(\alpha) = \alpha^m(1 - \alpha)^n \quad (6)$$

The autocatalytical model is an empirical model capable to describe kinetics of solid state processes, although the parameters of this model have no physical meaning. However, from the mathematical point of view they have to fulfil some conditions [36], e.g.,  $m < 1$ .

The parameters of the model can be determined by numerical fitting method [37] or can be determined by the rearrangement of the experimental data. The parameters of autocatalytical model using rearrangement of the data are determined in two consecutive steps. First the ratio  $m/n$  is determined as is described in Eq. (7) and then the dependence according Eq. (8) is calculated [38].

$$\frac{m}{n} = \frac{\alpha_M}{1 - \alpha_M} \quad (7)$$

$$\ln \left[ \Phi \exp \left( \frac{E}{RT} \right) \right] = \ln(\Delta HA) + n \ln [\alpha^{m/n} (1 - \alpha)] \quad (8)$$

Equation (8) is valid in the interval  $0.2 < \alpha < 0.8$ . The parameter  $n$  is determined directly from the slope of this dependence and then the parameter  $m$  using Eq. (7). Also the pre-exponential factor  $A$  can be calculated from the section of the dependence (8) because the  $\Delta H$  value is known directly from DSC (Tables I and II). It is well known that the value of  $\alpha_M$  strongly depends on the value of  $E$  [39]. Therefore, for a reliable kinetic analysis it is important to determine correctly the value of activation energy.

The values of parameters of autocatalytical model and pre-exponential factor calculated according to Eqs (7) and (8) and describing dehydration of COT are summarized in Table I for the first effect and in Table II for second effect. Never-

