Análisis Térmico Controlado por la Muestra y Termogravimetría de Alta Resolución. Influencia de las condiciones experimentales sobre los parámetros cinéticos calculados

Sample controlled thermal analysis and high resolution thermogravimetry. Influence of experimental conditions on calculated kinetic parameters

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Resumen

El Análisis Térmico Controlado por la Muestra y la Termogravimetría de Alta Resolución fueron empleados para estudiar la deshidratación del $BaCl_2 \cdot 2H_2O$. Los modelos controlados por el avance interfacial bidimensional (R_2) y la energía de activación de 26 kJ/mol fueron calculados cuando se aplicaron las técnicas de ATCM; el modelo cinético difusivo tridimensional (D_3) y la energía de activación de 40 kJ/mol fueron determinados cuando se aplicó la Termogravimetría de Alta Resolución. Se demostró la influencia de la atmósfera y particularmente de la presión residual en los alrededores de la muestra sobre los parámetros cinéticos calculados.

Palabras clave: Cinética, ATVC, TG Alta Resolución, $BaCl_2 \cdot 2H_2O$.

Abstract

Sample Controlled Thermal Analysis and High-resolution Thermogravimetry are used for to study the dehydration of $BaCl_2 \cdot 2H_2O$. Model controlled by 2-dimensional interfacial advancement (R_2) and activation energy of 26 kJ/mol were calculated when the technique SCTA was applied and a 3-dimensional diffusive kinetic model (D3) and activation energy of 40 kJ/mol were determined when Hi- Res ATG was applied. The influence of atmosphere and particularly of the residual pressure in environment of the samples on the calculated kinetic parameters was demonstrated.

Keywords: Kinetics, CRTA, Hi Res ATG, $BaCl_2 \cdot 2H_2O$.

Introducción

It has often been reported in the literature that the calculated thermoanalytical curves and kinetic parameters in solid state reactions depend on the experimental conditions and it is difficult to accept them as intrinsic constants of the investigated reaction. Many papers have illustrated this problem when the Conventional Thermal Analysis is used. It

has been showed the influence of heating rate, sample weight, crystallite size, gas flow and shape of the crucible on the calculated kinetic parameters [1].

In the particular case of the control of atmosphere in environment of the sample, two procedures have been employed:

i) Experiments with permanent vacuum in the reaction zone. The gaseous products are eliminated in a continuous form.

ii) Experiments in dynamic atmosphere. It is used a continuous and constant gaseous flow that carries out the reaction products.

Criado and Rouquerol assert that it is a mistake to suppose that the use of the mentioned procedures (vacuum or flow) is sufficient to depreciate the adverse influence of the atmosphere in environment of the sample. The authors also say that the experimental results may depend on the mentioned conditions [1].

Then, the calculated kinetic parameters by Conventional Thermal Analysis are considered constant of the procedure and operational parameters. These aspects show the vulnerability of obtained kinetic parameters under arbitrary experimental conditions.

It is suggested the effective control of the temperature and pressure gradients, as well as the control of the atmosphere in the environment of the sample to reduce the inconvenience of the influence of the experimental conditions over the calculated kinetic parameters [1].

A new procedure to study the thermal behavior of a substance, based on the control of reaction rate appears. In the decade of 70 this idea was separately developed in Marseilles by Rouquerol and in Budapest by Paulik-Paulik. Rouquerol proposes a new approach known as Constant Decomposition Rate Thermal Analysis (CRTA) and the control of the flow of self-generated gas in the reaction. Paulik´s, in the mean time, suggests other approach known as the Quasi-isothermal and Quasi-isobaric Thermal Analysis (QIQITA) and the control of mass change rate obtained, differentiating electronically the mass signal [2].

In 1989 Rouquerol propose the Controlled Transformation Rate Thermal Analysis (CRTA) with the aim of to give a unified presentation to the modern trends of the Thermal Analysis.

The Controlled Transformation Rate Thermal Analysis can be defined as a general thermoanalytical method where a physical or chemical property X of a substance is modified, following a predetermined program X = f (t) under an appropriate action of temperature [2]. Recently the same author proposed the expression Sample Controlled Thermal Analysis for this same definition [3].

