

Langmuir Aggregation of Nile Blue and Safranin T on Sodium Dodecylbenzenesulfonate Surface and Its Application to Quantitative Determination of Anionic Detergent

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We studied the interaction of sodium dodecylbenzenesulfonate (SDBS) with Nile Blue (NB) and Safranin T (ST) by a spectral correction technique. The aggregations of NB and ST on an SDBS surface obeyed Langmuir isothermal adsorption. The adsorption ratios of NB and ST to SDBS were both 0.5, and the adsorption constants of the aggregates were 1.80×10^5 and 9.49×10^4 . The aggregations were applied to the quantitative determination of anion detergent in samples; the recovery of SDBS was between 90.3 and 106% together with an RSD of 3.78%.

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Introduction

In the present supersensitive detection of trace amounts of a component, the use of a surfactant is often essential. The following models were earlier proposed and applied as an explanation of the synergism (*e.g.* solubilization, stabilization, enhanced sensitivity) of surfactant: micelle extraction,¹ synergism perturbation,² electrostatic field aggregate,³ hydrogen bond formation,⁴ micelle catalysis,⁵ asymmetric microenvironment⁶ and so on. An ion surfactant molecule usually has a long chain and various aggregation forms in an aqueous solution, *e.g.* spherical, worm-like, tubules and lamellae. Recently, the study of surfactant molecular aggregation has still been very active.^{7,8} Understanding the aggregation of a micelle and its assembly with other organic ions, *e.g.* stain, is very significant for synthesizing a new-type of efficient detergent.

A surfactant molecule (S) exists in a monomer when S is less than its critical micellar concentration (CMC) (Fig. 1(1)) and the aggregation of S molecules forms a large electrostatic global micelle when S is over CMC (Fig. 1(2)). The charge monomer and micelle can both adsorb a dye probe (L) with a contrary charge (Fig. 1(1) and (2)) until kinetic equilibrium is established. The electrostatic attraction results in the solubilization of L. If a metal (M) is added into the S solution, the sensitive complexation of M with L adsorbed on the S surface would occur. Because the concentration of L on a micellar surface is much higher than that in the aqueous phase, the complex reaction changes very sensitively and rapidly. This causes an enhancement of the sensitivity. The aggregation of L on the S surface occurs in only a monolayer, like a biomacromolecule.⁹ It obeys Langmuir adsorption¹⁰ and the following equilibrium occurs: L (aqueous phase, C_L) \rightleftharpoons SL_N (micelle phase, C_S) in L-S solution. The Langmuir equation,

$$\gamma = \frac{KN C_L}{1 + K C_L}, \quad (1)$$

is used, where K is the adsorption constant and C_L is concentration of the excess L. N indicates the maximal adsorption ratio of L to S and γ the molar ratio of L adsorbed to S. With an increase in the L concentration, γ will approach a maximum, called the adsorption ratio (N). If $K C_L$ approaches infinity, γ approaches N . Conversely, $\gamma = K N C_L$ if $K C_L$ approaches zero. Therefore, we calculated the binding constant, $K = S/N$, where the symbol S indicates the tangent slope of γ vs. C_L at the grid origin. Of course, we can also calculate K by measuring a certain solution, where its γ/N is between 0 and 1. Both C_L and γ are calculated by the following equations:¹¹

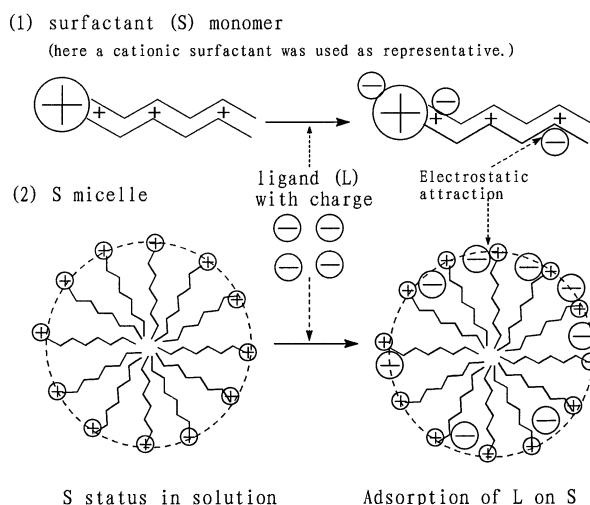


Fig. 1 Adsorption of stain anions (L) on a surfactant (S) monomer and a micellar surface (a cationic surfactant as representative).

