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ORIGINAL CONTRIBUTION

Stoichiometric complexes of polyelectrolyte and azo-functionalized surfactant

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Abstract The Stoichiometric (1:1) complexes, comprising of a quaternary ammonium surfactant derived from azobenzene and the anionic polyelectrolyte poly(styrene sulfonate), were studied in solution. The studies were based on UV/Visible spectroscopy. Furthermore, aqueous solutions were prepared by the addition of excess surfactant. The kinetic data ($t_{1/2}$ and % *cis*) for the complexes in water with added dodecyltrimethylammonium bromide (DTAB) were collected, which suggests that the 1:1 complexes are resolubilized in water by the additional DTAB.

Keywords Polyelectrolyte · Surfactant · Azobenzene · Complexes

Introduction

The practical importance [1] of the interactions between charged polymers and surfactant molecules, in the pharmaceutical, cosmetics, paint and coating industries, has led to intensive research within this area [2–4]. The mixing of polyelectrolytes and oppositely charged surfactants leads to the formation of aggregates with different three-dimensional structures, due to electrostatic and hydrophobic interactions. The type of structure formed is heavily dependent on the charge stoichiometry of the complex. For example, ratios of charged groups of polyelectrolyte > surfactant lead to a “string-of-pearls”-like morphology of surfactant micelles lined up along the polymer backbone [5], whereas stoichiometric charge ratios of polyelectrolyte and surfactant form highly stable and water-insoluble structures. These latter configurations, more commonly known as 1:1 complexes, are soluble in organic solvents [6] and may form nano- or micro-scale structures (e.g., lamellar) in solid films. The ease of preparing the 1:1 complexes and the wide range of different polyelectrolytes and surfactants that can be used provide an attractive way to tailor the macroscopic properties of materials. They have been investigated in both (organic) solutions and in the solid state by Antonietti et al. [7–10], MacKnight et al. [11–13], and Bazuin et al. [14–16] among others [17–20].

Modification of these 1:1 complexes by incorporation of specific functionalities offers a unique avenue for the formation of “smart” responsive materials with a high degree of order that can be easily and cheaply fabricated. We have been developing such 1:1 complexes that contain molecular switch that could lead to their use in optical storage devices[21–23], sensors [24], viscosity modifiers [25], and biomaterials [26, 27]. One such common switch is azobenzene. This switch undergoes *trans* → *cis* isomerization upon photoirradiation, and reverse process of *cis* → *trans* can be triggered both photochemically and thermally [28, 29]. The isomerization causes a decrease in the distance between the para carbon atoms in azobenzene from about 9.0 Å in the *trans* form to 5.5 Å in the *cis* form. The dipole moments are also different; *trans*-azobenzene has no dipole moment while the *cis* isomer has a dipole moment of 3.0 D. Thermal reversion of the *cis*- to *trans*-azobenzene occurs in the dark and generally follows first-order kinetics. In substituted azobenzene moieties, the

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thermal reversion process is influenced by microenvironment properties such as polarity, viscosity, and free volume. Hence, the azobenzene moiety not only provides a mechanism by which the structure of these complexes in solution can be probed [30], but also may give rise to stimuli responsive materials, an aspect of this work we will discuss in a forthcoming publication.

The goal of this work is to study 1:1 complexes, comprising of a quaternary ammonium surfactant derived from azobenzene and the anionic polyelectrolyte poly (styrene sulfonate) (PSS), in solution. Studies were based on UV/Visible spectroscopy. Furthermore, aqueous solutions prepared by the addition of excess surfactant were also studied.

Experimental

Materials

All solvents and starting compounds were purchased from either VWR Scientific or Aldrich and used as received, except poly(styrene sulfonate) (Aldrich, PSS, M_n~70,000) which was purified by precipitation from water into a propanol/methanol (3:1 *v*/*v*) mixture, and dodecyltrimethylammonium bromide (Aldrich, DTAB) which was purified by recrystallization from acetone. All water used was deionized.

