Influence of alcohol on the morphology of BaSO$_4$ crystals grown at the air–water interface

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Paper

Control over the crystallography and morphology of technologically important minerals is an important goal in the area of crystal engineering. Charged insoluble surfactant monolayers at the air–water interface (Langmuir monolayers) have proven to be popular mineralization templates. In this paper, we investigate the influence of trace quantities of alcohol (ethanol) in the aqueous subphase on the crystallography and morphology of BaSO$_4$ crystals grown in the presence of anionic Langmuir monolayers at two largely different supersaturation ratios. It is observed that the crystals grow in the barite structure with interesting differences in morphology of the crystals grown with and without alcohol in the subphase. Preferential adsorption of ethanol molecules at the air–water interface is expected to influence not only the organization of the surfactant Langmuir monolayer but also to alter the dielectric properties of the interface and, consequently, the electrostatic binding of the ions with the Langmuir monolayer prior to mineralization.

Introduction

The synthesis of advanced inorganic materials increasingly requires the ability to grow crystals of controllable structure, size, morphology and, indeed, assembly of the crystals into predefined superstructures. In this context, biominerals have served as an inspiration to crystal engineers.[1–4] It is now established that an important requirement for biomineralization is epitaxy between the crystal nucleating face and the underlying bio-organic surface and, consequently, biomimetic surfaces such as those presented by Langmuir monolayers,[5–9] self-assembled monolayers (SAMs) on planar[10,11] and nano-scale curved surfaces[12–14] as well as functionalized polymer surfaces[15,16] have been studied in great detail. Control over the morphology of crystals grown in solution *via* the addition of suitable crystallization inhibitors/promoters[17–19] is a well-studied and understood approach,[20] as is carrying out crystal growth in constrained environments such as those afforded by microemulsions.[21]

Crystal growth at the air–water interface is an important area of research that involves the use of Langmuir monolayers of surfactant molecules as molecular templates for the oriented nucleation of organic and inorganic crystals by an epitaxial process.[7,22] The interfacial region between a charged surface and an electrolyte is central to many processes such as those occurring during electrodeposition, ion transport through biological membranes, the preparation of Langmuir–Blodgett (LB) films, biomineralization[23] and oriented nucleation of inorganic systems under Langmuir monolayers.[22] Langmuir monolayers have been shown to induce oriented crystallization from solutions of proteins[24,25] and other organic and inorganic compounds.[26] Mann *et al.* studied the oriented crystallization of CaCO$_3$ under monolayers of stearic acid and observed that it resulted in oriented disk-shaped vaterite formation.[23,27] Heywood and Mann studied the oriented nucleation of BaSO$_4$ under compressed Langmuir monolayers of long chain alkyl phosphonate, which resulted in plate-like out growth as well as bow-tie morphology,[6] and under an n-eicosyl sulfate/eicosanoic acid monolayer it resulted in unusual and complex morphology of the BaSO$_4$ crystals.[7]

In this paper, we investigate the role of trace quantities of alcohol (ethanol) in the aqueous subphase on influencing the crystallography and morphology of BaSO$_4$ (barite) crystals grown in the presence of charged anionic Langmuir monolayers at two largely different supersaturation ratios. We have chosen BaSO$_4$ as a model system since a considerable body of information exists in the literature on barite morphology control,[6–9,17–19,21] possibly due to the importance of this mineral in cosmetics, papermaking and off-shore oil field applications. Dramatic changes are observed in the morphology of BaSO$_4$ crystals grown with and without ethanol in the subphase. These differences are attributed to small but significant changes in the dielectric properties of the interface due to preferential adsorption of ethanol under the Langmuir monolayers. Preferential adsorption of ethanol molecules at the air–water interface is expected to influence not only the organization of the surfactant monolayer but also to alter the dielectric properties of the interface[28–31] and, consequently, the electrostatic binding of the ions with the Langmuir monolayer prior to mineralization. It has been reported that hydrophobic additives such as 4-methoxy-(E)-cinnamic acid in water result in the formation of highly ordered aggregates of the additive at the air–solution interface.[32] Such an ordering of ethanol molecules at the air–water interface could also contribute significantly to the control of BaSO$_4$ morphology in this study.[32] Presented below are the details of this study.

