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Infrared spectroscopic investigation on the reaction mechanisms of urea with manganese(II), cadmium(II), magnesium(II) and calcium(II) formate at elevated temperature

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ABSTRACT

The manganese(II), cadmium(II), magnesium(II) and calcium(II) carbonates, respectively, were achieved by a novel synthetic route through the reaction of aqueous solutions of $Mn(HCOO)_2 \cdot xH_2O$, $Cd(HCOO)_2$, $Mg(HCOO)_2 \cdot 2H_2O$, or $Ca(HCOO)_2$ with a low cost precursor like urea at $\sim 85^\circ C$ for 12 hrs. The infrared spectra of the results indicate absence of the individual bands of urea, but exhibited of the characteristic bands of ionic carbonate, CO_3^{2-} . A general reaction mechanisms describing the preparation of Mn(II), Cd(II), Mg(II) and Ca(II) carbonate compounds were discussed.

Keywords: carbonate CO_3^{2-} , Infrared spectra, Elemental analyses, Urea.

INTRODUCTION

Urea is physiologically very important. It is the chief nitrogenous product of protein metabolism. Urea has a melting point of $132^\circ C$, soluble in water and ethanol, but insoluble in ether. Urea is used for preparing formaldehyde-Urea resin (plastics) [1], barbiturates [2], and fertilizers [3-6]. Urea is also extensively used in the paper industry to soften cellulose and has been used to promote healing in infected wounds and many other applications in the field of biological and organic synthesis [7-10].

Yamaguchi and Stewart [11, 12] were assigned all of the observed frequencies in the spectra of urea and urea-d₄. The two vibrations of the frequencies at 1686 and 1603cm^{-1} were assigned as

the 1686 cm^{-1} band due to CO stretching vibration and the 1603 cm^{-1} band for NH_2 bending motion. The calculations studied by Yamaguchi showed that for the band at 1686 cm^{-1} , the contribution of the NH_2 bending motion is greater than that of CO stretching motion. The infrared bands of urea- d_4 observed at 1245 and 1154 cm^{-1} are assigned to ND_2 bending vibrations. This assignment is consistent with the observed depolarization degrees of the Raman lines. The 1464 cm^{-1} frequency of urea is assigned to the CN stretching vibration. The corresponding frequency of urea- d_4 is observed at 1490 cm^{-1} . The 1150 cm^{-1} band is assigned to NH_2 rocking vibrations.

The reactions between transition metal ions and urea at room temperature have been studied extensively [13-17]. The infrared spectra of these complexes clearly indicated that urea molecule behaves as a mono dentate ligand and coordinates to the metal ions through the oxygen atom and not the nitrogen atom.

The nature of the reaction products depend strongly on the type of metal ions and so the metal salt used. The novelty in our previously studies [18-27] were oriented to the reaction of urea ligand with different metals such as Co(II), pb(II), Sn(II), Cr(III), Fe(III), Au(III), Sn(IV), V(V) and Mo(IV) at high temperature which demonstrate that the types of metal ions beside their anions have a pronounced effect on the nature of the reaction products. The published papers were trended for the reaction of urea with different metal salts at elevated temperature lead to discovering a novel method for preparation pbCO_3 and CoCO_3 [21], lanthanide carbonates [23,27], limonite, $\text{FeO}(\text{OH})$ [20], $2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$ [19], $\text{SnOCl}_2 \cdot 2\text{H}_2\text{O}$ [18], (Cr_2O_3 , MnO_2 , MoO_3 and WO_3) oxides resulted from a novel oxidation reduction reaction between (K_2CrO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$), KMnO_4 , Na_2MoO_4 and Na_2WO_4 , respectively, with urea in an aqueous solution at $\sim 85\text{ }^\circ\text{C}$ [27].

The bright side in this study was undertaken to identify the nature of the reaction mechanisms of the products resulted during the reaction of urea with $\text{Mn}(\text{HCOO})_2 \cdot x\text{H}_2\text{O}$, $\text{Cd}(\text{HCOO})_2$, $\text{Mg}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$, or $\text{Ca}(\text{HCOO})_2$ at $85\text{ }^\circ\text{C}$ for 12 hrs in aqueous media. The reaction products were isolated as solids and characterized by elemental analysis, infrared spectroscopy.

