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The Effect of Surfactant on Formation of Calcium Carbonate

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Calcium carbonate was precipitated by rapidly mixing calcium chloride solution, sodium carbonate solution, and aqueous surfactant solution at 25 °C in order to elucidate the effect of addition of surfactant on the formation. The samples obtained were examined by scanning electron microscopy, X-ray powder diffraction, and a specific surface area study. The sample without surfactant proved to be calcite crystals. When a cationic surfactant was added, the crystal structure was transferred from calcite and vaterite to calcite with an increase of the concentration of the cationic surfactant. On the other hand, the addition of a lower concentration of an anionic surfactant provided a mixture of calcite and vaterite, but in higher concentration, amorphous material was obtained. The samples with nonionic surfactant were vaterite crystals. It was found that the spherical particle ratio (N_{sp}) and the vaterite crystal ratio (F_v) in the sample depend on the concentration of the nonionic surfactant.

The preparation of the spherical particles of inorganic compounds has been the subject of many studies.[1–14] However, the spherical particles can be obtained only under limited synthesis conditions, depending on the concentration of solution, temperature, reaction rate, pH, and the ripening method.

Anhydrous calcium carbonate as an inorganic compound is known to exist in three crystalline modifications: calcite, aragonite, and vaterite. Calcite is a stable form at ordinary temperatures and pressures. Aragonite and vaterite are metastable modifications which transform to calcite on heating.[10–12]

Miyata and Nakahara[13] have reported that vaterite was prepared by an interfacial reaction method in which calcium carbonate was formed by the reaction of K_2CO_3 aqueous solution emulsified in benzene with $CaCl_2$ aqueous solution. Inoue and Kanaji[11] prepared vaterite by reacting the concentrated aqueous solution of $CaCl_2$ with Na_2CO_3 and the same process was also employed in the system of $Ca(NO_3)_2$ with Na_2CO_3. Enomoto *et al.*[14] obtained vaterite by mixing $CaCl_2$, $NaHCO_3$, and NH_3 at 45 °C to attain a final pH of 6.8.

In this work, calcium carbonate was precipitated by mixing $CaCl_2$–Na_2CO_3 solutions in the presence of aqueous surfactant solution at 25 °C. The effects of addition of aqueous surfactant solution on the morphology and polymorphism of calcium carbonate were examined.

Experimental

Preparation of Calcium Carbonate. Nonionic surfactants used in this experiment were supplied by Nikko Chemicals Co., Ltd.; other chemicals were of reagent grade.

Calcium carbonate was precipitated by rapidly mixing 2.5×10^{-2} mol dm^{-3} of $CaCl_2$ solution, 2.5×10^{-2} mol dm^{-3} of Na_2CO_3 solution, and aqueous surfactant solution at 25 °C. The concentrations of the surfactant added were 5.0×10^{-5}, 9.0×10^{-4}, and 5.0×10^{-3} mol dm^{-3} (cationic surfactant: hexadecyltrimethylammonium bromide, CTAB), 5.0×10^{-5}, 3.2×10^{-3}, and 8.0×10^{-3} mol dm^{-3} (anionic surfactant: sodium dodecyl sulfate, SDS), and 5.0×10^{-6}, 1.0×10^{-5}, 5.0×10^{-5}, 1.0×10^{-4}, 5.0×10^{-4}, and 1.0×10^{-3} mol dm^{-3} (nonionic surfactant: poly(oxyethylene) nonylphenyl ether, NP-n: n=10, 20). Each solution was mixed for 10 s and unstirred thereafter. Precipitation commenced less than 5 s after mixing, with a rapid onset of turbidity, and crystals gradually settled out of the solutions. In this experiment, the precipitate of calcium carbonate adhered tenaciously to the walls and bottom of the reaction cell after 3 h of aging. The precipitate obtained was washed with water to remove unreactive salts and by-products, washed again with methanol to remove the surfactant, then dried *in vacuo*. Each dried precipitate was used as a sample.

pH Measurement. The pH of the supernatant was measured by a Corning pH meter 130.

Scanning Electron Microsopy (SEM). The morphology and polymorphic composition of samples obtained were taken with a JEOL JSM-T20 SCANNING MICROSCOPE and a AKASHI ALPHA-10 after coating by the thick 30 nm of gold on each sample was carried out by a JEOL COAT ION SPUTTER JEC-1100. Further, the spherical particle ratio (N_{sp}) was determined by counting the number of spherical and unspherical particles on the microphotgraphs taken with different fields.

