

Interaction of Indigo Carmine with Cetyltrimethylammonium Bromide and Application to Determination of Cationic Surfactant in Wastewater

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Received May 28, 2003

The microsurface adsorption - spectral correction (MSASC) technique has been applied to the interaction of indigo carmine (IC) with cetyltrimethylammonium bromide (CTAB). The aggregation of IC on CTAB obeys Langmuir isothermal adsorption. The results show that both the monomer complex IC·CTAB and the micellar complex (IC·CTAB)_N were formed. The binding constant of the monomer complex was calculated to be $K_{IC·CTAB} = 2.20 \times 10^5 \text{ L} \cdot \text{mol}^{-1}$, and the molar absorptivity of the micellar complex was calculated to be $\epsilon_{(IC·CTAB)_N}^{560 \text{ nm}} = 8.58 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. The aggregation was applied to the determination of cationic surfactant in wastewater.

Key Words : MSASC technique, Langmuir aggregation, Indigo carmine, Cetyltrimethylammonium bromide, Determination of cationic surfactant

Introduction

Surfactant is extensively used in our daily life and various industrial productions, for example in chemicals, oil, mine-selecting, photosensitive materials, medicines, metallurgy and others. In many chemical analyses, a surfactant is often essential. Studies of surfactant solutions are still very active.¹⁻⁴ The investigation into the interaction between a surfactant and a small molecule or ion is helpful to analyze the mechanism of surfactants in washing, emulsification, separation and synergism. Understanding the aggregation of a surfactant with other small molecules or ions is still very significant to synthesize the new types of efficient detergents. Some earlier models *e.g.* solubilization, stabilization and sensitization, micelle extraction, synergism perturbation,⁵ hydrogen bond formation,⁶ asymmetric microenvironment⁷ were proposed and applied to explain surfactant activity.

In the present work, the microsurface adsorption - spectral correction technique (MSASC) is described and applied to study the aggregation of indigo carmine (IC) on cetyltrimethylammonium bromide (CTAB). The structure of IC is given in Figure 1. It forms a bivalent anion in a wide pH range and is adsorbed on CTAB. The aggregation of IC on CTAB has been characterized. The maximal binding number



Figure 1. The molecular structure of indigo carmine (IC).

of IC on CTAB is $N=1$, and the adsorption constant is $K_{CTAB-IC} = 2.20 \times 10^5 \text{ L} \cdot \text{mol}^{-1}$ of the monomer complex. This aggregation has been applied to quantitative detection of cationic surfactant in wastewater with satisfactory results.

Principle

In a surfactant (S) solution, the aggregation of S forms an electrostatic global micelle (Fig. 2, left) when the concentration of S is greater than the critical micellar concentration (CMC). The electrostatic attraction of a negatively charged dye (L) occurs^{8,9} on the micellar microsurface until the kinetic equilibrium (Fig. 2, right) is reached. The electrostatic attraction results in the solubilization of L in S solution. Similarly, the same phenomenon happens on S

(1) surfactant (S) monomer

(here a cationic surfactant was used as representative)

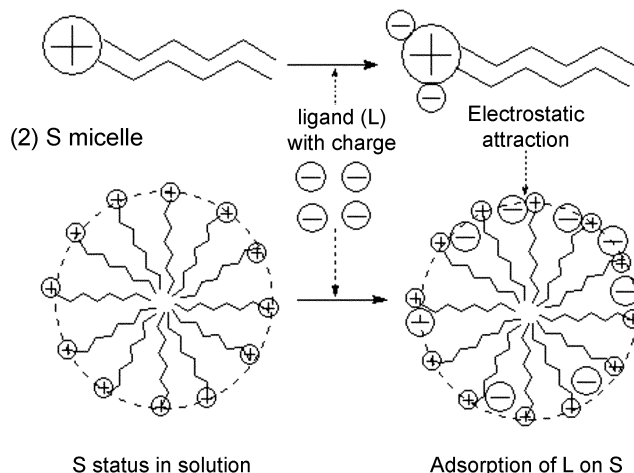
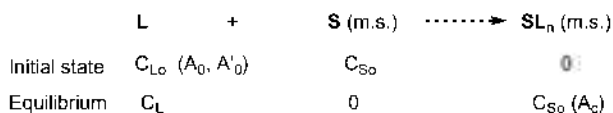


Figure 2. The aggregation of negatively charged dye (L) on cationic surfactant (S): 1- S monomer and 2- S micelle.

