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SHORT COMMUNICATION

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Control of calcium carbonate particle size and shape by precipitation from CTAB/alcohol/hexadecane mixtures

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Abstract When used as a precipitation media, emulsified mixtures of cetyltrimethylammonium bromide/*n*-butanol (E), hexadecane (O) and water (W), controls the size and shape of calcium carbonate particles. Monodisperse 2-micron spherical-calcite particles were obtained in a water-rich region of the mixture, while 2-micron rhombohedral-calcite particles with an aspect ratio near one were obtained in the middle region of the mixture. Replacing *n*-butanol with *i*-butanol led to consistent formation of monodisperse spherical particles, while using *n*-propanol in place of *n*-butanol limited the number of spherical particles produced in the water-rich region.

Key words Monodispersed – calcium carbonate – precipitate – spheres – microemulsion

Introduction

Microemulsions and other organized media have a profound effect upon precipitation and crystallization processes [1–7]. Variations in particle size, phase, and porosity all reflect upon the structural identity of the mesophase from which precipitation or crystallization occurs. The phase and shape of growing crystallites are influenced as surfactants and other polar organic components of these media adhere to the surface of a growing particle [2, 8], while the complex solution structure of these mesophases affects the porosity of the precipitated solid [9–11].

To understand the influence of a complex media upon crystal growth, the composition of an emulsified mixture was varied and its effect upon the precipitation of calcium carbonate explored. We elected to investigate reactions producing calcium carbonate since its controlled precipitation is important to its use as a filler and whitener in paper [12]. Control of the phase, particle size and the layering of calcium carbonate are also of biological importance where aragonite and calcite are commonly found in the endo and exoskeleton of marine organisms [6, 7, 13]. In this work, monodisperse 2-micron spherical and 2-micron rhombohedral calcite particles were obtained at specific compositions of the emulsified mixture.

Experimental

Materials

Reagent grade cetyltrimethylammonium bromide (CTAB), *n*-butanol, *i*-butanol, *n*-propanol, hexadecane, ammonium carbonate and calcium chloride dihydrate were purchased from Aldrich Chemical Company Inc. and were used without further purification.

Equipment

All electronmicrograph images were recorded on an environmental scanning electronmicroscope (Electroscan model E3). To obtain a thin layer of the solid, the samples were dispersed in water, and the dispersion was placed on a standard platform where the water was allowed to evaporate. Powder X-ray diffraction (XRD) data for all samples were collected at 25 °C on a modified Phillips XRG 2000 diffractometer (Cu K) interfaced with a RADIX databox and an MDI software system. Data were matched against the Powder Diffraction File of inorganic phases published by the International Center for Diffraction Data [14].

Preparation of emulsified mixtures

Optically clear mixtures of CTAB/*n*-butanol (1 : 1 by weight, 1 : 5 molar ratio) (E), water (W) and hexadecane (O) were prepared as described by Mackay and coworkers [15]. The four areas of the phase map investigated were: (a) water; (b) a water-rich region composed of 50% emulsifier, 0–4% hexadecane, and 46–50% water by weight; (c) a middle region consisting of 75% emulsifier, 5–12.5% hexadecane and 12.5–20% water; and (d) an oil rich region with 50% emulsifier, 6% water, and 44% hexadecane (Fig. 1). Four other emulsified mixtures were prepared by replacing the CTAB/*n*-butanol emulsifier with CTAB/*i*-butanol (1 : 1 by weight), and CTAB/*n*-propanol (55 : 45 by weight) at regions (b) and (c) of the phase map. The reagents of the emulsified mixtures were combined, warmed to 30 °C and stirred for an hour to ensure dissolution of the surfactant.

Precipitation of 1–3 μm spherical calcite particles

Ammonium carbonate (25 mg, 0.26 mmol) was dissolved in mixture (b) (20 g) and added with rapid stirring to calcium chloride dihydrate (380 mg, 2.6 mmol) dissolved in mixture (b) (6 g). The reaction was stirred for 5 min as a precipitate formed. The reaction mixture was centrifuged and the precipitate collected, resuspended in 50 ml of water and centrifuged five times. The resulting solid was air dried.

Precipitation of 1–3 μm rhombohedral calcite particles

Ammonium carbonate (100 mg, 1.0 mmol) was dissolved in 14 g of mixture (c) by warming to 30 °C. The mixture was cooled to 22 °C and added dropwise to calcium chloride dihydrate (150 mg, 1.0 mmol) in 3 g of mixture (c). The reaction was stirred for 5 min as a precipitate formed. The reaction was centrifuged and the precipitate collected, resuspended in 50 ml of water and centrifuged five times. The resulting solid was air dried.

