REPRINTS
Spectral behaviour of eosin Y in different solvents and aqueous surfactant media

Moumita Chakraborty, Amiya Kumar Panda*

Department of Chemistry, University of North Bengal, Darjeeling 734013, West Bengal, India

A R T I C L E   I N F O

Article history:
Received 16 March 2011
Received in revised form 11 June 2011
Accepted 16 June 2011

Keywords:
Eosin Y
Cationic surfactants
Solvent polarity
Interaction constant
Stokes shift
Anisotropy

A B S T R A C T

Photophysical behaviour of the anionic xanthene dye, eosin Y (EY) was investigated in solvents of different polarities as well as in the presence of aqueous cationic surfactants. From the correlation between $E_I(30)$ and Kosower $Z$ values of EY in different solvents, subsequent parameters for EY were determined in the presence of surfactants. A red shift, both in the absorption and emission spectra of EY, was observed with decreasing solvent polarity. Dimersisation of EY was found to be dependent on solvent polarity. Cationic surfactants retarded the process of dimerisation, which were evident from the lower dimerisation constant ($K_d$) values, compared to that of in pure water. Dye–surfactant interaction constants were determined at different temperatures (298–318 K) and subsequently the thermodynamic parameters, viz., $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$ were evaluated using the interaction constant values. The fluorescence spectra of EY followed the same trend as in the absorption spectra, although with lesser extents. Stokes shifts were calculated and correlated with the polarity of the medium. Fluorescence of EY was initially quenched by the cationic surfactants in their pre-micellar region, which then followed a red shift with intensity enhancement. Fluorescence quenching was found to be of Stern–Volmer type where the excited state lifetime of EY remained unchanged in different surfactant media. However, the anisotropy value of EY was changed in the post micellar region of surfactants.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Surfactants have a tendency to accumulate at the air–liquid interface and thus they can change the properties of interface. In addition, because of their amphiphatic structures, they can congregate to form a stabilized entity, called micelle, after the attainment of critical micelle concentration (CMC) [1]. Among the different industrial applications, surfactants are used in dye industry as they can wet [2] and help in the dispersion of dyes, especially which are poorly soluble. Examples include industrial cleaners, cosmetics, plasticizers in cements and concretes, etc. [3,4]. Thus the study of dye–surfactant interaction is important from the fundamental understanding point of view as well as industrial applications. Photophysical studies of dyes in aqueous surfactant solution are also important to understand the mimicking bio-membranous interfaces [5]. According to Bhowmik and Ganguly [6], dye molecules form 1:1 charge transfer complex with oppositely charged surfactants. Surfactants are also used as solubilizers for water insoluble dyes, as disaggregating agent for dyes, which accelerates the adsorption of dye on fibres [7]. Besides, dye–surfactant interaction studies can effectively determine the critical micelle concentration of surfactants [8,9].

Eosin Y (EY) belongs to the xanthene group of dyes and studies on the interaction of surfactant with different xanthene dyes have been performed for a substantial period of time [5,10–12]. EY is a xanthene derivative and finds many applications, viz., in solvent polarity determination [10], lasers, CMC determination [9], the characterization of super conductors, etc. [13]. EY sensitized nanoparticles can produce hydrogen by photocatalytic decomposition of water [14]. Although several studies have been made involving dye–surfactant interactions, yet this particular field of research is still important for improvised dyeing process in terms of theoretical, technological, environmental as well as economic point of view [15]. According to Gökçüre and Tunaç [16], a dye molecule exhibits spectral changes in the presence of varying amount of surfactants consistently and there exist sequential equilibria between surfactant monomers, micelles, dye aggregates and pre-micellar dye–surfactant complex, etc. Solvents also play important role on the spectral and aggregation behaviour of dye molecules, which subsequently find many applications as described by De et al. [10]. Effect of solvent polarity on the aggregation behaviour of EY has been studied by De et al. [10], where a significantly high concentration of dye was used (as high as $10^{-3}$ M). However, practical applications, which count for economy, environmental issues and lesser usage of dye molecule, photophysical studies of EY in the dilute region, are believed to be more important. In addition to this, a systematic investigation on the photophysical behaviour of EY in a variety of solvents is also not common in literature. Photophys-
tical studies of EY in the presence of different surfactants are also not very common [5,10].

The present study deals with the photophysical behaviour of EY in solvents of different polarities and cationic surfactants. The endeavour was to undertake a physico-chemical investigation on the effects of different solvents (protic and aprotic) on EY. The solvents used were water, methanol, ethanol, n-propanol, n-butanol, n-pentanol, DMF and DMSO. Also, systematic studies on the interaction between EY and different cationic surfactants were undertaken with the variation of surfactant head group, chain length, as well as the number of hydrocarbon chains. The surfactants used were hexadecyltrimethylammonium bromide, hexadecylpyridinium chloride, didodecylmethylammonium bromide and didecylmethylammonium bromide. As the polarity of a solvent controls the photophysical characteristics of a dye at the molecular level, hence such studies are assumed to provide information involving the solvation capacity of the dye molecules and their aggregation behaviour. These parameters could directly be estimated using the Kosower Z values, dielectric constants and the refractive indices of the media. Effect of solvent polarity on the self-aggregation of dye molecules can also be estimated from such studies. Dye–surfactant interaction studies are believed to shed information on the polarity of the medium (governed by added surfactants), nature and extent of interactions between dye and surfactant molecules as well as the self-aggregation behaviour of dye in the presence of the surfactants.

2. Materials and methods

2.1. Materials

The anionic xanthene dye, 2-(2,4,5,7-tetra bromo-6-oxido-3-o xo-3H-xanthen-9-yl) benzoate, disodium salt (eosin Y, EY) was a product from Sigma–Aldrich, USA. The cationic surfactants, hexadecyltrimethylammonium bromide (CTAB, Aldrich, Germany), hexadecylpyridinium chloride (CPC, SRL, India), didodecylmethylammonium bromide (DDAB) and didecylmethylammonium bromide (DeDAB, Fluka, Switzerland) of >99% purity were used. Solvents used, viz., methanol (MeOH), ethanol (EtOH) and n-butanol (ButOH)/(SD Fine Chem. Ltd, India); n-propanol (ProOH)/(SRL, India); n-pentanol (PentOH) (Lobe Chemie Pvt. Ltd, India); dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) (E. Merck, India) were of HPLC grade. A.R. grade glycerol was a product from SRL, India. Water used in this study was deionised and doubly distilled.

2.2. Methods

A stock solution of 1.0 mM EY was prepared to perform the experimental works after proper dilution as per requirement. The visible absorption spectra were recorded on a UVD-2950 spectrophotometer (Labomed Inc., USA). Spectra were recorded in the range 400–600 nm using a matched pair of quartz cuvette of 1.0 cm path length. The fluorescence spectroscopic measurements were performed using a bench-top spectrofluorimeter (Quantamaster-40, Photon Technology International Inc., NJ, USA). Fluorescence data were recorded at controlled room temperature. The excitation wavelength for EY was set at 500 nm (λex) and the emission spectra were recorded in the range of 500–650 nm. Fluorescence anisotropy measurements were performed at an emission wavelength of 540 nm (λem). Steady state fluorescence anisotropy (r) was determined according to the expression:

\[ r = \frac{k_{VV} - G_k_{HH}}{k_{VV} + 2G_k_{HH}} \]  

where \( G = \frac{k_{VV}}{k_{HH}} \), \( k_{VV} \) corresponds to the intensity obtained when the excitation and the emission polarizers are oriented vertically. \( k_{HH} \) is the intensity obtained for vertical excitation polarizer and horizontal emission polarizer. \( k_{VV} \) and \( k_{HH} \) refer to similar parameters as above for the horizontal positions of the excitation polarizer [17].

Fluorescence lifetime measurements of EY were recorded with the same fluorimeter where a nano LED (Photon Technology International Inc.) of 505 nm wavelength was used to excite the dye. Fluorescence decays were obtained by Ströbe technique [18].

3. Results and discussion

3.1. Absorption spectra of EY

3.1.1. Effect of dye concentration on the absorption spectra of EY

Fig. 1A describes the visible absorption spectra of aqueous EY at different concentrations (2–20 μM). The aqueous solution of EY exhibits an intense band at 517 nm with a shoulder at 496 nm. The present observation was found to be comparable with previous reports [9,10]. The band at 517 nm corresponds to the monomeric form of EY while the shoulder at 496 nm is due to the dimeric form of EY. According to De et al. [10], EY dimerizes through the stacking of two monomers (Type A), alternately known as H-aggregates. With the increasing concentration of the dye in water, intensity of both the bands increased. However, the relative enhancement in the intensity of 496 nm shoulder was found to be higher than that of the 517 nm peak. Results clearly suggest that with increasing EY concentration in water the process of dimerisation through the stacking of monomers increases. Thus the ground state population of the dimeric form increases with increase in dye concentration [19–21]. As in the present study, the maximum concentration of dye in water was 20 μM, therefore, no higher aggregates, other than the dimers were expected [10]. The absorption spectra of EY were resolved using principal component analysis method, as detailed in different publications of Estelrich et al. [20,21] and De et al. [10]. Briefly, the spectra were fitted to two overlapping Gaussian

![Fig. 1](image-url)
curves with the help of Gaussian curve fitting, as shown in Fig. 1B. As already stated, the resolved spectra of EY in water comprise of two peaks. Therefore, it could be assumed that there exists equilibrium between the monomer (M) and the dimer (D) at a particular temperature. If we consider the following equilibrium (ignoring the existence of higher aggregates other than the dimer):

\[ 2M \leftrightarrow D \]  

then the equilibrium constant \((K_D)\) could be expressed as:

\[ K_D = \frac{C_D}{C_M} \]  

(3)

where \(C_D\) and \(C_M\) stand for molar concentration of dimeric and monomeric form of EY.

Thus, the total absorbance of EY at a particular wavelength \(A(\lambda)\) is contributory effect of both the monomeric and dimeric form of EY. Therefore one can make a following expression:

\[ A(\lambda) = \varepsilon_M(\lambda)C_M + \varepsilon_D(\lambda)C_D \]  

(4)

The term \(\varepsilon_M(\lambda)\) stands for the molar absorption co-efficient at a particular wavelength \(\lambda\). The ultimate solution for resultants of equation takes the following form as:

\[ A(\lambda) = \varepsilon_D(\lambda) \left( \frac{C}{2} - \frac{1 \pm \sqrt{1 + 8K_D C}}{8K_D} \varepsilon_M(\lambda) \right) \]

\[ + \varepsilon_M(\lambda) \left( \frac{1 \pm \sqrt{1 + 8K_D C}}{4K_D} \right) \]  

(5)

\(K_D\) can suitably be determined by the iterative method as described by Estelrich et al. [20]. If one plots the molar absorbance, \(A(\lambda)\), as a function of dye concentration \(C\) at any wavelength, one can determine the molar absorptivity of monomer, \(\varepsilon_M(\lambda)\), dimer, \(\varepsilon_D(\lambda)\) and the dimerisation constant, \(K_D\). The non-linear least square regression analysis of the above equation was done using Microsoft Excel (Solver) program. Initially, some hypothetical value of \(\varepsilon_M(\lambda)\) and \(\varepsilon_D(\lambda)\) were provided to the solver. The molar absorptivity of the lowest concentration of the dye was approximated for the monomeric form while that of the dimeric form was considered as highest concentration. The iterative method of MS Excel (Solver) program minimises all the values and hence \(K_D\) can be determined. \(K_D\) value of aqueous EY in the studied concentration range \((2–20 \mu M)\) was found to be \(9.7 \times 10^7\) M\(^{-1}\). The present result for the \(K_D\) value was found to be higher than that reported by De et al. [10] \((3.0 \times 10^4\) M\(^{-1}\)). In their study, the concentration range of EY was much higher than the present concentration range, where the probability of higher aggregate formation was less than the reported systems of De et al. [10].