Experimental

Measurement of pressure–area (π–A) isotherms and the preparation of LB films were carried on a computer controlled NIMA 611 model trough equipped with a Wilhelmy plate for surface pressure sensing. 50 μL of a 1 mg mL^{-1} solution of stearic acid (used as-received from Aldrich) in chloroform was spread on the surface of a 1×10^{-2} M aqueous solution of barium chloride (pH 6.0) as the subphase in the trough. After evaporation of the solvent (typically 15 min after spreading the monolayer) the pressure–area (π–A) isotherms were monitored at room temperature as a function of time at a compression/expansion rate of 50 cm^2 min^{-1}. π–A isotherms of the stearic acid–barium chloride system were recorded after 15 min and

after 1 h of spreading of the stearic acid Langmuir monolayer. After the π–A isotherm measurements of the stearic acid–barium chloride system had been taken, 60 μL of ethanol (final concentration of ethanol in the aqueous subphase is 1.7×10^{-3} M) was injected into the non-monolayer side (near the barrier) of the trough. Pressure–area (π–A) isotherms were recorded after 10 min, 1 h and 3 h of addition of the ethanol to the subphase. Thereafter, 100 mL of 1×10^{-2} M sodium sulfate solution in water was added to the subphase. Care was taken to remove an equal quantity of the barium chloride solution prior to sodium sulfate addition, thereby maintaining a constnat water level in the trough. This leads to a super-saturation ratio (S_R) of ca. 400 in the salt solution. After addition of Na_2SO_4, crystals of $BaSO_4$ were observed to form at the interface after 24 h. LB films of the $BaSO_4$ crystals were formed by the vertical lifting method onto Si (111) substrates for X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements at a surface pressure of 40 mN m^{-1} and a substrate withdrawal rate of 20 mm min^{-1}. In a similar manner, the crystallization of $BaSO_4$ was also carried out at a supersaturation ratio of ca. 50.

In order to determine the role played by ethanol in controlling the morphology of the $BaSO_4$ crystals grown at air–water interface, control experiments were performed wherein the $BaSO_4$ crystallization was accomplished without the addition of ethanol to the subphase at the two super-saturation ratios mentioned above.

XRD analysis of all the $BaSO_4$ samples was carried out on a Philips PW 1830 instrument operating in the transmission mode at 40 kV voltage and a current of 30 mA with CuKα radiation. SEM measurements were carried out on a Leica Stereoscan-440 scanning electron microscope equipped with a Phoenix EDAX attachment.

Results and discussion

The interaction of alcohols with aqueous interfaces plays an important role in a variety of physical and chemical processes.[28] Wilson and Pohorille[28] have shown that ethanol exhibits a pronounced free energy minimum at the air–water interface and, therefore, has positive adsorption at this interface. Taylor et al.[29] have studied the mass accommodation of ethanol at the liquid–vapor interface and have shown that the ethanol molecule will stay in equilibrium with the water molecules at the air–water interface. Gericke et al.[30] have discussed that water soluble solvents (e.g. ethanol) may alter the properties of the spread film. They have also shown that a small quantity of ethanol reduces the surface tension of a pure water subphase and that these water soluble ethanol molecules will remain in the hydrophobic region of the surface film or influence the adjacent water layer and the head group structure. In aqueous solutions, the hydrophobic chain of ethanol induces a new structure of the interface exhibiting less entropy (hydrophobic effect).[30] Donaldson and Anderson have studied the formation of critical clusters of solvent that have no free energy barrier for transport between the interfacial and bulk regions.[31] As mentioned briefly in the introductory section, Weissbuch, Leiserovitz and Lahav have shown the sponta-neous formation of aggregates of 4-methoxy-(E)-cinnamic acid on the surface of water.[32] It is clear that the addition of trace quantities of additives such as alcohol would considerably modify the properties at the air–water interface in different ways, thus providing a versatile means of modulation of the crystal morphology.