EXPERIMENTAL SECTION

2-1- Materials and synthesis

All chemicals used throughout this work were analytical pure. MCO_3 ($\text{M} = \text{Mn}(\text{II})$, $\text{Cd}(\text{II})$, $\text{Mg}(\text{II})$ or $\text{Ca}(\text{II})$) were prepared by mixing an aqueous solutions (50 ml) of 0.1M of urea with 0.01M of the respective $\text{Mn}(\text{HCOO})_2 \cdot x\text{H}_2\text{O}$, $\text{Cd}(\text{HCOO})_2$, $\text{Mg}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$, or $\text{Ca}(\text{HCOO})_2$. The mixtures were heated at $85\text{ }^\circ\text{C}$ for 12 hrs in a hot plate. The solid products compounds were filtered off, washed several times with hot water, dried at $120\text{ }^\circ\text{C}$ in an oven for 3 hours and then placed in *vacuo* over anhydrous calcium chloride. The yields of the obtained Mn(II), Cd(II), Mg(II) and Ca(II) carbonates were varied in the range 60-to-75% depending upon the type of metal as well as on the counter ions associated with the metal ion.

The elemental analyses for MCO_3 ($\text{M} = \text{Mn}(\text{II})$, $\text{Cd}(\text{II})$, $\text{Mg}(\text{II})$ and $\text{Ca}(\text{II})$) (Table 1) obtained during the reaction of urea with the respective metal formate salts almost the same and indicate the absence of nitrogen element.

2-1- Instruments

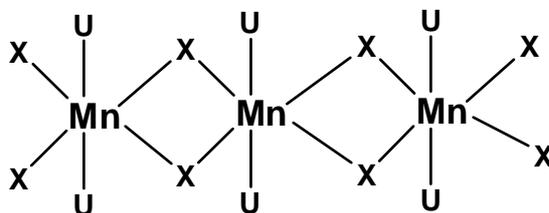
Carbonate content in the four compounds were determined by dissolving a sample of each product in excess standard HCl and the excess of HCl was determined using standard sodium carbonate [28]. The percentage of manganese(II), cadmium(II), magnesium(II) and calcium(II) in their compounds were determined gravimetrically method till constant weight and stable formula. The infrared spectra of urea, all reactants and products were recorded in potassium bromide discs using a Shimadzu FT-IR Spectrophotometer.

RESULTS AND DISCUSSION

The reaction of aqueous solutions of urea with formate salts of manganese(II), cadmium(II), magnesium(II) and calcium(II) at 85 °C produces a buff, white, white and white solid crystalline products, respectively. The infrared spectra of urea as well as the reaction products of different manganese(II), cadmium(II), magnesium(II) and calcium(II) salts with urea at elevated temperature were obtained from potassium bromide discs. The spectra of free urea ligand, manganese(II), cadmium(II), magnesium(II) and calcium(II) carbonates are shown in Fig. 1-5, respectively. The band assignments for the products are given in Table 2. The infrared spectra show no bands due to any of the reactants and of coordinated urea, but instead, a group of bands characteristic for the ionic Carbonate, $(\text{CO}_3)^{2-}$, is appeared [29]. Based on this fact, along with that obtained from elemental analysis data as well as the volumetric determination of $(\text{CO}_3)^{2-}$ group with standard solution of HCl and beside that the infrared spectra of the commercially obtained MnCO_3 , CdCO_3 , MgCO_3 and CaCO_3 are the same as that of the reaction products. The products obtained were identified as MnCO_3 , CdCO_3 , MgCO_3 and CaCO_3 . The infrared assignments agree quite well with those known [29] for the ionic carbonate $(\text{CO}_3)^{2-}$.

Previous studies [18-27] indicated that the nature of the reaction product obtained from the reaction of metal ions with urea at high temperature depends upon the type of metal ion and in some cases on the nature of the metal salts used.

The manganese(II)-urea complexes have been studied extensively [30-33] and it was found that, these complexes are of high spin and possess octahedral structures. These investigation have also shown that, all of the studied Mn(II)-urea complexes are of the general formula MnU_2X_2 ($\text{X}=\text{Cl}^-$ or Br^- , $\text{U}=\text{Urea}$). They have a chain like structure with halogen bridges, as shown by structure (formula 1).