3.1.2. Effect of solvent polarity

Solvent polarity plays a great role on the spectral behaviour of a dye molecule. Therefore, by suitably analysing the spectral behaviour of a dye molecule, a solvent can be characterised in terms of its polarity and solvation power. Spectra of EY were recorded in a number of solvents of different polarities. Two categories of solvents were used, viz., protic (water, methanol, ethanol, n-propanol, n-butanol and n-pentanol) and aprotic (DMF and DMSO). It may be mentioned that due to its ionic nature, EY was insoluble in solvents like n-alkanes, cyclo-alkanes, chloroform, carbon tetrachloride, etc. The absorption maximum (\(\lambda_{abs, max}\)) of EY was shifted to higher wavelength (red shift) with the decrease in solvent polarity. The \(\lambda_{abs, max}\) for EY followed the order: water < methanol < ethanol < n-propanol ≈ n-butanol ≈ n-pentanol < DMSO < DMF. Spectra of EY in different solvents have also been shown in Fig. 1C.

![Graph](Image)

Fig. 2. Kosower \(Z\) vs. \(E_T(30)\) profile for 10 μM EY in (A) solvents of different polarities and (B) surfactants at 298 K. Solvents and surfactants are mentioned inside the figure.

The solvent polarity parameter, \(E_T(30)\), of EY was evaluated using the following formula [23,24]:

\[ E_T(30) = \frac{28591}{\lambda_{abs, max}} \]  

(6)

Another parameter called Kosower \(Z\) value is also used as standard of solvent polarity [25], which are readily available in the literature. It was found that the Kosower \(Z\) value decreases linearly with the decrease in solvent polarity as shown in Fig. 2A. \(E_T(30)\) values of EY in the presence of different surfactants were also calculated using Eq. (6) (spectral behaviour of EY in the presence of surfactants will be discussed later). A good linear co-relation between the Kosower \(Z\) and \(E_T(30)\) values for EY and different surfactants were also observed as shown in Fig. 2B. Table 1 summarises the results of the spectral analyses of EY in different solvents and aqueous surfactant solutions.

While considering the process of dimerisation (the method of \(K_D\) determination has previously been described in detail), it was found that the \(K_D\) value decreased with the decrease in solvent polarity. This was as predicted. It is expected that with the decrease in solvent polarity the process of dimerisation (formation of H-aggregates) will be hindered. As surfactant in water also lead to the decrease in polarity, hence the \(K_D\) value of EY in surfactant medium should decrease compared to the \(K_D\) value in pure water. Besides, Coulombic interaction of EY with oppositely charged surfactant retards the process of dimerisation. Analysis of Table 1 reveals that the dimerisation constant of EY was almost the same in water and
methanol. Proti c solvents favoured the process of dimerisation than the aprotic solvents. The trend leads to the conclusion that the dielectric constant of the medium plays an important role in dye aggregation. Thus, hydrophobic interaction of dye molecules will be strong enough to overcome the electrostatic repulsion between the anions. Also, the –OH group present in water and alcohols promote aggregation, as hydrogen bonding plays an important role which is revealed by near similarity of K0 values for water, methanol and ethanol.

3.1.3. Effect of surfactants

Fig. 3 describes the effect of the surfactants (CTAB, CPC and DDAB) on the absorption spectra of 10 μM EY in water. The intensity of EY absorption decreased and subsequently the absorption maximum of EY was also shifted to higher wavelengths with the progressive addition of cationic surfactants. After a certain concentration of the surfactant was attained, there was no shift in the peak position (except didodecylmethylammonium bromide). However, there was increase in the absorbance value which eventually attained maximum. Such spectral shift in the presence of surfactants is not uncommon [5,10] in the presence of CTAB, CPC and DDAB, the absorption maxima were red shifted to 528, 531 and 536 nm respectively (for pure EY in water the value was at 517 nm), indicating electrostatic interaction between EY and oppositely charged cationic surfactants [6,22]. Between CTAB and CPC, CPC exhibited stronger interaction with EY, as it required lesser amount to cause significant spectral change. Both CPC and CTAB have similar hydrocarbon chain length, but the hydrophilic–lipophilic balance (HLB) value of CPC being higher [26,27], its hydrophilic interaction (which was prevalent electrostatic in nature) with the dye is higher. A surfactant having higher HLB value implies its stronger affinity towards water and vice versa. Besides, the presence of a planar pyridinium ring favours better stacking of the dye with CPC. A significant spectral change was also observed in case of the doubled tailed surfactant, DDAB. In fact, the hydrophobic interaction is definitely higher in case of DDAB compared to the other single tailed surfactants. Also, vesicle formation could play some role in this case [28–30]. Similar were the observations for DeDB (spectra not shown). The spectral data with a fixed concentration of EY and varying concentrations of the cationic surfactants (CTAB, CPC, DDAB and DeDB) have been utilized to calculate the binding constant (K0) of the dye with the surfactants using Rose and Drago’s absolute method [31]:

\[
\frac{(C_0-C_S)}{(A-A_0)} = \frac{1}{[K_0-L(\varepsilon_{Ds}-\varepsilon_D)]} + \frac{C_S}{[L(\varepsilon_{Ds}-\varepsilon_D)]} \tag{7}
\]

where C0 is the initial concentration of the dye, C_S is the initial concentration of the surfactant, A0 is the absorbance of the pure dye solution at λmax, A is the absorbance of the dye–surfactant solution at λmax, K0 is the binding constant of the dye with surfactant, εD is the molar absorption coefficient of the dye, εDS is the molar absorption coefficient of the dye–surfactant complex, and L is the optical path length of the solution. The values of (C0,C_S)/(A−A0) were plotted against C_S and a straight line was constructed (figure not shown to save space). From the slope and intercept of the linear plots, the binding constant, K0 was calculated. The K0 values for the surfactants were calculated at five different temperatures (298,
Table 2
Thermodynamic parameters for the interaction of EY with different surfactants.

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>T/K</th>
<th>$K_b \times 10^9$M$^{-1}$</th>
<th>$\langle -\Delta G^\circ \rangle$[kJ mol$^{-1}$]</th>
<th>$\Delta H^\circ$[kJ mol$^{-1}$]</th>
<th>$\Delta S^\circ$[J K$^{-1}$ mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB</td>
<td>298</td>
<td>4.62</td>
<td>26.69</td>
<td>-16.38</td>
<td>34.62</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>3.67</td>
<td>26.56</td>
<td>-35.28</td>
<td>-28.77</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>2.94</td>
<td>26.41</td>
<td>-54.49</td>
<td>91.12</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>1.94</td>
<td>25.77</td>
<td>-74.02</td>
<td>-154.16</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>1.15</td>
<td>24.80</td>
<td>-93.87</td>
<td>-217.19</td>
</tr>
<tr>
<td>CPC</td>
<td>298</td>
<td>13.52</td>
<td>29.36</td>
<td>-78.54</td>
<td>-165.03</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>7.16</td>
<td>28.25</td>
<td>-63.74</td>
<td>-117.12</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>6.69</td>
<td>28.54</td>
<td>-89.09</td>
<td>-65.41</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>3.99</td>
<td>27.65</td>
<td>-33.39</td>
<td>-18.33</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>3.83</td>
<td>27.99</td>
<td>-17.85</td>
<td>31.90</td>
</tr>
<tr>
<td>DDAB</td>
<td>298</td>
<td>6.75</td>
<td>27.06</td>
<td>-37.08</td>
<td>-31.70</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>5.70</td>
<td>27.67</td>
<td>-11.30</td>
<td>54.03</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>4.57</td>
<td>27.56</td>
<td>14.01</td>
<td>137.90</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>8.73</td>
<td>29.70</td>
<td>41.55</td>
<td>227.64</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>8.53</td>
<td>30.11</td>
<td>68.62</td>
<td>310.48</td>
</tr>
<tr>
<td>DeDAB</td>
<td>298</td>
<td>2.35</td>
<td>25.02</td>
<td>-53.48</td>
<td>-95.53</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>1.68</td>
<td>24.59</td>
<td>-35.87</td>
<td>-37.21</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>1.48</td>
<td>24.67</td>
<td>-17.96</td>
<td>21.79</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>1.38</td>
<td>24.88</td>
<td>0.02</td>
<td>80.27</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>1.45</td>
<td>25.41</td>
<td>18.74</td>
<td>138.86</td>
</tr>
</tbody>
</table>

10μM EY was used for study.

303, 308, 313 and 318K). From the $K_b$ values, the thermodynamic parameters like the standard Gibbs free energy change ($\Delta G^\circ$), the standard enthalpy change ($\Delta H^\circ$) and the standard entropy change ($\Delta S^\circ$) for the dye–surfactant complex formation were determined using standard thermodynamic expressions [32]:

$$\Delta G^\circ = -RT \ln K_b$$  \hspace{1cm} (8)

Changes in the standard enthalpy, $\Delta H^\circ$, were evaluated by the van’t Hoff equation:

$$\frac{\partial (\Delta G^\circ)}{\partial (1/T)} = \Delta H^\circ$$  \hspace{1cm} (9)

In the present study, $\Delta G^\circ$ vs. $T$ profile was found to follow a 2$^\text{nd}$ polynomial equation as [33]:

$$\Delta G^\circ = a + bT + cT^2$$  \hspace{1cm} (10)

where $a$, $b$ and $c$ are the polynomial coefficients.

The polynomial coefficients thus helped in determining the $\Delta H^\circ$ values described in the following expression:

$$\left[ \frac{d(\Delta G^\circ)}{d(1/T)} \right] = a - cT^2 = \Delta H^\circ$$  \hspace{1cm} (11)

The standard entropy change ($\Delta S^\circ$) for the dye–surfactant complex formation was then evaluated according to the following expression:

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$  \hspace{1cm} (12)

Thermodynamic parameters for the formation of the dye–surfactant complexes have been summarised in Table 2. Analysis of the table reveals that with the increase in the temperature, the binding constant ($K_b$) values decrease, revealing the binding process to be exothermic in nature. Negative $\Delta H^\circ$ values also support this, although few exceptions were observed in case of DDAB and DeDAB at higher temperatures. $\Delta G^\circ$ values reveal that the spontaneity of the dye–surfactant binding process is maximum at 298 K in case of single tailed surfactants. Also, the higher values of free energy change indicate the dye–surfactant interaction process to be governed both by electrostatic and hydrophobic forces [5,6,22].

