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Premicellar aggregates of Rose Bengal with cationic and zwitterionic surfactants

Piotr Bilski *, Ralph N. Holt, Colin F. Chignell

Laboratory of Molecular Biophysics, National Institute of Environmental Health Sciences, Research Triangle Park, P.O. Box 12233, Research Triangle Park, NC 27709, USA

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Abstract

Transition from non-micellar to micellar Rose Bengal (RB) may involve little known species which are usually called dye-rich-micelles or premicellar aggregates (PAs). We have studied the PAs formed between RB and a series of surfactants with a zwitterionic alkylsulfobetaine functionality, SB-*X*, where $X=8$, 10, 12, 14 or 16 carbon atoms in the alkyl chain. We have compared these aggregates to those formed between RB and the cationic surfactant cetylpyridinium chloride. In most of the PAs studied, the formation of aggregates broadened and red-shifted (~ 10 nm) Rose Bengal's absorption and fluorescence, and decreased the intensity compared to the absorption and fluorescence bands of free RB in water. Such properties are characteristic of J-aggregates in which the RB molecules are loosely organized in a 'head-to-tail' fashion. The formation of all PAs containing RB was increased by the addition of salts producing water-soluble aggregates. Addition of salts such as KCl, Na_2SO_4 or $MgCl_2$ (0.2–1.5 M) to the PAs formed exclusively between RB and SB-12 induced the formation of novel J-aggregates in which the dye absorption band was very narrow, red-shifted by 37 nm, and almost three times more intense. The novel PAs are stable in solution and even co-existed with RB in SB-12 micelles at high salt concentrations. They were not formed by eosine or salts having large polarizable anions such as ClO_4 or I . They also were not formed with other surfactants, except when SB-10 was used instead of SB-12 in $MgSO_4$ solution. The spectral properties of RB in novel J-PAs indicate a higher level of molecular organization, which may lead to free exciton transitions between the dye molecules as a result of strong dipole–dipole coupling. Our results also confirm that the formation of hydrophobic ion pairs between the RB dianion and the cationic center in surfactant molecules initiates premicellar aggregation (Bilski et al., J. Phys. Chem., 95 (1991) 5784). Some of the resultant salt-induced PAs must be highly structured, which strongly affects the spectral properties of Rose Bengal. © 1997 Elsevier Science S.A.

Keywords: Rose Bengal; Premicellar aggregates; Dye-rich-micelles; Surfactants; Cetylpyridinium chloride; Zwitterionic surfactants; Salts; Free exciton; Ion pairs

1. Introduction

Aggregation and aggregated species are of interest because of their importance in biology and other sciences. In aqueous media, hydrophobic stabilization [1] is a major driving force for aggregation, producing micelles, vesicles, liposomes and bilayers/membranes from their respective monomeric components [2,3]. In systems containing ionic dyes and charged surfactants, smaller species, which are described as dye-rich micelles or premicellar aggregates (PAs), are often formed prior to micelles [4–18]. An important step preceding such premicellar aggregation may be the formation of hydrophobic ion pairs between the ionic dye and oppositely charged surfactant molecules.

Aggregation usually affects the spectral properties of dyes, which in turn can provide information on the structure of the aggregates. The absorption spectra of the so-called H-aggregates ('sandwich aggregates') and J-aggregates ('head-to-tail aggregates'), differ in that the H-aggregates show a hypsochromic shift, while the J-aggregates show a bathochromic shift [19–22]. For most J-aggregated dyes in solution, the spectral bands become broad and structureless due to the irregular grouping of dye chromophores in an aggregate. Less frequently, one observes very sharp and intense absorption bands, which may be due to free exciton transitions [19–23]. Although distinct narrowing and intensification of spectral bands in solution is rare, this phenomenon has nevertheless been observed for some J-aggregated cyanine [24–26] and porphine dyes [27]. The exciton theory provides an explanation of the involvement of energy transfer

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* Corresponding author.

