



SYNTHESIS, SPECTRAL CHARACTERIZATION AND THERMOGRAVIMETRIC STUDIES OF SOME INORGANIC COMPLEXES

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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 maleoyl carboxymethyl cellulose (MACMC). The complexes have been characterized by elemental analysis, spectroscopic spectral measurements (IR, UV-Vis.), magnetic measurements and thermal studies. Tetrahedral structure was proposed for Mn(II) and Zn(II) complex while the square planar geometry was proposed for Cu(II) complex with MACMC. Octahedral structure was proposed for Ni(II) and Co(II) complexes of MACMC. The thermal decomposition study of the prepared complexes was monitored by TG analysis in dynamic atmosphere. TG studies confirmed the chemical formulations of these 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.

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Introduction

Each glucose unit in the cellulose chain has three hydroxyl groups, each of which is capable of hydrogen bonding to an adjacent molecule. Because of the abundance of hydroxyl groups, and their ability to hydrogen bond to a neighboring molecule, the chains are bound tightly together. Water molecules, at any temperature, cannot force their way in between the chains to hydrate them, thus cellulose is water insoluble. Sodium carboxymethyl cellulose (Na-CMC) is an anionic water-soluble polymer derived from cellulose. Due to its innocuousness, it is used as a stabilizer, binder, thickener, for suspension and as water retaining agent in food industry, pharmaceutical, cosmetic, paper, and other industrial areas[1-3].

Cellulose and its derivatives have been used in metal ion absorption [4]. 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. CMC presents the structure of a polyanion consisting of repeating units of b-1, 4-linked anhy-

droglucose 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 [5-8]. A paper in the literature outlined the importance of biopolymers as remediation agents in wastewater treatment [9].

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 maleoyl carboxymethyl cellulose (MACMC), 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 for the calculation of kinetic parameters [10-12].

Results and Discussion

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), Maleic acid (E.Merck, Germany). Manganous acetate, Cobaltous acetate, Nickel acetate (E.Merck, Germany), Cuprous acetate and Zinc acetate (S.D.Fine Chem., India).

Synthesis of Ligand

The ligand (MACMC) was synthesized by triturating the mixture of 10 g of finely powdered Na salt of CMC (low viscosity) and 30 ml of glycerol and adding in small amounts into the vertex of 0.2M aqueous Maleic acid solution and stirred electrically until a clear gel was formed. The synthesized ligand MACMC was stored in an airtight wide mouth bottle.

Synthesis of complexes

The inorganic polymers in the present work have been synthesized by refluxing 10 g of MACMC ligand and 100 ml of 0.2 M aqueous metal acetate at 100°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.

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 $[M(II)L]_n$ and $[M'(II)L \cdot 2H_2O]_n$ where $M=Mn(II)$ and $Zn(II)$, $M'=Ni(II)$, $Co(II)$ and $Cu(II)$ and $L=MACMC$. 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.

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°C to 800°C taking sample masses ranging from 2 to 4 mg and furnace heating rate of 10°C/min.

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

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

$$\frac{\Delta \log \left(\frac{dw}{dt} \right)}{\Delta \log W_r} \quad \text{vs} \quad \frac{\Delta \left(\frac{1}{T} \right)}{\Delta \log W_r}$$

Hence, a plot of $\frac{\Delta \log \left(\frac{dw}{dt} \right)}{\Delta \log W_r}$ vs $\frac{\Delta \left(\frac{1}{T} \right)}{\Delta \log W_r}$ 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 $W_r = W_c - w$, W_c is the weight loss at the completion of the reaction, w is the total weight loss up to the time t and T is the temperature in K . The following expression is used to evaluate E_a with Sharp-Wentworth method:

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

Where, dc/dt is the rate of change of mass with time t , T is the temperature and $\beta = \Delta T/dt$.

The thermal degradation curve for $M(II)MACMC$ shown in Figure 1 and the thermo analytical data and decomposition temperatures are given in Table 1.

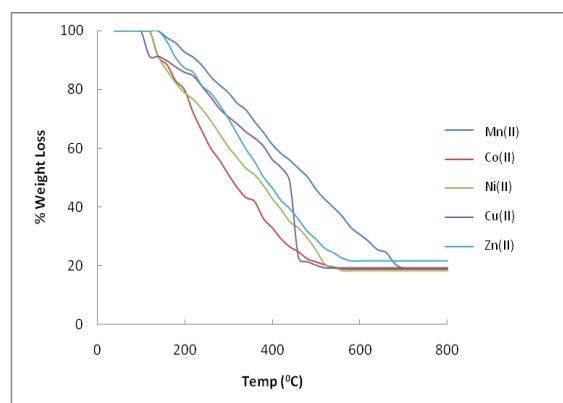


Fig. 1- Thermogram of $M(II)MACMC$ Complexes

Conclusion

Thermogram of $M(II)MACMC$ 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 $[\Delta S]$ 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 $[E_a]$ 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 $M(II)MACMC$ complexes in the higher temperature range.

Fairly straight line plots are obtained using the two methods. However, using the Freeman - Carroll method some abnormal points were ignored to get a clear picture about most of the points. Similarly, in the Sharp - Wentworth method, some points at the beginning or the end did not fall on straight line. This is expected, since, the decomposition of $M(II)MACMC$ is not obeying first order kinetics perfectly.

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Table 1- Kinetic Parameters of MACMC complexes

Complex	Decomposition Temp. (T) K	Activation energy kJ/mole			Kinetic parameters by FC			
		Freeman Carroll	Sharp Wentworth	Entropy Change ΔS (kJ)	Free Energy Change ΔF (kJ)	Frequency Factor Z, (S-1)	Apparent Entropy S* (kJ)	N (found)
[Mn(II)(MACMC)] _n	440	4.724	4.702	-167.38	124.07	16.03	-118.58	0.912
[Co(II)(MACMC)(H ₂ O) ₂] _n	400	10.904	10.929	-160.68	119.04	64.56	-108.18	0.988
[Ni(II)(MACMC)(H ₂ O) ₂] _n	440	11.29	11.324	-160.51	125.73	62.37	-107.49	1.205
[Cu(II)(MACMC)](H ₂ O) ₂ _n	370	8.294	8.294	-163.07	113.15	22.698	-117.34	0.897
[Zn(II)(MACMC)] _n	400	14.879	14.755	-157.91	121.15	250.03	-96.36	0.965