Another technique appears based essentially in the same principle and is known as High Resolution Thermogravimetric Analysis (Hi-Res TGA). In this technique, when no mass loss is occurring, it is possible to have a high heating rate (for example 50 °C/min), but when a minimum loss is detected, the heating rate is reduced towards zero or kept low until the mass again becomes nearly constant [4, 5]. The development of these techniques has allowed a best study of the kinetics parameters in the studied chemical process, what it is evidenced in some paper recently published [6, 7].

However, the effective control of temperature and pressure gradients that these modern techniques offer; sometimes is not sufficient and some researchers report the influence of the experimental conditions on calculated kinetic parameters.

In 1993, Rouquerol studies the kinetic of dehydration of $Li_2SO_4 \cdot H_2O$ by CRTA under a residual pressure selected in 10^{-5}–10^{-2} mbar range. This work shows that, as the controlled pressure is increased, the kinetic model progressively switches from a phase boundary (or first order) controlled type to a nucleation and growth of nuclei [8].

In 1996, Rouquerol using the same technique shows the influence of residual pressure on the kinetic model for the dehydration of uranyl nitrate trihydrate in the range of pressure between 10^{1} and 10^{-3} mbar. Two kinetic models are distinguished: in the upper pressure region a model of instantaneous nucleation and 2-dimensional nuclei growth occurs, lowering the pressure a 2-dimensional interfacial advancement model is favored [9]. In this paper, we compare the results obtained by Sample Controlled Thermal Analysis (SCTA) and High Resolution Thermogravimetric Analysis (Hi-Res TGA), using as reaction model the first dehydration of $BaCl_2 \cdot 2H_2O$ and show the influence of the experimental conditions on calculated kinetic parameters and particularly on the selected kinetic model.

Experimental

Material

In this study was used $BaCl_2 \cdot 2H_2O$ Panreac, purity 99 %.

Apparatus

The experiments were all carried out with:

- The thermolysis in SCTA equipment is carried out "under vacuum": The signal is produced by a Pirani gauge, which measures the total residual pressure of produced gases by the thermolysis. This signal is kept constant, controlling the furnace heating via a differential and integral, proportional regulation (PID). With this apparatus it is possible to work under a controlled residual pressure in the intervals from 10^{-3} to 100 mbar and in the temperature region among 30 and 100 °C. The dehydration of $BaCl_2 \cdot 2H_2O$ in a single experiment were carried out under a constant residual pressure of $1,86 \cdot 10^{-3}$ mbar and constant reaction rate C = 0,001 5 h^{-1}. When the rate jumps method is applied the ratio of the rate (r_r) is fixed at a value of 4 and the fasted decomposition rate does not exceed 0,02 h^{-1}.

- High Resolution Thermobalance, Hi-Res TGA (TA Instruments, mod. TG-2950). The experiments were done in flow of N_2 (100 ml/min). The heating rates were 10 and 20 °C/min in non-isothermal segments and the experimental resolutions used was 5. In all cases the weight sample was about 56 mg.

Kinetic procedure

The kinetic law may be assumed by simple comparing of the experimental curve transformation degree (α) versus Temperature (T), with the set of isokinetic theoretical curves reported by Criado and Ortega. In general, kinetic models of instantaneous nucleation and nuclei growth give rise to curves with a minimum α_m. Models limited by diffusion phenomena give rise to curves with an inflexion point (with exception of one-dimensional diffusion), and models governed by interfacial advancement produce curves which show neither a minimum nor an inflexion point [10].

Transformation degree can be calculated by the equation 1:

$$\alpha = \frac{(W_o - W)}{(W_o - W_F)} \qquad (1)$$

where

Wo, W, W_F: final and actual, initial values of the measured physical property.

The analysis of isokinetic data is further carried out in the following way [8, 10] (2):

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha)$$

(2)

where

α: Transformation degree.

A: Arrhenius pre-exponential factor.

E: Apparent activation energy.

T: Absolute temperature.