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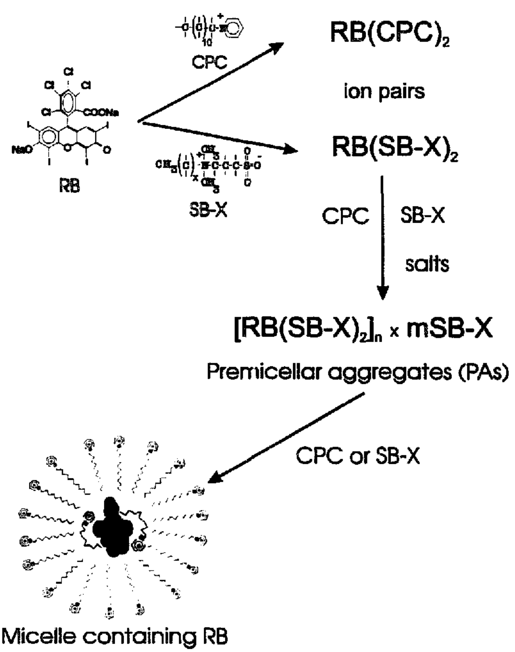

Fig. 1. Aggregated species produced in aqueous electrolytes containing RB and cationic (CPC) and zwitterionic SB-X surfactants.

[28–30] in determining the spectral properties of aggregated dyes [20,22,28,29].

Xanthene dyes, including the Rose Bengal (RB) dianion, are known to undergo aggregation in aqueous solution [31]. RB is an important photosensitizer that forms ion pairs with cationic surfactants [18]. Such ion pairs may aggregate by binding more surfactant molecules, which produces PAs along the route to micelles containing RB (Fig. 1). Zwitterionic surfactants also show some tendency to form PAs with RB [32]. However, unlike cationic surfactants, the presence of both the cationic and the anionic center in a zwitterionic detergent molecule may influence the hydrophilic/hydrophobic balance in the resulting PAs. Moreover, all ionic species (salts) present in solution may affect such a balance by acting as counter-ions for surface charges in the PAs.

In the present work, our purpose was to investigate the premicellar aggregates formed between RB and ionic surfactants when the surfactant concentration was insufficient to form micelles, especially in the presence of added salt. We have found that generally, under such conditions, 'loose' J-type PAs are formed in which RB shows a less intense and broad absorption band. However, when an appropriate salt is added to PAs formed from RB and SB-12, a novel J-aggregated species is produced, characterized by an intense and narrow absorption band in the visible spectral region. This absorption is indicative of a very high degree of molecular organization in such PAs, and is reported for the first time here for Rose Bengal.

2. Experimental section

Zwitterionic surfactants (sulfobetaines SB-8, SB-10, SB-14, and SB-16) were purchased from Calbiochem Co. (La Jolla, CA) as Zwittergents 3-08, 3-10, 3-14 and 3-16. Cetylpyridinium chloride (CPC) and lauryl sulfobetaine (SB-12) were purchased from Sigma Chem. Co. (St. Louis, MO). Rose Bengal, eosine and all inorganic salts (reagent grade or better) were obtained from Aldrich Chem. Comp., Inc. (Milwaukee, WI). All solutions were prepared in deionized water.

Absorbance spectra were measured using an HP 8451 Array Spectrophotometer (Hewlett Packard Co., Palo Alto, CA). Fluorescence spectra were measured on an SLM SPC 823/SMC 220 interfaced to a PC computer. For spectral deconvolutions, curve-fitting software Peakfit (Jandel Scientific, San Rafael, CA) was employed.

Aggregation of RB with surfactants can be quite a slow process. At low salt concentrations equilibration may take several hours, and the aggregate formation is sensitive to temperature. When the temperature was decreased, the aggregates usually grew bigger, as indicated by much stronger light scattering. However, we did not measure either the aggregation kinetics or the aggregate's sizes. All our measurements were performed on solutions that had achieved equilibrium regarding temperature and aggregation kinetics. The spectra of aggregated RB were stable and did not change over time when kept at room temperature where all our measurements were performed.

3. Results and discussion

3.1. Interaction of RB with ionic surfactants

At least four forms of RB may exist during the titration of the RB dianion by the surfactants CPC and SB-12 in aqueous solution (Fig. 1): uncomplexed RB, RB ion pairs, premicellar aggregates and micellar RB. The properties of uncomplexed RB are well known; micellar RB [32], and the RB ion pairs [33] have already been characterized and have proved useful in photosensitization studies [32,33]. However, the premicellar aggregates, the most elusive species previously observed in RB/surfactant systems [18,32], have not been characterized adequately.

