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CIRCULAR DICHROISM OF POLY-MOLECULAR ASSOCIATE, J-AGGREGATE, OF 1,1'-DIETHYL-2,2'-CYANINE CHLORIDE BY REGULAR STIRRING OF THE SOLUTION

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The circular dichroism of the poly-molecular associate of 1,1'-diethyl 2,2'-cyanine chloride, J-aggregate, has been induced by regular stirring of the solution.

1,1'-diethyl-2,2'-cyanine chloride(Fig. 1) is widely used for the spectral sensitization in photographic emulsions. In the aqueous solution at high dye concentrations, the poly-molecular associate of the dye shows a specific absorption band which is sharp and strong at a longer wavelength by ca. 1500 cm^{-1} than the monomer band. The absorption band is called as Jelley-Scheibe band(J-band) after the names of the discoverers[1]. The J-aggregate, which shows the J-band and is reported to be consisted of at least seven molecules[2], is important for the spectral sensitization in photographic emulsions because of the coincidence of the wavelength of the J-band in the solution with the sensitivity maximum in photographic emulsions[3].

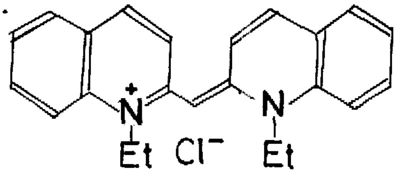

Fig. 1

Blout and Stryer reported that the circular dichroism(CD) of the J-aggregate is induced by α-helical, poly-α,L-glutamic acid in the neutral pH region[4]. Mason has observed the circular dichroism induced by potassium tartrate for the J-aggregate[5]. Maurous and Bird reported the splitting of the CD spectrum at the J-band[6]. Daltrozzo et al. have presented the schematic models of the J-aggregate from their observation of the induced Cotton effect by potassium tartrate[2]. In all the past works, chiral species have been used to determine the CD spectra. We have observed the circular dichroism in the solution of the J-aggregate formed by regular stirring of the solution without any chiral additives.

The sample of the dye afforded by Nihon Kanko Shikiso Co., Ltd. was dissolved in the twice distilled water to obtain 3×10^{-3} M dye solution which shows no J-band. A piece of potassium sulfate crystal was immersed in the clockwise swirling solution at ca. 1000 r.p.m. in a porcelain cruicible for 20 min. at room temperature to obtain the solution which contains monomers (525 nm), dimers(484 nm) and J-aggregates(572 nm) in a state of equilibrium. In this case, the J-aggregate would be small and the viscosity of the solution is not high. The absorption and CD spectra are shown in Fig. 2. After the measurement of the CD spectrum, the solution was stirred anticlockwise for 30 min., and the CD spectrum with the oposite signs of the elipticity to the former solution has been observed as also shown in Fig. 2. The CD spectrum at about 532 and 493 nm would not be due to monomers and dimers but to the J-aggregate, as reported by Daltrozzo et al[2]. This result would suggest that the dissymmetric J-aggregate has been formed by the regular stirring of the solution The circular dichroism has disappeared after standidng for about one day.

1 M potassium chloride aqueous solution was added into 6×10^{-3} M dye solution in 1:1 of volume ratio to obtain the solution which contains almost of only the J-aggregates and has high viscosity. The solution was once heated up to 70°C to break the J-aggregates into monomers and dimers[7] and stood for one day at room temperature in a dark room to obtain the solution of the J-aggregates dispersed randomly. The solution was stirred as in the same way as stated above for three minutes. In this sample, the splitting of the CD spectrum at the J-band has been observed(Fig. 3). This splitting has been remained for at least one day at room temperature. This splitting has been observed by Maurous and Bird at room temperature and in the unstable state by Daltrozzo et al. at liq.N_2 temperature. Cooper has observed the splitting of the J-band in absorption spectra at liq. N_2 temperature[8], not at room temperature. The splitting would be due to the interaction among the J-aggregates in the solution. In the solution with the high viscosity, the J-aggregate will grow to be large enough to interact with each other. The solution in a gel state without chiral additives as in this sample would keep the chirality in the stable state. For reference, the solution which contains monomers, dimers and J-aggregates in

