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Effect of different amphiphiles and their monolayers on the crystallization of $CuSO_4·5H_2O$ †

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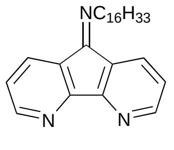
The crystallization of $CuSO_4·5H_2O$ under a series of monolayers, 9-hexadecylimino-4,5-diazafluorene (hidf), 5-hexadecyliminomethyl-8-hydroxyquinoline (hihq), 8-hexadecyloxyquinoline-2-carboxylic acid (hqa) and stearic acid (sa) has been studied. The results demonstrate that the selection of the amphiphile for controlling oriented crystallization is very important. The hidf monolayer is the best template for oriented nucleation and growth of $CuSO_4·5H_2O$ as its lattice structure can match the (010) face of $CuSO_4·5H_2O$ perfectly. Furthermore, between $CuSO_4·5H_2O$ and $Na_2SO_4·7H_2O$, only the hidf monolayer can choose $CuSO_4·5H_2O$ to nucleate under it. The selection of a suitable phase of each monolayer for controlling the oriented crystallization is also a key factor in the induced crystallization. For example, when a hqa monolayer is in the gas or liquid phase its ability to induce oriented crystallization of $CuSO_4·5H_2O$ is poor and the best state is not the most condensed one, rather a liquid–solid state. This is attributed to the co-ordination effect and the lattice matching between the inorganic and organic interfaces. The relationship between the surface pressure and area per molecule (π *vs.* A curves) and the monolayers' ability to control crystallization is also discussed.

Inspired by the investigations of biomineralization, the study of crystallization under organic ultra-thin films has become one of the most active fields in inorganic chemistry and in some related subjects such as physics, biology and materials science.[1–13] And it would lead to the development of new strategies in the controlled synthesis of inorganic nanophases, the crystal engineering of bulk solids, and the assembly of organized composite and ceramic materials.[4,7,9–15]

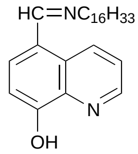
The most fashionable approach is the use of simplified organized surfaces, which are compressed surfactant films formed at air/water interfaces (Langmuir films), as substrates for inorganic crystallization from supersaturated subphases. In the past decade, the nucleation of some minerals under a monolayer has been reported and many interesting results obtained.[16–26]

In this paper we summarize our present studies in this field and discuss the influence of different head groups and different monolayer states on the ability to control crystallization of $CuSO_4·5H_2O$. We think these results will help understanding of the process of the crystallization under a monolayer and give useful reference data for further studies.

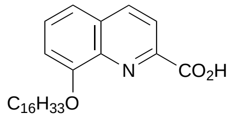
In our opinion, the process of crystallization under a monolayer can be interpreted in terms of a hierarchy of control levels. The first is that the monolayer should have effective sites for nucleation at the monolayer/water interface and the second is that it should possess the ability to choose certain crystals from a mixed solution containing more than one solute. As we know, although many salts dissolve in a biological system, only a few minerals can be deposited on a certain substrate. The organic matrix controls the crystallochemical properties of the biomineral. Similarly, as a good template, the monolayer should have this ability too, so that the head groups of amphiphiles packed in the monolayer should be able to recognize some ions. The third is that the monolayer should have the ability to induce oriented crystallization. Apparently, the inorganic composite materials formed in biological systems are distinguished from synthetic composites. In these systems the organic matrices are often various organic frameworks and their chemical, steric and structural properties are critical factors in the control and organization of bioinorganic solid formation. As a monolayer is an organized molecular film with functional groups, the crystallographic relationships between the overgrowth and the substrate should be controlled by the epitaxial matching of lattice spacings at the monolayer/crystal interface.



hidf



hihq



hqa

$CH_3(CH_2)_{16}CO_2H$

sa

Up to now, controlled crystallization under a monolayer at these three different levels has been achieved.[16–27] However, some mechanisms of these processes are not well understood. For example, which kind of monolayer should we choose to control the growth of a certain crystal? Which state of the monolayer is the best one and how can we find it? To answer these questions, we have studied systematically the induced crystal growth of $CuSO_4·5H_2O$ under a series of monolayers in different states.