R: Gas constant.

f (α): Function related to the kinetic model obeyed by the reaction (table 1).

TABLE 1. KINETIC MODEL FUNCTIONS f(α), USUALLY EMPLOYED IN SOLID STATE REACTIONS [4,10]

Model	Symbol	f(α)
One-dimensional diffusion	D1	½ α
Two-dimensional diffusion	D2	-1/ ln (1-α)
Three- dimensional diffusion (Jander)	D3	3 (1-α)2/3 / 2 [1- (1-α)1/3]
Three- dimensional diffusion (Ginstring- Brounshtein)	D4	3/2 [(1-α)-1/3- 1]-1
First order	F1	(1-α)
Phase boundary controlled	Rn (1 ≤n≤ 3)	n (1-α)1-1/n
Nucleation and growth (Avrami-Erofeev)	Am (0,5 ≤m≤4)	m (1-α)[-l n(1-α)]1-1/m

If dα/dt is a constant and logarithm is applied and reorganized the equation (2) we obtained the equation (3):

$$\ln f(\alpha) = \frac{E}{RT} + \ln\left(\frac{C}{A}\right)$$

(3)

The term ln(A/C) is a constant. Then it is plotted ln f(α) versus reciprocal temperature (1/T) for various functions f(α) and the linear regression coefficients, together with the values of E, are calculated. The kinetic law or kinetic model is obtained from the best regression coefficient and the activation energy is calculated from the slope. This indicates that it is possible to obtain the reaction kinetic parameters from one single experiment [4, 11].

Another way to calculate the activation energy is the following:

When expression (2) is applied for two decomposition rates, in isoconversion points ($\alpha_1 = \alpha_2$), it is possible to calculate the activation energy without previous knowledge of the reaction kinetic model [11]. The resulting expression (4) is:

$$E = R \ln \left[\frac{\left(\frac{d\alpha}{dt} \right)_2}{\left(\frac{d\alpha}{dt} \right)_1} \right] \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^{-1}$$

(4)

where

T_1 and T_2: temperatures resulting from the two decomposition rates $(d\alpha/dt)_1$ and $(d\alpha/dt)_2$ respectively.

In the particular case of rate jumps method applied in SCTA [8, 9], where the sample decomposes alternatively at two different decomposition rate with a ratio r_r, the equation (4) is simplificated to equation 5:

$$Ea = \frac{R T_1 T_2}{T_2 - T_1} \ln r_r$$

(5)

Results and discussion

Figures 1 and 2 show characteristic curves of single experiments of SCTA and Hi-Res TGA respectively, for the dehydration first stage of $BaCl_2 \cdot 2H_2O$. In the first case (figure 1) can be observed that reaction occurs under temperature and pressure constant conditions.
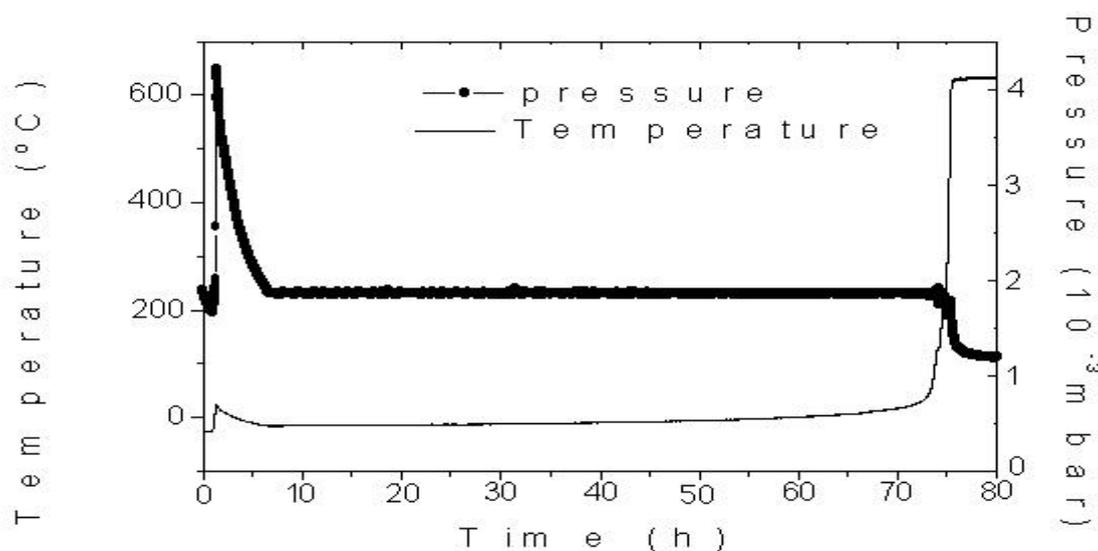

