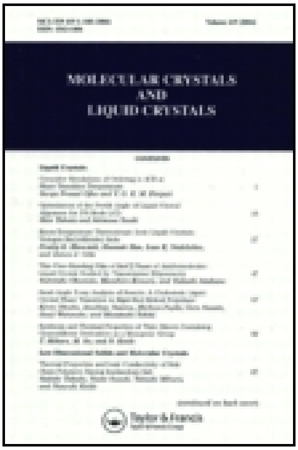

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SOME EXPERIMENTS ON THE TWO-DIMENSIONAL DISPOSITION CONTROL OF MOLECULAR CLUSTERS OF NM SIZE IN SPREAD MONOLAYERS OF A PARTIALLY FLUORINATED LONG-CHAIN AMPHIPHILE BY AFM

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Abstract Some experimental results are presented on the two-dimensional disposition control of molecular clusters of nm size in spread monolayers of a partially fluorinated long-chain acid by mixing with a rather short-chain perfluorinated acid. Cluster size does not change with mixing, but average inter cluster distance changes monotonously with increasing mixing ratio up to 70 %. However, regularity of the two-dimensional arrangement of clusters disappears at mixing ratio above 40 %.

INTRODUCTION

Langmuir-Blodgett films are made by successive deposition of insoluble monolayers at the water surface on to solid substrates. LB method is a supernatant technique to form molecularly ordered ultrathin organic films. However, it is difficult to control in-plane structures of the films by this technique.

We have found that partially fluorinated long-chain amphiphiles form two-dimensional monodisperse molecular clusters of a few tens nm size at the water surface using Atomic Force Microscope (AFM).[1)] The size and the shape of the two-dimensional molecular clusters change with changing molecular structures systematically.[2)]

This paper reports some attempts on the disposition control of two-dimensional molecular clusters in condensed monolayers by mixing with an amphiphile forming expanded monolayers.

EXPERIMENTAL

Film materials used are heptadecafluorononadecanoic acid (abbreviated hereafter as C19F17), and perfluoroundecanoic acid (abbreviated hereafter as C11F21). They were purchased from Wako Chemicals and were used without further purification. They were spread from solutions of spectrograde chloroform (Dojin Chemicals). Potassium hydroxide, cadmium acetate and lanthanum acetate used as source of metal ions in the subphase were of guaranteed grade (Wako Chemicals). Ultrapure water from Elgastat system was used as the subphase. Langmuir trough was that of computer-controlled one constructed in our laboratory. Details of the instrument was described elsewhere. [3] Atomic force microscope used was Nanoscope III and the tapping mode was used to avoid damages during observation of comparatively soft surface of one-layer LB films. Etched silicon cantilevers (125 μm length, 20-60 N/m, about 20 nm radius of curvature of the top of the probe pin) were used. One monolayer samples were transferred by scooping-up on to cover glass of optical microscope. Surface of the cover glass is smooth enough as the substrate for AFM observation of molecular films.

RESULTS and DISCUSSION

Figure 1 shows π-A isotherms of C19F17 at 10℃ on the subphase containing (a) potassium ion, (b) cadmium ion and (c) lanthanum ion, at concentration of 5×10^{-4} mol/l, respectively. As the valency of metal ions increases, isotherms shift to the smaller molecular areas. This means that multivalent metal ions have tendency to condense monolayers of C19F17 by forming metal salts. π-A isotherm of C11F21(Cd^{2+}) is much expanded (d).

Figure 2 represents top view images showing effect of changing metal ions on the molecular cluster of C19F17; (a) potassium ion, (b) cadmium ion, and (c) lanthanum ion. Size of the cluster does not appear to change except for the case of potassium ion where cluster

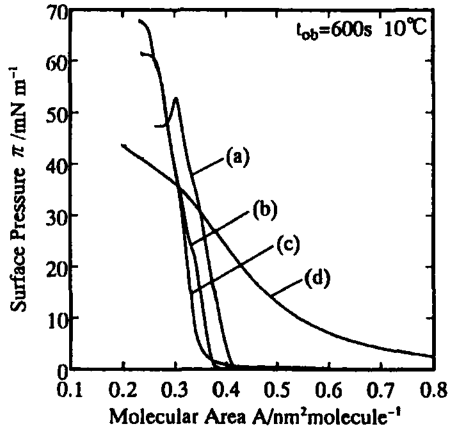

Fig. 1 π-A isotherms of C19F17 and C11F21.

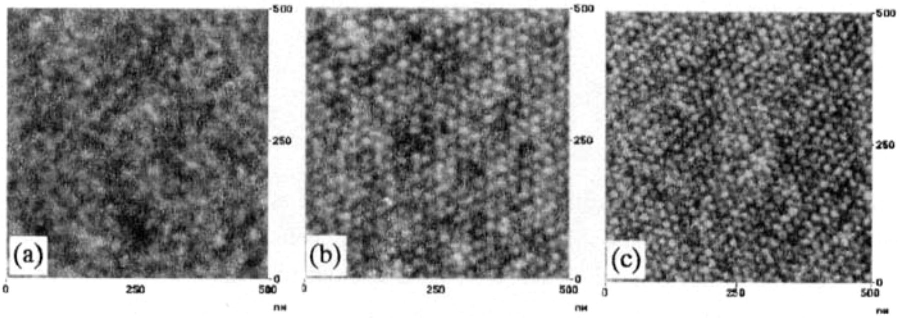

Fig. 2 Effect of metal ions on the cluster structure; (a) K^+, (b) Cd^{2+}, (c) La^{3+} (500×500 nm^2). (See Color Plate VII).

structure becomes diffuse, but the outline of the clusters becomes clearer as the valency of the metal ions increases. Molecular clusters are almost monodisperse and the average diameter of the clusters for the case of lanthanum salt is 19 nm. This figure means that one cluster is composed of several hundreds C19F17 molecules. Cross sectional analysis of the AFM image of Fig. 2(c) reveals that the height difference between the top and the bottom of the cluster is less than 1 nm which is about one third of the molecular length. High resolution AFM observation revealed that there is no regularity on the molecular arrangement in the clusters.