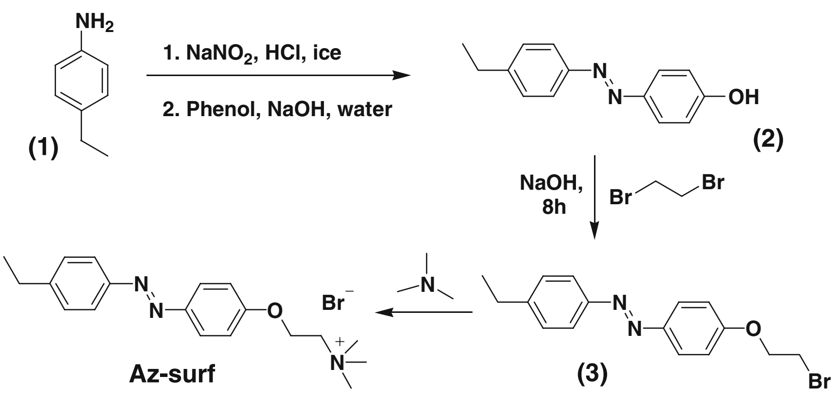
Azo-modified surfactant synthesis

The azo-modified surfactant (Az-surf) was synthesized in three steps following the previously reported procedure [31] (Scheme 1). Ice (10.0 g) and concentrated HCl (25.0 ml) were added slowly to a solution of (**1**) (15.5 ml, 0.12 mol) dissolved in 1:1 water/ethanol (75.0 ml) in an ice bath. Sodium nitrite (8.56 g, 0.12 mol), dissolved in 1:1 water/ethanol (75.0 ml), was added dropwise to the solution above to form the diazonium salt. Sodium hydroxide (9.9 g, 248 mmol) and phenol (17.5 g, 180 mmol) were dissolved in water (50.0 ml) and added dropwise to the diazonium salt solution in an ice bath with constant stirring for 90 min. The solution was acidified using concentrated HCl and left stirring at room temperature for 2.5 h. The solid formed (**2**) was filtered, washed thoroughly with water, recrystallized from ethanol/water, and left to dry overnight in a vacuum oven (yellow/brown solid, 25.0 g, 92%). (**2**) (5.0 g, 22 mmol), 2-dibromoethane (12.4 g, 66 mmol) and NaOH (2.2 g, 55 mmol) were dissolved in ethanol (60.0 ml) and refluxed for 10 h under nitrogen. The reaction mixture was left to stand at room temperature for 6 h, was then filtered, and washed with water. The product (**3**) was collected and dried in a vacuum oven overnight. The final step was reacting (**3**) (1.0 g, 3 mmol) with trimethylamine (2.2 ml, 33% by weight in ethanol) in THF (60.0 ml) under reflux for 48 h. The Az-surf formed precipitated out of THF, the mixture was filtered when hot, and was left to dry in a vacuum oven (50 °C) overnight (orange solid, 0.38 g, 32%).

Synthesis of 1:1 charge complexes

Two complexes with different amounts of Az-surf were synthesized with mole ratios of PSS/DTAB/Az-surf=1:0:1 (complex A) and 1:0.9:0.1 (complex B) (the mole ratio of the PSS is based upon each repeat unit). The surfactant(s) were dissolved in water and added dropwise to a stirring aqueous solution of PSS and left to stir for 1 h. For 1:1 complex A, 0.380 g (9.69×10^{-4} mol) Az-surf was dissolved in 10 ml water and added to 0.191 g (9.26×10^{-4} mol) PSS in 30 ml water. For 1:1 complex B, 2.575 g DTAB (8.34×10^{-3} mol), 0.361 g (9.20×10^{-4} mol) Az-surf were dissolved in 50 ml water and added to 1.91 g (9.26×10^{-3} mol) PSS in 150 ml water. The solution was decanted and the solid washed twice with water to remove NaBr and filtered. Complexes A and B were dried in a vacuum oven (50 °C) overnight.

