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Spectrophotometric investigation of the monomer–dimer process of C.I. Basic Blue 9 in aqueous polymer–surfactant system

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ABSTRACT

The monomer–dimer process of C.I. Basic Blue in an aq. solution of the anionic surfactant, sodium dodecyl sulfate and the nonionic polymer, polyvinyl alcohol, was investigated spectrophotometrically. The effective dimerization constant of the dye (${}^{\mathrm{eff}}K_D$) was determined in the presence of the surfactant and polymer, both individually and in combination, from a low ionic strength buffered aq solution; the value of ${}^{\mathrm{eff}}K_D$ increased in the order: PVA $<$ SDS $<$ PVA–SDS $<$ H_2O. Aggregation of the dye in the polymer–surfactant system was exothermic and displayed large negative ΔH^o and negative ΔS^o values. Below the CAC, the presence of surfactant facilitated dye dimerization whereas $>$ CAC the dye dissolved monomerically in the surfactant/polymer complex; the monomer–dimer process of the dye was influenced by hydrophobic interactions.

1. Introduction

Aqueous polymer–surfactant systems have been the subject of intense research owing to their extensive industrial, cosmetic and pharmaceutical applications [1–5]; they also mimic many biological systems [1,3]. The interaction of dyes with surfactants and with polymer–surfactant systems are often used to determine changes in the physiochemical properties of aqueous biological systems, as well as the determination of the critical micelle concentration (CMC) and critical aggregation concentration (CAC) and the modelling of dye–surfactant and polymer–surfactant interactions [2,3,6,7].

The thiazine dye, C.I. Basic Blue 9 (BB9), is known to aggregate in aqueous solution [6–11]. It is widely held that the dye undergoes self association to form dimers, trimers and higher aggregates. The forces responsible for such aggregations are believed to be hydrogen bonding, van der Waal's forces, London dispersion forces and hydrophobic interactions [9–13]. The strength of such molecular aggregation depends upon both the concentration and structure of the dye, temperature, pressure, solvent and other factors [14–20]. However the monomer–dimer process of BB9 in aqueous micellar medium has not been clearly established, nor has it been extensively investigated in polymer–surfactant systems.

The present work concerns the spectrophotometric investigation of the monomer–dimer process of C.I. Basic Blue 9 in aqueous medium, in the presence of the anionic surfactant, sodium dodecyl sulfate (SDS), the nonionic polymer, polyvinyl alcohol (PVA) and in the presence of both SDS and PVA. The concentration of the dye was maintained in the range 10^{-6} to 10^{-3} M so that only monomer–dimer equilibrium exists [7].

2. Experimental

Methylene blue (3,7-bis[dimethylamino] phenazothionium-chloride) (C.I. Basic Blue 9 (BB9)) obtained from S.D Fine Chemicals, India was recrystallized from ethanol. Sodium dodecyl sulfate (SDS) obtained from Aldrich was stirred overnight in ether and then recrystallized from ethanol. Polyvinyl alcohol (PVA) (M.W 14 000) obtained from Central Drug House, Mumbai, India were used as such. All solutions were prepared in doubly distilled water.

The spectra were recorded in Thermo Electron UV1 spectrophotometer using thermostated cell holder. The temperatures were maintained within ± 1 K. Buffer solutions were prepared following the Tables of Perrin having ionic strength of 0.001 [2].

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3. Results and discussion

3.1. Effective dimerization constant ($^{eff}K_D$)

In the experimental concentration range of MB it was assumed that only monomer–dimer equilibrium is possible, in accordance with the process;

$$2M \overset{K_D}{\rightleftharpoons} D \tag{1}$$

where M and D are the monomer and the dimer species of MB respectively and K_D is the dimerization constant which can be defined as;

$$K_D = C_D/(C_M)^2 \tag{2}$$

where C_D and C_M are the concentrations of the dimers and the monomers, respectively. The components concentration can be expressed by the following mass balance equation;

$$C_M + 2C_D = C_0 \tag{3}$$

where C_0 is the analytical molar concentration of the dye.