Formula 1: Manganese urea complex

This structure is supported by electronic spectral measurements and the magnetic susceptibility data [34] but could not be checked by infrared spectroscopy because of the Mn-X-M bridging vibration frequency lying below 200cm^{-1} .

The trans-octahedral complex $[\text{MnU}_4(\text{NCS})_2]$, (U=urea) has been prepared and investigated [35]. The ligand, urea is coordinated through its oxygen atom while the thiocyanate through the nitrogen atom. These results are supported by the crystallographic data of Tsintsadze *et al* [36] obtained on the $[\text{MnU}_4(\text{NCS})_2]$ complex.

The trifluorobis(urea)manganese(III) trihydrate, $[\text{MnF}_3(\text{urea})_2] \cdot 3\text{H}_2\text{O}$ complex is prepared and its infrared spectrum is obtained [37]. The characteristic features of the infrared spectrum of this complex are the absorptions due to coordinated urea, coordinated fluoride and lattice water. The important bands of coordinated urea have been observed at 3425 and 1535cm^{-1} , assignable to $\nu(\text{NH}_2)$ and $\nu(\text{CO})$ modes, respectively. The unaltered position of $\nu(\text{NH}_2)$ and a significant lowering of $\nu(\text{C}=\text{O})$ band frequencies compared with those for the free urea suggest that urea is coordinated with the metal in an unidentate manner through its oxygen atom. However, there is a shift to the lower frequency in the position of the $\nu(\text{Mn}-\text{F})$ mode indicating that, the fluoro ligands are involved also in the formation of bridges among the contiguous Mn centers in the crystal lattice.

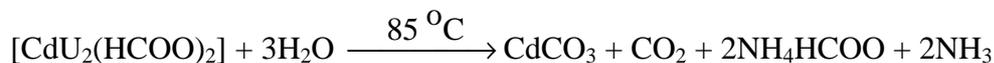
Oxalato urea complexes of manganese(II) $[\text{MnU}_2(\text{C}_2\text{O}_4)]\text{H}_2\text{O}$ (U=Urea) was prepared [38] from the reaction of $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and urea at pH ~3 in 1:1, 1:2, 1:3 and 1:4 molar ratios. This complex was characterized by its IR-spectrum, X-ray diffraction, and thermal analysis. The data obtained indicates that, the oxalato group and the H_2O molecule are in the inner-sphere. The thermal analysis data indicate that, this complex $[\text{MnU}_2(\text{C}_2\text{O}_4)]\text{H}_2\text{O}$ decomposes at 400°C in three stages to Mn_3O_4 as the final product.

At high temperature the role of Mn(II) ions in decomposing the coordinated urea in the form of $[\text{MnU}_2(\text{HCO}_2)_2]$ could be understood according to the following reactions;



Adducts of $\text{ZnX}_2 \cdot 2\text{urea}$ (X = Cl, Br, I), $\text{CdX}_2 \cdot 2\text{urea}$ (X = Br, I), $\text{CdX}_2 \cdot \text{urea}$ (X = Cl, Br, I) and $\text{HgX}_2 \cdot \text{urea}$ (X = Cl, Br) have been characterized [39]. The shifts of the stretching vibrations to low frequency (νCO) and to high frequencies (νCN and νNH) indicated that urea is oxygen-bonded to the metals.