Specific Surface Area. The specific surface area of calcium carbonate was measured by a Shimadzu GAS CHROMATOGRAPH GC-7A connected with a Shimadzu SORPTOGRAPH ADS-1B. The area was determined by applying the BET method to the nitrogen adsorption at liquid nitrogen temperature.

X-Ray Powder Diffraction.[15] An X-ray powder diffraction was measured by a Rigaku Denki Geigerflex RAD-IIIA MJ 200 DX with nickel filtered copper $K\alpha$ radiation (35 kV and 10 mA). To evaluate the crystal transfer ratio in vaterite to calcite in the presence of surfactant, the following equations were employed:

$$F_c = \frac{I_{104(c)}}{I_{110(v)} + I_{104(c)} + I_{112(v)} + I_{114(v)}} \times 100, \tag{1}$$

$$F_c + F_v = 100. \tag{2}$$

Here diffraction intensities (I) of the (104) reflection of calcite and of the (110), (112), and (114) reflections of vaterite are obtained and the vaterite (F_v) and calcite (F_c) crystal ratios can be determined by the X-ray diffraction measurement using Eqs. 1 and 2.

Results and Discussion

The crystals obtained in the absence of surfactant had a characteristic calcite(rhombohedral) morphology, as shown in Fig. 1. Further, the X-ray powder diffraction

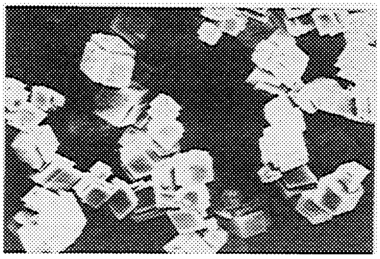

Fig. 1. SEM photomicrograph of calcium carbonate crystals precipitated in the absence of surfactant.

analysis showed the calcite (ASTM No. 5-586) diffraction peak. The pH values of each reacting solution, with and without the surfactant solutions, were 10.30, and 10.30—10.40, indicating that the effect of pH on the formation of calcium carbonate by the addition of surfactant will be negligibly small.

Figure 2 shows a scanning electron microphotograph of the powders prepared in the presence of CTAB, whose critical micelle concentration(cmc) is 9.0×10^{-4} mol dm^{-3}. The samples obtained in the presence of 5.0×10^{-5} mol dm^{-3} of CTAB were a mixture of characteristic calcite and vaterite(hexagonal) whose morphology is shown in Fig. 2(A). With an increase of the concentration of CTAB (9.0×10^{-4} and 5.0×10^{-3} mol dm^{-3}), the morphology became that characteristic of calcite, as shown in Figs. 2(B) and (C). The above results indicate that the vaterite fraction in the samples decreases with an increase of the concentration of CTAB added. Especially. in the concentration of 5.0×10^{-5} mol dm^{-3} of CTAB, the spherical particle ratio (N_{sp}), the vaterite crystal ratio (F_v), and the specific surface area were 82.5%, 47.0%, and 2.8 m^2/g, respectively. The decrease in the vaterite crystal ratio with an increase of the concentration of CTAB might be caused by the slow diffusion of water owing to the thick layer of CTAB adsorbed around the calcium carbonate particles.

Figure 3 gives the SEM pictures of the powders prepared in the presence of SDS, whose cmc is 8.0×10^{-3} mol dm^{-3}. The morphology of the samples obtained in the presence of 5.0×10^{-5} mol dm^{-3} of SDS exhibited a mixture of calcite and vaterite, as shown in Fig. 3(A). The addition of higher concentrations of SDS (3.2×10^{-3} and 8.0×10^{-3} mol dm^{-3}) provided amorphous precipitates, as shown in Figs. 3(B) and (C). Thus, vaterite and calcite crystals become amorphous with increasing the concentration of SDS added. In the concentration of 5.0×10^{-5} mol dm^{-3} of SDS, N_{sp}, F_v, and specific surface area were 70.0%, 32.0%, and 2.3 m^2/g, respectively.

