

Effects of sodium dodecyl benzenesulfonic acid (SDBS) on the morphology and the crystal phase of CaCO_3

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Abstract—The effects of anionic surfactant on the morphology and crystallization of calcium carbonate precipitated from CaCl_2 and Na_2CO_3 were investigated. Although reaction temperature did not have an effect on the morphology of calcium carbonate, it did have an effect on the cluster size. The cluster size became bigger with high reaction temperature. With the addition of sodium dodecyl benzenesulfonic acid (SDBS), the morphology of precipitated calcium carbonate changed from cubic to porous spheres with over 98% of the crystal phase transformed from calcite to vaterite. The analysis of precipitates formed by the reaction of CaCl_2 solution (from limestone (CaO 50% content)) and Na_2CO_3 found that the morphology of precipitated calcium carbonate changed from cubic to spherical, and the crystal phase changed from calcite to over 94% vaterite with the addition of sodium dodecyl benzenesulfonic acid. These vaterite structures were solid spheres rather than hollow ones.

Key words: Calcium Carbonate, Anionic Surfactants, Calcite, Vaterite, Drug Delivery System

INTRODUCTION

Calcium carbonate (CaCO_3) has calcite, aragonite and vaterite crystal structures, with calcite the most stable. In natural conditions, vaterite is thermally unstable, and thus is easily re-crystallized to calcite [1-4]. To control calcium carbonate crystallization, $\text{Ca}(\text{OH})_2$ - CO_2 - H_2O systems and CaCl_2 - Na_2CO_3 system are used. In the former, controlling the phase of calcium carbonate is difficult, first because of the ductility factor of limestone during calcining for 1 to 2 hours at 1,000 °C in a kiln, and second because lime milk ($\text{Ca}(\text{OH})_2$) is manufactured by the hydration of CaO. Cubic, calcite calcium carbonate usually then forms from the lime milk and CO_2 due to the effects of SiO_2 , MgO, Fe_2O_3 , Al_2O_3 impurities in the limestone and the reaction with lime milk [5]. A kiln's fuel differs depending on the kiln type, which affects CaO morphology [6]. Therefore, the formation of vaterite structures in calcite is studied through controlling CaCl_2 - Na_2CO_3 systems [7-9].

The crystal structure of CaCO_3 can be controlled by additives in the CaCl_2 - Na_2CO_3 system. Polymorphs of CaCO_3 can be produced by forming chains of Ca^{2+} and CO_3^{2-} ions in organic media [10]. Vaterite CaCO_3 with spherical structures is thermally stable in aqueous solutions and is synthesized with organic acid additives [11-16]. Also, spherical vaterite CaCO_3 can be synthesized by adding amino acids in bio-mineralization systems [17,18]. Polymorphous CaCO_3

can also be synthesized with inorganic additives [19] or enzymes [20,21].

Encapsulation through self-assembly can coat functional substances with outer layers, with variously sized macro-, micro-, or nano capsules and also multilayer capsules possible. Encapsulation protects the inner material from the outside environment, and thus protects it from oxidation and other degradation, maintaining its capability and stability. Encapsulation also facilitates the coated substance's application in various systems by controlling its release through the coating substance that can be chosen for its behavior in various environments [22-25].

Recently, porous spherical vaterite CaCO_3 has been synthesized by layer-by-layer (LBL) self-assembly encapsulation and applied to drug delivery systems (DDS). Shape and crystallization can be controlled through the use of additives during calcium carbonate growth in layer-by-layer self-assembly systems. Such systems can be used to control the release of such as proteins, antibiotic and anti-cancer agents with the use of anionic PSS (poly(sodium 4-styrenesulfonate)) and cationic PAH (poly(allylamine hydrochloride)) electrolytes [26-37].

Vaterite CaCO_3 has been studied though adding SDBS, an anionic surfactant similar to the anionic electrolyte PSS, to CaCl_2 - Na_2CO_3 systems [38-41,43-46]. According to the studies, hollow-type vaterite CaCO_3 could be synthesized by adding commercial CaCl_2 .

This work aimed to synthesize vaterite CaCO_3 of solid spheres rather than hollow ones. For the purpose, the anionic surfactant and CaCl_2 solution through the Solvay process with the use of lime-

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stone (CaO, 50%) were employed instead of commercial CaCl_2 .

EXPERIMENTAL

1. Materials and Characterization

CaCl_2 of purity >74%, MW 110.99 was supplied by OCI Company, Korea. Na_2CO_3 of purity >99.2%, MW 116 was supplied by OCI Company, Korea and used without further purification. Limestone with 50% CaO content was supplied by BeakKwang Mineral Material Co. Ltd., Korea. The anionic surfactant was SDBS (sodium dodecyl benzenesulfonic acid 50%, $\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$, JUNSEI, MW 348.48). HCl and NaOH (OCI company, Korea) of 98% purity were used.

The crystal shape and quantity of CaCO_3 were analyzed by an x-ray diffraction system (D/MAX2500V/PC, Rigaku, Japan) with maximum power 18 kW, voltage 60 kV, current 300 mA, and Cu/K-alpha radiation. Particle size of CaCO_3 was measured by the particle size analyzer (LS13320, Beckman Coulter, U.S.A.). A field emission scanning electron microscope (FE-SEM model: S-4300, HITACHI, Japan) was used to analyze the microstructure and shape of the CaCO_3 . CaO content of the limestone was analyzed by an x-ray fluorescence spectrometer (ZSX Primus II, Rigaku, Japan). The purity of $\text{Ca}(\text{OH})_2$ was analyzed by adding NaOH (2 mol) to the manufactured CaCl_2 . The vibrational frequencies of the CO_3^{2-} ions of the synthesized CaCO_3 were analyzed by Fourier transform infrared spectrometry (FT-IR, Vertex 70, Bruker Optics, Germany).