3.2. Fluorescence spectral studies

3.2.1. Effect of dye concentration

When excited at 500 nm, an aqueous solution of 2 μM EY emits maximum radiation at 535 nm ($\lambda_{\text{max}}$). Unlike the absorption spectra EY did not exhibit any significant shoulder in its emission spectra. Fig. 4A reveals that with the increasing EY concentration in water, the fluorescence intensity was enhanced and the $\lambda_{\text{max}}$ was progressively shifted to higher wavelengths up to 545 nm. However, in case of absorption spectra no spectral shift occurred with increasing dye concentration. The enhancement in the fluorescence intensity (F.I.) with increasing dye concentration and the absence of any significant dimeric band in the emission spectra proves that the excited state is predominantly populated with the monomeric form of EY and therefore, excited state aggregation is not permitted. In the case of absorption spectra, absorbance vs. concentration profile for EY at $\lambda_{\text{abs}}$ was linear. But in aqueous medium, F.I. vs. [EY] plot was linear up to 10 μM, beyond which a negative deviation from linearity was noted in all the cases. Such phenomenon was probably due to the self quenching of the dye molecules.

3.2.2. Effect of solvent and surfactant on the emission spectra of EY

Emission spectral shift in different solvents followed the same sequence as in the absorption spectra. Emission spectra of EY in different solvents have been present in Fig. 4B.

Stokes shift ($\Delta \lambda = \lambda_2 - \lambda_1$, where $\lambda_2$ and $\lambda_1$ are the frequencies of the corresponding absorption and fluorescence maximum respectively) for EY in different environments was also evaluated using the standard procedure [34–36]. In the present case, Stokes shift has been found to increase with increasing solvent polarity. Results are summarised in Table 1 along with other spectral data. In case of alcohols, behaviour of n-propanol, n-butanol and n-pentanol did not follow the generalization. Stokes shift value decreased for methanol, compared to water, which also decreased further in case of ethanol. In case of n-propanol, the value was increased. The value did not change systematically among n-propanol, n-butanol and n-pentanol. The results indicate that the increasing hydrophobicity of the higher alcohols could not significantly and systematically control the spectral shift of EY. The anomalous behaviour in the presence of higher alcohols could also be due to the limited solubility. However further studies are warranted to make a final conclusion in this regard. Increase in Stokes shift with increas-
ing solvent polarity indicates stronger solvation of EY. EY, being ionized, is expected to be better solvated with a solvent of higher polarity (exceptions being n-propanol and DMF). Results also suggest that excited state dipole moment was increased in solvents of higher polarity. Larger magnitudes of Stokes shift also indicate the difference between the excited state and the ground state geometry [36].

Similar to the absorption spectroscopic studies, effect of cationic surfactants on the fluorescence spectra of 10 μM EY were also undertaken. Results are graphically presented in Fig. 5 for CTAB, CPC and DDAB. Unlike the absorption spectra, the emission spectral shift was less induced by cationic surfactants. Emission maximum of EY was only significantly shifted above the critical micelle concentration of all the four surfactants. Surfactants quenched the fluorescence of EY in their pre-micellar region. The cationic surfactants could bind to the anionic dye by way of electrostatic interaction, which finally led to the decrease in fluorescence. Quenching was found to be of Stern–Volmer type, assuming that the fluorescence quenching of EY is due to the formation of the excited state complex with the oppositely charged surfactants. Stern–Volmer constant (the interaction constant between dye and surfactant in the excited state) has been calculated using standard method [10] and also the relation $K_{SV} = k_q \tau_0$ ($k_q =$ quenching constant and $\tau_0 =$ lifetime of the fluorophore), was found to be valid for all the four studied surfactants. As, $\tau_0$ did not significantly change within the studied concentration range for a particular surfactant, hence the product of $k_q$ and $\tau_0$ remained constant, i.e., $K_{SV}$ could easily be calculated from the slope of $F_0/F$ vs. [Q] plot. Stern–Volmer plot for CTAB and DDAB have been shown in Fig. 6 as representative. Related results for all the surfactants are summarised in Table 3. Although the excited state lifetime did not change significantly among the four different surfactants, however, the dynamic quenching constants ($k_q$) varied among the surfactants significantly. For CPC, the value was higher than that of CTAB. Due to the presence of pyridinium ring in CPC there occurred better stacking of EY over CPC, which was not so favourable in case of CTAB. For the double tailed surfactants, the values of $k_q$ were found to be lower even than CTAB. Results indicate retarded interaction between the surfactant head group and EY. Presence of two hydrocarbon tails may hinder the surfactants to be in the proximity of EY. It, therefore, could clearly be concluded that the excited state

### Table 3

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>$10^{-3} \times K_{SV}$ /M$^{-1}$</th>
<th>$\tau_0$/ns</th>
<th>$10^{-13} \times k_q$/(M$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB</td>
<td>8.81</td>
<td>2.50</td>
<td>3.52</td>
</tr>
<tr>
<td>CPC</td>
<td>9.41</td>
<td>2.52</td>
<td>3.73</td>
</tr>
<tr>
<td>DDAB</td>
<td>4.68</td>
<td>2.60</td>
<td>1.80</td>
</tr>
<tr>
<td>DeDDAB</td>
<td>4.85</td>
<td>2.54</td>
<td>1.90</td>
</tr>
</tbody>
</table>

10 μM EY was used for study. $\lambda_{ex} = 500$ nm. $\lambda_{em} = 540$ nm.
interaction between dye and oppositely charged surfactants were governed by Coulombic interactions [6,37].

3.2.3. Fluorescence lifetime measurements

Time-resolved fluorescence studies were carried out to determine the emission decay parameters for EY in different solvents and surfactants. 10 μM EY exhibited a lifetime 2.50 ns. The lifetime did not change significantly with the variation of solvent polarity and surfactant concentration. Similar results were observed by other researchers [10]. The fluorescence decay curve of EY was found to be single exponential in water and in the presence of all the surfactants used (as shown in Fig. 7).

3.2.4. Steady-state fluorescence anisotropy

Fluorescence anisotropy provides important information about the micro-viscosity of the medium around a fluorescent dye molecule [38,39]. When a dye molecule binds to oppositely charged micelle, the micro-viscosity of the dye–micelle interface gets significantly changed [40]. Variation of fluorescence anisotropy with the surfactant concentration has been shown in Fig. 8. Pure EY in water has an anisotropy value of 0.057. A mild increase in the anisotropy value was observed in aqueous salt solution (0.057 in water to 0.067 in 1.0 mM NaCl solution). The increase in the fluorescence anisotropy with increasing salt concentration was a direct consequence of viscosity enhancement of aqueous salt solution. Among the different alcohols, anisotropy increased with increasing alcohol chain length (data not shown). DMF and DMSO exhibited similar behaviour as that of water. Surfactants could significantly alter the anisotropy value of EY in water. A significant increase in the fluorescence anisotropy of EY was noted in the post-micellar region. Hence, one could employ the anisotropy measurement technique as a tool to determine the critical micellar concentration of surfactant. As already been mentioned that there is a direct correlation between the fluorescence anisotropy and viscosity of the medium [17,40], therefore, one needs to correlate the anisotropy with viscosity. In the inset of Fig. 8, anisotropy dependence of EY on glycerol concentration in water has been shown as reference. It is believed that EY could electrostatically bind at the micellar interface, which restricts the segmental motion of the dye molecule. Hence, the micro viscosity around dye–micelle interface becomes significant than the viscosity when the dye just binds electrostatically to a surfactant in its pre-micellar region.

4. Summary and conclusions

Absorption and emission spectral behaviour of the anionic xanthene dye, EY was investigated in the solvents of different polarities as well as in different aqueous cationic surfactant solution. By suitably analysing the spectral data of EY in the presence of surfactants in their pre-micellar region, dye–surfactant interaction constant values were determined both in the ground and excited states. Stokes shifts were calculated and correlated with the polarity of the medium. Steady state fluorescence anisotropy values were evaluated in the pre- and post-micellar regions of surfactants in aqueous medium. A significant change in the anisotropy values was observed for EY.

Based on the experimental results the following conclusions could be drawn:

(1) The ground state is predominantly populated with the dimeric form of EY as revealed from the absorption spectra. On the contrary, emission spectra of EY prove that the excited state is predominantly populated with the monomeric form of EY and hence excited state aggregation is not permitted.
References

Effect of colloidal silica on the spectral behaviour of 7-hydroxycoumarin in aqueous medium

Moumita Chakraborty, Soumik Bardhan, Swapan K. Saha, Amiya K. Panda

Department of Chemistry, University of North Bengal, Darjeeling 734 013, West Bengal, India

Highlights

- Imperfections in colloidal silica were incorporated by thermal heating.
- Interaction of silica and 7HC was studied by absorption, emission and FTIR spectroscopy.
- Mechanism on the effect of H-bonding on excited state energy transfer process was rationalized.

Abstract

Absorption and emission spectroscopic studies, in combination with FTIR measurements, were carried out for 7-hydroxycoumarin (7HC) and nanocolloidal dispersion of silica. Attempt has been made to identify the characteristics of excited state H-bond formed between colloidal silica and 7HC in aqueous medium. Both the absorption and emission spectra of 7HC was found to be dependent on the concentration of silica. At lower silica concentrations, the absorption spectra decreases with increasing silica concentration, on the other hand, at higher concentration a bathochromic shift occurs in the absorption spectra of 7HC. Fluorescence behaviour followed the opposite trend in comparison to the absorption spectra. It is proposed that at lower silica concentration, excited state H-bond was formed between 7HC and silica dispersions. At higher concentration, the decrease in fluorescence intensity is attributed to the self-quenching of adsorbed dye molecules over silica surface following the mechanism of Homo Förster resonance energy transfer (HFRET). Results were correlated with the size and surface charge of colloidal silica as measured by dynamic light scattering and zeta potential studies.

Introduction

Semiconductor nanoparticles have gained importance for their multifarious applications as they possess favourable optical properties, viz., high quantum yield, enhanced photostability, capability of cell imaging [1], etc. Among different semiconductor nanocrystals, silica has got special importance because it can be used in different forms for solute pre-concentration and immobilization of analytical reagents [2]. Besides, silica has got special attention for other specific properties like optical transparency [3], high hydrophilicity [4] and negative surface charge in aqueous media [5].

