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Syntheses of Amphiphilic Benzothiazolium Azo Dyes and Behavior of their Monolayers on a Water Surface

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ABSTRACT

Syntheses of several 2-(4'-alkylaminophenylazo)-N-methylbenzothiazolium perchlorates having octadecyl groups were carried out in order to investigate the spreading properties of the monolayers on a water surface.

These amphiphilic azo dyes were prepared by the reaction of N-octadecylated aromatic amines with a 3-methyl-2-benzothiazolinone hydrazone hydrochloride in acetic acid containing lead dioxide. When the chloroform solution containing the dyes was developed on water, it found that the dyes formed stable monolayers at the air–water interface, respectively. From the results of π–A isotherms and occupied molecular area measurements, it can be considered that the chromophores appear to be oriented in the monolayer, having a degree of c. 80–85° to the water surface. The degree of the orientation in the mixed monolayers with arachidic acid (AA) are only slightly larger than that in the pure monolayer systems.

1 INTRODUCTION

There has been a great deal of interest in the Langmuir–Blodgett (LB) deposition technique over the last 10 years. The ability to control the film thickness to within a single monomolecular length and the possibility of fabricating supermolecular arrays of novel, interesting organic materials have attracted much enthusiasm in the hope that such capabilities will

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lead to the development of new electronic and optical devices. The LB films of azo dyes have been a subject of keen interest because of their utility in photovoltaic cells, optical information storage, photochromic and nonlinear optical materials.[1-10] Many of these studies concerned azo dyes of the azobenzene configuration, but the monolayer and multilayers for other than azobenzene derivatives has not been well investigated.

In this paper we report the syntheses of new amphiphilic azo dyes, viz. 2-(4'-alkylaminophenylazo)-*N*-methylbenzothiazolium perchlorates and 2-(4'-(*n*-octadecylamino)-1'-naphthylazo)-*N*-methylbenzothiazolium perchlorates, and how chromophores can be arranged in a monolayer at a water surface.