2. Syntheses of CaCO_3

2-1. Without Anionic Surfactant

Samples a, a-1, a-2 and a-3 were formed from equimolar portions of CaCl_2 and Na_2CO_3 agitated for 1 hour at pH=9. The samples were thrice washed with distilled water and then dried for 12 hours

at 70 °C. The four samples were synthesized at room temperature, 40 °C, 60 °C, and 80 °C, respectively (Fig. 1).

2-2. With Anionic Surfactant

Samples b, b-1, b-2, b-3 and b-4 were similarly formed from equimolar portions of CaCl_2 and Na_2CO_3 agitated for 1 hour at pH=9. They too were thrice washed with distilled water and dried for 12 hours at 70 °C. The samples' molar SDBS contents relative to either CaCl_2 or Na_2CO_3 were 0.3%, 0.1%, 1%, 50% and 100% respectively (Fig. 1).

2-3. With Anion Surfactant using Limestone

Limestone (CaO content 50%) was pulverized to 2-5 mm and further diminished by a water mill. 125 μm particles were used after sieving. After reacting 1 kg limestone powder with 6 M HCl, pure CaCl_2 solution was produced by two cycles of filtering through glass fiber. Reacting a 1 : 1 : 1 molar ratio of Na_2CO_3 , SDBS and the CaCl_2 solution produced CaCO_3 (sample b-5). Sample b-6 CaCO_3 was similarly synthesized but without the surfactant. The impurities of the CaCl_2 solution were assayed by synthesizing $\text{Ca}(\text{OH})_2$ (sample b-7) with a 1 : 2 molar ratio of CaCl_2 and NaOH (Fig. 1).

RESULTS AND DISCUSSION

1. The Effect of Temperature on CaCO_3 Synthesis

The crystallization of CaCO_3 polymorphs in the CaCl_2 - Na_2CO_3 system can be controlled by pH, the presence of additive and seed, temperature, and concentrations/super-saturation [7-9].

In this study, the effects of temperature on the CaCl_2 - Na_2CO_3 system without surfactant were tested (Fig. 1). Eq. (1) describes the system's reaction.

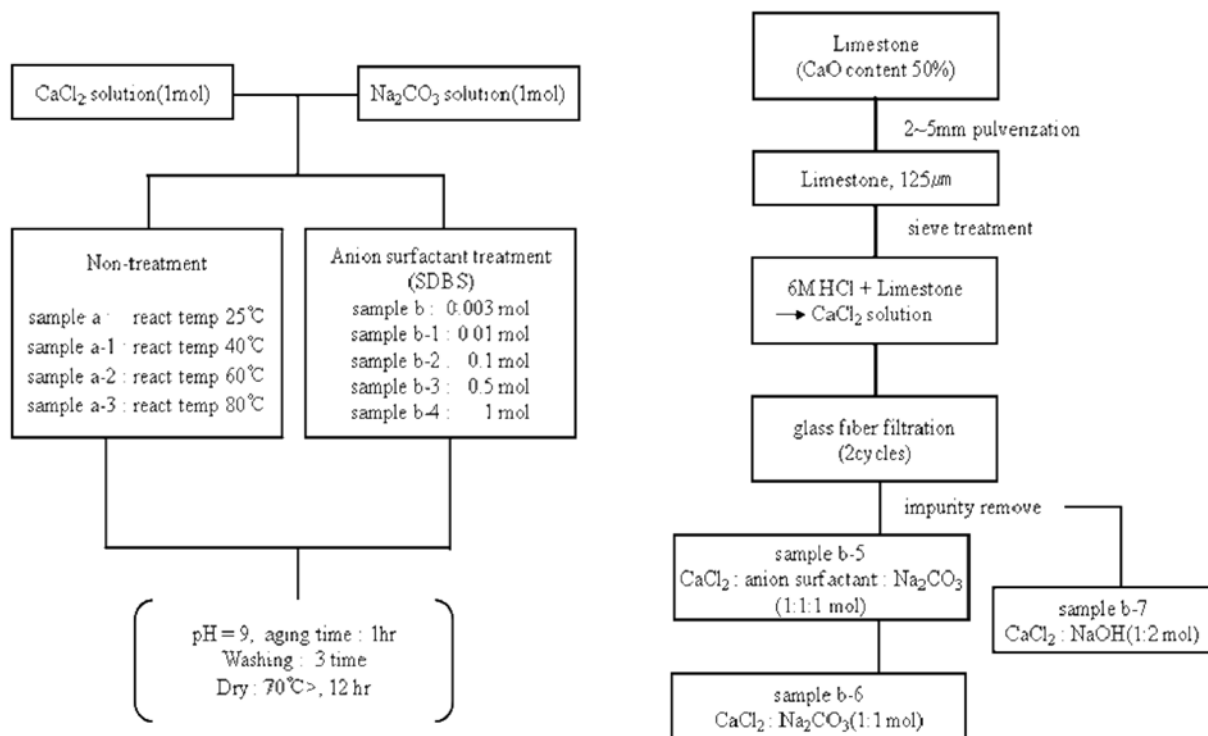


Fig. 1. Syntheses of CaCO_3 .

