



THERMOGRAVIMETRIC ANALYSIS OF LANTHANIDE ALKANOATES

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ABSTRACT

The thermogravimetric results reveal that the thermal decomposition of lanthanide octanoates, i.e., lanthanum, cerium, praseodymium and neodymium octanoates, is kinetically of zero order with energy of activation lying between 7-9 K.Cal mole⁻¹.

Keywords: Lanthanide Octanoate, Energy of activation, thermal decomposition, order of reaction.

INTRODUCTION

The study of lanthanide Octanoates is becoming increasingly important in technological as well as in academic fields. It has been a subject of intense investigations in the recent past on account of its role in such diversified fields as detergents, softeners, stabilizers, catalysts, antioxidants, lubricants, emulsifiers, water proofing and wetting agents. Nevertheless the studies on these octanoates are limited, with the result that only few references [1-10] are available.

Now-a-days metal Octanoates have widely been used as thermal stabilizers in different industries in China and Japan [11-14] so the present paper includes thermal analysis of lanthanide Octanoates. The results of thermogravimetric analysis have been used to determine the order of reaction and energy of activation for the decomposition reaction.



EXPERIMENTAL

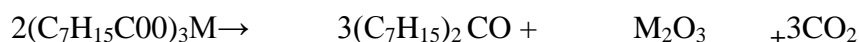
Lanthanum nitrate, cerium chloride, praseodymium nitrate and neodymium nitrate (Indian rare earths Ltd) and Octanoic acid (BDH) were used for the preparation of lanthanide octanoate. The lanthanum, cerium, praseodymium and neodymium octanoates were prepared by direct metathesis of the corresponding potassium Octanoate with the required amount of lanthanum nitrate, cerium chloride, praseodymium nitrate and neodymium nitrate solutions at 50-60°C under vigorous stirring. The precipitated octanoates were filtered and washed with distilled water and alcohol and recrystallized with a mixture of benzene and methanol and dried under reduced pressure.

The thermogravimetric analysis of lanthanum, cerium, praseodymium and neodymium octanoates were carried out by a Perkin-Elmer thermo gravimetric analyzer (TG-S-2) in nitrogen atmosphere at a constant heating rate of 10⁰/min maintaining similar conditions throughout the experiments.

RESULT AND DISCUSSION

The results of the thermogravimetric analysis of lanthanum, cerium, praseodymium and neodymium Octanoate are given in Table 1. It is found that the final residue is metal oxide and the weights of the residue are in agreement with the theoretically calculated weight of lanthanum oxide, cerium oxide, praseodymium oxide and neodymium oxide from the molecular formulae of the corresponding Octanoates. A white substance is found deposited at the cold part of the sample tube surrounding the sample and it is identified as Octanone (mp 39°C)

The thermal decomposition of these Octanoates can be expressed as





Meta octanoate (soap) octanone (ketone) Metaloxide (residue) Carbon dioxide (gas)

Where M stands for La, Ce, Pr and Nd, respectively. The thermogravimetric data were used to calculate the energy of activation and to find the order of reaction for the decomposition of lanthanum, cerium, praseodymium and neodymium Octanoates using the equations of Freeman and Carroll [15] which may be written as

$$\frac{\Delta \log \left(\frac{dw}{dt} \right)}{\Delta (\log W_r)} = - \frac{E}{2.303R} - \frac{\Delta (1/T)}{\Delta (\log W_r)} + n$$

E= Energy of activation

R= Gas Constant

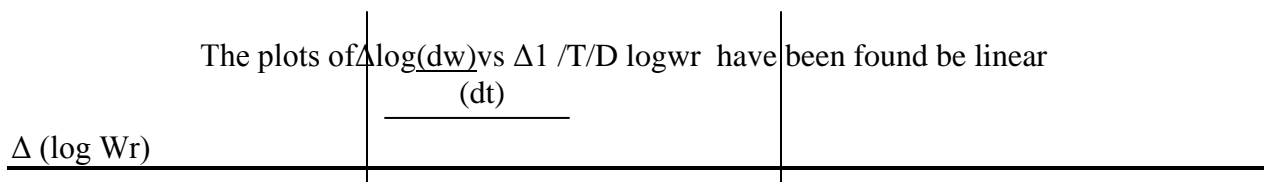
N= Order of decomposition reaction

T= Temperature on absolute scale

W= Difference between the total loss in weight and the loss in weight at time t.i.e. $W_0 - W_t$.

and $\left(\frac{dw}{dt} \right)$ = Rate of weight loss obtained from the loss in weight vs time curves at appropriate times.

