KINETIC STUDY OF THERMAL DECOMPOSITION OF METAL DIALKANOATES

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Abstract—The thermal solid phase-decomposition of zinc and cadmium dialkanoates (butanedioate and hexanedioate) was studied thermogravimetrically. Various kinetic parameters viz. Energy of activation, E, Entropy of activation, ΔS, Free energy of activation, ΔG, Enthalpy of activation, ΔH, and Frequency factor, Z have been calculated using Freeman-Carroll's equation, Coats-Redfern's equation integral method and Horowitz- Metzger's equation approximation method. The trend of kinetic parameters was found to be different from that of thermal stability order. The low values of frequency factor, negative values of entropy of activation and positive values of free energy of activation and enthalpy of activation indicate slow nature of decomposition process and exothermic nature of system.

IndexTerms—Thermogravimetry, Metal dialkanoates, Frequency factor, Activation energy, Entropy of activation.

I. INTRODUCTION

Surface active agents are characterized by the possession of both polar and non-polar groups in the same molecule. This dual nature is responsible for the phenomenon of surface activity, and micellization and solublization. The dual nature of a surfactant is typified by metal alkanoates, can be called association colloids, indicating their tendency to associate in solution, forming particles of colloidal dimensions. This characterization of metal alkanoates has been exploited in a number of industrial applications.

The survey of the literature reveals that major development has taken place in the study of metal alkanoates of mono-carboxylic acid; the study of dialkanoates is limited [1-7] with few references, which have a great importance in industries and research. Burrows et al [1] synthesized di-carboxylic acid metal soaps by metathesis and Ikhuoria et al [2] studied the effect of temperature on the stability of metal soaps of dicarboxylic acids. Liu et al [3] used metal dialkanoates as thermal stabilizers for PVC. Workers [4-7] studied spectroscopic and thermal behavior of metal dialkanoates. The application of metal alkanoates largely depends on their physico-chemical properties such as physical state, thermal stability, chemical reactivity and solubility in polar and non-polar solvents. A number of workers have used ultrasonic measurements of metal alkanoates for the determination of ion-solvent interaction in organic solvents. Viscometric conductometric measurements and thermodynamic parameters of the solution of lanthanide and transition metal alkanoates have been determined in different organic solvents [8-14].

The present investigation deals the thermal stability of zinc and cadmium dialkanoates (butanedioate and hexanedioate) and evaluation of kinetic parameters employing the differential Freeman-Carroll equation [15], the integral method Coats-Redfern equation [16] and the approximation method Horowitz- Metzger's equation[17],.

II. EXPERIMENTAL

All chemicals used were of BDH/AR grade. zinc and cadmium dialkanoates (butanedioate and hexanedioate) were synthesized by direct metathesis in alcohols of corresponding potassium alkanoates as mentioned in our earlier publications [13-14]. The purity was checked by elemental analysis and their melting points and absence of hydroxylic group and formation of metal-oxygen bond was confirmed by IR spectra. The reproducibility of the results was checked by preparing two samples of the same alkanoates under similar conditions.

The thermograms were recorded using a Perkin-Elmer thermogravimetric analyzer (TG-S-2) in nitrogen atmosphere at a constant heating rate of 10º/min maintaining similar conditions throughout the investigation under a wide temperature range(0ºC to 1200ºC). Kinetic data were evaluated from TG traces using the equations noted in Table 1.

III. RESULTS AND DISCUSSION

The thermogravimetric analysis (TGA) of zinc and cadmium dialkanoates (butanedioate and hexanedioate) are given in Fig.1 thermogravimetric analysis a technique which measures the weight change in a material as a function of temperature and time in a control environment. This can be very useful to investigate the thermal stability of material to investigate its behavior in different environment (Inert or oxidizing).