Figure 1. SCTA characteristic curves for the first dehydration of $BaCl_2 \cdot 2H_2O$.
Temperature and pressure versus time curves.

In the second case (figure 2) is appreciated an isothermal process. A similar result (isothermal process) is obtained when is applied the Paulik brother technique (QIQITA). These results show the control of temperature and pressure gradients attained with these techniques, which are essential factors to guarantee a best reproducibility and representability of calculated kinetic parameters. These aspects is not attained when are used the techniques of Conventional Thermal Analysis.
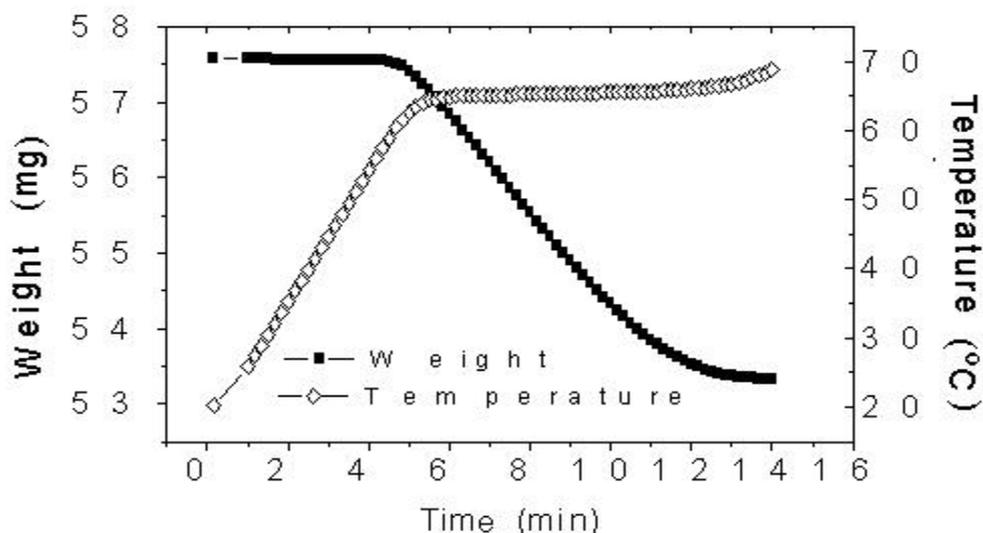

Figure 2. Hi-Res TGA characteristic curves for the first dehydration of BaCl$_2$·2H$_2$O. Weight and temperature versus time curves.