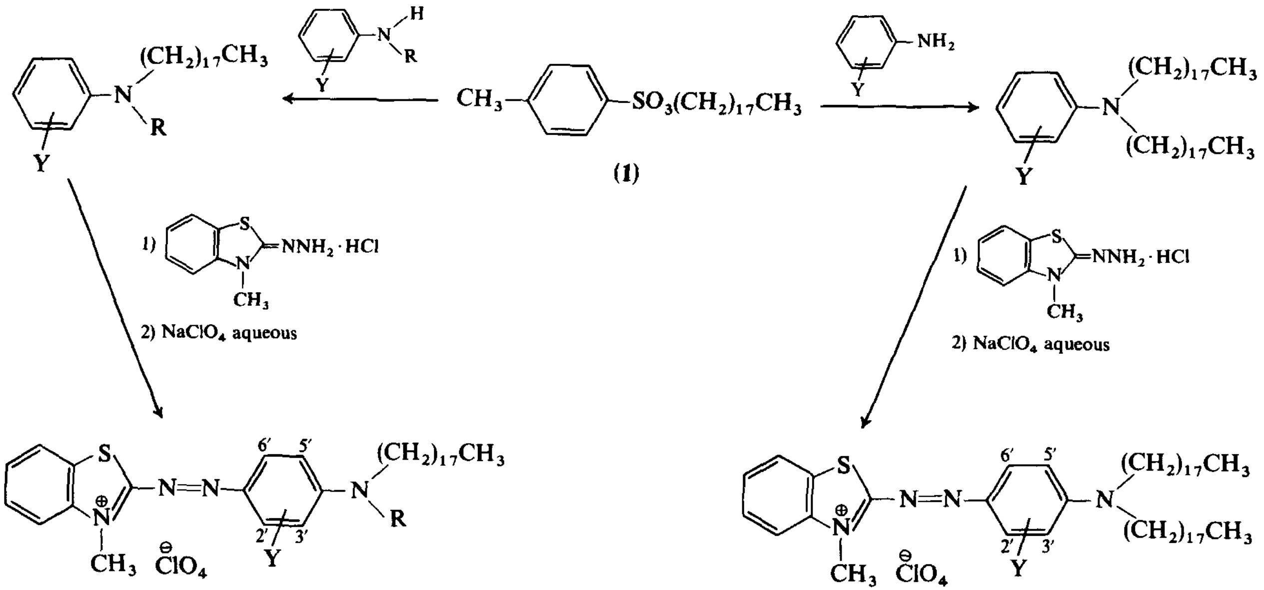
2 RESULTS AND DISCUSSION

2.1 Preparation of amphiphilic benzothiazolium azo dyes

2-(4'-alkylaminophenylazo)-*N*-methylbenzothiazolium perchlorate **3a-3g** having one or two octadecyl groups were synthesized by the processes demonstrated in Scheme 1.

An octadecyl *p*-toluenesulphonate (**1**) was prepared in 75% yield from *n*-octadecylalcohol and *p*-toluenesulphonyl chloride (Tokyo Kasei Co. Ltd) according to the literature.[11,12] Octadecylation of aromatic amines such as aniline, *N*-ethylaniline, *N*-ethylaminophenol, *m*-chloroaniline, *m*-nitroaniline and 1-naphthylamine with (**1**) was carried out at 140–160°C in the presence of anhydrous sodium carbonate.[13,14] Typically, a mixture of *N*-ethyl-*N*-octadecylaniline (**2a**) and 3-methyl-2-benzothiazolinone hydrazone hydrochloride in acetic acid containing a small amount of lead dioxide as catalyst[15] was reacted for 3 h at room temperature to give a purple-coloured solution. The solution was poured into 10% aqueous hydroperchloric acid and the precipitate product was filtered. It was purified by column chromatography on silica gel, using chloroform as eluent, to give (**3a**) (dark red-coloured powder) in 28% yield. The absorption maximum for (**3a**) was at 607 nm, with a weak shoulder at around 580 nm.

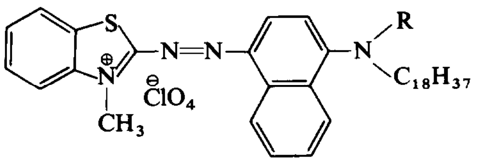
In a similar manner dyes, (**3b**)–(**3e**) were obtained in 7 ~ 20% yields; (**3f**) and (**3g**) were obtained in only poor yield, due to the presence of electron attracting substitutents in the arylamine. The λ_{max} for (3g) showed a red-shift at about 30 nm in methylene chloride. Similarly, reaction of *N*-monooctadecylated 1-naphthylamine with 3-methyl-2-benzothiazolinone hydrazone hydrochloride gave (**4a**) (Scheme 2), 2-(4'-(*n*-octadecylamino)-1'-naphthylazo)-*N*-methylbenzothiazolium perchlorate,



(3a) R=C_2H_5, Y=H
(3c) R=C_2H_5, Y=3′—CH_3
(3d) R=CH_3, Y=2′—CH_3
(3e) R=C_2H_5, Y=2′—OH

(3b) Y=H
(3f) Y=2′—Cl
(3g) Y=2′—NO_2

Scheme 1. Synthetic results for the amphiphilic azo dyes.



	R
(4a)	$C_{18}H_{37}$
(4b)	H

Scheme 2. Structures of (**4a**) and (**4b**).

in 17–20% yield. Dye (**4a**), purified by column chromatography showed a visible absorption band at 620 nm in methylene chloride. Dye (**4b**) λ_{max} 620 nm was also obtained in 29% yield after the appropriate treatments as described above. The results are summarized in Table 1.

2.2 Visible, IR and Raman spectra of the products

Figure 1 shows typical visible-absorption spectra for dyes (**3a**) and (**3e**). The observed absorption maxima (λ_{max}) are shown in Table 1. Substituent effects in the phenyl ring could be roughly evaluated by the λ_{max} values. The introduction of —CH_3 and —OH groups into the 2'-position produced a 7–27 nm hypsochromic shift in comparison with the parent dye (**3a**). On the other hand, the presence of —Cl and —NO_2 groups, electron-withdrawing substituents, produced a bathochromic shift of 3 nm in (**3f**) and 33 nm in (**3g**), respectively.