The adsorption of SDS onto calcium carbonate powder has been studied by Chibowski.[16] According to his report, in the low concentration of SDS, the adsorption in the synthesis reaction step of calcium carbonate was appreciable, while in the highcon centration, this solution dissociated similarly to Eq. 3, and Ca^{2+} and $2DS^-$ in this solution produced $Ca(DS)_2$ after reacting like Eq. 4. Since this reaction affects significantly the reaction of calcium carbonate, it is considered that calcite and vaterite crystals become amorphous by the addition of SDS.

$$\text{Na–Ds} \longrightarrow \text{Na}^+ + \text{DS}^-, \tag{3}$$

$$\text{Ca}^{2+} + 2\text{DS}^- \longrightarrow \text{Ca(DS)}_2. \tag{4}$$

Thus, cationic and anionic species of the surfactant play important roles in the formation of calcium carbonate. As nonionic surfactants have no charge groups, the formation of calcium carbonate in the presence of nonionic surfactant proceeds without taking into consideration the charge effect.

Figure 4 gives the SEM pictures of the powders prepared in the presence of NP-10, whose cmc is (7.5—9.0) $\times10^{-5}$ mol dm^{-3}. The samples in the presence of NP-10 (5.0×10^{-6} and 1.0×10^{-4} mol dm^{-3}) had a characteristic calcite and vaterite morphology, as shown in Fig. 4(C). The vaterite crystal ratio (F_v) calculated

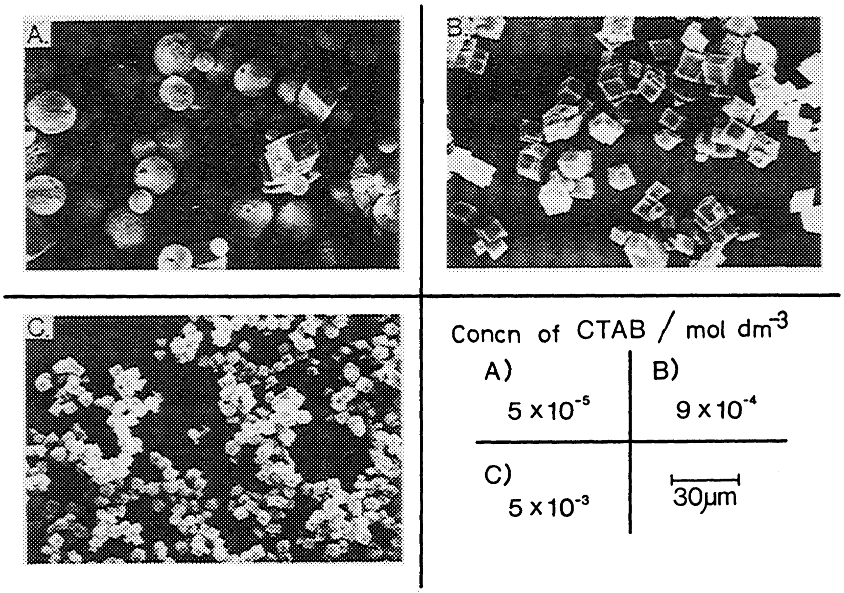

Fig. 2. SEM photomicrographs of calcium carbonate crystals precipitated in the presence of various concentrations of CTAB.