Experimental

Four amphiphiles were chosen in our experiment: 9-(hexadecylimino)-4,5-diazafluorene (hidf), 5-hexadecyliminomethyl-8-hydroxyquinoline (hihq), 8-hexadecyloxyquinoline-2-carboxylic acid (hqa) and stearic acid (sa), in which hidf, hihq and hqa were synthesized in our laboratory and sa was obtained from Shanghai Chemical Reagents Co. Although the compounds have the same hydrophobic part, which is the long alkyl chain containing sixteen carbon atoms, their hydrophilic parts are dissimilar: hidf's head group is a diazafluorene Schiff-base

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segment containing two nitrogen atoms with lone-pair electrons; hihq's head group is a quinoline containing a nitrogen and an oxygen atom as the co-ordination sites; hqa's head group is a quinoline acid containing one nitrogen atom and two oxygen atoms, but its long alkyl chain is connected at the C[8] position of the quinoline ring; the hydrophilic part of the sa is a carboxylic acid and there is no nitrogen atom in its structure.

The characteristics of the monolayers of the four amphiphiles on different subphases were measured by a KSV-5000 Langmuir–Blodgett system. Three subphases, pure water, an aqueous solution of $CuSO_4$ (1×10^{-2} mol dm^{-3}) and a mixed aqueous solution of $CuSO_4$ (1×10^{-2} mol dm^{-3}) and Na_2SO_4 (1×10^{-2} mol dm^{-3}), were used for the later study on crystallization. The four amphiphiles were dissolved in chloroform at a concentration of 1.0×10^{-3} mol dm^{-3} and spread on the subphases. Generally 15 min were allowed for chloroform evaporation, the monolayer was then compressed by two movable Teflon barriers at a rate of *ca.* 20 mm min^{-1}. The isotherm of surface pressure (π) *vs.* area per molecule (A) was recorded automatically. All these studies were carried out in a dust-free box at 20 °C. The compressed monolayers were transferred to a clean substrate (glass) and these Langmuir–Blodgett films were examined by an ESCALAB MK-II electron spectrometer (X-ray photoelectron, XPS, mode) to gather information on the interaction between ions and the amphiphiles.

The salt $CuSO_4 \cdot 5H_2O$ was chosen as its stability and morphology have been studied thoroughly and its crystal face could be examined easily. A mixed solution including $CuSO_4$ and Na_2SO_4 was also used for study at the second level. The preparation of a supersaturated solution at 20 °C was described in our previous paper:[27] $CuSO_4$ (32 g) was added to water (100 g) at 40 °C. After the solute had dissolved the temperature was reduced to 20 °C and the solution filtered. The filtrate, a supersaturated solution of $CuSO_4 \cdot 5H_2O$ at 20 °C, was transferred to a mini trough of a KSV-5000 Langmuir–Blodgett system and the temperature of the subphase was increased to 25 °C then reduced to 22 °C. A monolayer was carefully and slowly spread from the 1.0×10^{-3} mol dm^{-3} solution in $CHCl_3$. Next, by means of the Langmuir–Blodgett system, a suitable state was chosen through the π *vs.* A curve, meanwhile the temperature of the subphase dropped to 20 °C. Thus, the crystallization of $CuSO_4 \cdot 5H_2O$ in the trough was studied under different conditions. The crystals formed at the interfaces or in solution were examined by optical microscopy and the crystal faces by a D/Max-RA X-ray diffractometer by measuring the distances (d) of the crystal faces and using A.S.T.M. cards. The study of crystallization in the mixed solution of $CuSO_4$ and Na_2SO_4 was similar except that $CuSO_4$ (25 g) and Na_2SO_4 (10 g) were added to water (100 g).