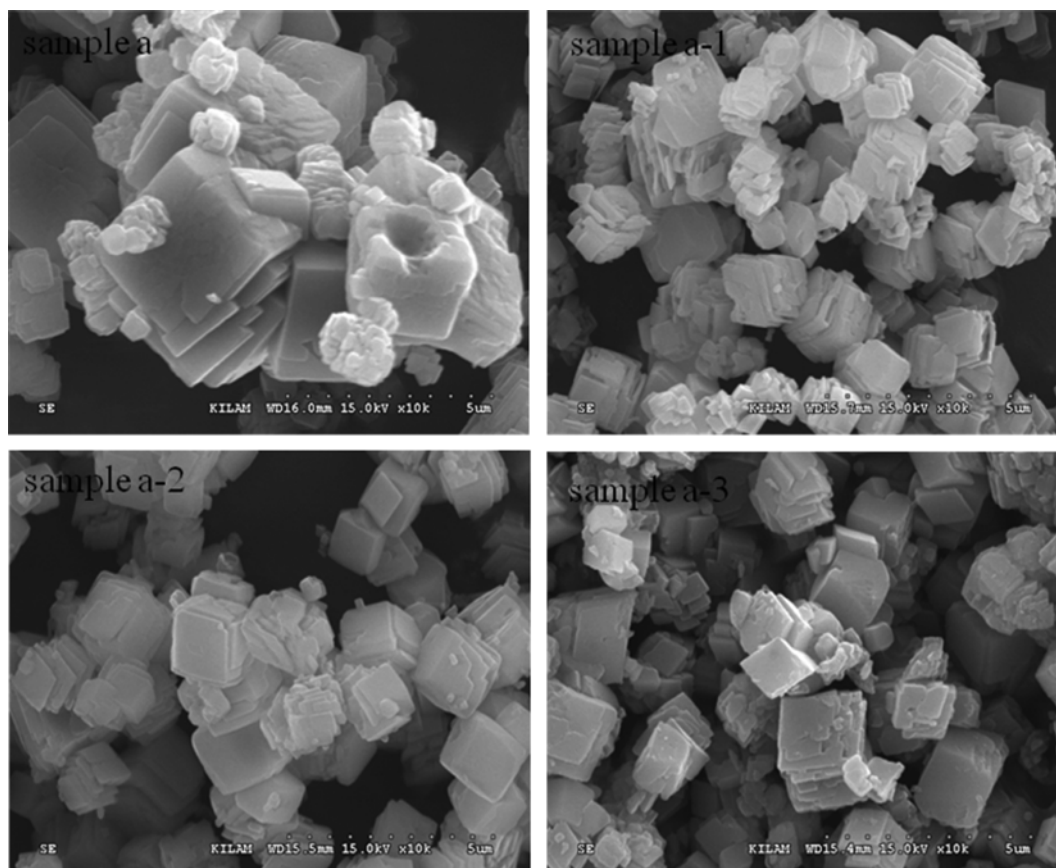


Fig. 2. SEM images of samples a (room temp.), a-1 (40 °C), a-2 (60 °C), a-3 (80 °C) (pH=9, CaCl_2 : Na_2CO_3 1 : 1 molar ratio).

The syntheses were performed at pH 9, and a 1 : 1 mol ratio of CaCl_2 and Na_2CO_3 . Temperatures ranged from room temperature to 80 °C. SEM images of the samples indicate that they were not affected by temperature: all formed the most stable structure, cubic calcite (Fig. 2) [2,7-9]. XRD analysis confirmed their calcite structures (Fig. 6). However, vaterite CaCO_3 has been reported from CaCl_2 - Na_2CO_3 systems [31-37]. The sudden mixing of CaCl_2 and Na_2CO_3 with agitation for 30 s at room temperature followed by their undisturbed settling for 10 to 15 minutes can form amorphous, spherical, micro-crystals slowly through the transformation of calcium carbonate. Through the physical or chemical adsorption of anionic or cationic electrolytes to these micro-spheres, proteins and other useful substances can be loaded. In particular, D. V. Volodkin [36] noted the instability of vaterite CaCO_3 through its recrystallization (>80%) to the calcite structure in aqueous solution over 24 hrs. In the same work vaterite CaCO_3 was stabilized by electrolyte (PAH/PSS)₃ and could withstand storage for one week at room temperature. This indicates that cores formed through volume disorder by PSS of $\text{Ca}(\text{R-SO}_3)_2$ and CO_3^{2-} ion through reaction with R-SO_3^- (Fig. 4).

Results indicated that the crystal morphology of calcium carbonate was not affected by temperature. On the other hand, the cluster size was affected by temperature (d_{50} =3.35 μm at 40 °C, d_{50} =4.41 μm at 80 °C).

2. The Effect of Anionic Surfactant on CaCO_3 Synthesis

2-1. Effects of SDBS on the Morphology of CaCO_3

Equimolar ratio CaCl_2 and Na_2CO_3 systems for CaCO_3 synthe-

sis were tested with various amounts of SDBS additive from 0.003 to 1 mol with the aim of synthesizing vaterite CaCO_3 through its controlled crystallization using limestone. A low molecular weight anionic surfactant was used for this, whose structure is similar to that of the anionic electrolyte PSS [38-41]. Samples' SEM images are shown in Fig. 3 and indicate that sample b (0.003 mol SDBS) was calcite CaCO_3 , similar to sample a, and that samples b-1 (0.01 mol SDBS), b-2 (0.1 mol SDBS) and b-3 (0.5 mol) exhibited both calcite and vaterite structures. With anionic surfactant, white $\text{Ca}(\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3)_2$ formed through the reaction of Ca^{2+} and CO_3^{2-} ions with the SDBS, while calcite and vaterite CaCO_3 formed through the reaction of Ca^{2+} and CO_3^{2-} ions with Na_2CO_3 . In sample b-4 (1.0 mol SDBS) CaCO_3 was synthesized with a hollow, vaterite structure. Thus hollow, spherical CaCO_3 vaterite structures were created through the formation of cores by the reaction of Ca^{2+} : $\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$: CO_3^{2-} with CaCO_3 core grains gathering by volume disorder from the surfactant's covalent electrons. This process showed similar results to the vaterite CaCO_3 synthesis reported by D. V. Volodkin that employed PSS rather than SDBS [36].

