

## COMPARISON OF THE DEHYDRATION KINETICS OF SOLID STATE COMPOUNDS OF 2-METHOXYBENZYLIDENEPYRUVATE WITH SOME DIVALENT METAL IONS

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**Resumo:** o sal de sódio de 2-metoxibenzalpiruvato assim como os complexos metálicos do ligante 2-metoxibenzalpiruvico com os íons Fe, Co, Ni, Cu e Zn foram preparados e analisados no estado sólido. Curvas termogravimétricas (TG) destes compostos foram obtidas com massa de amostra em torno de 1 e 5mg em atmosfera de nitrogênio. Diferentes razões de aquecimento foram utilizadas para caracterizar e estudar estes compostos sob o ponto de vista cinético. A energia de ativação e o fator pré-exponencial foram obtidos com a aplicação, nas curvas TG, do método proposto por Wall-Flynn-Ozawa. Os dados obtidos foram avaliados e os valores obtidos de energia de ativação foram relacionados em função do grau de conversão ( $\alpha$ ). Os resultados apresentaram que devido a massa de amostras, diferentes energias de ativação foram obtidos. Os resultados também foram discutidos tendo em vista a dependência entre a energia de ativação e o fator pré-exponencial, onde foi verificado o efeito de compensação cinética (KCE) e possível relação linear entre as etapas de desidratação destes compostos.

**Palavras chave:** íons divalentes, 2-metoxibenzalpiruvato; cinética não isotérmica.

### Introduction

2-methoxybenzylidenepyruvate is an organic compound synthesized from pyruvic acid and phenyl-substituted compounds [1,2]. Several works have been accomplished with different metal ions starting from these syntheses, since this ligand forms complexes easily. The thermal behavior of these compounds has been evaluated thoroughly, especially by thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) as well as X-ray powder diffractometry, infrared spectroscopy, which have been used to characterize these compounds [3-9].

The aim of these work is the comparison of the dehydration kinetics using non-isothermal

procedures of the solid-state compounds of bivalent Fe, Co, Ni, Cu and Zn with 2-methoxybenzylidenepyruvate (2-MeOBP). By applying the isoconversional method proposed by Wall-Flynn-Ozawa on the TG curves, the data provide information concerning the activation energy ( $E_a$  kJ mol<sup>-1</sup>) versus the conversion degree ( $\alpha$ ) as well as the pre-exponential factor ( $\ln A$  min.). Furthermore, the isoconversional method was used as way of obtaining reliable and consistent kinetic information and also because avoids the use of explicit kinetics models [10]. The dependence of the activation energy was also considered in terms of the pre-exponential factor, where it was possible to verify the effect of kinetic compensation (KCE) of these compounds.

## Experimental

2-methoxybenzylidenepyruvic acid (2-MeO-BP·H<sup>+</sup>) and its sodium salt, 2-methoxybenzylidenepyruvate (2-MeO-BP·Na<sup>+</sup>), were synthesized, purified and prepared, first the acid and then the salt, as described in literature [1]. All the complexes of the general formula M<sup>m+</sup>L<sub>m</sub>nH<sub>2</sub>O, where M are the divalent metal ions Fe, Co, Ni, Cu, Zn and L is the sodium salt. The solid-state compounds were prepared by dropwise adding the chlorides of the metal ions to the ligand solution (except for iron, where the sulphate was used) and this was done under continuous stirring until total precipitation was achieved. The precipitates were filtered and washed with water to totally eliminate the chloride (or sulphate) compounds and then dried at room temperature and stored until constant mass in a desiccator over anhydrous calcium chloride.

Kinetic evaluation of the dehydration steps were obtained using heating rates of 5, 10 and 20°C min<sup>-1</sup> from 30 to 500°C. The curves were obtained using a SDT 2960 thermoanalyser system from TA Instruments. Powered samples having a mass of 1 and 5 mg (±0.05mg) were placed in an alumina crucible, under a nitrogen flow of 100 mL min<sup>-1</sup>.

This compound also was examined using Scanning Electron Microscopy (SEM). The particles were sputtercoated with a thin and uniform layer of gold using a vacuum evaporator and then