Results and Discussion

At first we studied the crystallization of $CuSO_4 \cdot 5H_2O$ under the four monolayers. When a compressed monolayer is formed at an air/water interface the nucleation of $CuSO_4 \cdot 5H_2O$ occurs preferably under it and in spite of the different structural characters of the amphiphiles. Nevertheless, the ability to induce nucleation is influenced by the various states of the monolayer. The results obtained with hqa are typical. Unlike the other compounds, the π *vs.* A isotherm of hqa on the subphase of $CuSO_4$ solution has expanded (gas phase), plateau (liquid phase) and condensed (solid phase) regions at different surface pressures so that it is suitable for this purpose. In this experiment, seven typical states of the monolayer were selected and defined as **I**, **II**, **III**, **IV**, **V**, **VI** and **VII** in the π *vs.* A curve. When the monolayer is in state **II**, the probability of (010) crystal face of $CuSO_4 \cdot 5H_2O$ is more than half; with decreasing A, the probability increases rapidly. Nevertheless, when the monolayer is in state **IV**, which belongs to the liquid phase, all nucleation occurs at the interface. This is maintained until the monolayer collapses on the surface (state **VII**). Similar results were observed under the other amphiphile monolayers. Obviously, these results show that it is not necessary to synthesize a special amphiphile in order to promote nucleation under a monolayer. Rather, the key factor is the state of the monolayer, which should be in liquid or solid phase.

The result can be explained from the knowledge about nucleation.[28] A monolayer can be considered as a new kind of phase formed on the surface of a solution, instead of at the air/water interface, therefore this film can provide suitable sites for heterogeneous nucleation, which occurs much easier than homogeneous nucleation in the supersaturated solution. On the other hand, these amphiphilic ligands not only have the structural characteristics of common surfactants, but also the chemical properties of normal ligands. All these features result in an increase in the solute concentration in proximity to the monolayer. As a consequence the nucleation of $CuSO_4 \cdot 5H_2O$ occurs preferably under the monolayers. However, when the monolayer is in the gas phase, to some extent, as the nature of a monolayer/water interface is similar to that of an air/water interface, nucleation does not take effect.

At second level the experimental results obtained for the different amphiphiles are distinct. The proportions of $CuSO_4 \cdot 5H_2O$ and $Na_2SO_4 \cdot 7H_2O$ crystals formed under compressed monolayers are illustrated in Fig. 3. When a compressed hidf monolayer forms on the mixed supersaturated solution, the nucleation sites of the two crystals are separated: the $CuSO_4 \cdot 5H_2O$ crystals form at the monolayer/water interface and $Na_2SO_4 \cdot 7H_2O$ crystals appear at the bottom. However, under monolayers of hihq, hqa and sa, both $CuSO_4 \cdot 5H_2O$ and $Na_2SO_4 \cdot 7H_2O$ crystals can be found under the monolayers. However, the percentage of the $CuSO_4 \cdot 5H_2O$ crystals under the monolayers decreases in the order hihq > hqa > sa.

This interesting phenomenon can be explained by the principles of co-ordination and hard–soft acid–base theory. As a rule, N is associated with a soft base and O with a hard one; Cu^{2+} is a soft acid and Na^+ a hard one. Therefore, N is a better co-ordination site for Cu^{2+} than for Na^+ and O interacts with Na^+ well. Having two nitrogen atoms and no oxygen atom, hidf is a preferable ligand for copper ions and its local concentration under the monolayer is much higher than that in solution. Owing to ion exclusion, the concentration of Na^+ decreases. So the value of the supersaturation ratio S of $CuSO_4 \cdot 5H_2O$ is increased and that of $Na_2SO_4 \cdot 7H_2O$ is decreased in proximity to the monolayer. As a result, under a hidf monolayer the crystallization of $CuSO_4 \cdot 5H_2O$ is predominant. However, having one or more oxygen atoms in the head groups, hihq and hqa can co-ordinate with Cu^{2+} and Na^+ in the meantime, so that the ability to accumulate Cu^{2+} under their monolayers is weakened with increasing number of oxygen atoms in molecular structure. Nevertheless, because sa interacts with cations by Coulombic attraction it is hard for sa to recognize Cu^{2+} and Na^+ and $CuSO_4 \cdot 5H_2O$ crystals can coexist with $Na_2SO_4 \cdot 7H_2O$ under its monolayer.

