Effect of Temperature on the Binding and Distribution Characteristics of Thionine in Sodium Dodecylsulfate Micelles

Sinem Göktürk · R. Yeşim Talman

Abstract The interaction between thionine (a cationic thiazine dye) and anionic surfactant sodium dodecylsulfate in aqueous solution at different temperatures has been studied spectrophotometrically. The absorption spectra were used to quantify the dye/surfactant binding constants and surfactant/water partition coefficients of the dye by applying mathematical models that consider partitioning of the dye between the micellar and aqueous pseudophases. The Benesi-Hildebrand equation was applied to calculate the binding constants of thionine to sodium dodecylsulfate micelles over a temperature range of 293 to 333 K. To evaluate the thermodynamic aspects of the interaction of thionine with sodium dodecylsulfate micelles, Gibbs energy, enthalpy and entropy changes were determined. The effect of temperature on the critical micelle concentration of sodium dodecylsulfate in the presence of thionine was also studied and discussed. The binding affinity of thionine to the sodium dodecylsulfate micelles significantly decreased with increasing temperature because of the thermal agitation.

Keywords Dye-surfactant interactions · Thermodynamics · Thionine · Sodium dodecylsulfate · Spectrophotometry · Binding constant · Partition coefficient · Critical micelle concentration

1 Introduction

Surfactants are widely used in households and as industrial cleaners, in cosmetics, research laboratories and as wetting, dispersing and leveling agents for improving dyeing processes by increasing solubility, stabilizing the dispersed state and promoting a uniform distribution of the dye in the textile. In the dyeing process, many surfactants have been used as leveling agents and/or dispersing agents [1, 2]. Surfactants present in the dye bath are responsible

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for a considerable change in the state of the dye in solution, predominately caused by interactions between dye and surfactant. In order to design desirable dye-surfactant systems, it is essential to understand the nature of interactions between them [3]. In the last few decades, many investigations have been made on the interactions between surfactants and water soluble dyes in order to acquire information about dye-surfactant associations [4–10]. Although the interaction between dyes and surfactants has been reported in many papers, studies in this area are still important and interesting for improving the dyeing process from theoretical, technological, ecological and economical points of view. The investigations into the behavior of different dyes in aqueous surfactant solutions can give useful information for understanding the thermodynamics and kinetics of the dyeing process and the finishing of textile material. UV-Vis spectroscopy, conductometry and using surfactant selective electrodes are among the most widely used measurement methods for studying this subject [6, 8, 11–13]. There are also several studies about the effect of organic and inorganic solutes on the interaction between dyes and micelles [5, 6, 14], but to date very few studies have been made on the influence of temperature on the interaction between dyes and surfactants [2, 9, 13, 15].

Surfactants are composed of a hydrophilic surface and a hydrophobic core in aqueous media and their specific structure enables the micelles to establish chemical interactions with either hydrophilic or lipophilic molecules. These aggregates exhibit an interfacial region separating the polar bulk aqueous phase from the hydrocarbon-like interior. As a consequence, micellar solutions consist of a special medium in which hydrophobic, amphiphilic or ionic compounds may be solubilized and reagents may be concentrated or separated in aqueous solution. The phenomenon of solubilization plays an important role in detergents, the dyeing process in textile industries, and in pharmaceutical applications [16, 17]. Solubilization has been treated as partitioning of additive molecules between a micellar phase and an intermolecular bulk phase. Several models have been used to explain the theoretical principles that govern the solubilization process or the uptake of hydrophobic solutes in aqueous systems into micelles or the binding processes of solutes. Of these the pseudo-phase model is most often used. This model is based on three principles: 1) the micellar and aqueous phases, although in the same system, are compartmentalized; 2) solute molecules are distributed between the two phases; and 3) the distribution is in dynamic equilibrium. Among the various factors that undoubtedly contribute to solubilization in micellar systems, hydrophobic contributions are quite significant. A significant characteristic of the hydrophobic effect is that the entropy term is dominant, i.e., the transfer of the hydrocarbon solute from the hydrocarbon solvent to water is accompanied by an increase in the Gibbs transfer energy ($\Delta G > 0$). The decrease in entropy is thought to be the result of the breakdown of the normal hydrogen-bonded structure of water accompanied by the formation of differently structured water, often termed "icebergs" [18], around the hydrocarbon chain. To minimize the large entropy effect, the icebergs tend to cluster, in order to reduce the number of water molecules involved; the "clustering" is enthalpically favored (i.e., $\Delta H < 0$), but entropically unfavorable. The overall process has the tendency to bring the hydrocarbon molecules together, which is known as the hydrophobic interaction. Molecular interactions, arising from the tendency for the water molecules to regain their normal tetrahedral structure, and the attractive dispersion forces between hydrocarbon chains, act cooperatively to remove the hydrocarbon chain from the water "icebergs", leading to an association of hydrophobic chains [19]. The interactions between additive-water, additive-micelles and the water-micellar phase play a vital role in the partitioning/binding process. The thermodynamic process of the interaction of dye with surfactants and transfer of the dye between the micellar and bulk water phases is characterized by Gibbs energy changes, binding constants and partition coefficients, respectively [20–22]. The objective of this paper is to understand and characterize the role of

temperature on the interaction between oppositely charged dye and surfactant in aqueous solutions. In view of this interest, this work aims to investigate changes caused by temperature variations on the interaction of thionine (3,7-diamino-5-phenothiazinium acetate) with the anionic surfactant sodium dodecylsulfate (SDS) using spectrophotometric measurements. To evaluate the thermodynamic aspects of the binding of thionine (Thio) to SDS micelles, Gibbs energy (ΔG°), the standard enthalpy (ΔH°) and the standard entropy change (ΔS°) have been calculated. By using the pseudo-phase model, the partition coefficients of Thio between the bulk water and SDS micelles and binding constants of Thio to SDS micelles were calculated by applying different approaches. We have also undertaken this study to understand the role of temperature on variations in CMC values of SDS in the presence of fixed concentration of Thio.

2 Experimental

All the chemicals were of analytical reagent grade. SDS was a Sigma product. Thio was obtained from Fluka. Doubly distilled conductivity water was used for solution preparation. The spectroscopic measurements were performed with a double-beam UV-Vis spectrophotometer (Shimadzu UV-2100 S) equipped with a matched pair of cuvettes of 10.0 mm path length in a water-jacketed thermostatic cell-holder.

