Synthesis and Structural Studies of Some Inorganic Polymers of Succinoyl Carboxymethyl Cellulose

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Abstract: The inorganic polymers containing transition metals such as Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were synthesized by using succinoyl carboxymethyl cellulose (SCMC) in aqueous media. The newly synthesized polymers were characterized by elemental analysis, IR spectroscopy, TG analysis, UV reflectance spectra and magnetic moment. On the basis of these studies, the composition of the polymeric unit was found to be $[M(II)L]_n$, $[M'(II)L.2H_2O]_n$, $\{[M''(II)L.2H_2O]_n H_2O\}$, where $M = Zn(II)$, $M' = Mn(II)$, $Ni(II)$ and $Cu(II)$ and $M'' = Co(II)$, $L = SCMC$ ligand. On the basis of instrumental techniques, it has been found that the $[Zn(II)(SCMC)]_n$ inorganic polymer has tetrahedral geometry, whereas $\{[Cu(II)(SCMC)]_n.2H_2O\}$ has square planar geometry and $[Mn(II)(SCMC).2H_2O]_n$, $\{[Co(II)(SCMC).2H_2O]_n H_2O\}$ and $[Ni(II)(SCMC).2H_2O]_n$ have octahedral geometry. The decomposition temperatures of the inorganic polymers have been determined by TGA. The TGA reveal that the Mn(II) polymer of SCMC is highly thermally stable than rest of the polymers and these polymers can be used as thermal resisting materials.

Keywords: Carboxymethyl cellulose, SCMC, TGA, Thermal degradation

Introduction

Cellulose derivatives have gained acceptance for pharmaceutical, cosmetic, food, adhesives, textiles and packaging uses. They must be non-toxic, noncarcinogenic, biocompatible and in no way injurious in the biological environment. Cellulose ether is the most widely used cellulose derivative in food and pharmaceutical industries. They are obtained by replacing the hydroxyl groups with either alkyl or hydroxy-alkyl groups. Accordingly, a wide range of cellulose ethers are manufactured to meet specific needs of industrial applications¹. This is the case with sodium carboxymethylcellulose (Na-CMC), an anionic linear cellulose ether. CMC presents the structure of

a polyanion consisting of repeating units of anhydroglucose residues, substituted by sodium carboxymethyl groups. Cellulose derivatives such as carboxymethylcellulose (CMC) and hydroxypropylcellulose are biocompatible² and have been applied in drug delivery formulations³⁻⁶ and as components of therapies for preventing post surgical adhesions (*e.g.*, Genzyme's Septrafilm)⁷⁻¹¹. A number of papers have been published on the uses of chelating exchanges for trace element pre-concentration from various matrix 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 minerals¹²⁻¹⁵. A paper in the literature outlined the importance of biopolymers as remediation agents in wastewater treatment¹⁶.

The present work is a part of systematic investigation undertaken in the laboratory which includes the synthesis of thermally stable inorganic polymers, the mechanism of their formation and their structural aspects. The metal ions selected for the present work belongs to 3-d block transition elements *viz.* Mn(II), Co(II), Ni(II), Cu(II) and Zn(II).

Experimental

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), succinic acid (E.Merck, Germany), manganous acetate, cobaltous acetate, nickel acetate (E.Merck, Germany), cuprous acetate and zinc acetate (S.D.Fine Chem., India).

Instruments

Microanalysis of C, H, N were carried out on EAS superuser elemental analyser system GmbH, access: VarioEL superuser, NEERI. Infrared spectra in the region 4000-400 cm⁻¹ were recorded in the solid state (KBr Pallets) in pharmacy department, RTMNU, Nagpur, using FTIR – 101A Shimadzu. The kinetics of thermal decomposition was investigated by using non-isothermal manual thermal analyzer at Department of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur. The heating rate employed was 10 °C/min and the mass loss was recorded continuously. Magnetic susceptibility of inorganic polymers was determined by Gouy's method at room temperature using mercury tetrathiocyanatocobaltate(II) as standard.

Synthesis of ligands

The ligand is 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 0.2 M aqueous succinic acid solution and stirred electrically until a clear gel was formed. The synthesized ligand was stored in an airtight wide mouth bottle.

Figure 1. Succinoyl carboxymethyl cellulose (SCMC) ligand

Synthesis of inorganic polymers

The inorganic polymers in the present work have been synthesized by refluxing 10 g of SCMC ligand and 100 mL of 0.2 M aqueous metal acetate at 100 °C in an oil bath for 2 h. The inorganic polymers obtained were then cooled, filtered and washed with hot water to remove any metal acetate and unreacted ligand.

Figure 2. Synthesis of succinoyl CMC ligand $n = 2$ for succinic acid

Results and Discussion*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 $[\text{M}(\text{II})\text{L}]_n$, $[\text{M}'(\text{II})\text{L} \cdot 2\text{H}_2\text{O}]_n$, $\{[\text{M}''(\text{II})\text{L} \cdot 2\text{H}_2\text{O}]_n \cdot \text{H}_2\text{O}\}$, where $\text{M} = \text{Zn}(\text{II})$, $\text{M}' = \text{Mn}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ and $\text{M}'' = \text{Co}(\text{II})$, $\text{L} = \text{SCMC}$ ligand. On the basis of elemental analysis, infrared spectra, reflectance spectra, magnetic measurements and thermal studies, the proposed structure of these inorganic polymers shown in Figures 5 and 6. The elemental analysis of ligand and polymers is given in Table 1.