Vaterite structures crystallize in various ways and can become rose-shaped with growth in the x, y and z directions. Vaterite structures' crystallization can depend on the type of functional group (SO_3^-). The SEM images of samples b-2 (0.1 mol SDBS) and b-3 (0.5 mol SDBS) show their rose-shaped structures (Fig. 3) [39]. This kind of structure is believed due to the hydrophobic property of SDBS. The hydrophobic interaction between SDBS-plates might result in different angles and grow into rose-shaped.

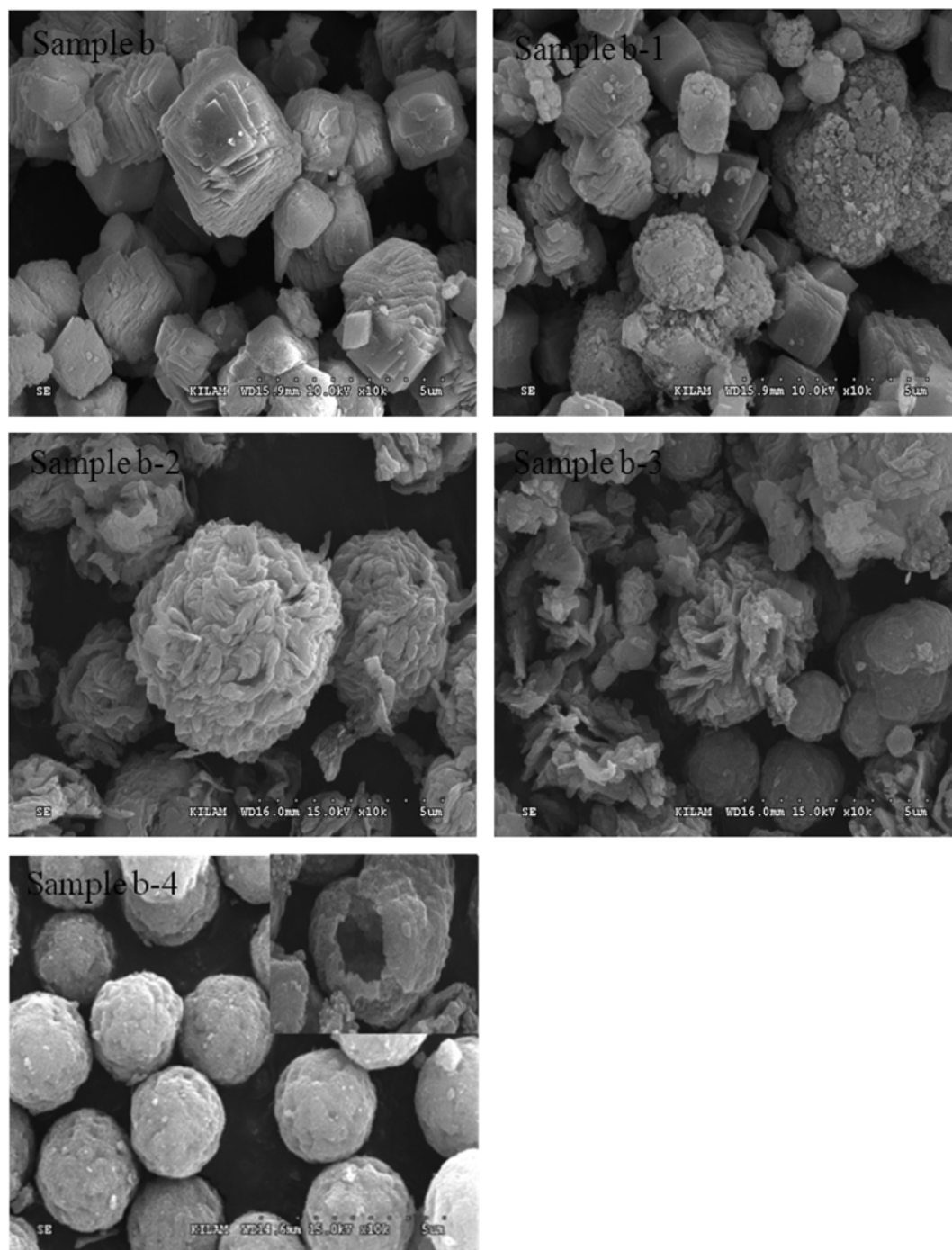


Fig. 3. SEM images of samples b (0.003 mol SDBS), b-1 (0.01 mol SDBS), b-2 (0.1 mol SDBS), b-3 (0.5 mol SDBS), b-4 (1 mol SDBS) (pH=9, CaCl_2 : SDBS : Na_2CO_3 (1 : 1 molar ratio)).

XRD analysis of the b-series (without b-7, Fig. 7) also shows that with increasing concentration of anionic surfactant, a transfer from calcite to vaterite structures occurred. As sample b-4 was found to be of vaterite structure, it was subjected to further quantitative XRD analysis (Fig. 9), which found hollow CaCO_3 structures of 1.5% calcite and 98.5% vaterite.

