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The Surfactant-Induced Formation of J- and H-Aggregates in Aqueous Pseudoisocyanine Solutions

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ABSTRACT

It is reported that J- and H-aggregates of pseudoisocyanine iodide can occur in water at low dye concentrations ($\sim 1 \times 10^{-5}$ M) *in the presence of some anionic surfactants (sulphonates, sulphates and their derivatives) at room temperature.*

1 INTRODUCTION

Cyanine dyes are known to form different types of aggregate. The J-aggregates of pseudoisocyanine (PIC) and other polymethine dyes are of substantial interest because of their perspective use in logic memory elements when used as Langmuir–Blodgett monolayers.[1,2]

J-aggregate formation in concentrated (approximately 10^{-2} M) aqueous solutions of unsubstituted PIC is widely known.[3] Such aggregates also occur at lower dye concentrations on addition to the PIC solutions of inorganic salts, polyelectrolytes and gelatine,[4] and also at low temperature,[5,6] in films with regulated structure,[7] in non-aqueous mixtures of polar and non-polar solvents,[8] and at colloidal silica surfaces.[9] Similar cyanines, such as merocyanines[10] and squarylium dyes,[11] also show J-aggregate formation. J-aggregates are characterised by an intense narrow absorption band, which is shifted to longer wavelengths relative to the monomer absorption. Other types of aggregates (for example, H-aggregates) can be formed at the Langmuir–Blodgett interface depending on the conditions and on the

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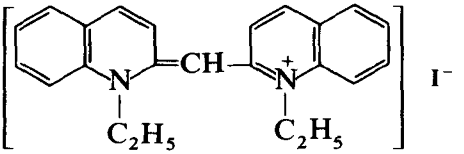
structure of the dye.[2] H-aggregates absorb at shorter wavelengths than the J-aggregates.

It is of interest to note that the appearance of aggregates can be observed in a variety of systems, e.g. in the solid phase (Langmuir films), colloids (gelatine, polyelectrolytes) and solutions (organic solvents and their mixtures). Aggregation can also be induced in dyes containing lower[11,12] and higher alkyl chains;[13,14] these facts led us to investigate the possibility of inducing aggregates of a number of cyanines using surfactants. Photometric studies revealed the formation of both J- and H-aggregates.

This paper deals with PIC aggregation in water in the presence of certain anionic surfactants.

2 EXPERIMENTAL

1,1′-Diethyl-2,2′-cyanine (PIC) was mainly used in the form of the iodide:



The chloride appeared to be less suitable because of its higher solubility and some previous investigations did not identify an aggregate when PIC chloride was used in experiments.[14,15] However, our studies indicated that the use of PIC chloride leads to similar results.

The following sodium salts of sulphates and of sulphonates containing alkyl, alkylbenzene and oxyethylene radicals were used as anionic surfactants, with critical micelle concentration (CMC) in parentheses, from our data or Ref. 16: (**I**) $C_{12}H_{25}OSO_3Na$—sodium dodecyl sulphate ($8{\cdot}4 \times 10^{-3}$ M);[16] (**II**) $C_{12}H_{25}(OC_2H_4)_3OSO_3Na$ ($1{\cdot}4 \times 10^{-4}$ M); (**III**) $C_9H_{19}—C_6H_4—(OC_2H_4)_{12}OSO_3Na$ ($9{\cdot}4 \times 10^{-5}$ M); (**IV**) $C_9H_{19}—C_6H_4—(OC_2H_4)_{12}—OCO—C_6H_4COONa$ (9×10^{-5} M); (**V**) $C_{12}H_{25}SO_3Na$ ($8{\cdot}5 \times 10^{-3}$ M);[16] (**VI**) $C_{12}H_{25}—C_6H_4—SO_3Na$ ($1{\cdot}2 \times 10^{-3}$ M);[16] (**VII**) $C_9H_{19}—CH{=}CH—CH_2SO_3Na$ — this sample was donated by P. A. Perov). Distilled water was used to prepare solutions of the reagents.