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$$\gamma = \eta \times \frac{C_{L0}}{C_S}, \quad (2)$$

$$C_L = (1 - \eta)C_{L0}, \quad (3)$$

where

$$\eta = \frac{A_c - \Delta A}{A_0}, \quad (4)$$

where both C_S and C_{L0} are the concentration of the S and L initially added, and η indicates the effective fraction of L. A_c , A_0 and ΔA are the real absorbance of the S-L product, the measurement absorbance of the reagent blank against water and that of the S-L solution against the reagent blank directly measured at the peak wavelength (λ_2). A_c is calculated by means of¹²

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

where $\Delta A'$ indicates the absorbance of the S-L solution, measured at the valley absorption wavelength (λ_1). In common, α and β are the correction constants, which can be calculated as follows:¹²

$$\alpha = \frac{\epsilon_{SL}^{\lambda_1}}{\epsilon_{SL}^{\lambda_2}}, \quad (6)$$

and

$$\beta = \frac{\epsilon_L^{\lambda_2}}{\epsilon_L^{\lambda_1}}, \quad (7)$$

where $\epsilon_{SL}^{\lambda_1}$, $\epsilon_{SL}^{\lambda_2}$, $\epsilon_L^{\lambda_1}$ and $\epsilon_L^{\lambda_2}$ are the molar absorptivities of SL_N and L at λ_1 and the peak wavelength (λ_2), respectively, directly measuring SL_N (when S is much more than the L concentration) and L solutions. In addition, the absorptivity (real $\epsilon_a^{\lambda_2}$, not apparent $\epsilon_a^{\lambda_2}$) of the adsorption aggregate SL_N at λ_2 is also directly calculated by the following relation:

$$\epsilon_a^{\lambda_2} = \frac{mNA_c}{\delta \gamma C_S}, \quad (8)$$

where m is the aggregation number of S micelle, δ the cell thickness (cm) and the others have the same meanings as in the equations above.

The cooperation of the Langmuir adsorption and spectral correction technique will provide a very helpful experimental strategy for studying the interaction of a surfactant with a stain and a metal. It clearly provides a synergism mechanism of a surfactant solution. In this work, we studied concrete interactions: sodium dodecylbenzenesulfonate (SDBS) with Nile Blue (NB) and Safranin T (ST). The aggregation of NB and ST on an SDBS surface obeys Langmuir isothermal absorption. The two interactions have been applied to the quantitative detection of an anion detergent in samples with satisfactory results.

Experimental

Apparatus

The absorption spectra were recorded on a UV/VIS 265 Spectrophotometer (Shimadzu, Japan). A conductivity meter,

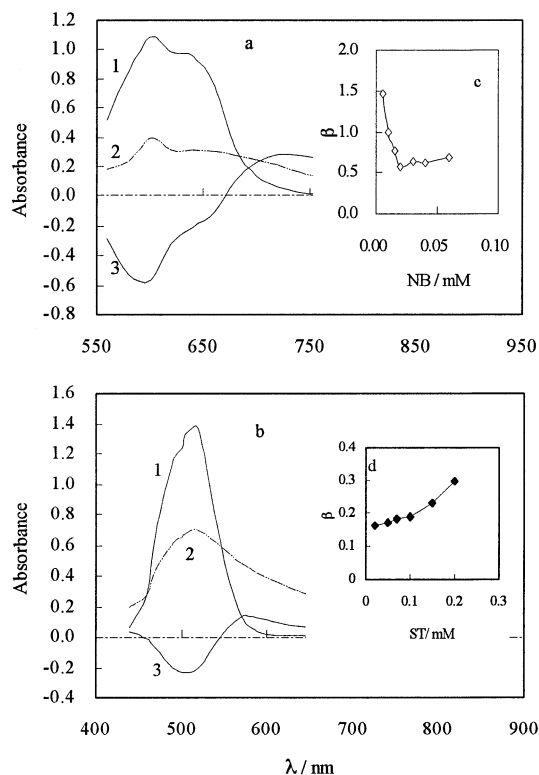


Fig. 2 Absorption spectra of NB, ST and their SDBS solutions: a1, 0.500 μmol of NB at pH 7; a2, 0.250 μmol of NB with 1.5 μmol of SDBS at pH 7; a3, 0.500 μmol of NB with 1.00 μmol of SDBS at pH 7; b1, 1.500 μmol of ST at pH 11; b2, 0.500 μmol of ST with 2 μmol of SDBS at pH 11; b3, 1.00 μmol of ST with 1.00 μmol of SDBS at pH 11, c, β variation of NB solution at pH 7; d, β variation of ST solution at pH 11. a3 and b3 against reagent blank and the others against water.