Kinetic of the dehydration according to SCTA

Figure 3 shows the dependency of transformation degree (α) with the temperature, in the interval of $0 \leq \alpha \leq 1$ for the first dehydration of BaCl$_2$·2H$_2$O. In this case, the single experiments were done under a residual pressure of $1,86 \cdot 10^{-3}$ mbar and a constant reaction rate C = 0,015 h^{-1}. This curve has a very interesting feature that offers information about of possible kinetic model of the reaction, when it is compared with the set of isokinetic theoretical curves reported by Criado and Ortega [8, 10]. The profile of this curve suggests that this reaction is controlled by models of interfacial advancement (R$_2$, R$_3$) or first order (F$_1$).
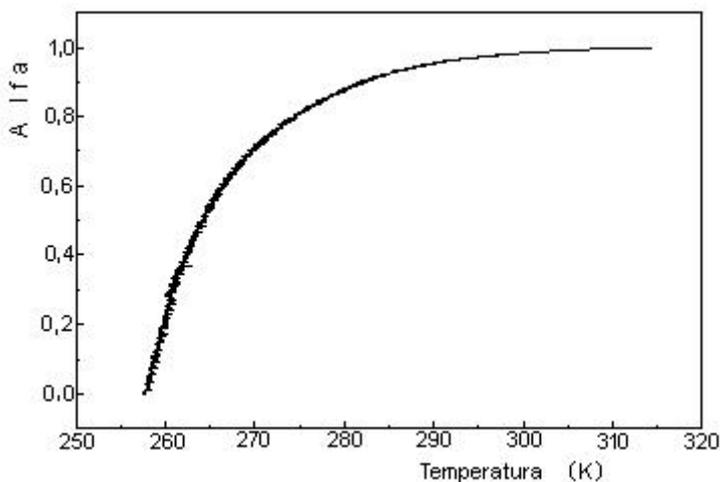
**Figure 3. Experimental α -T plots for the first dehydration
of BaCl$_2$·2H$_2$O. SCTA experiment.**

It is obtained a similar result when is applied the expression 3. These results are shown in table 2.

**TABLE 2. KINETIC RESULTS OF THE FIRST DEHYDRATION
OF BaCl$_2$·2H$_2$O, FROM EXPRESSION 3 AND SCTA EXPERIMENT**

Symbol of the Kinetic models	Coefficients of Regression	Standard Deviation	Activation Energy kJ/mol)
D$_1$	0,654	0,78	42
D$_3$	0,890	0,79	96
D$_4$	0,876	0,78	88
F$_1$	0,684	0,003	7
R$_2$	0,992	0,061	31
R$_3$	0,992	0,082	41
A$_2$	0,729	0,44	59
A$_3$	0,461	0,57	63
A$_4$	0,314	0,64	48

The values of calculated activation energy from this expression are 30 kJ/mol to R$_2$ and 40 kJ/mol to R$_3$. Besides, it is observed that the best fit correspond to the kinetic models R$_2$ y R$_3$; although can be difficult to unambiguously select the correct mechanism. This impossibility of calculation method to discriminate among the models a same group has been frequently reported in literature [1, 8]. Nevertheless, when the rate jumps methods and the equation (5) are applied, it can be identified the correct mechanism. Figure 4 represents the obtained results.
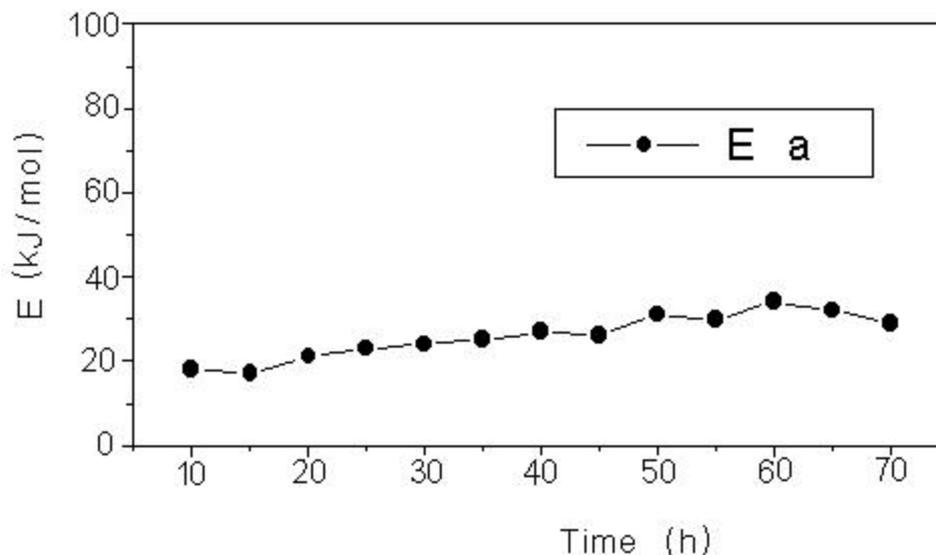
Figure 4. Dependency of the activation energy on time for the first dehydration of BaCl$_2$·2H$_2$O, from expression 5 and rate jumps method.

