

Impact of 2-Aminonicotinic Acid and/or β -Cyclodextrin on the Morphology of Metal Carbonates ($M = Ca^{2+}$ and Sr^{2+}) Crystallization

V. SREERAM^{1,*}, M.V. BASAVESWARA RAO² and KOYA PRABHAKARA RAO^{3,*}

¹P.G. Department of Chemistry, A.G. & S.G. Siddhartha Degree College of Arts & Science, Vuyyuru-521165, India

²Department of Chemistry, Krishna University, Machilipatnam-521001, India

³New Generation Materials Lab, Department of Science and Humanities, Vignan's Foundation for Science Technology and Research (VFSTR), Vadlamudi-522213, India

*Corresponding authors: E-mail: sreeramvenigalla2008@gmail.com; drkpr_sh@vignan.ac.in; kprao2005@gmail.com

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We examined the crystallization impact of the surfactant, 2-aminonicotinic acid and/or β -cyclodextrin on the formation of two anhydrous metal carbonates, MCO_3 ($M = Ca^{2+}$ and Sr^{2+}), from their respective calcium chloride and strontium chloride salts along with $NaHCO_3$ at room temperature. By varying the concentrations of this hybrid surfactant to the concentrations of MCO_3 during the preparations and examined their particle sizes by PXRD, FTIR, TGA and SEM. The characterization on these newly formed anhydrous metal carbonates clearly indicated that $CaCO_3$ formed with three different shapes such as truncated calcite, hexagonal calcite and rod shaped aragonite. Whereas, $SrCO_3$ formed with two different shapes such as hexagonal poles and bloom scale bars by varying concentrations of the surfactants. The mixed surfactant certainly made an impact on the metal carbonates formations with different shapes and sizes by varying surfactants concentrations and conditions.

Keywords: β -Cyclodextrin, Calcium carbonate, 2-Aminonicotinic acid, Strontium carbonate, Morphology.

INTRODUCTION

Nature utilizes many natural surfactants from plants and animals to control and direct the crystallization process during natural mineral formations. The natural and biological macromolecules could control the nucleation process during their formation to get various beautiful precious stones with amazing shapes and gem morphology. For example, natural network comprises of an auxiliary system of compromising hydrophobic macromolecules related to acidic macromolecules that go about as a nucleation surface for bio-mineralization. Later, these natural minerals give another course to integrate with various other minerals and materials to form a variety of new materials with desired properties and applications. In nature, the assortment of strong inorganic minerals and materials with intriguing properties and various leveled structures are solidified affected by natural surfactants [1]. Moreover, natural surfactants certainly impact the size, shape and morphologies of minerals and materials, which could certainly play a crucial

role in their physical, biological and mechanical properties of formed materials. In the literature, various studies were reported to investigate the impact of natural surfactants on the nucleation, development and morphology of inorganic materials [2-8].

Reused by the formation process of the biominerals utilizing natural layouts, along with new synthetic methodologies and processes achieved extraordinary materials in the field of biomimetic area of research and materials science [9-16] too. In fact, among the many important commonly used minerals, $CaCO_3$ is a seriously contemplated in light of its bounty as a biomineral in nature. Henceforth, for making a variety of morphologies of $CaCO_3$, various methodologies were tried including Langmuir monolayers [17], self-amassed monolayers [18], miscelles [19], microemulsions [20], etc. Moreover, as fluctuated dissolvable added substances such as manufactured peptides [21], dendrimers [22], microorganisms [23] and chiral compounds [24] have been studied to control polymorphs, directional conglomeration, size and shape control of $CaCO_3$ precious stones.

