Eclética Química

DEHYDRATION AND VOLATILIZATION NON ISOTHERMIC KINETIC OF THE SOLID STATE ALUMINIUM 8-HYDROXYQUINOLINATE

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ABSTRACT: $Al(C_9H_6ON)_3 \cdot 2.5H_2O$ was precipitated from the mixture of an aqueous solution of aluminium ion and an acid solution of 8-hydroxyquinoline, by increasing the pH value to 9.5 with ammonia aqueous solution. The TG curves in nitrogen atmosphere present mass losses due to dehydration, partial volatilisation (sublimation plus vaporisation) of the anhydrous compound followed by thermal decomposition with the formation of a mixture of carbonaceous and residues. The relation between sublimation and vaporisation depends on the heating rate used. The non isothermic integral isoconventional methods as linear equations of Ozawa-Flynn-Wall and Kissinger-Akahira-Sunose (KAS) were used to obtain the kinetic parameters from TG and DTA curves, respectively. Despite the fact that both dehydration and volatilisation reactions follow the linearity by using both methods, only for the volatilisation reaction the validity condition, 20£ E/RT£ 50, was verified.

KEY-WORDS: 8-hydroxyquinolinate, aluminium, kinetic parameters, TG, DTA, volatilisation.

Introduction

1. Aluminium 8-hydroxyquinolinate

It has been found out that the complete precipitation of the aluminium ion by the 8-hydroxyquinolinate anion to form $Al(C_9H_6ON)_3$, occurs from pH 4.2^9 to higher pH values. This reagent has been used to separate the aluminium ion from the beryllium, alkali earth metal and

magnesium cations as well as from the phosphate anion[2,3,9].

Borrel and Paris[4] studied the precipitation of several metallic oxinates, among them that of the aluminium ion. $Al(C_9H_6ON)_3$ was prepared in 0.1 mol L^{-1} HCl, with 10% excess of 8-hydroxyquinoline, heated up to 70-80°C, washed by hot water decantation, filtered under vacuum and stored at room temperature. TG curves showed dehydration and thermal decomposition with formation of Al_2O_3.

Charles and Langer[8] prepared complexes of aluminium ion in aqueous solutions, which were washed with distilled hot water in order to obtain total elimination of the ligand excess. The compounds were previously dried at room temperature and the drying was completed in vacuum at 50°C. TG curves allowed to verify the volatilisation of these compounds.

The thermal behaviour of aluminium quinolinate and their derivatives were studied by Wendlandt and Horton[18] through the differential thermal analysis in an argon atmosphere. The partial volatilisation of the aluminium complex was observed by Charles and Perroto[7] through TG and DTA curves also in argon atmosphere.

The thermogravimetric study of aluminium oxinate obtained by three different procedure was done by Keattch[13]. TG curves showed the dehydration and thermal decompositions to Al_2O_3 at 150 and 700°C, respectively.

Critical study using 8-hydroxyquinoline as gravimetric reagent for the aluminium ion was done by Chalmers and Mohammed Abdul Basit[6], through modification in experimental conditions described by Berg[9]. They verified the co-precipitation of 8-hydroxyquinoline and formation of polynuclear species, besides the volatilisation when this compound was submitted to heating.

2. Theoretical of non-isothermal integral isoconvertinal methods

The general equation[10] for the reaction rate in an isothermal condition has been written as:

$$\frac{d\alpha}{dt} = f(\alpha)\,A\,T^n e^{-\frac{E}{RT}} \tag{1}$$

in which da/dt is reaction rate, f(a) is reaction model, A is the pre-exponential factor, E is the activation energy, T is the temperature, and R is the gas constant.