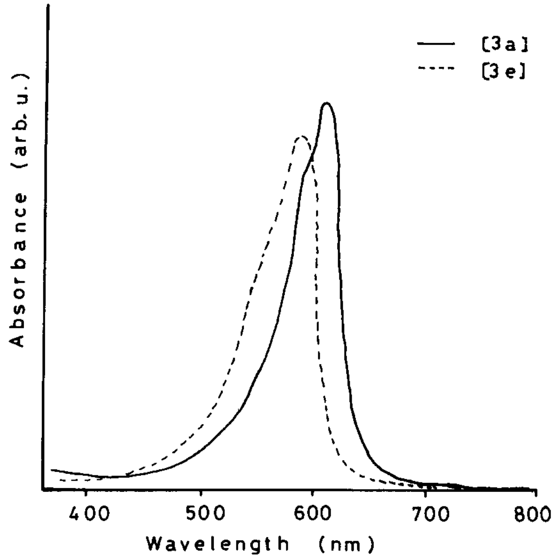


Fig. 1. Absorption spectra of (**3a**) and (**3c**) in methylene chloride.

TABLE 1
Characterization Data for some Amphiphilic Azo Dyes

Compounds	R_1	R_2	*Y*	*Yield (%)*	*m.p. (°C)*	λ_{max} *(nm)*[a] *(ε × 10⁴)*	*Analysis (%)*		
							H	*C*	*N*
(3a)	$C_{18}H_{37}$	C_2H_5	H	28·2	108–109	607, 580 (s)	8·61	63·27	8·17
						(9·6)	(8·23)	(62·89)	(8·63)
(3b)	$C_{18}H_{37}$	$C_{18}H_{37}$	H	19·5	138–139	610, 585 (s)	10·00	69·32	5·99
						(8·1)	(9·81)	(68·73)	(6·41)
(3c)	$C_{18}H_{37}$	C_2H_5	3'-CH_3	15·5	97–99	590	8·54	64·02	8·65
						(7·3)	(8·36)	(63·37)	(8·45)
(3d)	$C_{18}H_{37}$	CH_3	2'-CH_3	7 0	142–143	600, 580 (s)	8·49	63·84	8·47
						(10·0)	(8·23)	(62·89)	(8·63)
(3e)	$C_{18}H_{37}$	C_2H_5	2'-OH	7·4	93–94	580	8·86	63·01	7·68
						(5·4	(8 03)	(61 37)	(8·42)
(3f)	$C_{18}H_{37}$	$C_{18}H_{37}$	2'-Cl	2·0	105–106	610, 590 (s)	9·88	67·02	6·55
						(6·2)	(9·32)	(66 12)	(6 17)
(3g)	$C_{18}H_{37}$	$C_{18}H_{37}$	2'-NO_2	trace	—	640			
(4a)	$C_{18}H_{37}$	H	—	17·5	120–121	620	7·46	63·83	7·96
						(12·0)	(7 66)	(64 40)	(8·35)
(4b)	$C_{18}H_{37}$	$C_{18}H_{37}$	—	28·6	116–118	620	8·99	69·48	6 75
						(9·5)	(9·49)	(70·02)	(6·07)

[a] The values of λ_{max} were measured in methylene chloride.
(s), shoulder.

