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Analysis of TG Curves of Some Copper Complexes

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ABSTRACT

A method has been developed to extract kinetic parameters from TG curves. It has been checked by applying it some synthetic TG curves. Encouraged by finding in the case of synthetic TG curves the method has been applied to analyze TG curves of some copper complexes.

Keywords : *Thermogravimetry, kinetic parameters, activation energy .*

1. Introduction

Several methods of analytical chemistry are based on measuring chemical and physical changes in a sample while its temperature is raised in a controlled manner. The results of such measurements can often be expressed as a graph of one specific property (the heat content, its mass etc) versus the temperature of the sample. In the thermogravimetry (TG), the weight of the sample is recorded as a function of temperature or time.TG measurements have been widely used to study the kinetics of decomposition reactions and the main kinetic parameters associated with TG are, respectively, the activation energy(E), order of kinetics of the reaction(n) and pre-exponential factor (A)[1-5].

In the present work, we have developed a method for the determination of the kinetic parameters of a TG curve. The present method is checked by applying to some synthetic TG curves. Finally the method has been used to analyze TG curves of some copper complexes.

2. Theory

The basic equation generally employed for evaluating the kinetic parameters in non-isothermal method is given by [1-5]

$$- \frac{d\alpha}{dt} = A(1-\alpha)^n \ exp(-E/RT) \qquad (1)$$

Where α is the fraction of the sample which has been decomposed at time t and T is the corresponding temperature.R is the universal gas constant.

Equation (1) can be replaced by the equivalent equation [1]

$$\frac{dx}{dt} = Ax^n exp(-E/RT) \tag{2}$$

Where x =1-α represents the fraction of sample remaining undecomposed at time t . For a linear heating profile

$$T=T_0+\phi t \tag{3}$$

where T_0 is the temperature at t=0 and ϕ is the linear heating rate.From equations (2) and (3), we get

$$\frac{dx}{dT} = \frac{A}{\phi} x^n \ exp(-E/RT) \tag{4}$$

The solution of equation (4) is straightforward and can be expressed as [1]

$$x(T) = \left[1 + (n-1)\frac{A}{\phi}\int_{T_0}^{T} \exp(-E/RT')dT' \right]^{-\frac{1}{n-1}} \text{ (for } n \neq 1\text{)} \tag{5}$$

$$x(T) = \exp(-A/\phi) \qquad \text{(for } n=1\text{)} \tag{6}$$

In equation (1) without any loss of generality one can replace the lower limit T_0 of the integral $\int_{T_O}^{T} \exp(-E/RT')dT'$ by 0 [6] (zero) and as shown by Singh et al [7,8]

$$\int_{o}^{T} \exp(-E/RT')dT' = (E/R)\Gamma(-1,u) \tag{7}$$

with $u = \frac{E}{RT}$ and $\Gamma(-1,u)$ is the complementary incomplete Gamma function [8] evaluated by using its continued fraction representation [9].

In order to find out the kinetic parameters E, n and A associated with a TG curve we compute the mean deviation D_{md} and root mean square deviation D_{rmsd} defined, respectively, by

$$D_{md} = \frac{1}{N}\sum_{i=1}^{N} \left| (x_i)_{calc} - (x_i)_{obs} \right| \tag{8}$$

$$D_{rmsd} = \left\{ \frac{1}{N}\sum_{i=1}^{N} \left| (x_i)_{calc} - (x_i)_{obs} \right|^2 \right\}^{\frac{1}{2}} \tag{9}$$

where $(x_i)_{calc}$ is the calculated value of x_i(i=1,2,3 ….N, N is the number of data points) for a temperature T_i by using either equation (5) ($n \neq 1$) or equation (6) (n≠1). $(x_i)_{obs}$ is the corresponding value of (x_i) obtained from the synthetic or experimental TG curves.D_{md} =D_{rmsd} =0 means a complete coincidence of the

calculated and observed TG curves . An attempt has been made to find out the value of E,n and A which minimize D_{md} and D_{rmsd} by using a suitable minimization procedure [10].

3. Result and discussion

To check the method we apply it to the theoretical TG data of Zuru et al [11] corresponding to ϕ=5K/minute. In Table 1, we compare the kinetic parameters denoted by E_{cf},n_{cf} and logA_{cf} as calculated by the present analytical technique with the input values E_{Zu},n_{Zu} and logA_{Zu} used by Zuru et al [11] in computing theoretical TG curves. Excellent agreement has been obtained. Encouraged by our findings in the case of theoretical TG curves we consider experimental TG curves of complexes Cu(BSTCZ)(HCOO), Cu(BSTCZ)(CH_3CH_{2COO}) where BSTCZ denotes 1, 5 bis (Salicylindene) thiocarbohydrazone recorded with a constant heating rate ϕ = 10 ^{0}K/minute. The TG curves of the above copper complexes have been analysed by using the well known Coats and Redfern method [12]. Ortega et al [13] have demonstrated that Coates and Redfern method leads to a sufficiently accurate value of the activation energy. For the case of Coats and Redfern method, the order of kinetics has been determined by employing a statistical technique prescribed by Chakraborty [14]. The result are displayed in Table 2 and in figures 1and 2. We find a good agreement between the values of kinetic parameters $E_{cf,}$ n_{cf} and $logA_{cf}$ as calculated by the present method with those (E_{CR}, n_{CR} and logA_{CR}) calculated by using Coats and Redfern method[12].