Under non-isothermal condition, at a constant heating rate b =dT/dt, the explicit temporal dependence in equation (1) may be rewritten as:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt} \cdot \left(\frac{1}{\beta}\right) = \frac{A}{\beta} f(\alpha) T^n e^{-\frac{E}{RT}} \tag{2}$$

Considering the integral form and E/RT=x:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{AE}{R\beta}\left[\frac{E}{R}\right]^n \int_x^{x_0} \frac{e^{-x}}{x^{n+2}} dx = \frac{AE}{R\beta}\left[\frac{E}{R}\right]^n P_n(x,x_0) \tag{3}$$

Considering $-E/RT_0 \gg 1$, the integral temperature P_n may be obtained as being:

$$P_n(x, x_0) \approx P_n(x, \infty) \approx P_n(x) \tag{4}$$

Assuming n=0, the equation (4) may be simplified to the form p(x), whose Doyle§ approximation [1] from $20 \le x \le 46$ is given as:

$$\log p(x) = -2.315 - 0.4567(E/RT) \tag{5}$$

Using the Doyle§ approximation and logarithmic form of the equation (3) the linear equation of Ozawa-Flynn-Wall[12,15] can be obtained:

$$\log \beta = \log \frac{AE}{g(\alpha)R} - 2.315 - 0.4567\frac{E}{RT} \tag{6}$$

To small intervals and considering the same extension of reaction a in a series of experiments in different heating rate :

$$E = -\frac{R}{0.4567}\frac{d\log\beta}{d(1/T)} \approx -2.19R\frac{d\log\beta}{d(1/T)} \tag{7}$$

The pre-exponential factor, A, may be obtained through the following equation:

$$A \approx \frac{\beta E e^{E/RT}}{RT^2} \tag{8}$$

and the lifetime (t_f) may be estimated from Toop equation[16].

$$\ln t_f = \frac{E}{RT_f} + \ln\left[\frac{E}{\beta R}\right]p\left(\frac{E}{RT_p}\right) \tag{9}$$

where T_f is the temperature in which the system is exposed and T_p is the temperature at which the mass loss is 5%.

The Kissinger-Akahira-Sunose method[1,5,14], KAS method, may be originally obtained through derivation of the equation (2), logarithm application and posterior rearrangement as given bellow:

$$\frac{d^2\alpha}{dT^2} = \left[\frac{df(\alpha)}{d\alpha}Ae^{-E/RT} + \frac{\beta E}{RT^2}\right] \tag{10}$$

as $\dfrac{d^2\alpha}{dT^2} = 0$ (peak temperature)

$$\ln\frac{\beta}{T_p^2} = -\frac{E}{RT} + \ln\left[\left|\frac{df(\alpha)}{d\alpha}\right|\frac{AR}{E}\right] \tag{11}$$

This equation is valid at any given conversion and according to which, $20 \le x \le 50$:

$$p(x) \cong \frac{e^{-x}}{x^2} \qquad (12)$$

Experimental

An aqueous solution of aluminium ion was added, under constant stirring, to an excess of 8-hydroxyquinoline dissolved in acetic acid, and a precipitate was obtained when raising the pH to 9.5. The precipitate was washed with diluted ammonia aqueous solution to eliminate the excess of 8-hydroxiquinoline, dried at 60°C in a mechanical convection oven.

After wet digestion with a mixture of concentrated sulphuric acid and hydrogen peroxide 30% solution in water, the aluminium content was determined by gravimetric analysis[3] as Al_2O_3.

The 8-hydroxyquinolate content was determined by a bromatometric method using standard $Na_2S_2O_3$ solution and soluble amide as an indicator[3], as well as, by elemental analysis (C, N, H).

The water content was determined from the TG curves.

TG/DTA curves were obtained using a SDT 2960 equipment from TA Instruments in a dynamic atmosphere of N_2 (100 mL min^{-1}), a-Al_2O_3 crucible and sample weight of about 2 mg. The data were evaluated to obtain kinetic parameters by KAS method[1,14]. Ozawa[15] and Flynn et Wall[12] methods were also used by means of a software of the TA instruments.

Results and Discussion

Through analytical and thermal analytical methods it has been verified that the compound presents the composition $Al(C_9H_6ON)_3.2.5H_2O$, Table 01.

TABLE 01: Metallic, 8-hydroxyquinolate and water contents of the compound.

