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The Aggregation of a Merocyanine Dye in Solution and Film

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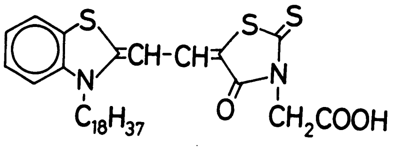
Two low-energy bands, one near 595 nm and the other near 630 nm, were observed in the visible absorption spectra of a merocyanine dye (3-carboxymethyl-5-[2-(3-octadecyl-2-benzothiazolinylidene)ethylidene]-2-thioxo-4-thiazolidinone) dissolved in methanol–water mixtures containing KOH and Triton X-100. From the dye-concentration dependence on the spectra, the band near 595 nm was assigned to the tetramer, and the one near 630 nm, (probably) to the hexamer of the carboxylate form of the dye. The same bands were observed in the dye films when they were soaked in aqueous solutions of pH$\geq$5.5. The relative intensities of the two bands were strongly affected by the ionic strength of the aqueous solution.

Merocyanine dyes have come to attract particular interest as materials for photoelectric[1–8] or photoelectrochemical[8–12] devices because of their high quantum efficiencies. We have reported previously[11] that a thin film of 3-carboxymethyl-5-[2-(3-octadecyl-2-benzothiazolinylidene)ethylidene]-2-thioxo-4-thiazolidinone (MD) showed two low-energy absorption bands near 595 and 625 nm. This spectral change seems of interest because it is induced by a simple treatment, *i.e.*, by soaking the MD film in an aqueous solution of an adequate pH and ionic strength, and also because it is accompanied by a drastic enhancement of the cathodic photocurrent at the MD-coated electrode.[11] Sugi *et al.* have also reported[6,7] that Langmuir multilayers containing MD or its analogue exhibited an enhanced photoconductivity in the lateral direction, associated with the appearance of a low-energy band near 595 nm. Although these low-energy bands have been taken as aggregates of MD,[6,7,11] only a limited number of experiments have so far been carried out, and little is known about the nature of the bands.

We have found that methanolic aqueous solutions of MD containing KOH show low-energy bands depending on the concentration of methanol as well as on that of MD. In this paper, the visible absorption spectra of MD in the solution system are investigated in order to characterize the low-energy bands. The spectral change in the MD film is also discussed with the aid of the results obtained for the solution system.



Experimental

The MD was obtained from the Japanese Research Institute for Photosensitizing Dyes and used without further purification, since preliminary tests showed that the purification of MD by means of column chromatography on silica gel (eluent; chloroform containing 10% v/v methanol) brought about no discernible change in the results. The other reagents used were of an analytical GR grade and were also used without further purification.

Methanolic aqueous solutions, each containing 0.01 M[†] KOH, were employed as solvents of MD, and 0.005% v/v of Triton X-100 was added to each solution in order to prevent the precipitation of MD. The visible absorption spectra of the MD solutions were recorded 2 h after the preparation of each solution using a Cary 17 DX spectrophotometer. An absorption cell with the optical path of 10 cm was mostly employed because the measurements had to be carried out on very dilute MD solutions.

MD films were prepared by means of the vacuum evaporation of the dye onto Pyrex-glass plates (size; 0.9 × 4.5 cm^2) below 5×10^{-4} Pa using a tungsten boat heated up to *ca.* 220 °C. Film with an absorption of 0.25 ± 0.01 at 516 nm was used for the experiments. For IR spectral measurements, CaF_2 single crystal plates were employed as bases of the MD films in place of the glass plates. The permeability of the MD film to an aqueous solution was checked by soaking the film on a water-soluble substrate in the solution. In the present study, a KBr tablet coated with epoxy resin on only one side was used as the substrate; MD was evaporated onto the uncoated side. A phosphate buffer solution (KH_2PO_4 plus K_2HPO_4, pH 7.0; ionic strength, 0.01) was prepared, and the ionic strength of the solution used for the experiments was adjusted by diluting the buffer solution with water or by adding KCl to it. The MD film on glass was placed in an absorption cell (size; $1.0\times1.0\times4.5$ cm^3), and the visible absarption spectra were recorded using a Shimadzu UV-220 spectrophotometer before and after adding an aqueous solution to the cell. The IR spectrum of the MD film soaked in an aqueous solution and then dried was measured using a JEOL JIR 40 IR spectrophotometer.

