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Visible Absorption Spectra of Cetyl Orange
Monolayers on the Water Surface

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Visible absorption spectra of spread monolayers of cetyl orange on water at pH 2.8, 4.2 and 10.0 were recorded *in situ* at various stages of monolayer compression. The results indicate that at pH 2.8 and 4.2 the molecules are in equilibrium between the azo and hydrazone forms of the azobenzene moiety. Upon monolayer compression, the equilibrium shifted toward the azo form which is originally in a more tightly condensed state than the hydrazone form. At pH 10.0, on the other hand, the cetyl orange molecules have the pure azo form, irrespective of the degree of monolayer compression, and attain the H-aggregated state upon compression.

KEY WORDS: Spread monolayers on water/ Cetyl orange/ Visible absorption spectra/ Azo hydrazone tautomeric equiliblium/ Aminoazobenzene derivatives/

INTRODUCTION

Recently, an increased interest in the Langmuir-Blodgett (LB) films consisting of well-organized molecular assemblies in the form of ultrathin films has provoked much attention to the molecular structure and aggregation state in spread mono-layers on the water surface from which the LB films are fabricated. In a previous paper, we reported resonance Raman spectra of LB films of cetyl orange (sodium p-dicetylaminoazobenzenesulfonate) prepared from spread monolayers on water at pH 8.7 and 1.5, which gave the azo and hydrazone forms (Fig. 1), respectively, of the trans azobenzene moiety[1]. On that occasion, we felt the necessity of studying the tautomeric equilibrium between the azo and hydrazone forms, as well as their aggregation states, on the water surface.

In the present work, therefore, we measured visible absorption spectra of cetyl orange monolayers on water at different pH values and at various stages of mono-layer compression, using a spectrophotometer equipped with optical fibers and a multichannel detector[2,3].

EXPERIMENTAL

Cetyl orange was kindly synthesized in Wako Pure Chemical Industries, Ltd, Osaka by the method described previously[4,5]. A Kyowa Kaimen Kagaku Model HBM-AP Langmuir trough with a Wilhelmy balance was used for π-A isotherm and visible absorption measurements. Water used as a subphase was purified by