Table 1: Application of the present method to some computer generated TG Curves [11]

E_{Zu} (KJ/mol)	n_{Zu}	log A_{Zu}	E_{cf} (KJ/mol)	n_{cf}	log A_{cf}
83.68	1	11.22	83.81	1	11.23
83.68	2	11.22	83.78	2	11.28

Table 2: Evaluation of kinetic parameters of experimental TG curves of some copper complexes [6] by present method of curve fitting.

Complex	E_{CR} (KJ/mol)	n_{CR}	log A_{cf} (KJ/mol)	E_{cf}	n_{cf}	logA_{cf}
Cu(BSTCZ)(HCOO)	163.01	2.4	13.56	163.54	2.3	13.56
Cu(BSTCZ)(CH_3CH_2COO)	152.86	2.4	10.89	156.49	2.4	11.18

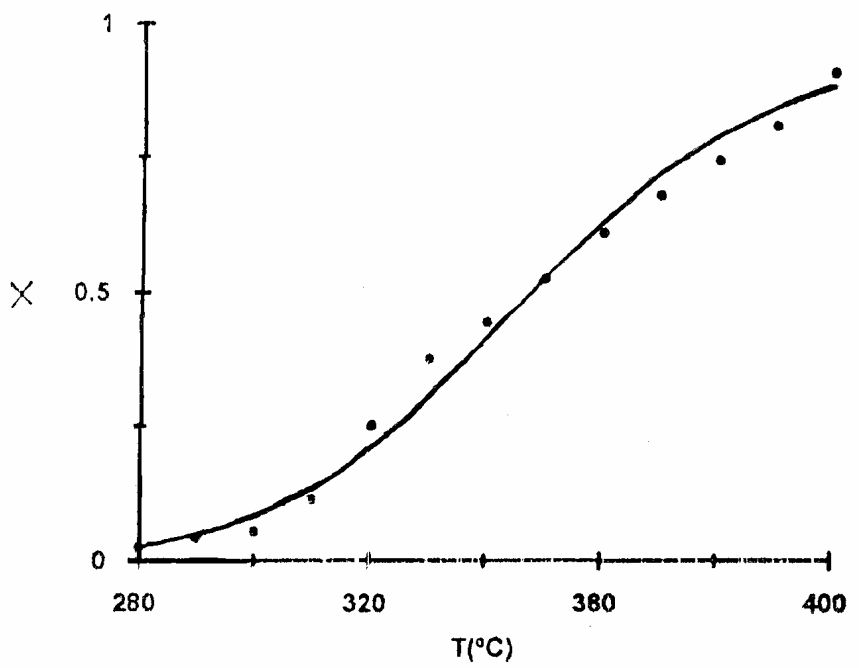

Figure 1. Curve fitting of TG curves of the complex Cu(BSTCZ)(CH_3CH_2COO). (• • •) denotes the experimental points and the continuous curve denotes the fitted peak.

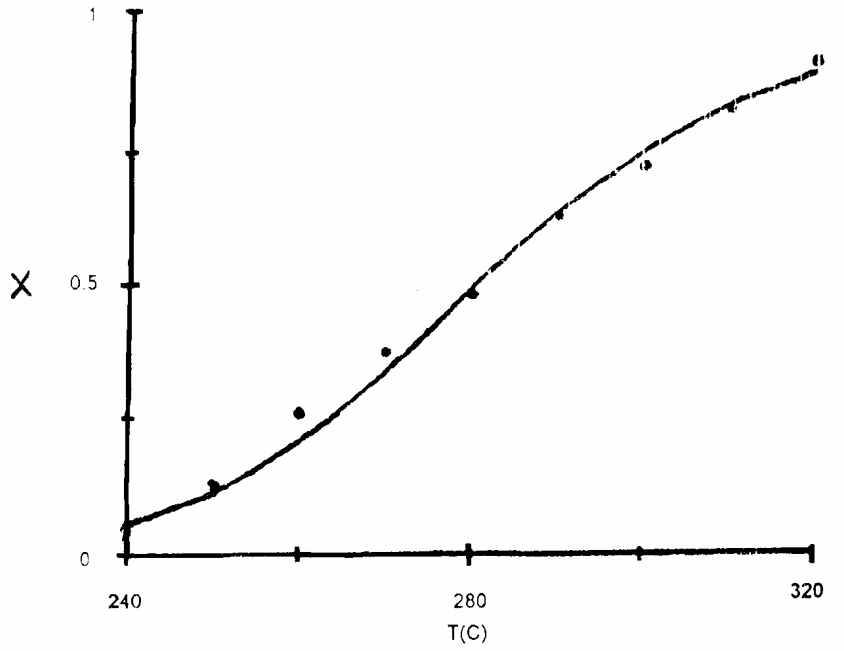

Figure 2. Same as Figure 1 but for the complex Cu(BSTCZ)(HCOO)

4. Conclusion

In the present paper we have developed an objective and accurate method of analysis of TG curves. By applying the method to synthetic and experimental TG curves of copper complexes, we have obtained results in reasonably good agreement with those obtained by other existing methods in the literature [11,12].

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