Model DDS-11A (Tianjin 2ed Analytical Instruments), was used to measure the conductivity together with a Model DJS-1 conductivity immersion electrode (electrode constant 0.98, Shanghai Tienkuang Devices) for the production of deionized water below 0.5 ($\mu\Omega\cdot\text{cm}$)⁻¹. The pH of a solution was measured on a pHs-2C acidity meter (Leici Instruments, Shanghai) and a Model 620D pH Pen (Shanghai Ren's Electronic). The temperature was adjusted and remained constant in an electrically heated thermostat bath, Model 116R (Changjiang Test Instruments of Tongjiang, China).

Reagents

A stock standard SDBS solution, (10.00 mM) was prepared by dissolving 1.742 g of sodium dodecylbenzenesulfonate (SDBS, Shanghai Chemical Reagents) in 500 ml a non-ionic surfactant; a 1.00 mM SDBS work solution was provided daily by diluting the stock solution. Organic dye solutions, 0.500 mM NB and 1.000 mM ST (purchased from Shanghai Chemical Reagents of Chinese Medicine Group), were prepared by dissolving in deionized water and stored at 4°C. Acetate, ammonium and phosphate buffer solutions (pH 3 - 12) were used to adjust the acidity of the solutions. 2 M NaCl was used to adjust the ionic strength of the aqueous solutions and 5% Na₂EDTA was prepared to mask any foreign metal ions which possibly coexisted in the samples. All of the reagents were of analytical grade and used without further purification.

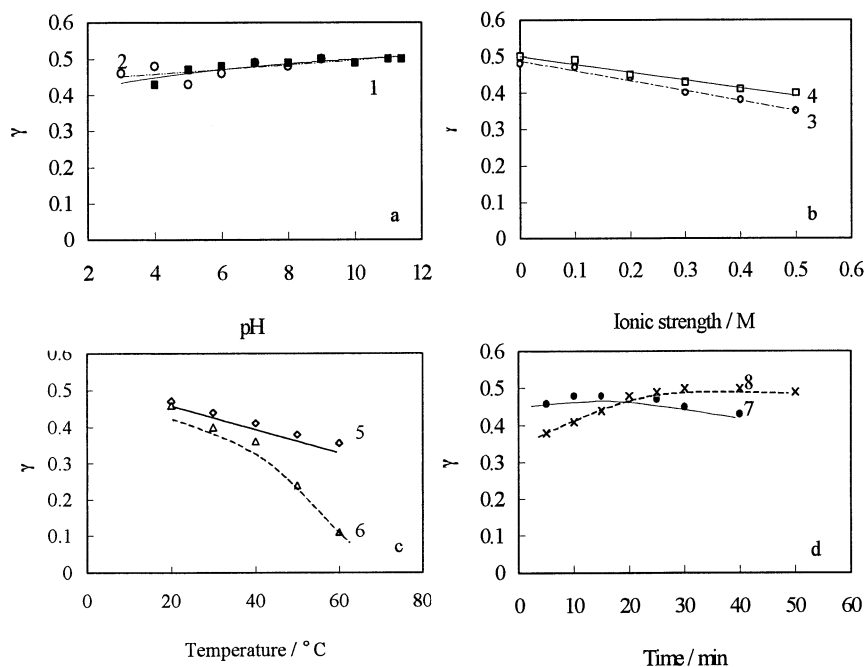


Fig. 3 Effect of the pH (a), ionic strength (b), temperature (c) and reaction time (d) on the binding ratio of NB and ST to SDBS. 1, 3, 5 and 7: 1.00 μmol of NB plus 1.00 μmol of SDBS at pH 7; 2, 4, 6 and 8: 1.00 μmol of ST plus 1.00 μmol of SDBS at pH 11.

Procedures

Into a 25 ml calibrated flask were added an appropriate working solution of SDBS, a 2.5 ml of buffer solution and an appropriate NB or ST solution. The mixture was then diluted with deionized water to 25 ml and thoroughly mixed. All of the absorption measurements were obtained against a blank treated in the same way without SDBS.

Two samples were prepared and analyzed. Sample 1 was from lake water; 2 mg of NH_4^+ , K^+ , Cl^- , SO_4^{2-} , NO_3^- , ethanol, amino acid, sugar, 0.2 mg of F^- , Fe(II) , Mg(II) , Zn(II) , Al(III) , 0.05 mg of Pb(II) , Ni(II) , 0.01 mg of Hg(II) and drops of SDBS solution were added. Sample 2 came from local sewage water. A known volume of a sample was taken into a 25 ml volumetric flask. Then, 1 ml of Na_2EDTA was added to complex metal ions, and the following procedures were the same as mentioned in the last paragraph.