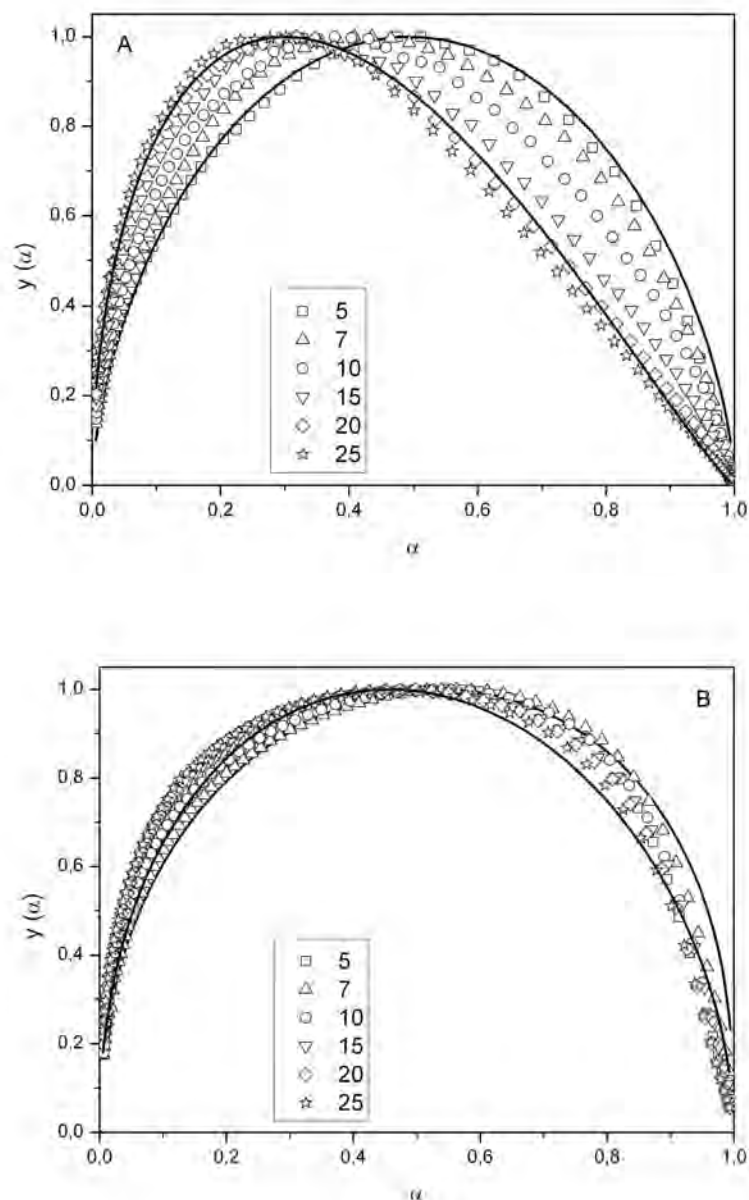


Fig. 4 Normalized  $y(\alpha)$  function obtained by transformation of non-isothermal data for COT dehydration of A) 2 molecules of water; and B) last molecule of water for different heating rates. The points represent experimental data and lines are values calculated using parameters from Tables I and II for the heating rates of 5 and 25  $\text{K min}^{-1}$

theless, the pre-exponential factor can be also calculated using the temperature and conversion corresponding to the maximum of observed peak,  $T_p$  and  $\alpha_{Tp}$ , respectively [40]

$$A = -\frac{\beta E_0}{RT_p^2 f'(\alpha_{Tp})} \exp\left(\frac{E_0}{RT_p}\right) \quad (9)$$