For this study, two anhydrous metal carbonates, CaCO_3 and SrCO_3 was chosen, since SrCO_3 crystallizes in strontianite form in most of the studies whereas CaCO_3 crystallize in three different morphologies *i.e.* calcite, aragonite and vaterite [25, 26]. Moreover, recently organisms control crystal morphology using various macromolecules, lipid membranes were reported [27]. However, to the best of our knowledge, there is no such study using 2-aminonicotinic acid and β -cyclodextrin on the mineralization process either CaCO_3 or SrCO_3 . In this article, the effect of this mixed surfactant, 2-aminonicotinic acid and/or β -cyclodextrin on the mineralization process of anhydrous metal carbonates, MCO_3 ($\text{M} = \text{Ca}^{2+}$ and Sr^{2+}) was studied. All the newly formed anhydrous metal carbonates minerals were characterized using PXRD, FTIR, TGA and SEM.

EXPERIMENTAL

Crystallization of calcium and strontium carbonates were completed in glass vessels. The chemicals CaCl_2 , SrCl_2 , NaHCO_3 , β -cyclodextrin and 2-aminonicotinic acid (corrosive) were kept for 24 h before the examination. All the chemicals used for this synthetic mineralization process were acquired from Merck/Aldrich and utilized moving forward without any more decontamination.

General mineralization process of MCO_3 ($\text{M} = \text{Ca}^{2+}$ and Sr^{2+}): At room temperature, 1 mM CaCl_2 (0.1470 g)/L 1 mM SrCl_2 (0.2662 g) was brought with three distinct extents of 2-aminonicotinic acid (0.2 mM, 0.1 mM and 0.05 mM) in 25 mL glass measuring cylinders. For this reaction mixture, 20 mL of distilled water was added by mixing altogether with the assistance of magnetic stirrer. Later, to the above reaction mixture, 2 mM NaHCO_3 (2 mL of 1.0 M) was added under continuous mixing. Finally, the reaction mixture was kept for 24 h for the crystallization process. The solid product washed few times with distilled water and dried at encompassing temperature. The dried anhydrous CaCO_3 and SrCO_3 were characterized by powder X-ray diffraction (PXRD), FT-IR, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM), *etc.* for understanding the morphology of these newly formed minerals.

Characterization techniques: Powder X-ray diffraction (PXRD) measurements were carried out using a Rigaku RINT powder X-ray diffractometer using $\text{Cu K}\alpha$ radiation. FTIR spectra were recorded using a Cary 639 FTIR with a Diamond ATR, Agilent Technologies, USA. SEM analysis was carried out using a JEOL JSM-6700F SEM. Thermogravimetric analyses (TGA) were carried out using a Hitachi STA 7200 under an N_2 flow with a 10 K min^{-1} ramp rate.

RESULTS AND DISCUSSION

Crystallization of calcium carbonate: A CaCO_3 crystal growth formation was monitored at various molar proportions of Ca^{2+} /2-aminonicotinic acid (ANA) at room temperature using the ratio of 5:1, 10:1, 20:1. Later, the crystallized products acquired at these conditions were characterized by SEM analysis are projected in Fig. 1. Without the usage of surfactant 2-aminonicotinic acid and/or β -cyclodextrin, thermodynamically most stable ordinary rhombohedral calcite crystal with particle size of around 30-60 μm as shown in Fig. 2. Moreover, surfactant

