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Study of the thermal behavior of the transition phase of Co(II)–diclofenac compound by non-isothermal method

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Abstract The Co(II)–diclofenac complex was evaluated by simultaneous thermogravimetry-differential thermal analysis (TG-DTA) and differential scanning calorimetry (DSC). The DTA curve profile shows one exothermic peak because of the transition phase of the compound between 170 and 180 °C, which was confirmed by X-ray powder diffractometry. The transition phase behavior was studied by DSC curves at several heating rates of a sample mass between 1 and 10 mg in nitrogen atmosphere and in a crucible with and without a lid. Thus, the kinetic parameters were evaluated using an isoconversional non-linear fitting proposed by Capela and Ribeiro. The results show that the activation energy and pre-exponential factor for the transition phase is dependant on the different experimental conditions. Nevertheless, these results indicate that the kinetic compensation effect shows a relationship between them.

Keywords Co(II)–diclofenac · DSC · Transition phase · Non-isothermal kinetic

Introduction

Diclofenac (2-[2-(2,6-dichlorophenyl)aminophenyl]ethanoic acid) is a well-known non-steroidal, anti-inflammatory drug and it has also been proven to be quite good for use as a ligand, especially for divalent metal complexes [1–3]. Bucci et al. [4] investigated the thermal behavior of the compounds originating from reacting diclofenac and some transition metals. However, the authors did not verify the transition phase of the cobalt compound and therefore, these steps were neither identified nor informed. In a previous study, the authors reported the prepared thermal characterization of iron(III)–diclofenac. In this study, the authors used mass samples of 2 and 5 mg, which allow a better evaluation of kinetic parameters [5]. Furthermore, recently the authors also related the preparation of zinc–diclofenac and calcium–diclofenac compounds and the investigation of the thermal behavior and kinetic parameters of the dehydration, thermal decomposition, and transition phase of this compound [6, 7].

The transition phase process of any material is of great interest because its physical–chemical properties, such as solubility, chemical stability, and dissolution, change in a significant way. The transition phase consists of complex reaction mechanisms in which the nucleation, crystal growth, or a diffusion process can be included; and these are dependent on experimental parameters, such as the amount sampled, the particle size, and heat transfer, among others [8–10]. In addition, the polymorphism phenomenon can occur in several organic compounds, which consist of the alteration of the molecular conformation into a determined space arrangement. Solid state compounds can be present in two main types of transition phase: enantiotropic and monotropic. First, a reversible transition of the

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structure occurs. Second, the transition occurs as an irreversible rearrangement of the structure.

In this study, the aim was the preparation of cobalt (II)–diclofenac (Co(Diclof)$_2$ in a solid state. This compound was evaluated by simultaneous thermogravimetry-differential thermal analysis (TG/DTA), differential scanning calorimetry (DSC), and X-ray powder diffractometry. The results of this study add to the knowledge on the transition phase of this compound. The kinetic parameters, such as the activation energy (E_a/kJ mol^{-1}) and the pre-exponential factor (ln A/min^{-1}) of the transition phase of Co(Diclof)$_2$ were evaluated by DSC analysis under non-isothermal conditions. Besides this, an investigation with four mass samples was carried out in order to determine the effect of changing the experimental variables as well as the kinetic behavior. Thus, the measurements are estimated at temperatures corresponding to fixed values of conversion degree (α) and the activation energy (E_a/kJ mol^{-1}). Data were obtained applying the isoconversional method proposed by Capela and Ribeiro [5–7, 11, 12].

Kinetic theory

Kinetic analysis under non-isothermal conditions is usually undertaken to consider the integral kinetic equation, defined by

$$\beta = \frac{AE}{Rg(\alpha)} \int_{E/RT}^{\infty} \frac{\exp(-z)}{z^2} dz, \tag{1}$$

where $\beta = \mathrm{d}T/\mathrm{d}t$ is a constant heating rate (T is the temperature and t is the time), $g(\alpha)$ is the integral form of the reaction model as a function of the extent of the reaction α, A is the pre-exponential factor, E is the activation energy and R is the gas constant.