Table 1. Elemental analysis of succinoyl carboxymethyl cellulose (SCMC) & its inorganic polymers

Inorganic Polymer	Empirical Formula	Formula weight	%C		%H		%M	
			Calcd	Found	Calcd	Found	Calcd	Found
SCMC	$\text{C}_{12}\text{H}_{15}\text{O}_{10}$	319	45.14	45.29	4.70	4.61	--	--
$[\text{Mn}(\text{II})(\text{SCMC})(\text{H}_2\text{O})_2]_n$	$\text{MnC}_{12}\text{H}_{19}\text{O}_{12}$	410.01	35.12	36.29	4.63	5.64	13.39	13.26
$\{[\text{Co}(\text{II})(\text{SCMC})(\text{H}_2\text{O})_2](\text{H}_2\text{O})\}_n$	$\text{CoC}_{12}\text{H}_{21}\text{O}_{13}$	432.01	33.30	32.28	4.39	5.06	13.64	13.08
$[\text{Ni}(\text{II})(\text{SCMC})(\text{H}_2\text{O})_2]_n$	$\text{NiC}_{12}\text{H}_{19}\text{O}_{12}$	413.77	34.80	33.20	4.59	4.87	14.18	14.54
$\{[\text{Cu}(\text{II})(\text{SCMC})(\text{H}_2\text{O})_2]\}_n$	$\text{CuC}_{12}\text{H}_{19}\text{O}_{12}$	418.62	34.40	33.70	4.50	4.80	15.17	15.90
$[\text{Zn}(\text{II})(\text{SCMC})]_n$	$\text{ZnC}_{12}\text{H}_{15}\text{O}_{10}$	384.38	37.46	36.67	3.90	3.50	17.00	17.26

Infrared spectral studies

The IR spectral data for SCMC and its inorganic polymers with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) are given in Table 2. Characteristic peak of functional groups was observed in the IR Spectra of SCMC: -OH group at 3400 cm^{-1} , -CH group at 2927 cm^{-1} , C=O group of non-conjugated ketones, carbonyls and in ester groups at 1718 cm^{-1} ^{17,18}, -COOH group at 1655 cm^{-1} . The IR spectra of polymers show few new weak absorption bands in the range of $600\text{ to }670\text{ cm}^{-1}$ which may be assigned to the M-O (Metal-Oxygen) bonds¹⁹. The weak band observed around $780 - 900\text{ cm}^{-1}$ may be assigned to coordinated water molecule. The infrared spectral assignments of ligand and inorganic polymers are tabulated in Table 2.

Table 2. IR spectral assignments of SCMC ligand and its inorganic polymers

Assignment	SCMC	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
O-H	3400	3450	3400	3440	3441	3500
C-H	2927	2928	2924	2920	2920	2910
C=O	1718	1718	1718	1718	1718	1718
COOH	1655	1655	1655	1620	1560	1637
COO-	1458	1458	1458	1458	1508	1458
C - O -	1043	1115	1050	1055	985	1066
H-O-H						
Coordinated	-	898	900	781	-	-
M-O	-	600	600	669	596	660

Magnetic moment and electronic spectral studies of SCMC inorganic polymers

The magnetic moment values of SCMC inorganic polymers are given in Table 3. These magnetic moment values support the octahedral geometry for Mn(II), Co(II) and Ni(II) inorganic polymers²⁰ and the tetrahedral geometry for Cu(II) polymers. Since $[\text{Zn(II)(SCMC)}]_n$ is a d10 system and hence is diamagnetic in nature, however, on the basis of elemental analysis, infrared spectra and thermal decomposition data, its most probable geometry is suggested to be tetrahedral.

Table 3. Magnetic moment data of SCMC inorganic polymers

Inorganic polymer	Gram Susceptibility $\chi_g \times 10^{-6}$ (CGS Unit)	Atomic susceptibility $\chi_A \times 10^{-3}$ (CGS Unit)	Corrected atomic susceptibility $\chi_A \times 10^{-3}$ (CGS Unit)	Effective magnetic moment B.M.	Stereo - chemistry
Mn-SCMC	36.28	14.87	14.99	5.93	Octahedral
Co-SCMC	21.45	9.26	9.38	4.69	Octahedral
Ni-SCMC	12.74	5.27	5.39	3.55	Octahedral
Cu-SCMC	3.30	1.38	1.50	1.87	Tetrahedral

Electronic spectral properties include the electronic transitions which take place between the ground levels of coordination clusters and the excited levels. The spectra of the coordination compounds may be classified into ligand field bands and charge transfer bands. The ligand field bands are essentially concerned with the transition between different *d*-orbital which results from the application of the ligand field. Electronic spectral assignments of SCMC inorganic polymers are given in Table 4.

