Molecular Orientation of a Nematic Liquid Crystal Induced by Mixing with Tetraalkylcalix[4]resorcinarenes at the Air–Water Interface

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Abstract. *O*-Octacarboxymethoxylated tetraalkylcalix[4]resorcinareanes (CRA-CMs) formed stable monolayers on a water surface, whereas their π-A isotherms were affected by the length of the alkyl residues. A double-layered structuring was observed for CRA-CM having four undecyl substituents (11CRA-CM) by compression, though CRA-CM with four eicosyl residues formed a stable monomolecular film. 11CRA-CM possessed the ability to form a host–guest monolayer film with liquid crystalline 4,4′-dihexylazobenzene at the air/water interface, leading to perpendicular orientation of C6Azo. The host–guest mixed monolayers displayed a double-layered structuring by compression.

Key words: tetraalkylcalix[4]resorcinarene, nematic liquid crystal, host–guest, bilayered structure

1. Introduction

We recently observed that phthalocyanine metal complexes having eight long alkoxy substituents (CnPcM) possess an ability to incorporate hydrophobic rod-shaped molecules in their hydrophobic cavity at the air-water interface to form homogeneous host-guest mixed monolayers [1, 2]. The orientation of CnPcM in floating molecular films were influenced by some factors including the length of substituents, central metal ions and subphase temperature [1–3]. The edge-on arrangement of the Pc ring plane was dominant in floating films when the peripheral substituents were hexyloxy or decyloxy, respectively, in the self-aggregation of the macrocycles on a water surface [3]. On the other hand, CnPcM having long alkoxy residues ($C_{18}H_{37}O$- and $C_{20}H_{41}O$-) and central metals such as Cu and Co preferred the flat-laid conformation as a result of the *van der Waals* interaction among the substituents of CnPcM and the enhanced hydrophilic nature of the Pc ring [3]. Furthermore, the filling effect of long-chain normal alkane and hydrophobic liquid

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R = $C_{11}H_{21}$: **C11CRA-CM**
= $C_{20}H_{41}$: **C20CRA-CM**
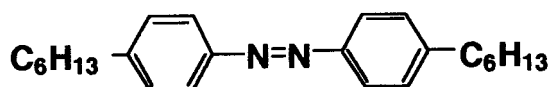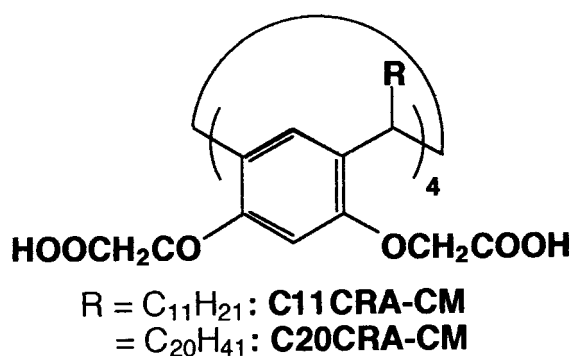
4,4'-dihexylazobenzene: **C6Azo**

T_{NI} = 20 °C (monotropic)

Figure 1. Structural formula of compounds.

crystals on the preferential formation of the flat-laid conformation of the CnPcM with eight long alkoxy substituents give rise to homogeneous mixed monolayers with improved stability [1]. In particular, host–guest mixed molecular films on water are interesting because of their unique structures, being regarded as a model for interfacial liquid crystals, whereas a water surface acts as a substrate covered with flat-laid phthalocyanine molecules with long-chain alkoxyls to determine the mode of LC alignment [4, 5].

The crown conformer of *O*-octacarboxymethoxylated calix[4]resorcinarenes (CRA-CM, Figure 1) has a cylindrical framework with the eight polar substituents at the upper rim, whereas hydrophobic alkyls are tethered to the lower rim so that this molecule can be regarded as a macrocyclic amphiphile. In this respect, CRA-CM is very attractive to fabricate this kind of model systems for an interfacial ultrathin LC layer, taking into account the fact that their floating monolayers are very stable on water [6]. This paper deals with the effect of the length of alkyl substituents on molecular assembly at the air–water interface and the fabrication and characterization of mixed floating molecular films formed by spreading with a nematic liquid-crystalline azobenzene (C6Azo, Figure 1).

