



Kinetics of thermal decomposition of gadolinium alkanoates

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Abstract: The thermal decomposition of gadolinium alkanoates (decanoate, dodecanoate, and tetradecanoate) 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.

Key words: Thermogravimetry, Metal alkanoates, Frequency factor, Activation energy, Entropy of activation.

I. Introduction

Surface active agents are characterized by the possession of both polar and non-polar regions in the same molecule. This dual nature is responsible for the phenomenon of surface activity, and micellization and solubilization. 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. In recent years, metal alkanoates have found extensive application in various industries. Wu et al¹ and Kanai² developed new technologies to synthesize metal alkanoates. Workers³⁻⁵ studied spectroscopic and thermal behavior of metal alkanoates. Effect of electrolytes on micellar behavior of metal alkanoates studied by Shukla et al⁶. A number of workers have used ultrasonic⁷⁻⁸ measurements of metal alkanoates for the determination of ion-solvent interaction in organic solvents. Viscometric⁹ conductometric¹⁰⁻¹¹ measurements and thermodynamic¹¹⁻¹² parameters of the solution of lanthanide and transition metal alkanoates have been determined in different organic solvents. 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. Although many references¹⁻¹² are available to explain their physico-chemical and acoustic behavior in liquid state still the study on the nature, structure and thermal behavior is limited¹³⁻¹⁵ which have a great importance in industries and research.

In continuation of our earlier work on gadolinium alkanoates (decanoate, dodecanoate, tetradecanoate and octadecanoate)⁷⁻¹¹ the present investigation deals the thermal stability of gadolinium alkanoates and evaluation of kinetic parameters employing the differential Freeman-Carroll equation¹⁶, the integral method Coats-Redfern equation¹⁷ and the approximation method Horowitz- Metzger's equation¹⁸.

II. Experimental

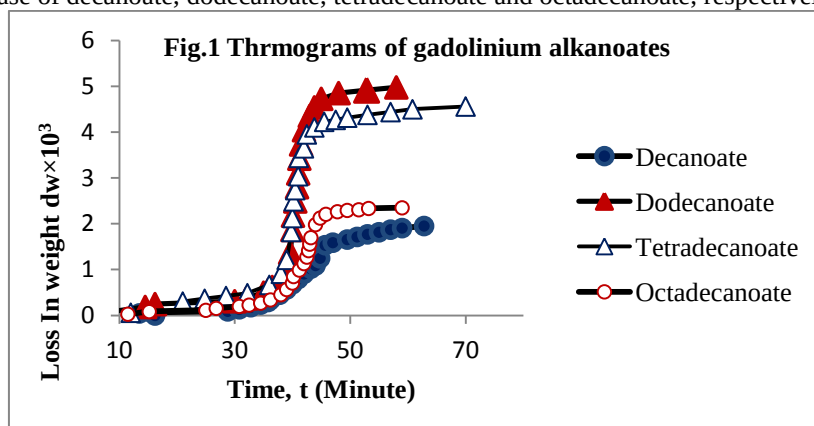
All chemicals used were of BDH/AR grade. Gadolinium alkanoates (decanoate dodecanoate, tetradecanoate and octadecanoate) were synthesized by direct metathesis of corresponding potassium alkanoates as mentioned in our earlier publications⁷⁻¹¹. The purity was checked by elemental analysis and their melting points (decanoate -98°C, dodecanoate -102°C, tetradecanoate-112°C, and octadecanoate-118°C) 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 10°/min maintaining similar conditions throughout the investigation under a wide temperature range(0°C to 1200°C). Kinetic data were evaluated from TG traces using the equations noted in Table I.

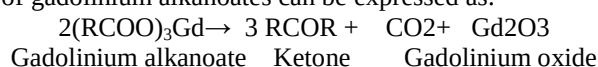
III. Results and Discussion

The thermogravimetric analysis of gadolinium alkanoates (decanoate, dodecanoate, tetradecanoate and octadecanoate) are given in Fig.1. It is found that gadolinium alkanoates were stable and non-hygroscopic, and the final residue is gadolinium oxide and the weights of the residue are in agreement with the theoretically calculated weight of gadolinium oxide from molecular formulae of the gadolinium alkanoates. A white

substance is found deposited at the cold part of the sample tube surrounding the sample and it is identified as decanone (M.P-58.8°C) dodecanone (M.P-69.4°C), tetradecanone (M.P-78.0°C), and octadecanone (M.P-88.4°C), in the case of decanoate, dodecanoate, tetradecanoate and octadecanoate, respectively.