Results and Discussion

Spectral analysis

Adsorption experiments of NB and ST on an SDBS surface were carried out. The absorption spectra of NB, ST and their SDBS solutions are shown in Fig. 2 (a and b). From curves a-1 and b-1, we can observe that the peak absorptions of the NB and ST solutions at pH 11 is located at 600 and 500 nm, respectively, and from curves a-2 and b-2; the peak absorptions of the SDBS-NB and SDBS-ST aggregates are at 540 and 520 nm. The spectral violet shift of the SDBS-NB aggregate is 40 nm and the spectral red shift of the SDBS-ST aggregate is 20 nm. However, from the relative spectra, a-3 and b-3, the peaks of the SDBS-NB and SDBS-ST solutions are located at 720 and 580 nm. Therefore, four wavelengths (600 and 720 nm, 500 and 580 nm) were used as work wavelengths. From curves a-2 and b-2, the correction coefficient of the NB-SDBS and ST-SDBS aggregates were calculated to be $\alpha = 1.39$ and 1.49,

respectively. The variation in β of NB and ST solutions are shown in Figs. 2c and 2d; the self-assemblies of NB and ST occur^{13,14} under the recommended operation.

Effect of variables

By varying the pH of the solution, the absorptions of SDBS-NB and SDBS-ST solutions were measured; the ratio of NB and ST to SDBS is shown in Fig. 3a. From curve 1, we can observe that the absorption of the former approaches a maximum at between pH 3 and 9, and that of the latter approaches a maximum at between pH 8 and 11. The NB cations at pH 3–9 and ST cations at pH 8–11 are easily formed and they were adsorbed on the SDBS surface. In the study, pH 7 and pH 11 were selected, respectively.

From Fig. 3b, we find that an increase in the ionic strength of a solution would cause a decrease in the adsorption ratio. This is attributed to the fact that much more Na^+ can also be adsorbed on the SDBS surface in place of the NB or ST molecules. This is in accord with the common nature of surface adsorption.

Under various temperatures, the relationship between the binding ratio and the NB and ST concentrations is shown in Fig. 3c. We have observed that the ratios decrease along with an increase in the temperature. This is in accord with the common nature of surface adsorption, which is different from the common chemical reaction. Curve 5 gives the ratio as increasing by 6% and for curve 6 by about 20% per increasing 10°C.

From Fig. 3d, the adsorption is seem to be complete within 10 min at room temperature (20°C) because the binding ratio approaches the maximum, and then remains constant.

Effect of the NB and ST concentrations and determining the adsorption constants

By varying the addition of NB and ST solutions, the absorption of dye-SDBS solutions was measured. The values of γ and C_L were calculated. Their relationship is shown in Fig. 4.

Table 1 Six replicated determinations of SDBS solutions with NB at pH 7 and ST at pH 11 and calculation results of the binding ratio, equilibrium constant and real absorptivity of SDBS products

Interaction	γ/N	K	$\epsilon/l \text{ mol}^{-1}\text{cm}^{-1}$
SDBS (0.500 μmol)	(0.243 ± 0.014)	$(1.80 \pm 0.21) \times 10^5$	6.90×10^3 (720 nm)
-NB (0.250 μmol)	/0.50		
SDBS (1.00 μmol)	(0.244 ± 0.003)	$(9.49 \pm 0.63) \times 10^4$	4.45×10^3 (580 nm)
-ST (0.500 μmol)	/0.50		

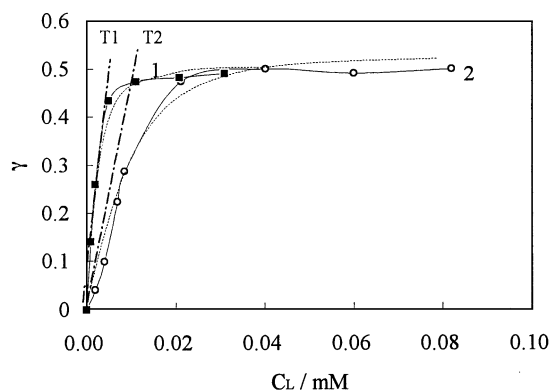


Fig. 4 γ vs. C_L : 1, NB solution containing 1.00 μmol of an SDBS; 2, ST solution containing 1.00 μmol of SDBS. The solid lines indicate measurement, the dashed lines indicate Langmuir adsorption, and the dotted-dashed-lines show the tangent line at 0 point.