2. Experimental

2.1. MATERIALS

2, 8, 14, 20-Tetraundecyl-4, 6, 10, 12, 16, 18, 22, 24-octacarboxymethoxyl-calix-[4]resorcinarene (C11CRA-CM) was prepared according to refs. [7, 8]. The synthesis of 4,4′-dihexylazobenzene (C6Azo) is described in refs. [5, 9].

2, 8, 14, 20-Tetraeicosyl-4, 6, 10, 12, 16, 18, 22, 24-octacar boxymethoxyl-calix[4]resorcinarene (C20CRA-CM). This was synthesized according to refs. [7, 8]. Mp = 163–165 °C. ^{1}H-NMR (90 MHz): δ = 0.80 (t, 12H, CH_3), 1.22, 1.72 (152H, CH_2), 4.05–4.55 (20H, Ar-CRH-Ar, Ar-OCH_2COOH), 6.35 (s, 4H, Ar-H), 6.58 (s, 4H, Ar-H). Found: C 71.0%, H 9.74%. Calculated for $C_{124}H_{200}O_{24} \cdot H_2O$: C 71.2%, H 9.67%.

2.2. π-A ISOTHERM MEASUREMENTS OF MONOLAYERS ON A WATER SURFACE

Measurements of surface pressure – area (π-A) isotherms were achieved on pure water (Milli-Q) filled in a Lauda FW-II film balance. Subphase temperatures were controlled at 20 °C by water circulation using RCS and RC6 (LAUDA). A spreading solution was prepared by mixing a THF and CHCl$_3$ (1 : 4) solution (v/v) of CRA-CMs (*ca.* 10^{-5} mol dm^{-3}) and C6Azo. After the completion of solvent evaporation for 10 min, a monolayered film was compressed at a speed of 25 cm^2 min^{-1}, and a π-A isotherm was recorded.

2.3. CHARACTERIZATION OF MONOLAYERS AT THE AIR−WATER INTERFACE

UV-visible absorption spectra of monolayers on water were recorded with a multi-channel photodiode MCPD-2000 (Ohtsuka Electronics) equipped with a quartz optical fiber [10, 11]. Brewster angle microscope (BAM) images were taken with an NLE-EMM633 (Nippon Laser Electronics).

3. Results and Discussion

3.1. MOLECULAR ASSEMBLY OF CRA-CMS ON A WATER SURFACE

π-A isotherms of C11CRA-CM and C20CRA-CM are shown in Figure 2. Surface pressures start to increase at A = around 2.0 nm^2 for both compounds, and estimated limiting areas per molecule were *ca.* 1.8 nm^2, being in agreement with the base area of the cylindrical macrocycle estimated by a space-filling molecular model (CPK-model). Consequently, a sharp rise in the surface pressure of π-A isotherms of CRA-CMs is due to the rigid molecular framework of the cylindrical macrocycle. It is worthy to note that π-A isotherms of CRA-CMs are influenced drastically by the length of the alkyl chains tethered to the lower rim of the cylindrical structure. In the case of C11CRA-CM, the first increment in surface pres-
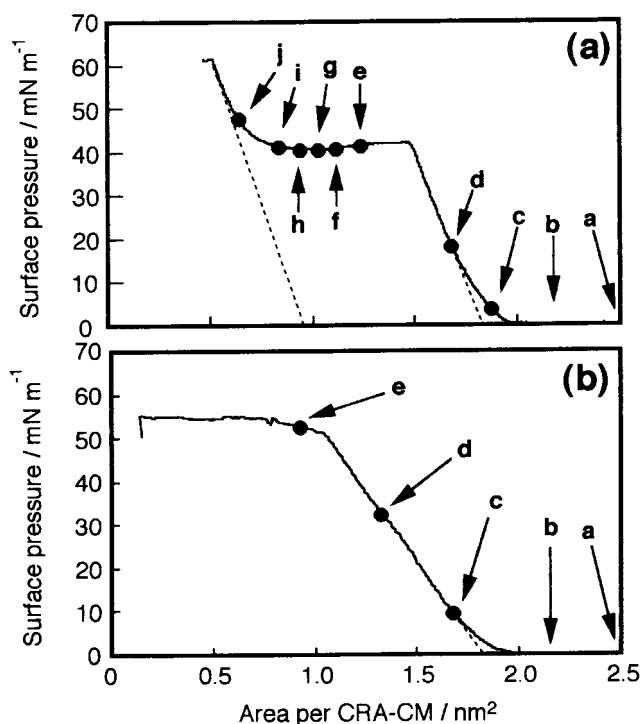
Figure 2. π-A isotherms of the monolayers (a) C11CRA-CM and (b) C20CRA-CM measured at 20 °C.

