ISSN: 2319-8753

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 11, November 2014

Thermal Study of Cadmium Levo-Tartrate Crystals

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ABSTRACT: Metal tartrate compounds find various applications. Lead tartrate is added in gasoline to prevent knocking in motors, while, cadmium tartarte crystals possess piezoelectric nature. In the present study, cadmium levo-tartrate crystals were grown using silica hydro-gel as growth medium. Yellowish white dendrite type crystals were obtained. The crystals were characterized by Thermo gravimetric analysis and kinetic as well as thermodynamic parameters were evaluated for the different stage of decomposition.

KEY WORDS: Cadmium levo-tartrate crystals, gel growth, thermo gravimetric analysis, kinetic parameters, thermodynamic parameters.

I. INTRODUCTION

The crystals are the pillars of modern electronic and the field of science and technology. The supply of natural crystals is limited, while the new materials in the crystalline form are required for the development. The crystals can be grown by various methods. In the present article, the gel method is used to grow the pure crystals of cadmium levo-tartrate. This is a simple technique and can be used at room temperature. This technique is one of the best alternatives for the growth of crystals which are relatively insoluble or sparingly soluble in water and decompose before their melting points. Gel acts as a 3 dimensional crucible which supports the growing crystal and at the same time yields to its growth without exerting major forces on it.

In the literature, many pure tartrate compounds are reported which have been grown by gel technique, for example, iron tartrate [1], cobalt tartrate [2-4] and lead tartrate [5].

In the present work, pure cadmium levo-tartrate crystals were grown by gel technique. The crystals were characterized by thermo gravimetric analysis and kinetic as well as thermodynamic parameters were evaluated for the different stage of decomposition.

II. MATERIALS AND METHOD

In the present study, the single diffusion method [5-8] was employed for the growth of cadmium levo-tartrate crystals. The silica hydro gel was used as a growth medium. To prepare the gel, a solution of sodium metasilicate of 1.05 specific gravity and 1 M solution of levo tartaric acid were mixed in such a manner that the pH of the mixture was set at 4.5. The gel solution was poured in to glass test tubes of 15 cm length and 2.5 cm diameter and allowed to set in the gel form. The supernatant solution containing cadmium nitrate solutions was poured on the set gel carefully without damaging the gel.

All the chemicals were of AR grade and obtained from Sigma Aldrich. The following reaction is expected to take place in the formation of cadmium levo-tartrate crystals.

$$Cd(NO_3)_2{\cdot}4H_2O + H_2C_4H_4O_6 + nH_2O \rightarrow CdC_4H_4O_6{\cdot}\, nH_2O + 2HNO_3 + 4H_2O \quad (1)$$

The amount of HNO_3 produced is very less in comparison to the nutrients being supplied to the growing crystals and hence no major limitation is imposed [5-8].

DOI: 10.15680/IJIRSET.2014.0311038

ISSN: 2319-8753

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Photograph of the grown crystals is shown in the figure 1.

Fig. 1. Dendritic crystals of cadmium levo-tartrate

III. CHARACTERIZATION TECHNIQUE

The grown crystals were characterized by Thermo Gravimetric Analysis (TGA). The TGA was recorder on Perkin Elmer make instrument, model Pyris-1 DSC, Pyris-1 TGA, DTA-7. The data were recorded from room temperature to 700^{o}C at a heating rate of 10^{o}C min^{-1} in atmosphere of air in standard Al_2O_3 crucible.

IV. RESULT AND DISCUSSION

There are reports available in literature on thermal studies on pure metal tartrate systems, for example, strontium iodate [9], mercuric iodate [10] and potassium hydrogen levo-tartrate crystals [11].

The TGA curve for cadmium tartrate crystals is shown in figure 2. There are three stages of decomposition starting from room temperature of 45 ^{o}C. The first stage of dehydration starts from 45 ^{o}C and continues up to 80 ^{o}C where the weight loss is about 12%. Then sample remains stable during the 80 to 260 ^{o}C temperature range. Then after second stage of decomposition starts from 270 ^{o}C and continues up to 320 ^{o}C where the weight loss is about 32%. At the end of second stage, the sample is converted into oxalate of cadmium. The third and final stage of decomposition occurs during the temperature range 320 to 360 ^{o}C where the mass loss is about 57%. At the end of this stage, the sample is converted into oxide of cadmium. Comparing the observed and calculated percentage weight losses suggests chemical formula for the given crystal to be $CdC_4H_4O_6 1.83H_2O$. The TGA result for cadmium levo-tartrate is shown table 1.