or,

$$X_i^M + X_i^D = 1 \tag{4}$$

where x_i^M and x_i^D are the respective mole fractions of the monomer and the dimer which can be defined as;

$$x_i^M = C_M/C_0 \tag{5}$$

$$\text{and } x_i^D = C_D/C_0 \tag{6}$$

Using eqn.' s (2), (4), (5) and (6) we have,

$$K_D = x_i^D/2C_0(x_i^M)^2$$

$$= (1 - x_i^M)/2C_0(x_i^M)^2 \tag{7}$$

Further, considering the monomer–dimer process in SDS–PVA system we have for the 1.0 cm path length cuvette,

$$A = \varepsilon_M^f C_M^f + \varepsilon_M^b C_M^b + \varepsilon_D^f C_D^f + \varepsilon_D^b C_D^b \tag{8}$$

where ε_M^f, ε_M^b, ε_D^f and ε_D^b are the molar extinction coefficient and C_M^f, C_M^b, C_D^f and C_D^b are the concentrations of the respective free and bound monomer and dimer species of BB9. Since the pH and the measuring wavelength are fixed, we can assume that $\varepsilon_M^f = \varepsilon_M^b$ and $\varepsilon_D^f = \varepsilon_D^b$. Then Eq. (8) reduces to;

$$A = \varepsilon_M C_M + \varepsilon_D C_D \tag{9}$$

where C_M and C_D are the total concentrations of the monomer and dimer species, respectively, i.e., $C_M = C_M^f + C_M^b$ and $C_D = C_D^f + C_D^b$ and ε_M and ε_D are the molar extinction coefficients of the monomer and dimer of BB9 at the monomer band maximum.

Regardless of the final location of the species (i.e., in water, micellar pseudophase or surfactant bound polymer surface), we can define the effective dimerization constant ($^{eff}K_D$) from the deviation value of absorbance from the absorbance value provided by Beer's–Lambert's law, ΔA as follows [9–11]:

$$^{eff}K_D = 2(\Delta A)(\Delta\varepsilon)/(2A - C_0\varepsilon_D)^2 \tag{10}$$

where, $\Delta A = (C_0\varepsilon_M - A)$ and $\Delta\varepsilon = (\varepsilon_M - \varepsilon_D/2)$.

Eq. (10) can be transformed into the following linear equation [10,11];

$$\frac{1}{\sqrt{\Delta A}} = (C_0/\Delta A)b - a \tag{11}$$

where $a = (\sqrt{2^{eff}K})/(\sqrt{\Delta\varepsilon})$ and $b = \sqrt{2^{eff}K_D\Delta\varepsilon}$

$\therefore \Delta\varepsilon = b/a$ and $^{eff}K_D = (ab)/2$.

$^{eff}K_D$ and $\Delta\varepsilon$ has been determined from the slope of the plot described by Eq. (11).

The molecular structure of C.I. Basic Blue 9 (BB9) is shown in Fig. 1. BB9 monomers and dimers have been characterized before and they have distinct absorbance spectra [4–7]. The spectral properties of methylene blue have been summarized in Table 1. The absorbance spectra of aqueous BB9 in absence and in the presence of SDS, PVA and SDS–PVA are shown in Fig. 2. In aqueous solution the two bands with absorption maxima at 612 and 664 nm can be attributed to the dimeric and monomeric forms of BB9 [6,9,11,18]. We have observed a small blue shift of the monomeric form in SDS and PVA–SDS system from 664 to 661 nm as shown in Fig. 2. For determination of $^{eff}K_D$ a series of solution at progressively increasing concentration of the dye, C_0 was prepared in water, in fixed concentration of SDS (3×10^{-3} M) and in fixed concentration of PVA (5%) for each set of experiment. The intensity of absorbance, A at 664 nm (monomer) was measured as a function of dye concentration in water and for the other systems the 661 nm was considered. The molar extinction coefficient of the monomer (ε_M) was determined from the absorbance of the most dilute dye solutions (i.e., 1.35×10^{-6} M) that were used. The molar extinction coefficient of the dimer (ε_D) was determined from the $\Delta\varepsilon$ value (as described earlier) and the value of ε_M. The values of ε_M and ε_D determined by the present method (Table 1) are in good agreement with the reported values. We did not find any reported value of ε_M and ε_D of BB9 in presence of SDS and PVA–SDS system. It may be noted that the present experiments were carried out in a well buffered medium of pH 7.0 (Perrin's table) [21]. The value of $^{eff}K_D$ determined for the above experiments are also in good agreement of those reported by other methods as shown in Table 2. We observed that the value of $^{eff}K_D$ of BB9 in water (3.88×10^3 M^{-1}) is about 10 times greater than its value in SDS micellar medium (3.61×10^2 M^{-1}), while its value is comparable to that observed in aqueous PVA–SDS system (2.25×10^3 M^{-1}). This indicates that there is decrease in hydrophobic interaction between the dye molecules in micellar medium compared with the hydrophobic interactions in water or in aqueous PVA–SDS system. In case of aqueous PVA–SDS system all the SDS micelles associates with the PVA chains and the excess polymer chain probably wraps around the micelles through transient bridge like structures as reported for similar systems [1,2]. As a result, the reduction of hydrophobic interactions between the BB9 molecules by micelles becomes less in the presence of PVA.