Scheme 1 Outline of the synthesis of Az-surf



Structural characterization of complexes

Composition of the complexes was confirmed using ^{1}H NMR. Further verification of A and B was obtained using UV/Vis spectroscopy via a Beer's law plot of the free Az-surf.

Kinetics of thermal reversion process

Thermal reversion of azo-containing compounds (*cis* → *trans*) was followed using a Perkin-Elmer UV/Vis spectrophotometer at 25 °C. The *cis* isomers were obtained upon irradiating the *trans* at 365 nm for 15 min using a hand-held UV lamp. Thermal reversion *cis* → *trans* in all compounds obeyed a first-order kinetic rate law. Stock solutions were made up of approximately 5 mg of each complex dissolved in 10 ml of solvent, then diluted further (into 2 ml solvent) until the total azo concentration was ~10^{-5} M.

Results and discussion

To probe the structure of the 1:1 complexes in aqueous and non-aqueous solutions, we prepared two compositionally different 1:1 complexes which would allow for the comparison in switching efficiency of an azobenzene-rich environment against a similar material yet with lesser quantity of the Az-surf. Complex A had mole ratios of PSS/DTAB/Az-surf=1:0:1 (i.e., 50 mol% Az-surf) while complex B had mole ratios of 1:0.9:0.1 (i.e., 5 mol% Az-surf). To characterize the switching efficiency of the azo group within the 1:1 complex, we have studied the kinetics of *cis* → *trans* thermal reversion of the azo-unit in the complexes dispersed in a polar organic solvent (dimethyl sulfoxide (DMSO)) and water.

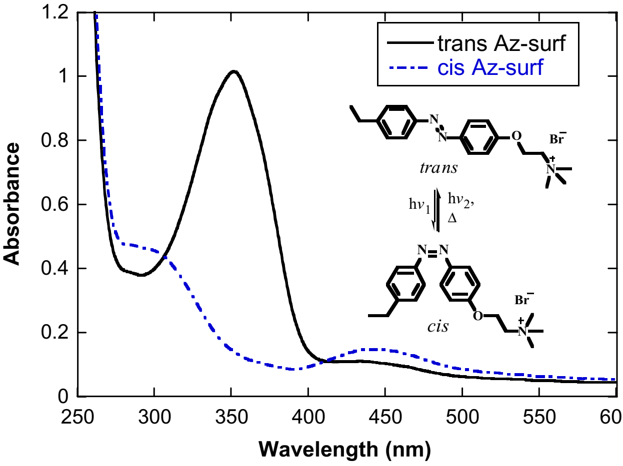


Fig. 1 UV/Vis absorption spectra of Az-surf in DMSO (4×10^{-5} M) upon UV irradiation

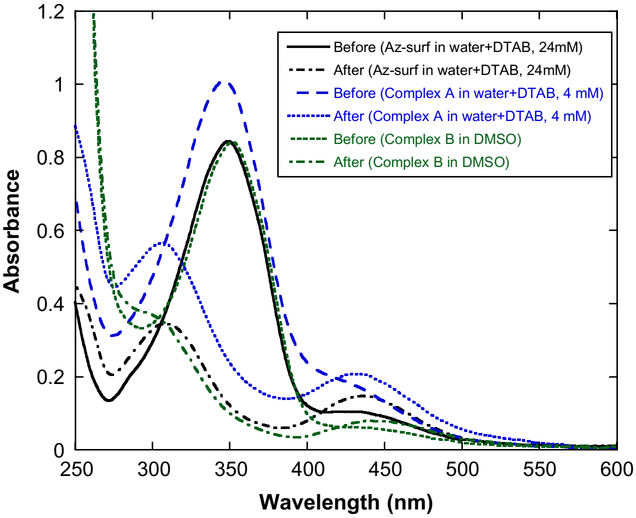


Fig. 2 UV/Vis absorption spectra, before and after UV irradiation: Az-surf in water with added DTAB (24 mM), complex A in water with added DTAB (4 mM), and complex B in DMSO. All solutions had Az-surf concentrations of ~4×10^{-5} M