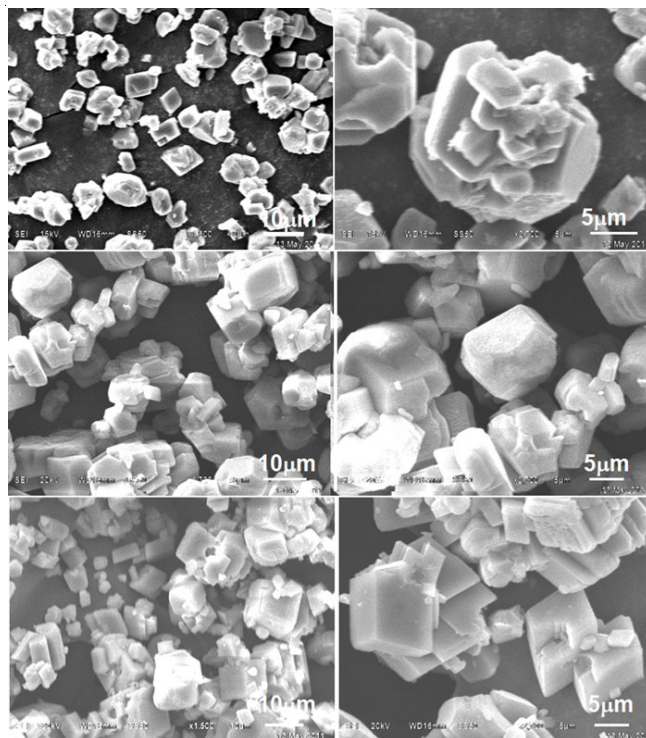


Fig. 1. SEM images of CaCO_3 particles with varying concentrations of ANA (left side) (a) 0.2 mM, (c) 0.1 mM and (e) 0.05 mM, (right side) (b), (d) and (f) with higher magnification, respectively

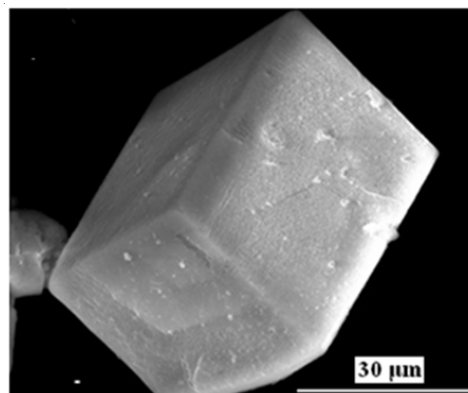


Fig. 2. SEM picture of CaCO_3 crystals in the absence of surfactant

concentrations controlled experiments at three different ways, only ANA (0.2 mM, 0.1 mM and 0.05 mM) and ANA (0.2 mM) + β -cyclodextrin and without any surfactant were also monitored.

SEM morphologies indicated that truncated calcite precious stones came about at lower (0.05 mM) and medium (0.1 mM) concentrations of 2-aminonicotinic acid (Fig. 1b-c), while on raising the concentration of ANA to 0.2 mM, hexagonal calcite gem developed on the rhombs shape (Fig. 1a). Whereas, when a mixture of 2-amino nicotinic acid (0.2 mM) and β -cyclodextrin were employed aragonite like calcite was noticed (Fig. 3). Without any surfactant ANA and/or β -cyclodextrin, calcite solid shapes are formed (Fig. 2).

PXRD analysis of CaCO_3 : The CaCO_3 crystals formed various synthetic conditions were carried out PXRD as shown in Fig. 4. The PXRD patterns indicated particular peaks that were normal for the (104), (006), (113), (202), (018) and (116)

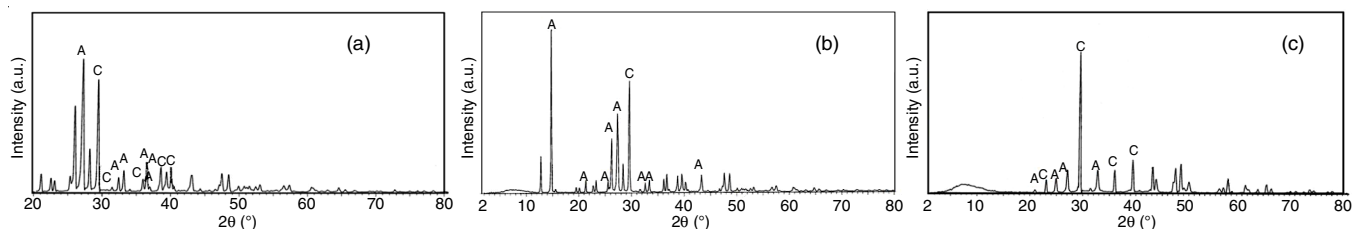


Fig. 4. Powder XRD patterns of CaCO_3 crystals in the presence of 2-aminonicotinic acid of 0.2 mM concentration (a); mixed surfactant of 2-amino nicotinic acid + β -cyclodextrin (b); and only β -cyclodextrin surfactant (c)