At pH 6, the carboxylate ions of the stearic acid Langmuir monolayer are expected to be fully charged leading to maximum attractive electrostatic interaction with the metal cations.[6–9] Thereafter, preferential adsorption of ethanol molecules at the air–water interface is expected to influence
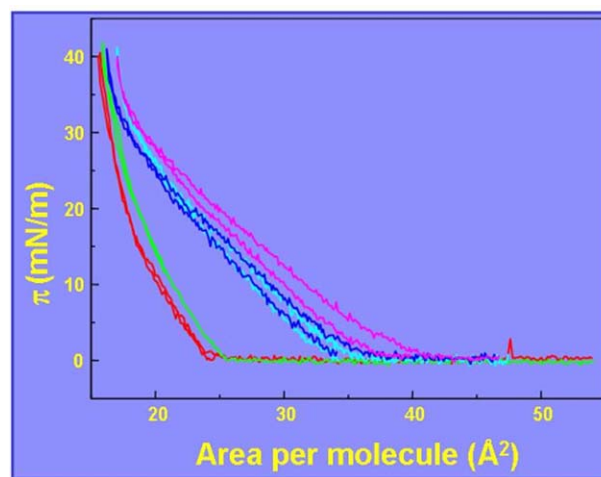

Fig. 1 π–A isotherms recorded from a stearic acid monolayer on an aqueous $BaCl_2$ solution before and after addition of ethanol into the subphase at various times (see text for details). Curves in red and green: π–A isotherms recorded 15 min and 1 h, respectively, after spreading of the stearic acid monolayer on the aqueous $BaCl_2$ subphase; curves in blue, cyan and magneta: π–A isotherms recorded 10 min, 1 h and 3 h, respectively, after addition of ethanol to the subphase.

not only the organization of the surfactant monolayer but also to alter the dielectric properties of the interface[28–32] and, consequently, the electrostatic binding of the Ba^{2+} ions with the carboxylate ions of the stearic acid molecule prior to mine-ralization. Thereafter, reaction of the Ba^{2+} ions with sulfate anions leads to the formation of $BaSO_4$ at the air–water interface.

In order to follow the complexation of the metal ions with the charged group of the surfactant molecules at the air–water interface, measurements of the surface pressure as a function of the monolayer area were performed. The π–A isotherms of the stearic acid monolayer on the aqueous barium chloride solution and after addition of a trace quantity of ethanol are shown in Fig. 1. Curves in red and green in Fig. 1 represent the π–A isotherm compression/expansion cycles of the stearic acid Langmuir monolayer on the barium chloride subphase at times of 15 min and 1 h, respectively. The expansion of the monolayer to a limiting area per molecule value of 23 Å^2 is observed which remained constant thereafter. It is clear that there is a fairly rapid expansion of the monolayer (curve in red), which indicates complexation of the barium ions with the carboxylic group of stearic acid. The π–A isotherms stabilize within 1 h of spreading of the monolayer. The curves in blue, cyan and magneta in Fig. 1 correspond to the π–A isotherm compression/expansion cycles after addition of a trace quantity of ethanol to the stearic acid–barium chloride subphase at times of 10 min, 1 h and 3 h, respectively. The expansion of the monolayer to a limiting area per molecule value of 33 Å^2 is observed which remained constant thereafter. We attri-bute this additional expansion of the stearic acid Langmuir monolayer to adsorption of ethanol at the air–water interface.