The chemical stability of MD during the course of the experiment was always checked by means of silica-gel thin layer chromatography.[3] No degradation products were observed on the silica-gel plate after soaking the film.

All the spectral measurements were carried out at 25 ± 1 °C.

Results and Discussion

Aggregation of MD in Solutions. Methanolic solutions of MD gave a single peak at 524 nm, along with a discernible shoulder at 495 nm, on their visible absorption spectra, and they followed Beer's law, at least in the concentration range from 0.1 μM to 14.0 μM (which corresponds to the saturated solution of MD). Since conformity to Beer's law was found at such a low concentration, the absorption of the methanolic solution can be assigned to the monomer of MD. The shape of the monomer-absorption spectrum of MD is typical of the monomers of polymethine dyes.[13,14] The peak absorption is induced by the $0\leftarrow0$ transition, and the shoulder on the high-energy side is a result of the

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[†] Throughout this paper, 1 M=1 mol dm^{-3}.

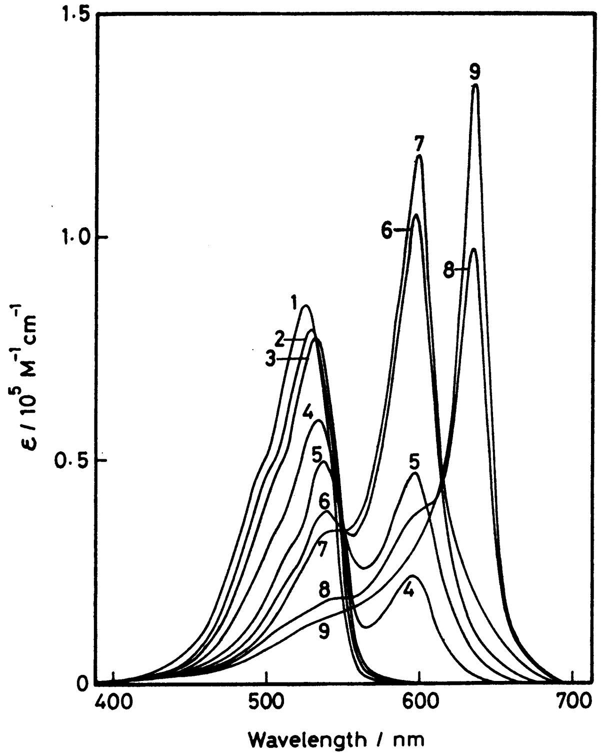

Fig. 1. Absorption spectra of 0.75 μM MD in methanolic aqueous solutions containing 0.01 M KOH and 0.005% v/v Triton X-100. The methanol concentrations in the solvents are given in M: (1) 22.5; (2) 20.0; (3) 17.5; (4) 15.0; (5) 13.5; (6) 12.5; (7) 11.0; (8) 9.0; (9) 7.5.

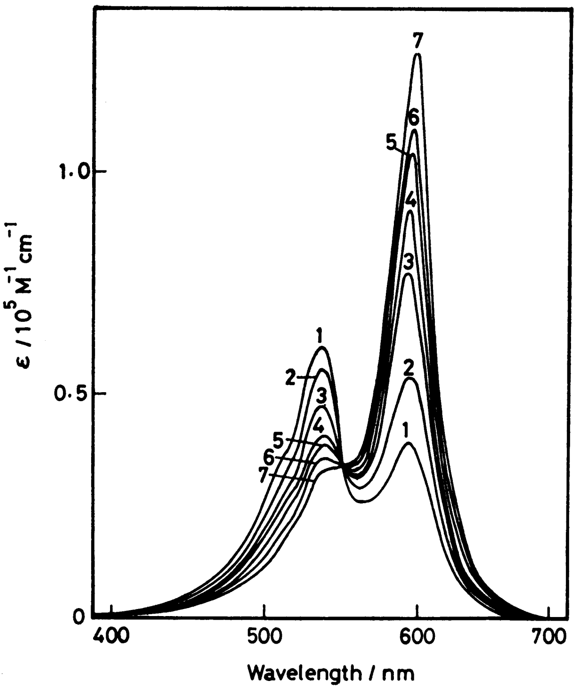

Fig. 2a. Absorption spectra of MD of various concentrations in 12.5 M methanol–water containing 0.01 M KOH and 0.005% v/v Triton X-100. MD concentrations are given in μM: (1) 0.2; (2) 0.3; (3) 0.4; (4) 0.6; (5) 0.75; (6) 1.2 (7) 1.4.