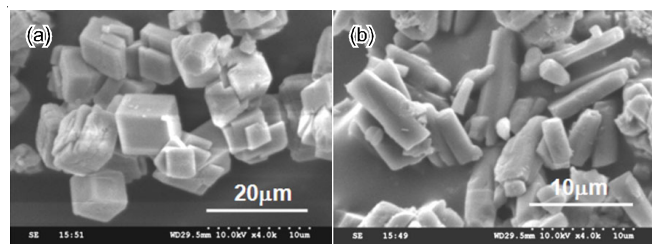


Fig. 3. SEM images of CaCO_3 crystals, (a) with β -cyclodextrin and (b) β -cyclodextrin and ANA (0.2 mM)

planes, indicated with unadulterated calcite crystals formation. These peaks corresponding the above mentioned plane were focused at $2\theta = 29.40^\circ$, 36.00° , 39.40° , 43.16° , 47.48° and 48.50° , individually. There was no other peaks were observed indicated that all the formed products were phase pure. This clearly indicated that the added surfactants in crystallization process have incredible impact on the size and morphology of CaCO_3 particles shapes. Moreover, the surfactant addition has no impact on CaCO_3 crystal structure of the subsequent calcite gems. Furthermore, when mixture of ANA + β -cyclodextrin was used as surfactant the aragonite peaks (A) more than calcite crystal (C), which would likewise be affirmed by the pole molded morphology acquired in SEM pictures.

FT-IR analysis of CaCO_3 : The FT-IR spectra of CaCO_3 particles formed at various synthetic conditions are shown in Fig. 5. The FTIR spectra confirmed the crystallization of the calcite crystal with characteristic peaks at 1706, 1322, 1031, 664, 581 cm^{-1} , relating to the corresponding to the ν_4 , ν_2 and ν_3 CO_3^{2-} absorption bands, respectively of calcite. Along with these characteristic peaks some other additional weak peaks seen which are related with the organic alkane and alkene C-H bond stretching peaks. This indicated that carboxylate and amino functional groups in these two surfactants remained firmly connected with the calcite crystals even after vigorous washing.

Crystallization of SrCO_3 : The SrCO_3 crystal growth formation was also monitored at various molar proportions of Sr^{2+} /2-aminonicotinic acid (ANA) ratio at room temperature. The crystallized products acquired at these conditions were also characterized.

At lower concentration levels of surfactant *i.e.* with molar ratio of 20:1 of Sr^{2+} /2-aminonicotinic acid, SrCO_3 crystal growth formation leads vaterite molded crystals are formed as shown in Fig. 6. While at higher concentration levels of the surfactant *i.e.* with molar proportion 5:1 of Sr^{2+} /2-aminonicotinic acid, SrCO_3 crystal growth formation to micro-rod hexagonal aggregates leads in the form of a flower like shaped structures were formed. SEM pictures of higher resolution indicated that these structures comprise nanosized particles. However, HRSEM