By comparing the measurement curves (solid line) with the Langmuir adsorption (dashed line), they can be seen to be close to each other. Therefore, the aggregations accord with the Langmuir isothermal adsorption in only a monolayer. The binding ratios of NB and ST to SDBS approach a constant value at 0.50 when the addition of NB and ST is over 0.50 μmol . From the tangent lines, T1 and T2, we calculated the adsorption constant of the SDBS-NB and SDBS-ST aggregate to be $K = 1.78 \times 10^5$ and 9.38×10^4 . In addition, we also determined K and ϵ of the aggregates by some replicated measurements of the solutions. The preparations of the solutions and the calculations of the factors are given in Table 1. We find that all K are near to those obtained from γ vs. C_L . In determining the adsorption constants, the spectral correction technique has special advantages in operation and principle by contrast of the classical methods, such as the Scatchard model,¹⁵ and the molar ratios.¹⁶

Calibration graph and precision

A standard series of SDBS solutions was prepared and measured when NB and ST solutions were added. The regression equations of the real absorption (A_c) of the aggregates are given in Table 2. They are linear within the recommended concentration scope. By comparing both the slopes and the correlation coefficients of the linear equations, we found that the spectral correction technique always has a higher sensitivity and a better precision than what can be obtained in ordinary spectrophotometry.

For an A_c of 0.010, we calculated the detection limit of SDBS to be 0.030 μmol with NB as the reactant and 0.07 μmol with ST as the reactant. Seven replicated determinations of 0.500 μmol of SDBS were carried out with NB as the reactant. The mean was $0.440 \pm 0.006 \mu\text{mol}$ and the mean recovery of SDBS was 88.0%. The relative standard deviation (RSD) was 1.37%.

Table 2 Linear regression equations for determining an anion detergent with NB at pH 7 and ST at pH 11 in the presence of EDTA

Dye reactant	Linear slope/ μmol	Regression equation	Correlation coefficient
NB	0 - 1.50	$A_c = 0.375x - 0.027$ $\Delta A = 0.319x - 0.021$	0.9980 0.9958
ST	0 - 3.00	$A_c = 0.148x - 0.007$ $\Delta A = 0.123x - 0.009$	0.9961 0.9953

Table 3 Determination of an anion detergent in samples with NB and ST as reactants in the presence of EDTA

Sample No.	Added SDBS/ μmol	SDBS found/ μmol	
		with NB	with ST
1	0	0.107 ± 0.003^a RSD 2.78%	0.100 ± 0.003^a RSD 3.78%
	0.200	0.287 ± 0.007^b Rec. 90.3%	0.311 ± 0.008^b Rec. 105%
2	0	0.300 ± 0.006^a RSD 2.54%	0.306 ± 0.005^a RSD 1.93%
	0.300	0.590 ± 0.008^b Rec. 96.7%	0.624 ± 0.010^b Rec. 106%

a. Six replicated determinations.

b. Three replicated determinations.

Similarly, when ST was used as the reactant, the mean was $0.447 \pm 0.017 \mu\text{mol}$ SDBS and the mean recovery was 89.4% with an RSD of 3.78%.

Effect of foreign ions

By the addition of EDTA- Na_2 (1 ml of 5%) in the general procedures, the influence of foreign substances on the determination of SDBS by using the spectral correction technique was tested at an ionic strength of 0.01. Because EDTA may mask most of the metals ions, a higher concentration of metal ions may be allowed. None of the following ions affected the direct determination of 1.00 μmol of SDBS (less than 10% error): 1 mg of K^+ , NH_4^+ , Ca(II) , SO_4^{2-} , CO_3^{2-} , 0.5 mg of Cl^- , F^- , PO_4^{3-} , NO_3^- , SO_3^{2-} , Ac^- , protein, amino acid, acetone, ethanol, 0.5 mg of Mg(II) , Al(III) , Fe(III) , Mn(II) , Zn(II) , Ti(IV) , Ge(IV) , Ni(II) , Co(II) , Sn(II) , 0.2 mg of Pb(II) , Cd(II) , Cu(II) , Be(II) , Hg(II) and 0.1 mg of cetyl trimethylammonium bromide (CTAB).

Sample analyzed

The determination of an anion detergent in two samples was carried out according to the procedures described in "Experimental"; and the results are given in Table 3. We observed that the recovery of SDBS was between 90.3 and 96.7% with an RSD of 2.78% with NB as the reactant and between 105 and 106% with an RSD of 3.78% with NT as the

reactant.

Conclusion

The investigation of the interaction of NB and ST with SDBS supports the Langmuir monolayer adsorption of small dye molecules or ions on an ionic surfactant. We have described the basic physics behind the cooperation of the Langmuir aggregation and the spectral correction technique, and surveyed some ongoing research concerning application to dye/surfactant/metal system. We understand that classical spectrophotometry can still play an important role in explaining micellar synergism.

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