sure occurs in the region of 2.0 nm^2 > A (an area per molecule) > 1.5 nm^2, whereas the second appears at A < 1.0 nm^2 through the plateau region. A estimated from the second steepest region was *ca.* 0.9 nm^2 and just a half of that estimated from the first one. The isotherm was reversible, whereas the isotherm during the expansion process showed a slight hysteresis when compared with that on compression. On the other hand, the π-A isotherm of C20CRA-CM showed a single steep rise and a high collapse pressure (*ca.* 50 mN m^{-1}), indicating the formation of a stable monomolecular film.

UV absorption spectral measurements of monolayers on a water surface were achieved to obtain further information concerning the collapse behaviour by monitoring absorbances at *ca.* 284 nm due to the aromatic ring of CRA-CMs. The results are given in Figure 3. Absorbances of C20CRA-CM increase slightly as the decrease in A. In a marked contrast, absorbances of C11CRA-CM increase with the decrement of A in the plateau region, and the absorbance was approximately twice of that of C20CRA-CM when the surface pressure showed the second steep rise ($A = ca.$ 0.7 nm^2).

Surface morphology of these monolayers on a water surface was directly observed using Brewster angle microscope (BAM). The formation of a homogeneous monolayer by applying surface pressure was shown in the case of C20CRA-CM
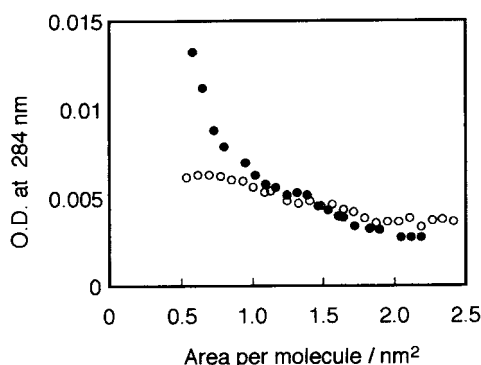
Figure 3. Absorbance changes of C11CRA-CM (●) and C20CRA-CM (○) at 284 nm as a function of area per molecule.

(Figure 4). Quite different BAM images were obtained for a C11CRA-CM monolayer (Figure 5). Photographs (a)–(d) were obtained using *p*-polarized light including a slight *s*-component to increase contrast between a monolayer and the water surface. The C11CRA-CM monolayer exhibits a homogeneous appearance (Figures 5(a)–(d)) in the first steep rise of surface pressure at $A = {\sim}1.3$ nm^2. When further reduction of A was made to give the plateau region, bright dots appeared and grew (Figure 5(e)–(j)). Since the brightness of films observed by BAM is affected by the thickness of films, the growing of bright dots of a C11CRA-CM floating molecular film suggests the generation of a multi-layered structuring as a result of further compression [12]. These results of π-A isotherms, UV absorption spectra and BAM measurements indicated that reversible double-layering occurs in a plateau region of the C11CRA-CM monolayer at the air–water interface.

3.2. MIXED MONOLAYER COMPOSED OF C11CRA-CM AND A NEMATIC LIQUID CRYSTAL

The formation and characterization of ultrathin molecular films incorporating a nematic liquid crystal were investigated under the anticipation that floating C11CRA-CM molecules at the air-water interface might act as a trigger for the perpendicular orientation of LC molecules in a mixed monolayer. In this study, the liquid crystalline azobenzene (C6Azo) was employed because the azo-chromophore gives us novel information concerning the orientational direction of guest molecules spectroscopically.

