APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 12, 341–346 (1998)

# Adsorption of Pseudoisocyanine on Silver Bromide Nanoparticles: Effect on the Stability of the Particles

Laurence Jeunieau* and Janos B. Nagy
Laboratoire de Résonance Magnétique Nucléaire, Facultés Universitaires Notre-Dame de la Paix, Rue de Bruxelles, 61 B-5000 Namur, Belgium

**Pseudoisocyanine (PIC) was adsorbed on colloidal silver halide nanoparticles where it formed aggregates (J-aggregates). The nanoparticles were prepared using a surfactant (AOT)/n-heptane/water microemulsion. The molecules of pseudoisocyanine replaced the molecules of surfactant (AOT) on the surface of the nanoparticles and caused an instability of the silver bromide dispersion. The stability could be improved by two methods: either by using an adsorption inhibitor (e.g. *p*-xylene) or by adding another surfactant (CTAB). The adsorption has also been carried out at low temperature: the stability of the particles was then improved, and the J-aggregates are smaller. © 1998 John Wiley & Sons, Ltd.**

*Appl. Organometal. Chem.* **12**, 341–346 (1998)

**Keywords: silver halides; nanoparticles; pseudoisocyanine; stability**

*Received 20 November 1997; accepted 20 January 1998*

## 1 INTRODUCTION

Cyanine dyes are used for spectral sensitization in the photographic industry. Many publications deal with the study of their adsorption and the mechanism of their spectral sensitization (e.g. Refs. 1, 2). However, these silver halide particles are always synthesized in a gelatine–water medium and they are generally in the order of 0.4 μm in size. In this work the cyanine dye, pseudoisocyanine (Fig. 1), was adsorbed on silver bromide particles synthesized in microemulsion systems.[3–5] In this case the particle size was very small (46 Å) and the medium was different: the particles were in contact with an organic phase and a surfactant was adsorbed on their surface.

## 2 EXPERIMENTAL

The silver bromide particles were synthesized in two microemulsion systems: AOT [bis(2-ethylhexyl)sodium sulphosuccinate]/n-heptane/water and AOT/*p*-xylene/water (Fig. 2).[6–8] The microemulsions were prepared from n-heptane (Aldrich; 99+% HPLC grade), AOT (Sigma; 99%) and aqueous solutions (using twice-distilled water) of 0.063 M silver nitrate (Janssen Chimica; p.a) and 0.064 M potassium bromide (Merck; Uvasol spectroscopy). The microemulsions were prepared with a 0.12 M solution of AOT in n-heptane and the aqueous solutions were added in order to reach a ratio $R = [H_2O]/[AOT]$ of 3.1:1.

A 5 ml portion of the microemulsion containing silver nitrate was poured into 5 ml of the microemulsion containing potassium bromide. The silver bromide particles formed were 46 Å in size. For the dye adsorption, a $10^{-3}$ M solution of PIC (Aldrich; 97%) in methanol was used. The number of PIC molecules per particle on the AgBr were 14 or 21. Part of the dye solution was added to 5 ml of the AOT solution. This mixture was finally added to the

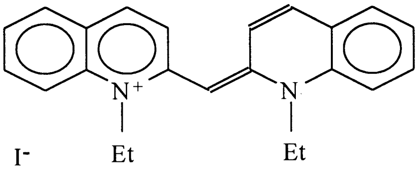

**Figure 1** Molecular structure of 1,1′-diethyl-2,2′-cyanine (pseudoisocyanine).

---

* Correspondence to: L. Jeunieau, Laboratoire de Résonance Magnétique Nucléaire, Facultés Universitaires Notre Dame de la Paix, Rue de Bruxelles, 61 B-5000 Namur, Belgium.
E-mail: laurence.jeunieau@fundp.ac.be