Infrared spectra of the products in the solid state were measured by using an FT-IR spectrophotometer with a micro-infrared attachment (Nippon Denshi Co. Ltd). Figure 2(a) shows a typical IR spectrum of dye (**3a**). Intense bands at 2922 and 2850 cm^{-1} are assigned to CH_2 asymmetric and symmetric stretching vibrations of a long hydrocarbon chain and a moderate band at 2953 cm^{-1} is due to the CH_3 asymmetric stretching. Bands at 1610 and 1520 cm^{-1} may be assigned to $^{+}N{=}C$ stretching and ν_{19} mode of the benzene ring. A moderately intense band at 1466 cm^{-1} may be due to CH_2 scissoring of the hydrocarbon chain. It is well known that azobenzene derivatives give a band due to =N—Ph stretching in the 1150–1160 cm^{-1} region;[16,17] the band at 1163 cm^{-1} probably arises from the =N—Ph stretching mode. There is little doubt that the band near 841 cm^{-1} is due to a CH out-of-plane deformation of the benzene ring. The intense band near 1090 cm^{-1} is ascribed to ClO_4^-[18] and the band at 1463 cm^{-1} in the resonance Raman spectrum (Fig. 2(b)) may be due to —N=N— (*trans*) stretching.[16–18] The appearance of N=N and =N—Ph stretching at 1463 and 1161 cm^{-1}, respectively, shows that (**3a**) contains an appreciable contribution from the resonance structure (**b**) in Fig. 3. IR and Raman spectra for other dyes also showed similar results.

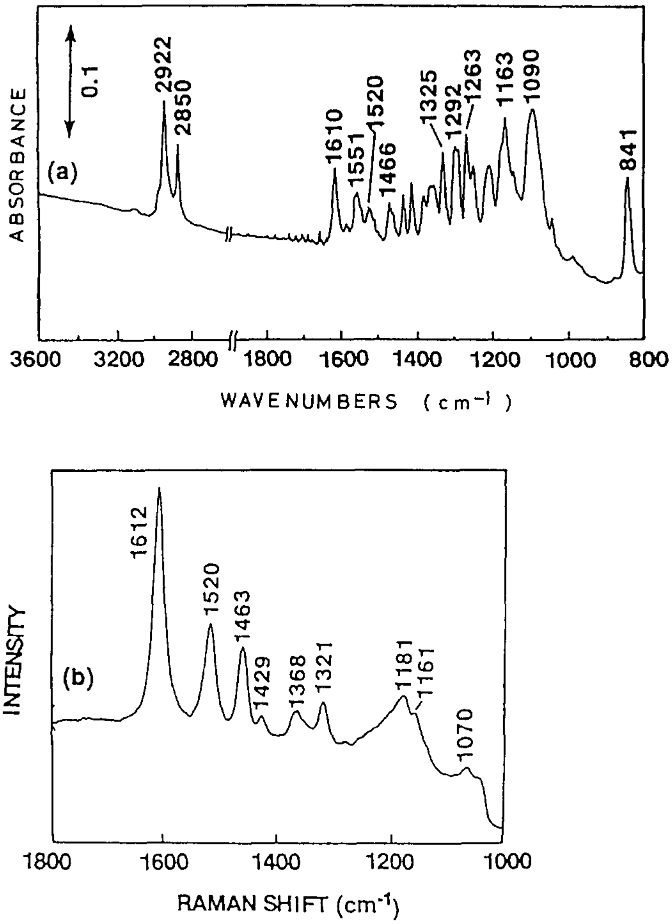
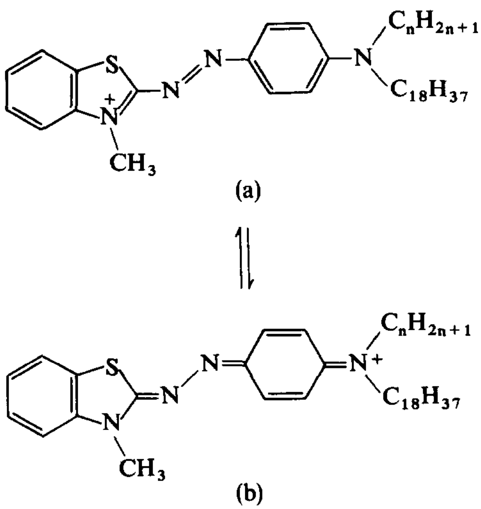


Fig. 2. FT-IR and resonance Raman spectra. (a) Infrared transmission spectrum of (**3a**) in a powdered microcrystalline state; (b) 514·5 nm excited resonance Raman spectrum of (**3a**) in acetone (1×10^{-4} M).