Complexes A and B were synthesized by coupling of PSS with Az-surf and DTAB. The ^{1}H NMR spectra for complexes A and B show the aromatic protons of the PSS overlapping with that of Az-surf; therefore, UV/Vis spectroscopy was used to determine the exact ratio of PSS/Az-surf in the complexes. Since Az-surf has distinct absorptions at 350 and 450 nm, it was possible to use the 450 nm region (where there is no absorption by the PSS) to obtain a Beer's law plot that was then used to determine the exact concentration of Az-surf in the complexes after measuring its absorption at that wavelength (ε=1,159.8 L mol^{-1} cm^{-1} at λ=432 nm). This method confirmed that complexes A and B had 50 and 5 mol% Az-surf, respectively.

The thermal *cis–trans* isomerization of azobenzene unit in Az-surf and complexes A and B was investigated. The *trans*-azo-unit was irradiated using a UV lamp for 15 min to obtain the *cis* isomer. Figure 1 shows the absorption spectra of *trans*- and *cis*-Az-surf in DMSO. The absorption spectra of Az-surf and the complexes all look similar before and after irradiation (see Fig. 2 for a selection of spectra; all have similar $\lambda_{\max}$, at approximately 348 nm). The *trans* isomer has an intense absorption band at 350 nm due to the π–π^* transition and a much weaker band around 450 nm due to the forbidden n–π^* transition. During the isomerization process of *trans*-Az-surf to the *cis* isomer, the band at 350 nm decreases and the band at 450 nm increases, until a photostationary state is reached. The thermal reversion (*cis* → *trans*) was then monitored at 350 nm and half-lives were calculated from first-order rate plots from the following equation:

$$\ln\frac{(A_{\mathrm{eq}}-A_0)}{(A_{\mathrm{eq}}-A_t)}=k_{\mathrm{c}}t \qquad (1)$$

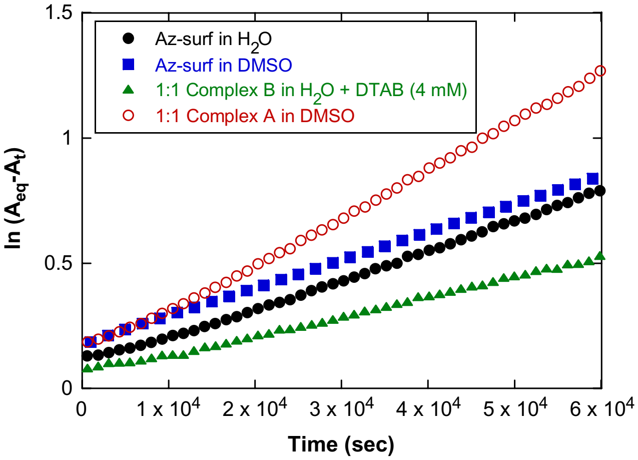


Fig. 3 The first-order rate plot of thermal reversion process of *cis*-Az-surf to the *trans* isomer (monitored at 350 nm) in water, DMSO, and as part of 1:1 complex A in DMSO and 1:1 complex B with added DTAB (4 mM)

where A_0, A_t, and A_{eq} are the initial absorbance, the absorbance at time t, and the absorbance at the photostationary state of the azo-unit at 350 nm, respectively. The rate constant of the thermal reversion is k_c. The first-order rate plots of Az-surf thermal reversion in various solvents and complexes are shown in Fig. 3. The thermal reversion of Az-surf and the complexes all followed first-order kinetic rate law.

The half-lives of the thermal reversion process for Az-surf and the two 1:1 complexes A and B in various solutions are recorded in Tables 1, 2, and 3, respectively. To determine the degree of isomerization (*trans* → *cis*) for each system, the % *cis* formation was quantified following irradiation of the *trans* isomer. The 1:1 complexes are insoluble in water, yet this “solvent” would possibly be the best choice for many potential applications of photoresponsive materials. Thus, to alleviate this issue, DTAB was added in different amounts (4 and 24 mM) to aid dissolution. The effect of this additional surfactant (and therefore also counter ions) in solution on the UV/Visible spectra of Az-surf is negligible, as evidenced in Fig. 2, where the addition of extra DTAB and/or the presence of PSS does not alter the absorption spectra. There is, however, an effect on the thermal reversion process (*vide infra*).