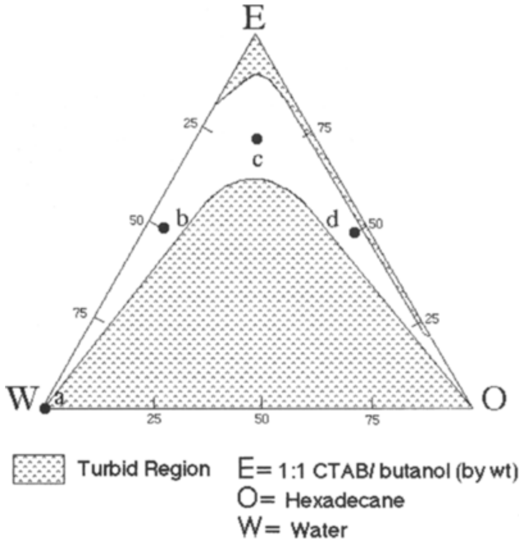


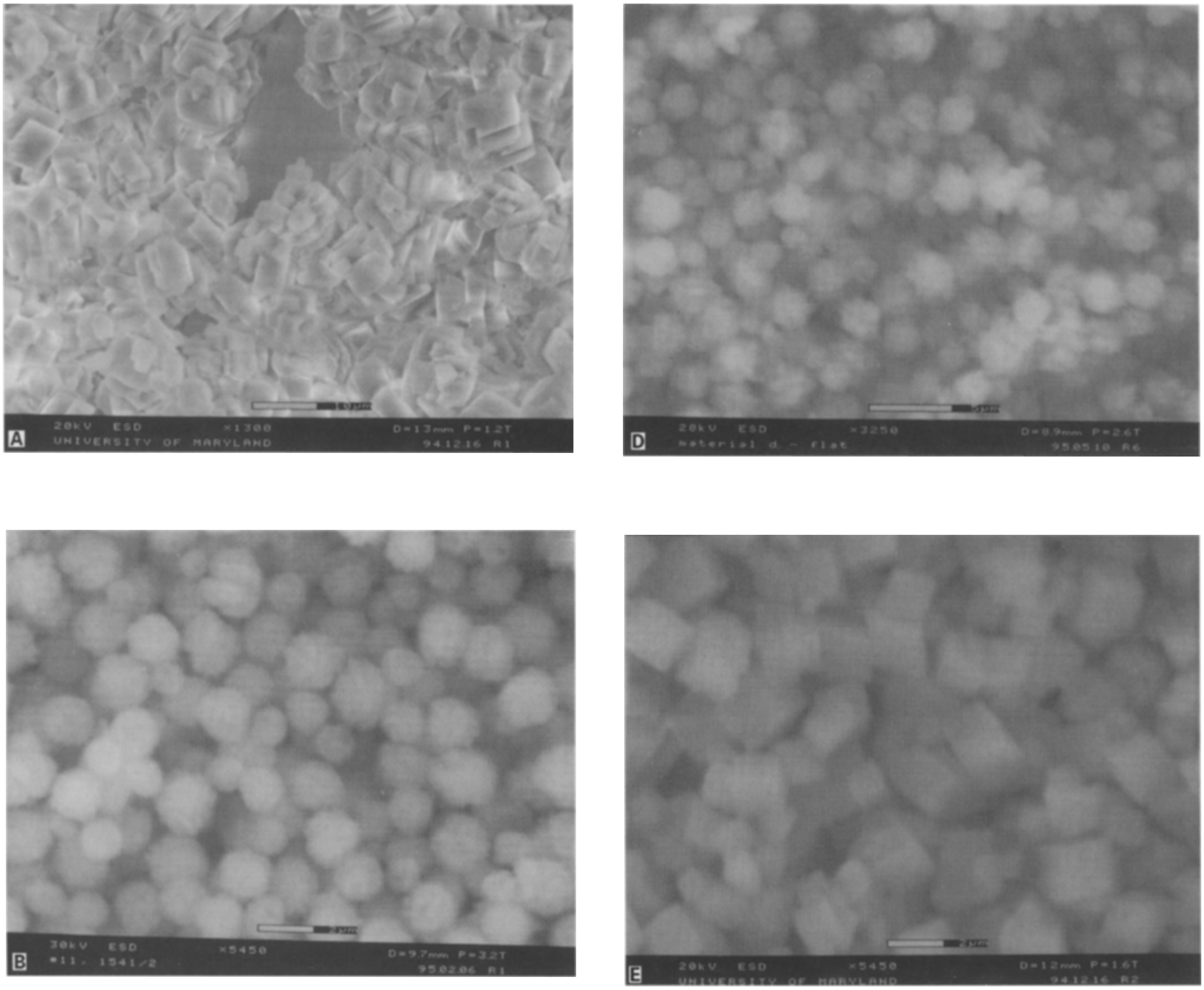
Fig. 1

Results and discussion

The emulsified system composed of cetyltrimethylammonium bromide (CTAB)/*n*-butanol (1 : 1 by weight) = E, water = W and hexadecane = O, was developed by Mackay and coworkers (Fig. 1) [15]. This system was selected as a precipitation media since the cationic surfactant (CTAB) was expected to interact with the carbonate anion, yet not precipitate under the relatively high calcium concentrations used in this study. Our studies were conducted at points (a)–(d) on the phase map (Fig. 1), and images of the precipitated calcium carbonate obtained at these points are shown in Fig. 2.

Precipitation in water at both a 1 : 1 and 10 : 1 calcium to carbonate ratio produced irregular rectangular platelets up to 10 mm in length with preferential growth along one plane. In contrast, at the mid-range region, (c), monodisperse 2 mm rhombohedral particles with an aspect ratio close to one precipated at both calcium to carbonate ratios. With a 1 : 1 calcium to carbonate ratio precipitations at region (b) produced 2 mm spherical particles in addition to the 2 mm rhombohedra. However, if the carbonate concentration was kept low (0.074% by weight) and a 10 : 1 calcium to carbonate ratio used, monodisperse 2-micron calcite spheres were precipated at region (b). These spherical particles were stable in water, but when allowed to stand in mixture (b), an irregular rhombohedral morphology was adopted in ≈12 h. Precipitation in the oil-rich region, (d), produced poorly formed 3–5 mm crystallites with little discernible structure.