The results of thermogravimetric analysis of metal dialkanoates are recorded in Table .1. it is found that the thermal decomposition of metal dialkanoates (butanedioate and hexanedioate) gives a number of products. The major components has been identified dione-1,4 cyclohexanedione and cyclopentanone respectively, a white substance deposited at the cold part of the sample tube surrounding the sample. The results show that metal dialkanoates are stable and non-hygroscopic, and the final residue is metal oxide and the weights of the residue are in agreement with the theoretically calculated weight of metal oxide from molecular formulae of the metal dialkanoates

Fig.1 Thrmograms of metal dialkanoates
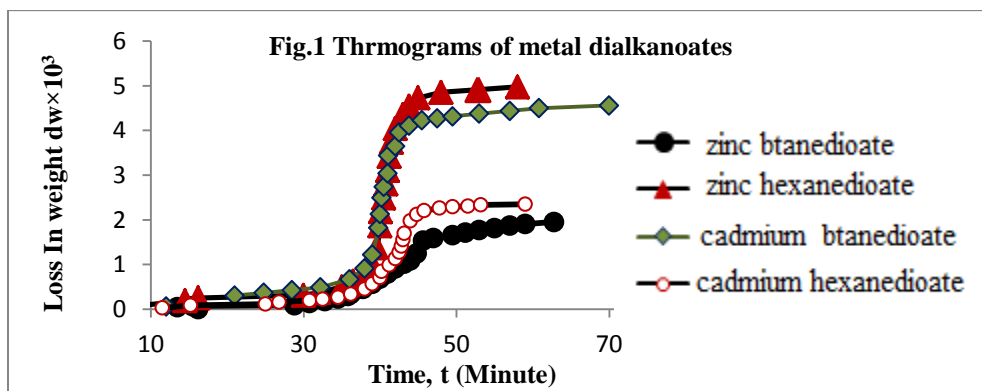
The thermal decomposition of metal dialkanoates can be expressed as:

$$2(RCOO)_2M\rightarrow \quad \text{Ketone} \quad + \quad MO \quad + \quad CO_2$$

Metal dialkanoate   Ketone   Metal oxide
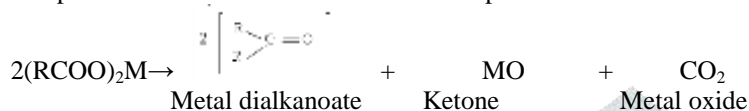
(Where, M is Zn^{+2} or Cd^{+2})

Freeman-Carroll equation: Freeman-Carroll equation which may be written in the form

$$\frac{(\Delta log(dW/dt)}{\Delta logW_r} = \frac{-(E/2.303R)\Delta(T^{-1})}{\Delta logW_r} + n \tag{1}$$

Where $W_r = W_\alpha - W$ is difference between the total loss in weight W_α, and the loss in weight W, at time t, T is the absolute temperature at time t, n is the order of reaction. R is the gas constant in calories and E is the energy of activation in K cal mol^{-1}. W_r and T can be directly obtained from the TG traces.

Plots of $\Delta log (dW/dt)/ \Delta(logW_r)$ vs. $\Delta(1/T)/\Delta(logW_r)$ have been found to be linear with intercept equal to zero (Fig.2.1-2.2), concluded that the order of reaction for the decomposition of metal dialkanoates is zero order. The temperature slopes dW/dT were converted into time slopes dW/dt, using the relationship[18-19]

$$\frac{dW}{dt} = \frac{dW}{dT}\cdot\frac{dT}{dt} = \left(\frac{dW}{dT}\right)\Phi \tag{2}$$