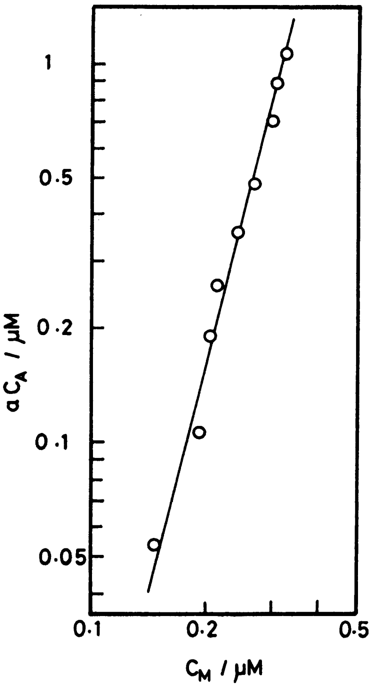

Fig. 2b. Determination of the aggregation number a, for the equilibrium $aC_M \rightleftharpoons C_A$. C_M and C_A are the concentrations of monomer and aggregate, respectively, and they derived from Fig. 2a.

"forbidden" transition of high energy due to molecular vibration.[13,14] The addition of an alkaline aqueous solution to the methanolic solution of MD strongly affected the shape of the absorption spectrum. Figure 1 shows the visible absorption spectra of 0.75 μM MD in mixed solution of methanol and water, each containing 0.01 M KOH and 0.005% v/v Triton X-100. The features of the spectra can be roughly classified into three groups, depending on the methanol concentration of the solution. The MD solutions containing 17.5 M or above methanol give an absorption similar in shape to that obtained in the methanolic solution (Lines 1—3). On the other hand, a new band starts to appear near 595 nm in addition to the above absorption, and the intensity of the new band increases with a decrease in the concentration of methanol, in the concentration range of methanol from 15.0 M to 11.0 M (Lines 4—7). Further decreasing methanol concentration below 11.0 M brings about the appearance of another low-energy band near 630 nm associated with a significant intensity lowering of the band near 595 nm (Lines 8 and 9).

The similarity of Lines 1—3 to the absorption of the methanolic solution of MD indicates that MD is in the monomeric form in the mixed solvents containing 17.5 M or more methanol. The MD in these solvents followed Beer's law over a relatively wide concentration range; *i.e.*, the solution containining 20.0 M methanol follows the low from 0.1 μM to 2.0 μM of MD. As can be seen from Lines 1—3, the monomer band of MD exhibits a small shift to the low-energy side and a lowering of the molar absorptivity, ε_M, with a decrease in the concentration of methanol in the mixed solvent; this could be explained by the increase in the dielectric constant of the solvent, since the monomer band obtained in methanol and in other organic solvents (such as benzene, tetrahydrofuran, acetone, *N*,*N*-dimethylformamide, and diethyl sulfoxide) showed a slight shift to the low-energy side with the increase in the dielectric constant of the solvent, and since the ε_M of the band decreased when the dielectric constant of the solvent was above *ca.* 30.

Deviations from Beer's law become noticeable when low-energy bands appear in addition to the monomer band. Figure 2a shows the dependence of the absorption spectra on the MD concentration in the solvent containing 12.5 M methanol. An isosbestic point is observed near 550 nm; this indicates that the monomer band and the band near 595 nm are expressed by a single equilibrium. Since the decreased intensity of the monomer absorption near 535 nm and the accompanied enhancement of the low-energy band near 595 nm are observed with a growing MD concentration, the curves in Fig. 2a can be analyzed in termes of an equilibrium between the monomeric and aggregate forms of MD:

$$aC_M \rightleftharpoons C_A, \quad K = C_A/(C_M)^a, \tag{1}$$

where C_M and C_A are the concentrations of the monomer and the aggregate respectively, a is the number of monomer units in the aggregate, and K is the association constant. Hence, the a-value is determined by plotting log aC_A and log C_M. The peak intensity of the monomer band and that of the aggregate band were evaluated according to the procedure of West and Pearce.[14] The molar absorptivity of the monomer at the peak, ε_M, was taken as 7.40×10^4 M^{-1} cm^{-1} in the solvent by extrapolating the ε_M *vs.* methanol concentration curve measured in the methanol-concentration region where only the monomer band is given. By subtracting the C_M thus determined from the total dye concentration, C_T, aC_M $(=C_T-C_M)$ was evaluated. As is shown in Fig. 2b, the plots follows a straight line, and the a-value is determined as *ca.* 4. Accordingly, the spectral change is explained by a monomer⇄tetramer equilibrium, and the low-energy band near 595 nm can be assigned to the tetrameric form of MD. The molar absorptivity of the tetramer at the peak, ε_4, was obtained as 6.27×10^5 M^{-1} cm^{-1}.

Similarly, the dependence of the band near 630 nm on the MD concentration was examined in the solvent containing 7.5 M methanol (Fig. 3a). In this case, however, the absorption change cannot be described by a simple equilibrium, because two bands, the monomer and the tetramer bands, appear in addition to the band near 630 nm. Since the relative intensities of the monomer and tetramer absorptions decreased and the absorption of the band near 630 nm increased with a growing MD concentration, the band near 630 nm may well be assigned to a higher-order aggregate. The following equilibrium is, therefore, proposed in addition to the monomer⇄tetramer equilibrium:

$$C_4 + bC_M \rightleftharpoons C_{(4+b)}, \quad K' = C_{(4+b)}/C_4\cdot(C_M)^b, \tag{2}$$

where $C_{(4+b)}$ is the concentration of the aggregate which shows the band near 630 nm; $(4+b)$, the number of monomer units of the aggregate; C_4, the concentration of the tetramer; and K', the association constant. If the total dye concentration is given by C_T, the following relations are obtained:

$$\log\,[(4+b)C_{(4+b)}/C_4] = b\log C_M + \log\,[(4+b)K'], \tag{3}$$

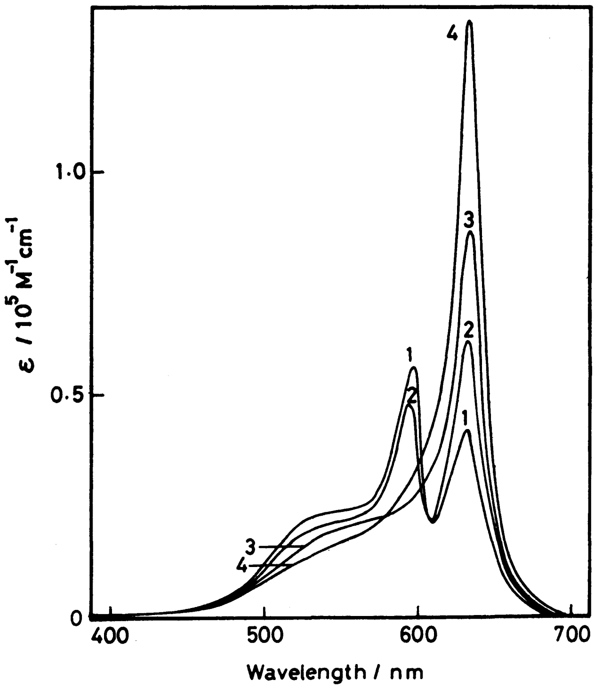

Fig. 3a. Absorption spectra of MD of various concentrations in 7.5 M methanol–water containing 0.01 M KOH and 0.005% v/v Triton X-100. MD concentrations are given in μM: (1) 0.1; (2) 0.2; (3) 0.5; (4) 0.75.