Keywords:
- Ludox®
- 7-Hydroxycoumarin
- Excited state hydrogen bonding
- HFRET
into various functionalities because of the presence of active –OH groups which make silica suitable for different purposes as mentioned above. Traditional organic fluorophores are usually photosensitive which could be overcome by conjugating with silica nanoparticles [9]. However, the process of conjugation between an organic dye and silica nanoparticles is not straightforward. While silica is highly hydrophilic, organic dyes are usually hydrophobic, which makes the aggregation process less favourable. There are several reports on the synthesis and characterization of silica coated fluorescent nanoparticles [6,10]. Although, fluorescent/dye-sensitized doped/fluorescent conjugated silica nanoparticles have several advantages, however, such systems suffer some limitations which are strongly dependent on their size and concentration [7]. According to Ha et al. [11] and Bringley [12] in some cases, fluorescence could even be quenched, compared to the free dye molecules. Therefore, a detailed spectral investigation on the absorption and fluorescence spectra of dye-silica aggregates are warranted for better technological applications as well as from the fundamental understanding point of view. Towards this initiative we have undertaken the spectroscopic investigations on colloidal silica–7HC aggregates in a wide concentration range of silica. In addition to the aforementioned point of interest, it is believed that physicochemical studies on dye–colloidal aggregates would have been equally important in the field of waste water treatment [13], lasing property [14], dye–sensitized solar cells [15], photocatalytic reactions [16], etc. Ludox® is commercially available spherical shaped silica particles suspended in aqueous medium which find different applications [17–22]. Therefore, colloidal silica in the form of Ludox® can be considered as an appropriate model system in investigating its capability to alter (both enhancement and quenching) the absorbance and fluorescence intensity of fluorophores in aqueous medium. The dye 7-hydroxychromen-2-one (7-hydroxycoumarin, 7HC), commonly known as “Umelliferone”, is a natural product of the coumarin family [23]. It is known to have antioxidant properties [24,25]. The ultraviolet activity of 7-hydroxycoumarin led to its use as a sunscreen agent and an optical brightener for textiles [26–29]. It is used as laser dyes and also as fluorescent indicator [27,30]. Although several reports are available in the literature which include the interaction between silica and a number of dyes [8,31–36], however, reports involving the interaction of Ludox® with 7-hydroxycoumarin are not common in literature. The occurrence of excited state H-bonding between silica and 7-hydroxycoumarin is supposed to be understood in a better way through fluorescence spectroscopic analysis, which could further be investigated via FTIR measurements.

The present study aimed at understanding the extent of interaction between 7-hydroxycoumarin and Ludox® (commercial form colloidal silica) through absorption and fluorescence spectroscopy, fluorescence lifetime and FTIR studies. Finally, size and zeta potential measurements using dynamic light scattering technique were carried out in order to understand the stacking behaviour of dye molecules over the silica surface.

Experimental

Materials

The dye, 7-hydroxychromen-2-one (7-hydroxycoumarin, 7HC), was a product from Chem Service, West Chester, USA (99% pure) and was used as received. Colloidal dispersion of silica (Ludox AM-30 colloidal silica, 30 wt.% suspension in water) was procured from M/S Sigma Aldrich, USA. HPLC grade acetonitrile from E. Merck, Germany was used for FTIR measurements. Double distilled water with a conductance of 2–4 μS/cm was used in preparing the solutions.

Methods

A stock solution of 7HC (1.0 mM) was prepared as described elsewhere [37] using double distilled water. This stock solution was diluted within the range 1–20 μM. Thirty weight percent of the supplied Ludox® solution was diluted to 10 wt.% which was used as the stock solution. This stock solution was heated at 80 °C for 2 h. The heating is supposed to cause defects/imperfections in the microcrystalline silica particles as reported by Banerjee et al. [38]. This solution was then diluted to required concentrations. This preheated colloidal suspension was used throughout all the experiments unless specifically mentioned. Henceforth, colloidal silica means silica microcrystalline suspensions comprising imperfections/defects.

DLS and zeta potential measurements of Ludox®, the dye (7HC) and the dye–Ludox® system were carried out by a Nano ZS 90 (Malvern, UK). A He–Ne laser of 632.8 nm wavelength was used and the data were recorded at a scattering angle of 90°. Steady state electronic absorption spectra were recorded on a UVD-2950 spectrophotometer (Labomed Inc., USA). Spectra were recorded within the range 200–400 nm using a matched pair of quartz cuvette of 1 cm path length, while the steady state fluorescence spectra were recorded in a bench-top spectrofluorometer (Quantamaster–40, Photon Technology International Inc., NJ, USA). The dye, in the presence and absence of Ludox®, was excited at 375 nm while the emission spectra were recorded in the range 400–600 nm. Fluorescence lifetime of the dye in the absence and presence of Ludox® was recorded at 450 nm using 310 nano LED as the light source. The fluorescence decay was found to be single exponential in nature and the χ² value was found to be greater than 1.0.

FTIR absorption spectra were recorded in the range of 400–4000 cm⁻¹ with a Shimadzu 83000 spectrometer (Japan) using a CaF₂–IR crystal window (Sigma–Aldrich) equipped with presslock holder with 100 number scans and spectral resolution of 4 cm⁻¹. All the measurements were carried out at ambient but controlled temperature.

Results and discussion

Characterization of Ludox® in the absence and presence of 7HC

Dynamic light scattering (DLS) and zeta potential measurements

Pure Ludox® within the range 0.004–0.02 wt.% exhibited an average particle size of 27 nm as obtained by dynamic light scattering measurement. Effect of heating was insignificant on the size of Ludox suspension. The size variation in the presence of 7HC was found to be insignificant. Zeta potential measurements were carried out to understand the electrostatic interactions between 7HC and Ludox® in aqueous medium. If there occurs such an electrostatic interaction, it is expected that the zeta potential of Ludox® would change with the addition of 7HC. Pure silica exhibited an average zeta potential of –35 mV in aqueous medium in absence of 7HC. Ludox suspension, without heating possesses a lower zeta potential value (–14 mV) compared to the thermally treated Ludox suspension. The increase in negative zeta potential value was due to the formation of defects which led to the generation of electron rich centres [39]. However, when Ludox® was added progressively to 10 μM 7HC, a variation in the zeta potential was noted as summarized in Table 1. At lower concentration (within 0.004–0.02 wt.%) with the progressive addition of Ludox® to the dye, initially the zeta potential value was found to be –23 mV, which eventually attained the value for pure Ludox®. When Ludox® is heated above 80 °C it leads to the formation of defects, which are rich in electrons. These point defects are capable of forming H-bonds with 7HC. Thus 7HC, through the process of adsorption on the defective sites, can delocalize the electron density on Ludox®.
is due to the oxygen free radical present in defective SiO
range up to 2 wt.% exhibited an absorption peak at 205 nm which
range. No spectral shifts were also recorded, confirming the ab-
This linear increment in the absorption and emission spectra re-
This linear increment in the absorption and emission spectra re-

The present study on the interaction of Ludox® within the range 2–
Upon increasing the concentration of the dye, both absorption and emission intensities increased line-
early in the studied concentration range. The molar absorption co-
efficient of 7HC at 324 nm was found to be 1.035 × 10⁴ M⁻¹ cm⁻¹. This linear increment in the absorption and emission spectra re-

While considering the spectral behaviour of Ludox® it is noted that the absorption and emission spectra are featureless for Ludox®
up to 0.02 wt.% in water. However, Ludox® at higher concentration range up to 2 wt.% exhibited an absorption peak at 205 nm which
is due to the oxygen free radical present in defective SiO₂ moiety. Above this concentration the absorption spectra of Ludox® became noisy with progressive red shifts (spectra not shown). This was due to the scattering of aggregated silica at higher concentration range. Effect of Ludox® on the spectral behaviour of 7HC is shown
Fig. 2. The present study on the interaction of Ludox® and 7HC
are divided into two parts: (a) lower concentration range, i.e.,

0–0.02 wt.% of silica and (b) higher concentration range, i.e.,
0.02–9.00 wt.% of silica. In the dilute range of Ludox®, the spectra
of pure Ludox® were featureless. However, on the progressive
addition of Ludox® to 10 μM 7HC solution, absorbance of 7HC is
suppressed. Absorbance at 324 nm, characteristic of 7HC, de-
creased linearly with Ludox® concentration (Fig. 2A). The linearity
is not observed when the Ludox® concentration exceeds the con-
centration of 0.02 wt.. The systematic linear decrease at 324 nm
on progressive addition of Ludox® at lower concentration range
was due to uniform adsorption of 7HC over the colloidal Ludox®
surface whereby monolayer of dye molecules were formed [40].
The noisy and non-systematic decrease in the absorption spectra
of 7HC in the presence of higher amount (<0.02 wt.%) of Ludox®
was due to the irregular adsorption of the dye over Ludox®
surface. While considering the absorption spectra in the higher concentra-
tion range (Fig. 2B), the spectra of 7HC was red shifted to 360 nm
due to the irregular stacking of dye molecules over the silica sur-
face whereby fine precipitates were found to settle down at the
bottom of the vial, visible through naked eye. The complete
adsorption of 7HC leads to the featureless spectra and the forma-
tion of precipitates. In Fig. 2B, the same spectra of 7HC (spectrum
7), as shown in Fig. 2A (spectrum 1), has also been presented for
comparison. Due to the large difference in the absorbance values
for two different systems (for panel A the absorbance scale is 0–
0.17 while for panel B it is 0–3.25), the spectra of 7HC (as shown
in panel B) appears insignificant compared to that of Ludox® at
higher concentration. A 2 wt.% silica, when excited at 375 nm, emits at 430 nm. Another shoulder appeared at 450 nm (Fig. 3).
Again, at higher concentration the spectra became noisy which is
due to the irregular scattering of the colloidal aggregates. Contrary
to the absorption spectra of silica-dye system in the low concen-
tration range, the fluorescence intensity (F.I.) of 7HC increased line-
arily with the increasing Ludox®-dye system in the low concentra-
tion range, the fluorescence intensity (F.I.) of 7HC increased line-
arily with the increasing Ludox®-dye system in the low concentr-
tion range. The significant enhancement in the F.I. of 7HC increased line-
arily with the increasing Ludox®-dye system in the low concentr-
tion range of Ludox® was due to the excited state H-bonding be-

tween the defects incorporated into silica nanoparticle (resulted by
heating) and the OH group of 7HC as shown in Scheme 1 [41]. The
formation of H-bond was further established by FTIR measurements
(to be discussed and shown in the subsequent section). The non-linear decrease in the F.I. of 7HC at higher concentration
range was due to the irregular adsorption and subsequent precip-
itation of 7HC over the Ludox® surface. According to Chen et al. [7],
the quenching mechanism was due to the involvement of non-radiative processes. When the fluorophores are closely packed within the solid matrix of Ludox, the intermolecular energy transfer process becomes more favourable. In the present study, a fast Homo Förster resonance energy transfer (HFRET) among the fluorophores (herein 7HC) become significant, which eventually lead to self quenching process \([42,43]\). The process becomes remarkable when no prominent Stokes shift occur for the fluorophores in the absence and presence of silica \([44]\). The change in fluorescence of a dye molecule in close proximity to a second molecule is attributed to Förster resonance energy transfer (FRET). FRET is a mechanism which describes energy transfer between two chromophores, one in the excited state and the other in its ground state \([45]\). When the transfer of energy occurs between two identical molecules the phenomenon is known as Homo Förster resonance energy transfer (HFRET) \([42,43]\). In the present study, at higher Ludox concentration, the dye molecules are very rigidly bound around the silica surface for which there are possibilities of energy transfer from an excited dye molecule to another dye molecule in the ground state. It is to be mentioned that the lifetime of 7HC (5.35 ns) was not significantly changed in presence of Ludox. The Stern–Volmer quenching phenomena help in understanding the kinetics of a photophysical intermolecular deactivation process. Stern–Volmer quenching process is usually valid for the systems where the lifetime of a probe does not change significantly in the presence of quencher \([46]\). However, in the present case, the decrease in the F.I. with added Ludox did not follow Stern–Volmer equation \([46]\):

Fig. 2. Absorption spectra 10 μM 7HC in the presence of varying amount of Ludox at 298 K. Ludox was used in the two different concentration (wt.%) ranges. (A) 1, 0; 2, 0.004; 3, 0.008; 4, 0.012; 5, 0.016 and 6, 0.02. In panel (B) spectra of 7HC is shown in the presence of 7, 0.0; 8, 2; and 9, 3 wt.% of Ludox. Note the differences in the units of absorbance axis in two panels.