CCC 0268–2605/98/050341–06 $17.50

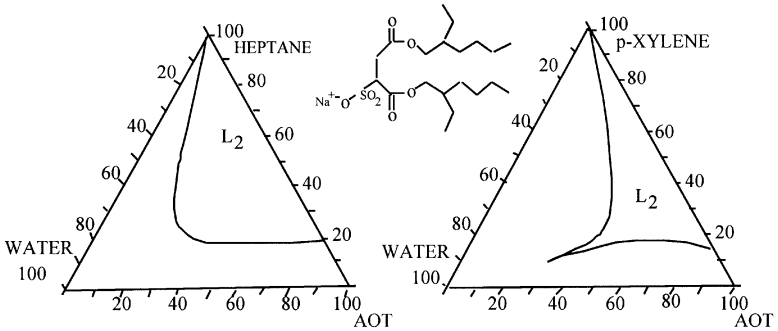

**Figure 2** The ternary microemulsions systems AOT/n-heptane/water and AOT/*p*-xylene/water[6–8] The area $L_2$ indicates the microemulsion zone.

colloidal suspension and stirred for 30 min. Time zero was taken at the end of the 30 min. A Uvikon 930 UV-spectrophotometer was used for the UV–visible absorption spectra (wavelength precision, 0.2 nm; optical path, 1 cm; reference in absorbance measurements, 0.12 M AOT solution in heptane).

## 3 RESULTS AND DISCUSSION

### 3.1 Stability of the particles

Many cyanine dyes form J-aggregates adsorbed on silver halide grains. J-aggregates are characterized by a sharp absorption band with a bathochromic shift of their absorption maxima. Figure 3 shows the decrease in the absorbance of the monomer and of the J-aggregate for 21.0 molecules of PIC per particle adsorbed on AgBr as a function of time. This decrease stemmed from the sedimentation of the particles, which was also confirmed by the aggregates detected by TEM.

The particles were stabilized by the surfactant molecules.[3–5] If PIC is adsorbed, AOT is removed from the surface and the particles are destabilized. The aggregation of the dye molecules on the silver halide nanoparticles decreased the stability of the particles: the aggregates removed the AOT molecules from a large area of the particle surface. The destabilization was increased by the growth of the J-aggregate with increasing time. This is illustrated by the increase in the absorbance maximum of the J-aggregate as a function of time (Fig. 4). The size of a given J-aggregate can be deduced from spectral properties.[9–11] The spectral shift for a linear and

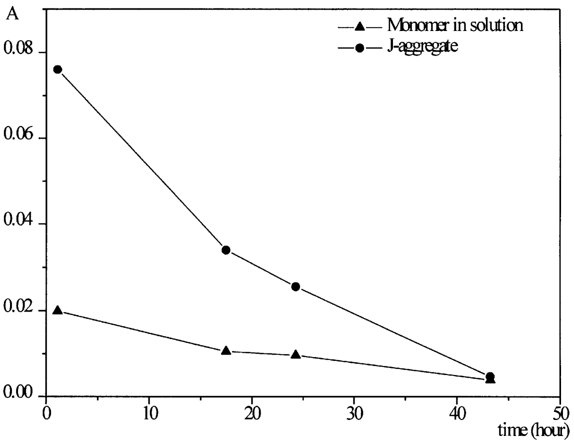

**Figure 3** Variation of the J-aggregate and monomer absorbance as a function of time.

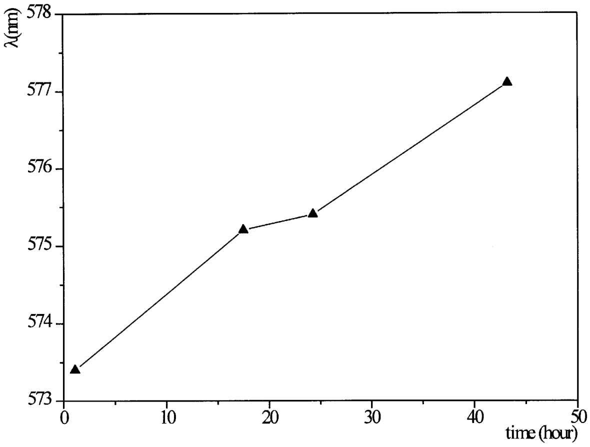

**Figure 4** Variation of the absorbance maximum of the J-aggregate of PIC adsorbed on AgBr.

**Table 1** Approximation of the average number of molecules per aggregate for different concentrations (1) for cyclic aggregates and (2) for linear aggregates.