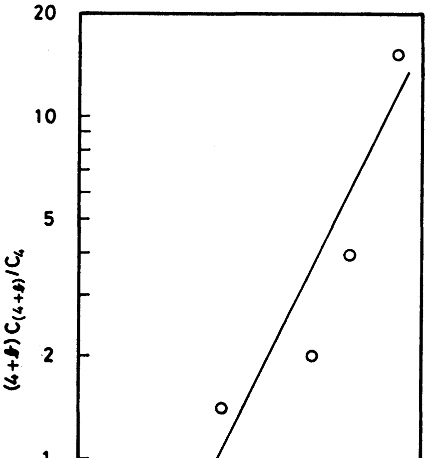

Fig. 3b. Determination of the b-value, for the equilibrium $C_4 + bC_M \rightleftharpoons C_{(4+b)}$. C_M, C_4, and $C_{(4+b)}$ are the concentrations of monomer, tetramer, and aggregate which shows the band near 630 nm, respectively, and they are derived from Fig. 3a. See Eqs. 2—4 and text for details.

$$(4+b)C_{(4+b)} = C_T - C_M - 4C_4. \quad (4)$$

By evaluating the peak intensities of the monomer and tetramer bands according to the procedure of West and Pearce[14)] and by applying the value of ε_M and ε_4 obtained for the mixed solvent containing 12.5 M methanol, C_M and C_4 were determined, and the values according to Eq. 3 were plotted. The results are shown in Fig. 3b. Although the data scatter somewhat, the b-value can be roughly estimated as 2. The low-energy band near 630 nm is, therefore, (probably) assigned to the hexamer of MD.

In the methanol–water mixtures containing KOH, MD is considered to be in the anionic form because of the dissociation of the carboxymethyl group of MD. For the formation of the above-mentioned tetramer and hexamer, the anionic form is concluded to be essential, since such aggregates were not formed when MD was dissolved in any methanol–water mixtures containing HCl, in which MD is considered to be in the neutral molecule form. As MD anions are polymerized by overcoming the electrostatic repulsive force between the anions, the addition of cations may play an important role in the screening effect.[13–16)] Our preliminary results indicate that the addition of KCl to the alkaline solution used in the present study enhanced the formation of both kinds of aggregates, especially of the hexamer. On the contrary, the increase in the concentration of Triton X-100 enhanced the intensity of the monomer band because of the dissociation of the aggregates, as has previously been reported in the case of a cyanine dye solution.[13)]

Aggregation of MD in Films. The vacuum-deposited MD film exhibits, similarly to the cast film of MD,[11)] two visible absorption peaks at 516 nm and at 546 nm. The peak at 516 nm has been assigned to the dimeric (or oligomeric) form, and the one at 546 nm, to the monomeric form, of MD molecules since a dicrease in the absorbance at 516 nm was observed in the cast film of MD which contained arachidic acid as a diluent.[11)] MD is insoluble in water as well as in aqueous solutions which are free from surfactants in the pH range from 0 to 13. Therefore, no coloration of aqueous solutions was observed when MD film was soaked in them. A slight alteration has been observed in the spectrum of the film soaked in a 0.5 M HNO_3 aqueous solution,[11)] while the monomer and the dimer (or oligomer) bands remain practically unchanged. Similar results were obtained for the film soaked in any aqueous solution with a pH below 5.5. When the film was soaked in aqueous solutions of pH 5.5 or above, on the other hand, the spectrum was changed to form two low-energy bands, at 595 nm and at 625 nm. Figure 4 shows the spectral change in the MD film in the aqueous solution of pH 7.0 and an ionic strength of 0.10. The observed absorption bands for the MD film at 595 nm and at 625 nm are very similar, with regard to the peak position and the band shape, to those near 595 nm and near 630 nm for the methanolic aqueous solutions of MD described in the preceding section. Therefore, it can be concluded that the observed low-energy band at 595 nm and at 625 nm for the film are also to be assigned to the tetramer and (probably) the hexamer of the MD anion respectively.