Fig. 3. Emission spectra of 2 wt.% colloidal silica in water. Temperature: 298 K; \(\lambda_{ex} = 375\) nm.

Fig. 4. Emission spectra of 10 μM 7HC in the presence of (A) lower wt.% (1, 0; 2, 0.004; 3, 0.008; 4, 0.012; 5, 0.016 and 6, 0.02) and (B) higher wt.% (2, 3, 4, 5, 6, 7, 8 and 9 wt.%) of Ludox at 298 K. Note: in the lower concentration range of Ludox, fluorescence of 7HC increased (Panel A) while the fluorescence of 7HC was quenched in the presence of higher amount of Ludox (Panel B).
\[
\frac{F_0}{F} = 1 + K_{sv}[Q]
\]

where, \(F_0\) and \(F\) are the fluorescence intensities of 7HC in the absence and presence of quencher, \(Q\); \([Q] = \text{Quencher concentration}\). Had there been a quenching of 7HC by Ludox\(\text{C}_{210}\), the plot of \(F_0/F\) vs \([Q]\) would be a straight line, which was not observed in the present case.

**Infrared spectroscopic study**

The IR spectral band of water in the OH stretching frequency region (\(\sim 3100\) to \(3750\) cm\(^{-1}\)) is usually very broad and structureless due to the continuum water structures with varying hydrogen bond strength. Anticipating that neat water, therefore, may not provide precise information of the dynamics of water via conventional IR spectroscopy, dilute water is employed for measurement in the present study. Assuming the concentration of neat water to be 55.5 M, sufficient amount of CH\(\text{C}_{3}\)CN was added to water to make it 1.0 M because under this condition, water molecules are mostly solvated by CH\(\text{C}_{3}\)CN and no water aggregates (even low order aggregates) are present [47]. Fig. 5 shows the IR spectra of 7HC (1.0 M) and water (1.0 M) in CH\(\text{C}_{3}\)CN on CaF\(_2\) plates. The peaks corresponding to the vibration of OH symmetric stretching of the weakly hydrogen bonded (3542 cm\(^{-1}\)) and nonbonded (3627 cm\(^{-1}\)) species of 7HC with CH\(\text{C}_{3}\)CN are resolved. These peaks are exactly superimposed on the peaks of dilute water (1.0 M) in CH\(\text{C}_{3}\)CN as observed previously (not shown here) [47]. On the other hand, Ludox\(\text{C}_{x}\) in dilute water yields a broad OH stretching band at 3602 cm\(^{-1}\). The IR spectra of the mixture of 7HC (1.0 M), water (1.0 M) and SiO\(_2\) (1.0 M) in CH\(\text{C}_{3}\)CN is interesting. For the quantitative evaluation,

**Fig. 5.** (a) IR spectra of 7-HC (1.0 M) and H\(_2\)O (1.0 M) in acetonitrile, (b) IR spectra of SiO\(_2\) (1.0 M) and H\(_2\)O (1.0 M) in acetonitrile, (c) IR spectra of 7-HC (1.0 M), H\(_2\)O (1.0 M) and SiO\(_2\) (1.0 M) in acetonitrile and Gaussian components from least squares fitting.
the spectra are deconvoluted into Gaussian profiles, which clearly yield three peaks at 3456 cm\(^{-1}\), 3556 cm\(^{-1}\) and 3632 cm\(^{-1}\), respectively [48]. It seems apparent that both the components of the OH stretching mode of 7HC are only slightly shifted to 3556 cm\(^{-1}\) and 3632 cm\(^{-1}\), respectively, while that of the hydrated silica is blue shifted to a great extent and resonate at 3456 cm\(^{-1}\). This shows that silica–OH donates proton to the OH oxygen of 7HC acceptor site in forming strong hydrogen bond between the two [49]. However, to make final conclusion on the morphology of Ludox\(^\circ\) in the absence and presence of 7HC through electron microscopic measurements are narrated. Besides, the adsorption kinetics of 7HC over silica surface, as measured by quartz crystal micro balance (QCM) studies would further highlight the detailed mechanism. These above mentioned components are considered to be the future perspectives of the present work.

Summary and conclusions

Physico-chemical studies on the interactions of the imperfect nanocolloidal dispersion of silica (Ludox\(^\circ\)) with 7HC have been undertaken with the aid of electronic absorption, emission and vibrational spectroscopic measurements. While the absorption and emission intensities of 7HC were increased with increasing dye concentration in the range of 0–20 \(\mu\)M, the enhancement of fluorescence intensity is brought about at the low concentration of silica. This enhancement of the fluorescence intensity of 7HC has been related to the strengthening of excited state H-bonds formed between Ludox\(^\circ\) and 7HC. It may be noted that the radiation less deactivation cannot dramatically influence the regulation of electronic states by H-bonding interactions and the fluorescence of chromophores in H-bonded surroundings may be quenched or enhanced by H-bonds [50]. At high concentration range of silica, strong and irregular adsorption of 7HC onto silica surface led to a red shift in the absorption spectra. The intermolecular fluorescence quenching, under the prevailing condition, is governed by the Homo Förster resonance energy transfer formalism. The size of the colloidal dispersion was independent of the concentration of silica and 7HC. Due to the stacking of dye molecules onto silica surface, negative zeta potential values of Ludox\(^\circ\) was suppressed compared to the systems without the dye. The adsorption kinetics of 7HC over silica surface, as measured by quartz crystal microbalance (QCM) studies would further highlight the detail mechanism. Besides, Raman spectroscopic studies are considered to be more informative in understanding the exact nature of H-bonding between Ludox\(^\circ\) and 7HC in aqueous medium. These components are considered to be the future perspectives of the present work.

Acknowledgements

The work has been financially supported by the Department of Science and Technology, Govt. of India. M.C. acknowledges the receipt of INSPIRE Fellowship from DST.

References

Surfactant-Assisted Synthesis and Characterization of Stable Silver Bromide Nanoparticles in Aqueous Media

Moumita Chakraborty,† Fang-Wei Hsiao,‡ Bappaditya Naskar,§ Chien-Hsiang Chang,‡ and Amiya Kumar Panda*†

†Department of Chemistry, University of North Bengal, Darjeeling 734 013, W.B., India
‡Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan
§Centre for Surface Science, Department of Chemistry, Jadavpur University, Kolkata 700 032, W.B., India

ABSTRACT: Colloidal dispersions of silver bromide (AgBr) in aqueous surfactant medium have been prepared using a surfactant-assisted synthesis approach with hexadecyltrimethylammonium bromide (CTAB). The surfactant acts both as source of bromide ion as well as the stabilizing agent. Upon progressive addition of silver nitrate to aqueous CTAB solution, stable AgBr dispersions were obtained. Formation of surfactant cation (CTA⁺) stabilized AgBr was confirmed by way of XRD, FTIR and NMR studies. Thermal behavior of the isolated nanoparticles was investigated by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA), where the occurrence of phase transition in the surfactant-stabilized nanoparticles was observed. Kinetics of the particle growth was investigated by dynamic light scattering measurements, which predicted the formation of surfactant bilayered structures associated with the nanoparticles of AgBr. Band gap of the nanoparticles was determined by suitably analyzing the UV−visible spectral data, which concluded that the particles behaved like insulators. Morphology of the particles, studied by TEM measurements, was found to be spherical. Finally, enthalpy of formation of surfactant-stabilized AgBr, determined calorimetrically, was found to be dependent on the concentration of the precursors.

INTRODUCTION

Because of their fascinating properties and multifaceted application potentials, research interests in the physicochemical investigations on synthesis and characterizations of nanoparticles are ever increasing since last few decades.¹−³ Nanoparticles find applications in various fields, viz., semiconductor,⁴−⁷ superconductor,⁸−¹² magnetic materials,¹³,¹⁴ opto-electronic devices,¹⁵−¹⁷ catalysts,¹⁸−²⁰ paint,¹,²² electrochemistry,¹−³,²³ biomedical devices,²⁴,²⁵ etc. As the nanoparticles have larger surface area than the bulk material, they become more reactive. The nanoparticles can be considered as a bridge between the bulk material and atomic/molecular entities.²⁶ There has been a significant increase in the synthesis and characterization of silver halide (AgX) nanoparticles due to their specific properties.¹−³ Silver halides are being used as photographic material for a long time.¹,¹²,²⁴,²⁷ According to Sambhy et al.,²⁴ AgBr nanoparticles have microbicidal activity.

Composite materials of AgCl and poly(methyl methacrylate) can be used as separation membranes.²⁷ Because of their high conductivity, AgX are used as solid ionic conductors.²⁸ However, the most important property of silver halides is their enhanced band gap emission in the nano range compared to the bulk material.²⁹ Besides the aforementioned properties silver halides are also used as catalysts.³⁰−³² Taking into account of different application potentials of nanoparticles of AgX, it is worth pursuing to study the convenient ways to prepare a stable dispersion of AgX. It has been reported that when present in pure crystalline form, silver halide salts are unstable.³³ Detailed mechanism for the degradation of Ag⁺ ions into metallic silver has been explained by Proudfoot.³⁴ However, if AgX salts are in a dispersed state, they become

Received: February 11, 2012
Revised: March 28, 2012
Published: April 18, 2012

Supporting Information

dx.doi.org/10.1021/la300615b | Langmuir 2012, 28, 7282−7290
stable.\textsuperscript{31} This has motivated the authors to undertake the investigations on the synthesis and characterization of colloidal silver bromide in aqueous surfactant medium. It has been reported by Lahtinen et al.\textsuperscript{35} that quaternary ammonium ion comprising a long hydrocarbon chain could stabilize the synthesized AgBr nanoparticle with a protective coating. Hexadecyltrimethylammonium bromide (CTAB) is one of the cationic surfactants that has been used by many researchers as stabilizers or templates for the synthesis of various novel materials.\textsuperscript{1−3,36} Sui et al.\textsuperscript{2,3} have used CTAB as a stabilizer in preparing positively charged silver nanoparticles. Chen et al.\textsuperscript{37} have used CTAB as a stabilizer, where seed mediated growth of silver nanodisks in aqueous media has been reported. Reports of Sui et al.\textsuperscript{2,3} and Nikhoobakt et al.\textsuperscript{38} have suggested that CTAB could act as a passivating agent in stabilizing the colloidal nanoparticles. Likewise, Liu et al.\textsuperscript{1} have proposed that hexadecyltrimethylammonium ion could form a bilayer like structure around colloidal AgBr particles, which was very much mimetic to vesicles.