The plausible mechanism of the formation of such monodisperse clusters in the monolayers of C19F17 is as follows. When a small drop of the spreading solution is set on the water surface, the drop expands instantaneously to form a very thin solution layer of less than 1 μm, and the solvent evaporates very quickly. The film molecules are left on the water surface in the higher supersaturation because the equilibrium spreading pressure of C19F17 is extremely low at this temperature. Then, numerous numbers of two-dimensional nuclei are generated at the same time and they grow up to the clusters. When the nuclei start to grow up, the degree of supersaturation drops very rapidly and the generation of nuclei is now suppressed. This is the reason of the very narrow distribution of size of the clusters. We have reported that for a series of partially fluorinated long-chain acids, cluster size increased from less than 20 nm of C19F17 to about 80 nm of C31F17 under the same spreading conditions, and the shape of the clusters also change from that of circular to irregular. Thermodynamic consideration predict qualitatively that the critical radius of clusters (r*) should be determined by degree of supersaturation (S) and the line tension (τ) between the clusters and the surrounding phase as the following equation gives, [2)]

$$r^* = A\tau / kT \ln S$$

where A is the molecular area. When S is larger than unity, and the nuclei occasionally getting radius larger than r* can grow spontaneously.

As we wish to control size, shape and disposition of the two-dimensional clusters in spread monolayers, we tried to mix C19F17 with some film materials forming rather ex-

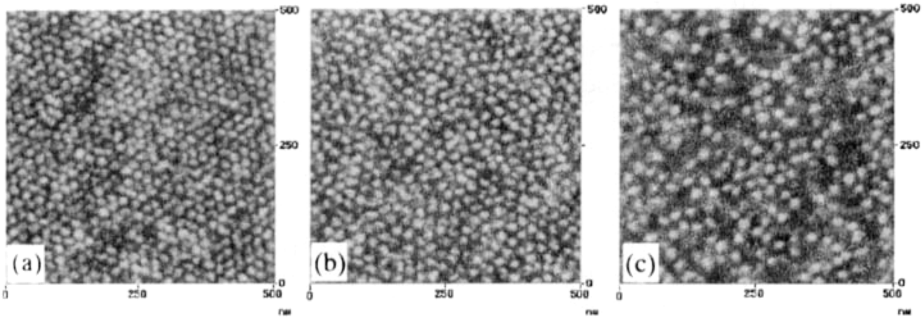

Fig. 3 Two-dimensional disposition control of C19F17 clusters by mixing with C11F21; (a) 20 %, (b) 40 %, (c) 60 % (500 × 500 nm^2).
(See Color Plate VIII).

panded monolayers such as methylmyristate. It was made clear by AFM observation that methylmyristate is not miscible molecularly with C19F17, and it forms microphases of lateral size of a few hundred nm in the mixed monolayer. We could not succeed disposition control of clusters in this case. Then, we use perfluoroundecanoic acid as a molecular diluent next. Figure 3 shows top view images of AFM of mixing samples of C19F17 with C11F21; (a) 20 %, (b) 40 %, (c) 60 %.

As seen from the images, the size of clusters does not appear to change with changing mixing ratio up to 60% at least. Figure 4 shows a relation between mixing ratio and the average inter-center distance of clusters. The inter-center distance increases monotonously with increasing mixing ratio up to 80 % but above 40 %, the disposition regularity was lost and the average distance shows large scatter.

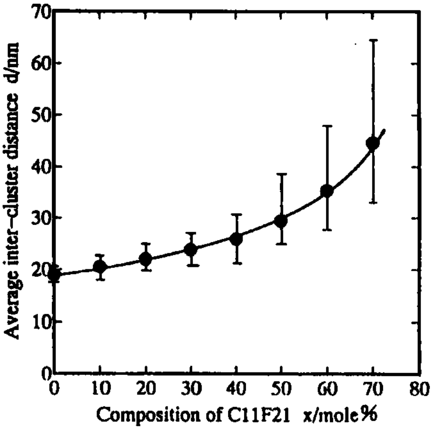

Fig. 4 A relation between mixing ratio and inter-center distance of clusters.

CONCLUSIONS

We have succeeded in the two-dimensional disposition control of molecular clusters of C19F17 in nm size by mixing with C11F21 without changing size. Requirements of mixing materials for the disposition control of the clusters are (1) they form rather expanded monolayers, and (2) they are miscible molecularly with the film materials which forms clusters. Average distance between clusters can be augmented by mixing up to 80 %, but the disposition regularity of clusters was lost above mixing ratio of 40 %.

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