Each of the above forms of Rose Bengal shows quite different spectral properties in aqueous solution. Representative spectral changes observed during titration with surfactant are shown in Figs. 2 and 3. Both the absorption and fluorescence bands of RB are red-shifted about 14 nm with complete micellization (Fig. 2(a)). The absorption coefficient of RB changes less, but reveals a shallow minimum due to premicellar aggregation (Fig. 2(b)), which is not evident in the plot of the spectral shift (Fig. 2(a)). The intensity of RB fluorescence (Fig. 3(A)) increases strongly and then saturates when micelles are formed (Fig. 3(a)). (Saturation points may be used to calculate the micellar aggregation number and the critical micelle concentration of surfactant [32] (Fig. 3(b)).) Although fluorescence may almost disappear in the region of premicellar aggregation (Fig. 3(a)), the fluorescence intensity is nevertheless the best parameter to investigate premicellar aggregation because it changes the most as the RB environment changes.

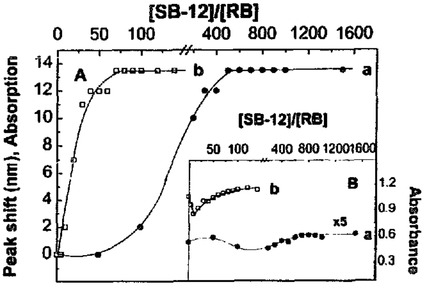

Fig. 2. Changes in the absorption spectrum of RB during titration with SB-12. (a) The shift of RB visible absorption maximum as a function of SB-12 to RB molar ratio; phosphate buffer pH 7, 16.7 mM. (b) The RB peak absorbance as a function of SB-12 to RB molar ratio; RB 5 μM, plot **a** (*Y* scale is multiplied five times), optical pathlength, 0.2 cm; RB 100 μM, plot **b** (optical pathlength, 0.1 cm).

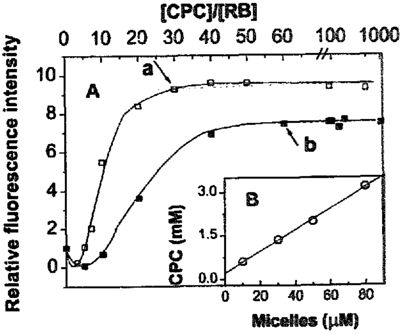

Fig. 3. The influence of CPC on the fluorescence spectra of RB. (a) Relative fluorescence intensity of RB as a function of CPC to RB molar ratio; samples contained 50 μM RB, **a** and 10 μM RB, **b**. (b) Plot of CPC concentration against the concentration of micelles containing RB molecules; phosphate buffer pH 7, 16.7 mM. Fluorescence amplitude at the λ_{max} of RB was used for calculation.

Ionic dyes can strongly interact only with the oppositely charged surfactant molecules; we observed no premicellar aggregation of the RB dianion with neutral Triton X-100 or with anionic sodium dodecyl sulfate (SDS) detergents. Therefore, the presence of the cationic center in the surfactant molecule is necessary for premicellar RB aggregation to occur.

3.2. Semi-organized premicellar J-aggregates

It is well known that in aqueous solution aggregation processes are generally affected by salts, and we have noted previously that the premicellar aggregation of RB with cationic surfactants depended on buffer concentration [18,32]. Here, we have examined in detail how different salts may influence the premicellar aggregation of RB with the cationic CPC and zwitterionic SB-12 surfactants. We have used KCl to enhance the aggregation of RB with CPC. For SB-12, we have selected $NaClO_4$ which only induced the formation of the semi-organized J-PAs, while other salts could produce a different type of PA with SB-12 (vide infra).

Titration of RB fluorescence in the region of the premicellar aggregates produced from SB-12 and CPC is shown in Fig. 4(a) and 4(b), respectively. At a CPC/RB ratio of exactly 2:1, the $RB(CPC)_2$ ion pair precipitated from water [18], but we observed no such precipitation when any of the