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$C_{16}H_{33}$

$C_{16}H_{33}$

Azo form

$-H^+$ | $+H^+$

$C_{16}H_{33}$

$C_{16}H_{33}$
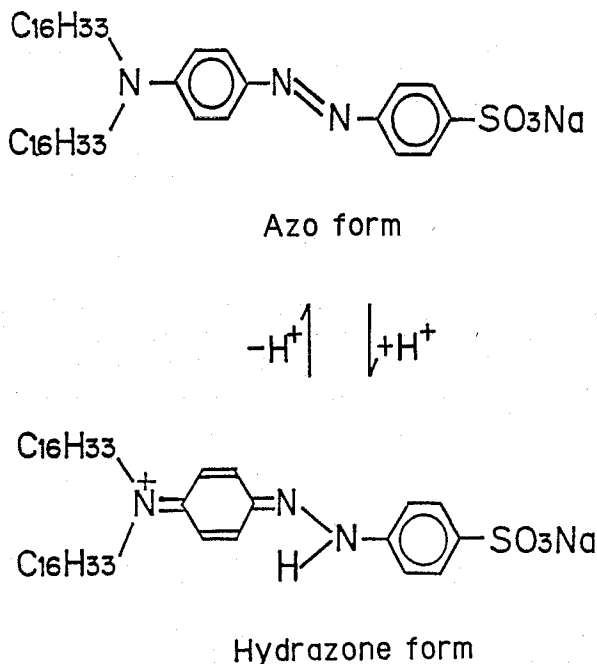
H

SO₃Na

SO₃Na

Hydrazone form

Fig. 1. Tautomeric equilibrium of cetyl orange

a modified Mitamura Riken automatic lab still consisting of a reverse osmosis module, an ion exchange column, and a double distiller. It was adjusted to pH 2.8 and 4.2 by aqueous HCl solution, or to pH 10.0 by aqueous NaOH solution. The temperature of the aqueous subphase was controlled to $20\pm0.3°C$ by a Neslab Cool-flow-25 refrigerated circulator. The monolayer of cetyl orange was spread from 1.34×10^{-3} M chloroform solution on the water surface. After 20 minutes for solvent evaporation, the monolayer was compressed at a constant rate of $10\ cm^2/min$ for
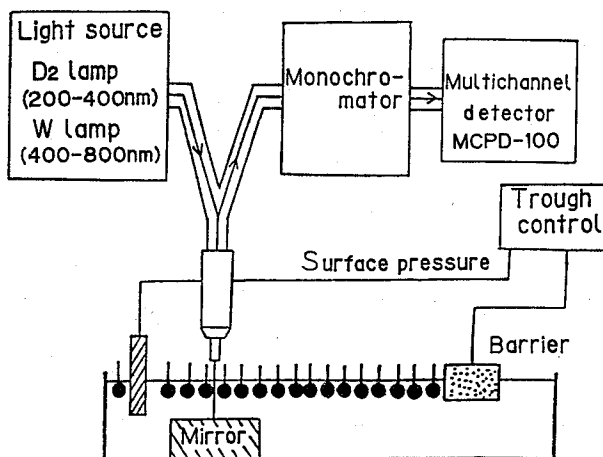
Fig. 2. Experimental setup for obtaining visible absorption spectra of spread monolayer of cetyl orange under compression.

the π-A isotherm measurements.

For visible absorption measurements, the monolayer was compressed at the same rate to a planned surface area and kept constant during the measurement, and then compressed again to the next surface area. Visible absorption spectra of the spread monolayers of cetyl orange on the water surface were recorded on an Otsu-ka Electronics Model MCPD-100 multichannel detector system shown in Fig. 2[2,3]. The light from the source was introduced through a branch of a Y-shaped optical fiber bundle to the surface of the spread monolayer. After passing through the monolayer the light was reflected back by a mirror placed horizontally in the water. After passing the monolayer again, the reflected light reentered the edge of the optical fiber and was led through another branch of the Y-shaped optital fiber bundle to a monochromator equipped with a multichannel detector. Reference spectra were obtained on the pure water surface.