2.3 Characteristics of monolayers on water

The spreading properties and orientation of azobenzene derivatives containing long alkyl chains, in monolayers on water, have been previously described,[4,5,19,20] but observations for benzothiazolium azo dyes have not yet been reported. In this present work, the spreading properties and orientation of dyes (**3a**)–(**3f**) were examined in monolayers on water. The dye monolayer was spread from a chloroform solution (2×10^{-3} M) on a water subphase containing $1{\cdot}4 \times 10^{-4}$ M $CdCl_2$ and $1{\cdot}7 \times 10^{-5}$ M $NaHCO_3$ at pH 6·3 and 17 ± 1°C. After evaporation of the solvent, the pressure-area (π–A) isotherm was measured at a compression speed of about 20 cm^2/min.



$n = 2$; (**3a**)
$n = 18$; (**3b**)

Fig. 3. Resonance structures of the azo dyes (**3a**) and (**3b**).

Figure 4(A–D) shows the π–A isotherms examined from the $CHCl_3$ solution of dye with or without arachidic acid (AA) as a matrix material. In all cases the area coordinate refers to the spread amount of the dye and arachidic acid per unit area. It was found that pure systems of these dyes formed stable monolayers on water. π–A isotherms of mixed systems of azo dye and AA in various molar ratios ranging from 1 : 1 to 1 : 10 were also obtained as sharp curves. However, the π–A isotherms of the pure or mixed monolayer for (**3d**) and (**3f**) showed that two 'collapse' points (by the conventional explanation) are seen at 36 and 30 mN/m (Fig. 4(C, D)). We assumed that these points represent the occurrence of two condensed states. A monolayer of arachidic acid alone collapsed near 50 mN/m and its limiting area was 21 Å^2 (see Fig. 4(D–E)). From the isotherms for 3(**a**)–3(**f**), occupied areas per dye molecule, which deducted the portion of arachidic acid from the apparent areas, are estimated. The occupied areas and collapse pressures are summarized in Table 2. Generally, it was found that the collapse pressures increased with increasing molecular ratio of AA, and that the limiting areas of the azo chromophore per molecule in the mixed monolayer were slightly smaller than those in pure dye systems. For dyes (**4a**) and (**4b**), having a naphthelene ring, analogous behaviour was also apparent, with a lower collapse pressure.

In the calculation for (**3a**), it is assumed that the area per molecule of the chromophore part is *c.* 89 Å^2 (14 Å × 6·4 Å) by using a molecular