The ratio of the rate (r$_r$) is fixed at a value of 4 and the fasted decomposition rate does not exceed 0,02 h^{-1}.

Thus, the activation energy can be estimated without previous knowledge of actual reaction mechanism. The estimated value is 26 ± 10 kJ/mol. This value is in good agreement with the calculated value to R$_2$ mechanism from expression (3). In this way, can be determined the actual mechanism and kinetic parameters by means of a combination of both analytical results.

Kinetic of the dehydration according to Hi-Res TGA

Figure 5 shows the dependency of transformation degree (α) with the temperature, in an interval of $0 \leq \alpha \leq 1$ and heating rates of 10 and 20 °C/min, for the first dehydration of BaCl$_2$·2H$_2$O.
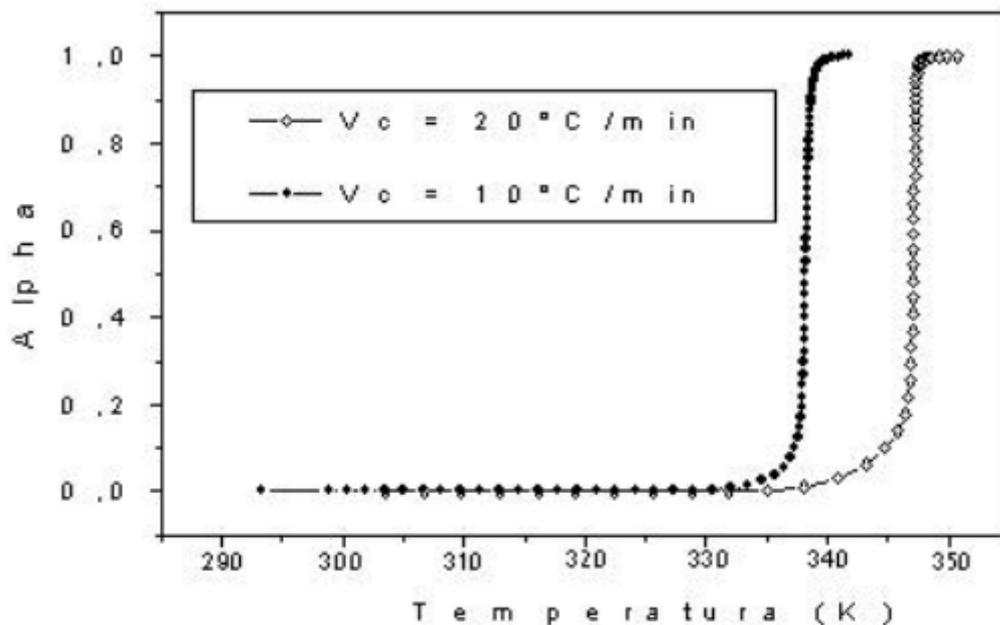
**Figure 5. Experimental α-T plots for the first stages of dehydration
of BaCl$_2$·2H$_2$O. Hi-Res TGA experiment.**

When comparing with the set of isokinetic theoretical curves [8, 10] the clearly sigmoide forms of the curves suggests diffusive process. Therefore, the slowest stage in the reaction is the diffusion of the molecules of water through the solid product [12].

Table 3 shows the obtained results to apply the expression 3, when the heating rate is 10 ℃/min. Similar results are obtained for the heating rate of 20 ℃/min. The best adjustments correspond to the kinetics models D$_1$, D$_2$, D$_3$ and D$_4$ although it cannot be select a kinetic model between the diffusive.