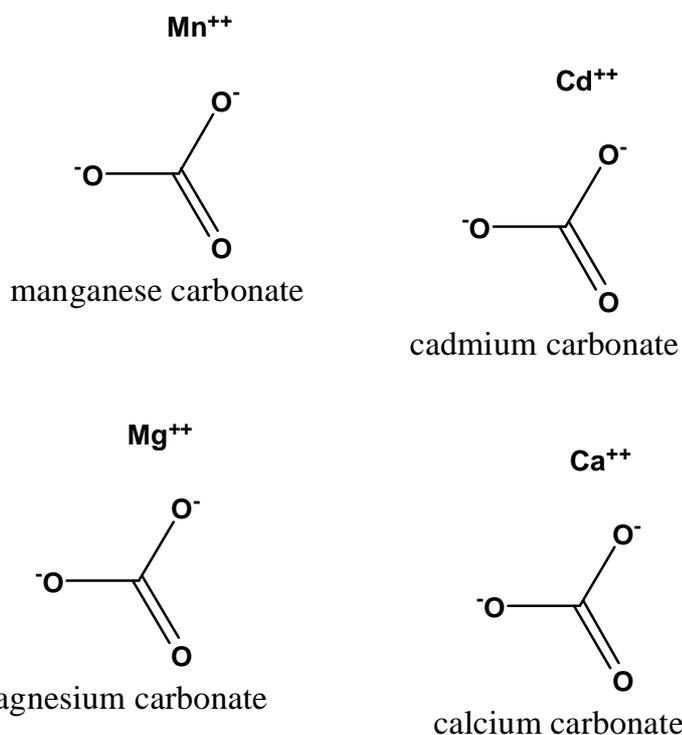
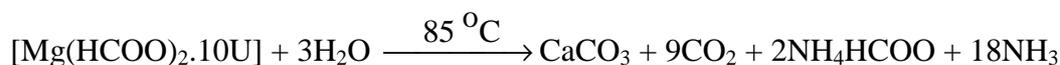
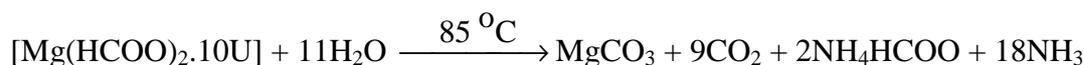
At high temperature the role of Cd(II) ions in decomposing the coordination urea in the form of $[\text{Cd}(\text{urea})_2(\text{HCOO})_2]$ could be understood as follows;



The inhibiting action of amides and alkaline earth element acetates on the corrosion of metals gives a practical importance to the investigation of their reaction in aqueous solutions. The reaction of urea with alkaline-earth metals in aqueous solutions has been studied by a number of workers [40-44]. In case of $\text{CO}(\text{NH}_2)_2\text{-M}(\text{CH}_3\text{COO})\text{-H}_2\text{O}$ (M=Mg, Ca, Sr or Ba) systems [45,46], the tendency of the alkaline earth elements to form complexes with urea decreases as its ionic radius increases. Thus magnesium(II) forms a complex with two molecules of urea, calcium(II) forms a complex with one molecule of urea, while strontium and barium acetates don't react. The complexes $[\text{2CO}(\text{NH}_2)_2\text{.Mg}(\text{CH}_3\text{COO})_2]$ and $[\text{2CO}(\text{NH}_2)_2\text{.Ca}(\text{CH}_3\text{COO})_2]$, are identified by elemental, X-ray phase, and thermogravimetric analysis.

The system $\text{MgCl}_2\text{-CO(NH}_2)_2\text{-H}_2\text{O}$ has been studied [40]. Its solubility isotherm at 0 °C consists of three branches. The two branches on the outside correspond to the crystalline of urea and $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$, while the middle branch corresponds to $\text{MgCl}_2\cdot 4\text{CO(NH}_2)_2$. With a further temperature rise to 15°, the hydrated complex $\text{MgCl}_2\cdot \text{CO(NH}_2)_2\cdot 4\text{H}_2\text{O}$ is formed. At 30° another complex, $[\text{MgCl}_2\cdot 6\text{CO(NH}_2)_2]$ is formed. All of these complexes are concurrently soluble and are precipitated in crystalline forms. At 45° the complex $[\text{MgCl}_2\cdot 10\text{CO(NH}_2)_2]$ is formed. The bond between MgCl_2 and urea is formed through the oxygen of the carbonyl group, as indicated by infrared spectroscopy.

The role of Mg(II) and Ca(II) ions in decomposing the coordinated urea at high temperature may be understood as follows.