The spectra of BB9 in the presence of increasing concentration of SDS and PVA at 298 K and pH 7.0 are shown in Fig. 3 and Fig. 4. It has been observed that in case of SDS initially with increasing SDS concentration there is increase in the absorption intensity at 612 nm at the cost of the absorption intensity at 661 nm. However as the concentration of SDS reaches 1×10^{-2} M the absorption

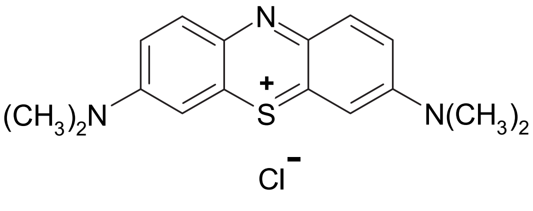

Fig. 1. Molecular structure of methylene blue (C.I. Basic Blue 9).

Table 1
Spectral properties of C.I. Basic Blue 9 (BB9).

Species	In aqueous solution		In SDS micellar medium		In SDS–PVA medium	
	λ/nm	$\varepsilon/10^4$ M^{-1} cm^{-1}	λ/nm	$\varepsilon/10^4$ M^{-1} cm^{-1}	λ/nm	$\varepsilon/10^4$ M^{-1} cm^{-1}
Monomer (BB9$^+$)	664 665[a]	8.3 7.3[b] 9.5[c]	661 665[e]	11.4	661	10.2
Dimer (BB9$^+$)$_2$	612 610[d]	12.8 13.2[c]	612 580[e]	15.6	612	14.8

[a] Ref. [8].
[b] Ref. [11].
[c] Ref. [26].
[d] Ref. [10].
[e] Ref. [6].

Table 2
Effective dimerization constants of C.I. Basic Blue 9 (BB9) at 298 K (±01).

Medium	Effective dimerization constant ($^{eff}K_D/10^3$ M^{-1})
Aqueous	3.88 3.80[a] 3.90[b]
Aqueous SDS (3×10^{-3} M)	0.361 0.295[a]
Aqueous PVA (5%)	0.213
Aqueous SDS–PVA [SDS] 3×10^{-3} M [PVA] 5%	2.25

[a] Ref. [6].
[b] Ref. [11].

intensity at 661 nm again increases and with higher concentration the spectrum becomes almost same as that of pure BB9 monomer as shown in Fig. 3. The increase in the dimerization at low concentrations of the surfactant was attributed by some researchers to a small volume of the micellar pseudophase under these conditions inducing higher local concentration of BB9 in the micelles enhancing dimer formation [3,6,19]. However, it can be noted that the increase in the dimerization has been observed when the SDS concentration is far below the cmc of the surfactant where micelle formation is unlikely. Moreover, reversal of the dye to the monomeric form at higher concentration of SDS indicates that the micelles rather favor the monomeric form.

On the other hand, the above observation can be conveniently interpreted in terms of formation of hydrophobicity induced close packed dye–surfactant ion pairs (DSIP) between the oppositely charged dye and surfactant at very low concentrations of the surfactant [22–25]. Micelle formation is unlikely when the concentration of SDS is very low. Under such conditions the cationic BB9 molecules are strongly attracted by the anionic monomeric SDS molecules leading to formation of closed packed DSIP like those reported in similar systems [22,24,25]. Due to the neutralization of the electric charge of the dye ion in the ion pair, the dye turns more hydrophobic and hence its dimerization increases. It is well known that the monomeric form of the dyes is favored when the dye molecules are incorporated to micelles. At high concentration of SDS, practically all the BB9 molecules are incorporated to the micelles and exist in the monomeric form [22–25].