Fig. 12 shows results of FT-IR analysis of samples, b to b-5 with CaCO_3 vibrational frequencies of CO_3^{2-} ions. The following peaks were observed for the samples: b, calcite ($713, 1,426 \text{ cm}^{-1}$) and vater-

ite (878 cm^{-1}); b-1, calcite ($712, 1,434 \text{ cm}^{-1}$) and vaterite (877 cm^{-1}); b-2 calcite ($712, 1,426 \text{ cm}^{-1}$) and vaterite (878 cm^{-1}); b-3, calcite ($713, 1,426 \text{ cm}^{-1}$) and vaterite ($745, 878 \text{ cm}^{-1}$); b-4, calcite ($1,440 \text{ cm}^{-1}$) and vaterite ($745, 877 \text{ cm}^{-1}$). The figure also indicates the to The SEM images of Fig. 3, the XRD analysis of Fig. 7 and the XRD quantitative analysis of Fig. 9 support the conclusion that an increase of anion surfactant facilitated the formation of CaCO_3 micro-particles, while maintaining their spherical shape through the volume disorder of the anion surfactant, which also stabilized them in aque-

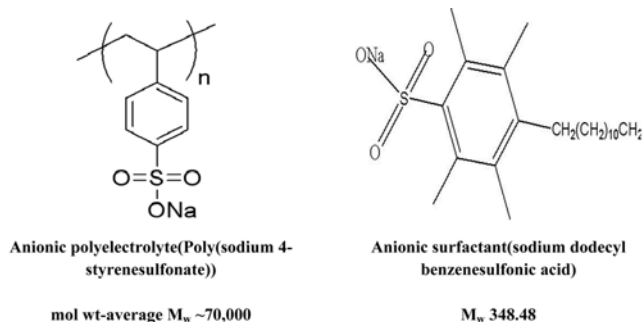


Fig. 4. Chemical structure of anionic polyelectrolyte (Poly(sodium 4-styrenesulfonate), left) and anionic surfactant (sodium dodecyl benzenesulfonic acid, right).

ous solutions.

2-2. Mechanism for the Crystallization of CaCO_3 with SDBS

Many researchers reported rose-shaped CaCO_3 with anionic surfactants [39,43-45]. Huang et al. [39] reported that the shape of CaCO_3 changed from monolayer to multilayer, and finally to rose-shaped type with SDSN as a surfactant. According to Matijevic group [43], rose-shaped vaterite was synthesized in urea solution (H_2NCONH_2) with SDSN and SDBS. They proposed that both preheating solu-

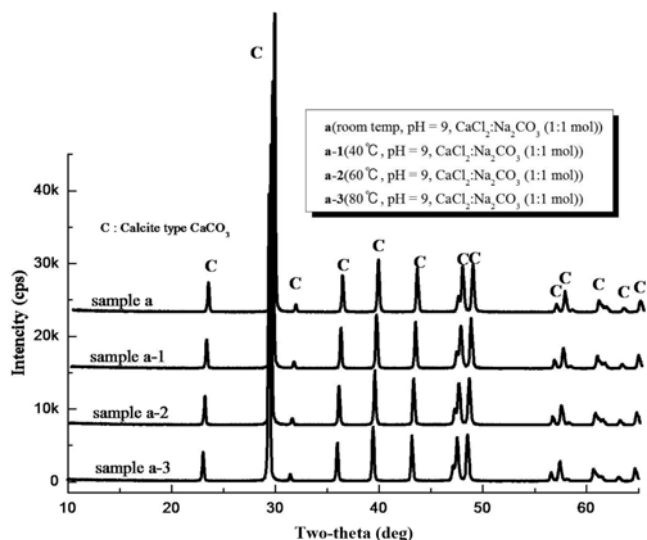


Fig. 6. XRD data of samples a (room temp), a-1 (40 °C), a-2 (60 °C), a-3 (80 °C) (pH=9, $\text{CaCl}_2 : \text{Na}_2\text{CO}_3$ (1 : 1 molar ratio)).

tion and increasing the concentration of urea offer more CO_3^{2-} and NH_4^+ through the hydrolysis of urea at 90 °C. It was reported that

