

Langmuir Aggregation of Thionin on Sodium Dodecyl Sulfate and Its Application¹

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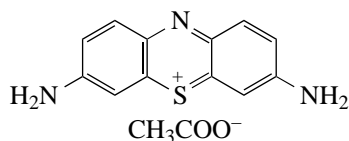
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Abstract—The microphase adsorption–spectral correction (MPASC) technique was applied to the interaction of thionin (TN) with sodium dodecyl sulfate (SDS) at pH 4.56. The synergism mechanism of SDS in solution was analyzed and discussed. The great electrostatic aggregation of TN on SDS obeys Langmuir monolayer adsorption. The property constants of the aggregate were determined and the quantitative determination of the anionic surfactant (AS) in samples was made in the presence of EDTA. Results showed that the large micellar aggregate is $(\text{TN}-\text{SDS}_2)_{31}$, the adsorption constant of the monomer aggregate is 1.85×10^5 (18°C), and its molar absorptivity is $4.45 \times 10^6 \text{ L mol}^{-1} \text{ cm}^{-1}$. For analysis of samples, the recovery is between 94.5 and 111% and the RSD is less than 7.62%.

Currently, for the supersensitive analysis of trace component, a surfactant, e.g., Triton X-100, sodium dodecyl sulfate (SDS), and so on, is often necessary because they enhance the sensitivity. The following models were earlier proposed to explain the synergism (e.g., solubilization, stabilization, and so on) of surfactants: micelle extraction, synergism perturbation [1], hydrogen bond formation [2], micelle catalysis [3], asymmetric microenvironment [4], and others. An ion surfactant molecule usually has a long chain and various aggregation forms in aqueous solution, e.g., spherical, worm-like, tubules, and lamellae [5]. Recently, the study of the surfactant molecular aggregation has become very active [6–9]. Understanding the aggregation of micelle and its assembly with other organic ions, e.g., stain is very significant to synthesize the new-type efficient surfactant.

In the present work, the microphase adsorption - spectral correction technique (MPASC) was described and applied to the study of the aggregation of thionin (TN) on SDS. The structure of TN is given below:



It forms cations in acidic solution and is adsorbed on anionic surfactants, e.g., SDS. Results showed that the binding ratio of TN to SDS is 1 : 2, and the binding constant of the monomer aggregate $K_{\text{SDS-TN}}$, 1.85×10^5 . The conventional quantitative detection of trace amounts of anionic surfactant (AS) in wastewater by spectrophotometry uses methylene blue [9]. The

extraction of the colored product must be carried out with chloroform [10–12]. The aggregation of TN on SDS has been applied to the determination of AS in samples. The reagent EDTA was added to mask metal ions possibly existing in samples in order to improve the detection selectivity. The mean recovery of SDS is between 94.5 and 111% with the RSD less than 7.62%.

EXPERIMENTAL

Apparatus and reagents. The absorption spectra were recorded on a TU1901 Spectrophotometer (PGeneral, Beijing) and the independent absorbance was measured on a Model 722 spectrophotometer. The DDS-11A conductivity meter (Tianjin 2nd Anal. Instruments) was used to measure conductivity together with a DJS-1 conductivity immersion electrode (electrode constant 0.98, Shanghai Tienkuang Devices); the deionized water had a conductivity below $0.3 (\Omega \text{ cm})^{-1}$. The pH of the solution was measured with a 320-S pH meter (Mettler–Toledo Instruments, Shanghai). The temperature was controlled and remained constant in a Model 116R electrical heated thermostat bath, (Changjiang Test Instruments of Tongjiang, China).