However in case of PVA the absorption intensity at both 661 nm and 612 nm decreases initially with increasing concentration of PVA and when the PVA concentration reaches 0.4% the absorption intensity at both the wavelength increases as shown in Fig. 4. This indicates specific hydrophobic interaction between the cationic dye and the nonionic polymer. As we have reported earlier there is stacking of the dye molecules both in monomeric and dimeric forms at low polymer concentration [2]. However when all the dye molecules are attached to the polymer chains, any further increase in polymer concentration only results in formation of transient network structures dislocating the stacked dye molecules which results in recovery of the absorption bands at both the wavelength [1,2].

The spectra of BB9 in PVA–SDS system as a function of SDS concentration at 298 K and *p*H 7.0 is shown in Fig. 5. In presence of PVA (5%) the absorption intensity of BB9 at 612 nm increases with the reduction in the absorption intensity at 661 nm indicating aggregation of the dye. With the addition of SDS the absorption intensity of BB9 at 661 nm initially decreases at the cost of the absorption intensity at 612 nm which is similar to the spectral feature of the dye in presence of SDS alone. However, when

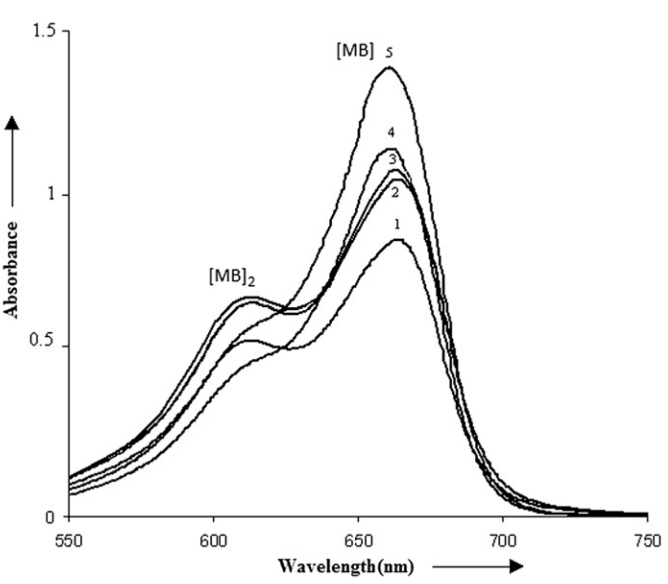

Fig. 2. The Spectra of BB9 (5×10^{-5} M) at *p*H 7.0 and 298 K (±01). [1{in water}; 2{in presence of 1.0% PVA}; 3{in presence of SDS (2.0×10^{-3} M and PVA (1.0%)}; 4{ in presence of SDS (1×10^{-1} M)}; 5{ in presence of SDS (1.6×10^{-2} M)}].

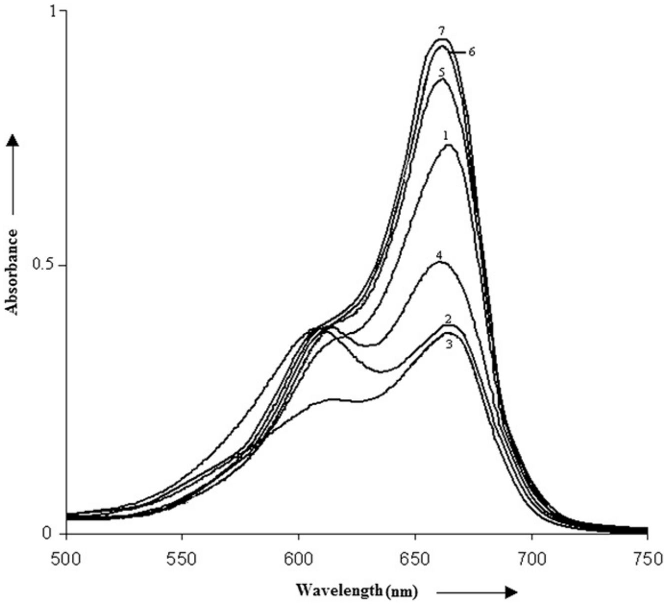

Fig. 3. Spectra of BB9 (5×10^{-5} M) at *p*H 7.0 in presence of various concentration of SDS at 298 K (±01). [SDS]/10^{-3} M: 1(2.0); 2(4.0); 3(6.0); 4(8.0); 5(10.0); 6(12.0); 7(14.0).