Compound		Contents (%)		
		expected	TG curves	analytical
$Al(C_9H_6ON)_3.2.5H_2O$	Al	5.35	5.35	5.30 (*g*)
pH 9	C_9H_6ON	85.72	85.83	84.40 (*b*)
	H_2O	8.93	8.75	--

(*b*) Bromatometric Method, (g) Gravimetric Analysis

Through the TG curves of the compound in a nitrogen atmosphere (Figure. 01) two steps of mass loss, the first due to dehydration at 210°C and the second attributed to sublimation/vaporisation of the anhydrous complex at 250-480°C, were observed. During the sublimation/vaporisation process

and probably in its very ending, which takes place until 500°C, some thermal decomposition is occurring, resulting in a mixture of carbonaceous and oxide residues. The DTG curves (Figure 01) indicate that the process of sublimation/vaporisation occurs through consecutive steps, Table 02.
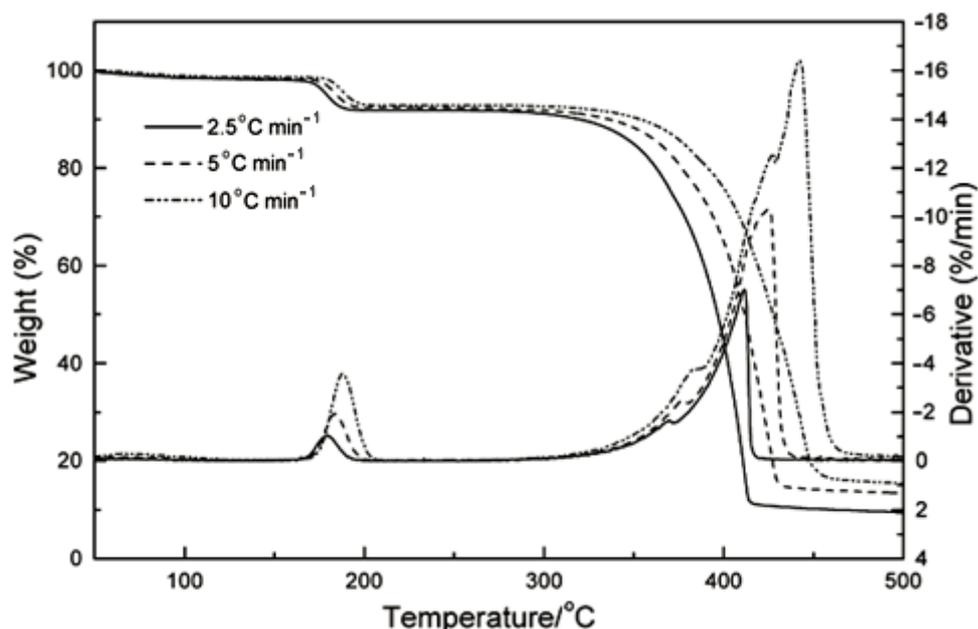
FIGURE 01: TG/DTG curves in N₂ atmosphere

TABLE 02 Data from TG-DTG-DTA curves

Corrected Heating rate (°C min⁻¹)	Δm (%)	Peak temperature (°C)	
		DTG	DTA
First stage - dehydration			
2.52	8.14	179.4	181.5
5.05	7.53	183.8	186.5
10.06	7.11	188.1	192.4
Second stage – sublimation/vaporisation and thermal decomposition			
2.50	81.12	369.7, 409.8	411.9
5.00	78.42	376.9, 423.3	(414.5*), 428.3
10.0	77.30	383.3, 427.1, 442.4	(414.0*), 446.1

*Onset temperature (fusion of the anhydrous Al(C₉H₆ON)₃)

The DTA curves showed a first broad endothermic peak due to dehydration (Figure 02 and Table 02). Regarding the sublimation/vaporisation and thermal decomposition process (Figure 03 and