Because of the manifold applications of AgBr nanoparticles, a number of reports are available in the literature.\textsuperscript{3,34,31,33−39,41} He et al.\textsuperscript{41} have prepared novel layered AgBr-based nanocomposite stabilized by CTAB. Lahtinen et al.\textsuperscript{35} have reported the preparation of surfactant monolayer protected silver bromide nanoparticles. Bai et al.\textsuperscript{42} have prepared and characterized AgBr nanoparticles in poly(vinylpyrrolidione) matrix. Photocatalytic activity of the synthesized AgBr nanoparticles as polymer composites has been reported by different authors.\textsuperscript{3,33,43} Preparation of AgBr nanoparticles has also been reported in water-in-oil microemulsion media by Husein et al.\textsuperscript{39} They have prepared AgBr nanoparticles in water-in-oil microemulsion where the existence of bulk water was possible for which the nanoparticles got precipitated in that water pool. In their case, basically formation of AgBr nanoparticles occurred in the confined water pool of water-in-oil microemulsion. However, in the present case, our proposition is different. We believe that AgBr nanoparticles are formed in aqueous medium first which then get stabilized by surfactant monolayers/bilayers. However, in all the cases, the wide applications of AgBr were not convenient because of the limited stability of AgBr nanoparticles as colloidal dispersions. Moreover, reports on the use of AgBr nanoparticles in the dilute concentration range (of the order of milli to micromolar) are not plenty in literature.

As already mentioned, although AgBr nanoparticles have many application potentials, it is difficult to obtain stable colloidal dispersions of AgBr, especially in the aqueous medium.

In this paper, the synthesis and characterization of colloidal dispersions of silver bromide using a very simple but novel approach are reported. Upon progressive addition of silver nitrate to aqueous CTAB solution, colloidal dispersions of AgBr are formed in the aqueous medium. The surfactant acts both as a stabilizing agent as well as the source for bromide ion. The colloidal dispersions of AgBr were stabilized by the layered structured surfactant cation assemblies. Although there are previous reports on the synthesis and characterization of AgBr nanoparticles, the studies in solution phase are not so common, which are essential for practical purposes. In the present case, the nanocolloidal dispersions of AgBr were found to be stable in the studied concentration range (10^{-6}−10^{-7} M) up to a year. Formation of nanoparticles of AgBr was confirmed by the way of XRD, FTIR, and NMR studies. Band gap of the nanoparticles in the dispersed state was investigated by UV−visible spectral measurements. Growth kinetics of the surfactant-protected nanoparticles (SPN) was studied by dynamic light scattering method. Thermal behavior of SPN was also studied by DSC/TGA analysis. Morphological studies were performed by TEM measurements. Our endeavor was to undertake a simple but novel one-pot synthesis of stable AgBr nanoparticles and its application in aqueous media.

## Experimental Section

### Materials

The cationic surfactant hexadecyltrimethylammonium bromide (CTAB) was a product from Sigma-Aldrich, USA. The surfactant was stated to be >99% pure and was used as such. A.R grade silver nitrate (AgNO\textsubscript{3}) was purchased from SD. Fine Chemical Ltd., India. All the chemicals were used as received. Double distilled water with a specific conductance of 2−4 μS cm\textsuperscript{-1} at 298 K was used for preparing the solutions.

### Methods

A stock solution of 1 mM AgNO\textsubscript{3} was prepared in water with which experimental works were carried out. 5.0 mL of colloidal dispersions of AgBr particles were prepared in 0.4 mM CTAB solution at five different concentrations (10, 20, 30, 40, and 50 μM). Quantitative amount of 1 mM AgNO\textsubscript{3} was added in 100 steps with constant stirring to obtain AgBr in the above-mentioned concentrations. It may also be mentioned that we had prepared and studied the AgBr nanoparticles in the concentration range of 10−50 μM with an interval of 5 μM. By the method of trial and error it was found that a 0.4 mM CTAB solution was the optimum concentration in obtaining a stable dispersion of AgBr up to 50 μM (shelf life = 1 year). Above the 0.4 mM concentration there is excess of Br\textsuperscript{-} ions which would cross the solubility limit and thus failed to stabilize the system despite of large amount of CTAB. On the contrary, there is deficiency of CTA\textsuperscript{+} ions to stabilize the system when the concentration of CTAB solution is below 0.4 mM. Henceforth, all the preparations would mean for a 0.4 mM CTAB solution in water. A stock solution of 1 mM CTAB was used for the study.

Surfactant-stabilized nanoparticles of AgBr were isolated in two ways. First, the method of Liu et al.\textsuperscript{1} was adapted to isolate AgBr from its aqueous dispersion. A 10 mL 20 mM aqueous AgNO\textsubscript{3} solution was added dropwise to 100 mL 0.4 mM CTAB solution under rigorous stirring and the dispersion thereby obtained, which was not as stable as the aforesaid preparation (stable up to 2 h), was centrifuged at 10000 rpm and the sediment was washed with water. It was then vacuum-dried at 80 °C. This isolate was termed as “aqueous extract”. In another method, surfactant-stabilized AgBr colloidal dispersion was extracted into chloroform layer and then the organic layer was dried under vacuum. The second category was termed as “chloroform extract”. XRD, FTIR, DSC, and TGA analyses were done on both the extracts.

The diffraction patterns of the isolated nanoparticles and the precursors were recorded in a RINT 2000, Rigaku diffractometer (Japan) using CuKα (0.15418 nm) radiation operated at 40 kV and 40 mA in the range of 5° to 70° at the rate of 3°/min. The FTIR spectral data were recorded in a Shimadzu 8300 FT-IR spectrometer (Japan) by taking the samples in the form of KBr pellets using standard procedure.\textsuperscript{1} H NMR spectra were recorded in 300 MHz FT-NMR by Bruker-Advance (5 mm BBO Probe) spectrometer (Switzerland) using tetramethylsilane (TMS) as an internal standard. The conductance measurements were undertaken by Eutech Instruments con 510 conductivity/TDS/FM meter. The UV−visible absorption spectra were recorded on a UVD-2950 spectrophotometer (Labomed Inc., USA) using a matched pair of quartz cuvette of 1 cm path length. Size of nanoparticles was determined by dynamic light scattering method using a dynamic light scattering spectrometer Nano ZS 90 (Malvern, U.K.). A He−Ne laser of 632.8 nm wavelength was used and the data were recorded at a scattering angle of 90°. Samples were filtered using Millipore hydrophobic membrane filter of 0.25 μm pore size. Thermal gravimetric analysis (TGA) of the isolated nanoparticles as well as CTAB was carried out on Mettler H10, Neo-Pharma Instruments Corp. from 50 to 325 °C and the differential scanning calorimetry (DSC) measurements were done on Pyris 6 DSC.
(Perkin-Elmer, USA). The samples were heated at a rate of 10 °C/min from 50 to 140 °C and the cooling was done at 5 °C/min. The instrument was calibrated with Indium before each experiment. The enthalpy changes for the formation of nanoparticles were measured in an OMEGA isothermal titration calorimeter (ITC) (Microcal Inc., Northampton, MA, USA). 1.8 and 1.325 mL CTAB solutions were taken in the reference and reaction cell, respectively. In the ITC experiment, enthalpy change associated with the interaction process was calculated under constant temperature accurately within 0.01 °C. As prepared samples of AgBr nanoparticles in surfactant medium were used for morphological studies by TEM. TEM images were recorded with an H-7500, transmission electron microscope (Hitachi, Japan), with an acceleration voltage of 80 kV. A drop of nanocolloidal dispersion of AgBr was dried on carbon-coated copper grid using the standard procedure.5

- RESULTS AND DISCUSSION

X-ray Diffraction Studies. Characteristic X-ray diffraction patterns of CTA+ -stabilized AgBr nanoparticles, isolated in two different ways, along with the precursors CTAB and AgNO3 are shown in Figure 1. X-ray diffractograms of CTAB and chloroform extracted CTA+ -stabilized AgBr bear the same features. Aqueous extract exhibited differences, although not so significantly. Pure CTAB bearing higher crystallinity exhibited sharp and intense peaks at 2θ values of 10.1, 13.4, 18.2, 20.3, 21.4, 23.9, 27.4, 30.8, and 38.1 degrees, respectively. Nanoparticles extracted by two different methods did not exhibit any characteristic peak for AgNO3. This suggests the complete conversion of AgNO3 to AgBr, which was not unexpected. Maximum concentration of added AgNO3 was 50 μM in presence of 0.4 mM CTAB. Therefore, it could be expected that all the Ag+ ions would be in the form of AgBr. Diffractograms of the nanoparticles isolated directly from aqueous media did not exhibit distinct, specific and intense peak for AgBr. The less intense diffractograms of any nanoparticle is not uncommon.1,24,44 Particles in the nano-dimensions are less crystalline and hence their X-ray diffractograms have fewer features than the corresponding bulk materials.28 Additionally, formation of lesser amount of AgBr compared to the amount of CTAB present resulted in the masking of AgBr diffractograms by CTAB. CTA+ -coated AgBr nanoparticles exhibited its characteristic peaks at 32.0, 49.0, and 67.5 deg, respectively. The results mildly deviated from the reported values 6,31,42 which is possibly due to the differences in the experimental conditions. In the present case, while obtaining the representative peaks for AgBr nanoparticles, we performed the analysis by expanding the corresponding zones. Individually expanded zones are presented in the supplementary section (Figure S1, Supporting Information). The interplanar distances corresponding to the above-mentioned peaks were 2.9, 2.0, and 1.7 Å respectively. Corresponding crystal planes (hkl) were (200), (220), and (400) respectively.42 Results confirmed the formation of crystals bearing the same structure as of cubic face centered bromargyrite (www.webmineral.com/MySQL/xray.php). Formation of AgBr was therefore established from the X-ray analysis.

