Short Communication

Crystallization study and morphology behaviour of calcium carbonate crystals in aqueous Surfactant-Pluronics® prototype

Bharatkumar Kanoje, Jigisha Parikh, Ketan Kuperkar

A Applied Chemistry Department, Sardar Vallabhbhai National Institute of Technology (SVNIT), Ichchhanath, Gujarat, India
b Chemical Engineering Department, Sardar Vallabhbhai National Institute of Technology (SVNIT), Ichchhanath, Surat, Gujarat, 395007, India

A R T I C L E   I N F O

Article history:
Received 28 April 2017
Accepted 12 October 2017
Available online 12 January 2018

Keywords:
Calcium carbonate
Surfactant
Pluronics®
Crystal growth
Diffraction
Scattering
Microscopy

A B S T R A C T

A facile procedure to fabricate the hydrophobic surfaces of calcium carbonate-polymer composites has been well described. Nano-sized highly ordered CaCO₃ clusters i.e. calcite/vaterite have been synthesized by simple precipitation in the presence of template made of cationic surfactant: cetyl trimethyl ammonium bromide (CTAB) and different non-ionic amphiphilic triblock copolymers comprising of PEO–PPO–PEO units: F98 and F127 commercially known as Pluronics® or Synperonics® or Poloxamers. The morphology of these nano-composites so formed was characterized in detail using spectroscopy, microscopy, diffraction, and scattering techniques. It was found that the surfactant-polymer prototype turned out to be an important parameter to tune and understand the shape-controlled morphology and crystallization in precipitated calcium carbonate (PCC). Our diffraction pattern depicted the presence of calcite/vaterite, while the microscopic investigations indicated the bunch/clusters of calcite (nano-flakes) arranged in stacks which could be attributed to the attractive hydrophobic interaction between the alky group of cationic surfactant and -PPO unit of the block copolymer. Similar assumptions were inferred by structural optimization using Gauss View 5.0.9. The scattering measurements described the polydispersity of nano-aggregates based on the scattering intensity. Results expounded the growth mechanism of CaCO₃ crystals to be a step-by-step build process with respect to the polarity.

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* Corresponding author.
E-mail: ketankuperkar@gmail.com (K. Kuperkar).

https://doi.org/10.1016/j.jmrt.2017.10.005
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1. Introduction

Controlled fabrication of inorganic compounds i.e., mineralization has become an attractive and challenging goal in materials chemistry research to tune well-desired and defined crystalline structures/shapes [1]. It involves different chemical synthesis route such as rapid mixing of calcium chloride and sodium carbonate, vapor diffusion, etc. [2]. However, the physico-chemical properties of such synthesized materials strongly depend on its morphology, size, crystal architecture and gets remarkably affected by various experimental conditions viz. pH, temperature, ageing time and presence of additives (templates) such as inorganic/organic salts, amino acids, surfactants, ionic liquids or polymers [3,4]. Calcium carbonate is one of such abundant minerals utilized extensively in paints, plastics, rubber, paper, cosmetics, electronics, medicine, catalysis, ceramics, etc. [5]. Amongst its three crystallographic phases, i.e., calcite, aragonite, and vaterite; studies have reported the former to be the most stable thermodynamically, while the later one is the least [6–8].

Recently, the amphiphilic block copolymers commonly known by their trade names as Pluronics® or Synperonics® or Poloxamers are found to be very effective in “crystal design” of CaCO3. These specially designed dysfunctional copolymeric surfactants have a symmetrical arrangement of poly(ethylene oxide)x–poly(propylene oxide)y–poly(ethylene oxide)z (PEO–PPO–PEO) blocks. They form micelles of core-shell architecture in aqueous solutions with hydrophobic core of –PPO unit and hydrophilic shell formed of –PEO unit (Scheme 1). However, the micellization process is again dependent on the polarity, compatibility between the polymer segments and their self-assembly behaviour in selective solvents. Pluronics® being non-ionic surfactant is relatively less toxic, eco-friendly and hence offer several industrial applications in and as detergents, dispersants, stabilizers, foaming agents, emulsifiers, etc. [9,10].