Figure 6 shows π-A iostherms of C11CRA-CM at 20 °C in the absence and in the presence of C6Azo at various mixing molecular ratios. The shape of these isotherms does not depend on the addition of C6Azo. They consist of the first steep rise of surface pressure at $A = ca.$ 2.0 nm^2, the plateau region and the second increment of surface pressure at $A = 1.0$ nm^2. UV absorption spectra of mixtures of C6Azo and C11CRA-CM at various molar ratios in solution and in floating
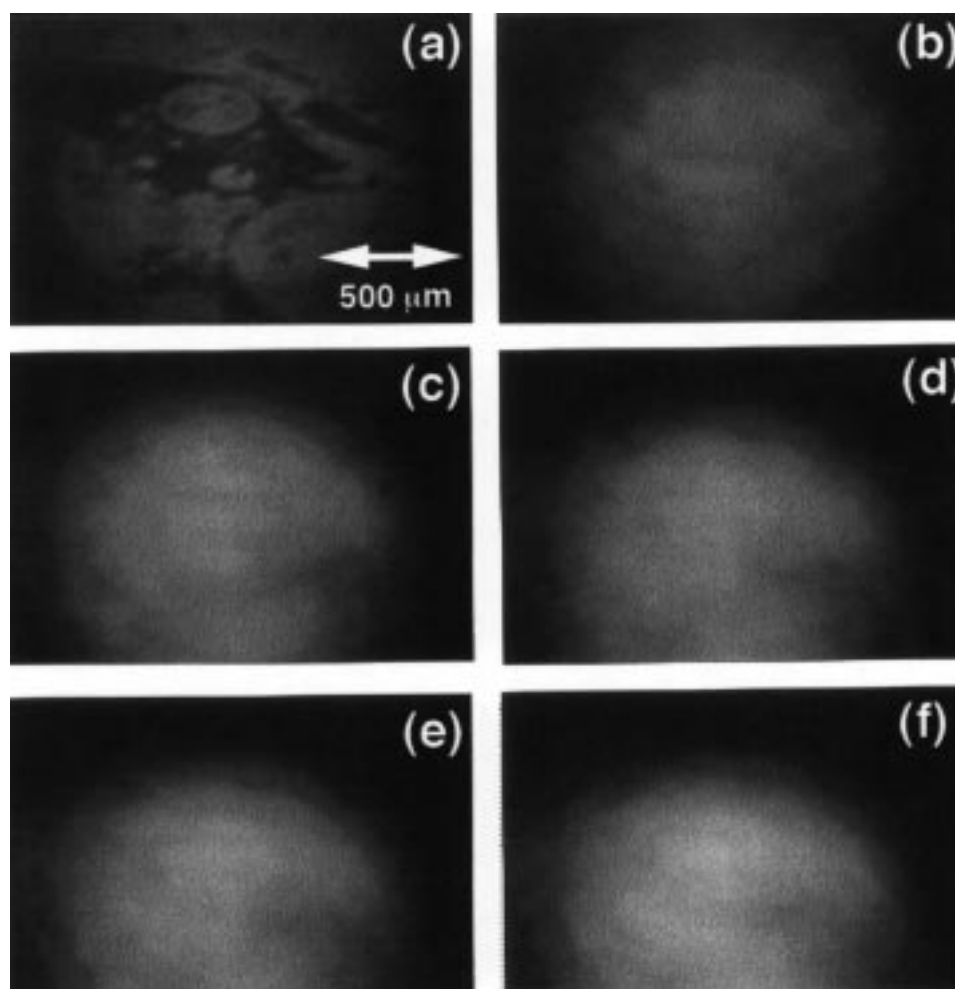
Figure 4. BAM images of the C20CRA-CM monolayer on a water surface at 20 °C. The images were taken at the points indicated in Figure 2b.