| Time | $\lambda_{\max}$ (nm) | (1) | (2) |
|---|---|---|---|
| 3 h 24 min | 574.6 | 6.9 | 4.7 |
| 21 h 45 min | 575.2 | 7.6 | 5.1 |
| 30 h 43 min | 576.0 | 8.9 | 5.6 |
| 47 h 44 min | 576.6 | 10.3 | 6.1 |

cyclic aggregate is a function of the aggregate size $N$ according to Eqn [1] for a cyclic aggregate, and Eqn [2] for a linear geometry, where $\Delta v_N$ and $\Delta v_\infty$ are the spectral shift of $N$-mer and $\infty$-mer with respect to the monomer, respectively, with $_{\max}(\mathrm{M}) = 541.2$ nm for the dye monomer adsorbed on AgBr and $\lambda_{\max}(\infty) = 580.7$ nm for an $\infty$-mer adsorbed on AgBr. The results are shown in Table 1. One can see that the average number increases with time and with the absorbance maximum of the J-aggregate.

$$(N-1)/N = \Delta v_N/\Delta v_\infty \qquad [1]$$

$$\cos[(\pi/(N+1)] = \Delta v_N/\Delta v_\infty \qquad [2]$$

This growth is described as the Ostwald ripening of the J-aggregates.[12] This process has been explained by the fact that the molecules at the ends of the J-aggregate are less stable than the other molecules which are in the middle part of the J-aggregate and hence the stability of the dye molecules increases with an increase in the size of the J-aggregate. The aggregates can grow through an adsorption–desorption sequence of the dye molecules on the grains during ripening. If the J-aggregate size is smaller, the destabilization of the particles by the dye adsorption will also be less.

Two methods were envisaged for the stabilization of the particles.

## 3.1 Particles synthesized in the AOT/*p*-xylene/water system

When the adsorption of the dye was carried out in the AOT/*p*-xylene/water system, the amount of adsorbed dye was very low. This must stem from the adsorption of the *p*-xylene on the surface of the particles inhibiting the adsorption of the dye molecules. This hypothesis was previously suggested in a study of the preparation of silver bromide nanoparticles in the same microemulsion.[4] After 30 min of stirring, 5 ml of *p*-xylene was poured into 15 ml of the colloidal suspension. The comparison between the absorbance of the monomer and of the J-aggregate with and without *p*-xylene (Fig. 5a) shows clearly the stabilization effect of *p*-xylene: the absorbance of the J-aggregates decreased more slowly as a function of time. This is a consequence of the smaller size of the J-aggregate: the absorbance maximum of the J-aggregate was lower (Fig. 5b). The competitive adsorption between the PIC and the *p*-xylene decreased the Ostwald ripening of the J-aggregate.

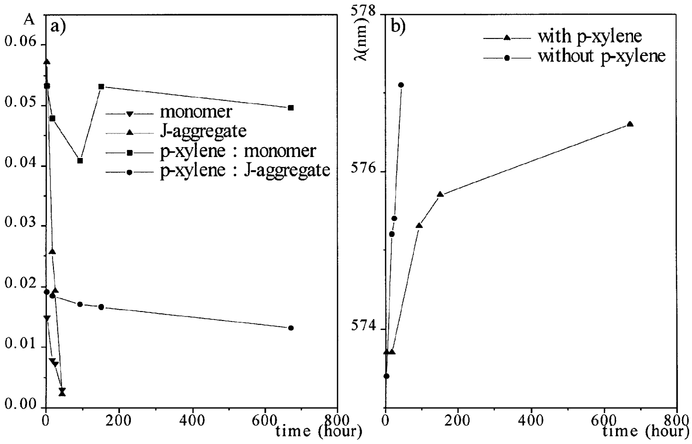

**Figure 5** (a) Variation of the absorbance of the J-aggregate adsorbed on AgBr and of the dye in solution. (b) Variation of the absorbance maximum of the J-aggregate, with and without *p*-xylene.