) it can be observed that for the 2.5°C min^{-1} rate only the sublimation occurs while for the 5 and 10°C min^{-1} rates three different processes can be verified: partial sublimation, fusion of the anhydrous compound at about 414°C and the vaporisation with probable thermal decomposition until 480°C. The relation between sublimated and vaporised complex and the remaining residues quantities depend on the heating rate.
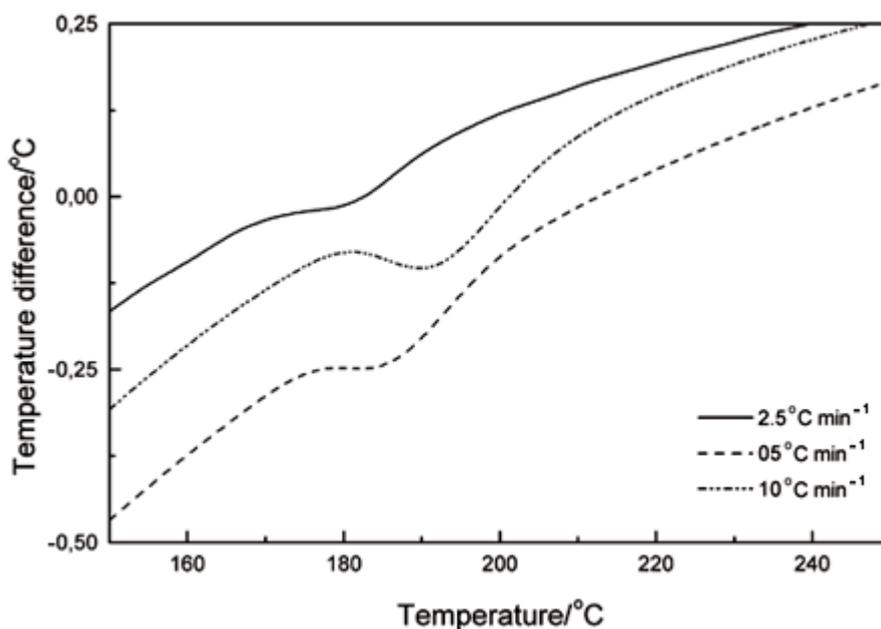
FIGURE 02: DTA curves in N$_2$ atmosphere. Dehydration step
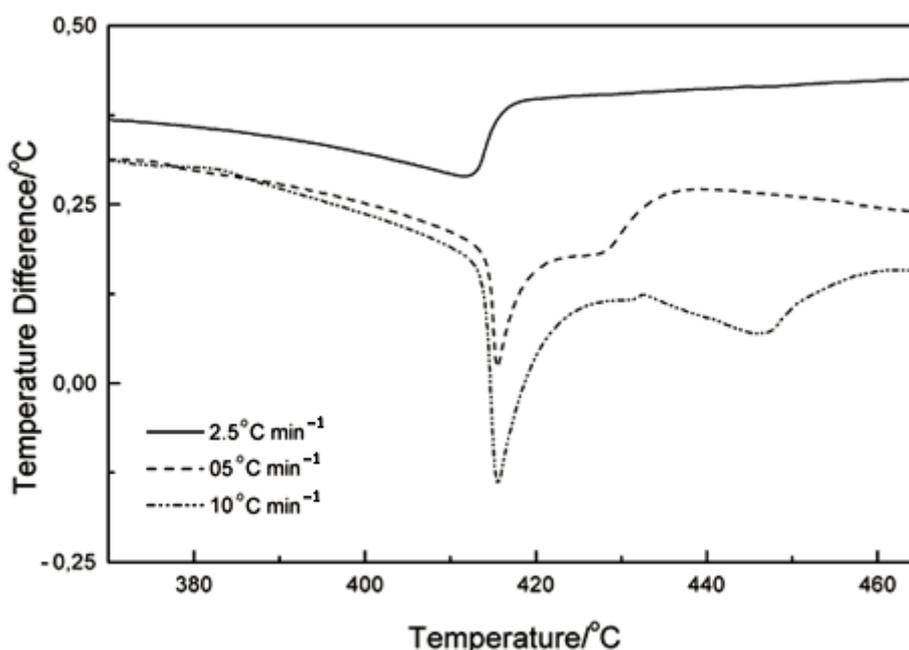
FIGURE 03: DTA curves in N$_2$ atmosphere. Sublimation/vaporisation step of the anhydrous complex.