Reported studies have explained the role of surfactant concentration in tuning the kinetics of precipitation, polymorphism and crystal size of precipitated calcium carbonate (PCC). Surfactants are further known to influence the steps involved in the crystallization steps viz., nucleation, crystal growth, and aggregation, which otherwise are not easily formed naturally [11]. Studies have shown that surfactant alone does not bring a significant affect on the CaCO3 in aqueous media. Therefore, the combined use of additives such as solvents, polymers morphosynthesis, etc. along with the surfactants is accounted as an important parameter in tweaking the crystallization [12,13].

In this work, we attempt to investigate the crystallization of calcium carbonate using the Surfactant-Pluronics® template to shed light on how the complexity of the template influences the polymorphs of calcium carbonate under vigorous stirring conditions. Further, we have tried to propose the probable mechanism for which we have chosen two Pluronics® F98 and F127 with approximate similar HLB values but varying lipophilic -PPO blocks lengths. Thus, the effect of the lipophilic block length on the formation of polymer-surfactant complexation has been systematically investigated.

2. Experimental

2.1. Materials

Cetyltrimethylammonium bromide (CTAB) (purity >99.5%), calcium succinate, sodium carbonate were procured from Sigma–Aldrich. Sample solutions were prepared using double-distilled water. Pluronics®: F98 (structure – EO118PO45EO118, mol. wt. – 13,000 g/mol and HLB – 28) and F127 (structure – EO100PO45EO100, mol. wt. – 12,600 g/mol and HLB – 22) were received as gift samples from BASF Corp., Parsippany, USA and were used without further purification. The average molecular weights and HLB values of the copolymers were provided by BASF while the reported CMC values were obtained using pyrene probe.

2.2. Synthesis

Surfactant-polymer templates were prepared by mixing CTAB (1.3 mM) with respective Pluronics® (1 g/L) to prepare 80 mL solution (stirring time 1 h). Simultaneous addition of calcium succinate and sodium carbonate solutions (1 M each) to the template solution immediately formed the desired precipitated calcium carbonate (PCC). The reaction mixture was further stirred for 30 min and filtered using vacuum filter, washed several times with distilled water and placed in an oven at 50 °C for 30 min to dry.

![Scheme 1](image-url) – Pluronics® (a) structural formula with PEO–PPO–PEO repeating units (with –H and –OH as the terminal ends) (b) core-shell micelle structure.
2.3. Instrumentation

A systematic morphology characterization of PCC was done by Fourier Transform Infrared Spectroscopy (FT-IR) recorded on FT-IR SHIMADZU-8400S and by powder X-Ray Diffraction using X’TRA powder X-ray diffractometer (XRD-BD111915-Rigiku). The PCC images were captured using Hitachi S-3400N field emission scanning electron microscopy (FE-SEM), while particle size distribution was obtained by Malvern Zetasizer Nano (Malvern, UK) Dynamic light scattering (DLS) instrument. PCC dimension was obtained using Anton Paar SAXS pace instrument where the scattering intensity, \( q \), was monitored using a 2D-CCD detector (pixel size 24 \( \mu \)m) within a range of 0.01–0.65 \( \text{Å}^{-1} \). The 2D-SAXS images were processed into 1D scattering profile and were corrected for transmission and background scattering using standard protocols in the SAXS quant software.

3. Results and discussion

3.1. Characterization

Fig. 1a shows the FT-IR spectra of the CTAB modified CaCO\(_3\) particles in different block co-polymeric templates. The characteristic absorption bands observed at 712, 870, 875 and 1475 cm\(^{-1}\) confirmed the formation of calcite. The absorption peak at 1645, 1672, 1790, and 1793 cm\(^{-1}\) indicated

![Fig. 1 (a) Spectral and (b) diffraction analysis of CTAB modified PCC product in presence of various block co-polymeric templates.](image-url)
the stretching vibration of C=O. Weak bands observed at 2802 and 2872 cm$^{-1}$ represented asymmetric and symmetric methyl and ethylene C–H stretching respectively indicating the fair association of CTAB molecules with the calcite crystals.