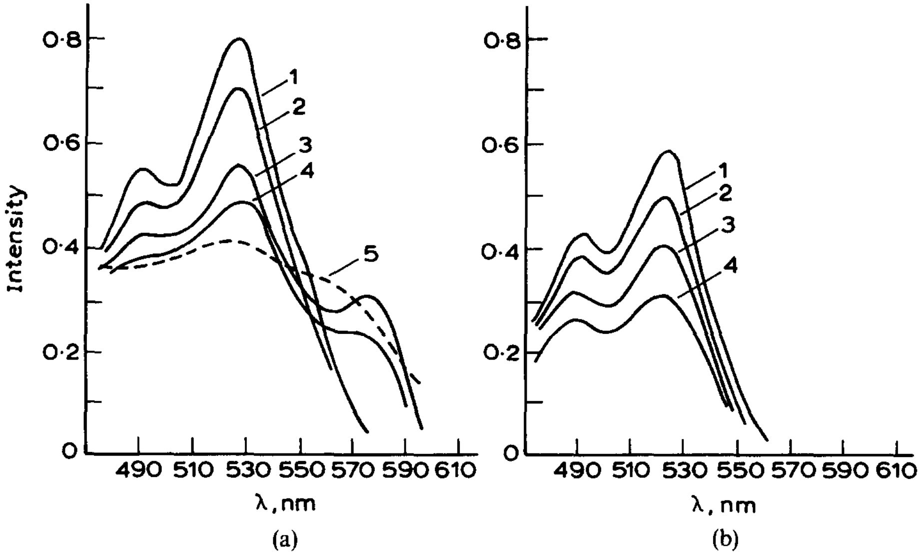
Absorption and fluorescence spectra were recorded immediately after mixing the dye solution with the surfactant solution at room temperature. Specord UV–VIS, Specord M40 and Hitachi 850 instruments were used for the measurements.

The following sequence of addition of components to the photometric flask was always used: first a solution of PIC, then a surfactant solution and finally water. In all about 70 series of spectra with various ratios of concentrations of PIC and surfactants were measured.

3 RESULTS AND DISCUSSION

The PIC aggregation was studied over a wide range of concentrations of both dye and anionic surfactant.

The absorption spectra of the system PIC–surfactant **I** are presented in Fig. 1. On adding **I** to aqueous PIC solution, an absorption of λ_{max} 578 nm appears, while the absorbance decreases in the region of the monomer maximum (524 nm) [Fig. 1(a)]. Further increase in the concentration of **I** leads to a decrease in intensity of the new band. This is similar to the 'metachromatic' effect, observed during the interaction between cyanines (or other dyes) and polyelectrolytes.[4] In the latter case, under the condition of excess of macro-ions, a decrease in the interaction (polymerisation) probability of the dye molecules, situated on the bead, results in the disappearance of the aggregate (dimer, J-aggregate, etc.) band. As shown in Fig. 1(b), there is a 'critical' ('border') PIC concentration below which the occurrence of the J-aggregates is impossible to observe at any concentration of **I**. For the PIC–**I** system this 'critical' concentration is about (0·9–1·0) ×



(a) (b)

Fig. 1. Absorption spectra of PIC–**I** system. (a) Concentration of PIC $1{\cdot}1 \times 10^{-5}$ M (constant); concentration of **I**: 1, 0 M; 2, 1×10^{-4} M; 3, $4{\cdot}5 \times 10^{-4}$ M; 4, 7×10^{-4} M; 5, $4{\cdot}5 \times 10^{-4}$ M (after 2 h). (b) Concentration of PIC $8{\cdot}5 \times 10^{-6}$ M (constant); concentration of **I**: 1, 0 M; 2, $6{\cdot}5 \times 10^{-5}$ M; 3, $1{\cdot}4 \times 10^{-4}$ M; 4, 5×10^{-4} M.

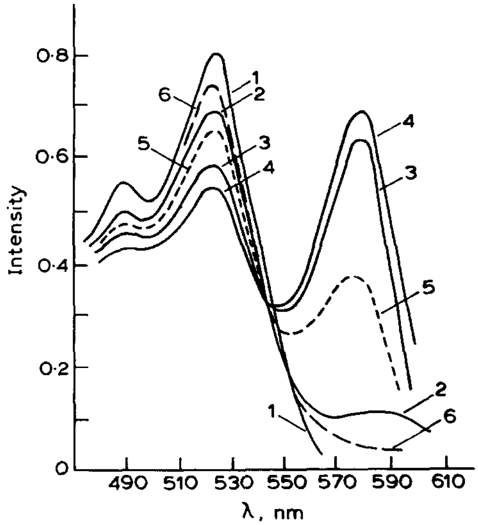


Fig. 2. Absorption spectra of PIC–II system. Concentration of PIC $1{\cdot}1 \times 10^{-5}$ M; concentration of **II**: 1, 0 M; 2, $4{\cdot}3 \times 10^{-4}$ M; 3, $1{\cdot}1 \times 10^{-3}$ M; 4, $1{\cdot}6 \times 10^{-3}$ M; 5, $2{\cdot}4 \times 10^{-3}$ M; 6, $2{\cdot}4 \times 10^{-2}$ M.