For a equal a constant, the plot log b vs. 1/T, Ozawa/Flynn/Wall method (Figures 4 and 5) show straight lines whose slopes give E_a/R values. From these values a number of activation energies are obtained depending on the extent of the conversion that consequently allows the obtainment of the pre-exponential factor and half-lifetime. In Table 03 are presented values of E_a, log A, $T_{1/2}$ and $t_{1/2}$ in 5% of conversion to both first and second stages of reaction.
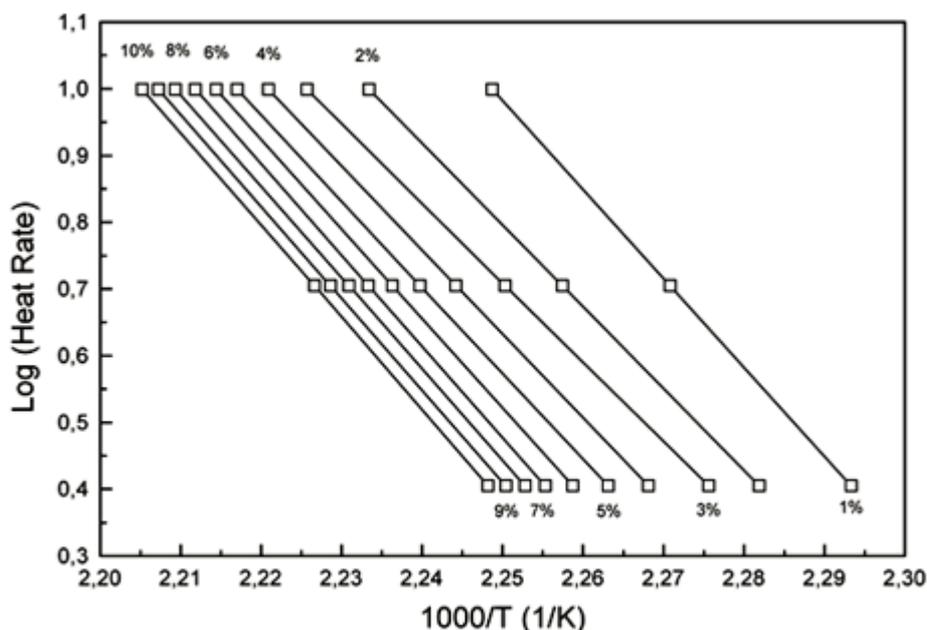
FIGURE 04: Log β vs. 1/T from Ozawa/Flynn/ Wall method. Dehydration step.
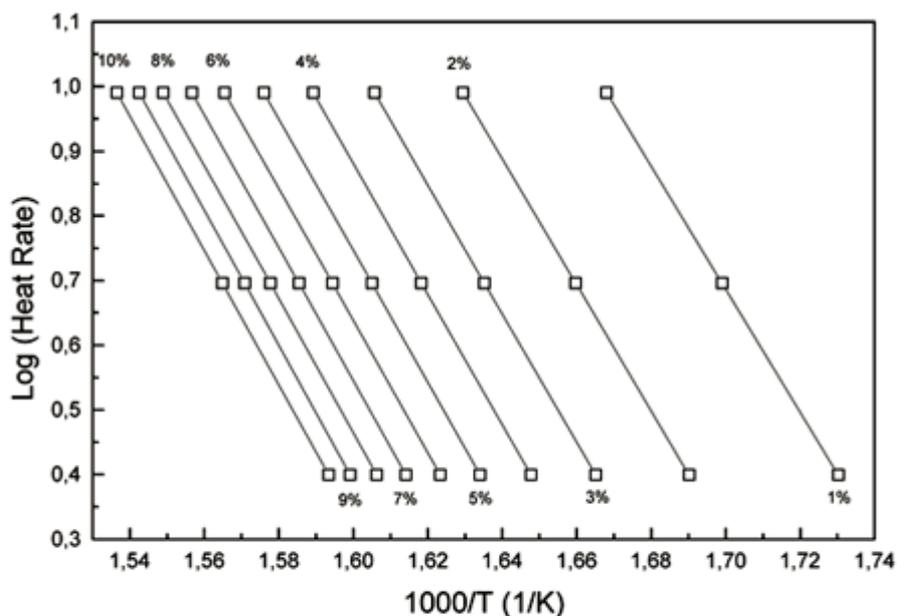
FIGURE 05: Log β vs. 1/T from Ozawa/Flynn/ Wall method. Sublimation/vaporisation step of the anhydrous complex.