The absorption spectra of 8.0×10^{-6} mol·dm^{-3} Thio solutions containing anionic surfactant SDS in the concentration range 1.0×10^{-5}–4.0×10^{-2} mol·dm^{-3} were recorded at the range of temperatures between 293 and 333 K. Dye/surfactant binding constants and micelle/water partition coefficients were determined from the absorbances of a series of solutions containing a fixed concentration of Thio (8.0×10^{-6} mol·dm^{-3}) and increasing concentration of SDS. The reproducibility for $\lambda_{\max}$ of the spectra was ± 0.01 nm. All measurements were done at least in triplicate. In this paper the CMC determination is based on the change in the absorption spectrum of Thio which indicates the onset of micelle formation.

3 Results and Discussion

The cationic dye Thio, having the structure shown in Scheme 1, exhibits a maximum absorption at 596 nm and a shoulder at 560 nm. In order to analyze the influence of temperature on aqueous solutions of 8.0×10^{-6} mol·dm^{-3} Thio, UV-Vis spectra were recorded. Figure 1a shows variation the UV-Vis spectra of Thio at different temperatures. The peak, which was obtained at 596 nm, did not change with increasing temperature. This peak has been attributed to the presence of the Thio monomer. It is well known that ionic dyes tend to aggregate in dilute solutions, leading to dimer formation, and sometimes even higher-order aggregates [23]. As temperature increases, the absorbance value of 8.0×10^{-6} mol·dm^{-3} Thio decreased. In the employed concentration range of 1.0×10^{-6} to 2.0×10^{-5} mol·dm^{-3}, the linear relation between absorbance and Thio concentration ($R^2 = 0.9999$) indicates the validity of Beer's law. The molar absorption coefficient of Thio at 596 nm, ε_{o}, was calculated
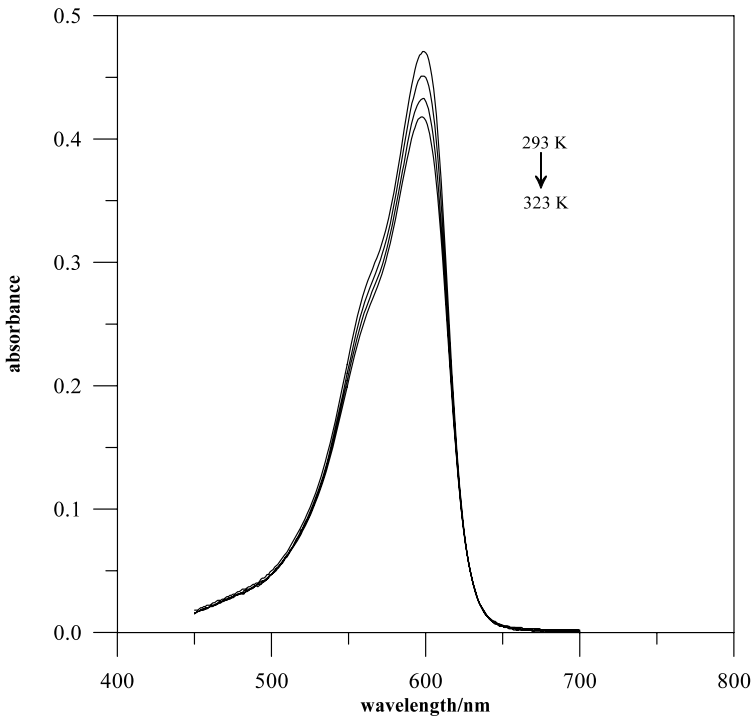
Scheme 1 Molecular structure of thionine
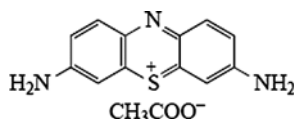
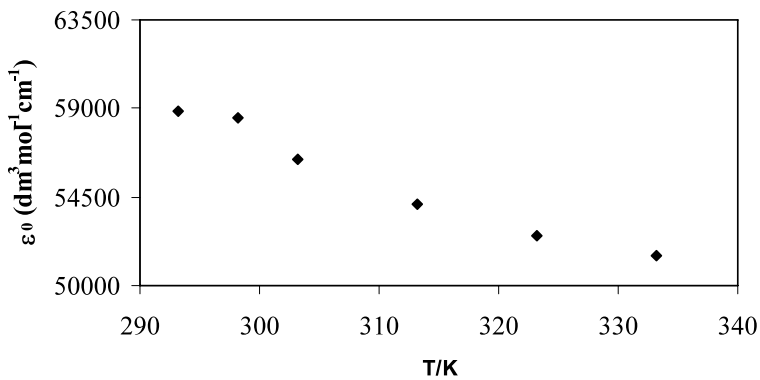**Figure 1a** UV-vis absorption spectra of 8.0×10^{-6} mol·dm^{-3} Thio at 293, 303, 313 and 323 K

Figure 1b Variation of ε_{o} values of Thio at 596 nm as a function of temperature