10^{-5} M. Increase in the concentration of **I** (at a constant content of PIC) leads only to a uniform decrease in the absorption intensity (curves 2, 3, 4) over the whole spectral range. A characteristic of PIC J-aggregates in the presence of **I** is their low stability with increase in time (Fig. 1(a), curve 5].

More stable J-aggregates are formed in the presence of surfactant **II**. Thus, at dye content about 5×10^{-5} M and **II** content of $(2\text{–}5) \times 10^{-5}$ M, the absorbance values of 578 nm do not change significantly over a period of a few months. The absorption spectra of PIC–**II** are shown in Fig. 2. The J-band configuration proves that the appearance of PIC J-aggregates is more typical in the case of **II** than in the case of **I** (at identical dye concentration). However, further increase in the concentration of **II** leads to dye disaggregation (curves 5, 6), as was observed when using surfactant **I**.

However, even under the conditions of their maximum yield in solution induced by **II**, J-aggregates coexist with non-fluorescent monomers (λ_{max} 524 nm). Measurement of the excitation spectra, however, allows characterisation of the band associated with J-aggregates to be made (Fig. 3). Induced by the surfactants, J-aggregates are characterised by a wider absorption band (40 nm width) than J-aggregates in concentrated aqueous solutions without any additives (with a 15 nm width[3]), and are similar to those in non-aqueous media at about the same dye concentration.[8] A small Stokes' shift occurs in the fluorescence spectrum of J-aggregates ($\lambda_{max}^{em} \approx 590$ nm) with respect to their absorption spectrum, in contrast to the situation in water, in which a narrow fluorescence band is observed. J-aggregates formed in the

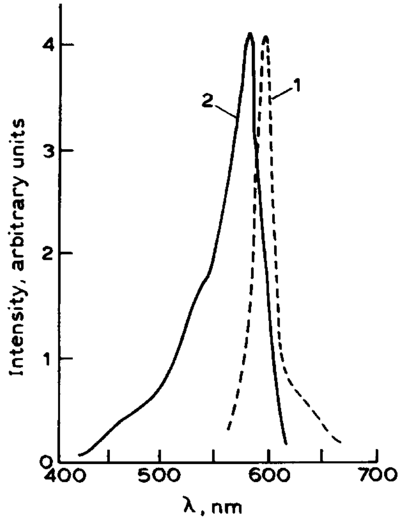


Fig. 3. Corrected fluorescence spectra (1) and excitation spectra (2) of J-aggregates for the PIC–II system.

presence of **II** seem to have a wider range of fluorescing centres with various conformations and molecule numbers, than those formed in water.

Studies using surfactants **III** and **IV** showed that they were unable to induce PIC J-aggregate formation within the range of dye concentrations examined.

Among the sulphonates investigated, only **VII** had the ability to induce J-aggregate formation, this taking place over a wider concentration range of **VII** and at a somewhat smaller value within this range (5×10^{-5} to 5×10^{-4} M). Compound **V** does not induce J-aggregate formation over a wide range of PIC concentrations.

From the experimental data, **VI** strongly enhances the formation of H-aggregates within the concentration range 1×10^{-6} to $\approx 1 \times 10^{-5}$ M (Fig. 4). On introducing **VI** into the PIC solution, a short-wavelength band with a maximum at 430 nm appears. (In the case of the 6-methyl-6,6′-dimethyl derivative of PIC we have observed the induction of H-aggregates with some anionic surfactants, but detailed discussion of this is not within the scope of this present report.) Increasing the concentration of **IV** to 1×10^{-4} M and above leads to a lowering of the intensity of the H-aggregate band, which is evidence of disaggregation. A feature of the induction of H-aggregates is the proportional dependence of the absorption at 430 nm on the concentration of **VI** within a comparatively wide range of surfactant concentration (1×10^{-5} to 1×10^{-6} M). This has been used by us as a basis for the development of a selective method for the quantitative determination of alkylbenzenesulphonates.[17]