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monomer (Fig. 2-1). The aggregation of L on S is only in a monolayer, like on a biomacromolecule.^{10,11} It obeys the Langmuir isothermal adsorption.¹² The S-L solution equilibrium occurs as follows (m. s. is microsurface phase):



The Langmuir isotherm equation is expressed as:

$$\frac{1}{\gamma} = \frac{1}{N} + \frac{1}{KNC_L} \quad (1)$$

where the symbol K is the binding constant, and both C_{S0} and C_{L0} are the initial molarities of S and L. C_L is the molarity of excess of L in equilibrium. The symbol γ is the molar ratio of L adsorbed to S. With an increase in L molarity, γ approaches a maximal binding number, N . From plots γ^{-1} vs. C_L^{-1} , N and K may be calculated. Both C_L and γ are calculated by means of:¹¹

$$\gamma - \eta \times \frac{C_{L0}}{C_{S0}} \quad (2)$$

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

where

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

where the symbol η indicates the effective fraction of L binding on S. A_c , A_0 and ΔA are the real absorbance of the S-L complex, the absorbance of L solution measured against water and that of the S-L solution measured against the reagent blank at a peak wavelength λ_2 . A_c is calculated by the relation:¹²

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

where

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

and

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

The symbol $\Delta A'$ indicates the absorbance of the S-L solution measured against the reagent blank at the valley absorption wavelength λ_1 . Both α and β are the correction constants.^{13,14} The symbols $\epsilon_{SL}^{\lambda_1}$, $\epsilon_{SL}^{\lambda_2}$, $\epsilon_L^{\lambda_1}$ and $\epsilon_L^{\lambda_2}$ are the molar absorptivities of SL and L at λ_1 and λ_2 , respectively. In addition, the molar absorptivity (real $\epsilon_r^{\lambda_2}$ not apparent $\epsilon_a^{\lambda_2}$) of the micellar complex is calculated by the relation:

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

where the symbol δ is the cell thickness (cm) and m is the micelle aggregation number of S.

Experimental Section

Apparatus and reagents. Absorption spectra were recorded on a TU1901 Spectrophotometer (PGeneral, Beijing) and independent absorbance was measured on a Model 722 spectrophotometer. pH of solution was measured on an pHS-2C acidity meter (Leici Instruments, Shanghai). The temperature was adjusted and remained constant in a Model 116R electronic heated thermostatic bath, (Changjiang Test Instruments of Tongjiang, China).

The standard solution of CTAB 1.00 mmol/l. was prepared by dissolving cetyltrimethylammonium bromide (CTAB) (A. R. Shanghai Chemical Reagents) in deionized water. IC solution 1.00 mmol/L was prepared by dissolving 0.5487 g of indigo carmine (content 85%, Beijing Chemical Industry) in 1000 mL of deionized water. The Britton-Robinson buffer solutions (between pH 1.8 and 9.62) were used to adjust the pH of the solution. NaCl 3 mol/L was used for adjusting ionic strength of the solution and improve the reaction sensitivity. The masking reagent was prepared by mixing 100 mL of 5% $\text{Na}_2\text{-EDTA}$, 100 mL of 2% ethylenediamine and 100 mL of 5% potassium sodium tartrate, and it was used for masking metal ions in the sample.

Recommended procedures.

Aggregation of IC on CTAB: Into a 25 mL calibrated flask, an appropriate working solution of CTAB, 2.5 mL of Britton-Robinson buffer solution, 5 mL of 3 mol/L NaCl and 1.00 mL of IC solution were added. The solution was diluted to 25 mL with deionized water and mixed thoroughly. After 10 min, the absorbances were measured at 560 and 610 nm, respectively, against a reagent blank treated in the same way without CTAB.

Preparation and analysis of samples: Two wastewater samples were analyzed: #1 from the Huaihe River and #2 from a local sewage pipe. A milliliter of the standard solution of CTAB was added to the samples (100 mL) before coloring. 10.0 mL of a sample was taken in a 25 mL flask. 0.5 mL of the masking reagent was added. The successive operations were carried out according to the above procedure.

Results and Discussion

Spectral analysis. The IC-CTAB binding reaction solution was measured and the absorption spectra of IC and its CTAB solutions are shown in Figure 3. By comparing spectrum 3 with 4, we found that the addition of NaCl could sensitize the binding reaction. From spectra 1 and 2, we observed that the spectral peak of the complex is located at 560 nm and that of IC at 610 nm. The peak blue shift of the complex was 50 nm. Such a great wavelength-shift is rare in similar systems.^{8,9,11} Are findings indicates that the IC-CTAB binding is firm in spite of the electrostatic attraction. Nevertheless, ordinary spectrophotometry is still unfit for characterization of the IC-CTAB aggregation because the resolution of