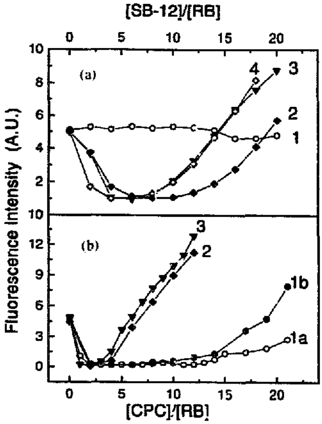

Fig. 4. The fluorescence intensity of RB (50 μM) during titration with surfactant in the region of premicellar aggregation. (a) The semi-organized J-PAs formed by RB and SB-12; no salt, **1**; $NaClO_4$ concentration: 0.2 M, **2**; 0.5 M, **3**; 1 M, **4**. (b) The semi-organized J-PAs formed from RB and CPC; no salt, **1a** (observed immediately after preparation), and **1b** (observed after one day storage); KCl: 0.2 M, **2**; 0.5 M, **3**. Fluorescence amplitude at the λ_{max} of RB was used for calculation.

zwitterionic surfactants SB-X interacted with RB. The fluorescence and absorption spectra of RB in the semi-organized PAs are broad and have been described previously [18]. For RB in water without an electrolyte, the PAs with CPC were formed immediately after sample preparation (Fig. 4(b) (**1a**), and changed little with time (**1b**). The presence of KCl (0.2 M, **2** and 0.5 M, **3** (Fig. 4(b)) significantly narrowed the relative CPC/RB concentration region where CPC PAs were present. For SB-12, there was no aggregation in the absence of electrolyte (Fig. 4(a), **1**), but $NaClO_4$ salt (0.2 M, **2**; 0.5 M, **3** and 1 M, **4**) induced PA formation starting at a 2:1 [SB-12]/[RB] molar ratio (Fig. 4(a)).

In addition to decreasing RB fluorescence, premicellar aggregation resulted in measurable light scattering, although the solutions remained transparent. This light scattering was easily observed at the excitation wavelength (Fig. 6(c)). Premicellar solutions of CPC and SB-X with various salts scattered no light when RB was omitted, indicating that larger particles (aggregates) were formed only in the presence of the RB anion. Similar light scattering was also observed for novel J-aggregates (vide infra). The light scattering data suggest that the size of the RB/surfactant aggregates may depend on the absolute component concentrations, because the number of ion pairs binding together in the aggregates may vary. However, such variation hardly affected the absorption and fluorescence spectra of the RB, except at the aggregation threshold, i.e. at very low concentrations of RB, surfactant and salt.

The fluorescence intensity of RB decreases more in CPC than in SB-12 PAs (Fig. 4), suggesting that RB has a greater propensity to aggregate premicellarly with CPC than with SB-12. This tendency is presumably due to the presence of two ionic centers in the zwitterionic SB-12 molecule (Fig. 1), which makes it less hydrophobic than the CPC cation. Thus, the PAs with CPC are sufficiently hydrophobic to aggregate easily, forming more compact PAs in which RB photobleaches faster than in the PAs from SB-12. The propensity of other SB-X surfactants to form PAs increases with increasing length of the alkyl chain: SB-16 and SB-14 formed RB PAs much more easily than SB-10, and SB-8 formed scarcely any PAs with RB. All the PAs in solutions without added salt were normal semi-organized J-aggregates.

The stoichiometry of the semi-organized RB J-PAs appears to be less well defined than that of the micellar RB, whose aggregation numbers are quite accurately measurable [32]. RB fluorescence in SB-12 and CPC PAs reaches a minimum at ratios of 2 < [SB-12]/[RB] < 15, and < 2[CPC]/[RB] < 5 respectively (Fig. 4(a) and 4(b)). For the PAs to be formed, this ratio must obviously be higher than 2, which is necessary for the electrical neutralization of the RB dianion in an ion pair. At ratios below the micellar aggregation numbers [32], the PAs may co-exist with micelles, or may exist alone, depending on salt and surfactant concentrations. The spectral changes that are observed for RB in the common PAs formed from CPC and from most SB-X are characteristic of 'loose' J-type aggregates in which the RB molecules are semi-organized in a 'head-to-tail' fashion.

3.3. *Novel, highly structured premicellar J-aggregates*

When salts smaller than $NaClO_4$, such as NaF, KCl, NaCl, KBr, $MgCl_2$, Na_2SO_4, $MgSO_4$ or $N(CH_3)_4Cl$, were added to an RB/SB-12 solution, they induced the formation of novel PAs. Such PAs could be induced when the [SB-12]/[RB] ratio was higher than 2 but lower than that necessary for micelle formation. Fig. 5(a)–5(d) shows the absorption spectrum of RB during its transformation into an aggregated form that has a very characteristic sharp absorption at 586 nm (Fig. 5(d)).