RESULTS AND DISCUSSION

Figure 3 shows surface pressure (π)-area (A) isotherms of the cetyl orange monolayer spread on water at 20°C and at pH 10.0, 4.2 and 2.8. The curve shifts to a larger area side with the decrease in pH value. To understand the reason of this shift, the visible absorption spectra of the spread monolayers with the surface area of 66 Å[2]/molecule were measured at pH 10.0 and 2.8. The results are shown in Fig. 4. At pH 10.0, a broad band with its center locating at about 440 nm appears. This band is typical of the 'K band' which is ascribed to the π-π* transi-
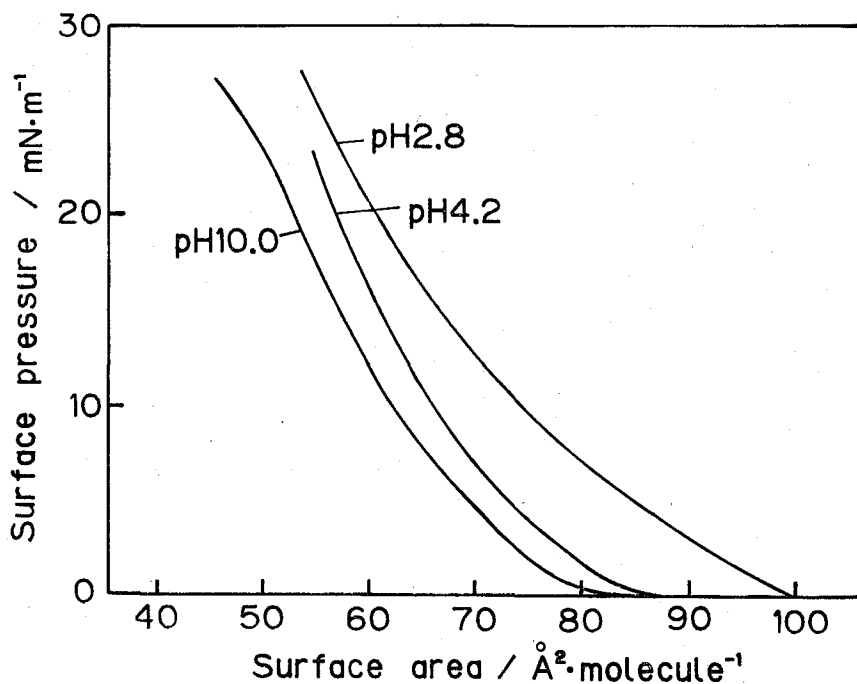
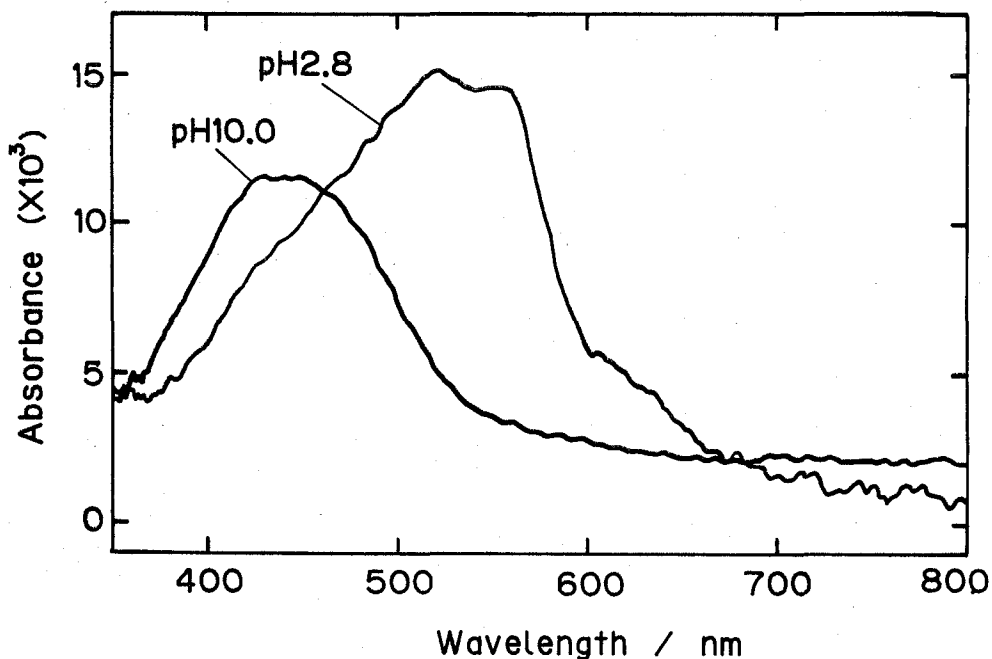Fig. 3. The π-A isotherms of spread monolayers of cetyl orange on water at 20°C at pH 10.0, 4.2 and 2.8.

Fig. 4. Visible absorption spectra of spread monolayers of cetyl orange on water at pH 10.0 and 2.8, 20°C, and at surface area of 66 Å²/molecule.

tion of the azo form of the trans azo-benzene moiety (Fig. 1)[1,6~8]. At pH 2.8, on the other hand, a peak at 519 nm is observed with a shoulder at 552 nm. This is typical of the 'Q band' which is ascribed to the same electronic transition of the protonated hydrazone form (or the quinoid form if the dicetylaminoazobenzene ring, i.e. N'-ring, is referred, Fig. 1)[1,7~9]. The peak at 519 nm is ascribed to the vibronic 0-1 component, while the shoulder at 552 nm to the 0-0 component[1]. Thus, the results of Fig. 4 indicate that the cetyl orange molecules at pH 10.0 and 2.8 are predominantly in the azo and hydrazone forms, respectively. Therefore, the ithotherm shift to the larger area side with decreasing the pH value can be interpreted by the equilibrium shift to the side of the hydrazone form which is in a more expanded state than the azo form on the water surface. This may be due to the fact that the hydrazone form has a positive charge on the nitrogen atom and therefore the repulsive forces between these charges may compel the distance between the neighboring molecules to be larger. At pH 4.2 the π-A isotherm in Fig. 3 falls between the above-mentioned two curves. This may suggest that both azo and hydrazone forms coexist at equilibrium on the water at this pH value. Actually, the visible absorption spectra of cetyl orange monolayers at this pH value show both azo and hydrazone bands, as will be described later.