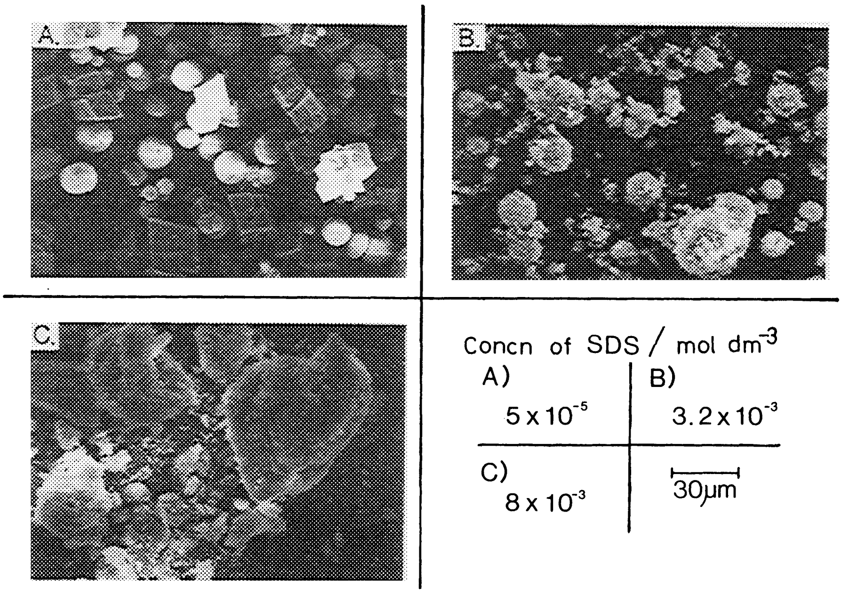

Fig. 3. SEM photomicrographs of calcium carbonate crystals precipitated in the presence of various concentrations of SDS.

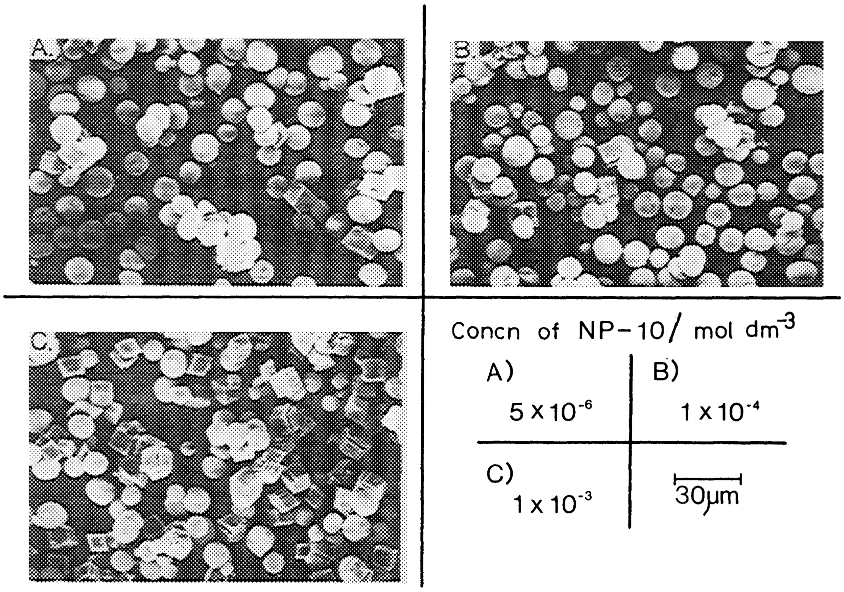

Fig. 4. SEM photomicrographs of calcium carbonate crystals precipitated in the presence of various concentrations of NP-10.

by Eqs. 1 and 2 is plotted against the concentration of surfactant shown in Fig. 5. In the case of NP-10, the F_v increased until the concentration of 5.0×10^{-5} mol dm^{-3}, then decreased slowly with an increase of the concentration until 1.0×10^{-4} mol dm^{-3}, and then decreased rapidly. In the case of NP-20, the F_v increased gradually with an increase of the concentration of surfactant. Thus, it is found that the vaterite crystal ratio depends on the concentration of the nonionic surfactant.

The spherical particle ratio (N_{sp}) is also plotted against the concentration of nonionic surfactant in Fig. 6. In the range of concentration of NP-10 from 5.0×10^{-6} to 5.0×10^{-4} mol dm^{-3}, the crystals were spheres, cubes, and amorphous. Further, at concentrations above 5.0×10^{-4} mol dm^{-3}, the N_{sp} decreased with an increase of the concentration of NP-10. Similarly, in the range of concentration of NP-20 from 5.0×10^{-6} to 1.0×10^{-3} mol dm^{-3}, the N_{sp} increased with an increase of the concentration of NP-20. The magnitude of N_{sp} obtained by using NP-10 is larger than that of NP-20.

The adsorption of nonionic surfactant onto inorganic powders has been studied by several investigators.[17–20] Akers and Riley[19] and Hsiao and Dunning[20] examined the adsorption of nonionic surfactants onto calcium carbonate or sands. They reported that the adsorption increases with decrease in the length of oxyethylene chain of the surfactant. According to their results, as the film thickness of the surfactant adsorbed on the powder particle increases with an increase of the concen-

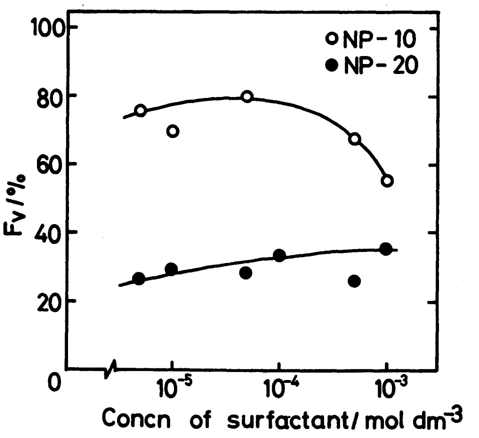

Fig. 5. Relation between vaterite ratio (F_v) in calcium carbonate and concentration of surfactant added.