At the third level, the experiment was carried on pure $CuSO_4$ supersaturated solution (not the mixed solution) and some interesting results were obtained under the different monolayers formed by the four amphiphiles.

(1) The best monolayer-forming agent of all is hidf. When the monolayer is in the compressed state (solid phase), especially where A and π are about 35 Å^2 and 35 mN m^{-1} [the lattice area of the (010) face of $CuSO_4 \cdot 5H_2O$[27] is 34.76 Å^2], all the millimetre-sized crystals are formed under the monolayer and their ladder shape [Fig. 4(*b*)] is different from that of the normal ones grown from solution in the absence of a monolayer which are plated [Fig. 4(*a*)] with three main faces (110), ($1\bar{1}0$) and (001). The X-ray diffraction patterns reveal a new and special face on the laddered crystal, (010), which is not the initial face of $CuSO_4 \cdot 5H_2O$ grown from aqueous solution. Thus the (010) face is a result of the control by the monolayer and is due to the

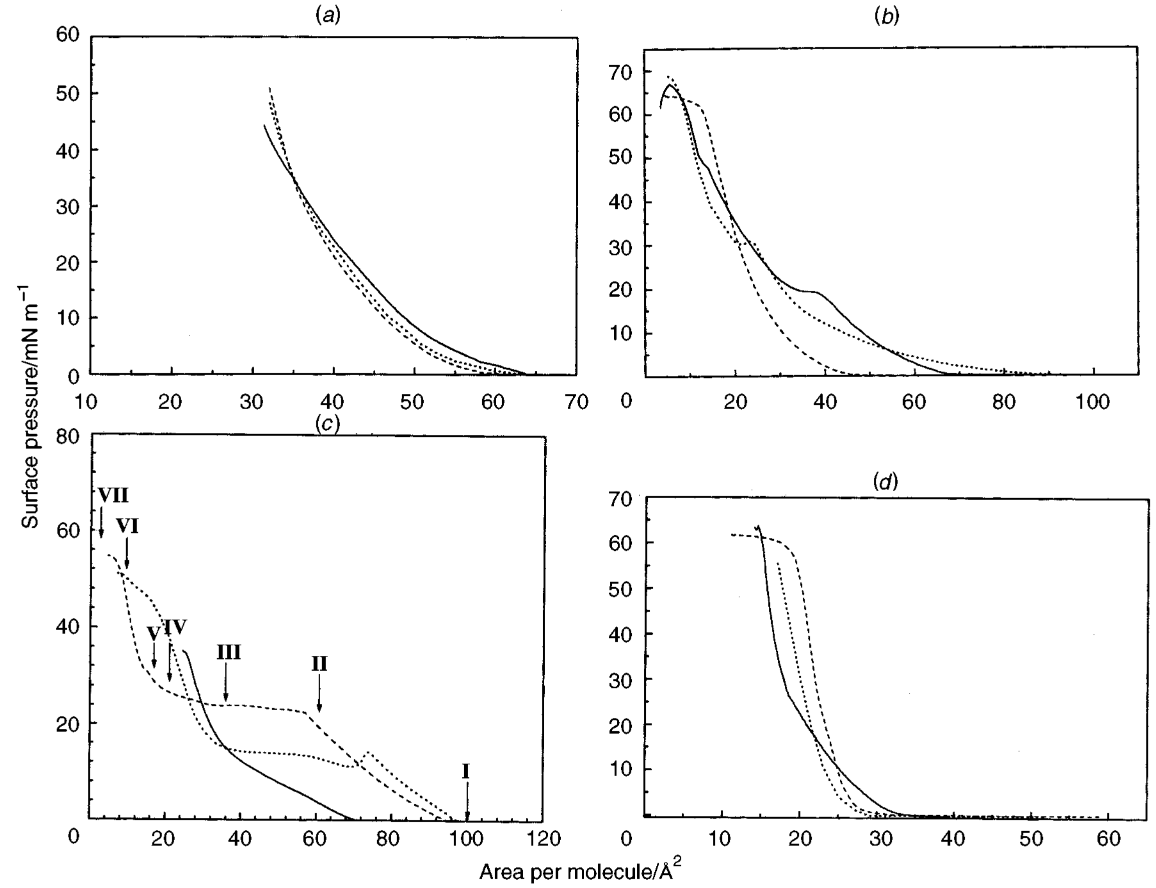

Fig. 1 Surface-pressure isotherms (π *vs.* A curves) of the four amphiphiles on different subphases, *i.e.* pure water (—), $CuSO_4$ (1.0×10^{-2} mol dm^{-3}) solution (– – –) and the mixed solution of Na_2SO_4 and $CuSO_4$ (concentrations of both solutes are 1.0×10^{-2} mol dm^{-3}) (· · ·): (*a*) hidf, (*b*) hihq, (*c*) hqa and (*d*) sa. Evidently, in comparison with those on pure water, the characteristics of the monolayers were changed remarkably except for hidf when $CuSO_4$ is added to the subphases. Furthermore, when Na_2SO_4 is added to the $CuSO_4$ solution only the curve of hidf is unchanged

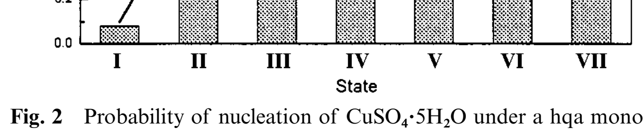

Fig. 2 Probability of nucleation of $CuSO_4{\cdot}5H_2O$ under a hqa monolayer in different states **I**–**VII**, defined by its π *vs.* A curve

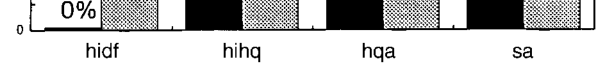

Fig. 3 Percentages of $CuSO_4{\cdot}5H_2O$ and $Na_2SO_4{\cdot}7H_2O$ crystals formed under the compressed monolayers of the four amphiphiles