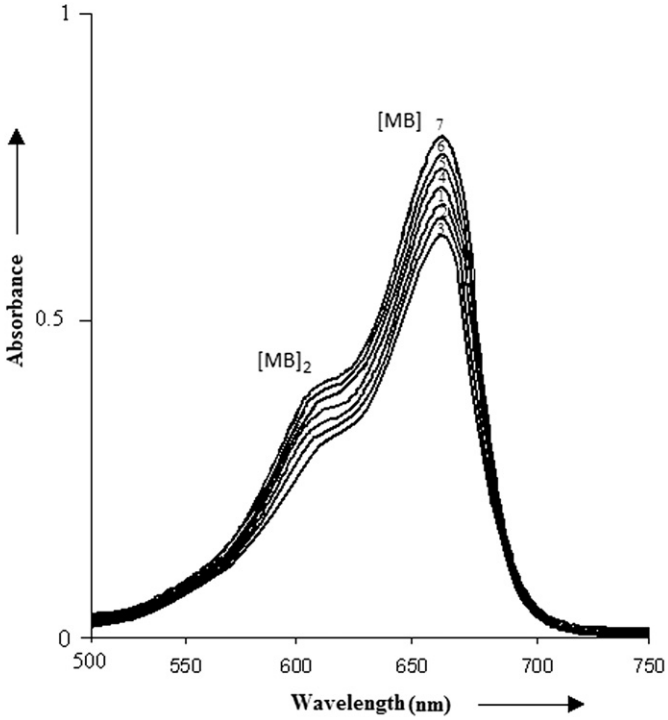

Fig. 4. Spectra of BB9 (5×10^{-5} M) at *p*H 7.0 in presence of various concentration of PVA at 298 K (±01). [PVA]:1(0.1%); 2(0.2%); 3(0.3%); 4(0.4%); 5(0.5%); 6(0.6%); 7(0.7%).

concentration of SDS exceeds 4×10^{-3} M there is recovery in intensity and a small shift of the monomer band towards shorter wavelength. At very high concentration of SDS the 612 nm dimer absorbance band completely disappears. A clear isobestic point was observed at 630 nm. The above spectral observations indicates that in surfactant free aqueous solution of nonionic polymer PVA, there is stacking of the cationic BB9 dye in both monomeric and dimeric forms leading to cooperative binding of the dye on the polymer domain. On addition of anionic surfactant SDS there is competition for binding site on PVA between BB9 and SDS, where SDS exhibits stronger binding to PVA [1,6]. When surfactant concentration is very high and probably exceeds the critical aggregation concentration (CAC), the dimer form of the dye almost disappears. This indicates that above CAC when surfactant aggregates are formed, the dye dissolves in monomeric form in the hydrophobic SDS–PVA complexes.

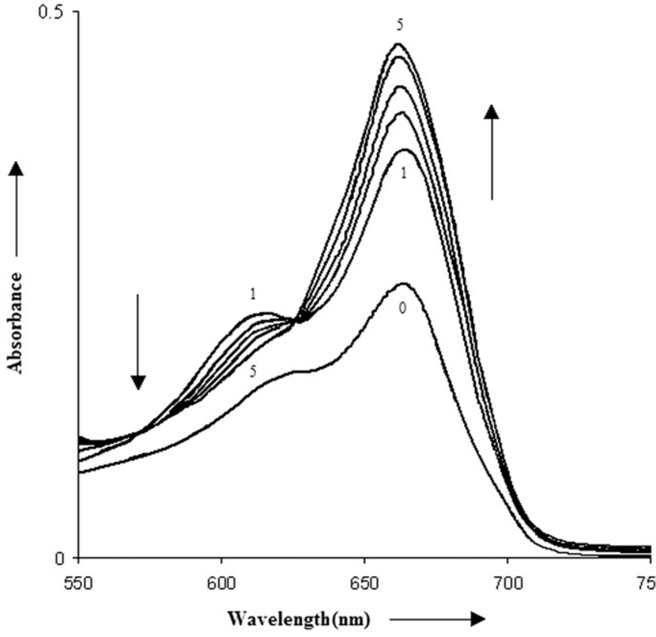

Fig. 5. Spectra of BB9 (4.5×10^{-5}) at *p*H 7.0 in aqueous solution of varying concentration of SDS in presence of 5.0% PVA (M.W 14000) at 298 K(±01). [SDS]/10^{-3} M: 0 (in water): 1(2.0); 2(4.0); 3(6.0); 4(8.8); 5(12.0).