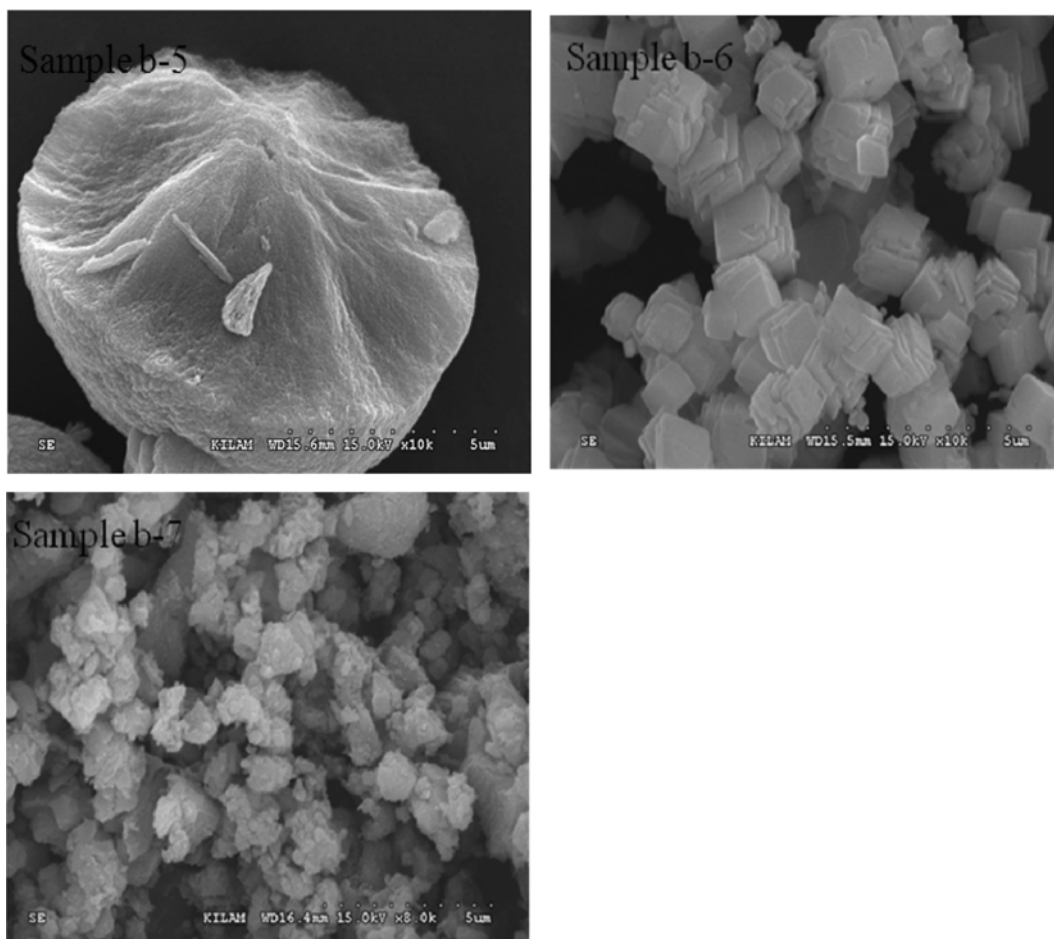


Fig. 5. SEM images of samples b-5 (1 mol SDBS), b-6 (no SDBS) (pH=9, $\text{CaCl}_2 : \text{SDBS} : \text{Na}_2\text{CO}_3$ (1 : 1 molar ratio)) and b-7 ($\text{Ca}(\text{OH})_2$, pH=9, $\text{CaCl}_2 : \text{NaOH}$ (1 : 2 molar ratio)).

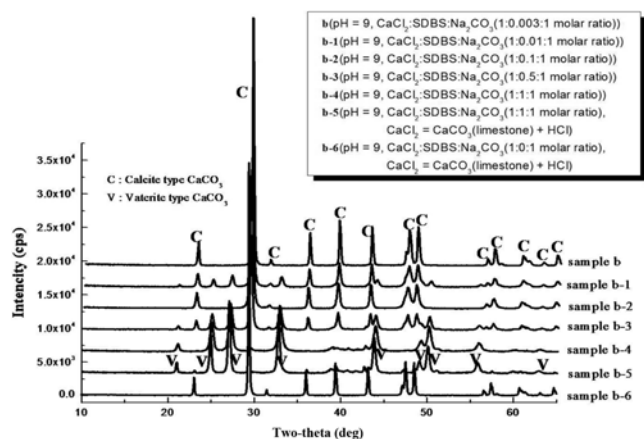


Fig. 7. XRD data analysis of sample b (0.003 mol SDBS), b-1 (0.01 mol SDBS), b-2 (0.1 mol SDBS), b-3 (0.5 mol SDBS), b-4 (1 mol SDBS), b-5 (1 mol SDBS), b-6 (no SDBS) (pH=9, $\text{CaCl}_2 : \text{SDBS} : \text{Na}_2\text{CO}_3$ (1 : 1 : 1 molar ratio)).

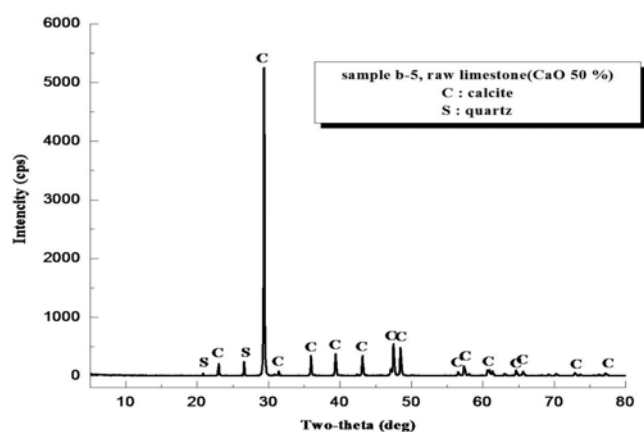


Fig. 8. XRD data analysis of limestone (sample b-5).

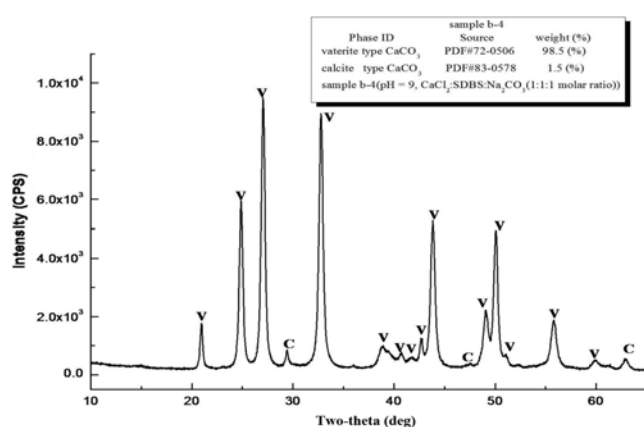


Fig. 9. XRD data and quantitative analysis of sample b-4 (pH=9, $\text{CaCl}_2 : \text{SDBS} : \text{Na}_2\text{CO}_3$ (1 : 1 : 1 molar ratio)).

the formation of vaterite in aqueous solution was favored under conditions of high ratio of $\text{CO}_3^{2-} : \text{Ca}^{2+}$ [44], and NH_4^+ can adsorb on the (001) faces of vaterite and act as a stabilizing agent [45]. Furthermore, Cölfen's [45] recent research suggested that ammonium ions

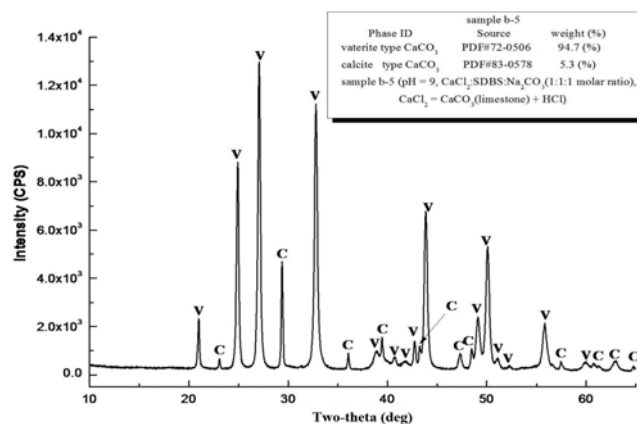


Fig. 10. XRD data and quantitative analysis of sample b-5 (pH=9, $\text{CaCl}_2 : \text{SDBS} : \text{Na}_2\text{CO}_3$ (1 : 1 : 1 molar ratio)).