molecular films are listed in Figure 7. There are two major absorption bands at 284 nm (Abs_{284}) due to the calix[4]resorcinarene and at *ca*. 335 nm (Abs_{335}) due to the azobenzene. The change in Abs_{284} provides information about the alteration of the two-dimensional concentration of C11CRA-CM assembling in a flat-laid conformation in floating mixed molecular films as shown in Figure 3. On the other hand, orientational information of C6Azo in the films is obtained by the change in Abs_{335}, since the longitudinal molecular axis of C6Azo is approximately parallel with π-π^* transitional moment [13]. This situation allows us to assume that Abs_{335}/Abs_{284} is a measure of the orientation of the liquid crystalline azobenzene. A smaller Abs_{335}/Abs_{284} suggests the preference of the perpendicular orientation of C6Azo.
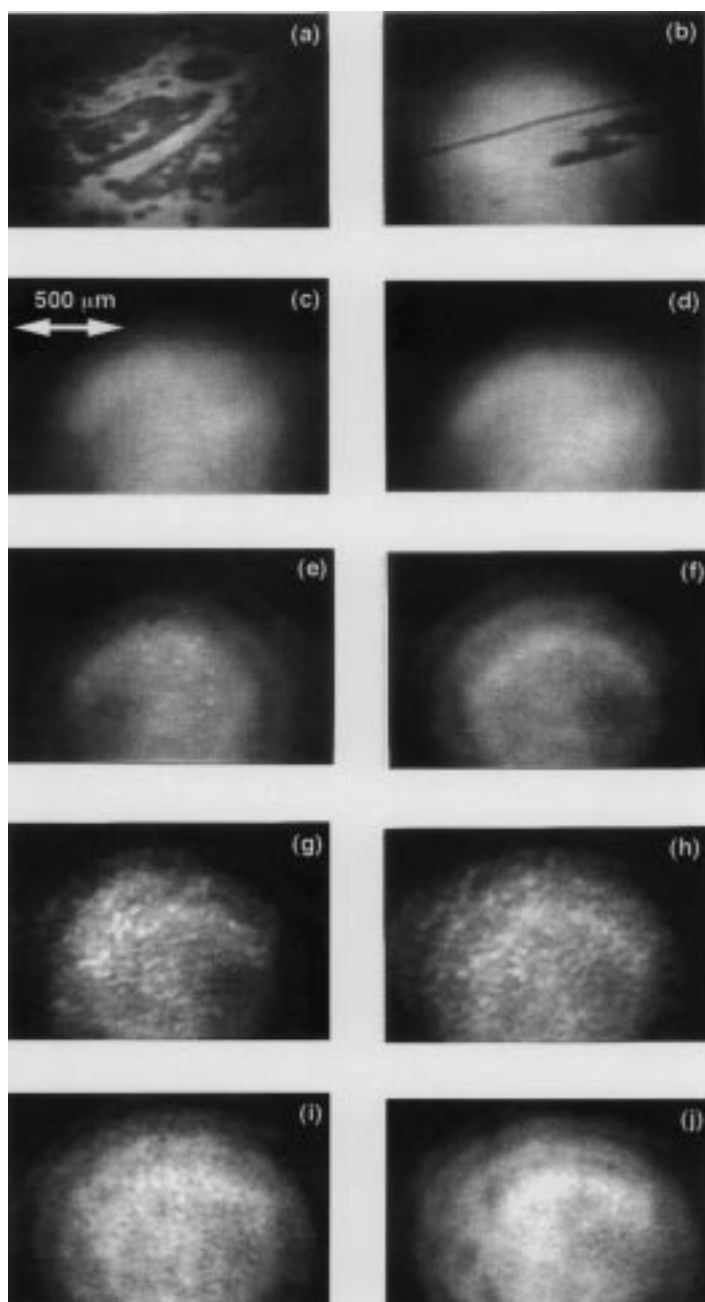
Figure 5. BAM images of the C11CRA-CM monolayer on a water surface at 20 °C. The images were taken at the points indicated in Figure 2a.
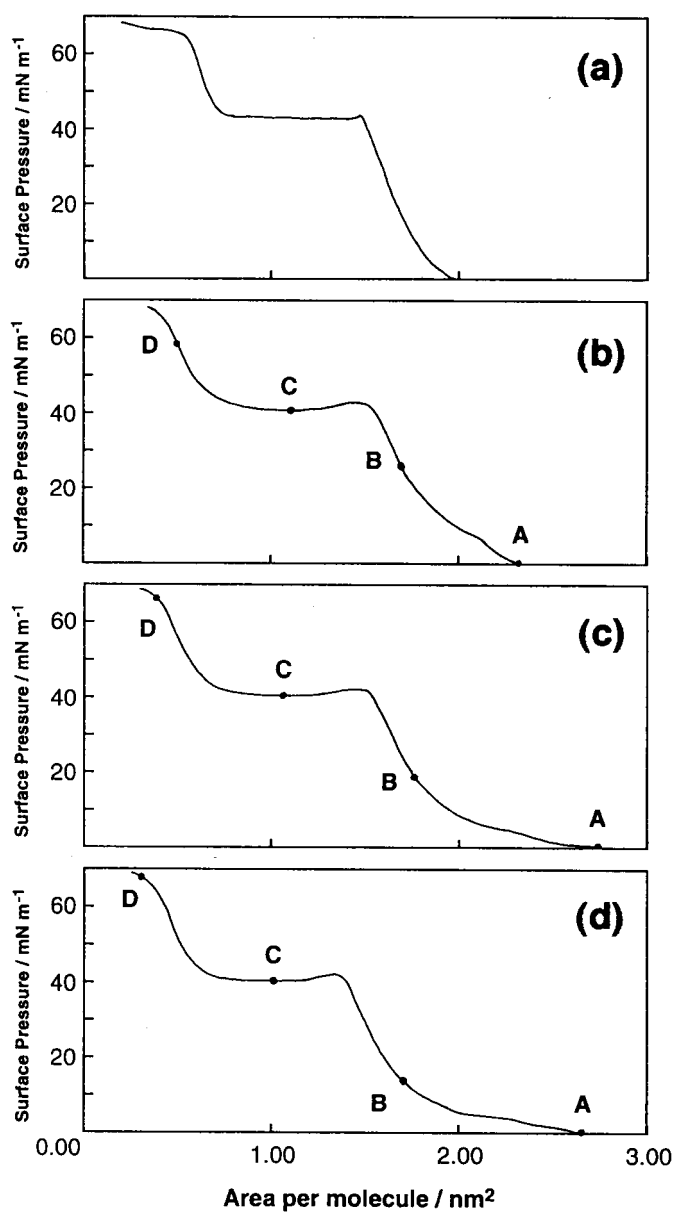
Figure 6. π-A isotherms of 11CRA-CM monolayers at 20 °C in the absence (a) and in the presence of C6Azo in (b) 1 : 1, (c) 1 : 3 and (d) 1 : 6 ratios.
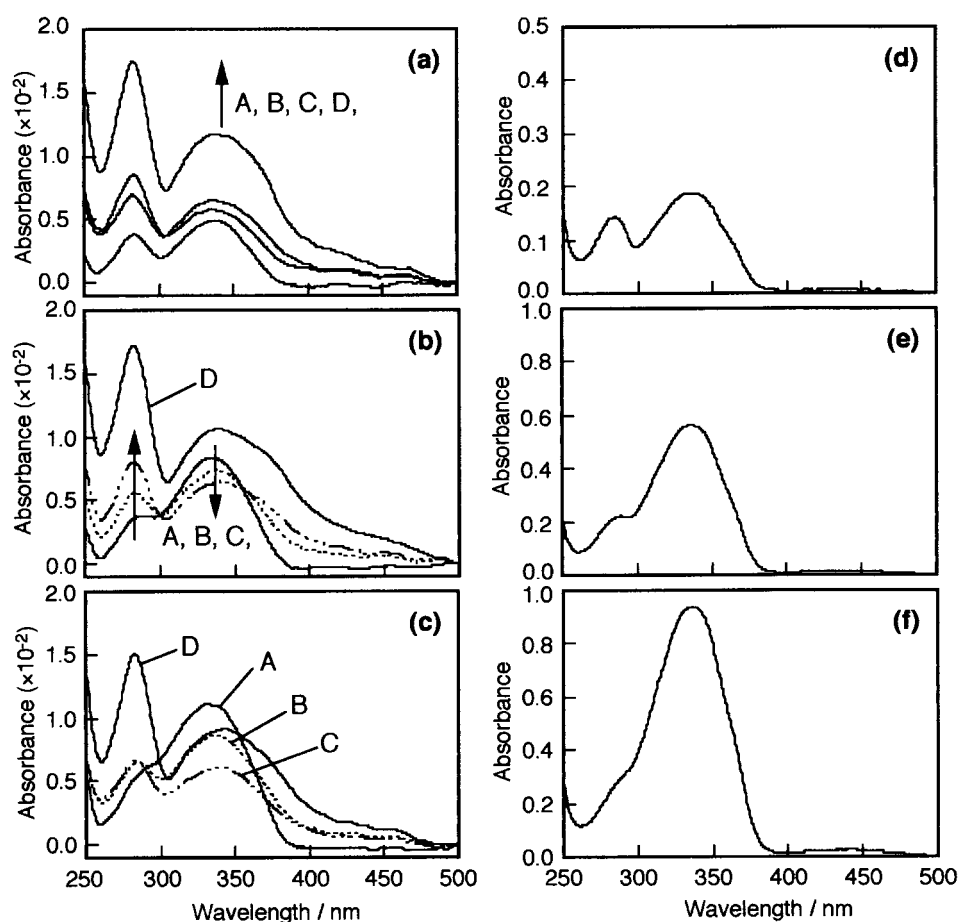
Figure 7. UV absorption spectra of the mixture of 11CRA-CM with C6Azo in the floating monolayers at (a) 1 : 1, (b) 1 : 3, and (c) 1 : 6 ratios, and in solution at (d) 1 : 1, (e) 1 : 3 and (f) 1 : 6 ratios, respectively. Absorption spectra A, B, C and D in (a), (b) and (c) were taken at the points indicated in Figure 6, respectively.