ISSN: 2319-8753

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(An ISO 3297: 2007 Certified Organization)

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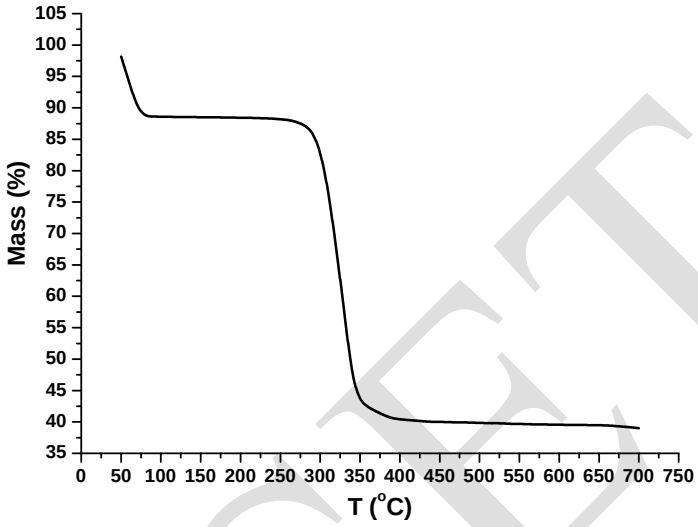

Fig. 2. TG curve for cadmium levo-tartrate crystals

Table 1. TGA result for cadmium levo-tartrate crystals

Temperature (°C)	Reactions involved	Theoretical mass loss (%) calculated	Experimental mass loss (%) from graph
30 – 50	$CdC_4H_4O_6 1.83H_2O \rightarrow CdC_4H_4O_6 + 1.6H_2O$	11.27	11.33
80 – 260	No decomposition	No mass loss	No mass loss
270 – 320	$CdC_4H_4O_6 \rightarrow CdC_2O_4 + 2CO + 2H_2$	31.75	32.37
320 – 360	$CdC_2O_4 \rightarrow CdO + 2CO + 1/2O_2$	56.32	57.30

Many researchers have used thermo gravimetric data to calculate the kinetic parameters of solid state reaction including mass [12-16]. By using kinetic parameters such as order of reaction, frequency factor and energy of activation, the shape of curve is determined. With the help of Coats and Redfern [14] relation the kinetic parameters were calculated. In the present study, the kinetic and thermodynamic parameters have been calculated for dehydration as well as for decomposition stage of crystals.

Coats and Tedfern relation is given by

$$\log_{10}\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \left\{\log_{10}\left[\frac{AR}{\alpha E}\right]\left[1-\frac{2RT}{E}\right] - \frac{E}{2.3RT}\right\} \quad (2)$$

where $\alpha = \frac{W_O - W}{W_O - W_f}$, W_o the initial weight, W the weight at time t, W_f the final weight, n the order of reaction, A the frequency factor, E the activation energy of the reaction, R a gas constant and α the heating rate in °C/min.

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To determine the the value of activation energy and order of reaction, a plot of $\log_{10}\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$ versus $\frac{1}{T}$ is drawn for different values of *n* and the best linear plot gives the correct value of *n*. This equation is valid for all values of *n* except *n = 1*.

Figure 3(a) and 3(b) is a plot of Coats and Redfern equation for the cadmium levo-tartrate crystals for the dehydration as well as decomposition stage, respectively.