Fourier Transform Infrared Spectra. In order to further establish the formation of CTA+ -coated AgBr nanoparticles, FTIR spectral measurements were carried out. The representative results are shown in Figure 2. The symmetric and asymmetric vibrations of pure CTAB appear at 2849 and 2917 cm−1 respectively. Isolated nanoparticles also bear the same fingerprint, which indicates the direct noninvolvement of hydrocarbons in stabilizing the AgBr nanoparticles. The observed peaks at 1486 and 1431 cm−1 for pure CTAB were due to the asymmetric and symmetric −C=−H vibration of the quaternary ammonium moiety.1−3 In case of isolated nanoparticles the peak at 1486 cm−1 was broadened and shifted to 1456 cm−1 and the peak at 1431 cm−1 was not present. Results suggest that AgBr clusters influenced the (CH3)3N+ vibration.

NMR Spectroscopic Studies. Coating ability of CTA+ over AgBr clusters was further evidenced through 1H NMR measurements.3,45−47 Spectral data of NMR studies are summarized in Table 1 and spectra are shown in Figure S2, Supporting Information. Peaks for pure CTAB appeared as follows: δ = 3.6 ppm (α-CH2−), δ = 3.47 ppm ((CH3)3N+), δ = 1.8 ppm (β-CH2−), δ = 1.36 ppm (γ-CH2−), δ = 1.25 ppm (−(CH3)−) and at δ = 0.88 ppm (terminal −CH3). For surfactant-stabilized nanoparticles, no shift in the terminal −CH3 and (−(CH3)−) protons occurred, which indicates that AgBr clusters could not perturb the terminal −CH3 protons. All the other proton signals were down shifted (approximately 0.13 ppm) indicating the partial attachment of the surfactant headgroup to AgBr nanoparticle.3,45−47

Conductometric Titration. Conductometric titration of an aqueous solution of 0.4 mM CTAB by AgNO3 is graphically presented in Figure S3, Supporting Information. Similar titration with 0.4 mM KBr is also shown for comparison. With the progressive addition of silver nitrate into the aqueous KBr solution, conductivity monotonously decreased. After the neutralization point, a further increase in conductance was

Figure 1. XRD patterns of (A) CTAB, (B) silver nitrate, (C) CTA+ -coated silver bromide nanoparticles isolated from water and (D) CTA+ -coated silver bromide nanoparticles isolated using chloroform.

Figure 2. FTIR spectra of (A) pure CTAB and (B) aqueous extract of CTAB-stabilized AgBr nanoparticles.
noted. When AgNO₃ solution was progressively added to KBr solution, instantaneous formation of AgBr particles occurred which remained as suspension. Usually, such titration leads to the replacement of Br⁻ ions with the NO₃⁻ ions along with the formation of insoluble component, AgBr. Conductivity of the replacement of Br⁻ ions. Therefore, there should not be any significant change in the conductance before the neutralization point. However, suspended AgBr colloids might hinder the mobility of the ions present in solution, which ultimately led to the decrease in conductance.

Conductance profile for CTAB solution followed the similar trend, although to lesser extent. The appearance of neutralization point at a lower concentration and also lesser conductance in the preneutralization point, compared to KBr, was not unexpected. CTA⁺ ions are involved in stabilizing the AgBr nanoparticles in the form of layers (to be discussed in detail later on). The conductivity of CTA⁺ ions is less compared to the K⁺ ions. Therefore, the conductometric titration curves for CTAB would always maintain a lower conductance in the preneutralization point at a lower concentration and also lesser conductance compared to KBr. According to Almgren and Rydholm,⁴⁹ CTAB micelles have much higher surface charge and hence a larger electric field for which Br⁻ ions can bind strongly as counterions to the micelles. Subsequently, the average mobility of the ionic species is decreased. In the previous published report,⁵ the surfactant ions could stabilize the nanoparticles through the formation of bilayer structures around them. Br⁻ ions would thus act as counterions, which lessen their availability compared to KBr solution of identical strength. However, it is to be mentioned that due to the formation of vesicle like entities the fraction of counterion dissociation would be higher compared to the CTAB micelles.

**UV−Visible Spectroscopy.** UV−visible spectra of colloidal AgBr, dispersed and stabilized in/by aqueous CTAB solution, were recorded in the range 200−350 nm at different concentrations of AgBr (viz., 10, 20, 30, 40, and 50 μM, some of which are shown in Figure 3). Colloidal dispersions exhibited a strong and intense peak at 212 nm against CTAB as blank. Absorbance at 212 nm increased with increasing AgBr concentration. The peak at 212 nm corresponds to the absorption of CTA⁺-coated AgBr in aqueous solution. Increase in intensity with increasing AgBr concentration implies the accumulation of CTA⁺ around AgBr nanoparticles. Results clearly indicate the clustering of the surfactant molecules which eventually stabilizes the nanoparticles. The exact orientation of surfactant molecules around AgBr nanoparticles will be discussed later on. Although not so sharp, another faint shoulder appeared at 270 nm which corresponds to AgBr nanoparticles.⁵⁹ The shoulder at 270 nm appeared faint in comparison to previously published reports³⁴,⁵⁰ because in the present case lower concentrations were used. It is also to be mentioned that pure AgBr in bulk state or in its vapor state appears light green.⁵⁰ However, in the present case we have failed to detect the corresponding peak in the visible region as the concentration of AgBr was in the micromolar range. Besides, the existence of larger amount of CTAB could have masked the greenish appearance of AgBr. The stabilizing agent, CTAB also protects the AgBr colloids from reduction to Ag metals, which is otherwise common for silver halides in their bulk state.

The absorbance-concentration profile at 212 nm obeyed Beer’s law and the molar absorption coefficient of CTA⁺-stabilized AgBr was found to be 6.88 × 10⁻³ M⁻¹ cm⁻¹ at 212 nm. Such kind of report for AgBr is not available in the literature. The spectral data were further analyzed to determine the optical band gap (εg) of CTA⁺-stabilized AgBr nanoparticles in aqueous medium using the Tauc relation:

\[ (\epsilon h\nu)^g = C(h\nu - \epsilon_b) \]  

(1)

where \( \epsilon \), \( h \), and \( \nu \) are the molar absorption coefficient, Planck’s constant, and frequency of light respectively and \( C \) is a constant. The exponent depends on the type of transition for direct allowed transition (here \( n = 1/2 \)). Liu et al.¹ have prepared AgBr nanoparticles using the present approach where the concentration of AgBr was fairly high, for which, the colloidal suspension exhibited peaks in the range 250−320 nm. According to them, the spectra correspond to the direct band gap of AgBr. We also have extended this approach to determine the direct band gap in the range 219−226 nm. From the linear portion of the plot of \( (\epsilon h\nu)^2 \) against \( h\nu \) (as shown in Figure 4), the band gap was determined from the ratio of the intercept and slope of the linear part. On an average, the band gap was found to be 5.35 eV for a 30 μM AgBr dispersion. With increasing AgBr concentration the band gap decreased, attained a minima at 40 μM AgBr (inset of Figure 4) which again increased up to 50 μM AgBr. Dispersions comprising higher than 60 μM AgBr became unstable. For bulk AgBr, the reported direct band gap is 4.29 eV.⁵² Higher band gap value for AgBr nanoparticles was attributed to the size confinement effect. It is not unexpected for the band gap to increase with the decrease in particle size.⁵¹ The decrease in band gap with increasing AgBr concentration was due to the formation of larger particles.

**Figure 3.** UV−visible absorption spectra of CTA⁺-coated AgBr nanoparticles in aqueous medium at 25 °C. Concentrations of AgBr (in μM): (1) 20, (2) 30, and (3) 50. A 0.4 mM CTAB solution was used as blank.

**Table 1. **¹H NMR Data of CTAB and CTA⁺-Coated AgBr Nanoparticles⁴

<table>
<thead>
<tr>
<th>System</th>
<th>terminal-CH₃</th>
<th>—(CH₂)₁₋₂</th>
<th>γ-(CH₂)₋</th>
<th>β-(CH₂)₋</th>
<th>(CH₃)₄N—CH₂—</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB</td>
<td>0.88 (3H, m)</td>
<td>1.26 (24H, s)</td>
<td>1.36 (2H, s)</td>
<td>1.8 (2H, br)</td>
<td>3.47−3.6 (11H, m)</td>
</tr>
<tr>
<td>aqueous extract of CTA⁺-coated AgBr</td>
<td>0.88 (3H, m)</td>
<td>1.26 (24H, s)</td>
<td>1.36 (2H, s)</td>
<td>1.76 (2H, br)</td>
<td>3.46−3.54 (11H, m)</td>
</tr>
<tr>
<td>CHCl₃ extract of CTA⁺-coated AgBr</td>
<td>0.88 (3H, m)</td>
<td>1.25 (24H, s)</td>
<td>1.34 (2H, s)</td>
<td>1.76 (2H, br)</td>
<td>3.38−3.47 (11H, m)</td>
</tr>
</tbody>
</table>

⁴Here, s, m and br, s denote singlet, multiplet, and broad singlet. CDCl₃ was used as solvent.
After the attainment of 40 μM AgBr concentration, smaller clusters are formed for which a further increase in the band gap occurred.

**DLS Studies and ζ Potential Measurements.** The kinetics for the growth in particle size as functions of AgNO₃ concentration and time were studied by dynamic light scattering method. Also, during the same studies, surface charges of the colloidal dispersions of CTA⁻ coated AgBr were investigated through ζ potential measurements. Results are summarized in Figure 5. With the increase in time, particles grew up to 24 h and then the size attains constancy. This implies that the growth process is completed within 24 h. Initially the size was around 50 nm. Within 6 h, there occurred a 2-fold increase in size. It is believed that initially randomly oriented CTA⁻ ions stabilized the colloidal particles of AgBr through the formation of monolayer, in the manner as shown in Scheme 1A. However, the kind of orientation, as shown in Scheme 1A, is not stable from both the thermodynamic and kinetic point of view, for which an enlarged bilayer-like structure is formed around the AgBr nanoparticle (shown in Scheme 1B), which becomes stable. The CTA⁻ bilayer formation in stabilizing nanoparticles has been reported earlier.1,2,38 Therefore, the increase in the hydrodynamic diameter of CTA⁻-stabilized nanoparticles is a contribution of colloidal growth of AgBr as well as the size enhancement due to the bilayer structure formation. Additionally, the increase in the bilayer density could contribute to the size enhancement of the surfactant-stabilized dispersion of silver bromide. The ζ potential values were found to increase with increasing time which subsequently attained constancy (data not shown to save space). Initially, the nanoparticles were stabilized by surfactant molecules through a monolayer coating with an irregular orientation (as shown in the Scheme 1A), with lower ζ potential value. However, after the bilayer-like structures were formed, the extent of dissociation of the counterions (bromide) increased and hence the ζ potential also increased. When the formation of the bilayer-like structures was completed, the ζ potential values attained constancy (data not shown). The formation of bilayer-like structures would lead to the creation of bigger entities as shown in Scheme 1. Hence, overall charge density would be less compared to the pure micelles. Accordingly, the extent of dissociation would be higher for the bilayer-like entities than the pure micelles of CTAB. As a result, the ζ potential for the bilayer-stabilized nanoparticle system will be higher than the corresponding micellar entities.