## 3.2 Use of CTAB

Another method for stabilization of the particles is to add another surfactant to the AOT/n-heptane/water microemulsion. In this experiment, the anionic surfactant (AOT) was replaced by a cationic one: CTAB (cetyltrimethylammonium bromide). CTAB is thought to be more adsorbed than AOT because of the slightly negative surface charge (due to 3% excess of KBr) on the molecules. CTAB was added in a solid form to the particle suspension and the mixture was placed for 15 min in an ultrasound bath. This indirect way of adding CTAB had to be used because the AgBr particles synthesized directly in the CTAB/hexanol/water microemulsion system were not stable.[13] The dye was adsorbed after the exchange of the surfactant molecules. Different concentrations of CTAB have been used, ranging between $1.02 \times 10^{-3}$ M and $7.88 \times 10^{-3}$ M. It must be noted that each concentration is sufficient to cover totally the AgBr particles. Indeed, as the surface occupied by the CTA$^{+}$ ion is 35 Å$^{2}$,[14] some 187 molecules of CTAB are enough to cover totally one particle of 46 Å diameter, and a concentration of $1.02 \times 10^{-3}$ M corresponds to 74 062 molecules of CTAB per particle. The variations of the absorbance of the monomer and of the J-aggregate both depended on

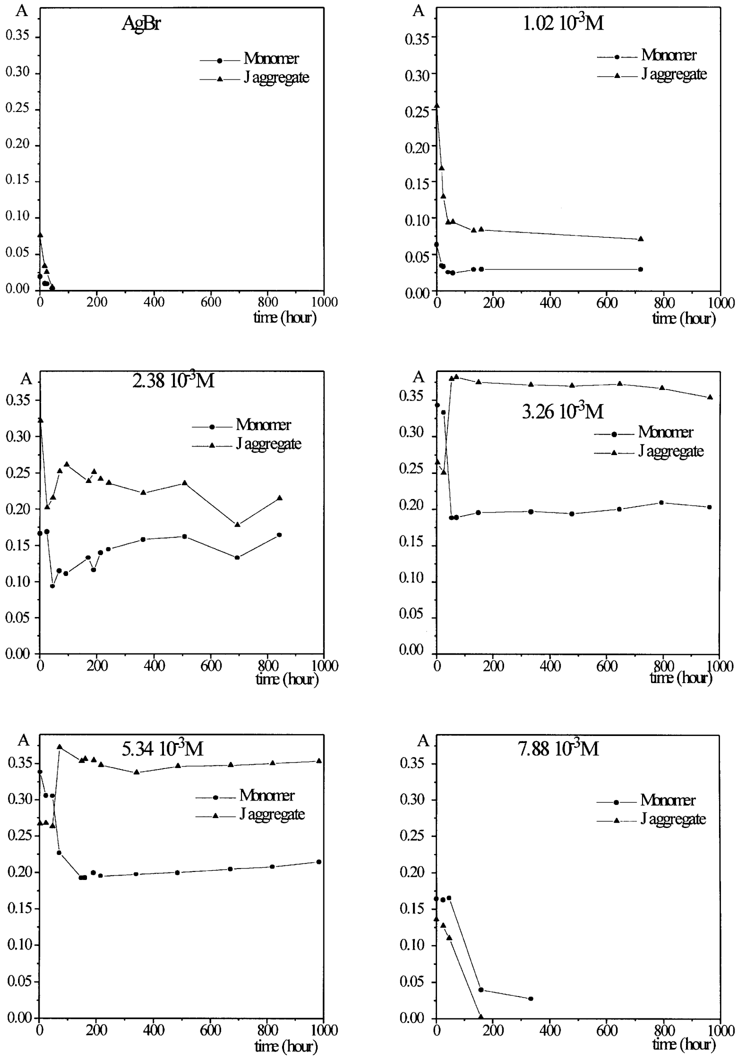

**Figure 6** Variation of the absorbance of the J-aggregate and of the dye in solution as a function of time.

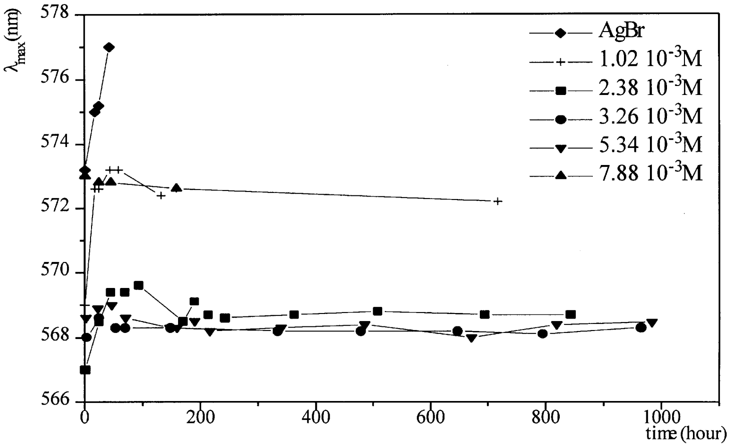

