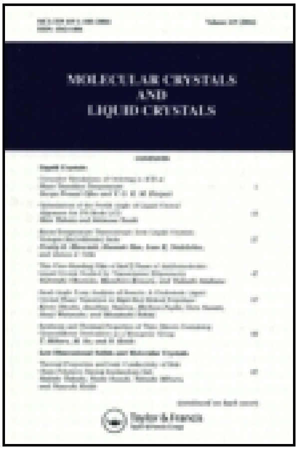

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Influence of Counter Ions on the Morphology of Cyanine Dye Aggregates at the Air/Water Interface

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Version of record first published: 24 Sep 2006

To cite this article: Takashi Watanabe, Makoto Shiga, Keisuke Asai & Kenkichi Ishigure (1999): The Influence of Counter Ions on the Morphology of Cyanine Dye Aggregates at the Air/Water Interface, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 327:1, 135-138

To link to this article: http://dx.doi.org/10.1080/10587259908026798

Mol. Cryst. Liq. Cryst., 1999, Vol. 327, pp. 135-138
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The Influence of Counter Ions on the Morphology of Cyanine Dye Aggregates at the Air / Water Interface

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(Received June 30, 1998; In final form July 15, 1998)

In a cyanine dye LB film, the J-aggregates of the dye molecules form domain structure. The shape and size of this structure are largely influenced by the conditions of film fabrication. We made a through investigation about the effects of counter anions of the dye molecules and ions as additives in the subphase on the domain structure in dye monolayers at the air/water interfaces and in LB films by using a fluorescence microscope. We found the conditions under which we can promote or prevent the growth of the domains, and discussed the influence of anions on π-A isotherm.

Keywords: cyanine dyes; domain structure; fluorescence microscopy; monolayer; J aggregates

INTRODUCTION

It is well known that cyanine dyes form J aggregates which have been attracting widespread attention in terms of their applicability to nonlinear optical devices[1] and photo-electro conversion devices, etc.[2]. The application to those devices requires us to incorporate the aggregates into thin solid films. The LB method is suitable for this incorporation. In the course of the application of this method prior to the transfer of a cyanine-monolayer containing J aggregates, the aggregates tend to organize themselves into crystalline domains at the air/water interface onto a substrate[3],[4]. This process largely influences the morphology of the J aggregates with the scale of micrometer which is directly related to their optical function on a mesoscopic scale and plays a critical role in their application. Therefore, the control of the J aggregate-morphology at the air/water interface is crucial. We found that the variation in the morphology is introduced by such parameters as spreading solvents, counter ions, ions contained in the subphase water. As a first step to realize how to control the morphology, we have closely studied the influence of counter ions on it by means of π-A isotherm measurement and fluorescence microscopy.

EXPERIMENTAL

Cyanine dyes used in this experiment are S120 series that differ only in counter anions (Fig. 1). By adding $NaClO_4$, NaF, KCl, KBr or KI to subphase, the sort and concentrations of ions (anions) in the subphase were varied. CH_2Br_2 was used as spreading solvent. Langmuir trough mounted with a fluorescence microscope was used for measuring π-A isotherms and observing dye monolayers at the air/water interface.

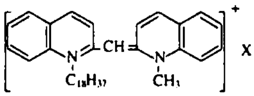
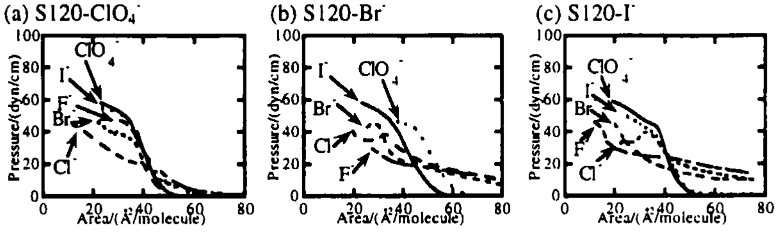


FIGURE. 1. Chemical structure of S120 cyanine dye. $X^- = ClO_4^-$, Br^- or I^-.