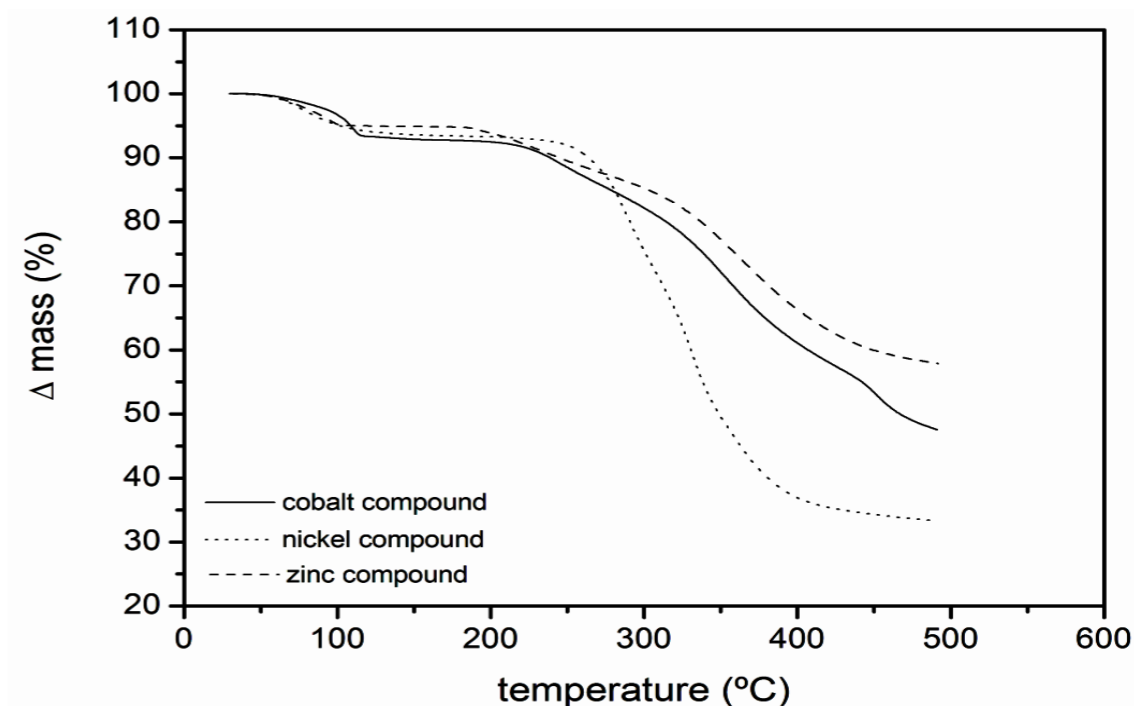
examined using a JEOL Scanning Microscope, model JSM-T-330A at an accelerating voltage of 20 kV.

## Results and discussion

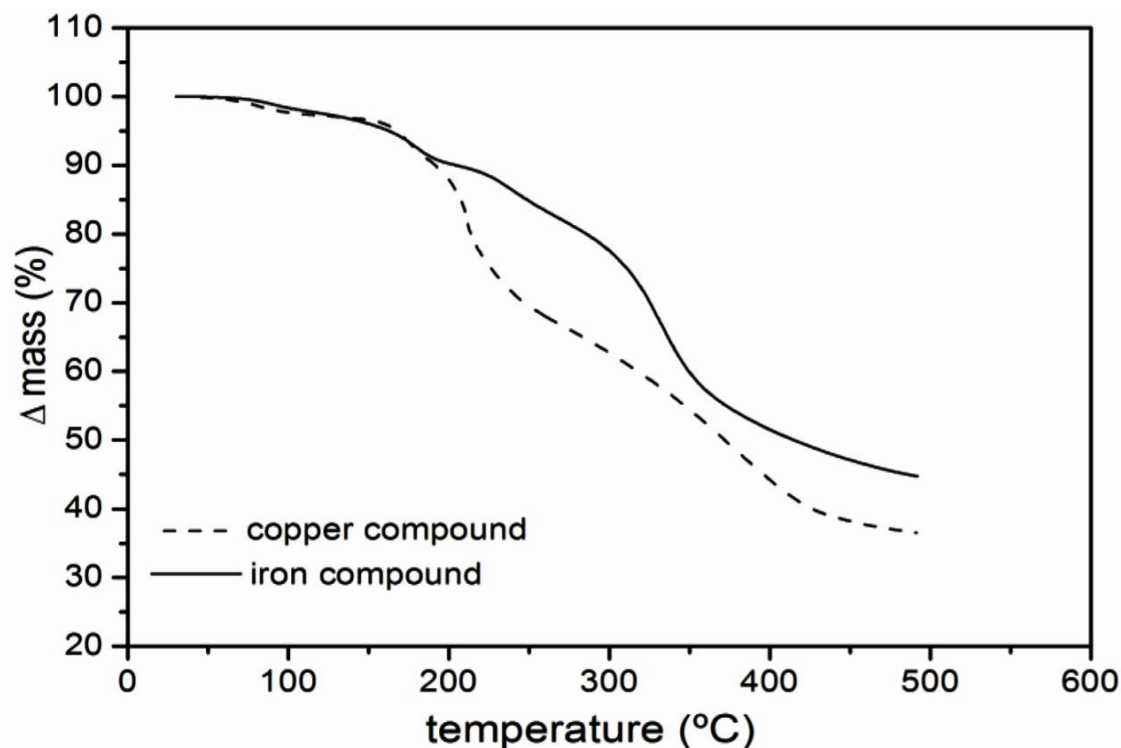
In a previous work, these were characterized by simultaneous TG-DTA and DSC curves (in dynamic air atmosphere), infrared spectroscopy and X-ray diffractometry [2]. These compounds are in agreement with the stoichiometry M:L<sub>2</sub>nH<sub>2</sub>O where M represents the bivalent metal ions, L is the ligand and n is the number of water molecules.

The kinetic parameters of dehydration of these compounds were evaluated from the TG curves shown in the Figures 1 and 2.