Next, we will deal with spectral changes upon compression of the monolayers at various pH values on water. Figure 5 shows visible absorption spectra of the spread monolayer of cetyl orange at various surface areas at pH 10. At large sur-
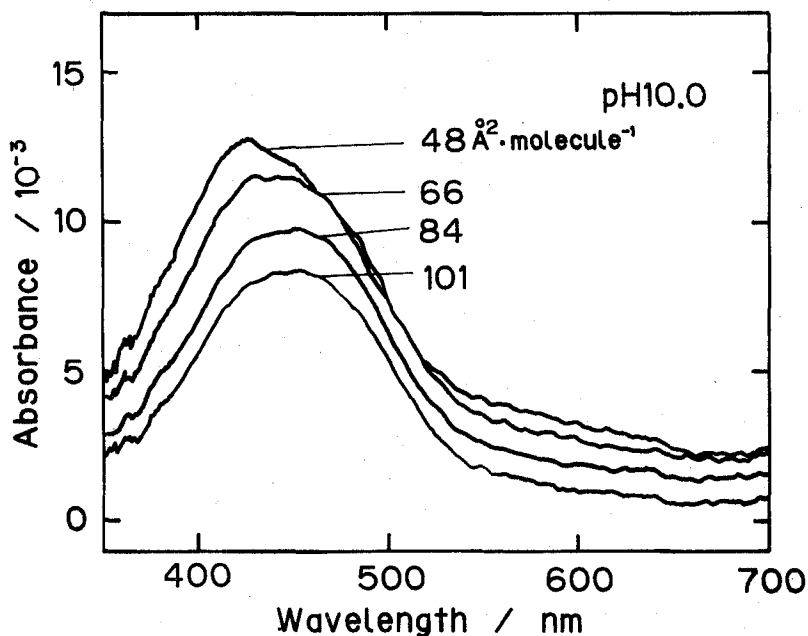
Fig. 5. Visible absorption spectra of spread monolayer of cetyl orange on water at pH 10.0 and 20°C at four different surface areas.

face areas of 101 and 84 Å²/molecule, the peak maximum is observed at ca. 450 nm, but at a small surface area of 48 Å²/molecule, it shifts to 425 nm. Similar blue shifts by monolayer compression were observed for the same π-π^* transition band of spread monolayers of azobenzene-containing long-chain fatty acids[3]. According to the molecular exciton model proposed by McRae and Kasha[10], these blue shifts were understood as due to the formation of the H-aggregates which are the linear aggregate of chromophores with their transition moments parallel to each other and ordered perpendicular (more precisely, with an angle greater than 54.74°) to the stacking direction. Therefore, the above-mentioned facts indicate that the degree of H-aggregation is gradually improved upon monolayer compression. In this regard, the bulk sample of cetyl orange consisting of microcrystallites with highly ordered molecules, exhibited an absorption maximum at ca. 400 nm, when measured as a KBr pellet. In a previous paper, we have also shown that the 10-monolayer LB film of cetyl orange prepared from a spread monolayer on water at pH 8.7 and 10°C and at the surface pressure of 40 mN/m showed an absorption peak at 415 nm. Since the absorption maximum (425 nm) of the compressed mono-layer at 48 Å²/molecule in Fig. 5 are higher than those (400 or 415 nm) for the solid states, the degree of H-aggregation may be lower in this compressed monolayer.

At pH 4.2 (Fig. 6), besides the azo band around 425 nm, the hydrazone bands at 519 and 552 nm also appear with the similar intensity to the azo band. There-fore, both tautomeric forms are highly in equilibrium with each other at this pH. In other words, pH 4.2 is within the transition interval of cetyl orange, and it
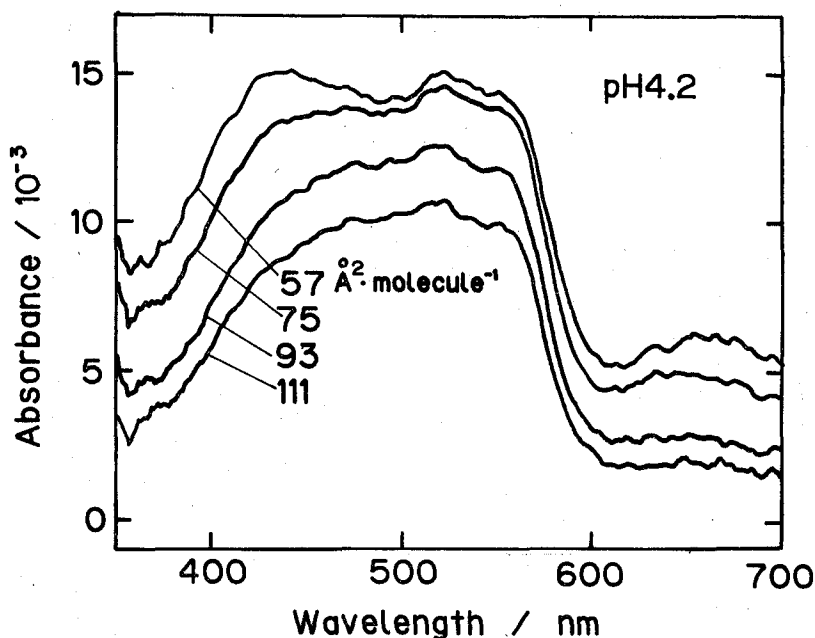
Fig. 6. Visible absorption spectra of spread monolayer of cetyl
orange on water at pH 4.2 and 20°C at four different
surface areas.