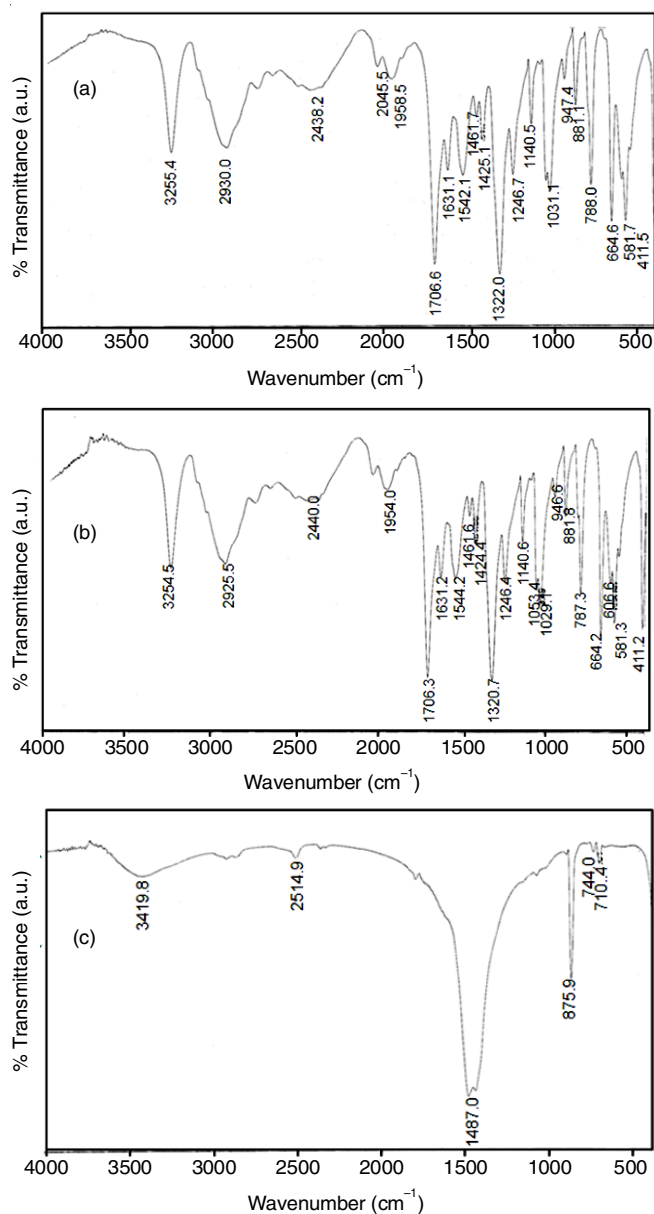


Fig. 5. FT-IR spectra of CaCO_3 crystals in presence of 2-aminonicotinic acid at 0.2 mM concentration (a); ANA + β -cyclodextrin (b); and only β -cyclodextrin surfactant (c)

morphology demonstrated that the crystals formed by using surfactants resulted microstructures (Fig. 7). From these SEM images, it is understood that the dendrite like morphology without any surfactant, converted into flower shaped structures under the influence of the surfactant ANA. Whereas, for the surfactant usage of ANA and β -cyclodextrin with three different concentrations, aragonite like SrCO_3 produced.

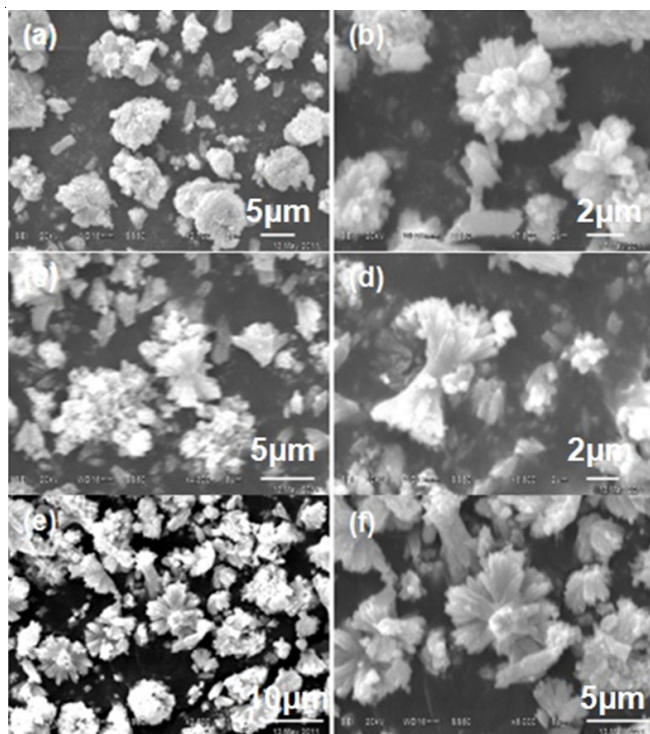


Fig. 6. SEM pictures of SrCO₃ particles with varying concentrations of 2-aminonicotinic acid, (left side) (a) 0.2 mM concentration, (c) 0.1 mM concentration and (e) 0.05 mM concentration, (right side) (b), (d) and (f) with higher magnification, respectively