Kinetic parameters are estimates by fitting the Eq. 1 to experimental data. As a consequence, the evaluation of the integral on the right side of the Eq. 1 is required and is known as the temperature integral. A difficulty results from the fact that this integral does not have an exact analytical solution. Thus, it is convenient to approximate the integral of temperature to some function that yields suitable estimations for these kinetic parameters.

In this study, the kinetic parameters are obtained from the isoconversional method using an approximation to the temperature integral based on the convergent of a Jacobi fraction, proposed by Capela et al. [11]. This approximation is a rational function, given by the following equation:

$$\int_{x}^{\infty} \frac{\exp(-z)}{z^2} \mathrm{d}z = \frac{\exp(-x)}{x} \frac{x^3 + 14x^2 + 46x + 24}{x^4 + 16x^3 + 72x^2 + 96x + 24} \tag{2}$$

A characteristic experimental curve presents the conversional fraction, α, as a function of the temperature for a given heating rate, β. For each fixed value of α, there are corresponding values of T_α for temperature, values of E_α for the activation energy and values of A_α for the pre-exponential factor.

Replacing the integral in Eq. 1 by the approximation given in Eq. 2, the following expression for the heating rate, β, is obtained as a function of $x_\alpha = 10^3/RT_\alpha$:

$$\beta = \frac{\exp(B_\alpha - E_\alpha x_\alpha)}{x_\alpha} \frac{E_\alpha^3 x_\alpha^3 + 14E_\alpha^2 x_\alpha^2 + 46E_\alpha x_\alpha + 24}{E_\alpha^4 x_\alpha^4 + 16E_\alpha^3 x_\alpha^3 + 72E_\alpha^2 x_\alpha^2 + 96E_\alpha x_\alpha + 24}, \tag{3}$$

where the activation energy is in kJ/mol and the parameter B_α is defined as

$$B_\alpha = \ln\left(\frac{10^3 A_\alpha}{Rg(\alpha)}\right) \tag{4}$$

The estimates of E_α and B_α can be obtained by the non-linear fitting of Eq. 3 to the β values as a function of x_α.

Once the $g(\alpha)$ function has been determined for each conversional fraction of α, the estimation of the Arrhenius pre-exponential factor can be obtained from Eq. 4 and is given by the following equation:

$$\widehat{A}_\alpha = \frac{R}{10^3} \exp(\widehat{B}_\alpha) g(\alpha) \tag{5}$$

Experimental

The Co(Diclof)$_2$ complex was prepared by the stoichiometric addition of cobalt (II) chlorides to an aqueous solution of potassium diclofenac salt. The obtained precipitate was filtered, washed with distilled water, dried at room temperature, and stored in a desiccator over anhydrous calcium chloride until a constant weight was achieved.

Simultaneous TG-DTA and DSC curves were obtained from a SDT 2960 and a DSC 2910, both from TA Instruments, respectively. The TG-DTA analysis experiment was performed using sample sizes of around 7 mg in an α-alumina crucible and heating rates of 20 °C min^{-1} in synthetic air atmosphere (100 mL min^{-1}). The DSC curves were obtained using several heating rates (5, 10, and 20 °C min^{-1}) from 30 to 210 °C. Powered samples having a particle size of around 250 μm and a mass of around 1, 2.5, 5, and 10 mg were placed in an aluminum crucible, either open or with crimped lids, and a nitrogen flow of 50 mL min^{-1}.

The diffraction patterns were obtained from a Siemens mod. D-500 X-ray diffractometer using CuKα radiation ($\lambda = 1.54$ Å) and settings of 40 kV and 30 mA.

Results and discussion

Thermal behavior

Simultaneous TG/DTA curves of Co(Diclof)$_2$ are shown in Fig. 1. The first mass loss (2.3%) between 30 and 128 °C corresponding to the endothermic peak below 100 °C is due to dehydration. The second and third mass losses occurred from 237 to 346 °C (59.1%) and from 346 to 640 °C (23.8%); the first of these occurred in a single step and the second in two overlapping steps. For both mass losses, the corresponding exothermic peak was attributed to the thermal decomposition of the ligand.