For the cobalt, nickel and zinc compounds (Figure 1), the TG curves to first mass loss seen between 30 and 110°C shown a pattern of dehydration and for the copper (130°C) and iron (150°C) compounds (Fig. 2), these correspond to another dehydration pattern. The initial temperature of thermal decomposition occurs for cobalt (185°C), nickel (240°C) and zinc (210°C); while for iron and copper occurs at 130°C and 150°C, respectively. The thermal decomposition in all the TG curves occurs in more than one consecutive step without the formation of stable intermediates or the respective oxides.



**Figure 1.** TG curves of the cobalt, nickel and zinc compounds, with mass sample of 1mg, at heating rate of 10°C min<sup>-1</sup> in nitrogen atmosphere.



**Figure 2.** TG curves of the sodium salt, copper, iron and ligand compounds, with mass sample of 1mg, at heating rate of  $10^{\circ}\text{C min}^{-1}$  in nitrogen atmosphere.

The kinetic parameters of the data was obtained using the isoconversional method of Flynn, Wall and Ozawa (FWO) because it is commonly used to avoid the kinetic model [11,12,13]. This method is based on fixed values of the degree of conversion ( $\alpha$ ) obtained from the experiments at different heating rates ( $\beta$ ):

$$\alpha_t = \frac{(C_t - C_0)}{(C_{\infty} - C_0)} \quad (1)$$

where C represents the reagent concentration, as well as other physical properties which are represented in the TG experiment. The subscript corresponds to the elapsed time,  $t$ , where the initial time is  $t = 0$  and the final time is  $t = \alpha$ .

The dependence of  $\alpha$  as a function of time can be expressed as the following differential equation [14]:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (2)$$

where  $k(T)$  is the temperature-dependent rate constant and  $f(\alpha)$  is a function that represents the reaction model. The  $k(T)$  usually employs the Arrhenius equation [15]:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (3)$$

where A is the pre-exponential factor, E is the activation energy and R is the gas constant.

For dynamic data obtained at a constant heating rate,  $\beta = dT/dt$ , this new term is inserted in the Eq. (3) to obtain the transformation [11]:

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{AE}{\beta R} p(x) \quad (4)$$

Thus, the non isothermal kinetics have resolved the major problem of the isothermal exper-

iment, which is that a sample requires some time to reach the experimental temperature undergoing some transformations that are likely to affect the kinetics results [16].

Based on the previous equation and considering that A,  $f(\alpha)$  and E are independent of T and that A and E are independent of  $\alpha$ , we obtain [11,16,17]:

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{AE}{\beta R} p(x) \quad (5)$$

where  $x = (E/RT)$ . For  $p(x)$ , where  $20 \leq x \leq 60$ , we can use Doyle's approximation of the integral temperature [11,17,18]:

$$\log p(x) \cong -2.315 - 0.4567x \quad (6)$$

However, a simpler expression has been developed by the substitution of Eq. (6) into Eq. (5) to obtain [11,17]:

$$\log g(\alpha) \cong \log \frac{AE}{R} - \log \beta - 2.315 - 0.457 \frac{E}{RT} \quad (7)$$

Thus, from the slope of a plot of  $\log \beta$  versus  $1/T$ , the activation energy can be calculated for fixed values of  $\alpha$  from the experiments at different heating rates testing the constancy of E with respect to  $\alpha$  and T [11,16,17].

The pre-exponential factor can be evaluated taking into account that the reaction is of the first-order and can be defined as [11]:

$$A = \frac{\beta E}{RT_m^2} \exp\left(\frac{E}{RT_m}\right) \quad (8)$$

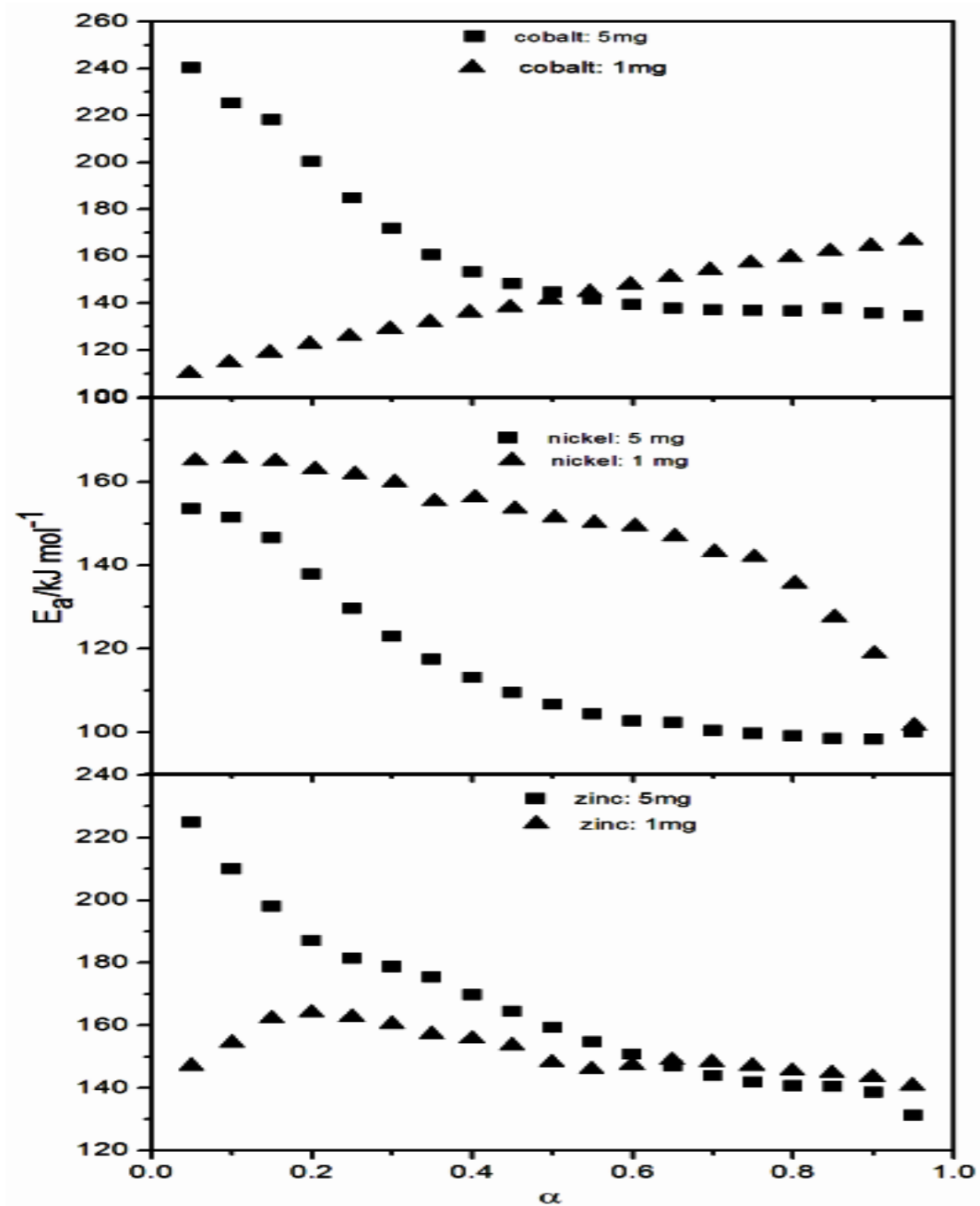
The average values of the activation energy of the kinetics data for all compounds are shown in Table 1, where the resulting correlation coefficient has a good linear close fit, showing that there is good correlation.

**Table 1:** Parameters  $E_a$  ( $\text{kJ mol}^{-1}$ ) and the correlation coefficient ( $r$ ) for the dehydration of the compounds.

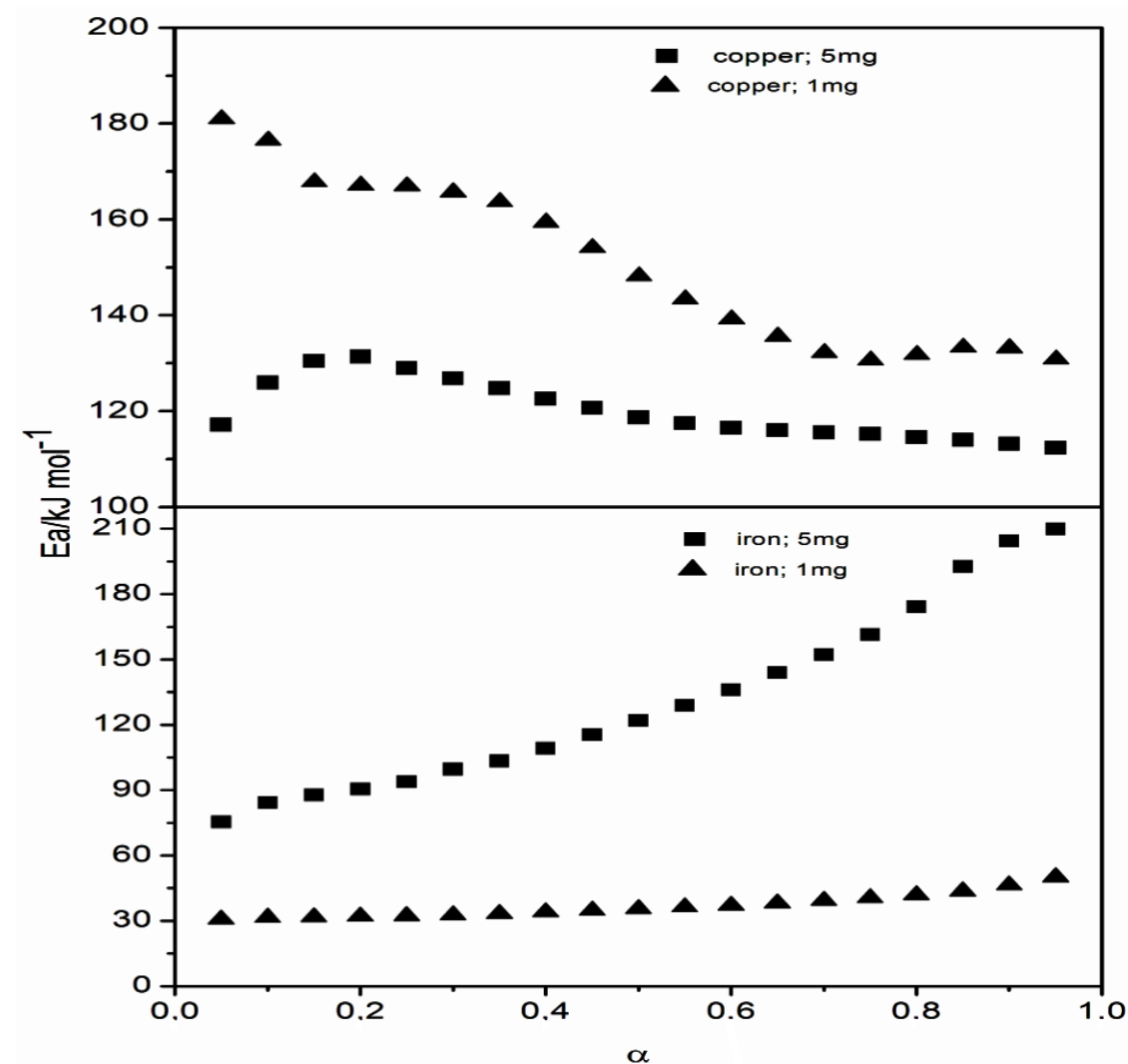
Compound	Mass	Dehydration	
		$E$ ( $\text{kJ mol}^{-1}$ )	$R^2$
Fe(L) <sub>2</sub> 0.5H <sub>2</sub> O	1mg	37.0 ± 0.2	0.99977
	5mg	130.8 ± 0.3	0.99979
Co(L) <sub>2</sub> 2H <sub>2</sub> O	1mg	141.0 ± 0.1	0.99979
	5mg	164.2 ± 0.2	0.99943
Ni(L) <sub>2</sub> 1.5H <sub>2</sub> O	1mg	147.8 ± 0.1	0.99847
	5mg	115.4 ± 0.2	0.99910
Cu(L) <sub>2</sub> 0.7H <sub>2</sub> O	1mg	150.6 ± 0.1	0.99926
	5mg	120.16 ± 0.05	0.96818
Zn(L) <sub>2</sub> 2H <sub>2</sub> O	1mg	150.69 ± 0.04	0.97043
	5mg	165.1 ± 0.2	0.99985