as $(5.85 \pm 0.1) \times 10^4$ dm^3·mol^{-1}·cm^{-1} at 298 K. A plot of ε_{o} versus temperature (T) also shows the decrease in absorbance at a fixed concentration of Thio with increasing in temperature (Fig. 1b). As seen in Fig. 1a and 1b, aqueous solutions of Thio are much significantly affected by temperature. In order to show the influence of temperature on the interaction of Thio with SDS, the variation of the absorption spectrum of Thio at the different temperatures in the presence of 0.3 mmol·dm^{-3} SDS (below the CMC) and 0.01 mol·dm^{-3} SDS (above the CMC) are shown in Fig. 2. It is apparent that an increase in temperature
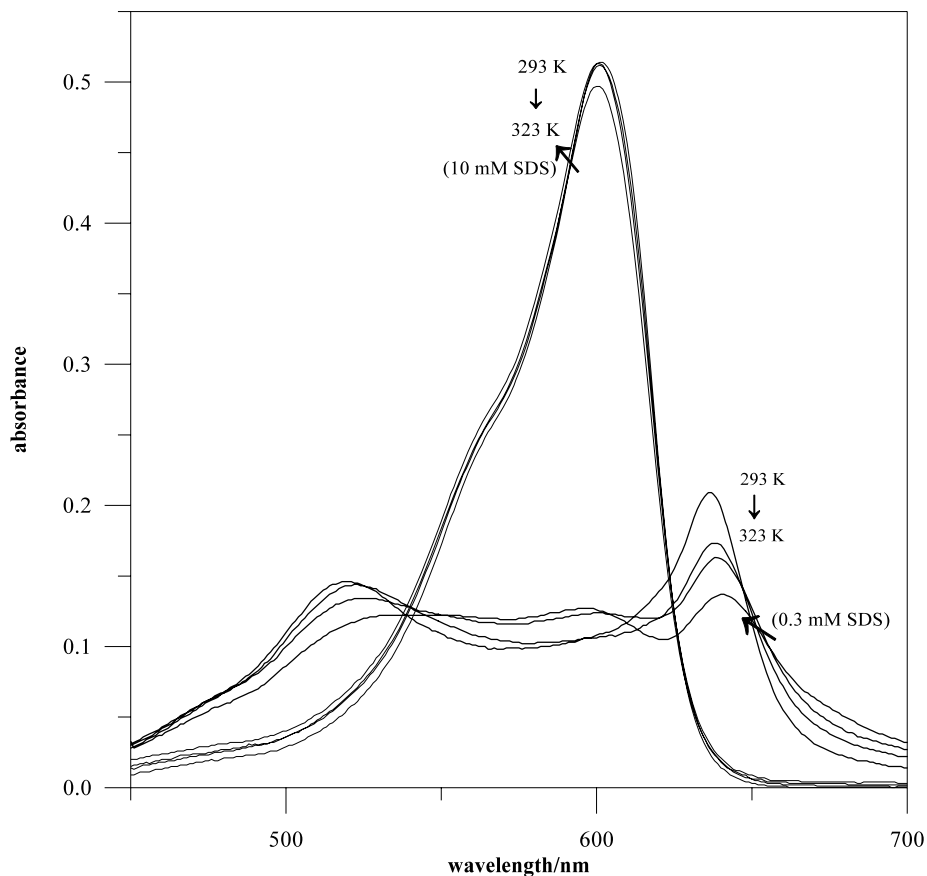
Figure 2 UV-Vis absorption spectra of 8.0×10^{-6} mol·dm^{-3} Thio at different temperatures in the presence of 0.3 and 10 mmol·dm^{-3} SDS concentrations

caused the absorbance values of Thio to decrease in the presence of SDS. The absorption spectra of 8.0×10^{-6} mol·dm^{-3} Thio in the presence of various concentrations of SDS recorded at 298 K are shown in Fig. 3a as a representative plot. For SDS concentrations up to 0.2 mmol·dm^{-3}, the absorbance of Thio sharply decreased without changing any of the spectral characteristics. Then a red shift with a shoulder at 635 nm was observed for SDS concentrations from 0.3 to 1.0 mol·dm^{-3}. The shoulder disappeared with further increasing SDS concentration, the absorption spectrum of Thio returned to its characteristic shape and the absorbance values increased with increasing SDS concentration and λ_{max} shifted to 601 nm. These shifts indicate that Thio interacts with SDS. Also the increase in absorbance with increasing surfactant concentration is regarded as being caused by penetration of the dye molecules into the micelles as observed in other cases [6, 12, 21, 22]. The same behavior was seen at all the temperatures studied i.e., an increase in temperature did not change the shape of spectrum of the Thio in the presence of various concentrations of SDS as shown in Fig. 3a. The absorbance change of 8.0×10^{-6} mol·dm^{-3} Thio over a wide range of SDS concentrations at different temperatures is shown in Fig. 3b. The absorbance of a fixed concentration of Thio initially decreased with increasing SDS concentration well below the CMC, reached a minimum value and then increased again with further increasing SDS con-
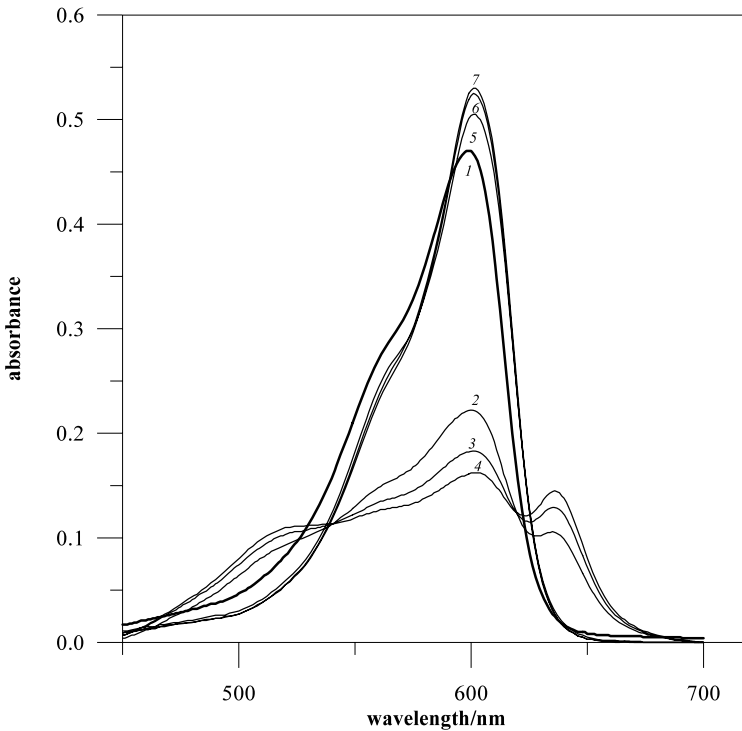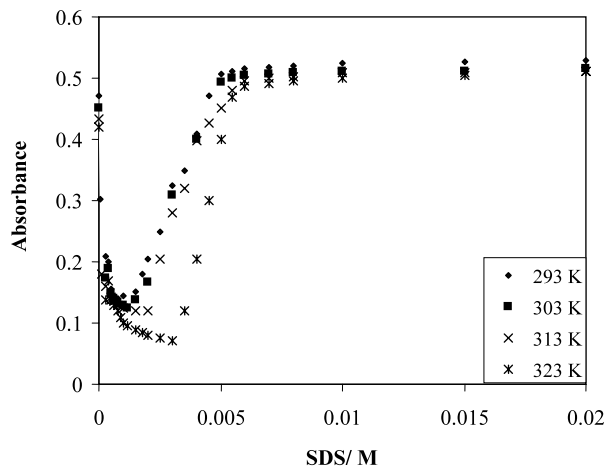
Figure 3a UV-Vis absorption spectra of 8.0×10^{-6} mol·dm^{-3} Thio at various concentrations of SDS at 298.15 K: *1*, in water; *2*, 0.3 mmol·dm^{-3}; *3*, 0.5 mmol·dm^{-3}; *4*, 1 mmol·dm^{-3}; *5*, 8 mmol·dm^{-3}; *6*, 10 mmol·dm^{-3}; *7*, 20 mmol·dm^{-3} SDS