The typical XRD patterns in Fig. 1b exhibited the calcite crystal nature of the obtained PCC in various fabricated Pluronic-surfactant templates (JCPDS: 33-0268). Diffraction peaks observed at 2$\theta$=29.4, 29.5, and 30 inferred the presence of higher amount of calcite form, while peaks at 2$\theta$=48.32, 48.52, 48.66, 48.68 and 48.88 indicated the composition of CaCO$_3$ microspheres exhibiting vaterite phase. As the polymer concentration increases, the intensity of all peaks decreases, implying the inhibition of crystallization and a reduction of crystallinity. Our XRD findings are evidently supported with those of FE-SEM images.

3.2. Growth morphology of PCC in Surfactant-Pluronics® template

The growth/nucleation of the PCC particles in F98 and F127 template solutions are presented in typical FE-SEM micrographs (Fig. 2).

A stack of rhomboedral crystals is found to be equally distant from one another, forming aggregates that can be taken approximately as a periodic lattice with period d. In amplified microscopic images, the overall stack geometry in case of F98 appeared to be somewhat disfigured with no sharp boundary due to the less attractive hydrophobic interaction between the alkyl group of CTAB and -PPO unit of block copolymer as compared to the hydrophilic F127, which exhibit more organized appearance due to fair association.

3.3. Molecular Optimization Study

Computational approaches have been used intensively to give the insight into the atomic studies of structure and dynamics in materials at different interfaces [14]. Based on our experimental findings, the quantum molecular simulations were performed using the semi-empirical method at a PM6 level, which inferred the electrostatic and hydrophobic interaction between CTAB and blocks of the copolymer (Fig. 3). The compact/overlap morphology was correlated with the calculated ionization potential, the total energy of molecular orbitals, dipole moment (l), highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital energies and the energy band gap ($\Delta E$) between them.

As could be seen from Fig. 3, the distance between Br$^-$ ion and N$^+$ ion is of about 3.402Å. Here the blue coloured N$^+$ ion of ammonium polar headgroup of CTAB gets bonded with the terminal end of the -PEO unit of the block copolymer forming the probable hydrogen bond with the bond length of 5.941Å. While the distance between N$^+$ ion and oxygens neighbouring -PPO units is around 5.078Å and 6.248Å. This could be attributed to the hydrophobic interaction of -PPO unit and hydrophobic chain of CTAB. The O$^-$ at the other terminal end of -PEO unit is at about 8.386Å from N$^+$. The quantum chemical parameters such as HOMO and LUMO regions represented in mesh form are found to be surrounding N$^+$ ion. After simulation, the value of $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ were evaluated as $\sim$0.2967 and $\sim$0.0003, respectively. It was found that the value of $E_{\text{HOMO}}$ is lower than $E_{\text{LUMO}}$, which clearly indicate the less probability of CTAB to donate the electrons to the polymer. Further, the $\Delta E$ (eV) which is the difference between the respective molecular orbitals is found to be very low, i.e., 0.2964 eV, thereby, indicating the system to be soft which could act as an adsorbent for the adsorbate CaCO$_3$. In addition, the
Fig. 3 – Optimized structure of CTAB with the general block co-polymer chain comprising of PEO–PPO–PEO units. The HOMO (red colour) and LUMO (green colour) are represented in coloured lobes. To avoid clumsiness in the optimized figure we have not shown the hydrogen atoms. Here the dotted line does not indicate the hydrogen bond and only represents the bond length.

Fig. 4 – Schematic mechanism showing the morphology modification and nucleation of PCC using Surfactant-Polymer template.
dipole moment \( \mu = 12.42 \text{Debye} \) of CTAB + Pluronic® is little higher which indicates a fair adsorption of polymer onto the CTAB.

3.4. Crystal growth mechanism of CaCO₃ polymorphs in surfactant-polymer templates

The underlying mechanism of “in situ” changes of crystal growth is attributed to the adsorption of surfactant at selected crystal/solution interface [15]. However, the crystallization and aggregation mechanism, i.e., the enrichment of Ca²⁺ on surfactant-polymer superstructures, is still unclear. We have proposed a probable mechanism to facilitate the PCC nucleation in presence of the template to facilitate a better understanding involved in organic-inorganic interactions. It has been reported that organic molecules when present in a crystallizing solution, dramatically influence the rates and/or mechanisms of crystallization thereby inducing the changes in the size distribution, morphology, and polymorphism.