The absorption spectrum of RB in these novel PAs is strongly red-shifted (about 37 nm) and very narrow (Figs. 5(d) and 6(a)). The absorption obeys the Lambert–Beer law, provided that the proper salt is used and an appropriate [SB-12]/[RB] ratio is maintained[1] (Fig. 6(b)). Under such conditions, the extinction coefficient $\epsilon_{568\ nm} = 2.8 \times 10^5$ M^{-1} cm^{-1} is almost three times higher than $\epsilon_{548\ nm}$ for free RB^{32}, and is one of the highest reported for RB. Similarly strong absorption bands have been observed for some aggregated forms of RB by Luttrull et al. [31b]. However, their spectra [31b] were broad and less red-shifted, and more

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[1] These rations were chosen to obtain a linear dependence originating at the zero RB concentration in order to measure the molar extinction coefficient of 'excitonic' RB.

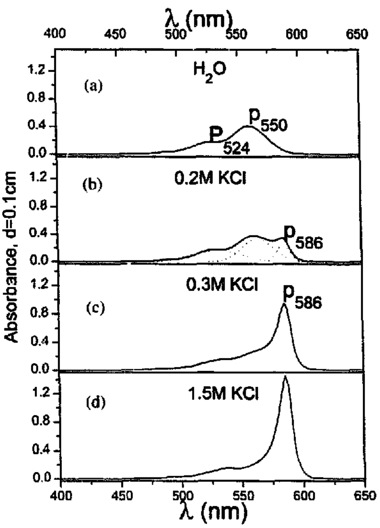

Fig. 5. Salt-induced transformation of RB (50 μM) from semi-organized J-PAs into highly structured novel J-PAs shown by the changes in RB absorption. SB-12 to RB molar ratio, 15. No salt (A); 0.2 M KCl (B); 0.3 M KCl, (C); 1.5 M KCl (D).

closely resembled the spectra of J-PAs in the solid state (Fig. 9(c)) than those observed in the salt solutions of SB-12.

Monitoring the new absorption band at 586 nm allowed us to measure a threshold for RB transformation into the novel PAs as a function of salt concentration (Fig. 7). The spectra were deconvoluted to follow the transformation more closely. Both the peak positions and the peak areas, plotted versus the salt concentration, produced similar plots (Fig. 7(a) and 7(b), respectively). The lowest threshold value where novel PAs start to form is around 0.1 M for KBr, but this value can increase to as much as 0.5 M when other salts such as NaCl are used. The same procedure and calculation using $Mg(ClO_4)_2$ revealed no such drastic spectral changes (Fig. 8); neither did potassium iodide (not shown).

One plausible explanation why both I^- and ClO_4^- anions block the formation of novel PAs may involve their competition with the RB dianion for the cationic center in the SB-12 molecules. I^- and ClO_4^- seem to be sufficiently polarizable to actually displace the RB anion when present at much higher concentrations than RB. This effect may prevent the formation of properly structured RB ion pairs with surfactant molecules, which is an essential step in premicellar aggregation.

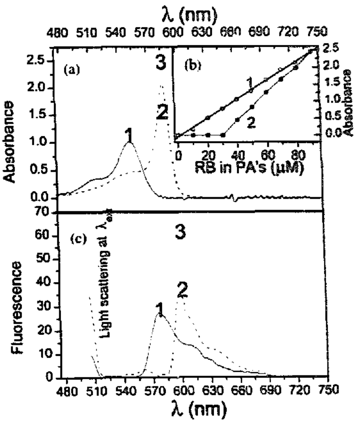

Fig. 6. Spectral changes observed during the transformation of free RB into salt-induced highly structured J-PAs. (a) Absorption spectra of RB (50 μM) in 0.5 M KCl solution at different SB-12 to RB molar ratio: no SB-12, spectrum 1; ratio 2, spectrum 2; ratio 20, spectrum 3. Inset (b) Absorbance increase at 568 nm with increasing RB concentration in novel PAs: KCl, 0.5 M; SB-12 to RB molar ratio was 3 for plot 2; the ratio was gradually decreased from 14 to 6 (respective to the experimental points in ascending order) to avoid micelle formation, line 1. (c) Fluorescence emission spectra of RB (50 μM) in 0.5 M KCl solution at different SB-12 to RB molar ratios: no SB-12, spectrum 1; ratio 2, spectrum 2; ratio 20, spectrum 3.