The SEM micrographs shown in Fig. 2 at different magnifications were obtained from the $BaSO_4$ crystals grown at the air–water interface with a stearic acid monolayer in presence of alcohol at an S_R of ca. 50. At lower magnification (Fig. 2A), a number of $BaSO_4$ crystals having bow-tie morpho-logy are observed. Spot profile EDAX (energy dispersive analysis of X-rays) measurements taken from within one of the crystals yielded a Ba : S : O ratio in excellent agreement with that expected for barite. It is clear from the low magnification images (Figs. 2A and B) that a number of the crystals are of very uniform size and are evenly distributed over the surface of the substrate. At higher magnification, finer details of the structure of the crystallites can clearly be resolved (Fig. 2C).
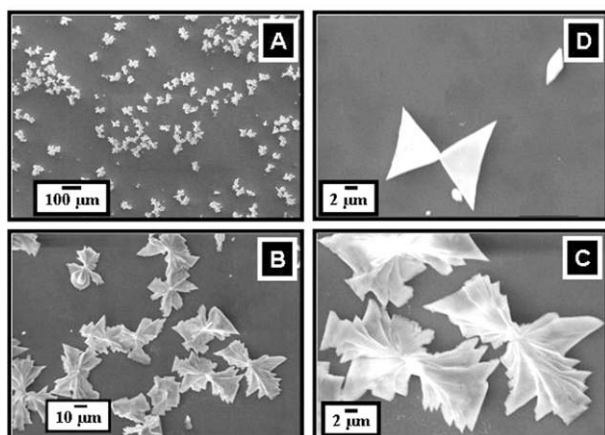
Fig. 2 A, B, C and D: SEM micrographs at different magnifications recorded from $BaSO_4$ crystals grown at the air–water interface with a monolayer of stearic acid in the presence of ethanol at an S_R of *ca.* 50.

The SEM picture shown in Fig. 2C clearly shows that the structures have 2-fold symmetry with well designed branching barite crystals whereas bow-tie structures with very smooth edges can be observed in Fig. 2D. As briefly mentioned in the Introduction, Heywood *et al.* have reported on the oriented nucleation of $BaSO_4$ crystals at an identical supersaturation ratio under compressed Langmuir monolayers of long chain alkyl phosphonates.[6] They have observed that a similar reaction process resulted in plate-like out growth of the barite crystals having a characteristic bow-tie morphology with rough edges.[6] This is in contrast to the smooth edges and dense crystal formation in this study. They have also reported that $BaSO_4$ growth under n-eicosyl sulfate/eicosanoic acid monolayers resulted in irregular and complex morphology of the crystals through the selective interaction of the developing crystal faces with the monolayer headgroups.[7] The XRD pattern recorded for the $BaSO_4$–stearic acid film of Fig. 2 is shown as curve 1 in Fig. 3. The XRD pattern was indexed with reference to the unit cell of the barite structure ($a = 8.87$, $b = 5.45$, $c = 7.15$ Å; space group *Pnma*).[33] For comparison, the XRD pattern recorded from the $BaSO_4$–stearic acid control film (without the addition of ethanol) grown at a similar supersaturation ratio is shown as curve 3 in Fig. 3. An
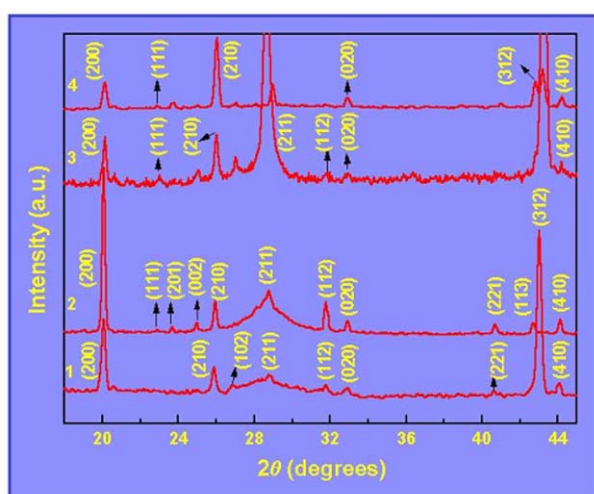