**Figure 7** Variation of the absorbance maximum of the J-aggregate as a function of time. The different concentrations of CTAB are indicated.

the CTAB concentration (Fig. 6). For a concentration of $1.02 \times 10^{-3}$ M and $2.38 \times 10^{-3}$ M, the two absorbances decreased but more slowly than without CTAB; hence the particles were stabilized. For concentrations of $3.26 \times 10^{-3}$ M and $5.34 \times 10^{-3}$ M, the stabilization was more complete; the absorbance of the J-aggregate increased at the expense of the absorbance of the monomer. However, for a greater concentration of CTAB ($7.88 \times 10^{-3}$ M, the particles were destabilized; the absorbances of the two species decreased rapidly with time. Figure 7 shows the variation of the absorbance maximum of the J-aggregate as a function of time. It is thus concluded that CTAB stabilized the size of the J-aggregate. Indeed, for CTAB concentrations of $2.38 \times 10^{-3}$ M, $3.26 \times 10^{-3}$ M and $5.34 \times 10^{-3}$ M, the absorbance maximum of the J-aggregate was nearly constant.

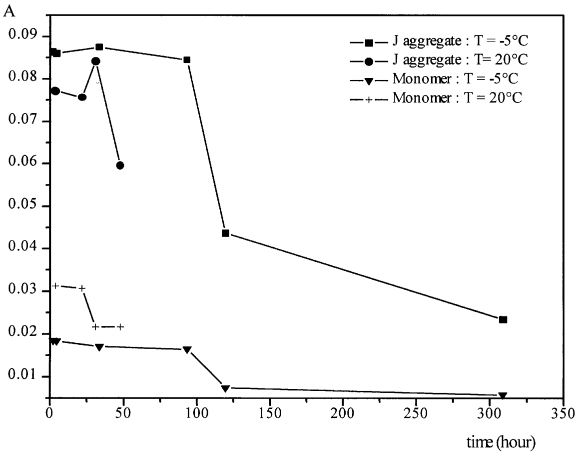

**Figure 8** Variation of the absorbance of the J-aggregate absorbed on AgBr and of the monomer in solution at −5 °C and at 20 °C.

## 3.3 Influence of the temperature

Although the adsorption of PIC was carried out at 20 °C, after 30 min of stirring the solution was kept at −5 °C. The amount of dye added corresponded to 14 molecules per AgBr particle. The absorbance of the monomer in solution was lower at −5 °C; hence the reaction of adsorption is exothermic (Fig. 8). However, the absorbance of the J-aggregate was greater at −5 °C, which showed that the low temperature stabilized the particles. The variation