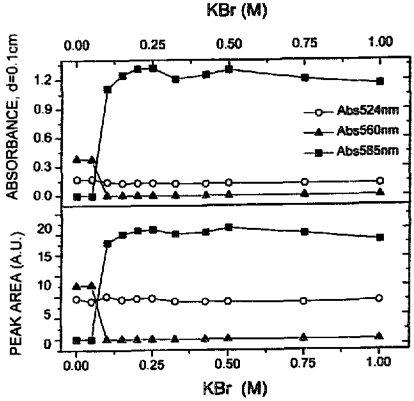

Fig. 7. Effect of KBr on the transformation of free RB into salt-induced highly structured J-PAs. Deconvoluted peak (a) and integral (b) absorbance of semi-organized (triangles) and novel RB J-PAs (squares). RB, 50 μM; SB-12 to RB molar ratio is 15.

These novel PAs are also not formed when eosine is substituted for RB, probably because eosine is not sufficiently polarizable. Nor were the novel PAs easily formed when SB-12 was replaced by other surfactants. Apparently the steric requirements necessary to produce the novel PAs from RB are fully satisfied only by SB-12. While one of its close homologs, SB-10, was able to induce free exciton transition

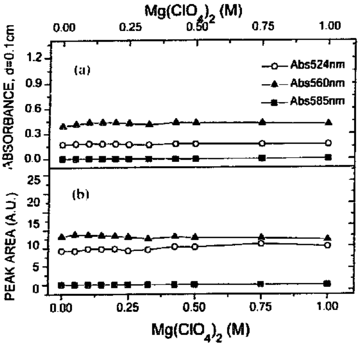

Fig. 8. Effect of $Mg(ClO_4)_2$ on the transformation of free RB into novel SB-12 J-PAs. Deconvoluted peak (a) and integral (b) absorbance of semi-organized (triangles) and missing novel J-PAs (squares); RB, 50 μM; [SB-12]/[RB] molar ratio, 15.1.

in the presence of some salts such as $MgSO_4$, the other SB-14 homolog failed to transform RB into the novel PA form. Even though a weak characteristic residual absorption peak at 585 nm appeared in very concentrated salt solutions containing SB-14, the peak was dominated by the absorption from either ordinary PAs or from the micellar RB, depending on the concentrations of the surfactant and salt.

In the presence of 1 M NaCl and SB-12 surfactant at a high enough concentration to start forming micelles [2], the RB micelles and the salt-induced novel PAs coexisted. This is evidenced by the gradual transformation of J-aggregated RB into a micellar RB upon increasing salt concentration, which is shown in Fig. 9(a). The arrow indicates the composite transitory spectrum [3] in Fig. 9(b) that was observed at that NaCl concentration. The coexistence of novel J-PAs and micelles suggests that under such conditions, the stability of the structured J-PAs may be comparable to micelles.

High stability of the novel PAs may be reflected in RB fluorescence: the fluorescence intensity in the novel J-PAs is higher than for free RB in water (Fig. 6(c), spectrum 3). This is in contrast to the strongly decreased fluorescence of RB in ordinary J-PAs (Fig. 4). The RB chromophores may be sufficiently separated in the novel PAs to prevent fluorescence self-quenching, in contrast to the proximity of RB molecules in the common premicellar aggregates, which usually promotes quenching [32]. It is also possible that the microenvironment in the novel PAs might be sufficiently aprotic to red-shift and enhance RB fluorescence [34]. Also, some J-aggregates can induce superradiance [35,36], which would increase fluorescence.