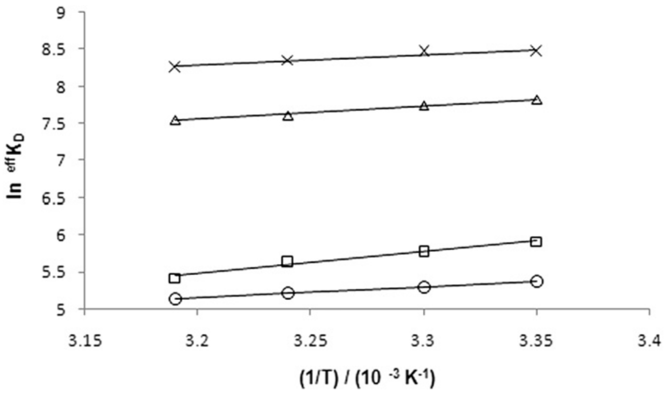

Fig. 6. van't Hoff plot for monomer–dimer process of BB9 at *p*H 7.0. Symbols: × (water); Δ (PVA–SDS); □ (SDS); ○ (PVA).

3.2. Thermodynamic parameters

Gibbs free energy change for the monomer–dimer process of BB9 has been determined by using Eq. (12).

$$\Delta G^0 = -\text{RT} \ln {}^{\text{eff}}K_{\text{D}} \tag{12}$$

ΔH^0 has been estimated from the slope of the approximating line according to the van't Hoff's relation;

$$\frac{\text{d}(\text{In}^{\textit{eff}}K_{\text{D}})}{\text{d}(1/T)} = \frac{-\Delta H^0}{R} \tag{13}$$

Some representative van't Hoff's plots are shown in Fig. 6. The linearity of the plots indicates the validity of the present method. ΔS^0 values were derived from ΔG^0 and ΔH^0 values.

$$\Delta S^0 = -(\Delta G^0 - \Delta H^0)/T \tag{14}$$

The values of the thermodynamic parameters are shown in Table 3. The relatively large negative ΔH^0 values indicate that the monomer–dimer process of BB9 in aqueous medium in the systems studied is exothermic. The ΔH^0 value is much lower in presence of surfactant or polymer as expected. The negative ΔS^0 values indicate

Table 3
Thermodynamic parameters for monomer–dimer process of C.I. Basic Blue 9 (BB9) at 298 K (±01).

Medium	$-\Delta G^0$/k J mol^{-1}	$-\Delta S^0$/J mol^{-1} K^{-1}	$-\Delta H^0$/k J mol^{-1}
Aqueous	20.5 20.0[a]	64.7 116[b]	39.8 59.1[b]
Aqueous SDS (3×10^{-3} M)	14.6	25.5	22.2
Aqueous PVA (5%)	13.3	7.7	15.6
Aqueous SDS–PVA [SDS] 3×10^{-3} M [PVA] 5%	19.2	31.8	28.7

[a] Ref. [11].
[b] Ref. [12].

that the monomer–dimer process of BB9 is not driven by entropy as expected for more ordered dimer formation. Hydrophobic interactions probably help the system to get rid of the thermodynamically unfavorable state which is reflected in the large negative ΔH^0. The results are also in consistent with dispersive van der Waals interaction of aromatic dye chromophore during aggregation. Such interactions are characterized by both negative enthalpy and negative entropy [12,14,19]. Hence monomer–dimer process of BB9 in aqueous medium, in presence of surfactant or polymer or both has an enthalpic origin.

4. Conclusion

Monomer–dimer equilibrium of BB9 been investigated spectrophotometrically in aqueous medium, in presence of SDS and in PVA–SDS system. It was observed that the value of ${}^{\mathrm{eff}}K_{\mathrm{D}}$ of BB9 in SDS is about ten times smaller compared to its value in water. However in PVA–SDS system the value of ${}^{\mathrm{eff}}K_{\mathrm{D}}$ is comparable to its value in water. Aggregation of BB9 in PVA–SDS system was found to be exothermic and driven by hydrophobic interactions. Below its CAC, presence of SDS facilitates dimerization of BB9 but above its CAC, the dye dissolves in the monomeric form in the hydrophobic PVA–SDS complex. The monomer–dimer process of BB9 in aqueous medium, in presence of surfactant or polymer or both has an enthalpic origin.

The reported spectroscopic method for determination of ${}^{\mathrm{eff}}K_{\mathrm{D}}$ and thermodynamics of monomer–dimer equilibrium of BB9 can be used for investigating the thermodynamics of aggregation of other dyes in similar systems.

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