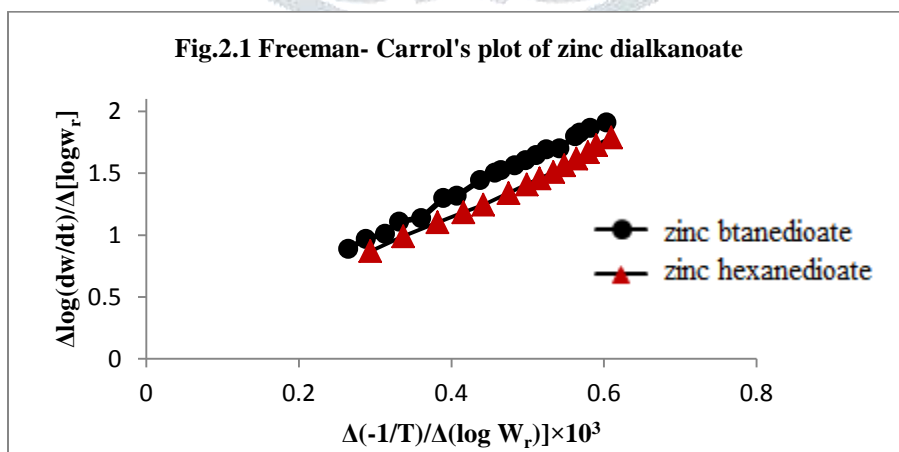Where Φ is the heating rate. The usual zero order rate law expression is,
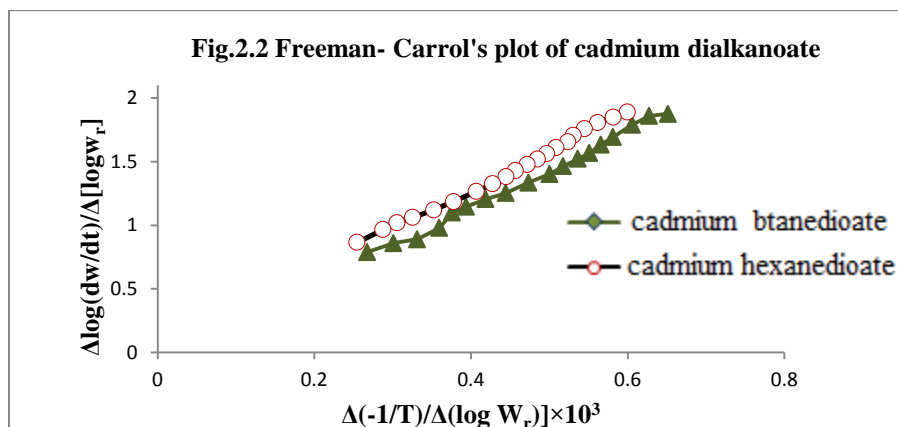
$$\frac{dW}{dt} = K \tag{3}$$

Combining this equation (3) with Arrhenius equation, $K= z\ exp^{(-E/RT)}$

$$K = \frac{dW}{dt} = z\ exp^{(-E/RT)} \tag{4}$$

Taking log of both side

$$log\left(\frac{dW}{dt}\right) = \frac{E}{2.303RT} + log Z \tag{5}$$

Fig.2.1 Freeman- Carrol's plot of zinc dialkanoate

Fig.2.2 Freeman- Carrol's plot of cadmium dialkanoate

Plot of log (dW/dt) against T^{-1} were drawn. They gave straight lines in all cases and the values of E, energy of activation were in agreement with the values obtained from Fig. (2.1-2.2). Z, frequency factor was calculated from the intercept and the entropy of activation ΔS was obtained from the relationship[18-19]

$$\Delta S = 2.303R \log(Zh/(kT_s)) \qquad (6)$$

Where k is the Boltzmann constant, h is the Plank constant and T_s is the peak temperature, ie., temperature on absolute scale at which the rate of decomposition is maximum from DTG. The free energy of activation ΔG, and enthalpy of activation ΔH, were calculated using the following relationship [18-19]

$$\Delta G = E - T_s \Delta S \qquad (7)$$
$$\Delta H = E - RT_s \qquad (8)$$

Coats-Redfern's   **equation:**

$$log \frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)} = \log[\frac{AR}{\Phi E}(1 - \frac{2RT}{E})] - \frac{E}{2.303RT} \qquad (9)$$