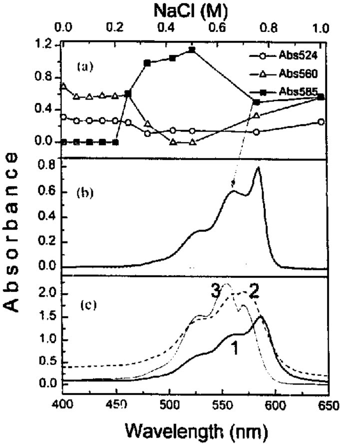

Fig. 9. Spectral changes observed during the transformation of J-PAs into micelles ((a), (b)) and after the induction/precipitation of J-PAs with $MgBr_2$ (c). (a) Transition of semi-organized J-PAs into novel J-PAs that were then transforming into micelles. The transformation was observed by plotting the deconvoluted peak absorbance at 585, 560, and 524 nm as a function of the NaCl concentration: RB, 50 μM; [SB-12]/[RB] = 17; an arrow connects the experimental point with the corresponding transitory spectrum. (b) The transitory spectrum showing RB coexistence in novel J-PAs and in micelles in NaCl solution. (c) The absorption spectra of RB observed during the precipitation of J-PAs by $MgBr_2$: spectrum **1**, 2 min after $MgBr_2$ addition (0.5 M) to the solution containing RB and SB-12 at 1:3 ratio; spectrum **2**, precipitated J-PAs spread on a quartz plate and dried; spectrum **3**, the same as **2** but after hydration in air.

3.4. Premicellar J-aggregates in solid state

A mixture of different types of J-PAs formed from RB and SB-12 could be precipitated from aqueous solution when $MgBr_2$ was used as an electrolyte. Such mixtures contained both semi-organized and structured J-PAs as evidenced by the absorption spectra. After $MgBr_2$ addition (0.5 M) to the solution containing RB and SB-12 at the 1:3 ratio, the color changed from red to violet, and a faint, silky precipitate started to form. The absorption spectrum taken a few minutes after $MgBr_2$ addition clearly showed the presence of a dominating peak at 585 nm that is characteristic of the novel J-aggregates (Fig. 9(c), spectrum **1**). After several days, the precipitate clumped together, forming a new phase that resembled more a liquid crystalline phase than a solid. This phase was very hygroscopic when separated and dried.

We spread the new phase on a quartz plate to measure the absorption spectra, which is shown in Fig. 9(c). The spectrum is broad, especially when measured for the dried aggre-

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[2] The aggregation number of the SB-12 micelles containing RB is lower in concentrated salt solution then in water (unpublished results).

[3] A similar spectrum was also observed when semi-organized J-PAs were transforming into highly structured J-PAs (not shown). This was because a contribution of novel J-PAs was comparable, and the position of RB absorption band in semi-organized PAs is similar to that in micelles. Despite the similarity in absorbance, both transitory regions could be distinguished by RB fluorescence, which was stronger in micelles and reduced in semi-organized PAs.

gates (spectrum 2). Nevertheless, novel J-aggregates seem to be confined within the absorption profile of the aggregates mixture, because a peak which may belong to the structured J-PAs started to reappeared upon hydration (Fig. 9, spectrum 3). These preliminary results suggest that the structured RB aggregates may be assembled in the solid state [4].

The peculiar spectral properties of RB can be caused by orderly 'stacking' of multiple RB chromophores in the molecular arrays of novel J-PAs. Such a high degree of organization may lead to strong dipole–dipole coupling [19–23] and free exciton transitions between the dye molecules [19–23]. This is in contrast to the weaker interaction and apparently less regular RB placement in semi-organized PAs. While the RB absorbance in the novel J-aggregates is quite characteristic of free exciton transition, more research is needed for absolute confirmation.

4. Conclusions

When the RB dianion interacts with the cationic center in zwitterionic and cationic surfactant molecules, it produces ion pair associates which may form premicellar aggregates, important transitory species preceding RB micelles. While electrolytes strongly enhance premicellar aggregation with cationic surfactants, they are essential for PA formation from zwitterionic surfactants whose ion pairs are less hydrophobic. All PAs we studied have a J-type structure. Most commonly formed are semi-organized premicellar RB aggregates with broad absorption spectra and strongly decreased fluorescence. Of the combinations we have studied thus far, only Rose Bengal with SB-12, in the presence of salts with non-polarizable anions, easily formed in solution a novel PA species with sharp absorption and increased fluorescence. These novel RB J-PAs are stable in aqueous solution, and may co-exist with micellar RB in concentrated electrolytes. Our findings suggest that the RB chromophores may show a free exciton transition while aggregated in an appropriate environment.

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[4] This may prove to be very useful because RB has such exceptionally strong photoredox and photosensitizing properties: the RB triplet state is formed with almost 100% efficiency [37]. Other J-aggregated dyes often featuring exciton transition such as carbocyanines [38], spiropyrans (merocyanines) [39], or porphines [27,40] have been investigated intensively. Highly structured J-aggregates are finding application in photography [41,42], and are promising as non-linear optical devices [39b].

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