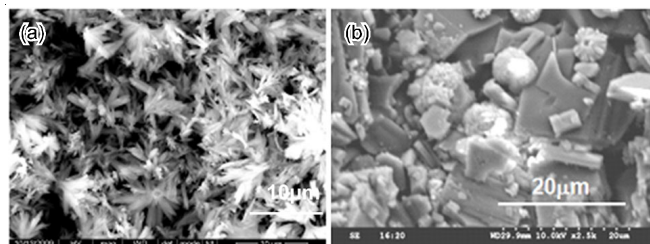


Fig. 7. SEM images of SrCO₃ crystals, (a) in the absence of 2-aminonicotinic acid and (b) in the presence of 2-aminonicotinic acid 0.2 mM concentration + β-cyclodextrin

XRD analysis of SrCO₃ samples: Powdered XRD patterns of SrCO₃ crystals formed under various synthetic conditions are shown in Fig. 8. The PXRD patterns indicated that all the peaks could be indexed in orthorhombic phase and no other impurity peaks were observed indicated the products obtained were of pure phase. The PXRD of obtained products indicated the characteristics peaks of the planes (111), (021), (002), (200), (130), (221) and (113) of pure strontianite crystals. The highest

intensity peak was (111) plane indicated that SrCO₃ crystallized predominantly along with the (111) plane. Moreover, PXRD pattern indicated that SrCO₃ crystallization using above synthetic method showed a very good crystallinity.

FTIR analysis of SrCO₃: In order to understand the impact of surfactant on the crystal growth of SrCO₃, of FT-IR spectra are recorded. The FTIR peaks at 1475, 1320 and 1323 cm⁻¹ comparable to the peaks of asymmetric stretching C-O bond. The sharp bands at ~857 and ~703, 857 and 664 cm⁻¹ are in plane and out plane bending of carbonate ion (CO₃²⁻). When compared the FTIR spectrum of SrCO₃ without ANA (Fig. 9a), the C-O stretching band at 1475 cm⁻¹ shifts higher wave number by 12 and 48 cm⁻¹ (1463 and 1427 cm⁻¹, respectively), when employed surfactants of ANA and β-cyclodextrin, respectively (Fig. 9c). Thus, FTIR results clearly indicated the influence of surfactants of ANA and β-cyclodextrin on the crystal growth formations.

Thermogravimetric analysis: TG/DTG thermograms of CaCO₃ and SrCO₃ crystals formed using the surfactant of 2-aminonicotinic acid are shown in Fig. 10. TGA analysis of CaCO₃ (Fig. 10a) indicated highest weight loss of 78 % observed in the temperature range of 290-340 °C. Besides, TGA profile of SrCO₃ crystals (Fig. 10b) also showed highest weight loss of 77 % in the temperature range of 300-360 °C. The CaCO₃ crystals using ANA surfactant indicated two stage weight losses. The first step weight loss observed in the temperature range of 290-340 °C is due to loss of 2-aminonicotinic acid. The 2nd step weight loss observed in the temperature range of 700-760 °C could be due to decomposition of CaCO₃ crystals into CaO and CO₂. Besides, SrCO₃ crystals using ANA surfactant indicated two stage weight losses. The 1st step weight loss observed in the temperature range of 300-360 °C, which is due to loss of 2-aminonicotinic acid. The 2nd step weight loss observed in the temperature range of 800-960 °C could be due to decomposition of SrCO₃ into SrO and CO₂.