The thermal decomposition of gadolinium alkanoates can be expressed as:



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

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

Where $W_r = W_\infty - W$ is difference between the total loss in weight W_∞ 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 $\Delta \log (dW/dt) / \Delta (\log W_r)$ vs. $\Delta(1/T) / \Delta (\log W_r)$ 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 gadolinium alkanoate is zero order. The temperature slopes dW/dT were converted into time slopes dW/dt , using the relationship¹⁹⁻²⁰

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

Where Φ is the heating rate. The usual zero order rate law expression is,

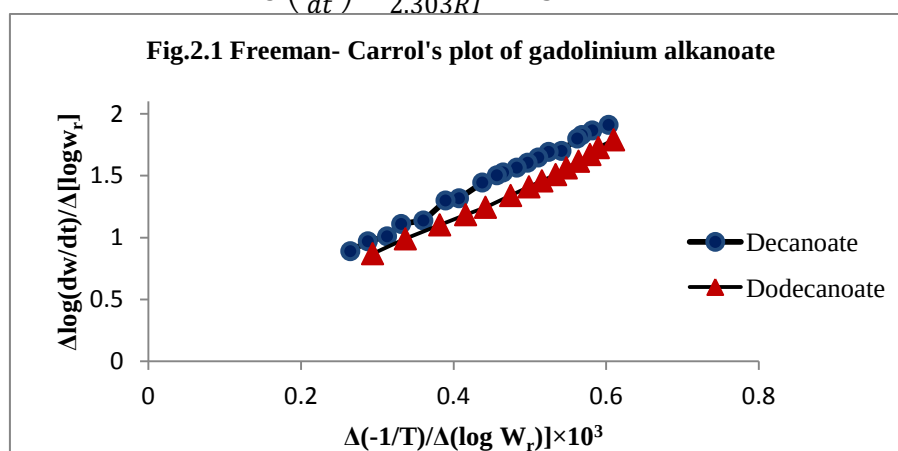
$$\frac{dW}{dt} = K \quad (3)$$

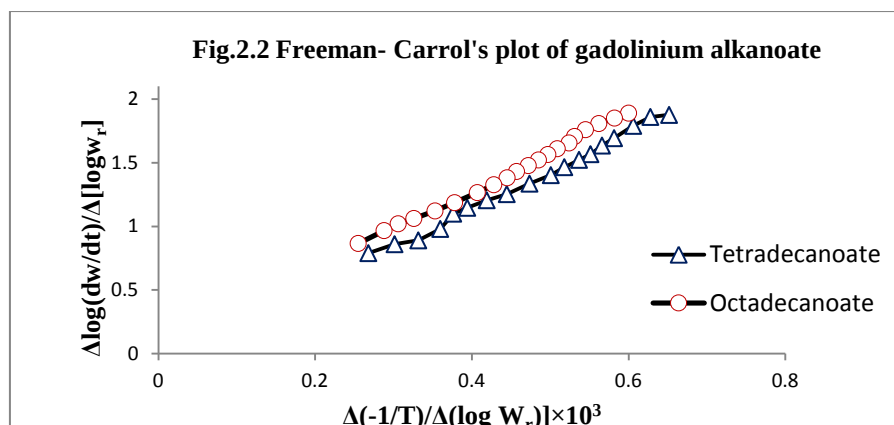
Combining this equation (3) with Arrhenius equation, $K = z \exp(-E/RT)$

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

Taking log of both side

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





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 relationship²⁰⁻²¹

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

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^{20,22,23}

$$\Delta G = E - T_s \Delta S \quad (7)$$

$$\Delta H = E - RT_s \quad (8)$$

Coats-Redfern's equation:

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

The equation for zero order reaction can be written as

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

α = Fraction of the surfactant decomposed,

T = Temperature on absolute scales,

R = Gas constant,

Z = frequency factor,

Φ = Rate of heating in $^{\circ}\text{C}$ per minute,

E = Energy of activation,

n = Order of reaction,

The plot of $\log (\alpha)/T^2$ 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 I

Table I. Kinetic parameters of gadolinium alkanoates

Gadolinium alkanoates	Energy of activation $E(\text{KJ mol}^{-1})$	Frequency factor $Z (\text{min}^{-1})$	Entropy of activation $-\Delta S (\text{KJ mol}^{-1}\text{K}^{-1})$	Free energy of activation $\Delta G (\text{KJ mol}^{-1})$	Enthalpy of activation $\Delta H (\text{KJmol}^{-1})$
Decanoate	64.9088	2.5	244.349	234.243	59.147
Dodecanoate	81.947	4.9	238.522	242.711	76.343
Tetradecanoate	68.57	3.6	241.135	232.059	62.933
Octadecanoate	75.80	4.1	240.024	240.660	72.883