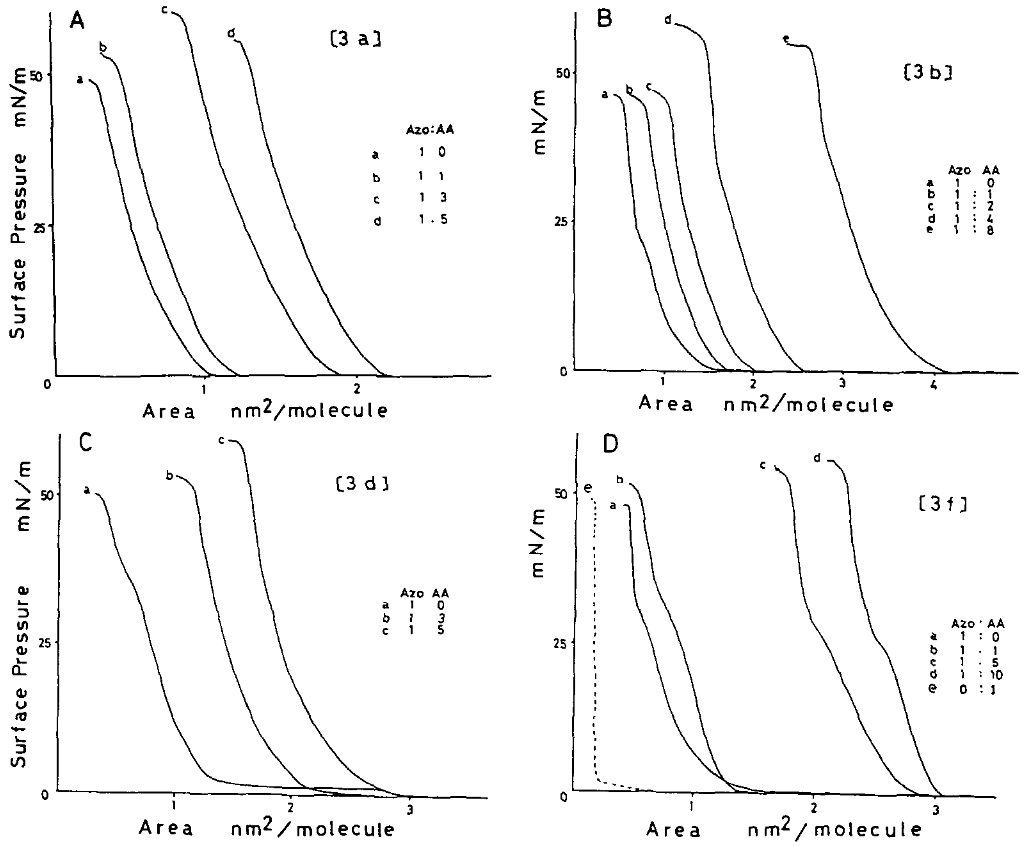


Fig. 4. Surface pressure–area isotherms of pure dye monolayers and mixed monolayers with arachidic acid (AA) on the aqueous subphase containing 1·4 × 10^{-4} M $CdCl_2$ and 1·7 × 10^{-5} M $NaHCO_3$ at pH 6·3 and 17°C.

TABLE 2
Monolayer Properties of Dyes on Water

Compounds	*Ratio of dye/AA*	*Limiting areas of dye (Å^2)*	*Collapse pressure (mN/m)*	*Probable angle of orientation to water surface (θ)*
(3a)	1 : 0	78	46	82·2
	1 : 1	70	52	82·7
	1 : 5	72	51	82·6
(3b)	1 : 0	69	46	82·7
	1 : 1	69	46	82·7
	1 : 4	66	54	82·9
(3c)	1 : 0	48	46	83·9
	1 : 5	42	54	83·9
	1 : 10	59	54	83·3
(3d)	1 : 0	107, 113	49	80·9, 80·7
	1 : 3	89	51	81·7
	1 : 5	99	58	81·3
(3e)	1 : 0	56, 76	47	83·4, 82·4
	1 : 1	58	43	83·3
	1 : 3	55	54	83·5
(3f)	1 : 0	60, 102	48	83·2, 81·1
	1 : 1	74	49	82·5
	1 : 10	68	51	82·8
(4a)	1 : 0	42	30	84·6
(4b)	1 : 0	48	32	84·8

scale model. The value (78 Å^2) for (**3a**) obtained from the π–A curve was smaller than the calculated molecular size. Because a single azo group has a water-attracting property,[11] the molecular area may be consistent with orientation of the aromatic nuclei in a vertical plane. Thus, it is suggested that the long axis of the chromophore of (**3a**) is neither perpendicular nor parallel to the air–water surface, but exists with some intermediate angle (Fig. 5).

Further, the detailed orientation of dye molecules at the air–water surface was studied by using the limiting area index and the angle θ to the horizontal axis, as shown in Fig. 6. The areas are consistent with the orientation of the dye molecules. This tentative consideration is based on the assumption that a long axis of the dye molecule rotates around with the same direction to the normal surface. In this simplifying assumption, the value of S in Fig. 6 is the limiting area of the dye molecule, and is related by eqns (1) and (2):

$$S = \pi r^2 \tag{1}$$

$$\theta = \cos^{-1}(r/l) \tag{2}$$

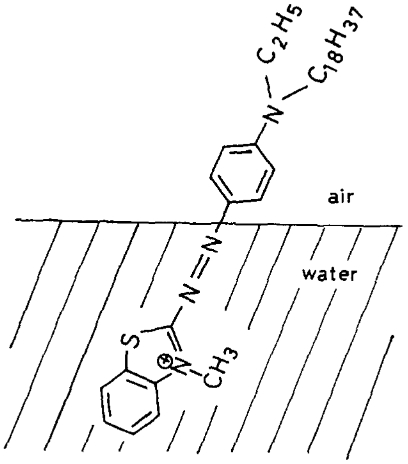


Fig. 5. Schematic representation of the molecular orientation of the benzothiazolium azo dye (**3a**) at the water surface.