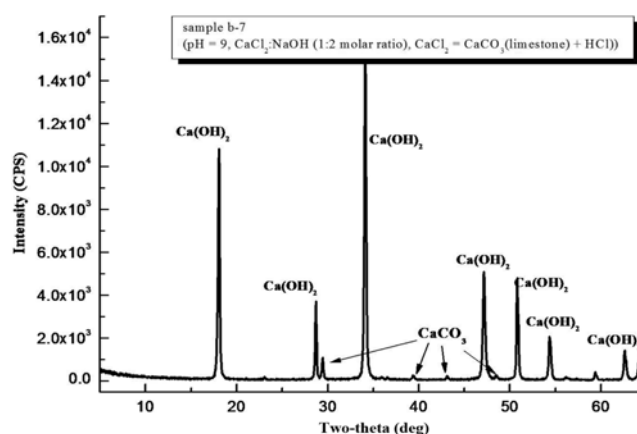


Fig. 11. XRD data of sample b-7 (pH=9, $\text{CaCl}_2 : \text{NaOH}$ (1 : 2 molar ratio)).

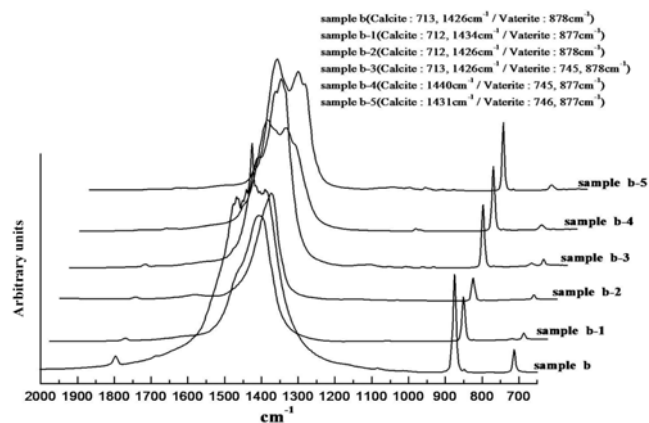


Fig. 12. FT-IR data of samples b, b-1, b-2, b-3, b-4, and b-5.

could play an important role in the formation of hexagonal vaterite.

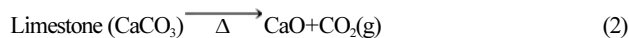
In the presence of SDSN, hydrophobic interactions [46] between surfactant molecules force the adjacent hexagonal plates to assemble together and these plates finally grow into petals in different layers. The more that monomers adsorb in the face, a hydrophobic interaction exists between hexagonal plates. In the presence of SDBS,

the hydrophobic interaction between plates, as well as coarse surfaces of the plate, make it possible that other plates can be mounted in it by different angles and grow into petals.

This is believed to be the mechanism that rose-shaped CaCO₃ was synthesized with SDBS in our experiments.

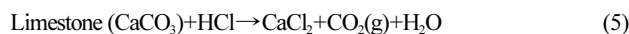
3. The Effect of Limestone on the Synthesis of CaCO₃

Limestone is generally used in the synthesis of CaCO₃ polymorphs through the following three reactions:



Limestone is a carbonate mineral theoretically composed of 56% CaO and 44% CO₂. Eq. (2) describes the production of CaO in shaft or rotary kilns that calcinate limestone [6]. Non-metallic minerals generally contain 1-3% impurities, lowering CaO content to 53-55%. Such impurities comprise Al₂O₃, Fe₂O₃, MgO and SiO₂, and they affect CaCO₃ by remaining throughout its synthesis [5,6].

The Solvay process is described in the following expression:



This process can form vaterite CaCO₃ by producing CaCl₂ solution (through the hydrochloric acid) which can be subsequently by

Table 1. XRF analysis of limestone and the product of the 6 M HCl + limestone reaction

Sample component	Limestone (mass%)	Remaining impurity after reacting 6 M HCl+limestone (mass%)
F		0.393
Na ₂ O	0.019	0.272
MgO	0.871	0.941
Al ₂ O ₃	0.77	19.6
SiO ₂	1.86	56.0
P ₂ O ₅	0.016	0.017
SO ₃	0.049	0.72
Cl	1.208	7.48
K ₂ O	0.144	5.37
CaO	94.2	5.78
MnO	0.031	
TiO ₂	0.047	0.899
V ₂ O ₅		0.07
Cr ₂ O ₃	0.023	0.13
Fe ₂ O ₃	0.65	2.07
NiO		0.026
CuO		0.009
ZnO		0.042
SeO ₂		0.003
Rb ₂ O		0.018
SrO	0.112	0.012
ZrO ₂		0.041
Nb ₂ O ₅		0.004
BaO		0.08
PbO		0.016
U ₃ O ₈		0.007

employed in the CaCl₂-Na₂CO₃ system.