corresponds with that (pH 3.1~4.4) of methyl orange[11]. Although the hydrazone
bands in Fig. 6 do not show any marked spectral change upon monolayer compres-
sion, the azo band shows similar blue shift to that in Fig. 5. Difference spectra
(not shown here) suggested that the relative intensity of the azo band to that of
the hydrazone band increased with decreasing surface area.

   At pH 2.8 (Fig. 7), the hydrazone bands at 519 and 552 nm appear with a long
tail toward shorter wavelengths. With decreasing surface area (upon compression),
the azo band around 425 nm increases in intensity. Therefore, the equilibrium
slightly shifts from the hydrazone form to the azo form upon compression. This
equilibrium shift is considered to occur following the Le Chatellier-Braun's law,
since the azo form is principally the more tightly condensed state than the hydra-
zone form, as mentioned above. It should be noted that the equilibrium shift
occurs against the increase in local pH value around the azobenzene chromophore,
since the proton is released by the transformation from the hydrazone to azo forms.

   Furthermore, we prepared LB films consisting of cetyl orange in the hydrazone
form from aqueous HCl subphases at low pH values, but they changed spontane-
ously to the azo form, loosing HCl. When we used H_2SO_4 instead of HCl, the
stability of the hydrazone form in the LB film was improved without appreciable
change in spread monolayer properties. These results will be reported elsewhere[12].

   Finally, we must add that properties of the cetyl orange monolayer on the acidic
subphases reported here are short-lived within a couple of hours after spreading
the cetyl orange monolayer. When these monolayars are allowed to stand for
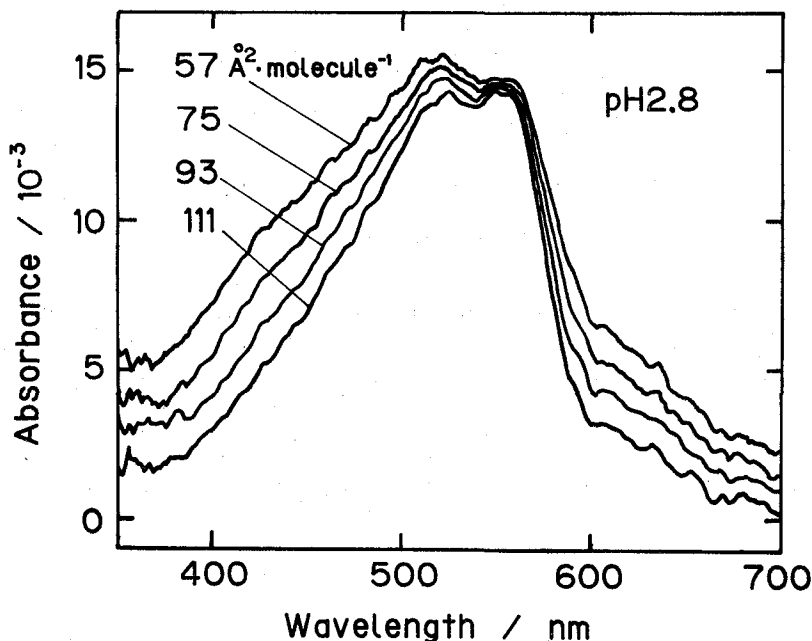
Fig. 7. Visible absorption spectra of spread monolayer of cetyl
orange on water at pH 2.8 and 20°C at four different
surface areas.

more than several hours in the atmosphere, they showed complex spectral changes
which await further clarification.

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