Figure 3b The absorbance change of 8.0×10^{-6} mol·dm^{-3} Thio (below and above CMC) with the concentration of SDS at various temperatures

centrations above the CMC. The concentration at the observed minimum is considered as the CMC in the presence of 8.0×10^{-6} mol·dm^{-3} Thio for each temperature studied. As seen in Table 1, CMC values of SDS determined spectrophotometrically in the presence of

Table 1 Physical parameters for the interaction of Thio with SDS at different temperatures

T	K_b	K_{ass}	K_S	K_x	CMC_0 [*]	$CMC_{exp.}$ [**]	$CMC_{eq.}$ [***] /	f^a	$\lambda_{max}{}^b$
K	$dm^3 \cdot mol^{-1}$	$dm^3 \cdot mol^{-1}$	$dm^3 \cdot mol^{-1}$		$mmol \cdot dm^{-3}$	$mmol \cdot dm^{-3}$	$mmol \cdot dm^{-3}$		
293	1201	994	879	48784	7.90	0.8	1.5	0.9150	601.2
298	1000	797	818	45440	8.05	1	1.9	0.9142	601.0
303	501	475	432	23976	8.50	1.2	2.5	0.8498	600.8
313	267	353	300	16650	9.44	2.0	3.4	0.7980	600.2
323	200	267	247	13708	9.57	3.0	3.6	0.7453	599.8
333	120	189	192	10656	11	3.5	4.0	0.6235	599.0

[*]The CMCs are taken from [22, 23]

[**]The CMCs were obtained spectrophotometrically

[***]The CMCs were obtained from Eq. 9

[a] f values at the concentrations of 0.01 mol·dm^{-3} SDS micelles

[b] λ_{max} is in nm for 0.01 mol·dm^{-3} SDS concentration

[c]Error limit in K values is ±5%. The correlation coefficients are higher than 0.9970

8.0×10^{-6} mol·dm^{-3} Thio are different from its CMC in pure water at room temperature and also at the other temperatures [19, 24].

It is well known that a solute can be arranged in various ways in the micelle. The spatial position of a solubilized molecule in a micelle will depend on its polarity: non-polar molecules will be solubilized in the micellar core and substances with intermediate polarity will be distributed along the surfactant molecules in certain intermediate positions. The solubilized molecule may enter completely inside the hydrophobic core or penetrate to a particular depth into the surface layer (the solute can be adsorbed on the surface of the micelle or, in the case of molecules containing polar substituents, be oriented with the polar portion of the molecule situated in the surface layer and the non-polar portion directed into the micelle). According to the molecular structure of Thio it can be seen that the cationic molecule has hydrophobic centers that make it suitable for both electrostatic and hydrophobic interactions with the anionic SDS. The change of the absorption spectrum of the cationic dye Thio due to incorporation into anionic SDS micelles allows the dye/surfactant binding constants and surfactant/water partition coefficients of dye to be determined with the following models.

3.1 Determination of Binding Constant

The values of the binding constants were obtained according to the methods described previously [6, 12]. The binding of the dye to the surfactant is in equilibrium as expressed by:

$$S_W + D_M \rightleftharpoons S_M, \tag{1}$$

$$K_b = \frac{[S_M]}{[S_W][D_M]} \tag{2}$$

where S_W and S_M represent the substrate (dye) concentrations in the aqueous phase and the micellar pseudophase, respectively, D_M is the concentration of surfactant molecules in micellar form, and K_b is the associated equilibrium or binding constant. K_b and the molar absorption coefficient, ε_m, can be determined using the Benesi-Hildebrand equation which

is valid for high surfactant concentrations [12, 25] in the following modified form

$$\frac{l[\text{Thio}]}{A - A_o} = \frac{1}{\varepsilon_m - \varepsilon_o} + \frac{1}{K_b[S_m](\varepsilon_m - \varepsilon_o)} \tag{3}$$

where [Thio] and [S_m] (S_m = total SDS concentration – CMC) are the initial molar concentrations of Thio and the micellized surfactant concentration, respectively, l is the optical path length of the solution, and A and A_o are the absorbances of Thio in the presence and absence of SDS, respectively, ε_m is the molar absorption coefficient of the dye fully bound to SDS micelles determined in a large excess of the micelles. The plot of l [Thio]/($A - A_o$) against $1/[S_m]$ was used to calculate K_b values at different temperatures from the slope and intercept, and are given in Table 1.

3.2 Determination of the Partition Coefficient

Absorbance values obtained at λ_{max} can be also used for the calculation of partition coefficient, K_x, defined according to the pseudo-phase model as [26, 27]

$$K_x = \frac{X_{\text{Thio}}^m}{X_{\text{Thio}}^w} \tag{4}$$

where X_{Thio}^m and X_{Thio}^w are the mole fractions of the cationic dye Thio in the micellar and aqueous phases, respectively. They are related to the concentrations of species in the solubilized system:

$$X_{\text{Thio}}^m = \frac{C_{\text{Thio}}^m}{C_{\text{Thio}}^m + C_{\text{surfactant}}^m}, \tag{5}$$

$$X_{\text{Thio}}^w = \frac{C_{\text{Thio}}^w}{C_{\text{Thio}}^w + C_{\text{surfactant}}^w + n_W} \tag{6}$$

where $C_{\text{surfactant}}^m$ and $C_{\text{surfactant}}^w$ represent the concentrations of surfactant in the micellar and monomeric states, and $n_W = 55.5$ mol·dm^{-3} is the molarity of water. Under the present experimental conditions $C_{\text{Thio}}^m + C_{\text{surfactant}}^w \ll n_W$. If we express $K_S = K_x/n_W$, we get the equation:

$$K_S = \frac{C_{\text{Thio}}^m/(C_{\text{Thio}}^m + C_{\text{surfactant}}^m)}{C_{\text{Thio}}^w} \tag{7}$$