SDS standard solutions, $1.00 \times 10^{-2} \text{ mol/L}$ and 100 mg/L , were prepared by dissolving sodium dodecyl sulfate (SDS) (Shanghai Chemical Reagents) in deionized water. SDS was used as the standard substance of anionic surfactant (AS). The TN solution, $1.25 \times 10^{-3} \text{ mol/L}$, was prepared by dissolving 0.1000 g of thionin (content 90%) in 10 mL of DMF and then diluting to 250 mL with deionized water. $1.25 \times 10^{-4} \text{ mol/L}$ TN was prepared by diluting the above solution. The Britton–Robinson buffer solutions (between pH 1.8 and 11.2) were prepared for adjusting

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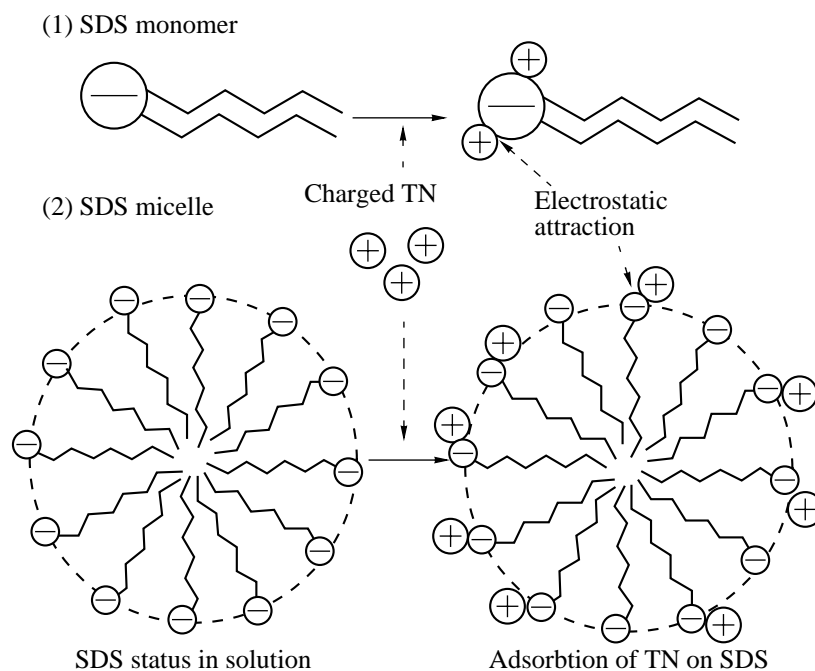


Fig. 1. The aggregation of TN on an SDS monomer and micelle.

the pH of solutions. 2.0 mol/L NaCl was prepared to adjust the ionic strength. 5% EDTA was used to mask foreign metal ions in samples.

MATERIALS AND METHODS

Aggregation of TN on SDS: Into a 10 mL calibrated flask were added an appropriate working solution of SDS, 1 mL of Britton–Robinson buffer solution and a known volume of TN solution. The mixture was diluted to 10 mL with deionized water and mixed thoroughly. The absorbance measurements were made at 595 and 630 nm, respectively, against the blank treated in the same way but without SDS.

Preparation and analysis of samples: Three samples were prepared. Sample 1 was sampled from Huahe River, sample 2 from local sewage pipe, and sample 3 from lake water. A sample should be filtered before coloring so as to remove the suspending solid. The order of the addition of the buffer and TN solutions corresponds with the procedure (1) above. In addition, 0.5 mL of 5% EDTA must be added to mask the metal ions possibly existing in the samples. The direct measurement is same as that above.

Principle and Calculation. In SDS (S) solution, the aggregation of S ions will form an electrostatic global micelle (Fig. 1 (1)) when the S concentration is higher than the critical micellar concentration (CMC). So, the electrostatic attraction of a ligand (L) with opposite charge occurs [13–16] in the micelle until the dynamic equilibrium takes place (Fig. 1 (2)). The electrostatic

attraction results in the solubilization of L on an S micelle. Similarly, the same electrostatic adsorption of L on an S monomer surface can occur when S is less than CMC (Fig. 1–(1)). The aggregation of L on an S surface is only for a monolayer like biomacromolecule [17, 18]. It obeys the Langmuir isothermal adsorption [19] and the following equilibrium occurs: L (aqueous phase, c_L) \leftrightarrow SL_n (micellar phase, c_S , S–CNC molecule). The Langmuir isothermal adsorption equation is used:

$$1/\gamma = 1/N + 1/KNc_L, \quad (1)$$

where K is the adsorption constant and c_L is the molar concentration of the excess L. The symbol γ is the molar ratio of L adsorbed to S. Within increase in the L concentration, γ will approach the maximal binding ratio N . The γ^{-1} on c_L^{-1} dependence is linear and we calculate N and K . Both c_L and γ are calculated by means of [20, 21]

$$\gamma = \eta(c_{L_0})/c_S, \quad (2)$$

$$c_L = (1 - \eta)c_{L_0}, \quad (3)$$

$$\eta = (A_c - \Delta A)/A_0, \quad (4)$$

where both c_S and c_{L_0} are the initial molar concentrations of S and L. η indicates the effective fraction of L adsorbed on S. A_c , A_0 , and ΔA are the real absorbance of the S–L aggregate, the measurement absorbance of the reagent blank (L solution) against water, and that of the S–L solution against the reagent blank directly mea-

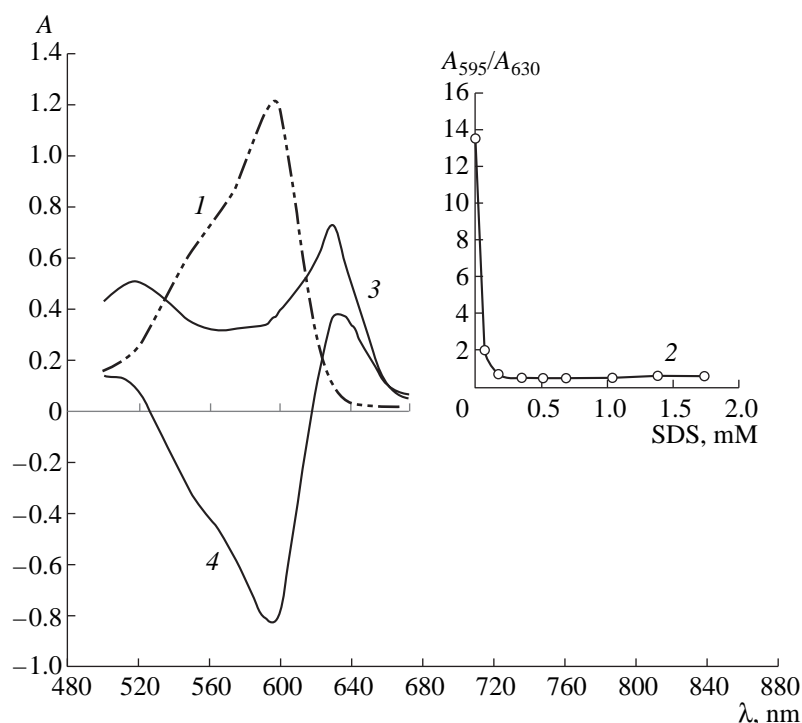


Fig. 2. Absorption spectra of TN-SDS solutions at pH 4.56: (1) TN (0.625 $\mu\text{mol/L}$) solution against water; (2) effect of SDS concentration on the absorbances ratio of solution at 595 and 630 nm initially containing 0.625 $\mu\text{mol/L}$ of TN against water; (3) TN (0.625 $\mu\text{mol/L}$), SDS (2.0 mg) solution against water; and (4) TN (0.625 $\mu\text{mol/L}$), SDS (0.50 mg) solution against reagent blank.