The effects of replacing the cosurfactant on calcite precipitation were investigated at regions (b) and (c) of the



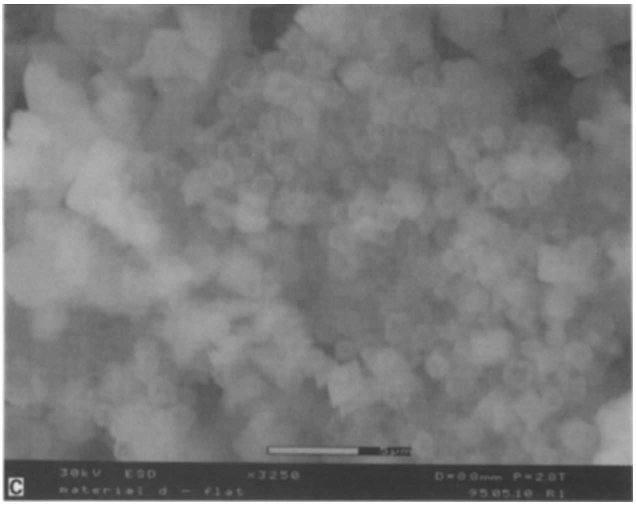


Fig. 2A Platelets of calcite formed in water (region "a"). **B** Calcite particles formed at region "b" of a CTAB/*n*-butanol emulsified mixture with a 10:1 calcium:carbonate molar ratio. **C** Calcite particles formed at region "b" of a CTAB/*n*-propanol emulsified mixture with 10:1 calcium:carbonate molar ratio. **D** Calcite particles formed at region "b" of a CTAB/*i*-butanol emulsified mixture with 10:1 calcium:carbonate molar ratio. **E** Rhombohedral calcite particles formed at region "c" of a CTAB/*n*-butanol emulsified mixture with a 1:1 calcium:carbonate molar ratio

phase map using both a 1:1 and 10:1 calcium to carbonate ratio. Using similar CTAB to alcohol molar ratios, *n*-butanol was replaced by *n*-propanol and *i*-butanol. Calcite precipitated at the (c) region using either *n*-propanol or *i*-butanol as cosurfactant produced crystallites that were essentially identical in shape, size, and phase to those obtained with *n*-butanol as the cosurfactant. However, when the precipitation conditions were optimized for obtaining spherical particles in the water rich region (b), the

CTAB/*n*-propanol emulsified mixture produced only a limited number of spherical particles, while spherical particles similar to those from the CTAB/*n*-butanol emulsified mixture were obtained from the CTAB/*i*-butanol emulsified system (Fig. 2).