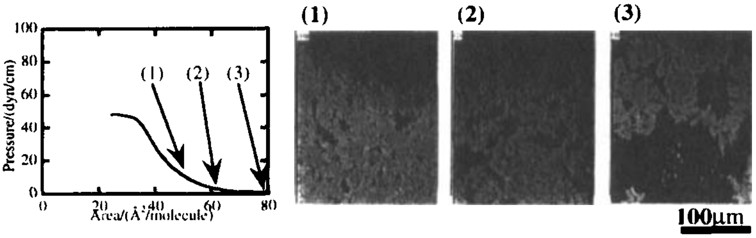
RESULTS AND DISCUSSION

π-A isotherm

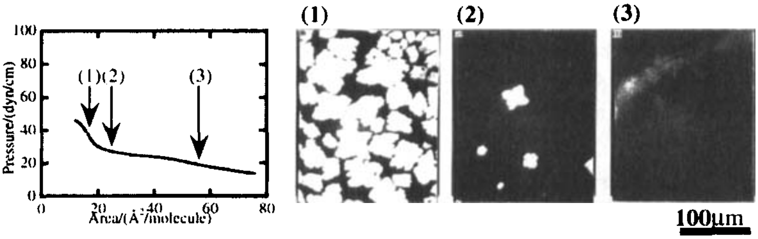
We found that the shape of the isotherm of S120 changed markedly with the varying combinations of the counter and subphase anions (Figs. 2), and classified the isotherms measured into two types, "low surface pressure type"(L type) and "high surface pressure type"(H type). While the monolayers of L type formed J aggregate domains even at the large molecule area of 100 $Å^2$/dye molecule or above (Figs. 3), the monolayers of H type formed domains when the monolayers were compressed to molecule area of 50 $Å^2$/dye molecule or below (Figs. 4). The marked difference in the molecule area dependence of the surface pressures between the two types was considered to arise from the extent of the dissociation


(a) S120-ClO_4^- (b) S120-Br^- (c) S120-I^-

FIGURES 2. π-A isotherms of S120 monolayers measured in various combination of dye counter anions and anions in the subphase.



FIGURES 3. π-A isotherm and fluorescence micrographs of an L type monolayer.

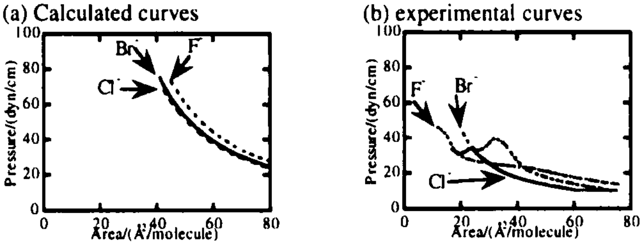


FIGURES 4. π-A isotherm and fluorescence micrographs of an H type monolayer.
(See Color Plate I at the back of this issue)

of the bond between the chromophore cation and counter anion of the cyanine dye. In the H type monolayer where the bond is largely dissociated, strong repulsive force works among the positively charged dye molecules and the high surface pressure would be generated at the large molecule area. In case of the strong repulsive force working among the dye molecules, the monolayer is compressed, the molecule area comes to be small and then the J aggregate domains would be formed. While in case of undissociated monolayers, only attractive force works. This would lead to the formation of the J aggregate domains at the large molecule area.

Theoretical interpretation of π-A isotherm

The high surface pressures observed at the large molecule area in the H type monolayers was explained quantitatively using Gouy-Chapman theory based on the assumption that the chromophore dye cations make a uniform surface layer with an electric double layer of the ions in the subphase. The electrostatic contribution (π_{el}) to the surface pressure (π) is given by a relation, $\pi_{el} = \int_0^{\psi_0} \sigma_0 d\psi$, where ψ is potential from the air/water interface to the bulk, ψ_0 and σ_0 are potential and charge density at the air/water interface. Defining x as distance from the interface to the bulk, we have a relation, $\sigma_0 = -\frac{\varepsilon}{4\pi}\left(\frac{d\psi}{dx}\right)_{x=0}$ from Poisson equation. Finally, the next relation $\pi_{el} = \sqrt{\frac{8\varepsilon k_B^3 T^3 C_0}{\pi e^2}}\left(\cosh\frac{e\psi_0}{2k_B T} - 1\right)$ is obtained from Gouy-Chapman theory. It was found that Stern layer has to be taken into account to explain the π-A curves measured, especially at the large molecule areas, using this theoretical treatment. Defining *r* as radius of the hydrated anions, a contribution (π_{el}) to the surface pressure from Stern layer is derived $\Delta\pi_{el} = \frac{4\pi\sigma_0^2}{\varepsilon} r$. From the above, $\pi = \Delta\pi_{el} + \pi_{el} = \frac{4\pi\sigma_0^2}{\varepsilon} r + \sqrt{\frac{8\varepsilon k_B^3 T^3 C_0}{\pi e^2}}\left(\cosh\frac{e\psi_0}{2k_B T} - 1\right)$. In Figs. 5 are shown the π-A curves calculated based on the above equation and the experimental curves for F⁻, Cl⁻ or Br⁻. The calculated curves indicate that the surface pressure decrease with increase of radius of hydrated anions. From comparing between the calculated and experimental curves, it is found that these curves have the same tendency in the order and also in the values, at the large molecule areas.


(a) Calculated curves

(b) experimental curves

FIGURES 5. Calculated curves and experimental curves of H type π-A isotherms.

CONCLUSION

Anions in the subphase change strikingly π-A isotherm of cyanine dye monolayers at the air/water interface and also the structures of J aggregate domain. These changes were considered to arise from the dissociation of the dye molecules and their interactions with the anions in the subphase.

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