Formula 2: Structure of Mn(II), Cd(II), Mg(II) and Ca(II) carbonate compounds

The $(\text{CO}_3)^{2-}$ ion is planar and therefore, it belongs to the D_{3h} symmetry. It is expected to display four modes of vibrations, $A_1' + A_2'' + 2E'$ (E' is a doubly degenerate motion). The vibration A_1' is only Raman active while the other ν_2 , ν_3 and ν_4 are infrared active. The stretching vibrations of the type; $\nu(\text{C-O})$; $\nu_3(E')$ is observed as a strong broad band in the range of $1500\text{-}1370\text{ cm}^{-1}$ while the stretching vibration $\nu(\text{C-O})$; $\nu_1(A_1')$ is observed in the region $\sim 1070\text{ cm}^{-1}$ as a medium-to-weak band. It should be indicated here that this motion (A_1') should be infrared inactive, its weak appearance in the spectrum of MgCO_3 could be related to weak solid-solid interactions causes the symmetry of CO_3^{2-} to be lowered than D_{3h} . The out of plane of vibration $\delta(\text{OCO})$; $\nu_2(A_2'')$ is

observed in the range of $\sim 860\text{ cm}^{-1}$ as a strong band while, the angle deformation bending vibration $\delta(\text{OCO})$; $\nu_4(\text{E}^-)$ appear in the range of 720 cm^{-1} as a medium strong. The infrared spectra of metal(II) carbonate, MCO_3 (formula 2), show that, some these products are hygroscopic and its clearly have moisture water. The band related to the stretching vibration $\nu(\text{O-H})$ of uncoordinated H_2O is observed as expected in the range of $\sim 3000\text{ cm}^{-1}$ Table 2.

Table 1: Elemental analyses data of Mn(II), Cd(II), Mg(II) and Ca(II) carbonate compounds

Compounds	Mwt.	Elemental analyses/ Found (Calc.)							
		%C		%H		%Metal		% CO_3^{2-}	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
MnCO_3	114.95	10.45	10.41	---	0.16	47.79	47.72	52.19	52.04
CdCO_3	172.42	6.97	6.93	---	0.11	56.20	56.11	34.80	34.39
MgCO_3	84.31	14.25	14.16	---	0.12	28.83	28.77	71.16	71.07
CaCO_3	100.09	12.00	11.94	---	0.10	40.04	39.97	59.94	59.88

Table 2: Infrared frequencies (cm^{-1}) and assignments of the products obtained from the reaction of (a): $\text{Mn}(\text{HCOO})_2 \cdot x\text{H}_2\text{O}$, (b): $\text{Cd}(\text{HCOO})_2$, (c): $\text{Mg}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ or (d): $\text{Ca}(\text{HCOO})_2$ with urea at 85°C temperature.

Frequencies*, cm^{-1}				Assignments
a	b	c	d	
2964 2925	3071 2954 2925	3649 3513 3446 2966 2925	2966 2925	$\nu(\text{O-H}); \text{H}_2\text{O}$
1463 1376 1070	1468 1077	1480 1467 1420 1378	1460 1383 1378	$\nu(\text{C-O}); \text{CO}_3^{2-}$
863 726	860 836 723	886 853 722	876 846 722 713	$\delta(\text{OCO}); \text{CO}_3^{2-}$