The molar quantity of hydrochloric acid for the reaction with limestone was optimized by reacting 125 μm limestone particles with 6 M HCl, with impurities removed by filtering through glass fiber. Remaining impurities in the CaCl₂ solution were determined through the following reaction:



By mixing CaCl₂ and NaOH at a 1 : 2 molar ratio, the theoretic reaction molar ratio, Ca(OH)₂ (sample b-7) was produced. Fig. 8 shows XRD data of limestone (sample b-5), indicating that it was composed of calcite and quartz, an impurity. Fig. 11 shows the XRD analyses of sample b-7 (pH=9, CaCl₂ : NaOH 1 : 2 molar ratio), indicating the lack of other impurities, with peaks from mainly Ca(OH)₂ and also CaCO₃. The existence of CaCO₃ was attributable to HCO₃²⁻ ions in the water. Table 1 shows the results of the XRF analyses of limestone and what remained after it reacted with 6 M HCl. In the table, the molecular weight of limestone became 50.2 after the subtraction of the molecular weight of CO₂(g) (44) from the 94.2 of CaO. Table 2 shows the results of XRF analysis of Ca(OH)₂ (sample b-7), indicating that CaO was 99.5%.

CaCO₃ of vaterite structure was synthesized using limestone with equimolar ratios of CaCl₂ : anionic surfactant (SDBS) : Na₂CO₃, found through reactions using the surfactant. After the CaCl₂ solution and anionic surfactant were mixed, a white solid formed, and further mixing with Na₂CO₃ solution led to vaterite CaCO₃ forming. After NaOH was mixed into the produced CaCl₂ solution at a 2 : 1 molar ratio, Ca(OH)₂ (sample b-7) was produced.

Fig. 5 shows SEM images of samples b-5 (1 mol SDBS), b-6 (no SDBS) and b-7 (Ca(OH)₂). Sample b-5 had spherical vaterite structures of CaCO₃, different from those of sample b-4, that were filled rather than the hollow spheres of sample b-4. The CaCl₂ af-

Table 2. XRF analysis of Ca(OH)₂ (sample b-7)

XRF analysis result		
No.	Component	Result (mass%)
1	F	0.254
2	Na ₂ O	0.0252
3	MgO	0.0264
4	Al ₂ O ₃	0.0025
5	SiO ₂	0.0203
6	SO ₃	0.0353
7	Cl	0.0972
8	CaO	99.5
9	SrO	0.0089
	Ig-loss	0.0302

Table 3. The vibrational frequencies of CO₃²⁻ ions of calcium carbonate minerals

Calcium carbonate minerals	Vibrational frequencies of CO ₃ ²⁻ ion			
	γ ₁ (cm ⁻¹)	γ ₂ (cm ⁻¹)	γ ₃ (cm ⁻¹)	γ ₄ (cm ⁻¹)
Calcite [42]		857	1426	712
Aragonite [42]	1082	859	1485	712, 699
Vaterite [42]	1085, 1070	870, 850, 830	1490, 1420	750

affected the growth of CaCO_3 cores due to the slight amount of impurities remaining after the reaction of limestone and hydrochloric acid. It was reacted with NaOH to assay these remaining impurities, with the resulting $\text{Ca}(\text{OH})_2$ (sample b-7) containing *ca.* 0.5% impurities of F (0.254%), Na_2O (0.0252%), MgO (0.0264%), Al_2O_3 (0.0025%), SiO_2 (0.0203%), SO_3 (0.0353%), Cl (0.0972%), SrO (0.0089) and Ig-loss (0.0302%). Other synthesis conditions were the same as for the anionic surfactant treatment of sample b. Sample b-6 was found to be calcite CaCO_3 , similar to sample a, when the CaCl_2 solution was used at room temperature without surfactant (Fig. 5). Fig. 5 also shows an SEM image of sample b-7 ($\text{Ca}(\text{OH})_2$) synthesized from the CaCl_2 solution.

The XRD data in Fig. 7 show that sample b-5, like sample b-4, was vaterite CaCO_3 , while sample b-6 was confirmed of calcite structure, like sample a. The XRD data and quantitative analysis of sample b-5, show it to be composed of 94.7% vaterite and 5.3% calcite (Fig. 10). Compared with sample b-4, sample b-5 was found to contain more calcite by 3.8 percentage points, likely due to the effect of impurities in the CaCl_2 solution. The FT-IR data, confirmed that sample b-5 was composed of calcite (1431 cm^{-1}) and vaterite ($746, 877\text{ cm}^{-1}$) (Fig. 12) [42].

CONCLUSIONS

The crystalline phase CaCO_3 in a $\text{CaCl}_2\text{-Na}_2\text{CO}_3$ system was controlled by adding surfactant. Without surfactant, calcite CaCO_3 was synthesized at pH 9 with equimolar reactant amounts of the theoretic reaction ratio. Although the crystal morphology of CaCO_3 was not affected, the cluster size was affected by temperature changes. Vaterite CaCO_3 was found to form in the presence of anionic surfactant (SDBS) under similar conditions where commercial CaCl_2 (purity >74%) was supplied. And XRD analysis found hollow vaterite structures accounting for up to 98.5% of the CaCO_3 .

CaCl_2 solution was produced through the decomposition of limestone with hydrochloric acid using the Solvay process. The produced CaCl_2 solution was used in the $\text{CaCl}_2\text{-Na}_2\text{CO}_3$ system with and without added surfactant. XRD analysis showed that vaterite structures accounted for 94.7% of the CaCO_3 formed in this way in the presence of surfactant, with the remainder calcite. These vaterite structures were solid spheres rather than hollow ones.

Limestone was shown to be potentially useful in protein encapsulation by PSS, an anionic electrolyte, and PAH, a cationic electrolyte, in $\text{CaCl}_2\text{-Na}_2\text{CO}_3$ systems. CaCO_3 synthesized employing Solvay process and SDBS in this study can be used for such purpose.

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