TABLE 3. KINETIC RESULTS OF THE FIRST DEHYDRATION OF BaCl₂·2H₂O FROM EXPRESSION 3 AND Hi- RES TGA EXPERIMENTS

Symbol of the Kinetic models	Coefficients of Correlation	Standard Deviation	Activation Energy (kJ/mol)
D_1	0,995	0,004 7	29
D_2	0,992	0,078	14
D_3	0,986	0,128	40
D_4	0,990	0,094	52
F_1	0,939	0,112	96
R_2	0,939	0,056	73
R_3	0,939	0,075	88
A_2	0,78	0,084	23
A_3	0,797	0,077	10
A_4	0,798	0,103	15

The dependency of the activation energy $(E)_\alpha$ on α is shown in the figure 6, when is applied the equation (4) in points of isoconversion, for two experiments done to different decomposition rates.
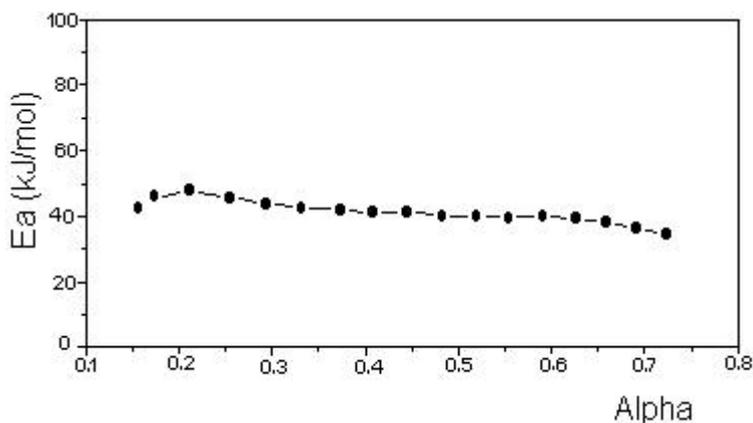

Figure 6. Dependency of the activation energy $(E)\alpha$ on α, for the first dehydration of BaCl₂·2H₂O, from the expression 3 and Hi-Res ATG.

The figure 6 shows in the $0,13 \leq \alpha \leq 0,7$ range, that the values of $(E)_\alpha$ are essentially constant, with a slight tendency to decrease. Therefore, it is evidenced that activation energy is independent of the transformation degree. The estimated value of activation energy is 40 kJ/mol. The combination of the obtained analytical results from the equations (3) and (4) allows selecting the D_3 kinetic model as the most probable, when Hi-Res ATG is used.

General considerations

The most important experimental consideration is deduced when are compared the obtained results by both techniques. In spite of the effective control of temperature and pressure gradients, when are used these experimental procedures, is evident the adverse influence of experimental conditions on the calculated kinetic parameters. The dependency of kinetic parameters and particularly of the kinetic model on the control of atmosphere in immediate vicinity of the sample is demonstrated.

The results suggest the residual pressure as experimental parameter that originates this difference. The experience for SCTA uses lower pressures (vacuum conditions) and a model of interfacial advancement limits the dehydration, while the Hi-Res ATG is carried out to greater pressure and is limited by diffusive process.

The interval of pressures established in each experiment allows favoring one or another kinetic model. In the table 2 for SCTA is observed that, the second models more probable are the diffusives and in the table 3 for Hi- Res ATG, the second models more probable are those characterized by the interfacial advancement.

Rouquerol coincides with Eyraud when asserts, sometimes the vacuum condition eliminate adsorption and diffusion process [13]. This affirmation can explain because during the experience of SCTA, the diffusive process is not determinant.

The literature refers that variations of pressure in 10^{-5}–10^{-2} mbar range during the study by SCTA of dehydration of the $LiSO_4 \cdot H_2O$, cause changes of the kinetic model as was referred [8]. It is important to emphasize that the obtained differences in the kinetic models do not alter the values of calculated activation energy from both techniques.

Conclusions

The influence of atmosphere and particularly of the residual pressure in environment of the samples on the calculated kinetic parameters is demonstrated, for the first dehydration of $BaCl_2 \cdot 2H_2O$. Model controlled by 2-dimensional interfacial advancement (R_2) and activation energy of 26 kJ/mol are calculated when is applied the technique SCTA; a 3-dimensional diffusive kinetic model (D_3) and activation energy of 40 kJ/mol are determined when Hi- Res ATG is applied. The limited validity of the expression (3) in the discrimination of reaction kinetic model was also demonstrated.

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