TABLE 03: Kinetic parameters

Method	E_a KJ mol^{-1}	Log A min^{-1}	$T_{1/2}$ °C	$t_{1/2}$ min
First stage - dehydration				
Ozawa 5% conversion	251.2	27.99	165.2	61.10
KAS	280.6	31.98		
Second stage – sublimation/vaporisation				
Ozawa 5% conversion	195.3	14.59	344.2	56.06
KAS	173.4	12.34		

In the Figures 6 and 7, the plot log b/T^2 vs. 1/T, KAS method, show a straight line obtained through linear fit, whose slope gives –E$_a$/R value from which is obtained the activation energy that gives subsides to estimate the pre-exponential factor, Table 03.
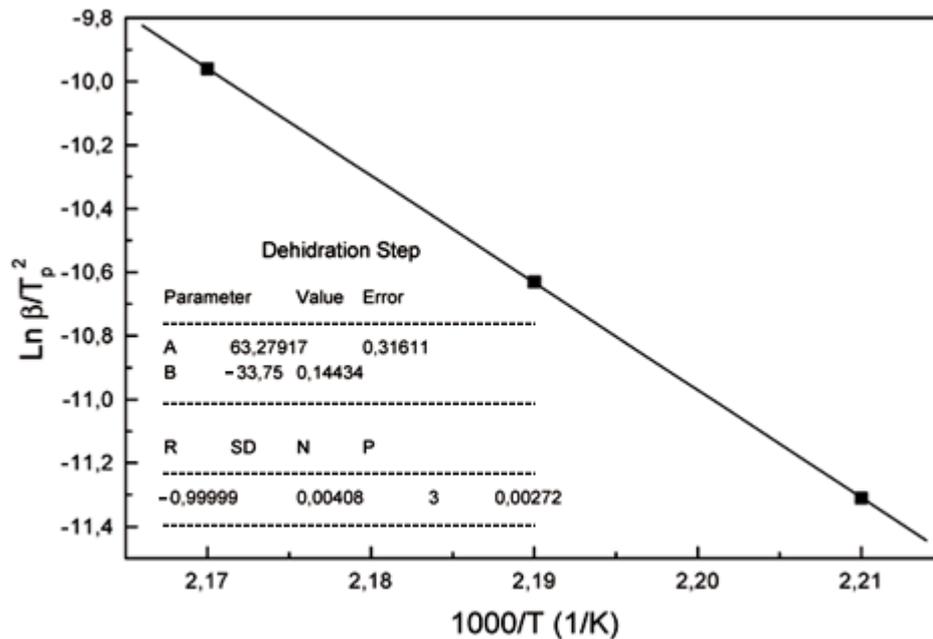
FIGURE 06: Log β/T$_p$^{2} vs. 1/T from KAS method. Dehydration step.
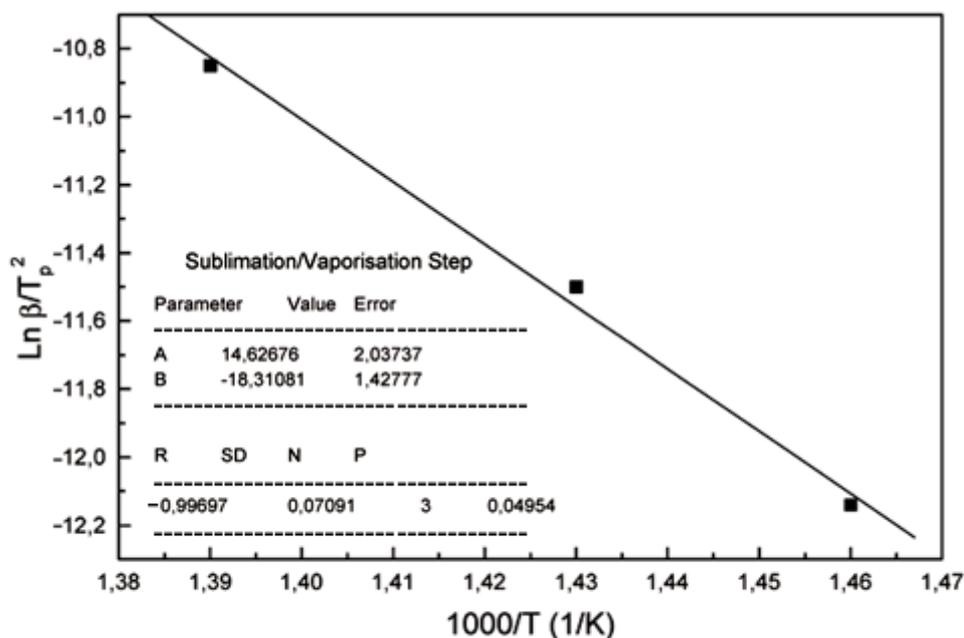
FIGURE 07: Log β/T_p^2 vs. 1/T from KAS method. Sublimation/vaporisation step of the anhydrous complex.