<sup>1</sup> L= ligand 2-methoxybenzilidene ;<sup>2</sup>Average

The activation energy ( $E_a$ ) versus conversion degree ( $\alpha$ ) values for the dehydration are shown in the Figures 3 and 4.



**Figure 3.** The calculated  $E_a/\text{kJ mol}^{-1}$  as a function of  $\alpha$  for the dehydration stage of the cobalt, nickel and zinc compounds.



**Figure 4.** The calculated  $E_a/\text{kJ mol}^{-1}$  as a function of  $\alpha$  for the dehydration stage of the copper and iron compounds.

For cobalt, nickel and zinc compounds, which apparently has the same dehydration pattern, the values of the activation energy vary for each compound. For the masses samples of 5mg, the dehydration step there are tendencies of the plots maintain the same contour and run parallel to each other. So this indicates that dehydration kinetic occurs by same way for every extension of  $\alpha$ . However, the mass sample of 1mg, the kinetic behavior does not occurs in a same tendencies for every extension of  $\alpha$ . These fact were attributed the differences in the thermal conductivity, which

is dependent of the characteristics of each compound. In addition, recently Kobelnik et. al observer that different mass sample, the activation energy continually vary in function of degree conversion as numerical values at open and the crimped lids crucibles [18]. Therefore, it suggested that these facts favors parallel reactions and besides, the heat of reaction associated with the thermal conductivity also lead to changes in the reactions. Furthermore, this not a general rule because the variation of the activation energy depends on several factors, such as the type of studied sample,



the presence or not of cover on the crucible, etc [20-22]. Furthermore, it is clear that the values of activation energy for first dehydration step are variable, which indicate that can be regarded as single step reaction. Additionally, the particle size or non-homogeneous particles of each compound can also alter the kinetic behavior. Figures 5 to 8 show SEM images of particles of the cobalt and copper compounds. For the cobalt compound, can be seen different sizes of the particles before and after the dehydration. This was attributed to destruction of the structure and subsequent contraction of the sample mass. For the copper compound, can be seen that there was a contraction in the volume without destroy the structure. Thus, the activation energy indicates that only the thermal conductivity alters the kinetic behavior.