Conclusion

Impact of surfactants 2-aminonicotinic acid and/or β-cyclodextrin on anhydrous metal carbonates, MCO₃ (M = Ca²⁺ and Sr²⁺) crystal formations at various concentrations and crystallization conditions were performed. The CaCO₃ crystals shown with truncated calcite, hexagonal calcite and pole formed aragonite morphology were formed at various conditions. Similarly, SrCO₃ particles with different morphologies, sizes and shapes were produced with shapes such hexagonal rods, flower like structures. When mixture of surfactants 2-aminonicotinic acid and β-cyclodextrin were employed for CaCO₃ crystallization

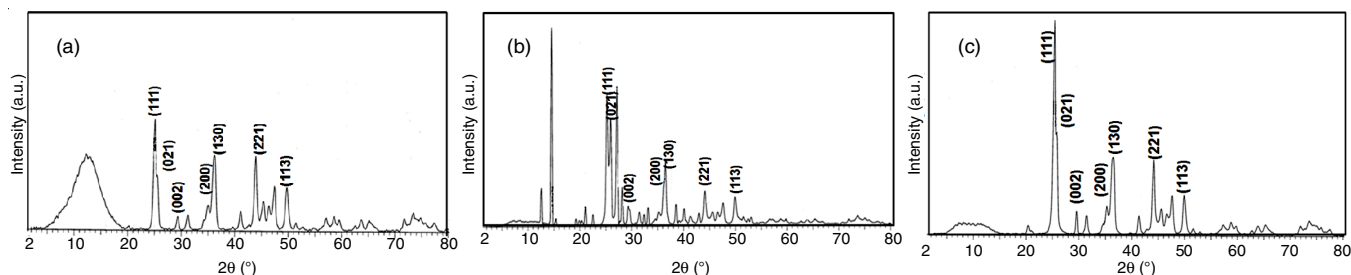


Fig. 8. Powder XRD patterns of SrCO₃ crystals in the absence (a) and in presence of 2-aminonicotinic acid at 0.2 mM concentration (b); 2-aminonicotinic acid + β-cyclodextrin (c)