Calculations based on the mass loss up to the final temperature are in agreement with the formation of Co_3O_4 as the final residue. An exothermic peak seen between 176 and 205 °C, having its maximum at 183 °C, which did not show a corresponding mass loss in the TG curves, is attributed to the transition phase of the anhydrous Co(Diclof)$_2$. The X-ray powder diffraction patterns showed that this compound was in its amorphous state (Fig. 2) and after heating, this compound presents a crystalline structure (Fig. 3).

Figures 4 and 5 show the DSC curves for Co(Diclof)$_2$ in nitrogen atmosphere at heating rates of 5, 10, and 20 °C min^{-1}, either open or with crimped lids, respectively. The DSC endothermic events from 30 to 100 °C correspond to water mass losses in agreement with the TG-DTA curves. The transition phase stage occurs progressively between 163 and 191 °C.

Kinetic data

In Fig. 6, the plot of the heating rate, β, is shown as a function of $X_\alpha = 1000/RT_\alpha$ It can be observed that the adjustment has a low variation for E1 values, which corresponds to the activation energy.

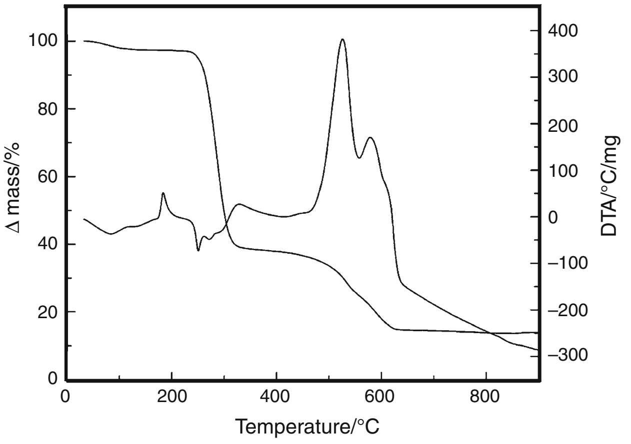

Fig. 1 Simultaneous TG-DTA curves of the Co(Diclof)$_2$ compound in synthetic air and heating rate of 20 °C min^{-1}

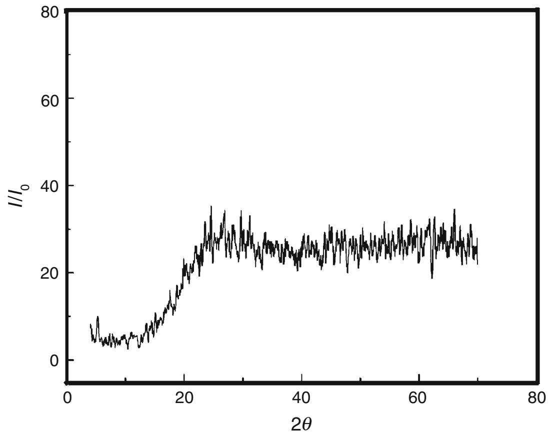

Fig. 2 X-ray powder diffraction patterns of the Co(Diclof)$_2$ complex before the crystallization

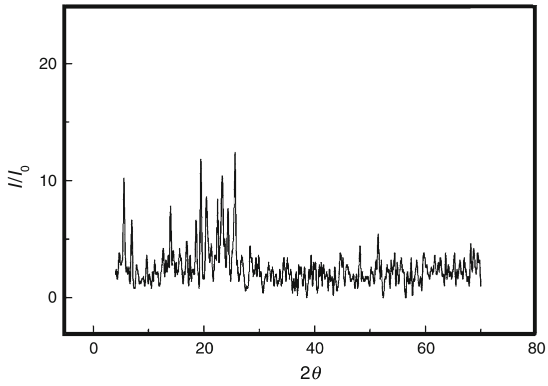

Fig. 3 X-ray powder diffraction patterns of the Co(Diclof)$_2$ complex after the crystallization

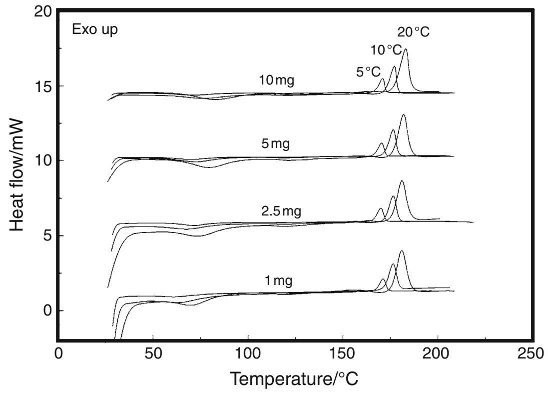

Fig. 4 DSC curves of Co(Diclof)$_2$ compound in nitrogen atmosphere at heating rate of 5, 10, and 20 °C min^{-1}, in aluminum crucible (open)