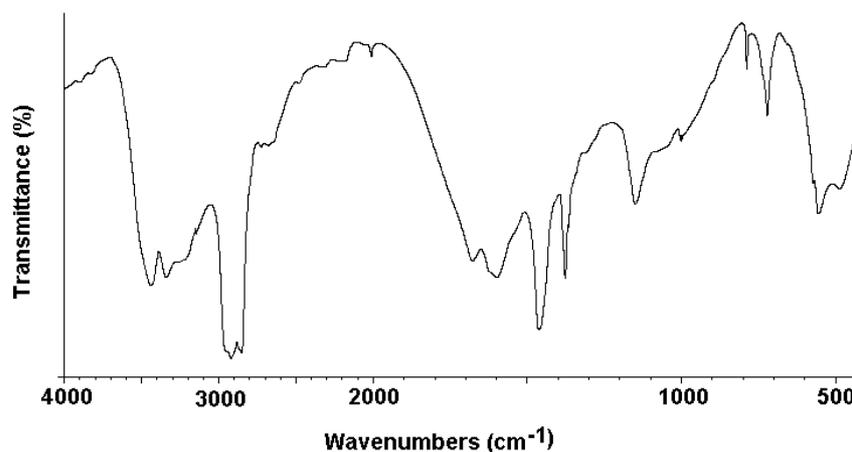


Fig. 1: Infrared spectrum of urea free ligand

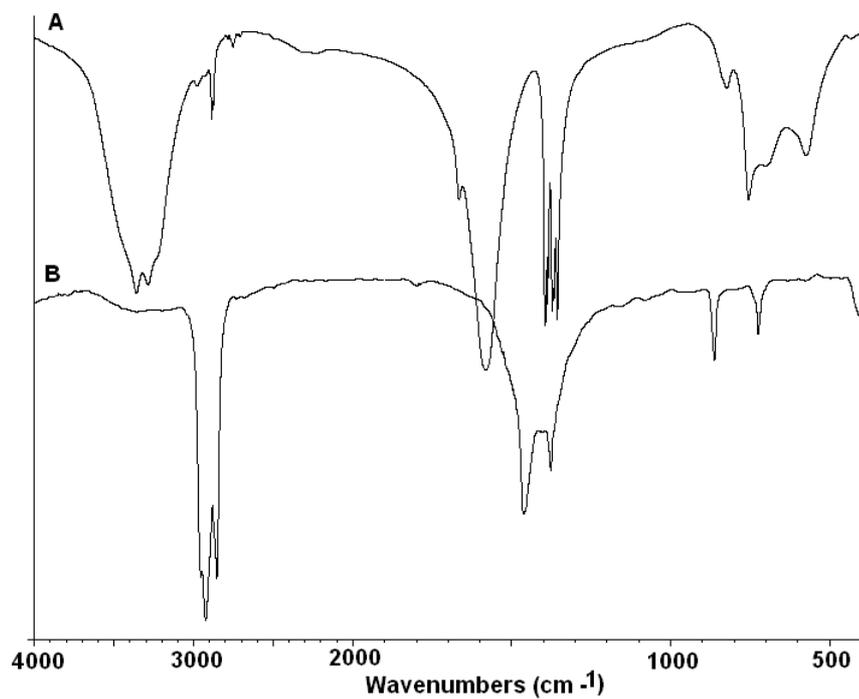


Fig. 2: Infrared spectra of Mn(HCOO)₂.xH₂O (A) and MnCO₃ (B) compounds

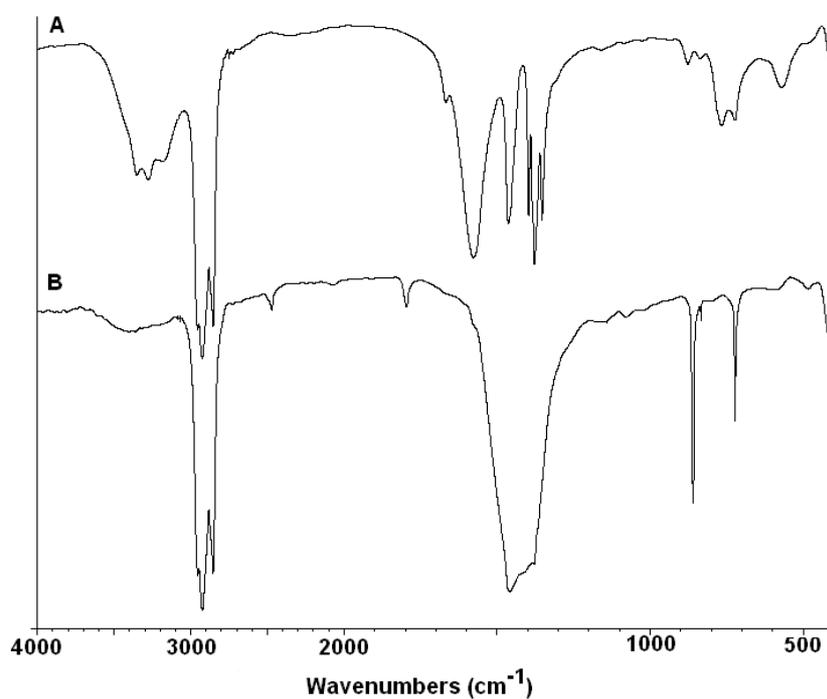


Fig. 3: Infrared spectra of Cd(HCOO)₂ (A) and CdCO₃ (B) compounds