Here surfactant-polymer-CaCO₃ template interface region functions like the chemical microenvironment where nucleation of CaCO₃ occurs [16]. The CTAB micelles exhibit small particle size distribution, but its combination with the polymer leads to the chemical interactions with the growing PCC and thereby influences the crystal morphology. However, the variation in the hydrophobicity and molecular weight of co-polymer plays a drastic role in influencing the morphology of CaCO₃, which reflect the influence of polymer polarity. The resultant complexation exhibit uniform size distribution with polymer chain orientation, which was justified by the optimized results. Thus, mechanism of nucleation/growth in CaCO₃ occurs under the co-operative effect of the CTAB micelles and adsorption of the block co-polymer chains resulting in distorted/sharp edges in stack architectures. Such behaviour could be due to the hydrophobicity of F98 and F127, which interact with CTAB by strong intermolecular interaction and undergo complexation with CaCO₃ (Fig. 4).

3.5. Dimension of PCC in Pluronics®-Surfactant template

Scattering techniques are reported to make important contributions in understanding the characterization of complex and their internal structures on a mesoscopic scale.

The calcite form of the material gave rise to a consistent scattering profile with little/no structural complexity (Fig. 5a). The scattered intensity \( I(Q) \) due to this kind of aggregate is well fitted and explained by the Debye, Anderson and Brumberger model [17]. The curves in the insight are divided into three regimes, i.e., scattering at low Q region is dominated by a steep linear decay owing to the large external facets of the powder grains (regime-I), whereas, small nanostructural features within the mineral particles give rise to a slide bent curve shape (regime-II and -III). Such minor deviation in the scattering curve is most likely due to surface roughness [18]. The evaluated correlation length in homogeneous CTAB modified calcite mixture using F98 is 14.6 nm and 28.5 nm in F127, which gets well supported by the distribution results obtained by DLS (Fig. 5b). Such behaviour could be attributed to the polymer polarity, i.e., the degree of hydrophilicity of F127 is more than F98, which makes it more feasible in tuning the crystal morphology.

Fig. 5 – Analysis for powdered samples of calcite in Pluronics®-surfactant template: (a) SAXS analysis of the orientation-averaged plot of the scattering intensity versus the modulus of the scattering vector Q (log-log representation). The control sample showed an intensity decay of \( I(Q) \propto Q^{-4} \) over the entire Q-range, thus indicating the absence/little structural complexity at the length scale of nanometres. In the scattering profile recorded, there is a deviation from porod-like behaviour in the low Q regime, which might be attributable to the rough-textured topography of the particle surfaces. The profile of both specimens presented (insight) is the magnified region with the slope is \( Q^{-4} \). (b) Observed size distribution curves recorded using DLS.

4. Conclusion

This study offers a systematic characterization using spectral, diffraction, scattering and microscopy techniques to
understand the crystallization behaviour and morphology design of the mineralized PCC using Pluronics®-surfactant prototype. Our findings indicated the dependence of the carbonate particles onto the structure of the segmented blocks of PEO–PPO–PEO in the copolymer which facilitates the complexation and redefines the bunch/stack like calcite/vaterite morphology. This could be inferred to the sufficient particle size distribution, which is a combinational effort of CTAB with the copolymer thereby influencing the crystal morphology, as CTAB micelles alone do not exhibit a wide particle size distribution. The obtained scattering results could be due to the influence of polymer polarity and to the attractive hydrophobic interaction between the alkyl group of cationic surfactant and -PPO unit of block copolymer, which was well supported by molecular optimization study. Thus, such behaviour in CaCO$_3$ is due to the co-operative effect of the surfactant micelles and the polymer chain adsorption resulting in the controlled functional architectures which could be of interest in materials research.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

Authors express sincere thanks to Dr. P.A. Hassan, Scientist, Chemistry Division, BARC-INDIA, Technical Education Quality Improvement Programme-II (TEQIP-II) for financial aid, Indian Institute of Technology Gandhinagar, Gujarat and Sardar Vallabhbhai National Institute of Technology, INDIA for instrumentation facility.

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