The size of the AgBr colloids stabilized by CTA⁻ was also found to be dependent on the concentration of AgNO₃, as shown in the inset of Figure 5. An increase in the size of the particle was observed up to 25 μM AgBr dispersion, which then decreased mildly, followed by a further linear increase after 45 μM. Precipitation occurred when the final AgBr concentration exceeded 60 μM. It is therefore evident that the optimum concentration to get a stable colloidal dispersion of AgBr in 0.4 mM aqueous CTAB solution is 30 μM as marked with an asterisk in the inset of Figure 5. With increasing concentration of AgBr initially the particles grow bigger with a smaller number of nuclei. This is possible because of the presence of relatively larger amount of stabilizing agent CTAB. When a certain concentration is reached (25–30 μM) formation of a larger number of nuclei of nanoparticles of AgBr superseded the growth processes. The growth rates of smaller nuclei were thus smaller than the growth rate of AgBr at lower concentration. At lower concentrations, number density of nanoparticles was low; the stabilizing agent was relatively abundant compared to the formed nanoparticles which results in the formation of fairly stable and larger aggregates. When the concentration of AgBr exceeds 40 μM, there would not be enough supply of the stabilizing agent for the growth of so many nuclei, resulting in smaller nanoparticle formation. Hence, number density of nuclei would increase. Subsequently, collision probability and formation of localized clusters would increase.

The rate of the particle growth was evaluated as the rate process followed a first order kinetics. As the concentration of CTAB was much higher than the AgNO₃ concentration, use of first order kinetics is justified. The following first order rate expression could therefore be used:35

\[
t = \frac{2.303}{k} \log \left( \frac{d_f - d_i}{d_f - d_i} \right)
\]

Here \( t = \) time, \( k = \) first order rate constant, \( d_i = \) initial particle size, \( d_f = \) particle size at time \( t \), \( d_f = \) final particle size.

There was no significant difference in the growth rate for different concentrations of AgNO₃. The average rate constant for the particle growth was found to be 5.63 × 10⁻³ h⁻¹.

**DSC–TGA Analysis.** Figure 6A denotes the TGA curves for pure CTAB, aqueous and chloroform extracts of CTA⁻-stabilized AgBr nanoparticles. For pure CTAB, two weight loss steps were observed at 160–170 and 170–240 °C of 10 and 77%, respectively. The thermal decomposition of aqueous extract of CTA⁻-stabilized AgBr was reflected through four
weight loss steps at 140–190, 190–220, 220–270 and 270–
290 °C of 10,6,16 and 24%, respectively. On the contrary, the
chloroform extract of CTA\(^+\)-coated AgBr was decomposed
through two weight loss steps of 15 and 39% at 140–200 and
200–230 °C, respectively. The weight loss for the aqueous
extract was higher than that for the corresponding chloroform
extract, which was obvious; for the nanoparticles stabilized by
bilayered structures, there would be a larger number of
surfactant molecules than the corresponding monolayer
protected systems (chloroform extract). The weight losses are
due to the thermal decomposition of CTAB (150–300 °C)\(^54\)
by a self-combustion process.\(^53\) According to Mukherjee et al.\(^53\)
and others\(^55\) when CTAB undergoes thermal decomposition
there occurs formation of some solid carbon for which the
attainment of 0 wt % in TGA analysis was not observed. In case
of aqueous extract there is a bilayer of CTA\(^+\) around the AgBr
nanoparticles, which makes the system more stable compared
to chloroform extract and hence the weight loss takes place at
higher temperature. Also, the % weight loss in case of
surfactant-coated AgBr nanoparticles was less than pure
CTAB. Pure CTAB undergoes thermal decomposition in this
range of temperature whereas the surfactant-coated AgBr
decomposes at a much higher temperature. The results suggest
two different states of CTA\(^+\) around AgBr nanoparticles and the
formation of CTA\(^+\) bilayers on the AgBr clusters. The two
different states of CTA\(^+\) ion around the AgBr nanoparticles
correspond to the two different orientations: first kind includes
the CTA\(^+\) ions where the head groups are oriented toward the
nanoparticles while for the other, the surfactant head groups are
protruding out of the nanoparticles. It is believed that extracting
the CTA\(^+\)-coated nanoparticles in chloroform eliminates the
bilayer structure and the CTAB molecules contributing to the
second layer will be collected as part of the solid phase when
the chloroform is evaporated.

![DSC profiles for heating and cooling of the pure CTAB and
isolated nanoparticles in the temperature range of 40–140 °C.
In the studied temperature range, pure CTAB exhibited a sharp
endothermic peak at 108 °C, whereas, the endothermic peaks for
the aqueous and chloroform extracts appeared at 93 and 100 °C.
These endothermic peaks, in the three cases, are not the result of
any weight losses. Rather, these very observations attribute to
the melting of the ordered regions of hydrocarbon chains in free
CTAB and CTA\(^+\) bilayers.\(^56\) The AgBr nanoparticles isolated
from chloroform showed the endothermic peak in between pure
CTAB and aqueous extract. The reason could be the formation
of monolayer-protected nanoparticles, which make them more
rigid, compared to those isolated from the aqueous media,
thereby having a higher melting point than the aqueous extract
but lower than pure CTAB. On the other hand, during cooling,
only pure CTAB and chloroform extracted nanoparticles
exhibited peaks within the temperature range of 60–80 °C.

**Isothermal Titration Calorimetry (ITC).** Isothermal
titration calorimetry has been found to be a very sensitive
tool in estimating the enthalpy of formation of nanoparticles.
It has previously been reported\(^53\) that when otherwise water
insoluble materials were synthesized in nano dimension using compartmentalized system, the problem of precipitation could easily be avoided. Not many reports are available in literature on these aspects of nanomaterials. Advantage of ITC studies to estimate the formation of nanoparticles at different precursor concentrations lies in the fact that, with suitable processing, the parameters related to the precipitation could easily be avoided. Results of the microcalorimetric titration of aqueous AgNO\(_3\) (taken in the syringe against aqueous CTAB solution) for different initial AgNO\(_3\) concentrations are shown graphically in Figure 7. It has been observed that with the increasing concentration of AgBr, there is a decrease in the enthalpy change. The decrease is attributed to the formation of a larger number of crystals. \(\Delta H_f\) vs [AgNO\(_3\)] profile was linear in nature. The study was carried out at five different concentrations and then the plot was extrapolated to zero. The enthalpy change for formation of AgBr nanoparticles was thus found to be 13.24 kcal mol\(^{-1}\). The exothermic nature of the reaction is proved by the negative values of the enthalpy change.

**Transmission Electron Microscopy.** Representative TEM images of the nanocolloidal dispersions of silver bromide, stabilized by CTAB, are shown in Figure 8. Particle morphology was found to be strongly dependent on the concentration of AgBr. Particles were spherical in shape although in some cases rice grains like morphologies were also observed (at 10 and 30 \(\mu M\) AgBr concentrations). Particles were mostly clustered whereby the size increased with increasing AgBr concentration up to 30 \(\mu M\), beyond which a decrease in the particle size was again observed. In case of 50 \(\mu M\) AgBr dispersion, smaller particles were found to be clustered. The observation in dynamic light scattering studies was thus further confirmed by TEM studies. It is to be mentioned here that EDX measurements carried out on the same spot exhibited the absence of artifacts.

At very low concentrations of AgBr, particle density was low, as observed in Figure 8A. With increased AgBr concentration, particles grew bigger. However, beyond 30 \(\mu M\) AgBr concentrations, a size constriction effect was observed. When AgBr concentration was sufficiently high, the surfactants failed to provide proper protection. Additionally, with the increased AgNO\(_3\) concentration, the rate of AgBr formation became faster. These two combined effects led to the formation of smaller particles in the higher concentration range. Size analysis of Figure 8B reveals the particle to be about 60 nm. The shape of the 30 \(\mu M\) AgBr was like rice grains. As shown in Figure 8E, the particles were clustered together, suggesting their formation following the same mechanism as in Figure 8D, but with a higher rate. The clustering of smaller particles (as in Figure 8E)
was due to the process of Ostwald ripening. When the samples were irradiated with high energy electron beam some Ag$^+$ ions could have been reduced to Ag$^0$. However, this reduction did not lead to any significant morphological changes. In the present case, chances of decomposition of AgBr by electron beam radiation are less, as AgBr particles enjoy additional protection from the surfactant bilayer-like entity. Similar method of TEM measurements has previously been reported by Liu et al.$^1$ However, it is noteworthy that the morphological characterization by low energy SEM would have been more reliable, which is considered as the future perspective.

## CONCLUSIONS

Surfactant-stabilized colloidal dispersions of AgBr have been prepared and characterized. The optimum concentration of CTAB used was 0.4 mM. To obtain the stable colloidal dispersions, the molar ratio of AgNO$_3$ to CTAB was maintained in the range of 1:40–1:8. The formation of the nanocolloidal dispersions has been supported by the conductometric and the calorimetric studies. The formation process was found to be exothermic in nature. The complete conversion of AgNO$_3$ to AgBr has been established from the XRD measurements. Formation of CTA$^-$-coated AgBr nanoparticles was established from XRD, TEM, FTIR, NMR and UV–visible spectral studies. The DSC–TGA analysis confirms two different states of CTA$^-$ around AgBr nanoparticles and the formation of the CTA$^-$ bilayer like structure was thus ensured. The formation of the bilayer like structure was further confirmed from the DLS results, where a 2-fold increase in size occurred within few hours from the time of the formation of the nanocolloidal dispersions. The morphology of the nanocolloidal dispersions was examined by TEM measurement and the particles were mostly found to be spherical in shape except for 10 and 30 μM AgBr solutions where the shape was rice-grain like.

## ASSOCIATED CONTENT

### Supporting Information

Expanded X-ray diffractograms, NMR spectra, and conductance profiles. This material is free of charge via the Internet at http://pubs.acs.org.

### AUTHOR INFORMATION

**Corresponding Author**

*Telephone: +91943334710. Fax: +913532699001. E-mail: akpanda1@yahoo.com.*

**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The work has been financially supported by the University Grants Commission (UGC), New Delhi, India. M.C. acknowledges the receipt of INSPIRE Fellowship from the Department of Science and Technology, Govt. of India. C.-H.C. and A.K.P acknowledge the financial assistance from the Confederation of Indian Industries, India and National Science Council, Taiwan (NSC100-2923-E-006-003-MY3) for sponsoring academic exchange program. We are grateful to CSS, JU for allowing us to carry out the calorimetric measurement. Valued guidance and suggestions from Prof. S. P. Moulik, CSS, JU is gratefully acknowledged.

## REFERENCES


dx.doi.org/10.1021/ja300615b | Langmuir 2012, 28, 7282–7290

7289
Langmuir