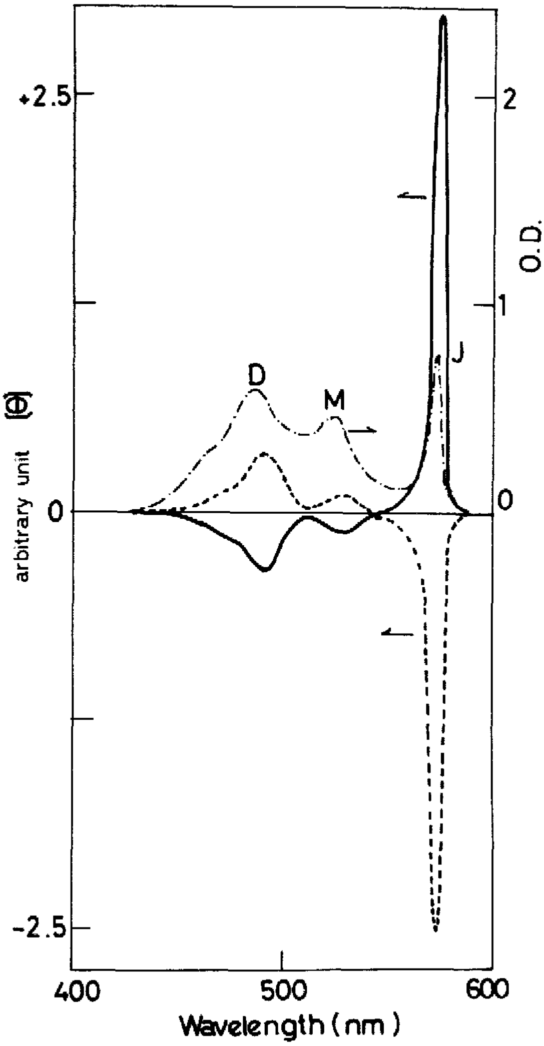

Fig. 2. Absorption and CD spectra*.

—·— :absorption.

------ :clockwise.

——— :anticlockwise.

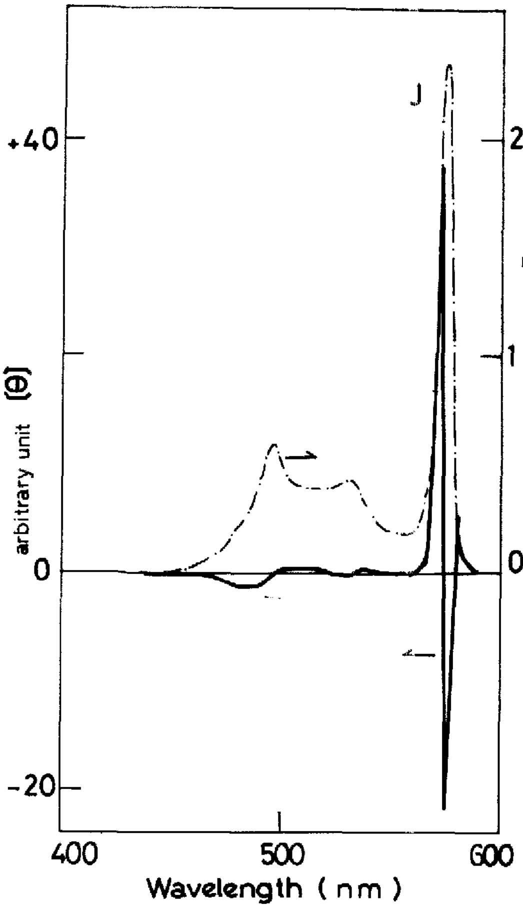

Fig. 3 Absorption and CD spectra*.

—·— :absorption

——— :CD

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* 100 μ light pass length for absorption and CD spectra.

a state of equilibrium formed by potassium tartrate was stirred in ong direction, but the stirring did not work on the solution. The mechanical factor, such as the stirring would be weaker than the perturbation by chiral species.

The formation of the dissymmetric molecular associate by the regular stirring of the solution can be applied to the measurement of the CD spectra of the J-aggregate of sodium 1,1'-diethyl-3,3'-disulfobutyl-5,5',6,6'-tetrachlorobenzimidazolocarbocyanine (Fig. 4) which is an anion dye[9]. For this dye, potassium tartrate does not induce the Cotton effect in the solution, because of the coulombic repulsion. However, we have observed the formation of the dissymmetric J-aggregate by the regular stirring of the solution. We have also observed the circular dichroism of the solution of the J-aggregate of 3,3',9-triethyl-5,5'-dichlorothiacarbocyanine chloride (Fig. 5) by the regular stirring. Therefore, the technique of the formation of the dissymmetric molecular associate by the regular stirring of the solution would have an capability to be generally applied to the other species.

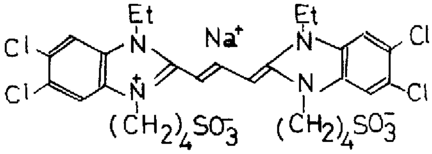

Fig. 4

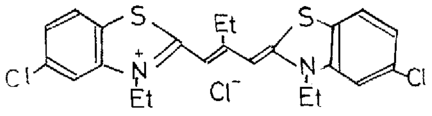

Fig. 5

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