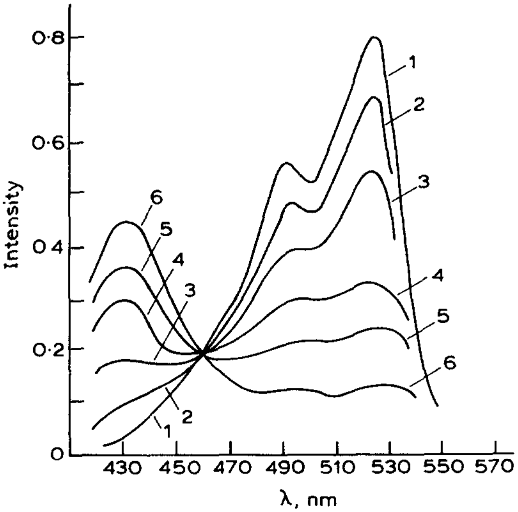


Fig. 4. Absorption spectra of the PIC–IV system; H-aggregate formation.

The results obtained lead to the conclusion that **VI** is a specific PIC H-aggregate inductor within the surfactants studied. In contrast to J-aggregates, the H-aggregates do not fluoresce, while their formation occurs over a wider range of surfactant concentrations (see the scheme in Fig. 5). It should be mentioned that in the PIC concentration range 5×10^{-6} to 1×10^{-4} M it was not possible to propose a single surfactant which had the ability to induce both types of PIC aggregates. On further increase of dye concentrations in the PIC–surfactant system, there occur more noticeable dimerisation (polymerisation) processes.

Each surfactant has its own upper value beyond which the dye aggregation (J- or H-type) is repressed. As a rule, this concentration does not surpass the surfactant CMC value (see adduced values of CMC, in Section 2, and Fig. 5, scheme).

We would emphasise that the band intensity of the J-aggregates formed depends not only upon the absolute value of the resulting concentration of the surfactants and/or PIC (the so-called analytical concentrations), but also upon the 'local' concentrations (i.e. the concentration at the instant of the components of the stock solutions coming into contact). Therefore, the spectra of J-aggregates obtained at the same initial concentrations of components can differ in intensity. Thus, if solutions are prepared using a different sequence and different concentrations of stock solution, the reproducibility of the results will be rather low. This is understandable, since it is well known that dye polymerisation, and especially J-aggregate formation, is not always a reversible process, obeying the law of thermodynamic equilibrium.

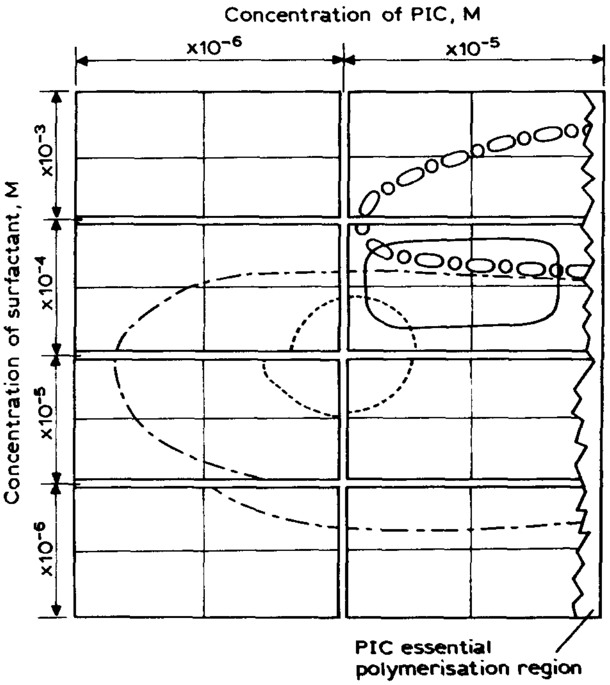


Fig. 5. Concentration areas corresponding to J- and H-aggregate formation of PIC. —— **I**, J-aggregates; O⊂⊃O **II**, J-aggregates; –·–·– **VI**, H-aggregates; ······ **VII**, J-aggregates.

It should also be noted that the addition of non-ionic surfactants destroys the aggregates; acetone and alcohols act similarly. The spectra of such systems were similar to those of the monomer PIC, but with a slight solvatochromic shift. Probably, the solubilisation of the hydrophobic dye ions by the micelles, or solvation of them by organic solvents, competes with aggregation processes. The role of the surfactants in the formation of aggregates is probably relatable to their anions being included in the corresponding particles as counterions. Hence, mixed micelle formation can be presumed; under conditions of excess surfactant the homomicelles with isolated dye monomers adsorbed on their surface predominate.

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