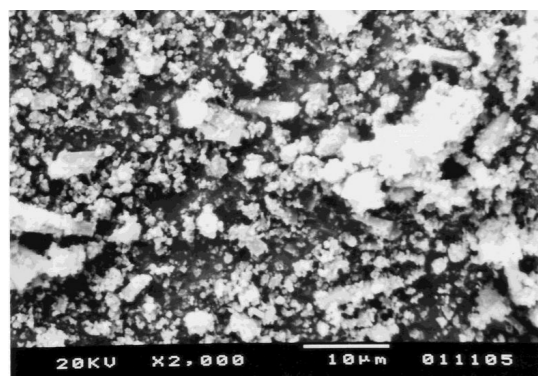


Figure 5. SEM hydrated cobalt compound

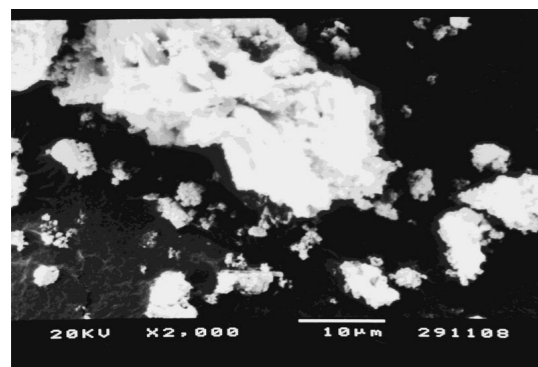


Figure 6. SEM dehydrated cobalt compound

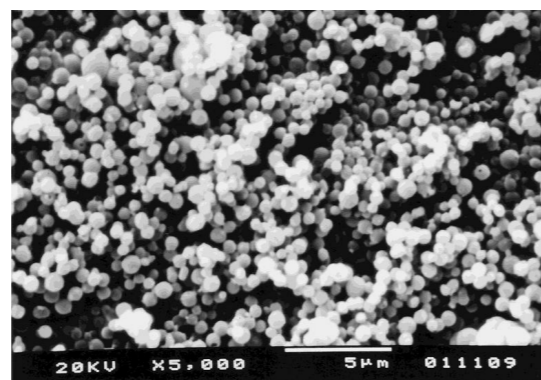


Figure 7. SEM hydrated copper compound.

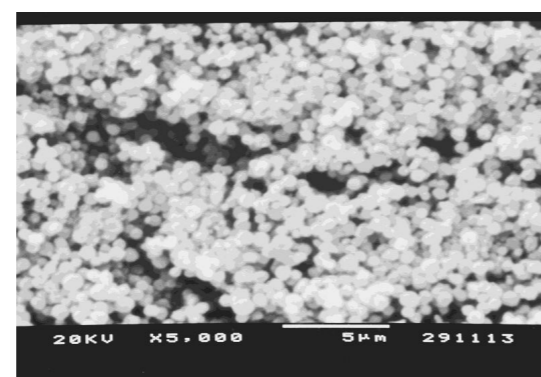


Figure 8. SEM dehydrated copper compound

From the information obtained, we can use the values of the activation energy and the pre-exponential factor to make the following correlation [23-25]:

$$\ln A = a + bE$$

where  $a$  and  $b$  are the compensation constants. The average values found for the plots of the activation energy and pre-exponential factor are commonly called of kinetic compensation effect (KCE). The existence of the “kinetic compensation effect” has been observed in literature for several groups of heterogeneous reactions. The linear relationship between  $\ln A$  and  $E_a$  for the dehydration reactions and thermal decomposition allows us to group them according to their similarities [23,26].

For the dehydration, as shown in Figure 9, evidence for the KCE was seen, but there was not relationship between the numbers of water mole-

cule losses. Additionally, in Figure 10 e 11, are shown the average values for 1 and 5mg masses of the activation energy as a function of the pre-exponential factor in a lower ( $0.5 < \alpha$ ) and a higher ( $0.5 > \alpha$ ) range of conversion degree. This artifact was used to demonstrate that there are variations in two intervals of the conversion degree. It may be observed that there was displacement between the compounds. But once again, there was no observed relationship between the water molecule losses for the dehydration.

This demonstrate that even if we just considered the average values of the two intervals, the KCE would not give clear information regarding the dehydration behavior. Additionally, this fact occurs because the dehydration of these compounds also undergoes different steps during the conversion degree ( $\alpha$ ).