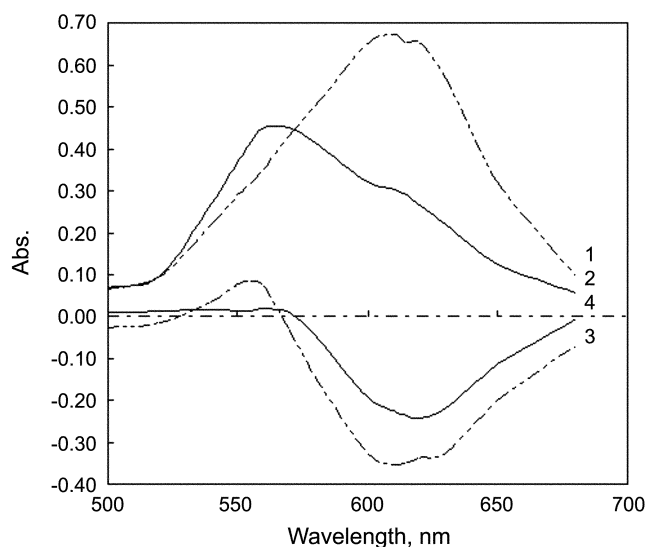


Figure 3. Absorption spectra of IC and its CTAB solutions containing 0.6 mol/l. NaCl: 1- IC (1.00 $\mu\text{mol}/25\text{ mL}$) solution against water. 2- IC (1.00 $\mu\text{mol}/25\text{ mL}$) - CTAB (10 $\mu\text{mol}/25\text{ mL}$) solution against water, which does not contain free IC. 3- IC (1.00 $\mu\text{mol}/25\text{ mL}$) - CTAB (1.00 $\mu\text{mol}/25\text{ mL}$) solution against a reagent blank and 4- same as 3 but in absence of NaCl.

spectra is not high enough. From spectrum 3, the peak of the IC-CTAB solution is located at 560 nm, and its valley is at 610 nm. Such two wavelengths were used. From spectra 1 and 2, the correction constants were calculated to be $\beta = 0.523$ and $\alpha = 0.500$, so $A_c = 1.44(\Delta A - 0.523\Delta A')$. A_c was used for calculating the real absorbance of the IC-CTAB complex in the mixed solution.

Effect of pH. Absorbance of the IC-CTAB solutions was measured for a variety of pH values. γ is shown in Figure 4. We could not see any change in the binding ratio as the pH increased. This particular dye has two very strong acid groups ($-\text{SO}_3\text{H}$). CTAB structure will not change and IC^{2-} can be formed between pH 1.8 to 9.62. This is the reason for

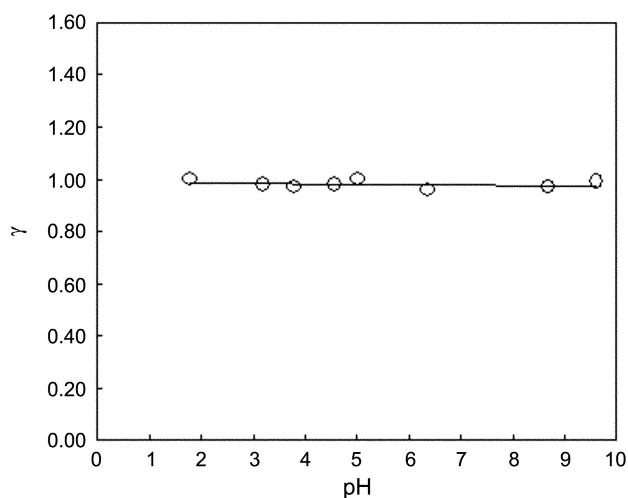


Figure 4. Effect of pH on γ of the solutions containing 1.0 μmol IC/25 mL and 1.00 μmol CTAB /25 mL and pH between 1.8 and 9.62.

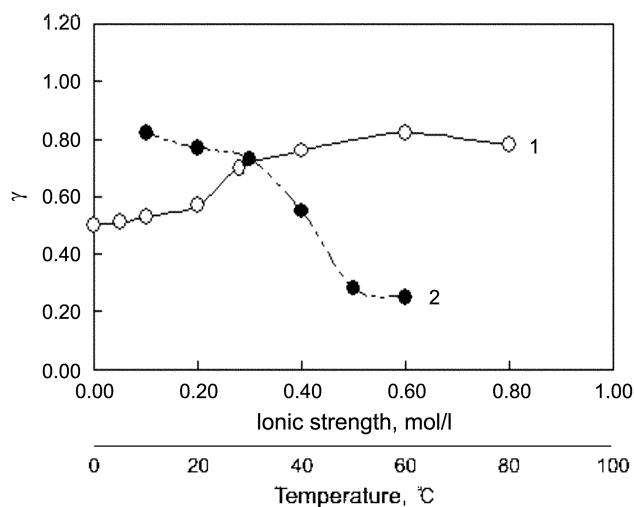


Figure 5. Effect of the operation conditions on γ of the solutions containing 1.0 μmol IC/25 mL and 1.00 μmol CTAB/25 mL: 1- ionic strength and 2- temperature.

keeping γ as a constant. In this work, pH 5.02 buffer solution was added.