Fig. 3 XRD patterns recorded from $BaSO_4$ crystals grown at the air–water interface near stearic acid Langmuir monolayers in the presence and absence of ethanol at S_R values of *ca.* 400 and *ca.* 50. Curve 1: in the presence of ethanol (S_R *ca.* 50); curve 2: in the presence of ethanol (S_R *ca.* 400); curve 3: in the absence of ethanol (S_R *ca.* 50); and curve 4: in the absence of ethanol (S_R *ca.* 400).
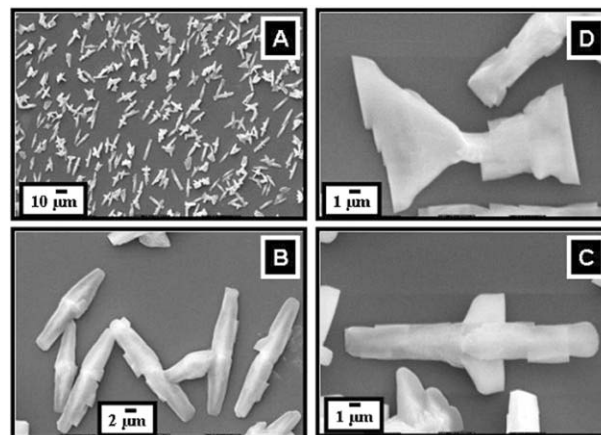

Fig. 4 A, B, C and D: SEM micrographs at different magnifications recorded from $BaSO_4$ crystals grown at the air–water interface with a monolayer of stearic acid in the presence of ethanol at an S_R of *ca.* 400.

interesting observation is the intense [3 1 2] Bragg reflection in the $BaSO_4$ film grown in the presence of ethanol that is considerably weaker in the film of the control experiment. This clearly indicates that face-specific nucleation and growth of the barite crystals occurs when crystallization is carried out in the presence of ethanol.

The SEM micrographs shown in Fig. 4 at different magnifications were obtained from the $BaSO_4$ crystals grown at the air–water interface with a stearic acid monolayer in presence of ethanol at an S_R of *ca.* 400. The lower magnification image (Fig. 4A) shows a number of well-formed barite crystals of fairly uniform size and with faceted surfaces. Higher magnification SEM images of the $BaSO_4$ crystals show the structure in greater detail (Figs. 4B and C). It is seen that the $BaSO_4$ crystals have an elongated, needle-shaped morphology, this morphology being quite different from the more compact structure of the crystals obtained at S_R 50 (Fig. 2). The SEM picture of one of the $BaSO_4$ crystals is shown in Fig. 4D and clearly reveals that some of the particles exhibit a bow-tie structure at a fundamental stage of growth. The morphology of the crystals is much smoother and quite unlike the more branched structure observed under lower supersaturation conditions (Fig. 2). Spot profile EDAX analysis of one of the crystallites yielded a composition consistent with $BaSO_4$. The XRD pattern from these crystals yielded sharp Bragg reflections characteristic of highly ordered crystalline barite (curve 2, Fig. 3).

The crucial role played by ethanol in modulating the morphology of the $BaSO_4$ crystals was determined by carrying out control experiments wherein the crystals were grown at the air–water interface in the presence of a stearic acid monolayer but without the addition of ethanol to the subphase. These experiments were carried out at both the supersaturation ratios of *ca.* 50 and *ca.* 400. Fig. 5 shows the SEM micrographs at different magnifications obtained from the $BaSO_4$ crystals grown at the air–water interface with a monolayer of stearic acid in the absence of ethanol at an S_R of *ca.* 50. At lower magnification (Fig. 5A), a number of $BaSO_4$ crystals with a highly irregular morphology can be seen, this morphology being radically different from the more regular bow-tie morphology of the barite crystals observed for similar supersaturation conditions in the presence of alcohol (Fig. 2). At higher magnification, the finer details of the crystals can clearly be resolved (Figs. 5B, C and D). The XRD pattern recorded for this film is shown as curve 3 in Fig. 3 and is characteristic of crystalline barite.