The average values of the activation energy from the kinetic data for all experimental conditions are shown in Table 1, where the resulting correlation coefficient has a good close linear fit, showing that there is good correlation.

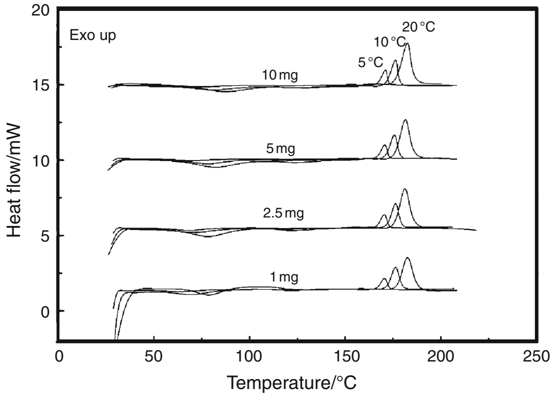

Fig. 5 DSC curves of Co(Diclof)$_2$ compound in nitrogen atmosphere at heating rate of 5, 10, and 20 °C min^{-1}, in aluminum crucible (crimped lids)

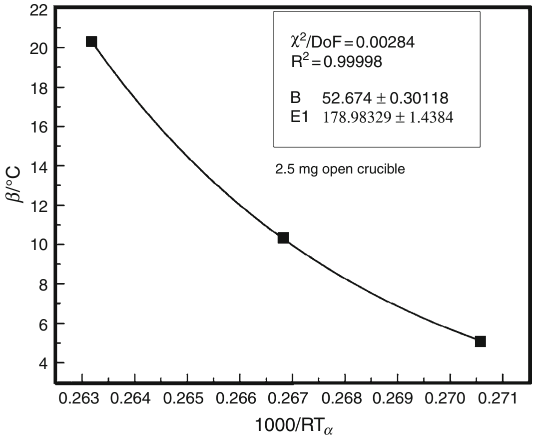

Fig. 6 Diagram of dispersion of β versus α (80%) for 2.5 mg in open crucible with the adjustment function

The average values of the activation energy and the pre-exponential factor were used to arrive at the following correlation [13, 14]:

$$\ln A = a + bE$$

where *a* and *b* are the compensation constants. These plots are commonly called the kinetic compensation effect (KCE). The existence of the "KCE" has been observed in literature for several groups of heterogeneous reactions [15, 16]. The KCE shown in Fig. 7 may suggest that the mechanism of the transition phase stage was not influenced by a change in the amount of mass, neither by the presence nor the absence of the crimped lids on the crucibles. This was so even with the differences observed in Fig. 8.

The activation energy versus the conversion-degree function is shown in Fig. 8. From these curves, a tendency can be observed where the plots maintain the same shape and almost run parallel to each other. But the values of the activation energy vary for each compound due to the dependence on the mass of the sample and the conditions of the crucible. This indicates that the transition phase does not occur in a homogeneous way for every extension of α.

Table 1 Parameters E_a/kJ mol^{-1}, pre-exponential factor/ln A and the correlation coefficient/r for the transition phase stage

Sample mass^a	Crucible	Ea/kJ mol^{-1a}	ln A/min^{-1a}	r
1 mg	Open	228 ± 42	58 ± 3	0.99892
	Crimped lids	177 ± 29	44 ± 2	0.99979
2.5 mg	Open	210 ± 37	53 ± 3	0.99435
	Crimped lids	206 ± 41	52 ± 3	0.99857
5 mg	Open	188 ± 31	47 ± 2	0.99989
	Crimped lids	191 ± 18	48 ± 2	0.99878
10 mg	Open	177 ± 32	44 ± 1	0.99989
	Crimped lids	183 ± 35	45 ± 2	0.99980

