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Synthesis and Thermal Properties of Complexes of Carboxymethyl Cellulose with Some Divalent Metals

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Abstract

A series of new complexes of manganese (II), cobalt(II), nickel(II), copper(II) and zinc(II) have been synthesized with pimeloylcarboxymethyl cellulose (PCMC). The complexes have been characterized by elemental analysis, spectroscopic spectral measurements (IR, UV, Vis.), magnetic measurements and thermal studies. Tetrahedral structure was proposed for Ni(II) and Zn(II)complex while the square planar geometry was proposed for Cu(II) complex with PCMC. Octahedral structure was proposed for Mn(II) and Co(II) complexes of PCMC. The thermal decomposition study of the prepared complexes was monitored by TG analysis in dynamic atmosphere. TG studies confirmed the chemical formulations of theses complexes. The kinetic parameters were determined from the thermal decomposition data using the graphical methods of Freeman Carroll and Sharp Wentworth method. Thermodynamic parameters were calculated using standard relations.

Keywords: TGA, Thermal degradation, Freeman Carroll, carboxymethyl cellulose.

1. Introduction:

Cellulose is renewable and due to its abundance in nature it offers materials for cost effective technologies of ion exchange (Nada et al, 2006, Sokker et.al. 2006) and hydrogel (Chauhan et.al 2005, Kawabara et.al 1996). Cellulose and its derivatives have been used in metal ion absorption [1]. Depletion of petroleum based products created interests in cellulose and cellulose derivatives as a renewable resource. Alkali cellulose and carboxymethyl cellulose (CMC) are the most important cellulose derivatives.

Cellulose derivatives have gained acceptance for pharmaceutical, cosmetic, food, adhesives, textiles, and packaging uses. This is the case with sodium carboxymethylcellulose (CMC), one anionic linear cellulose ether. CMC presents the structure of a polyanion consisting of repeating units of b-1, 4-linked anhydroglucose residues, substituted by sodium carboxymethyl groups. A number of papers were published on the use of chelating exchanges for trace element pre-concentration from various matrices using cellulose as solids sorbents for the separation of the transition metals in analyses such as: GFAAS spectrometry, ICP-MS for reduction and aggregation of silver, copper, and cadmium ions in aqueous solutions of gelatin and CMC, and with dichromate for separation of copper–lead in secondary copper minerals [2–5]. A paper in the literature outlined the importance of biopolymers as remediation agents in wastewater treatment [6].

The present work is a part of systematic program undertaken in the laboratory which includes the synthesis of thermally stable complexes of transition metals and pimeloylcarboxymethyl cellulose (PCMC), the mechanism of their formation and

their structural aspects. The metal ions selected for the present work belong to 3-d block transition elements viz. Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). The Freeman – Carroll and Sharp- Wentworth methods have been applied forthe calculation of kinetic parameters [7-9].

2. Results and Discussion:

2.1 ***Materials:*** All the chemicals used as starting materials in the synthesis of ligand and its inorganic polymers were of extra pure quality. Sodium carboxymethyl cellulose (E.Merck, Germany), Pimelic acid (E.Merck, Germany).Manganous acetate, Cobaltous acetate, Nickel acetate (E.Merck, Germany), Cuprous acetate and Zinc acetate (S.D.Fine Chem., India).

2.2. Syntheis of Ligand: The ligand (PCMC) was synthesized by triturating the mixture of 10 g of finely powdered Na salt of CMC (low viscosity) and 30 ml of glycerol with mortar and pestle. The triturated mixture is added in small amounts into the vertex of 0.2M aqueous Pimelic acid solution and stirred electrically until a clear gel was formed. The synthesized ligand PCMC was stored in an airtight wide mouth bottle.

2.3 Synthesis of complexes: The inorganic polymers in the present work have been synthesized by refluxing 10 g of PCMC ligand and 100 ml of 0.2 M aqueous metal acetate at 100^{0}C in an oil bath for 2 hrs. The inorganic polymers obtained were then cooled, filtered and washed with hot water to remove any metal acetate and unreacted ligand.

2.4 Composition of the Polymeric Unit: The composition of the polymeric unit was assigned on the basis of elemental analysis. The presence of water of crystallization was ascertained on the basis of thermal studies. The Composition of polymeric unit was found to be $[M(II)L]_n$,$[M'(II)L.2H_2O]_n$and $\{[M''(II)L]_nH_2O\}$ where M=Ni(II) and Zn(II), M'=Mn(II) and Co(II), M''=Cu(II) and L= PCMC. On the basis of elemental analysis, infrared spectra, reflectance spectra, magnetic measurements and thermal studies, these complexes are found to have octahedral, square planar or tetrahedral geometry.