In Figure 7, values of Abs_{335}/Abs_{284} measured at 0 mN m^{-1} (spectrum-A) are larger than 1, and the shapes of the spectra were approximately the same to that in solution. From the first steep rise of surface pressure (spectrum-B) to the plateau region (spectrum-C), Abs_{335}/Abs_{284} is reduced as A decreases. This result means that the compression of the floating film induces the perpendicular orientation of C6Azo molecules. It is noteworthy that absorbances at the second steep rise of surface pressure (spectrum-D) is almost twice those in spectrum-C without a change in the shape of the spectra, indicating that mixed molecular films form a double-layered structure at this point.

Slight changes were observed in the absorption maximum of the azobenzene (A_{azo}) due to the compression (Figure 7b and c). A_{azo} in spectrum-C of the mixed

monolayers of $1:3$ and $1:6$ mixing ratios are 340.5 and 341.5 nm, respectively, although A_{azo} in solution was 335 nm. Furthermore, A_{azo} in spectrum-D of the $1:6$ mixed film is 343.0 nm. A new absorption band centered at *ca.* 380 nm appeared as a shoulder in spectrum-C and spectrum-D of these two mixed monolayers. This is caused by the J-aggregation of azobenzene molecules because of dense packing. Absorption spectra of the $1:1$ mixed film (Figure 7a) show a monomeric increment of absorption intensity, during compression, relfecting no molecular reorientation in the floating film.

The two-dimensional free space of C11CRA-CM surrounded by four alkoxy substituents with a cross-sectional area = 0.2 nm^2 tethered to lower rim is *ca.* 1.0 nm^2. Thus, four azobenzene molecules in perpendicular orientation can be included in the space, as the cross-section area of azobenzene is *ca* 0.25 nm^2. The π-A isotherm and UV absorption spectra of the $1:3$ mixed film suggested that a monomolecularly assembled layer of C6Azo with perpendicular orientation is formed on a layer of C11CRA-CM at the air-water interface by compression. Even in the presence of an excess amount of C6Azo in a $1:6$ mixture, a multi-layer structure with perpendicular orientation of the liquid crystalline azobenzene was generated. This may be due to a long-range order of LCs [14].

The observation of surface morphology of mixed floating molecular films consisting of 11CRA-CM and C6Azo at a $1:3$ ratio was carried out using a Brewster angle microscope. The results are listed in Figure 8. Before applying surface pressure, bright domains probably composed of C6Azo appear, displaying phase separation in the mixed monolayer. Further compression leads to the disappearance of the domain structure and to the formation of a uniform surface morphology indicating an uniform pattern at the plateau region. Finally, the increment of brightness of the film was detected, while the uniform pattern remains. This observation confirms the dynamic process of the molecular assembly leading to the multilayered structuring, being in line with the results obtained by π-A isotherm measurements, absorption spectra and BAM observation.