Table 4. Electronic spectral assignments of SCMC inorganic polymers

Inorganic polymer	kK	Assignments	Stereochemistry
Mn-SCMC	25.64	6A1g→4E(g)(D)	Octahedral
Co-SCMC	18.51	4A1g→4T1(g)(P)	Octahedral
Ni-SCMC	20.82	3A2g→3T1g(P)	Octahedral
Cu-SCMC	12.65	C.T.	Tetrahedral

Figure 3. Electronic spectra of SCMC inorganic polymers

Thermogravimetric analysis of SCMC inorganic polymers

The mass loss of SCMC inorganic polymers at various temperatures have been shown in Figure 4. TG curve of Mn(II)(SCMC) polymer shows no mass loss up to 140 °C giving an indication of absence of water of crystallization. It shows mass loss of 8.7% between 140 – 240 °C due to the loss of two coordinated water molecules. It then shows a gradual decrease from 280 °C up to 540 °C which may be due to decomposition of the ligand attached to the metal ion, hereafter no further mass loss was observed due to the formation of stable metal oxide. The decomposition temperature was found to be 380 °C.

TG curve of Co(II)(SCMC) polymer shows presence of lattice water as there is 3.72% mass loss was observed between 100 – 120 °C. It shows mass loss of 7.68% between 120 – 210 °C due to the loss of two coordinated water molecules. After 260 °C it shows gradual decrease in mass up to 500 °C which may be due to decomposition of the organic species attached to the metal ion; after 500 °C no further mass loss was observed, may be due to the formation of stable metal oxide. The decomposition temperature was found to be 350 °C.

In TG curve of Ni(II)(SCMC) polymer, no mass loss is observed up to 150 °C giving an indication of absence of water of crystallization in the polymer. It shows mass loss of 8.41% between 150 - 220 °C due to the removal of two coordinated water molecules. It then shows a gradual mass loss from 250 °C up to 560 °C which may be due to decomposition of the ligand which is attached to the metal ion. Hereafter no further mass loss was observed indicating the formation of stable metal oxide. The decomposition temperature was found to be 350 °C.

The Cu(II)(SCMC) inorganic polymer shows presence of two lattice water as there is 8.5% mass loss was observed between 100 – 140 °C. This polymer shows absence of coordinated water, since no mass loss was observed between 140 – 200 °C, after 200 °C gradual decrease in mass up to 520 °C was observed which may be due to the decomposition of the ligand attached to the metal ion hereafter no further mass loss was observed due to the formation of stable metal oxide. The decomposition temperature was found to be 360 °C.

TG curve of Zn(II)(SCMC) shows no mass loss up to 240°C indicating absence of lattice and/or coordinated water in the polymer. It then shows a gradual decrease up to 580°C which may be due to the decomposition of the ligand attached to the metal ion; after which formation of stable metal oxide takes place. The decomposition temperature was found to be 330°C . The Thermoanalytical data of these inorganic polymers have been reported in Table 5.

Table 5. Thermoanalytical data of SCMC inorganic polymers

Inorganic polymer	% Loss due to lattice water	% Loss due to coordinated water	% Loss due to decomposition	Decomposition temperature range, $^\circ\text{C}$	Decomposition temperature, $^\circ\text{C}$	Rate of heating $^\circ\text{C}/\text{min}$
$[\text{Mn(II)(SCMC)(H}_2\text{O)}_2]_n$	-	8.76	78.34	280-540	380	10
$\{[\text{Co(II)(SCMC)(H}_2\text{O)}_2](\text{H}_2\text{O})\}_n$	3.72	7.68	74.41	260-500	350	10
$[\text{Ni(II)(SCMC)(H}_2\text{O)}_2]_n$	-	8.41	78.27	250-560	350	10
$\{[\text{Cu(II)(SCMC)}](\text{H}_2\text{O)}_2\}_n$	8.50	8.50	57.55	200-520	360	10
$[\text{Zn(II)(SCMC)}]_n$	-	-	85.12	240-580	330	10

Figure 4. Thermogram of SCMC-M inorganic polymers

Figure 5. Proposed structure of six coordinated inorganic polymers

Figure 6. Proposed structure of four coordinated inorganic polymers

Conclusion

On the basis of elemental analysis, infrared spectra, reflectance spectra, magnetic moment data and thermal studies, the $\{[\text{Cu(II)(SCMC)}](\text{H}_2\text{O)}_2\}_n$ and $[\text{Zn(II)(SCMC)}]_n$ inorganic polymers

have tetrahedral geometry, whereas $[\text{Mn(II)(SCMC)(H}_2\text{O)}_2]_n$, $\{[\text{Co(II)(SCMC)(H}_2\text{O)}_2](\text{H}_2\text{O})\}_n$ and $[\text{Ni(II)(SCMC)(H}_2\text{O)}_2]_n$ inorganic polymers are octahedral in nature. On the basis of thermal degradation studies, $[\text{Mn(II)(SCMC)(H}_2\text{O)}_2]_n$ has been found to be highly thermally stable than rest of the polymers reported in this paper. Since these inorganic polymers are highly thermally stable and form films, therefore, they can be used as thermally stable coating material.

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