Fig. 6 shows the SEM micrographs at different magnifications obtained from the $BaSO_4$ crystals grown at the air–water interface with a monolayer of stearic acid in the absence of
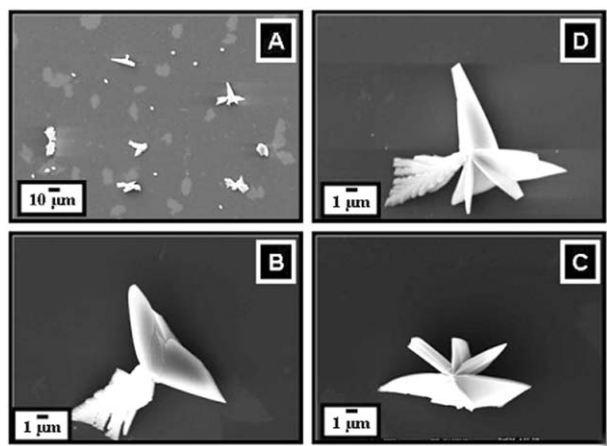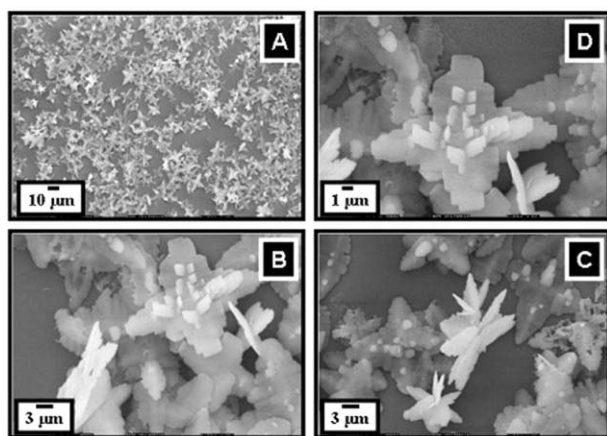
Fig. 5 A, B, C and D: SEM micrographs at different magnifications recorded from $BaSO_4$ crystals grown at the air–water interface with a monolayer of stearic acid in the absence of ethanol at an S_R of *ca.* 50.

Fig. 6 A, B, C and D: SEM micrographs at different magnifications recorded from $BaSO_4$ crystals grown at the air–water interface with a monolayer of stearic acid in the absence of ethanol at an S_R of *ca.* 400.

ethanol at a supersaturation ratio of *ca.* 400. At low magnification, a number of star-shaped structures of very uniform size can be seen and which are evenly distributed over the surface of the substrate (Fig. 6A). At higher magnification, the finer details of the structure can be clearly resolved (Fig. 6B, C and D).

The structures in Fig. 6 have 4-fold symmetry and appear to be composed of assemblies of crystallites, possibly due to secondary nucleation on the crystallites organized along the two perpendicular axes, and are completely different from the morphology of barite crystals obtained in the presence of ethanol at the air–water interface with a similar supersaturated solution (Fig. 4). In gross detail, the $BaSO_4$ structures shown in Fig. 6 are rather similar in morphology to the barite crystals obtained by Bromley *et al.*[17] They observed that at certain concentrations of additives containing (iminodimethylene) diphosphonate motifs, crystal growth along the [0 1 0] direction was more severely inhibited than along the [1 0 0] direction, which taken together with rounding along the [1 0 0] direction resulted in rounded, star-shaped single crystals of $BaSO_4$. Spot profile EDAX measurements well within one of the $BaSO_4$ stars yielded a Ba : S : O ratio in excellent agreement with the expected composition. The XRD pattern recorded for this film is shown as curve 4 in Fig. 3.

Conclusions

It has been demonstrated that trace quantities of surface-active additives such as ethanol during the growth of $BaSO_4$ crystals

at the air–water interface in the presence of stearic acid Langmuir monolayers resulted in a dramatic variation of the barite crystal morphology. While the exact reasons leading to the morphology variation in the presence and absence of ethanol are not understood at this time, it is believed that they may be due to a combination of two factors. The preferential adsorption of ethanol at the air–water interface is expected to affect the organization of stearic acid molecules in the Langmuir monolayer and, thus, the templating action of the Langmuir monolayer. Accumulation of ethanol at the subphase surface would also reduce the dielectric constant of the interfacial region and thus lead to enhanced binding of barium ions at the interface. The use of the surface-active adsorbates at the air–water interface throws open the exciting possibility of tailoring the physical and chemical properties of the interface and thereby modifying the morphology of the crystals nucleating and growing at the interface.

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