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Aqueous Dye Aggregates as Liquid Crystals

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Aqueous solutions of cyanine dyes can be made to aggregate by the addition of a salt, such as NaCl; the most unusual state observed in the range of transformations from true solution to precipitated crystals is an intermediate phase consisting of microscopic, thread-like aggregates of the dye molecules.(1,2) We have found that this phase may show large optical activities at the position of the absorption bands of the dye, which appear immediately upon mixing salt into the aqueous dye solution and which can be altered in magnitude and sign by rotating or shaking an optical cell containing aggregated dye solution.

This note will be restricted to observations made with the dye 1,1′-diethyl-2,2′-carbocyanine iodide (Koch-Light). Circular dichroism (CD) spectra were recorded on a Durrum-Jasco Spectropolarimeter, Model J-20. The magnitude of optical activity increases with dye concentration, but the spectropolarimeter cannot operate when the absorbance is greater than about 2.0; this restricts measurements in the region of the absorption bands to relatively low concentrations. The iodide dye salts are not very soluble in water; a typical experiment uses a nearly saturated solution at c. 5×10^{-5} M. CD is first detected when the added NaCl is at a concentration of c. 5×10^{-2} M, and generally increases in magnitude with the addition of salt until the dye begins to flocculate and settle out of solution. The limit of flocculation is avoided by using a small amount of salt. After the initial mixing, subsequent rotation of the cylindrical optical cell several times around its own axis produces a much larger optical activity with a CD spectrum that might be different in shape and opposite in sign from the original. This large, mechanically-induced result decreases in magnitude during the first half-hour after rotation. From that time on, the spectrum may change shape slightly, but the overall magnitude of the CD remains nearly constant for as long as we care to wait, which in one case was five days. Such a series of CD spectra is shown in Fig. 1. At the end of any such experiment the cell can be rotated again to yield a very different spectrum which would then evolve in time as stated above, ending with a new, apparently permanent CD.

In terms of the induction of optical activity we can distinguish four classes of salts producing aggregation in these dye solutions:

1. Inorganic salts such as NaCl and $MgSO_4$, with effects described above.
2. Small, optically active amino acid and α-hydroxy acid salts.
3. Salts of polymers where the monomeric unit is optically active and the polymer may exist either in a helical or random coil form.
4. Salts of polymers where the monomeric unit is optically inactive and the polymer forms no helix.

A number of active monomer salts of the second class was used to aggregate the dye, with induced activity occurring in nearly all cases. Mason(3) saw an induced effect with a (+)-tartrate salt opposite in sign to that with the (−)-tartrate. From our observations and those of Scheibe *et al*(4) the sign does not consistently depend upon that of the aggregating salt. The CD spectra of these aggregates can also be changed by agitation or rotation of the optical cell. Strong induced CD is also seen with the racemic forms of aspartate and lactate salts. Presumably, much of the activity in the dye spectrum in these cases is of the same type as that arising with NaCl, although there may also be a component associated with the binding of the dye to the asymmetric salt anion. No induced CD has been observed in aggregates formed with divalent salts of active monomers (e.g. Mg *l*-aspartate and Ca *l*-lactate) even though divalent inorganic salts are as effective as NaCl in giving rise to activity.

Induced optical activity in dye-polymer aggregates is well known.(4–6) As an example of the third class we have studied aggregates of our dye with the sodium salt of polyglutamic acid (Pilot, molecular weight 55 000), using a ratio of acid residue to dye of about 1 : 2. Induced CD is observed in the absorption bands of the