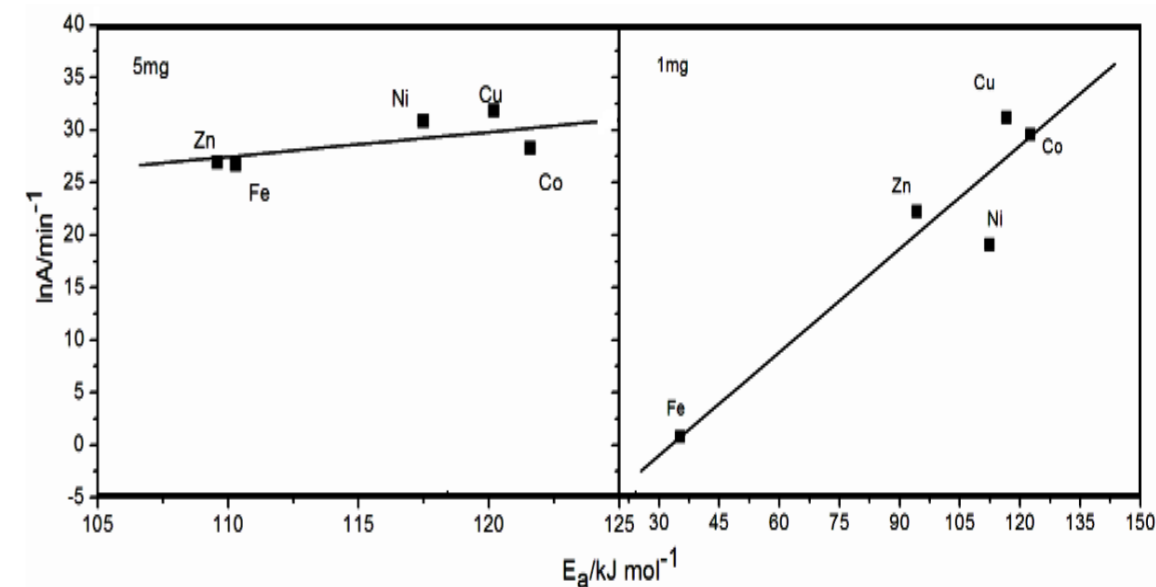
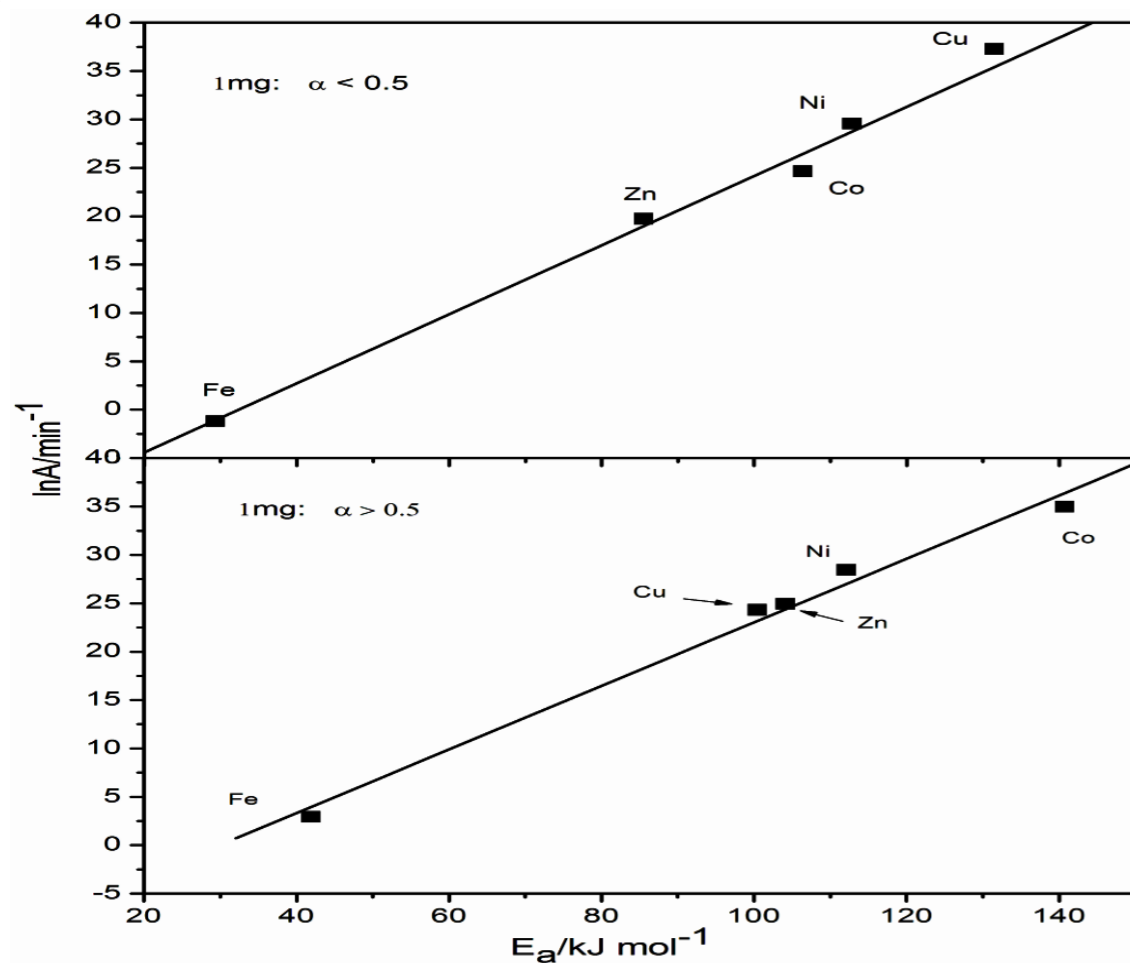
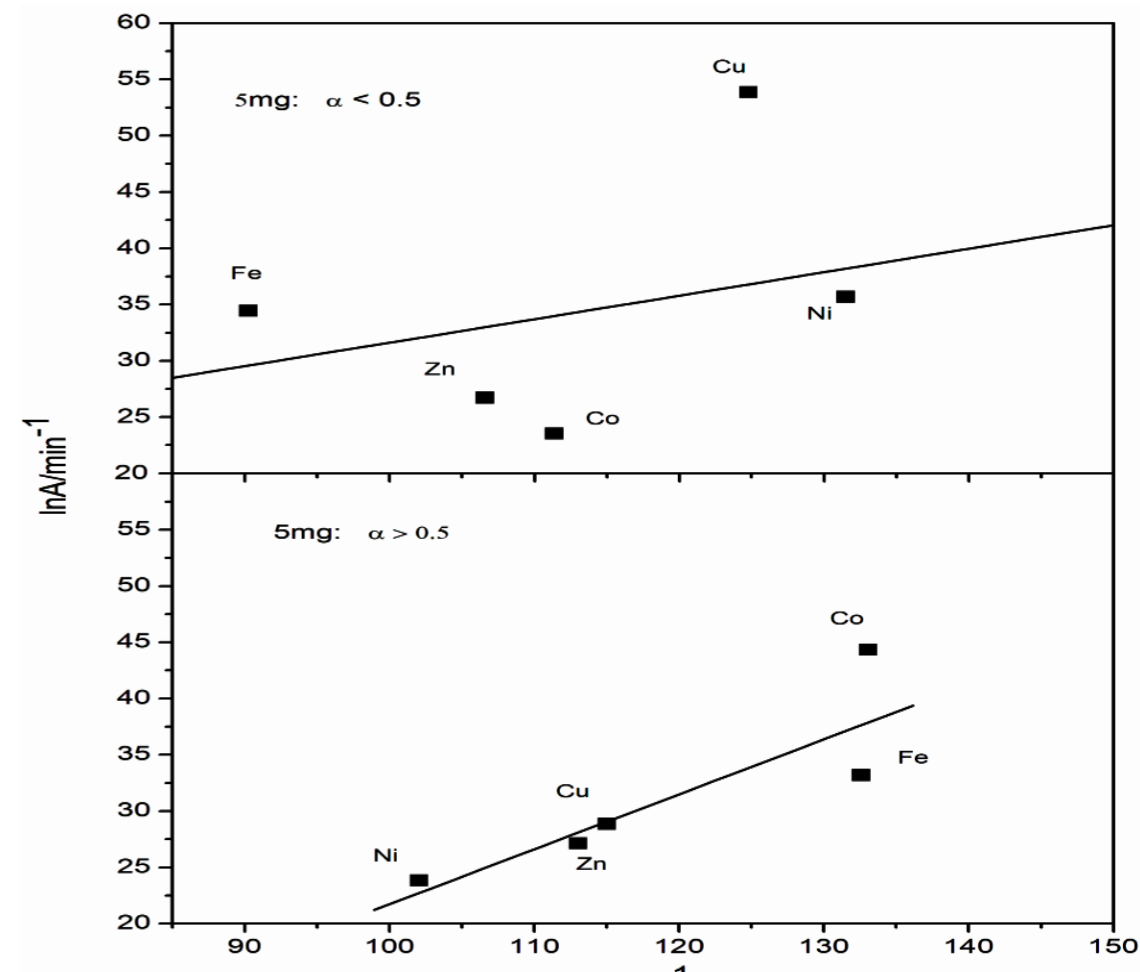