The fraction of the associated Thio (f) may be defined as:

$$f = \frac{C_{\text{Thio}}^m}{C_{\text{Thio}}} \tag{8}$$

At a certain C_{Thio}, f is equal to zero in the non-micellar region up to the CMC and increases with increasing concentration of surfactant above the CMC. As $C_{\text{surfactant}}$ increases to infinity, f approaches unity because all added dye should be solubilized in the micelles. The value of f can be directly calculated from the experimental data using Eq. 8:

$$f = \frac{\Delta A}{\Delta A^\infty} \tag{9}$$

where $\Delta A = A - A_w$ and $\Delta A^\infty = A^\infty - A_w$, A^∞ being the absorbance of Thio completely bound to SDS. The change in f with temperature is shown in Fig. 4 in the presence of
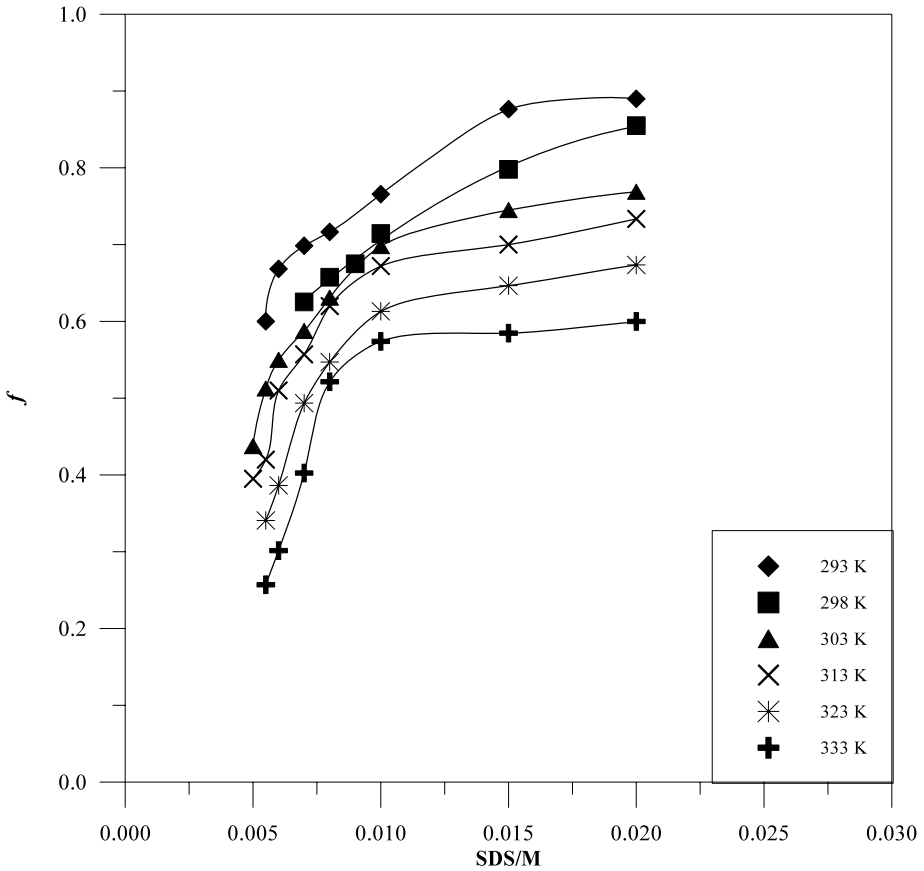
Figure 4 Fraction of bound Thio to SDS micelle at the different temperatures

0.01 mol·dm^{-3} SDS micelles. It can be seen in Fig. 4 that the increase in temperature caused a decrease in the fraction of Thio bound to SDS micelles. By using Eqs. 7, 8 and 9, Eq. 10 can be written in a linear form:

$$\frac{1}{\Delta A} = \frac{1}{\Delta A^{\infty}} + \frac{1}{K_S \Delta A^{\infty}(C_{\text{Thio}} + C_{\text{surfactant}} - \text{CMC})} \quad (10)$$

K_S and $K_x (K_S = K_x/n_W)$ are obtained from the slope of the plot of $1/\Delta A$ versus $1/(C_{\text{Thio}} + C_{\text{surfactant}} - \text{CMC})$. The results at the different temperatures are summarized in Table 1. We also calculated the binding constants with a more quantitative approach provided by the following treatment [28]:

$$\frac{f}{1-f} = K_{\text{ass}}(C_{\text{surfactant}} - C_{\text{Thio}})f - K_{\text{ass}}[\text{CMC}] \quad (11)$$

A plot of $f/(1-f)$ versus $(C_{\text{surfactant}} - C_{\text{Thio}})f$ gives a straight line where the slope and the intercept are K_{ass} and $K_{\text{ass}}[\text{CMC}]$, respectively. Association constant (K_{ass}) and the CMC of SDS in the presence of a fixed concentration of Thio for the different temperatures are shown in Table 1 using by Eq. 11. In the presence of 8.0×10^{-6} mol·dm^{-3} Thio, as seen in

Table 1, the CMC values are always significantly lower than the corresponding CMC values of SDS at all the studied temperatures. This confirms that Thio is capable of interacting with SDS, inducing the formation SDS aggregates. The CMC values obtained from both Eq. 11 and experimentally were found to be similar to the binding constants determined from the different approaches. As seen in Table 1, Thio interacts with SDS more weakly with increasing temperature. It is clear that as the temperature increases, the tendency to form Thio-SDS decreases.