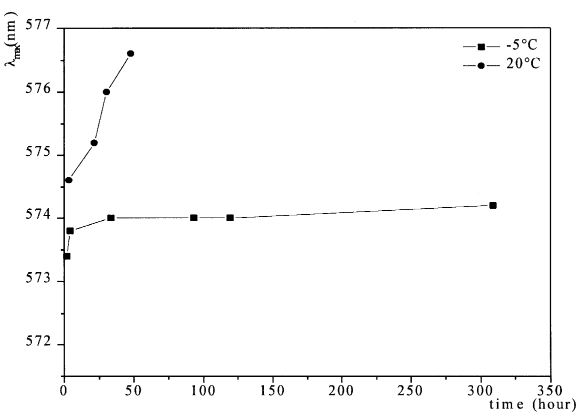

**Figure 9** Variation of the absorbance maximum of the J-aggregate at 20 °C and at −5 °C.

of the absorbance at low temperature is discontinuous: this break point maybe indicated the beginning of sedimentation. The J-aggregate was smaller at low temperature (Fig. 9): the absorbance maximum of the J-aggregate was lower. It can thus be concluded that the Ostwald ripening of the J-aggregates was disfavoured at low temperature.[15]

## 4 CONCLUSIONS

The adsorption of pseudoisocyanine on colloidal silver bromide nanoparticles causes an instability of the particles. Two methods have been found for the stabilization of the particles: the use of *p*-xylene as an adsorption inhibitor and the addition of CTAB, which decreases the rate of dye adsorption. In both cases the J-aggregate size is smaller; this factor explains the improved stabilization of the particles. Carrying out the reaction at low temperature also has a stabilization effect: the Ostwald ripening of the J-aggregates is disfavoured.

*Acknowledgment* Laurence Jeunieau thanks the **F.R.I.A.** for financial help.

## REFERENCES

1. T. H. James, *The Theory of the Photographic Process*, Eastman Kodak, New York, 1977.
2. T. Tani, *Photographic Sensitivity*, Oxford Series on Optical and Imaging Science, Oxford University Press, New York, 1995.
3. Ph. Monnoyer, A. Fonseca and J. B. Nagy, *Colloids Surf.* **100,** 233 (1995).
4. J. B. Nagy, D. Barette, A. Fonseca, L. Jeunieau, Ph. Monnoyer, P. Piedigrosso, I. Ravet-Bodart, J.-P. Verfaillie and A. Wathelet, *Nanoparticles in Solids and Solutions. An Integrated Approach to their Preparation and Characterisation,* Fendler, J. and Dékany, I. (eds), Kluwer, Dordrecht, 1996, p. 71.
5. Ph. Monnoyer, J. B. Nagy, V. Buschman, A. Fonseca, L. Jeunieau, P. Piedigrosso and G. Van Tendeloo, *Nanoparticles in Solids and Solutions. An Integrated Approach to their Preparation and Characterisation,* Fendler, J. and Dékany, I. (eds), Kluwer, Dordrecht, 1996, p. 505.
6. C. Cabos and P. Delord, *J. Appl. Crystallogr.* **12,** 502 (1979).
7. J. Rouvière, J. M. Couret, M. Lindheimer, J. L. Dejardin and R. Marrony, *J. Chem. Phys.* **76,** 3 (1979).
8. P. Ekwall, L. Mandell and K. Fontell, *J. Colloid Interf. Sci.* **33,** 215 (1970).
9. J. Moll, Forschunbericht 214: *Exciton-dynamics in J-aggregates of an Organic Dye,* Bundesanstalt für Materialforschung und Prüfung, Berlin, 1995.
10. T. Tani, T. Suzumoto, K. Kemnitz and K. Yoshihara, *J. Phys. Chem.* **96,** 2778 (1992).
11. A. Muenter, D. V. Brumbaugh, J. Apolito, L. A. Horn, F. C. Spano and S. Mukamel, *J. Phys. Chem.* **96,** 2783 (1992).
12. T. Tani, *J. Imag. Sci.* **34,** 143 (1990).
13. C. Ista, Bachelor Thesis, FUNDP, 1994.
14. A. Gourgue, PhD Thesis, FUNDP, 1981.
15. K. Kemnitz, K. Yoshihara and T. Tani, *J. Phys. Chem.* **94,** 3099 (1990).