Table 1 Half-lives and % *cis* of thermal reversion process of Az-surf in different solvents

Solvent	$t_{1/2}$ (min)	% *cis*
DMSO	1,020	85
Water	1,020	83
Water + DTAB (4 mM)	1,020	85
Water + DTAB (24 mM)	1,740	86

Table 2 Half-lives and % *cis* of thermal reversion process of 1:1 complex A in different solvents

Solvent	$t_{1/2}$ (min)	% *cis*
DMSO	660	90
Water + DTAB (4 mM)	1,620	71
Water + DTAB (24 mM)	2,100	75

To first provide a reference point, the Az-surf was examined by itself. There are different factors that affect the *cis–trans* isomerization process of azobenzene derivatives: polarity, viscosity, and free volume [30]. The thermal reversion of azobenzene and its derivatives in different solvents has been well investigated in the past [32, 33]. It was concluded that isomerization is enhanced in polar aprotic solvents [34, 35]. In our system, at Az-surf concentrations (~10^{-5} M) well below the expected critical micelle concentration (CMC), comparable half-lives in DMSO and in water (1,020 min) were obtained (Table 1).

When DTAB (4 mM) is added into the aqueous solution of Az-surf, below its CMC (16 mM) [5], the half-life of the thermal reversion remains the same as in pure water (1,020 min), due to little or no interaction between the DTAB and Az-surf molecules. Increasing the concentration of DTAB (24 mM), however, leads to the formation of micelles that incorporate a mixture of Az-surf and DTAB molecules. Consequently, the environment surrounding the azo-unit becomes more hydrophobic, increasing the half-life of the back reaction (1,740 min).

To confirm that a polarity change occurs when DTAB forms micelles with Az-surf, Reichardt’s dye [2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridino)phenoxide], a common polarity indicator [36], was used. Solvent polarity was determined by monitoring λ_{max}, using UV/Vis spectroscopy, of this zwitterionic dye in each solution; a decrease in solvent polarity is accompanied by an increase in λ_{max} of the dye. Figure 4 shows the absorption spectra of Reichardt’s dye in (1) water, (2) in a solution of Az-surf in water + DTAB (4 mM), and (3) in a solution of Az-surf in water + DTAB (24 mM). When a small amount of DTAB is added, below its CMC, the dye behaves just like it is in water, hence no change in λ_{max} between solutions 1 (456 nm) and 2

Table 3 Half-lives and % *cis* of thermal reversion process of 1:1 complex B in different solvents

Solvent	$t_{1/2}$ (min)	% *cis*
DMSO	600	90
Water + DTAB (4 mM)	1,260	60
Water + DTAB (24 mM)	1,440	62

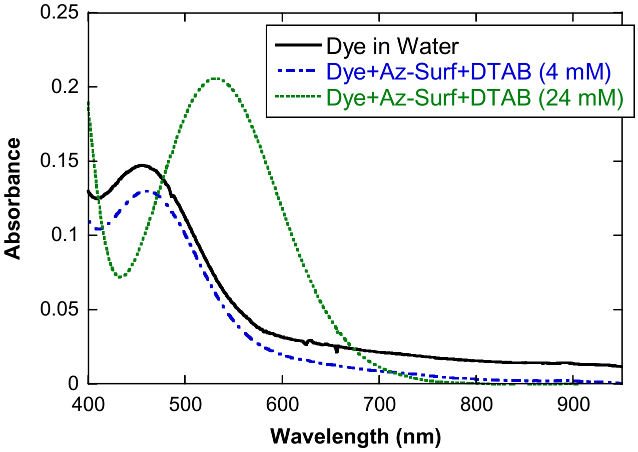


Fig. 4 Absorption spectra of Reichardt's dye in different solutions containing various amounts of DTAB (concentrations given in the figure legend)