All of the precipitated calcium carbonate was rhombohedral (hex) calcite with a well resolved X-ray diffraction pattern. Infrared spectra taken of the solid when crushed and pressed into KBr pellets showed no bands other than those associated with carbonate. This suggests that there was no encapsulated or residual surfactant, cosurfactant or oil.

Although the emulsified system within the boundaries of the phase map are clear and homogeneous in appearance, their micro-structures vary with the ratios of their components. In region (b) an oil-in-water microemulsion/or micelle is present, at region (c) a lamellar or continuous biphase is present, and in region (d), an inverse microemulsion, or water-in-oil microemulsion is likely [16]. Formation of small and regular rhombohedral particles at region (c) may be due to the surfactant in the lamellar media or the continuous biphase adhering equally to all faces of the growing crystal, supporting non-preferential growth. In region (b), where the formation of spherical particles is observed, the carbonate that is associated with the cationic ends of the surfactant on the surface of the aggregates may be serving as a seed surface for the growth of the spherical calcite particles. The low carbonate concentration necessary to obtain only spherical particles ensures that all of the carbonate is associated with the aggregate surface, and the high calcium to carbonate ratio promotes rapid precipitation. Uniform precipitation of spheres did not occur when the size of the cosurfactant was changed by substituting *n*-propanol for *n*-butanol. Since the smaller cosurfactant is likely to decrease the microemulsion or micellar surface area, less carbonate can associate with the surface and hence fewer spheres are obtained. In all cases, it is likely that the viscosity of the emulsified mixture limits particle size [17, 18].

Conclusions

The size and shape of calcite crystallites precipitated from a complex emulsified system can be controlled. The shape of these particles reflect upon the solution structure of the mesophase. Microemulsion/micellar micro-structure of region (b) serves as a nucleation site for spherical particles, while the laminar/biphasic microstructure of (c) leads to the precipitation of regular rhombohedral particles. The size of these particles, 1–3 μm, appears to be limited by the viscosity of the emulsified mixture. Since precipitation of silicates from surfactant containing water solutions has been shown to lead to the production of desirable microporous materials [9, 10], porosity measurements of the calcite spheres are underway.

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References

1. Harding PQ (1872) J Microsc Sci 12: 118–123
2. Fendler JH (1987) Chem Rev 87: 877–899
3. Mann S, Heywood BR, Rajam S, Birchall JD (1988) Nature 334:692–695
4. Heywood B, Mann S (1994) Chem Mater 6:311
5. Meldrum F, Heywood B, Mann S (1993) J Colloid Interface Sci 161:66
6. Mann S (1990) New Scientist 125:42
7. Mann S, Heywood B (1989) Chem Brit 25:698
8. Sugimoto T (1987) Adv Colloid Interface Sci 28:65–108
9. Tanev PT, Pinnavaia TJ (1996) Chem Mater 8:20268–2079
10. Beck JS, Vartuli JC, Roth WJ, Leonowicz ME, Kresge CT, Schmitt KD, Chu CT-W, Olson DH, Sheppard EW, McCullen SB, Higgins JB, Schlenker JL (1992) J Am Chem Soc 114:10834–10843
11. Huo Q, Margolese DI, Clesia U, Feng P, Gler TE, Sieger P, Leon R, Petroff PM, Schuth F, Stucky GD (1994) Nature 368:317–321
12. (a) Reisch M, Synthetic Mineral Know-How Aids Minerals Technologies Growth (1995) January 9th issue, C&EN. (b) Greenwood NN, Earnshaw A (1994) Chemistry of the Elements. Pergamon Press Ltd. Cambridge, pp 133–135
13. Lowenstam HA, Weiner S (1989) On Biomineralization Oxford University Press Inc, New York
14. Powder Diffraction File of Inorganic Phases, International Center for Diffraction Data
15. Mackay RA, Hermansky C (1981) J Phys Chem 85:739–744
16. Israelachvili J (1994) Colloids Surfaces 91:1–8
17. Eshuis A, Koning CAJ (1994) Colloid Polym Sci 272:1240–1244
18. Celikkaya A, Akinc M (1990) J Am Ceramic Soc 73:2360