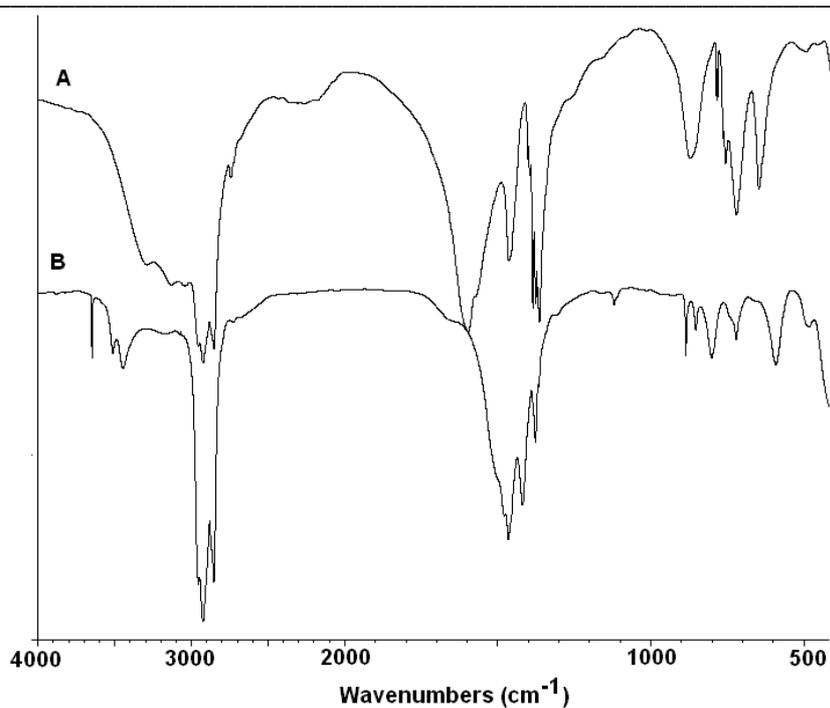


Fig. 4: Infrared spectra of Mg(HCOO)₂·2H₂O (A) and MgCO₃ (B) compounds

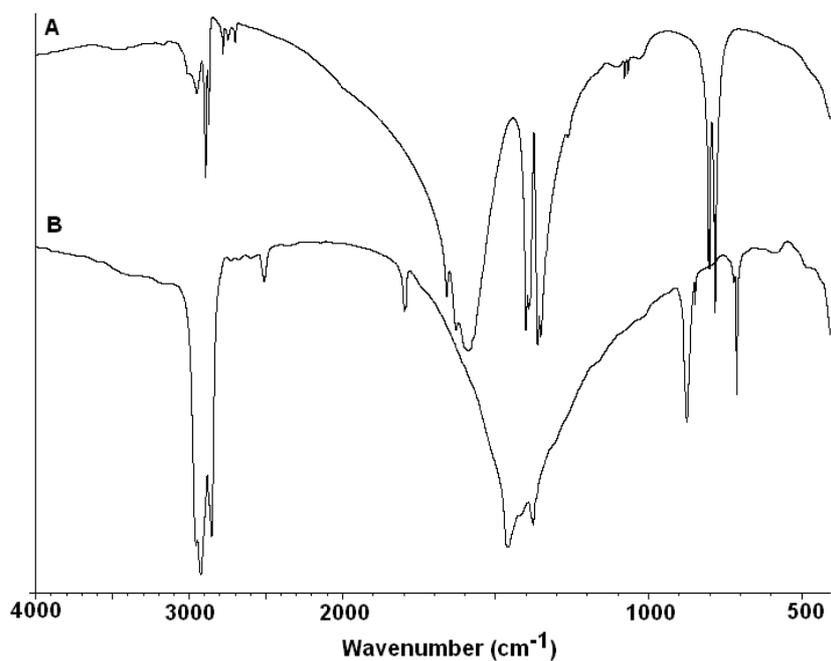


Fig. 5: Infrared spectra of Ca(HCOO)₂ (A) and CaCO₃ (B) compounds

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