The equation for zero order reaction can be written as

$$log \frac{(\alpha)}{T^2} = \log[\frac{AR}{\Phi E}(1 - \frac{2RT}{E})] - \frac{E}{2.303RT} \qquad (10)$$

α = Fraction of the surfactant decomposed,
T= Temperature on absolute scales,
R= Gas constant,
Z= frequency factor,
Φ= Rate of heating in ^{0}C per minute,
E= Energy of activation,
n= Order of reaction,

The plot of log (α)/T^2 against T^{-1} was drawn which gave straight lines in all cases with a slope of (–E/2.303R) from which the values of activation energy, E, was calculated. The values of frequency factor, Z, were calculated from the intercept of the same plot. The entropy of activation ΔS, free energy of activation ΔG, and enthalpy of activation ΔH, were obtained from equation 6-8, which were in agreement with the values obtained from Freeman-Carroll equation Table 1.

Table 1. Kinetic parameters of metal dialkanoates

Metal dialkanoates		Energy of activation E(KJ mol^{-1})	Frequency factor Z (min^{-1})	Entropy of activation -ΔS (KJ mol^{-1}K^{-1})	Free energy of activation ΔG (KJ mol^{-1})	Enthalpy of activation ΔH (KJmol^{-1})
Zinc	Butanedioate	51.603	5.5	237.549	205.953	40.488
	Hexanedioate	65.529	5.8	238.524	249.756	52.526
Cadmium	Butanedioate	44.676	3.8	241.434	207.612	39.047
	Hexanedioate	56.321	4.5	240.673	243.619	49.844

Horowitz- Metzger's equation: Horowitz- Metzger's equation can be written in the form-

$$\log[\log(1 - \alpha)^{-1}] = \frac{E\theta}{2.303RT_s^2} - log2.303 \qquad (11)$$

α = Fraction of the surfactant decomposed at time,t
R = Gas constant,
T_s= Peak Temperature
θ= T-T_s
E= Energy of activation,
From the slope of linear plot of log[log(1-α)$^{-1}$] vs. θ the values of activation energy, E was calculated. Frequency factor Z, was calculated from equation

$$\frac{E\theta}{RT_s^2} = A/\varphi \exp(-\frac{E}{RT_s})]\qquad\qquad(12)$$

The entropy of activation ΔS, free energy of activation ΔG, and enthalpy of activation ΔH, were obtained (Table I) from the equation 6-8. The values of energy of activation, E, obtained from Freeman-Carroll equation, Coats-Redfern's equation and Horowitz- Metzger's equation lies in the range of 50-53, 63-66, 43-46 and 54-57 KJ mol^{-1} for decanoate, dodecanoate, and tetradecanoate, respectively. The values of frequency factor, Z calculated from same equations lies in the range 5.4-5.6, 5.7-5.9, 3.6-4.0 and 4.4-4.6 respectively, indicate the slow nature of the decomposition reaction[18-19]. The negative values of entropy of activation, ΔS was found in the range of 237-240 and positive values of free energy of activation, ΔG, 205-249, which indicate that decomposition process of metal dialkanoates have less ordered structure than the product[18-19]. The results from this study show that energy of activation, E and thermal stability of metal dialkanoates are fairly heat stable, with the hexanedioate being more stable, than the butanedioate..

IV. CONCLUSION

The analysis of data using the Freeman-Carroll equation shows zero order kinetics of the decomposition reaction of zinc and cadmium dialkanoates (butanedioate and hexanedioate). The negative values of entropy of activation ,ΔS and positive values of free energy of activation, ΔG indicate that decomposition process of these activated alkanoates have more ordered structure than the reactants and further the low values of frequency factor, Z indicate the slow nature of the decomposition reaction. It also suggests that the system is not a spontaneous process and it is to be an exothermic process. The kinetic parameters show somewhat different trend in thermal stability of metal dialkanoates. This may be due to the fact the decisive criteria in kinetics are often quite different from those which decide thermal stability.

V. ACKNOWLEDGMENT

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