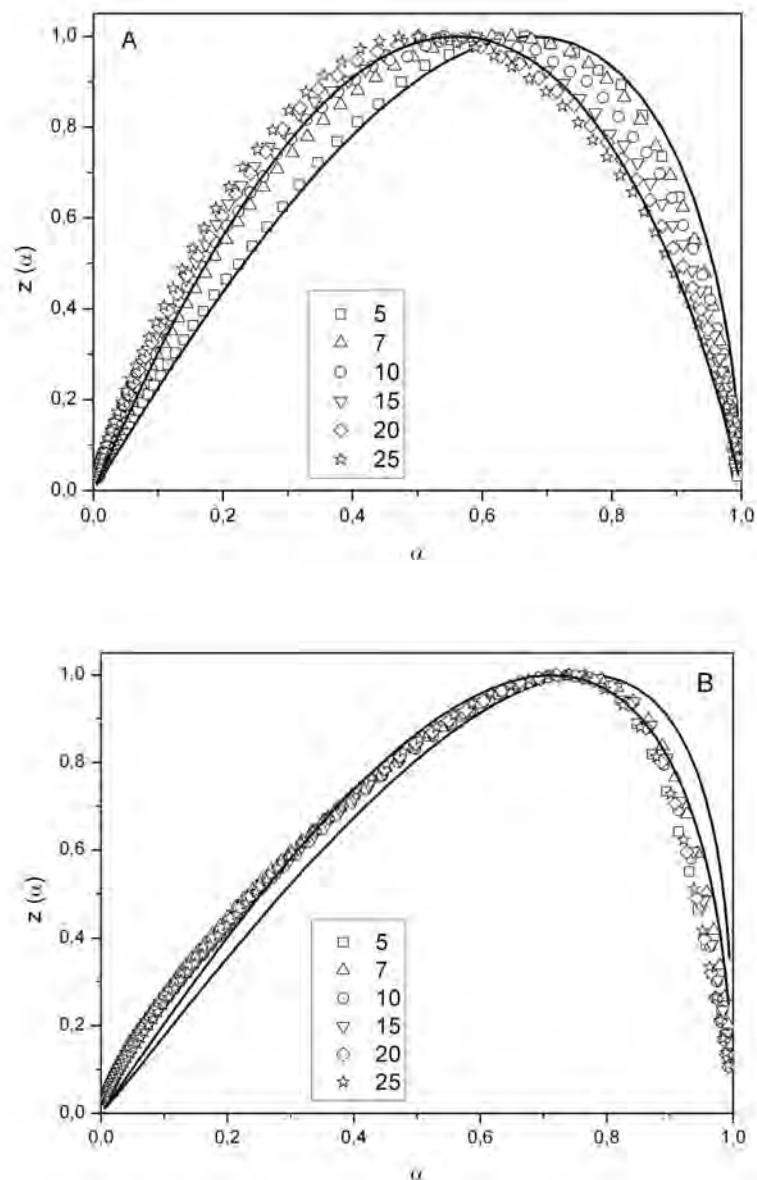


Fig. 5 Normalized  $z(\alpha)$  function obtained by transformation of non-isothermal data for COT dehydration of A) 2 molecules of water and B) last molecule of water for different heating rates. The points represent experimental data and lines are values calculated using parameters from Tables I and II for the heating rate 5 and  $25 \text{ K min}^{-1}$

where  $E_0$  is average value of the apparent activation energy, in our case the value determined by Kissinger method as was used also in previous calculations. The values of conversion  $\alpha_{Tp}$  corresponding to the maximum of the peak and  $\ln A$  calculated according to Eq. (9) are summarized in Table III for all heating rates and both the dehydration effects. As is seen,  $\alpha_{Tp}$  is close to the half of conversion for the first dehydration effect. But for the second effect the conversion  $\alpha_{Tp}$  is far from 0.5; it is around 0.7, which correlates with the asymmetric shape of DSC peaks in Fig. 2B. The pre-exponential factor calculated using  $\alpha_{Tp}$  and  $T_p$  according to Eq. (9)

Table III Global reaction order ( $m + n$ ), conversion ( $\alpha_{Tp}$ ) corresponding to the maximum of DSC peak and pre-exponential factor ( $A$ ) calculated from Eq. (9) for the first and second dehydration effect

Heating rate K min <sup>-1</sup>	First effect			Second effect		
	$\alpha_{Tp}$	$m + n$	$\ln(A/s^{-1})$	$\alpha_{Tp}$	$m + n$	$\ln(A/s^{-1})$
5	0.67	1.24	23.73	0.74	0.85	16.01
7	0.58	1.28	23.79	0.77	0.77	16.09
10	0.60	1.27	23.49	0.71	0.80	15.90
15	0.53	1.29	23.59	0.73	0.83	15.95
20	0.53	1.57	23.78	0.72	0.93	15.89
25	0.53	1.66	23.73	0.68	1.01	15.77
Average			23.7 ± 0.1			15.9 ± 0.1

has for the first effect lower value and for the second effect higher value as compared to the pre-exponential factors calculated from the section of dependence described by Eq. (8).

The theoretical dependences of the heat flow on the temperature calculated using the parameters summarized in Tables I and II for each heating rate are compared with the experimental data in Fig. 2 and also in the form of  $y(\alpha)$  and  $z(\alpha)$  functions for selected rates in Figs 4 and 5. As seen a relatively good agreement between theoretical and experimental data was obtained. The applied autocatalytical model has two parameters. Calculating  $m + n$ , we can estimate the value of global reaction orders, which are given in Table III for both the dehydration effects. For the first effect is  $m + n > 1$  for the second dehydration effect it is  $m + n \leq 1$ . Again, we can try to compare the second effect with the results obtained for dehydration of COM, where Liqing and Donghua [21] described the isothermal DSC data by reaction order model with parameter  $n = 1.4-2.4$  which is significantly higher than our results.

## Conclusion

The DSC method was used to study the dehydration of calcium oxalate trihydrate. The dehydration proceeds in two steps where first two molecules of water are lost around the temperature of 100 °C and then the last molecule of water dehydrates at temperature around the temperature of 200 °C. As was confirmed by thermogravimetry, any moisture caused by preparation, storage or handling of the samples did not significantly influence the dehydration effect obtained around the

temperature of 100 °C. The kinetic analysis of both the dehydration effects was done and the autocatalytical model was determined as the most suitable one. The strong dependence of value of effective activation energy on conversion indicates that probably the basic kinetic equation is not sufficient to describe dehydration data and that the model should be extended with the part reflecting the partial pressure of water vapour.

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