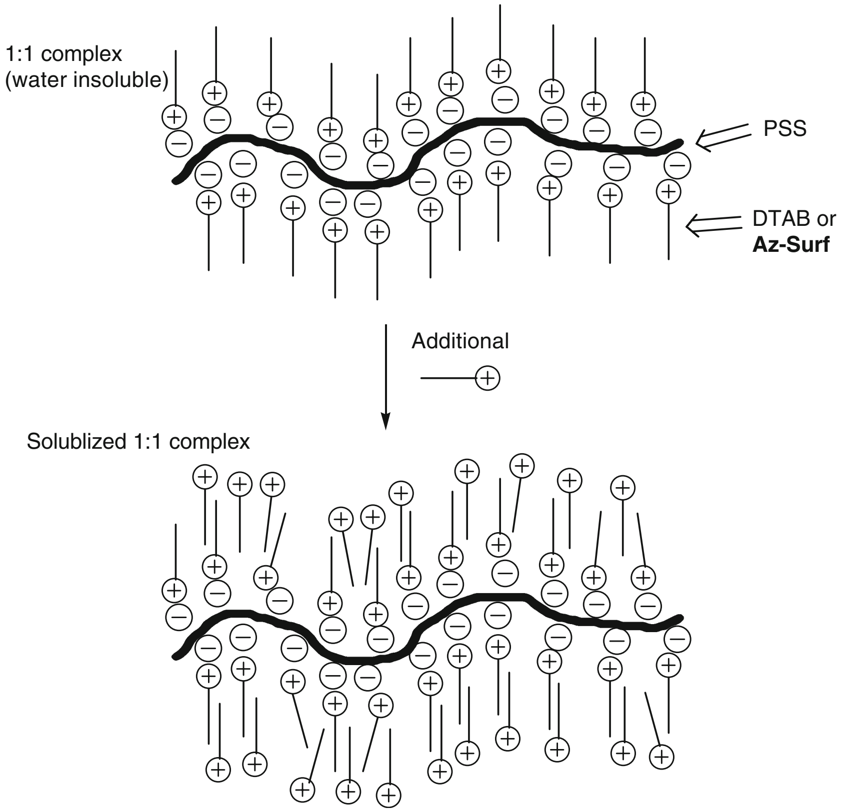
(458 nm). However, λ_{max} shifts to higher wavelength (532 nm) when DTAB concentration is above the CMC, this is because the dye is encapsulated in the micelles and therefore surrounded by the hydrophobic tails of the surfactants.

The % *cis* formation often indicates the ease with which the forward reaction (*trans* → *cis*) occurs [28]. If the free volume around the azobenzene unit is not enough for the *trans* to undergo the isomerization process then the % *cis* formation decreases [37]. For Az-surf in either DMSO or water (free or in the micellar form) the % *cis* formation is comparable (ca. 85%) indicating no difference in the amount of free volume available around the azo-unit (Table 1).

We performed the same set of studies using the 1:1 complexes A and B as was done with the Az-surf to ascertain if they can be solubilized in aqueous solutions, and if so, what type of structure(s) results. It seems that from previous studies that dissolution of the 1:1 complex into its constituent parts depends on the nature of the solvent; polar organic solvents exhibit polyelectrolyte behavior [8], while non-polar (or low polarity) solvents do not dissociate [38]. Theoretical studies [39, 40] predict that the addition of surfactants along the backbone of the polyelectrolyte chain will have the effect of stiffening the chain due to the crowding of the tails of the bound surfactant; hence, the complex forms a semi-flexible rod in solution. Thus, in the two solvents used here (DMSO and water), there are several possible structures that the 1:1 complexes A and B may adopt, depending on solvent conditions.