3.3 Effect of Temperature on the CMC

It is well known that micellization is affected by various factors including the surfactant species (hydrophobic volume, chain length and head group area), temperature, pressure, ionic strength, pH, etc. The effects of temperature changes on the CMC of surfactants in aqueous solution have been found to be quite complex. For electrolytes and amphoterics, micellization is affected by temperature as the hydrophobic and head-group interactions change. Accordingly, the CMC versus temperature studies were performed by da Silva et al. [29]. It was also confirmed by Ruso et al. regarding SDS micelles, at temperatures close to ambient, that no significant changes were observed of the CMC values or aggregation numbers [30]. As temperature is raised, SDS micelles are known to reduce their aggregation numbers, for instance, by 30% from 20 to 40 °C [31]. The effect of increasing temperature on the CMC of surfactants in aqueous solutions is usually ascribed to two opposing factors: (i) the dehydration of hydrophilic head groups that favors micellization, (ii) the break down of water structure surrounding the hydrophobic groups that disfavors micellization. The increase of the CMC with temperature in the present case clearly shows the dominance of the latter over the former. The effect might be assigned to increased repulsion among less hydrated head groups, less counter-ion binding, and increased thermal vibrations of the hydrophobic tails inside the micelles that loosen the micelle structure.

The CMC values of SDS obtained in the presence of Thio have a direct relation with the studied temperature range. Although it is widely known that the CMC is affected by temperature, the exact relationship between the two has not been identified. The temperature dependence of the CMC in ionic surfactants can usually be described by a power law [32–34]. Such a power-law description is quite desirable, because CMCs can then be predicted at any temperature of interest. Thus, a polynomial-function description of the CMC with respect to Thio has been used for the system studied here. By fitting a polynomial function of temperature to the CMC data obtained both experimentally and from Eq. 11, shown in Fig. 5, the correlation coefficients are:

$$\mathrm{CMC_{eq.}} = 3.0 \times 10^{-4} T^2 - 0.1183 T + 9.2077, \quad R^2 = 0.9869$$

$$\mathrm{CMC_{exp.}} = -1.4 \times 10^{-3} T^2 - 0.9246 T - 151.31, \quad R^2 = 0.9886$$

3.4 Thermodynamics Parameters

From the values obtained for K_b and K_x at different temperatures, the values of the Gibbs energy of interaction (ΔG_b^{o}) and the Gibbs energy of the transfer of dye from bulk water phase to micellar phase (ΔG_x^{o}) can be obtained from the following equation:

$$\Delta G^{\mathrm{o}} = -RT \ln K \tag{12}$$

Figure 5 CMC values of SDS in the presence of 8.0×10^{-6} mol·dm^{-3} Thio as a function of temperature. The broken and solid lines are the second-order polynomials for the CMC values measured and obtained from Eq. 11, respectively
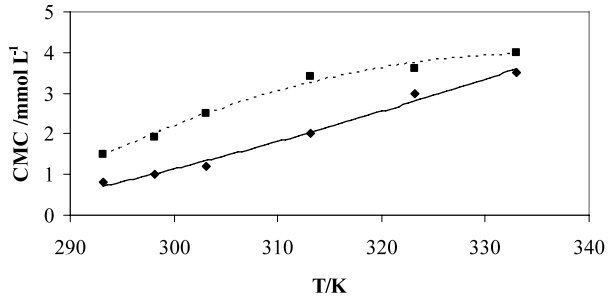

Table 2 Thermodynamics parameters for the interaction of Thio with SDS micelles for the binding and partitioning processes

T	Binding			Partitioning		
K	ΔG_b^o	$T \Delta S^o$	ΔH^o	ΔG_x^o	$T \Delta S^o$	ΔH^o
	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
293	−17.27	−30.14		−26.30	−5.73	
298	−17.11	−30.30		−26.27	−5.45	
303	−15.66	−31.76	−47.42	−25.40	−6.61	−30.97
313	−14.54	−32.88		−25.30	−6.72	
323	−14.22	−33.19		−25.58	−6.44	
333	−13.25	−34.17		−25.67	−6.34	

The values of ΔG_b^o and ΔG_x^o and related binding constants and partition coefficients calculated for the different temperatures are summarized in Table 2. The values of ΔH^o and ΔS^o for the association of Thio with SDS can be calculated as follows:

$$\Delta H^o = \frac{\partial (\Delta G^o / T)}{\partial (1/T)}, \tag{13}$$

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \tag{14}$$

It can be seen from Eq. 13 that if $\Delta G^o / T$ is plotted against $1/T$; the slope of the curve at any temperature is equal to ΔH^o at that temperature. However, we assume that ΔH^o is independent of temperature over the measured temperature range. A plot of $\Delta G^o / T$ versus $1/T$ should be straight line with a slope equal to ΔH^o (Fig. 6). The corresponding thermodynamic parameters are given in Table 2. The negative standard Gibbs energy change, which is in direct correlation with binding constants and partition coefficients, indicates the tendency of association of Thio to SDS micelles. The negative values of ΔH^o indicate that the interaction between Thio and SDS is exothermic. This means that major attractive force for the binding of Thio to SDS micelles is a hydrophobic interaction [17, 19, 35] and is accompanied by the negative values of ΔS^o (Table 2). The negative values of ΔS^o for dye-surfactant interactions indicate that the binding of surfactant to dye caused an increase in the order of the system. As the temperature increased, the hydrogen bonds diminished and so the entropy effect decreased. Meanwhile, as the temperature increased the size of the iceberg decreased due to melting, and so less energy was required to break up the three-dimensional water structure. Thus, ΔH^o became more exothermic and its effect very significant. Taking
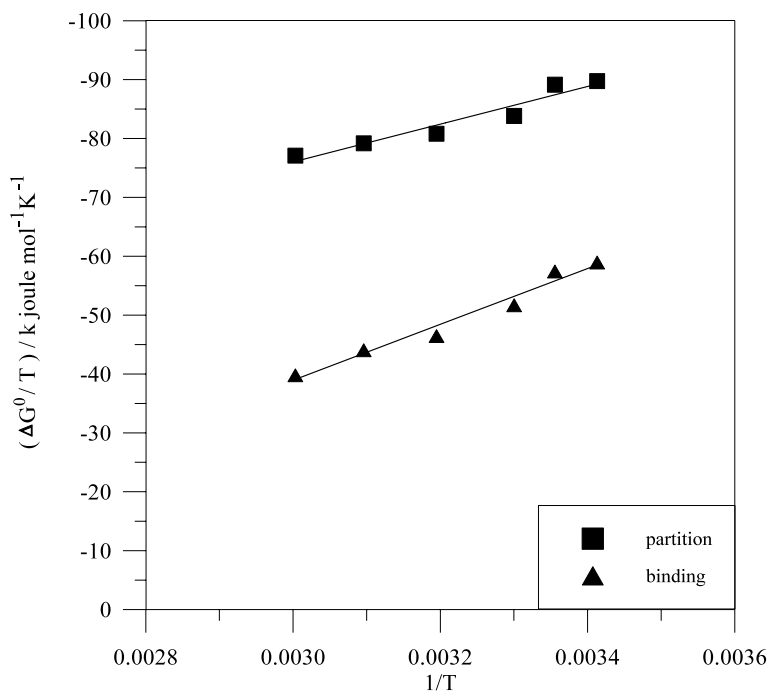
Figure 6 Plots of $\Delta G^{\mathrm{o}}/T$ versus $1/T$ for the binding and partition of Thio to SDS micelles