Figure 9. Linear plot of  $\ln A/\text{min}^{-1}$  versus  $E_a/\text{kJ mol}^{-1}$  for the dehydration of the compounds: (A) = 1mg and (B) = 5mg.



**Figure 10.** Linear plot of  $\ln A/\text{min}^{-1}$  versus  $E_a/\text{kJ mol}^{-1}$  for the dehydration reaction with mass sample of 1 mg in two intervals of conversion degree.



**Figure 11.** Linear plot of  $\ln A/\text{min}^{-1}$  versus  $E_a/\text{kJ mol}^{-1}$  for the dehydration reaction with mass sample of 5 mg in two intervals of conversion degree.

### Conclusion

The presented results clearly showed that the use of the different sample masses, influenced a decrease or an increase of the activation energy ( $E_a$ ) values. Besides the kinetic dependence on the experimental condition in a dynamic procedure, it can be seen from the resemblance between different conditions allows a better evaluation of kinetic parameters. The activation energy of the dehydrations steps suggests the occurrence of a multi-step process steps. Furthermore, the KCE leaves much doubt as to the reaction type that occurs during the dehydration steps because those compounds are not homogeneous. Thus, the KCE

relationships can be used only in an empirical manner, but this is not conclusive to evaluate or determine the complex reaction mechanism.

### Acknowledgments

CAPES/CNPQ and IPT – Instituto de Pesquisas Tecnológicas do Estado de São Paulo by TG curves.

**Abstract:** Divalent metal complexes of ligand 2-methoxybenzylidenepyruvate with Fe, Co, Ni, Cu and Zn as well as sodium salt were synthesized and investigated in the solid state. TG curves of these compounds were obtained with masses sample of 1 and 5mg under nitrogen atmosphere. Different heating rates were used to characterize and study these compounds from the kinetic point of view. The activation energy and pre-exponential factor were obtained applying the Wall-Flynn-Ozawa method to the TG curves. The obtained data were evaluated and the values of activation energy ( $E_a$  / kJ mol<sup>-1</sup>) was plotted in function of the conversion degree ( $\alpha$ ). The results show that due to mass sample, different activation energies were obtained. The results are discussed mainly taking into account the linear dependence between the activation energy and the pre exponential factor, where was verified the effect of kinetic compensation (KCE) and possible linear relations between the dehydrations steps of these compounds.

**Keywords:** bivalent metal ions, 2-methoxybenzylidenepyruvate, non-isothermal kinetics, dehydration

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