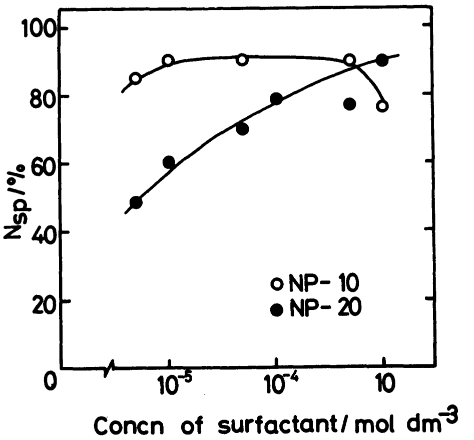

Fig. 6. Relation between spherical particle ratio (N_{sp}) in calcium carbonate and concentration of surfactant added.

tration of the surfactant, the film prevents the surface of the particle from contacting the water. Thus, the increase of the vaterite crystal ratio might be caused by preventing the vaterite particle from coming into contact with the water; this would result in stability of the vaterite crystal. On the other hand, at higher concentrations of the surfactant, the decrease in the vaterite crystal ratio is due to the slow diffusion of water through the thick film layer of the surfactant adsorbed around the particle. The above results show that the N_{sp} and F_v depend on the concentration of the surfactant and the length of their oxyethylene chain. Here, the N_{sp} in the case of NP-10 and NP-20 were 20—30% and 40—50% greater than those of their F_v, respectively. This difference might be interpreted if some of the sherical particles in the preparation of the above conditions are amorphous vaterite rather than vaterite crystals.

The mean particles size (arithmetic mean diameter, D) and specific surface area (S_N, S_D) of calcium carbonate are given in Table 1. The S_D value was determined by calculating from the mean particle size, employing Eq. 5:

$$S_D = 6/D \times \rho, \tag{5}$$

where D is an arithmetic mean diameter estimated from the SEM pictures and ρ is the specific gravity, 2.65. The S_N value was also determined by the BET method from the nitrogen adsorption. From Table 1, it is seen that the S_N value is larger than that of the S_D, indicating that the calcium carbonate formed by the addition of nonionic surfactant is porous. Further, to elucidate the surface morphology of vaterite crystal, the SEM picture was taken and is shown in Fig. 7. It is found that, as predicted by the S_N/S_D value, the surface of vaterite seems to have many pores.

TABLE 1. MEAN PARTICLE SIZE AND SURFACE AREA OF CALCIUM CARBONATE PRECIPITATED IN THE PRESENCE OF SURFACTANT

Surfactant mol dm^{-3}	Mean particle μm	S_N m^2 g^{-1}	S_D m^2 g^{-1}
None	10.50	1.48	0.22
NP-10			
1×10^{-5}	14.12	3.56	0.16
5×10^{-5}	12.32	3.02	0.18
1×10^{-4}	11.56	3.74	0.20
5×10^{-4}	10.56	4.81	0.21
NP-20			
5×10^{-6}	13.69	2.05	0.17
1×10^{-5}	12.57	2.80	0.18
5×10^{-4}	10.36	2.58	0.22
1×10^{-3}	12.44	4.59	0.18

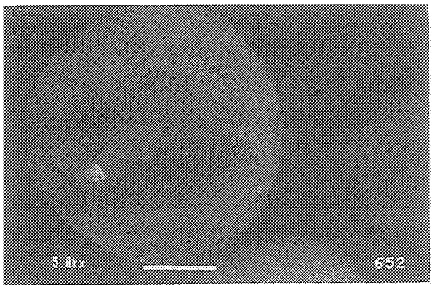

Fig. 7. SEM photomicrograph of a vaterite crystal enlarged.

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