4. Conclusion

CRA-CMs as macrocyclic amphiphiles form stable monolayers on a water surface, and the π-A isotherms are markedly influenced by the length of substituents tethered from the lower rim of the cylindrical structure. A π-A isotherm of C20CRA-CM having long-alkyl residues show a linear increment of surface pressure along with the decrement of A, and subsequently a collapse takes place at $>$ 50 mN m^{-1}. On the other hand, a π-A isotherm of C11CRA-CM displays three regions; the first steep rise, the plateau region and the second steep rise of surface pressure. On the basis of UV absorption spectral measurements and BAM observation, it was revealed that the plateau region is corresponding to the transition between a monolayer structure and a double-layered one. In other words,
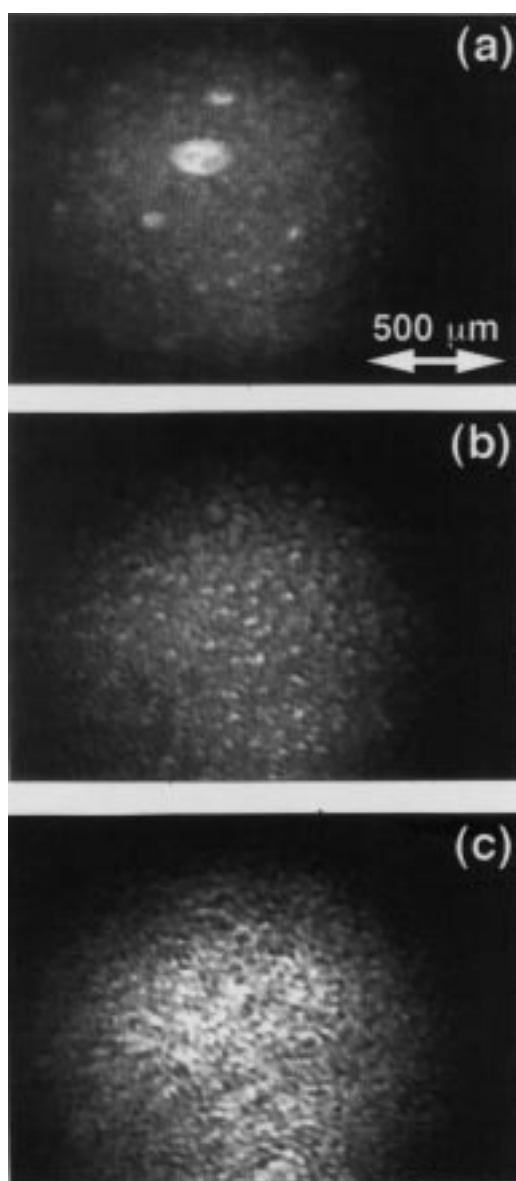
Figure 8. BAM images of the mixed monolayer composed of 11CRA-CM and C6Azo. (a) Before compression, (b) at plateau region and (c) at the second steepest region of surface pressure.
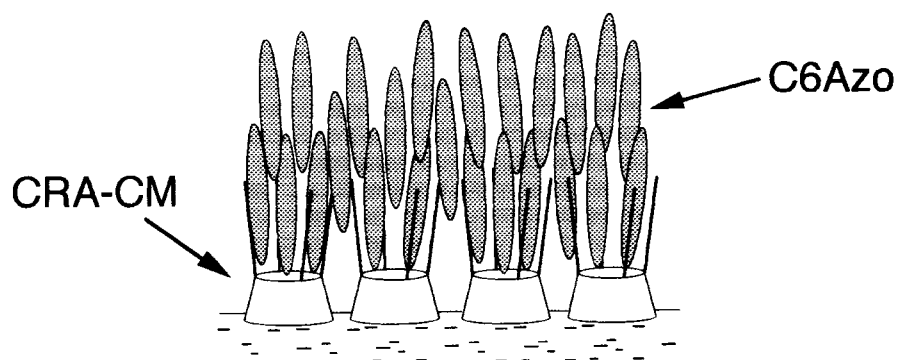
Figure 9. Illustrative presentation of a possible molecular assembly of a 1 : 6 mixture of 11CRA-CM and C6Azo in a floating molecular film.

the bilayering of CRA-CM molecular films is readily performed at the air-water interface by compression.

Because of the ability to form stable monolayers, C11CRA-CM having a hydrophobic free space acts as a trigger (host) to align C6Azo guest molecules perpendicularly on a water surface. Based on changes in UV-absorption spectra and BAM observation of the mixed monolayers at various surface pressures, it was revealed that the azobenzene as a guest displays reorientation of the molecular axis so that its longitudinal axis becomes perpendicular to a water surface owing to the applied surface pressure. These results indicate that the formation of a molecular layer of the nematic liquid crystal assisted by CRA-CM as a macrocyclic amphiphile provides a novel model system mimicking an interfacial region between a liquid crystalline layer and a substrate surface (Figure 9).

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