The most precise approximation to kinetic parameters, that is, when 20£ x£ 50, was only obtained in the second stage by using both methods, despite the fact the linearity has also been obtained in the first stage which is the dehydration reaction.

Comparing the results of the kinetic parameters from both methods it can be verified differences between values found. The lower E_a value obtained in the second stage through KAS method may be ascribed to the influence of the partial thermal decomposition, generally an exothermic reaction, on the sublimation/volatilisation process which is endothermic. It might not have happened in the Ozawa method because the evaluation was done at the beginning of the process, probably still without any contribution of the thermal decomposition.

Although the E_a values to dehydration reaction eliminate the validity interval required to x, it has been shown by Vyazovkin[17] that the linear procedures gives quite satisfactory values of E_a at x>13 to KAS method.

Concluding Remarks

The isoconversional methods allow the E_a to be determined as a function of the extent of conversion and/or temperature. This dependence is determined without making any assumptions about the reaction model.

Both of the advantages that can be attributed to KAS method are that it can locate the peak maximum temperature besides the unnecessary knowledge of the reaction mechanism to calculate the E_a. Nevertheless its dependence on the accuracy of the peak position may be the main disadvantage of the method.

Considering the difficulty in locating the values the a maximum and other parameters associated with the peak maximum temperature by using KAS method, the Ozawa method probably gave better results.

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RIBEIRO, C. A. et al. Cinética não isotérmica de desidratação e volatilização do 8-hidroxiquinolinato de alumínio no estado sólido. *Ecl. Quím.* (São Paulo), v.26, p. , 2001.

RESUMO: Al$(C_9H_6ON)_3$.2,5H$_2$O foi precipitado a partir de mistura de solução aquosa do íon alumínio e solução ácida de 8-hidroxiquinolina, e o pH ajustado a 9,5 com solução aquosa de amônia. Curvas TG em atmosfera de nitrogênio apresentam perdas de massa devido a desidratação, volatilização parcial (sublimação e vaporização) do composto anidro seguido por decomposição térmica com a formação de uma mistura de resíduos carbonaceos. A relação entre sublimação e vaporização dependem da razão de aquecimento utilizada. Os métodos isoconvenciais integrais não isotérmicos como as equações lineares de Ozawa-Flynn-Wall e Kissinger-Akahira-Sunose (KAS) foram usados para obter parâmetros cinéticos a partir de curvas TG e DTA, respectivamente. Apesar das reações de desidratação e de volatilização seguirem a linearidade por ambos métodos, somente foi verificado a condição de validade, 20£ E/RT£ 50, para a reação de volatilização.
PALAVRAS-CHAVE: 8-hidróxiquinolinato, ion alumínio, parâmetros cinéticos, termogravimetria, análise térmica diferencial, volatilização.

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