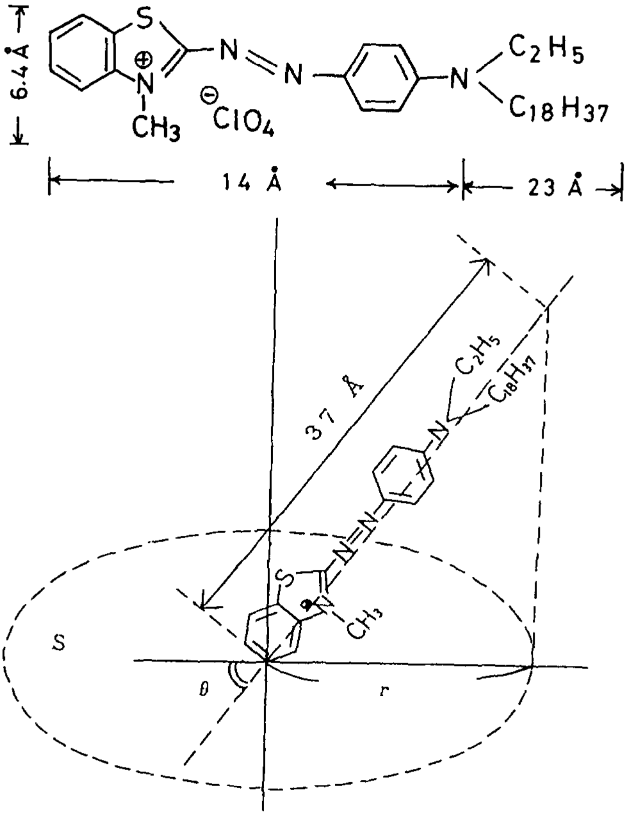


Fig. 6. A model showing the probable orientation of the molecules at the water–air interface; long axis of the dye molecule rotates around to the normal surface with an angle θ in the region of 80–85°.

Here, *r* defines radius of the revolution, and *l* is a molecular length in the long axis. As a typical result, it was found that the monolayer of (**3a**) has an orientation degree of *c*. 82° to the water surface. The degree of orientation in the mixed monolayers is slightly larger than that of the pure monolayer. Similar observations were also obtained for other dyes, as shown in Table 2.

3 EXPERIMENTAL

3.1 Preparation of octadecylated aniline intermediates

An octadecyl *p*-toluenesulphonate (**1**) was prepared from *n*-octadecylalcohol and *p*-toluenesulphonyl chloride (Tokyo Kasei Co. Ltd) according to the literature.[11,12] A mixture of *N*-ethylaniline (12·1 g, 0·10 mol), octadecyl *p*-toluenesulphonate (20·4 g, 0·05 mol) and anhydrous sodium carbonate 5·3 g (0·05 mol) was stirred for 22 h in an oil bath heated at 160 ~ 165°C. The reaction mixture was washed with 500 ml of hot water and cooled. The solidified mixture was poured into 200 ml of methanol, and the liquor was filtered to remove insoluble material. After evaporation of solvent from the filtrate, *N*-ethyl-*N*-octadecylaniline (**2a**) was obtained in 60% yields (m.p. 34–35°C). In a similar way, (**2c**)–(**2e**) were prepared from (**1**) and *N*-ethyl-*o*-toluidine, *N*-methyl-*m*-toluidine or *N*-ethyl-*m*-aminophenol, respectively.

Aniline (8·6 g, 0·09 mol), *n*-octadecyl *p*-toluenesulphonate (39·1 g, 0·09 mol), and 5·3 g of anhydrous sodium carbonate were stirred for 18 h in a 300 ml^3 three-necked flask at 140–145°C. The brown product was washed four times with hot water, dried, and then treated with successive portions of hot methanol, the solution being decanted from the insoluble material. After cooling the methanol solution in an ice-bath, the precipitated solid was separated, dried, and dissolved in ether. A small amount of hydrochloric acid was added to the ether solution, giving the insoluble amine hydrochloride. Treatment of the ether-insoluble salt with dilute aqueous sodium hydroxide (boiling 10 min), followed by crystallization of the solid from methanol yielded only trace amounts of *N*-*n*-octadecylaniline.