sured at the peak wavelength 2, respectively. A_c is calculated by the relation [21–23]

$$A_c = (\Delta A - \beta \Delta A') / (1 - \alpha \beta), \quad (5)$$

where $\Delta A'$ indicates the absorbance of the S-L solution measured at the valley absorption wavelength 1 against a reagent blank. α and β are the correction constants

$$\alpha = \varepsilon_{\text{ML}\gamma}^{\lambda_1} / \varepsilon_{\text{ML}\gamma}^{\lambda_2} \quad (6)$$

and

$$\beta = \varepsilon_{\text{L}}^{\lambda_2} / \varepsilon_{\text{L}}^{\lambda_1}, \quad (7)$$

and they are calculated by the relations [19–23]: where the symbols $\varepsilon_{\text{SL}}^{\lambda_1}$, $\varepsilon_{\text{SL}}^{\lambda_2}$, $\varepsilon_{\text{L}}^{\lambda_1}$, and $\varepsilon_{\text{L}}^{\lambda_2}$ are the molar absorptivities of SL_N and L solutions measured at λ_1 and λ_2 , respectively. In addition, the molar absorptivity (real $\varepsilon_r^{\lambda_2}$, not apparent $\varepsilon_a^{\lambda_2}$) of the micellar aggregate at λ_2 may be directly calculated by the relation

$$\varepsilon_r^{\lambda_2} = mNA_c / \delta \gamma c_S, \quad (8)$$

where δ is the cell thickness (cm) and m is the aggregation number of S in micelle. In fact, the spectral correction technique is also one of the dual-wavelength spectrophotometric approaches. However, it is different from the others [24–26], and only it can eliminate the optical absorption interference of the free L in its S

equilibrium solution. Thus the detection precision and accuracy may be improved and the property constants of the product can be determined and calculated easily.

RESULTS AND DISCUSSION

Spectral Analysis. The interaction of TN with SDS was carried out. The absorption spectra of TN and SDS-TN solutions are shown in Fig. 2. From curve 1, the spectral peak of TN is located at 595 nm. From curve 2, the absorbance ratio of the SDS-TN solution measured at 595 and 630 nm approaches a minimum when SDS is over 2.00×10^{-4} mol/L in the presence of 6.25×10^{-5} mol/L TN. Therefore, the free TN approaches zero in such SDS-TN solutions where the molar ratio of SDS to TN is more than 3 : 1. Curve 3 gives the absorption spectrum of such a solution and it indicates that the spectral peak of the aggregate is located at 630 nm. The peak red shift is only 35 nm. From the relative spectrum 4, we can see that the absorption peak and valley of the TN-SDS solution are located at 630 and 595 nm, respectively. Both wavelengths were used in this work. From curves 1 and 3, the correction constants were calculated to be $\beta = 0.074$ and $\alpha = 0.494$ from equations (6) and (7).

Effect of pH on interaction. By varying the pH of solution, the absorption of TN on SDS was measured. The γ of TN to SDS is shown in Fig. 3. We observe that

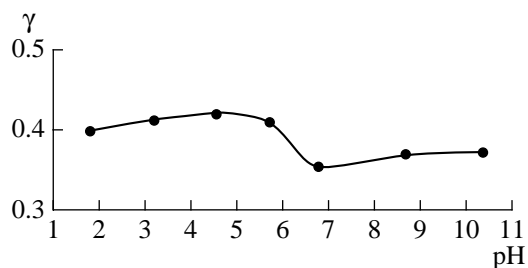


Fig. 3. Effect of the pH on the adsorption ratio of TN and SDS in the solution containing 0.937 $\mu\text{mol/L}$ of TN and 0.500 mg of SDS.

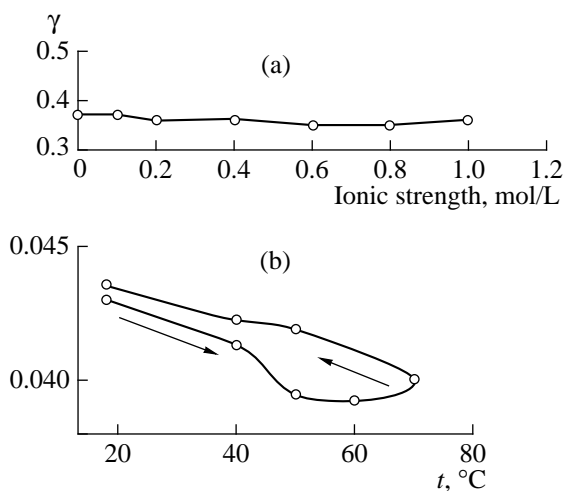


Fig. 4. Effect of the temperature on the adsorption ratio of (a) TN (0.075 $\mu\text{mol/L}$) and (b) SDS (1.50 $\mu\text{mol/L}$).