the values of the thermodynamic parameters into consideration, it can be said that the interaction between Thio and SDS is an enthalpy-driven process. The ΔG^{o} is the sum of the enthalpic and entropic contributions, and it can be seen in Fig. 7 that the enthalpic contribution plays the major role in the interaction of Thio with SDS at the studied temperature range.

In general, but not always, micelle formation is found to be an exothermic process, favored by a decrease in temperature. The enthalpy of micellization may therefore be either positive or negative depending on the system and conditions. The process, however, always has a substantial positive entropic contribution to overcome any positive enthalpy term, so that micelle formation is primarily an entropy-driven process. Micelle formation of sodium n-alkyl sulfates is driven mainly by the positive ΔS^{o}, which is due to breaking of bulk water structure around the molecules. This leads to more disorder in the structure of water and favors micellization. As the temperature is increased, the structure of water is partially broken down, and hydrophobic interactions become less significant. The negative values of enthalpy suggest the importance of London-dispersion interactions as an attractive force contribution to micellization [36]. Also, the observed exothermicity can be attributed to possible surfactant-solvent interactions. In the present study, the increase in temperature leads to an increase in the CMC value of SDS, i.e., inhibited micelle formation. In other words, decreased hydrophobic interaction is required for micelle formation. On the other hand, the degree of counter-ion dissociation in the surfactant micelles also increases regularly with increasing temperature due to a decrease in the charge density at the micellar surface caused by the decrease in the aggregation number of micelle i.e., inhibition of the binding of Thio to SDS micelles. The binding or association constant is related to the distribution coefficient
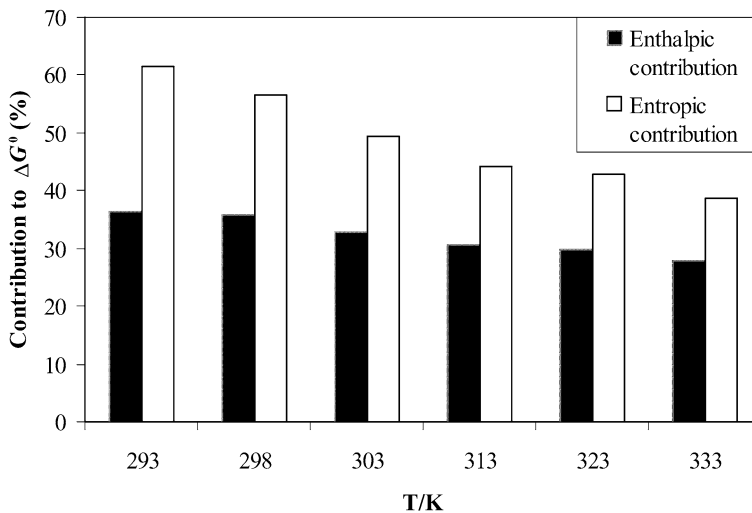
Figure 7 Enthalpic and entropic contributions to the Gibbs energy of binding of Thio to SDS micelles

through Eq. 7. It might be said that the high values of K_x also imply that most of the Thio is located or solubilized in the micellar pseudo-phase. This can be confirmed by the observed maximum absorption values in the absence and presence of SDS micelles given in Table 1.

4 Conclusions

Based on the presented results it can be generalized that the association of the cationic dye, Thio, with the anionic surfactant, SDS, is exothermic and spontaneous; as indicated by the thermodynamic parameters. The main contribution to ΔG^o comes from the enthalpy term, and both binding and partitioning of Thio into the SDS micelles are thus enthalpy-driven processes. Increase in temperature leads to a decrease in the equilibrium constant values. The results obtained from the different approaches are in good agreement for the effect of temperature on decreasing the interaction of Thio with SDS micelles. The increase in the CMC of SDS with temperature is indicative of a de-micellization process. It may be concluded that from these results, hydrophobic forces play an important role in the dye-micelle interactions.

References

1. Gao, H.W., Qian, Y., Hu, Z.J.: Tetraiodophenolsulfonphthalein as a spectral substitute to characterize the complexation between cationic and anionic surfactant. Dyes Pigments **279**, 244–252 (2004)
2. Abe, M., Kasuya, T., Ogino, K.: Thermodynamics of surfactant-dye complex formation in aqueous solutions. Sodium alkyl sulfates and azo oil dye systems. Colloid Polymer Sci. **266**, 156–163 (1988)
3. Khan, M.N., Sarwar, A.: Study of dye-surfactant interaction: Aggregation and dissolution of yellowish in *N*-dodecylpyridinium chloride. Fluid Phase Equilib. **239**, 166–171 (2006)
4. Diaz Garcia, M.E., Sanz-Medel, A.: Dye-surfactant interactions: A review. Talanta **33**, 255–264 (1986)
5. Tavcer, P.F., Span, J.: Dye-surfactant interactions studied using Job's method. Text. Res. J. **69**, 278–284 (1999)
6. Gökturk, S., Tunçay, M.: Spectral studies of safranin-O in different surfactant solutions. Spectrochim. Acta A **59**, 1857–1866 (2003)