The methanol-insoluble material in the above was also dissolved in ether, and the treatments by hydrochloric acid and aqueous sodium hydroxide were carried out. Recrystallization of the product from a mixture of methanol–ether (1 : 1, v/v) resulted in 13·3 g of *N*,*N*-di-*n*-octadecylaniline (**2b**), m.p. 51–52°C (52% yield). In similar procedures (**2f**) and

(**2g**) were prepared from (**1**) and *m*-chloroaniline or *m*-nitroaniline in 35 ~ 45% yields.

3.2 Preparation of amphiphilic benzothiazolium azo dyes

N-Ethyl-*N*-*n*-octadecylaniline (**2a**) (7·5 g, 0·02 mol) was reacted for 4 h at 20–22°C with 3-methyl-2-benzothiazolinone hydrazone hydrochloride (MBTH, 4·7 g, 0·022 mol) (Tokyo Kasei Co. Ltd) in 100 ml^3 of glacial acetic acid containing lead dioxide (5 g). After reaction, 10% sodium perchlorate (105 ml) was poured into the reaction mixture, which was then kept for 3 h at room temperature. The precipitated product was filtered and dried. The crude product was purified by passing through a silica gel column with chloroform as eluent. 2-(4'-Ethyloctadecylaminophenylazo)-*N*-methylbenzothiazolium perchlorate (**3a**) was obtained in 28·2% yield (3·4 g, m.p. 108–109°C) after evaporation of the solvent. In a similar manner dyes (**3c**)–(**3e**) were obtained in 6–8% yield from the corresponding amine derivatives.

N,*N*-Di-*n*-octadecylaniline (2b) (6·8 g, 0·01 mol) was reacted for 3 h at 20–22°C with MBTH (2·7 g, 0·012 mol) in 270 ml^3 of glacial acetic acid–methylene chloride (9 : 1, v/v) containing lead dioxide (6 g). The reaction mixture was poured into 10% aqueous sodium perchlorate (250 ml). After leaving overnight, the precipitated product was filtered and washed with diethyl ether and ethylacetate. The product was purified by column chromatography (silica gel) using chloroform–methanol (10 : 1, v/v) as eluent; 2-(4'-dioctadecylaminophenylazo)-*N*-methylbenzothiazolium perchlorate (**3b**) was obtained in 20% yield as dark-bluish crystals. Dyes (**3f**) and (**3g**) were obtained in lower yields. In a similar procedure, dyes (**4a**) and (**4b**) were obtained in 18–29% yields.

The visible and IR spectra of the dyes were measured using a Shimadzu UV-250 and Nippon Denshi FT-IR spectrophotometer, respectively. Elemental analyses were recorded on a Yanaco CHN recorder MT-2. Synthetic data are summarized in Table 1.

3.3 Measurements of surface pressure–area isotherms

The measurements of the surface pressure-area (π–A) isotherms of monolayers on the water surface were performed with a Wilhelmy-type film balance (Kyowa Kaimen Kagaku, model HBM-AP, Japan). Pure water from a milli-Q system (Millipore Ltd) was used for the preparation of the aqueous subphase. The pure monolayers of dyes were spread from chloroform solutions (2×10^{-3} M) onto the water containing $1{\cdot}4 \times 10^{-4}$ M $CdCl_2$ and $1{\cdot}7 \times 10^{-5}$ M $NaHCO_3$ at pH 6·0 and, usually, at 17°C. The mixed monolayers were formed by spreading chloroform solutions of dyes and arachidic acid (Tokyo Kasei Co. Ltd) on the same aqueous subphase. After evaporation of the solvent, the monolayers were compressed at a constant rate of 20 cm^2/min.

Preparations and properties of LB films from these dyes will be described in the next report.

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