epitaxial matching of lattice spacings of the specific crystal plane at the monolayer/crystal interface. The XPS study shows hidf can interact with Cu^{2+} giving a 1 : 1 complex Cu^{2+}–hidf and the (010) face is formed first as the Cu^{2+}–hidf structure (Fig. 5): hidf is a good template for copper ions, and the copper ions also act as the template for the (010) crystal face on which further growth is based.[27]

Crystallization under a hidf monolayer which is not so compressed gave similar results but non-oriented crystallization occurred and some plate-shaped crystals with the initial faces existed under the monolayer. The proportion of the non-oriented crystallization is increased with decreasing π. According to Mann,[10,14,29] the transcription synthesis involves a reorganized, self-assembled and relatively stable organic architecture for the use of chemical and structural templates for patterned materials deposition. The organized structure of films is generally considered to be of fundamental importance. Under a disordered template lattice matching and epitaxial growth were impossible and the crystallization of $CuSO_4{\cdot}5H_2O$ can not be oriented and controlled well. Perhaps, to some extent, the proportion of the non-oriented crystallization reflects the degree of disorder and defects in the monolayer.

(2) The compound hihq also gave good results. When the monolayer is in a state such that π and A are 40 mN m^{-1} and 20 Å^2 respectively, the crystals formed under the monolayer are plate-shaped as normal [Fig. 4(*c*)] but attached to the monolayer *via* the (110) face. This fact indicates that crystallization under a hihq monolayer is also oriented, though the induced face is an initial face. For different monolayer-forming agents, the local environment under a monolayer will be changed in physical properties such as the electric field, energy and mass