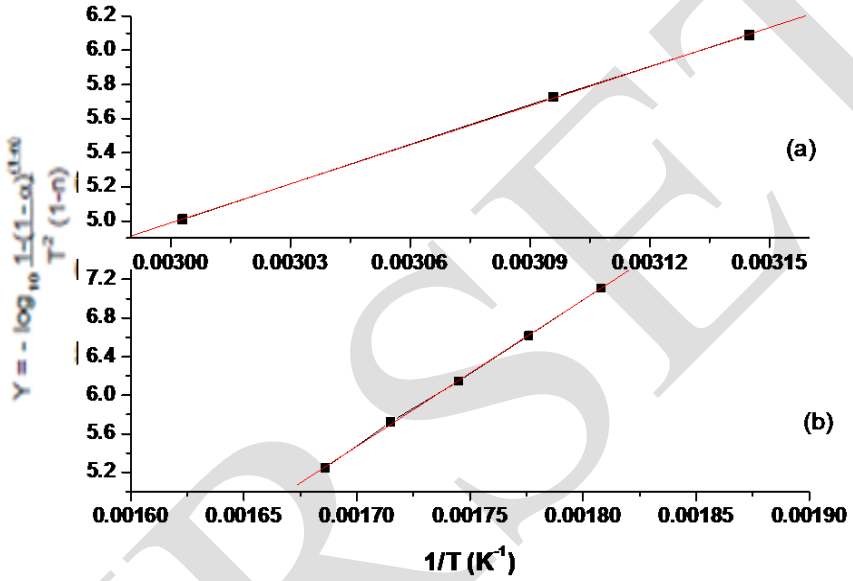

Fig. 3. A plot of Coats and Redfern relation for cadmium levo-tartrate crystals

The values of order of reaction, activation energy and frequency factor for the dehydration as well as decomposition stage are listed in the table 2.

Table 2. Kinetic parameters for cadmium levo-tartrate crystals

Stage	n	Activation energy (kJ mol^{-1})	Frequency factor
Dehydration	2	146.09	1.73×10^{33}
Decomposition	0.5	290.40	1.05×10^{37}

The thermodynamic parameters have been evaluated for the dehydration as well as decomposition stages by using the standard relations [17]. The standard enthalpy of activation $\Delta^{\#}H^{o}$ was calculated by using the relation 3.

$\Delta^{\#}H^{o} = E - 2RT$ (3)

The standard entropy of activation $\Delta^{\#}S^{o}$ was calculated by using relation 4.

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$$\Delta^{\#}S^{o} = 2.303 \times R \times \log_{10}\left[\frac{Ah}{kT}\right] \quad (4)$$

where, *k* is the Boltzman constant, *h* the Planck constant, *T* the temperature and *A* is the frequency factor.
The standard Gibbs free energy of activation $\Delta^{\#}G^{o}$ is estimated by using the relation 5.

$$\Delta^{\#}G^{o} = \Delta^{\#}H^{o} - T\,\Delta^{\#}S^{o} \quad (5)$$

The values of standard enthalpy, standard entropy and standard Gibbs free energy for the dehydration as well as decomposition stage are listed in the table 3.

Table 3. Thermodynamic parameters for cadmium levo-tartrate crystals

Stage	Standard enthalpy $\Delta^{\#}H^{o}$ (kJ mol^{-1})	Standard entropy $\Delta^{\#}S^{o}$ (kJ mol^{-1})	Standard entropy $\Delta^{\#}G^{o}$ (kJ mol^{-1})
Dehydration	140.72	0.390	140.33
Decomposition	280.88	0.457	280.42

Positive values of the standard enthalpy and the standard entropy of activation suggest that the process is spontaneous at high temperatures and the positive values of standard Gibbs free energy suggest that the process is thermodynamically unstable [6].

V. CONCLUSION

Pure cadmium levo-tartrate crystals were grown in silica gel by using 1 M cadmium nitrate solution as supernatant solution. From TG curves, it was found that the crystals were thermally unstable. Upon heating, they become anhydrous and decomposed into metal oxide through a single stage of oxalate. The kinetic parameters were evaluated for both the stages by using Coats and Redfern relation. The thermodynamic parameters were evaluated for both the stages by using the standard relations. The presence of water molecules was detected and calculated. The exact chemical formulation for the pure cadmium levo-tartrate crystals were suggested.

ACKNOWLEDGMENTS

The author (Harshkant Jethva) is thankful to the Principal and the Management of Maharaja Shree Mahendrasinhji Science College, Morbi for encouragements.

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