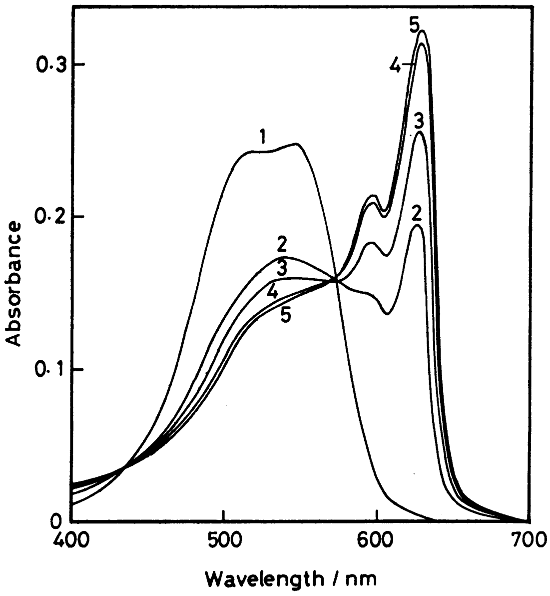

Fig. 4. Absorption spectra of the MD film (1) before and after sorking in an aqueous solution of pH 7.0 and ionic strength 0.10 for (2) 5 min, (3) 30 min, (4) 2 h, and (5) 24 h.

When the MD film on a KBr tablet was soaked in an aqueous solution of pH 7.0 with an ionic strength of 0.10, the tablet immediately began to dissolve (within a few seconds). The finding indicates that the solution can permeate rapidly into the film. Accordingly, the dissociation of the carboxymethyl group of MD in the bulk of the film is expected to proceed immediately after soaking the film in the aqueous solution. The formation of the MD anion in the bulk of the film was ascertained by IR measurements. The deposited film shows a C=O stretching absorption band for –COOH at 1740 cm^{-1}. The intensity of the absorption band becomes almost negligible after the film is dipped in the solution, probably because of the formation of the carboxylate form. The spectral change in the MD film is, on the contrary, very slow, as is shown in Fig. 4; the film needs *ca.* 2 h to give an almost stationary spectrum after being soaked in the aqueous solution. Therefore, slow processes for the aggregation, such as the re-arrangement, of MD anions proceed after the fast permeation of the aqueous solution into the film.

As has been described in the preceding section, the addition of KCl to the solution (which corresponds to the increment in the ionic strength of the solution) significantly affects the relative intensities of the two low-energy bands. In the case of the MD film/solution system, the change in the ionic strangth of the aqueous solutions also showed a marked effect on the relative intensities of the two bands. The results are given in Fig. 5, where the values of absorbance at 595 nm and at 625 nm are recorded after the MD film has been soaked for 2 h in each solution. As is shown in Fig. 5, the lowering of the ionic strength below 0.08 brings about a decrease in the absorbance at 625 nm and a simultaneous increase in that at 595 nm; further, only

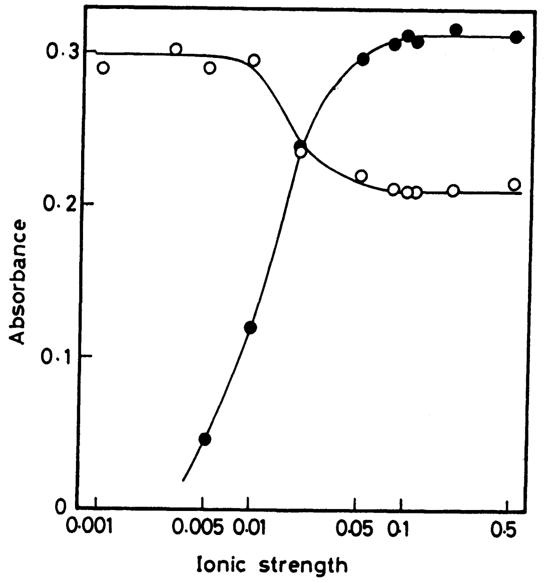

Fig. 5. Role of ionic strength of aqueous solutions on the absorptions of (○) the peak at 595 nm and (●) that at 625 nm.

the band at 595 nm is observed below the ionic strength of 0.003. Similar results were given by Sugi *et al.*7) and also by Nakahara *et al.*;17) they found7,17) that the MD containing monolayer which was spread on an aqueous subphase of 0.4 mM $CdCl_2$ (pH *ca.* 6.5 and ionic strength *ca.* 0.001) exhibited only a low-energy absorption near 595 nm. The results given in Fig. 5 clearly indicate that very concentrated cations surrounding MD anions lead to a highly-ordered aggregation.

The dye film with aggregate(s) which shows a low-energy band is of practical importance as a photosensitizer7,11,18–22) because of its high quantum efficiency, broad spectral response, and high stability. The change in the electrochemical behavior of the MD-coated electrode due to the formation of the aggregates will be described in detail in the following paper.

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