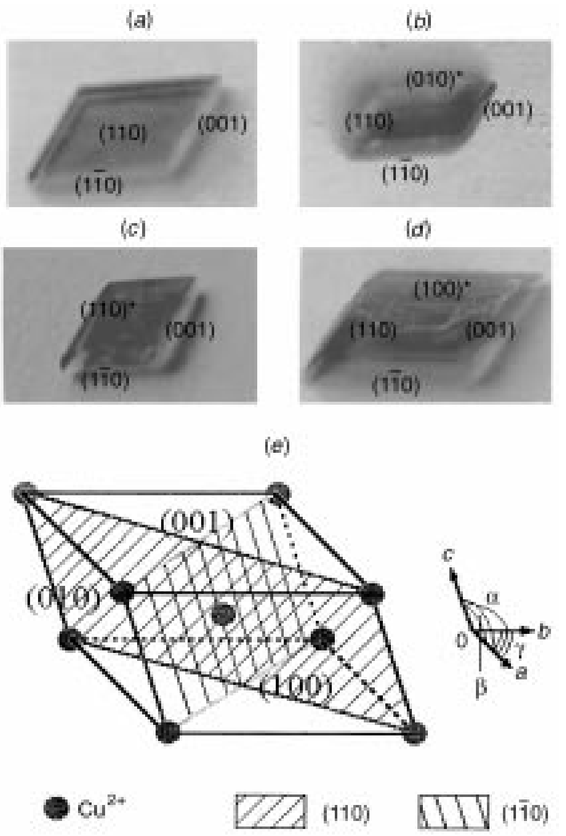

Fig. 4 Topographies of $CuSO_4{\cdot}5H_2O$ crystals with crystal faces labelled: (*a*) normal crystal grown without a monolayer; (*b*) crystal obtained under compressed monolayers of hidf, hqa and sa respectively; (*c*) crystal induced by compressed monolayer of hihq; (*d*) one of the crystals grown under a less compressed monolayer of hihq. The faces labelled with an asterisk are the induced faces, attached to the monolayers during crystallization. (*e*) Packing diagram of copper ions in a crystal cell of $CuSO_4{\cdot}5H_2O$ and the faces relevant to the results: $a = 7.26$, $b = 10.71$, $c = 5.96$ Å and $\alpha = 97.6$, $\beta = 125.3$, $\gamma = 94.3°$

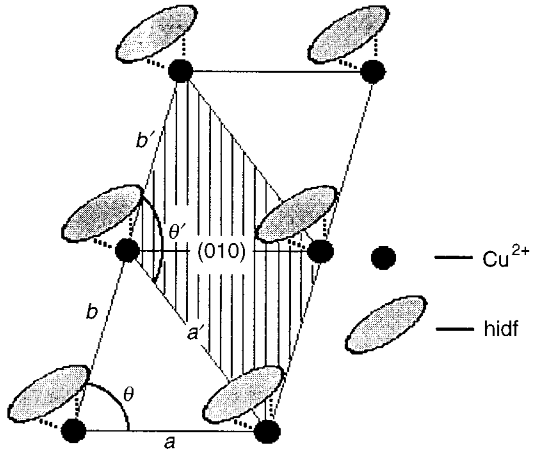

Fig. 5 Matching between the Cu^{2+}–hidf monolayer and the (010) crystal face of $CuSO_4{\cdot}5H_2O$. The computed result for the monolayer is $a = 6.2$, $b = 6.0$ Å and $\theta = 73°$; the corresponding lattice parameters of the (010) crystal face are 6.12, 5.96 Å and 72.8° (the lattice parameters are equated to $a' = 7.26$, $b' = 5.96$ and $\theta' = 125.3°$). Thus, the arrangement of the copper ions under the hidf monolayer is in close agreement with that on the (010) face of $CuSO_4{\cdot}5H_2O$

transmission, *etc.*, and some chemical properties related to the crystallization. As a result, the growth rates of some faces are also changed and the shape of the (110) face induced by a hihq monolayer changes from the normal shape, a parallelogram, into a lozenge. Clearly, this phenomenon implies that the different monolayers can influence the morphology of the crystal face too.