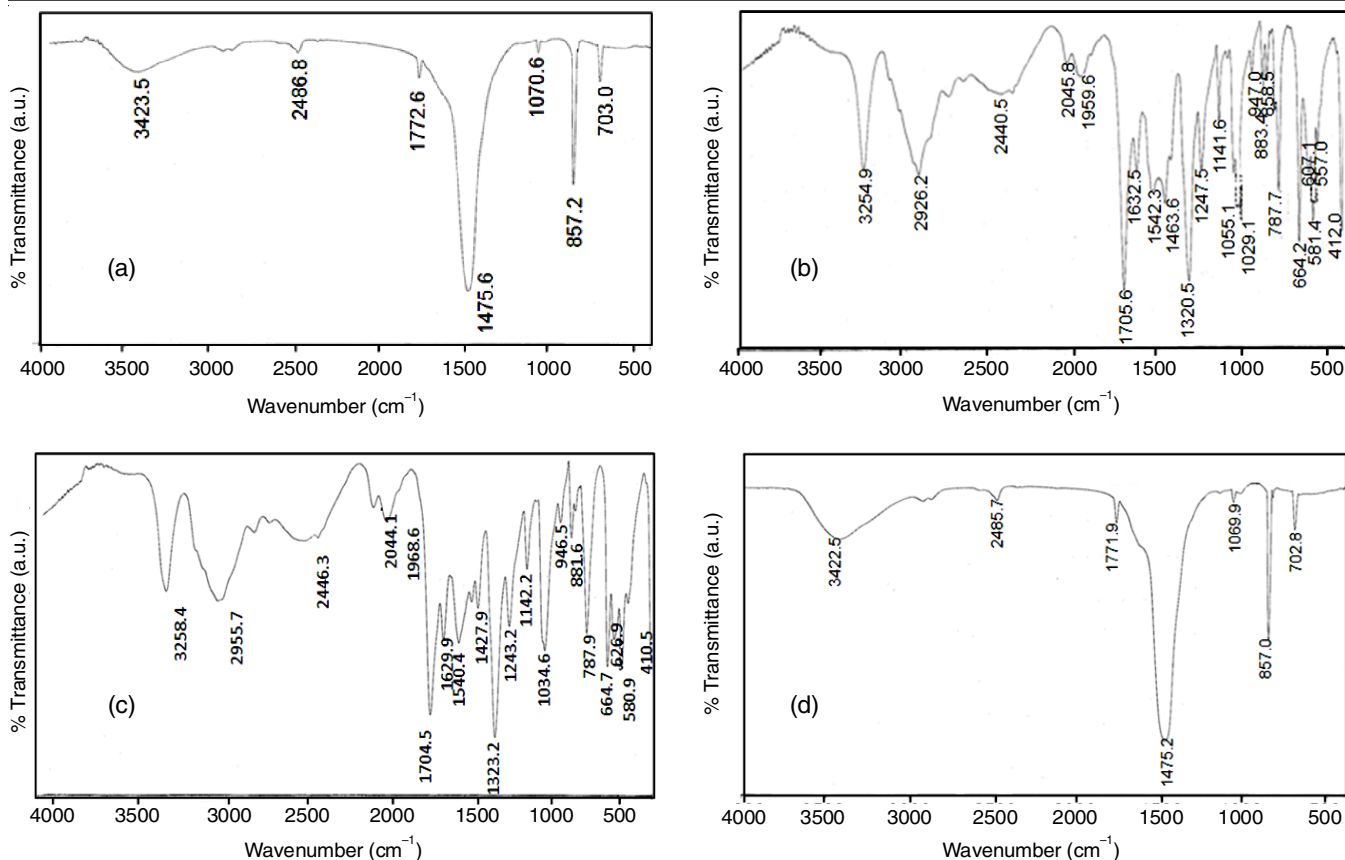


Fig. 9. FT-IR spectra of SrCO_3 crystals in absence of 2-aminonicotinic acid (a) and in the presence of 2-amino nicotinic acid at 0.2 mM concentration (b); in the presence of 2-aminonicotinic acid + β -cyclodextrin (c); and in the presence of only β -cyclodextrin (d)

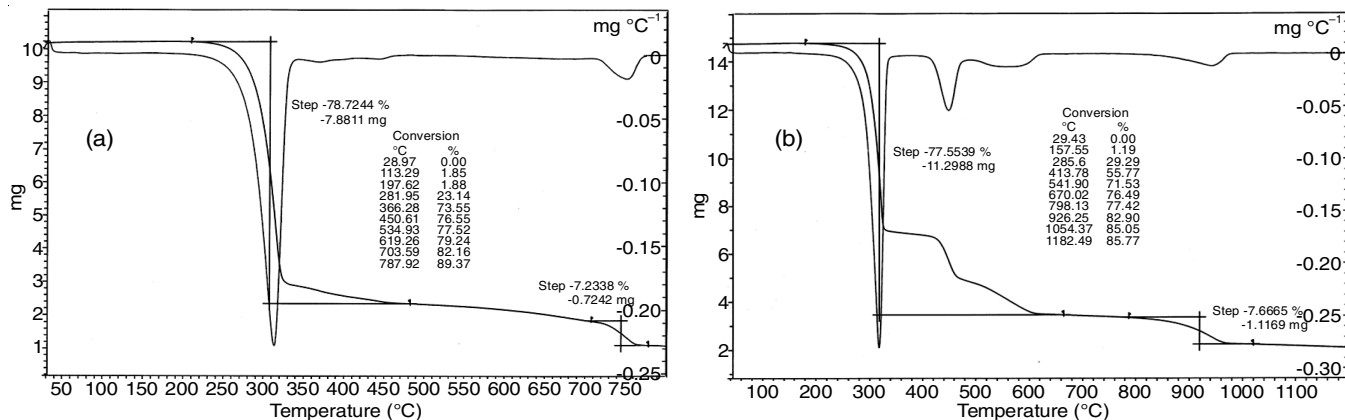


Fig. 10. TGA-DTA thermograms for CaCO_3 (a) and SrCO_3 (b) crystals in the presence of 2-aminonicotinic acid

leads to the formation of aragonite like structures. Moreover, at higher concentration, surfactants were employed for SrCO_3 crystal growth leads more predominantly flower like structures. From this study, it is concluded that the impact of surfactants used *viz.* 2-aminonicotinic acid and/or β -cyclodextrin on the crystal growth formation of metal carbonates, which leads to the structure-directing agents in the formation of microstructural minerals.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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