2.5 Thermogravimetric Analysis: The kinetics of thermal decomposition was investigated by means of non-isothermal TG technique using non-isothermal manual thermal analyzer. These measurements were carried out from 40^{0}C to 800^{0}C taking sample masses ranging from 2 to 4 mg and furnace heating rate of 10^{0}C/min.

Figure 1 shows the TG curves obtained for M(II)PCMC where M = Mn, Co, Ni, Cu and Zn. The Freeman – Carroll and Sharp- Wentworth methods have been employed for thecalculation of kinetic parameters of the newly synthesized polymer with help of dynamicTG curve. The following expression is used to evaluate various kinetic parameters:

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

Hence, a plot of $\frac{\Delta \log\left(\frac{dw}{dt}\right)}{\Delta \log W_r}$ vs $\frac{\Delta\left(1/T\right)}{\Delta \log W_r}$ should give a straight line with an intercept on Y- axis equal to the value of n (the order of reaction) and the slope m= E/2.303R. Where, dw/dt is the rate of change of weight with time and in expression Wr=Wc –w, Wc is theweight loss at the completion of the reaction, w is the total weight loss up to the time t and T isthe temperature in k. The following expression is used to evaluate Ea with Sharp-Wentworth method:

$$\log \frac{\left(dc/dt\right)}{(1-c)} = \log\left(A/\beta\right) - \left[\frac{E_a}{2.303R}\right].\frac{1}{T}$$

Where, dc/dt is the rate of change of mass with time t, T is the temperature and β = ΔT/dt.

The thermal degradation curve for M(II)-PCMC shown in Figure 1 and the thermoanalytical data and half decomposition temperatures are given in Table 1.

Table 1.Kinetic Parameters of PCMC complexes.

Complex	Decomposition Temperature (T) K	Half Decomposition Temperature (T*) K	Activation energy kJ/mole		Kinetic parameters by FC				
			Freeman – Carroll FC	Sharp – Wentworth SW	Entropy Change ΔS (kJ)	Free Energy Change ΔF (kJ)	Frequency Factor Z, (S^{-1})	Apparent Entropy S* (kJ)	N (found)
$[Mn(II)(PCMC)(H_2O)_2]_n$	693	733	15.168	15.116	-157.57	124.36	254.68	-96.65	1.304
$[Co(II)(PCMC)(H_2O)_2]_n$	683	733	14.26	14.262	-158.22	122.32	124.73	-102.59	1.138
$[Ni(II)(PCMC)]_n$	653	723	13.728	13.799	-158.55	117.26	85.7	-105.82	1.295
$[Cu(II)(PCMC)](H_2O)_2\}_n$	663	733	9.765	9.759	-161.68	116.96	68.7	-107.54	0.930
$[Zn(II)(PCMC)]_n$	663	713	6.561	6.554	-165.26	116.13	23.76	-116.60	0.884

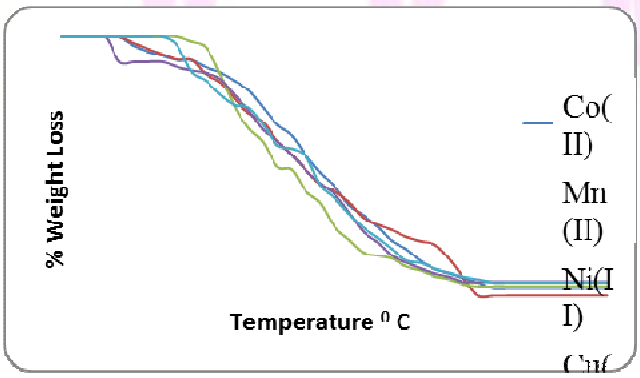

Figure 1 Thermogram of M(II)-PCMC Complexes

Conclusion :

Thermogram of M(II)PCMC polymeric complexes shows activation energy calculated by the Freeman – Carroll and Sharp Wentworth methods in good agreement with each other. Thermodynamic parameters have been calculated on the basis of thermal activation energy and values are given in Table 1. Due to abnormally low value of frequency factor [Z] it may be classified as a slow reaction and no other obvious reason can be given. The value of entropy [ΔS] indicates that the activated polymer has more ordered structure than the reactants and the reaction are slower than normal. This is further supported by low Z values. It is very difficult to draw any unique conclusion from the magnitude of thermal activation energy [Ea] as decomposition mechanism is expected to be complicated. Positive values of activation energy under present investigation correspond to the energy of activation due to oxidation –reduction process of M(II)PCMC complexes in the higher temperature range.

Fairly straight line plots are obtained using the two methods. However, using theFreeman- Carroll method some abnormal points were ignored to get a clear picture aboutmost of the points. Similarly, in the Sharp- Wentworth method, some points at the beginningor the end did not fall on straight line. This is expected, since, the decomposition ofM(II)MCMC is not obeying first order kinetics perfectly.

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