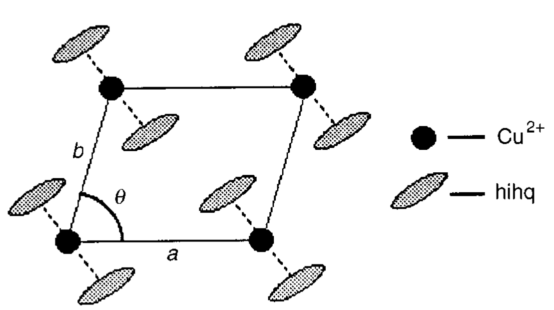

Fig. 6 Matching between Cu^{2+}–2hihq and the (110) face of $CuSO_4{\cdot}5H_2O$. Each Cu^{2+} ion is co-ordinated by two hihq molecules and the arrangement of the Cu^{2+} under the monolayer is $a = 7.0$, $b = 6.0$ Å and $\theta = 72.5°$, similar to the values on the (110) face of $CuSO_4{\cdot}5H_2O$ crystal (6.97, 5.96 Å and 72.8°). For copper ions under a hqa monolayer the values of the parameters are changed and the crystal face (010) is induced

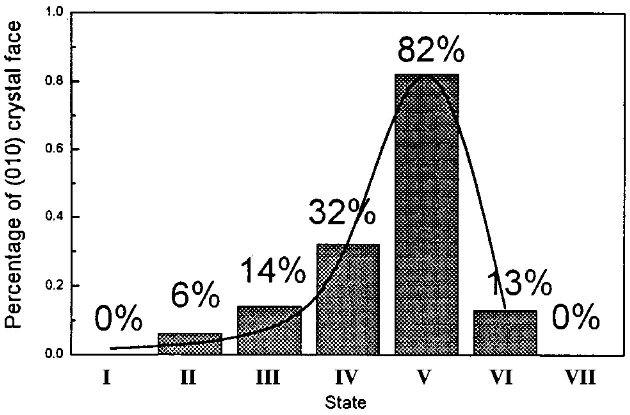

Fig. 7 Probability of the induced face (010) of $CuSO_4{\cdot}5H_2O$ under different states (from **I** to **VII**) of the hqa monolayer

Why is the (110) face formed under the monolayer? Obviously, the answer is similar to that for the (010) face formed under a hidf monolayer. However XPS studies show that each copper ion contacts two hihq molecules giving a 1 : 2 complex under the monolayer. The lattice area of the copper ions at the monolayer/water interface is about 20 × 2 = 40 Å^2, coinciding well with that of the (110) face of $CuSO_4{\cdot}5H_2O$, 39.67 Å^2 (Fig. 6).

When the hihq monolayer is less compressed and its A is in the region of 30–40 Å^2 a few special crystals are observed [Fig. 4(*d*)], *i.e.* a part of the (110) face disappeared and a new non-initial face (100) is formed. The lattice area of the (100) face is about 64 Å^2 and its half is 32 Å^2, this value is just located in the region selected.

(3) The situation of hqa is most complicated, there being seven typical states **I**–**VII** in its π *vs.* A curve. Interestingly, the best state of the hqa monolayer for controlling oriented crystallization is not the **VI**, the compressed one, but **V**. All results are summarized in Fig. 7. Both the plate- and ladder-shaped crystals can be obtained under all the seven states of the monolayer. Since none of the initial faces could alone be selected, therefore the proportion of the non-initial face (010) was used as reference for the ability to induce growth of $CuSO_4{\cdot}5H_2O$. This figure shows that when the monolayer is in states **II**–**IV** its ability to induce oriented crystallization is poor. However, with increasing π (or decreasing A) the monolayer becomes more and more organized, and the proportion of induced (010) face is also increased. When the monolayer is in state **V** not all the induced crystal faces are (010) (the proportion is about 80%); the rest are other initial faces of $CuSO_4{\cdot}5H_2O$. Further compression results in a decrease in the controlling ability and the proportion of (010) face drops to zero in state **VII**, where the monolayer collapses.