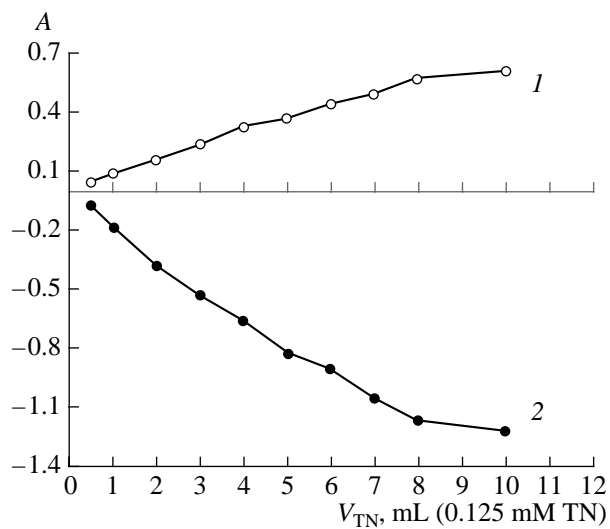


Fig. 5. Effect of the TN concentration on the absorbances of the solution containing initially 0.500 mg of SDS at pH 4.56: (1) at 630 nm and (2) at 595 nm, both against the blank reagent.

the aggregation of TN on SDS is more sensitive in acidic solution. This is attributed to the protonation of the TN-amines to form TN^{2+} and TN^{3+} . They can be attributed closely on SDS surface. In this work, pH 4.56 buffer solution was added.

Effect of the ionic strength, temperature, and time on the interaction. In order to investigate the effect of the ionic strength on the aggregation of TN on SDS, we added NaCl in solution and its effect is shown in Fig. 4. We see that the γ of TN to SDS decreases only 5% in 1.0 mol/L NaCl. This is attributed to the fact that TN cations have a much stronger electrostatic attraction than Na^+ .

The effect of the temperature on the γ of TN to SDS is also shown in Fig. 4. We observe that γ decreases slowly with an increase in temperature. This is attributed to the higher temperature causing the desorption of TN from SDS. This appearance is in accordance with the objective nature of a surface adsorption. From the return of the curve, we know the aggregation of TN on SDS is reversible.

At a temperature of 18°C, we found that the aggregation of TN on SDS is complete in 5 min. The absorbance measurement of the solution should be carried out after 5 min.

Effect of the TN concentration on the interaction.

By varying the addition of 1.25×10^{-4} mol/L TN, the absorption of the TN-SDS solutions was measured, and their curves are shown in Fig. 5. From curves 1 and 2, the absorbances increase with an increase of the TN concentration and approach maximums when the addition of TN solution is over 8 mL. In the quantitative determination of AS, 9.0 mL of 1.25×10^{-4} mol/L TN was added and then both the γ and c_L of each solution above were calculated. Their relationship is shown in Fig. 6. The γ^{-1} vs. c_L^{-1} curve is linear, which shows that the interaction of TN on SDS obeys the Langmuir isothermal adsorption. The regression equation is $\gamma^{-1} = 10.8c_L^{-1} + 2.1$

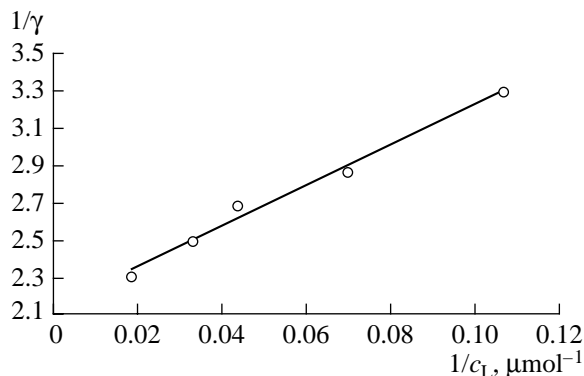


Fig. 6. γ^{-1} vs. c_L^{-1} .