7. Yang, J.: Interaction of surfactants and aminoindophenol dye. J. Colloid Interface Sci. **274**, 237–243 (2004)

8. Kubicek, V., Nemcova, K.: Study of the interaction phenomena of cetyl-trimethyl-ammonium bromide, cetylpyridinium chloride and benzethonium chloride with C.I. Acid Orange 52 and picric acid by two spectral methods. Dyes Pigments **68**, 183–189 (2006)

9. Tunç, S., Duman, O.: Investigation of interactions between some anionic dyes and cationic surfactants by conductometric method. Fluid Phase Equilib. **251**, 1–7 (2007)

10. Simoncic, B., Kert, M.: Influence of the chemical structure of dyes and surfactants on their interactions in binary and ternary mixture. Dyes Pigments **76**, 104–112 (2008)

11. Jocic, D.: Conductivity measurement—a simple method for determining dye/surfactant interaction. Text. Res. J. **65**, 409–416 (1995)

12. Göktürk, S.: Effect of hydrophobicity on micellar binding of carminic acid. J. Photochem. Photobiol. A Chem. **169**, 115–121 (2005)

13. Simoncic, B., Span, J.: A study of dye-surfactant interactions. Part 3. Thermodynamics of the association of C.I. Acid Orange 7 and cetylpyridinium chloride in aqueous solutions. Dyes Pigments **46**, 1–8 (2000)

14. Bracko, S., Span, J.: Anionic dye-cationic surfactant interactions in water-ethanol mixed solvent. Dyes Pigments **50**, 77–84 (2001)

15. Simoncic, B., Kert, M.: Thermodynamics of anionic dye-cationic surfactant interactions in cationic-nonionic surfactant mixtures in comparison with binary systems. Dyes Pigments **71**, 43–53 (2006)

16. Elworthy, P.H., Florence, A.T., Macfariane, C.B.: Solubilization by Surface-Active Agents. Chapman and Hall, London (1968)

17. Myers, D.: Surfactant Science and Technology. Wiley-Interscience, New York (2006)

18. Frank, H.S., Evans, M.W.: Free volume and entropy in condensed systems III. Entropy in binary liquid mixtures; partial molal entropy in dilute solutions; structure and thermodynamics in aqueous electrolytes. J. Chem. Phys. **13**, 507–532 (1945)

19. Rosen, M.J.: Surfactants and Interfacial Phenomena. Wiley, New York (1978)

20. Bunton, C.A., Sepulveda, L.: Hydrophobic and Coulombic interactions in the micellar binding of phenols and phenoxide ions. J. Phys. Chem. **83**, 680–683 (1979)

21. Mishra, A., Behera, R.K., Mishra, B.K., Behera, G.B.: Dye-surfactant interaction: chain folding during solubilization of styryl pyridinium dyes in sodium dodecylsulfate aggregates. J. Photochem. Photobiol. A: Chem. **121**, 63–73 (1999)

22. Shah, S.S., Khan, M.S., Ullah, H., Awan, M.A.: Solubilization of amphiphilic hemicyanine dyes by a cationic surfactant, cetyltrimethylammonium bromide. J. Colloid Interface Sci. **86**, 382–386 (1997)

23. Niazi, A., Yazdanipour, A., Ghasemi, J., Kubista, M.: Spectrophotometric and thermodynamic study on the dimerization equilibrium of ionic dyes in water by chemometrics method. Spectrochim. Acta Part A **65**, 73–78 (2006)

24. Shah, S.S., Jamroz, N.U., Sharif, Q.M.: Micellization parameters and electrostatic interactions in micellar solution of sodium dodecylsulfate (SDS) at different temperatures. Colloids Surfaces A: Physicochem. Eng. Aspects **178**, 199–206 (2001)

25. Benesi, H.A., Hildebrand, J.H.: A spectrophotometric investigation of the interaction of iodine with aromatic hydrocarbons. J. Am. Chem. Soc. **71**, 2073–2707 (1949)

26. Sepulveda, L., Lissi, E., Quina, F.: Interactions of neutral molecules with ionic micelles. Adv. Colloid Interface Sci. **25**, 1–57 (1986)

27. Kawamura, H., Manabe, M., Tokunoh., T., Saiki, H., Tokunaga, S.: Partition coefficients of ω-phenyl-alkanols between water and sodium deoxycholate micelles. J. Solution Chem. **20,**, 817–828 (1991)

28. Saikia, P.M., Kalita, A., Gohain, B., Sarma, S., Dutta, R.K.: A partition equilibrium study of sulfonephthalein dyes in anionic surfactant systems: determination of CMC in buffered medium. Colloids Surf. A: Physicochem. Eng. Asp. **216**, 21–26 (2003)

29. Da Silva, R.C., Loh, W., Olofsson, G.: Calorimetric investigation of temperature effect on the interaction between poly(ethylene oxide) and sodium dodecylsulfate in water. Thermochim. Acta **417**, 295–300 (2004)

30. Ruso, M.J., Taboada, P., Mosquera, V., Sarmiento, F.: Thermodynamics of micellization of n-alkyl sulfates in an alkaline medium at different temperatures. J. Colloid Interface Sci. **214**, 292–296 (1999)

31. Van Stam, J., Almgren, M., Lindblad, C.: Sodium dodecylsulfate-poly(ethyleneoxide) interactions studied by time-resolved fluorescence quenching. Prog. Colloid Polymer Sci. **84**, 13–20 (1991)

32. Stead, J.A., Taylor, H.: Some solution properties of certain surface-active N-alkylpyridinium halides: I. Effect of temperature on the critical micelle concentrations. J. Colloid Interface Sci. **30**, 482–488 (1969)

33. Flockhart, B.D.: The effect of temperature on the critical micelle concentration of some paraffin-chain salts. J. Colloid Sci. **16**, 484–492 (1961)

34. Kim, H.U., Lim, K.H.: A model on the temperature dependence of critical micelle concentration. Colloids Surf. A: Physicochem. Eng. Asp. **235**, 121–128 (2004)
35. Tanford, C.: The Hydrophobic Effect: Formation of Micelles and Biological Membranes, 2 edn. Wiley, New York (1980)
36. Jaap, J., Nusselder, H., Engberts, J.B.F.N.: Toward a better understanding of the driving force for micelle formation and micellar growth. J. Colloid Interface Sci. **148**, 353–361 (1992)