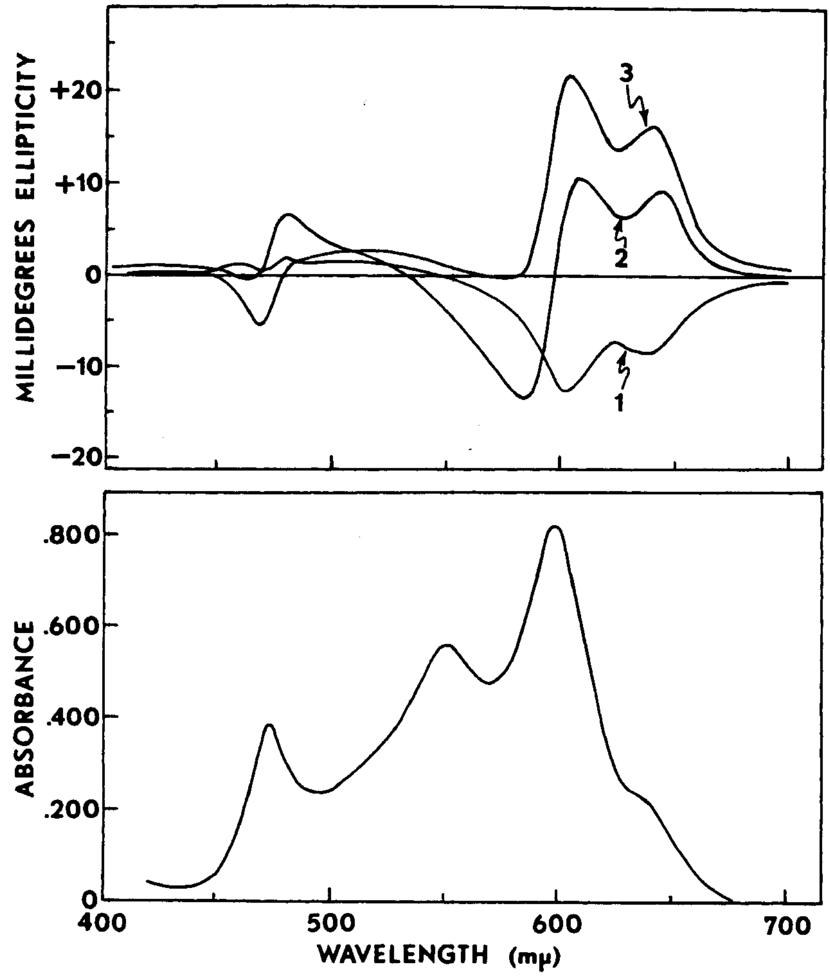

Figure 1. Spectra of the aqueous aggregate of 1,1′-diethyl-2,2′-carbocyanine iodide with NaCl in 1 cm. cell. Circular dichroism (CD) in units of millidegrees ellipticity given in upper part: 1, initial mixture; 2, twenty minutes after rotating the optical cell five times; 3, ten hours later. The absorption spectrum remains unchanged throughout the course of events depicted in the CD spectra.

dye at pH 4.0 when the polymer is in a helical conformation and also with the random coil at pH 7.0. In neither case can the CD spectrum be changed by rotating or shaking the optical cell. The fourth case listed above was studied with the sodium salts of polystyrene sulfonic acid and of a polyacrylic acid (Polysciences. Approximate molecular weight 40 000 for the polystyrene salt and 125 000 for the polyacrylate); although aggregation was evident from the changed absorption spectrum, no optical activity was detected with either salt.

These experimental observations are all consistent with the assumption that the dye aggregates produced with simple salts (e.g. NaCl) form a system with long-range order, i.e. a liquid crystal. Large optical activities are characteristic of the cholesteric type of liquid crystal. Also, liquid crystals are susceptible to large-scale reordering by added chemicals and by external fields.(7) The aqueous medium allows for manipulation of the optical activity by the simplest of mechanical means as, for example, by rotating the optical cell. This property may be of interest in speculation about the origin of optical activity in primitive biological systems.

When polymers are present in solution long-range order is prevented. If the polymer is optically active the dye cations can still show an induced activity as the result of association with anionic sites of the polymer. Therefore, it is not always possible to draw conclusions on the nature of the aggregate from the presence of induced optical activity alone.

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