When the 1:1 complexes are dissolved in the polar DMSO (see first entries in Tables 2 and 3), the complexes could be expected to dissociate into polyelectrolyte and surfactant ions [8]. Under these conditions, the azobenzene units have a similar free volume to the Az-surf simply dissolved in DMSO; they are not restricted since the Az-

Scheme 2 Schematic representation of a 1:1 complex upon addition of excess DTAB



surf is not attached to the polyelectrolyte anymore; hence, the % *cis* formation is high (90%). This supports the dissociation model described above. However, there is an unexpected difference in the half-life in DMSO of the Az-surf in the 1:1 complexes (ca. 600 min) and the free Az-surf (1,020 min). This decrease in half-life would be indicative of an *increase* in the polarity of the medium around the azobenzene moiety when the 1:1 complexes are dissolved in DMSO. This could be due to a counter ion effect. In this case, PSS is the counter ion when the complex dissociates, while a bromide ion is the counter ion when the free surfactant is dissolved in DMSO.

With the simple addition of the 1:1 complex to water, the complex is of course insoluble. To induce solubilization, we added additional surfactant in the form of DTAB. The second and third entries in Tables 2 and 3 show the results of the thermal reversion experiments and % *cis* formation for complexes A and B with either a low (4 mM) or high (24 mM) concentration of additional DTAB added to the solutions. For complex A (Table 2), the $t_{1/2}$ is longer than in DMSO for both aqueous solutions, with the higher DTAB concentration having a longer $t_{1/2}$ than the lower DTAB concentration. The same trend in $t_{1/2}$ is observed for complex B (Table 3). The % *cis* formation for complex A is 71% and 75%, which is lower than the Az-surf by itself (Table 1). For complex B, the % *cis* formation is 60% and 62%, which is similarly lower than for Az-surf by itself.

We expect that when DTAB is added to a solution of the insoluble 1:1 complex in water, two possibilities arise. In the first case, the excess DTAB molecules in solution may cause the surfactant molecules on the polyelectrolyte chain to dissociate and form micelles, leaving the polyelectrolyte chain charged in water; hence, the solution becomes clear. In such a case, the now free Az-surf should give similar data as given in Table 1. However, the results in Tables 2 and 3 do not support this possibility because the half-lives and % *cis* obtained are not the same as that of the free Az-surf in water.

The second scenario involves the extra DTAB molecules using their hydrophobic tails to interact with the tails of the Az-surf on outer layer of the 1:1 complex (Scheme 2). This causes the polarity of the medium surrounding the Az-surf in the complexes to shift to a more non-polar environment. Thus, the polarity around the azobenzene group should decrease. This is observed in the half-life of the thermal reversion process of the azo-unit in the complexes (Tables 2 and 3). The half-life increases going from DMSO, to water + DTAB (low concentration, 4 mM), to water + DTAB (high concentration, 24 mM). We attribute this trend to a gradual decrease in the polarity and an increase in the rigidity of the medium. The entrapment of the complex by the DTAB increases the rigidity of the environment surrounding the azo-unit, hence the decrease in the % *cis* formation, ca. 70% and 60% in both complexes A and B in water, respectively. Furthermore, complex B, which begins with more DTAB present, is expected to form more ordered (and therefore rigid) 1:1 complexes based on previous work by other workers [8, 10, 11, 20], thus shows a lower % *cis* formation than complex A.

Conclusions

A surfactant incorporating an azobenzene unit (Az-surf) was synthesized and utilized with DTAB in preparing 1:1 complexes of PSS to surfactant, A, and B. Composition of the complexes was confirmed using NMR and UV/Vis spectroscopy. Kinetics of the thermal reversion of the azo-unit in the free surfactant, and in the complexes, was studied in DMSO and water with added DTAB. $t_{1/2}$ of the thermal reversion process *cis* → *trans* of free Az-surf and the complexes A and B increases with a decrease in polarity of the solution by addition of extra DTAB.

The kinetic data ($t_{1/2}$ and % *cis*) for the complexes in water with added DTAB support our model which suggests that the 1:1 complex is surrounded by DTAB that solubilizes the complex in water. Work is currently underway to confirm this model. Further studies on the kinetics of the thermal reversion process in the solid state, in addition to molecular and property changes in film upon irradiation, are currently under investigation.

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