The plots of the loss in weight of the soap, w against t-time, t are shown in Fig. 1 and the values of dw/dt are obtained from these curves by drawing tangents at appropriate time.





with intercept equal to zero (Fig 2) It is, therefore, concluded that the order of reaction for the decomposition of lithium octanoates is zero and the values of energy of activation from the slope ($-E/2.303R$) of the plots (Fig.2) are 7.7, 7.8, 9.2 and 7.9 Kcal mole⁻¹ for lanthanum, cerium, praseodymium and neodymium octanoates respectively.

The aforesaid fact that the process of decomposition of metallic alkanoates is kinetically of zero order, is in harmony with the fact that the surface of the soap molecules remains completely covered all the time by the molecules of the gaseous product and so the decomposition is fast and the rate of decomposition becomes constant.

Fig 1 THERMO-GRAMS OF CAPRYLATES OF LANTHANIDE SOAPS

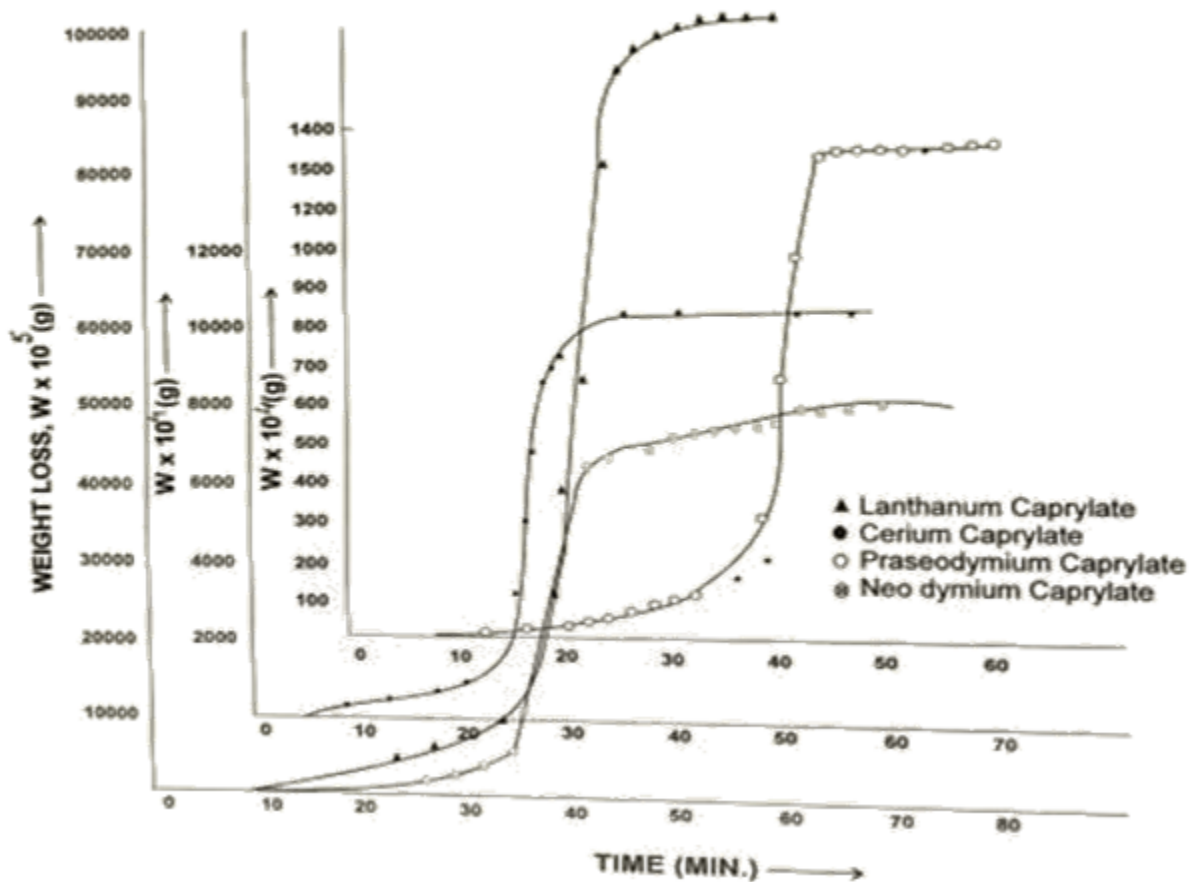
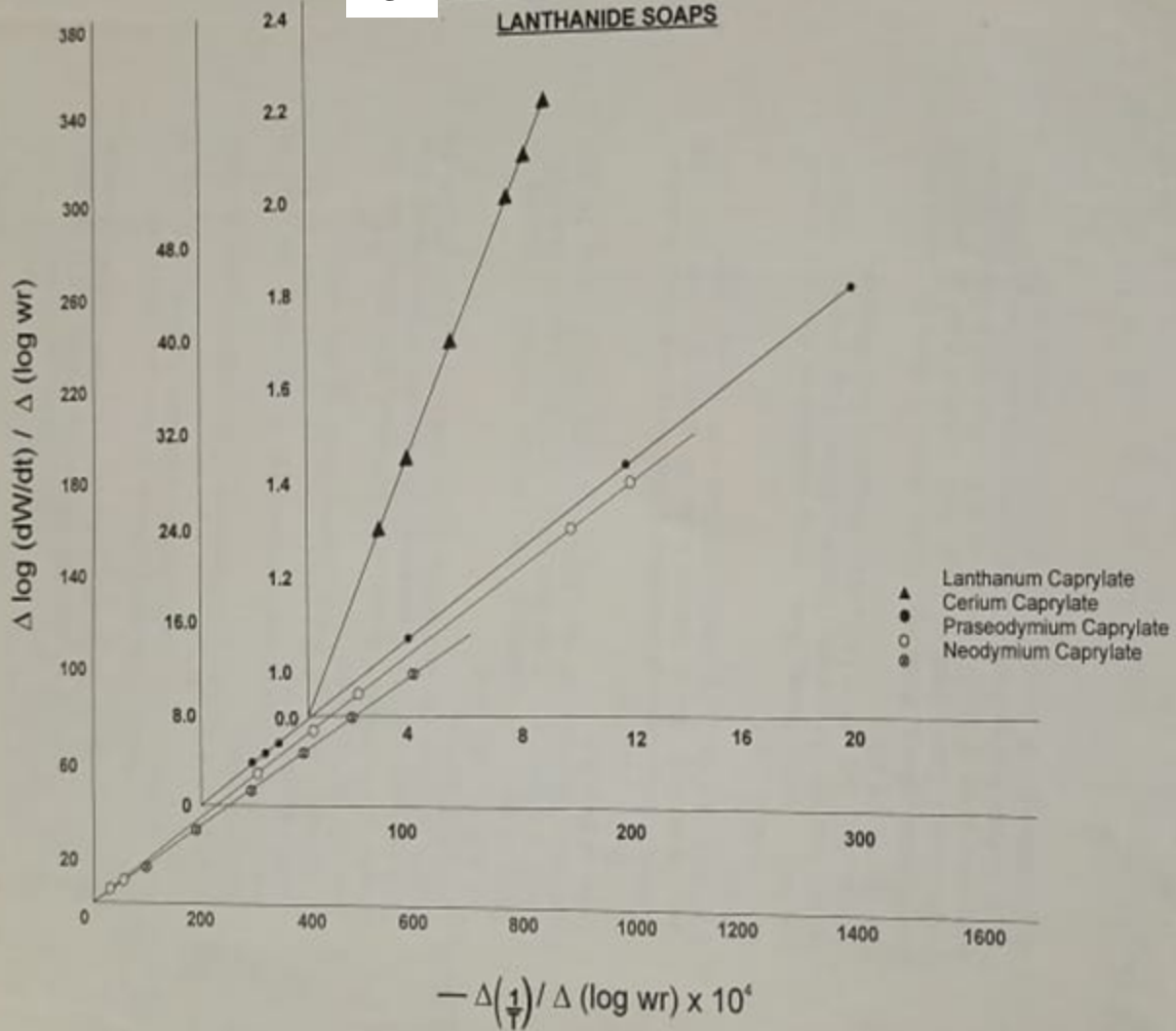


Fig 2

FREEMAN - CARROLL'S TYPE PLOTS OF
LANTHANIDE SOAPS





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