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

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

α = Fraction of the surfactant decomposed at time, t

R = Gas constant,

T_s = Peak Temperature

$\theta = T - T_s$

E = Energy of activation,

From the slope of linear plot of $\log[\log(1 - \alpha)^{-1}]$ vs. θ the values of activation energy, E was calculated. Frequency factor Z , was calculated from equation

$$\frac{E\theta}{RT_s^2} = A/\phi \exp\left(-\frac{E}{RT_s}\right) \quad (12)$$

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 64-66, 78-81, 68-74 and 75-77 KJ mol⁻¹ for decanoate, dodecanoate, and tetradecanoate, respectively. The values of frequency factor, Z calculated from same equations lies in the range 2.5-3-1, 3.6-3.9, 4.8-5-3 and 4.1-4.2 respectively, indicate the slow nature of the decomposition reaction^{20,24}. The negative values of entropy of activation, ΔS was found in the range of 238-244 and positive values of free energy of activation, ΔG , 232-242, which indicate that decomposition process of gadolinium alkanoates have less ordered structure than the product^{20,25}. Results show that energy of activation, E and thermal stability do not depend on chain length of fatty acids.

IV. Conclusion

The analysis of data using the Freeman-Carroll equation shows zero order kinetics of the decomposition reaction of gadolinium alkanoates. 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 gadolinium alkanoates. This may be due to the fact the decisive criteria in kinetics are often quite different from those which decide thermal stability.

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References

- [1]. Maoying Wu and Chesmin Xiao (Department of Chemical Engineering, Guangdong University of Industry, Canton, Peop. Rep. China. 510090) *Riyong Huaxue Gongye, Qinggongye bu Kexue Jishu Qingbao yanjiuso*, **5**, 19-21(1998).
- [2]. Hiroyuki Kanai (Shinko K.K., Japan) *Jpn. Kokai Tokkyo Koho JP.* **11** 349, 980 (99 349, 980) (Cl. C 11 B13/00), 21 Dec 1999, Appl. 1998/ 175, 435, 8 Jun1998; 4 pp.
- [3]. Guangdong Da-Guang Gongye Daxue Xuebao, Guangdong Gongye Daxue, **16**, 109-113(1999)
- [4]. K.N Mehrotra, R.K. Shukla and M., Chauhan, *Tenside Surfactant and Detergents*, **34**,124-127(1997).
- [5]. Kouhei Sawada, and Miki Konaka, *Journal of Oleoscience, Japan Oil Chemist's Society*, **53**,627-640(2004).
- [6]. R.K. Shukla, M. Shukla and V. Mishra, *Acta Acustica*, **45**, 345-349(2007).
- [7]. M. Shukla, S. Kumari and R.K. Shukla, *Acta Acustica*, **96**, 63-67(2010).
- [8]. S.K. Upadhyaya, *Indian J. Chem. Sect. A; Inorg. Bio-inorg., Phys., Theor. Anal. Chem.*, **39A**, 537-540(2000).
- [9]. K.N. Mehrotra and M. Anis, *J. Colloid and Surfaces*, **122**, 27-32(1997).
- [10]. Huseyin TOPALLAR and Y`uksel BAYRAK, *Tr. J. of Chemistry*, **22**, 167-173(1998).
- [11]. M. Shukla, S. Kumari and R.K. Shukla, *Journal of Dispersion Science* (2011) -Accepted.
- [12]. N. Levine, *Physical Chemistry*, Fourth Edition, New York: McGraw-Hill Inc (1995).
- [13]. K.N. Mehrotra, M. Sharma and A.S. Gahlaut, *Recl. Trav. Chim. Pays-Bas.*, **107**, 310 (1988); **108**, 256 (1989) *Procd. V National Symp. Anal. Spec.* **126** (1988).
- [14]. K.N. Mehrotra, M. Chauhan, and R.K. Shukla, *Tenside Surf. Det* **34**, 2 (1997)
- [15]. K. Binnemas and C. G rller-Walrand, *Chemical Reviews*, **102**, 2303-2346(2002).
- [16]. E.S Freeman and B. Carroll, *J. Phys. Chem.***62**, 394(1958).
- [17]. A. W. Coats and J. P. Redfern, *Nature*, **201**,68(1964).
- [18]. H. H. Horowitz and G. Metzger, *Anal. Chem.*,**35**, (1963).
- [19]. S. S. Mishra and Dinakar, *J. Indian Chem. Soc.*, **49**,6,(1972)
- [20]. K.G. Mallikaerjun, *E- Journal of Chemistry*, **1**(2),105-109(2004).
- [21]. J. Chacko and G. Parmeshwaran, *J. Therm. Anal.* **29**, 3(1984).
- [22]. J. Zsako, C. S. Varhelyi and E. Kekedy, *J. Inorg. Nucl. Chem*, **28**, 2637(1966).
- [23]. B. R. Puri, L. R. Sharma and M. S. Pathania, *Physical Chemistry*, 696(2000-2005).
- [24]. S. S. Sawhney and A. K. Bansal *Thermochim. Acta* **66**, 347(1983).
- [25]. P. V. Khadikar, S. M. Ali, B Heda., *Thermochim. Acta* **82**.253(1984).