Determination of the anionic surfactant samples with TN as the reactant at pH 4.56

Sam-ple no.	Added SDS, mg/L	Found an. surf., mg/L	RSD, %	Rec. %
1	0	3.12 ± 0.10	3.2	94.5
	2.00	5.01 ± 0.13	2.6	
2	0	0.92 ± 0.07	7.6	108
	1.00	2.00 ± 0.09	4.0	
3	0	8.13 ± 0.18	2.2	111
	10.0	19.2 ± 0.32	1.7	

(linear correlation coefficient $R^2 = 0.9862$, c_L , mol/L). From the intercept, the maximum binding ratio of TN to SDS is calculated to be $N = 0.5$. Therefore, the monomer aggregate is $TN \cdot (SDS_2)$. The large micellar aggregate is expressed as $(TN \cdot (SDS_2))_{31}$ (the micellar aggregation number = 62) when SDS is higher than CMC at 8.2×10^{-3} mol/L. From the slope of the line, the equilibrium constant of the monomer aggregate was calculated to be $K = 1.85 \times 10^5$. The real (not apparent) molar absorptivity of the micellar aggregate at 630 nm was calculated to be 4.45×10^6 mol⁻¹ cm⁻¹. For the determination of the formation constant of the aggregate, the spectral correction technique has special advantages in operation and principle in comparison to classical methods, such as the Scatchard model [27], molar ratios [28], and so on.

Quantitative determination of anionic surfactants. (1) *Calibration Graph and Precision:* The standard series of SDS solutions were prepared and measured at pH 4.56. The regression equation is that $A_c = 2.00x - 0.0151$ between $x = 0$ and 0.300 mg of SDS (linear correlation coefficient 0.999) and it is used in the determination of AS in samples. We have found that the A_c vs. x curve is more linear and more precipitous than the ΔA vs. x line. Therefore, the spectral correction technique has higher sensitivity and better accuracy than ordinary spectrophotometry. Six replicated determinations of 0.100 mg of standard SDS were made. The mean was 0.106 ± 0.005 mg ($n = 6$), and the relative standard deviation (RSD), 4.72%.

(2) *Effect of Foreign Ions:* By adding the masking reagent in the procedures, the influence of foreign substances was studied at pH 4.56. None of the following ions and compounds affected the direct determination of 0.500 μ mol/L of SDS (less than 10% error): 1 mg of Ca^{2+} , F^- , Mg^{2+} , NH_4^+ , PO_4^{3-} , $C_2O_4^{2-}$, glucose, or amino acid; 0.5 mg of Al(III), Mn(II), 0.2 mg of Fe(II, III),

Zn(II), or Co(II); and 0.1 mg of Cu(II), Ni(II), Pb(II), or Cd(II).

(3) *Samples Analyzed:* The determination of AS in three samples and the recovery of standard SDS are given in table. We see that the recovery of SDS is complete and the precision is satisfactory.

CONCLUSIONS

The cooperation of both the Langmuir adsorption and the spectral correction technique (MPASC) provides a very helpful experimental strategy for the study of the aggregation of a stain on a surfactant. The investigation to the aggregation of TN on SDS supports the Langmuir isothermal adsorption of stain molecules on ionic surfactant. Though MPASC technique has not given a sensitivity higher than other methods, such as RLS [29], it meets precision and accuracy criteria and offers the additional benefits of simplicity and versatility. In addition, we understand the classical method can still play important role in study of the synergism (such as solubilization, enhanced sensitivity, etc.) of surfactant micelle and application to the determination of super microamounts of a component.

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