^{a} Average values

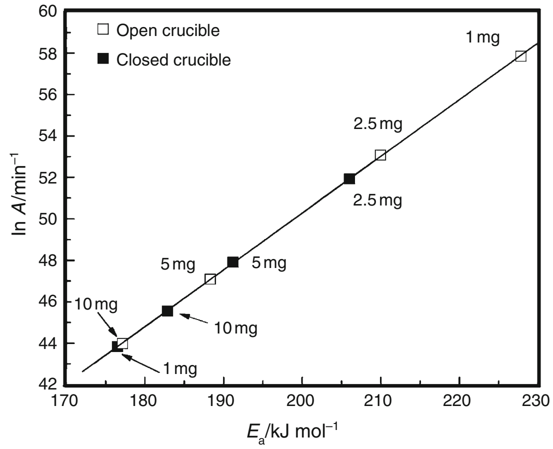

Fig. 7 Linear dependence of pre-exponential factor (ln A/min^{-1}) on activation energy (E$_a$/kJ mol^{-1})

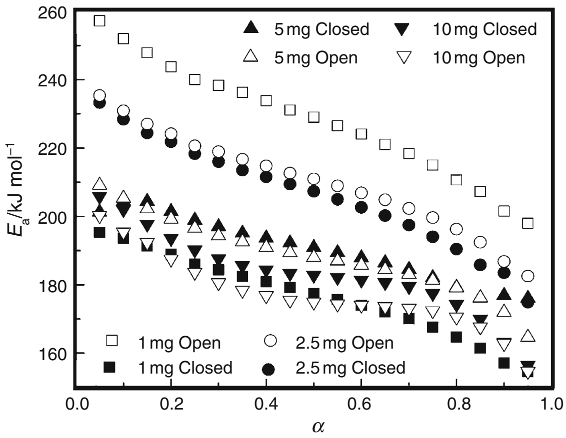

Fig. 8 The calculated E$_a$/kJ mol^{-1} as a function of α for the transition phase stage

Whether equal sample masses were comparatively evaluated or used in an open or a closed crucible, it was observed that there is a great difference between the plots of activation energy versus the conversion degree.

This was especially true for the 1 mg mass (in a closed crucible) for which the E_a versus α curve almost overlapped with those of the 2.5 and 5 mg masses (both in closed crucibles). This difference between them may be attributed to the fact that there is a better transfer of energy from the medium through the cover of the crucible over the sample, and thus, it propitiates the decrease in the activation energy. In the open crucible, this does not occur because there is the flow of nitrogen over the sample, which easily dissipates the generated energy and consequently cools the sample. In this way, this phenomenon will make the activation energy increase in relation to an equivalent sample in a closed crucible. Along with this, the smaller quantity of sample (1 mg) propitiates a better homogeneity by distributing the energy throughout the sample. However, with an increase in the sample mass, it can be seen that the differences between the values of the activation energy tend to disappear. This fact may be attributed to the increase of the mass, because the presence of a greater amount of sample makes a difference to the thermal conductivity decrease. Therefore, for the samples, in both open and closed crucibles, there is a very small difference in the values of the activation energy.

Conclusions

In this study, it was observed that there is an alteration in the values of the activation energy for all the compounds, both when using or not using the cover on the crucible as well as for increased sample masses. Nevertheless, it is also evident that the apparent activation energy becomes lower with an increase in the mass of the sample. In a previous study, Kobelnik et al. observed that for $Zn(Diclof)_2$ there is an increase in the activation energy for a sample mass of 5 mg in static atmosphere as numerical values. The others obtained results demonstrate that during the analysis conditions have the same behavior, independent of the atmosphere or sample mass conditions [7]. Besides, recently the authors reported the kinetic parameters of the transition phase stage of $Ca(Diclof)_2$. This study showed that the difference between the values of the activation energy was small, which was attributed to a difference in the thermal conductivity of the sample mass [6].

Furthermore, in this study, it was observed that the different kinetic results are conditioned by the contributions of different component factors, as well as by the variation in the conditions during the transition phase stage. Finally, KCE relationships were observed for a similar reaction behavior, along with a similar range in activation energy depending on variations in the experimental conditions.

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