The characteristic of hqa on the $CuSO_4$ solution is similar to that of hihq, *i.e.* a copper ion is co-ordinated by two hqa molecules. Using the *A* value of state **V**, 17 Å^2, and the (010) face's lattice area, 34.76 Å^2, the result can be explained well. However state **V** is not in the compressed phase; there are some defects in this state like those in the liquid phase. The induced crystal faces under the monolayer are not all (010) faces. Although the monolayer is most condensed in state **VI**, the area per molecule is too low to match well any crystal face of $CuSO_4 \cdot 5H_2O$. This fact also demonstrates that the lattice structural matching between the organic template and induced crystal face is very important in the oriented crystallization. In addition, when the monolayer is in state **IV** the area per molecule, 20 Å^2, is larger than the limiting area, 18 Å^2, obtained by extrapolating the surface pressure to zero for the condensed region, and can be considered as the critical point of the solid phase. Therefore state **IV** remains much more characteristic of the liquid phase than does **V**. This is the reason why its ability to induce oriented crystallization is much lower than that of **V**.

(4) It seems difficult for the sa monolayer to choose a certain crystal face of $CuSO_4 \cdot 5H_2O$ and almost all faces mentioned above can be obtained simultaneously [but the proportion of the (010) face is more than those of any other in the compressed phase] under every state of the monolayer. This is due to mismatching between the monolayer and crystal face structure. Computer simulation[30,31] shows that at the compressed state its *a*, *b*, θ are nearly 5, 5 Å and 60° respectively and it is far away from any face of the $CuSO_4 \cdot 5H_2O$ crystal.

The different amphiphiles have different π *vs*. *A* curve shapes for the same subphase system and some useful information about the monolayer's ability to induce inorganic crystals can be obtained by these curves. First, we note that the π *vs*. *A* curve of the hidf on $CuSO_4$ solution is unchanged in comparison with that on pure water. Therefore, when a hidf monolayer is transferred from pure water to a substrate and then its Langmuir–Blodgett film is placed into $CuSO_4$ supersaturated solution the results obtained from both are the same. However, the results obtained from hihq, hqa and sa Langmuir–Blodgett films are always different. This is due to the fact that their π *vs*. *A* curves of the $CuSO_4$ solution are changed remarkably in comparison with the curves of pure water. This means the ability to control crystal growth is not related to the curve of pure water, but to that of the $CuSO_4$ aqueous solution.

Next, as Na^+ coexists with Cu^{2+} in the subphase, the shapes of the curves of hihq, hqa and sa on the mixed solution are different from those on pure $CuSO_4$ solution. However, this does not occur for hidf. Obviously, only Cu^{2+} can interact with hidf, the Na^+ is exclusively under the monolayer and the π *vs*. *A* curve mainly reflects the characteristic of the interface. In other words, when the curve of the subphase containing solutes A and B is similar to that of subphase A, the monolayer can recognize and select A from the mixed system.

Finally, the best state of hidf and hihq is just at the intersection of the two curves representing pure water and $CuSO_4$ solution respectively. This implies that the monolayer structures on pure water and on $CuSO_4$ solution are very similar and perfect matching perhaps occurs at this point. It is also demonstrated by computer simulation. We think this is very interesting and will repay further study in the future. However, as the intersection point of hqa is located in the liquid phase of the monolayer on $CuSO_4 \cdot 5H_2O$, at this point hqa does not show special characteristics.

Conclusion

In this paper we have shown that it is important to select a suitable amphiphile and a suitable monolayer state in research on controlled crystallization under a monolayer. Some useful information about the monolayer's ability to induce inorganic crystals can be got directly from the characteristics of the π *vs*. *A* curves. According to the three hierarchical control levels, in short, at the first level the key point is the selection of the monolayer state, which should be a liquid or solid phase and the selection of amphiphiles is not important. However, at the second level, the key point is the selection of a suitable head group for the amphiphile and, at the third level, the matching of lattice structures at the monolayer/water interface, which involves both the selection of the amphiphile and of the monolayer state.

Acknowledgements

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