Effect of ionic strength, temperature and time. To investigate the effect of ionic strength on aggregation of IC on CTAB, we added NaCl to the solution, and its effect on γ is shown in Figure 5. We observed that γ heightens slowly when the ionic strength is less than 0.2 mol/L. γ increases and then remains a constant when the ionic strength is more than 0.2 mol/L. This is the reason for the firm binding between IC and CTAB. In addition, the addition of inorganic salt results in an obvious decrease in CMC of the ionic surfactant, and the CTAB micelle has a higher attraction microsurface than the CTAB monomer. Therefore, the presence of NaCl can sensitize the IC-CTAB binding reaction. In this work, 0.6 mol/l. NaCl was added (to what??).

The effect of temperature on γ is shown in Figure 5. γ decreased significantly with an increase in the temperature over 30 $^{\circ}\text{C}$. The electrostatic attraction among molecules is destroyed easily in a high temperature environment^{9,10} because the binding strength of the electrostatic attraction is always much less than that of a chemical bond. Besides, an increase in temperature results in an increase in the CMC of S more than to a decrease the attraction microsurface of S. This is in accordance with the objective nature of surface adsorption.

The effect of the reaction time on γ indicates that the aggregation of IC on CTAB is very rapid at 10 $^{\circ}\text{C}$. The color fading appears in 20 min. This is attributed to the fact that the aggregation of IC on CTAB causes the formation of flocculate in solutions of high ionic strength. The measurement of absorbance of the solutions should be carried out within 10 min of the formation of the flocculent. (Check!)

Characterization of the IC-CTAB interaction. By varying the addition of 1.00 mmol/L IC, the IC-CTAB solutions were measured, and absorbance change is shown in Figure 6. From curve 3, A_c approaches a maximum when

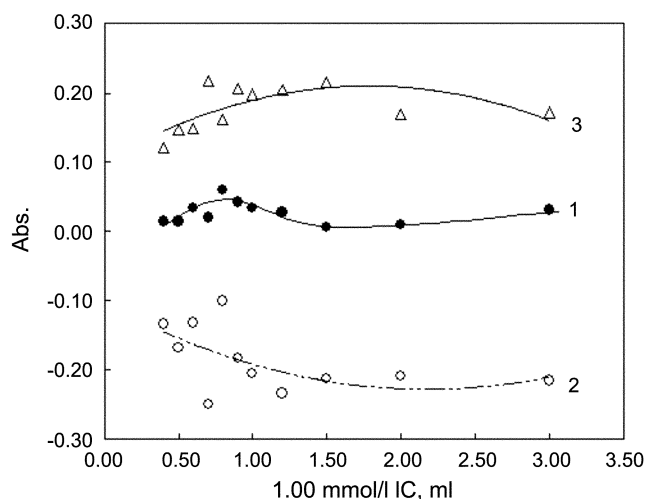


Figure 6. Effect of IC on the absorbance of the solutions containing 0.500 μmol CTAB/25 mL: 1- measured against reagent blank at 560 nm, 2- same as 1 but at 610 nm and 3- calculated A_c .

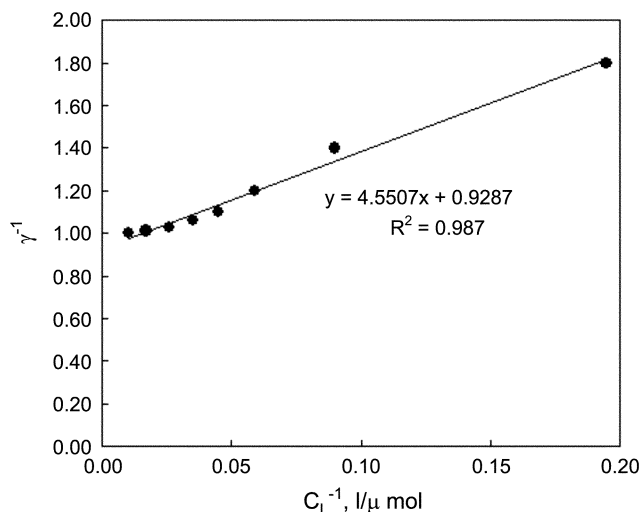


Figure 7. Plots γ^{-1} vs. C_L^{-1} .

the addition of IC solution is between 0.9 and 1.5 mL. In the quantitative detection of cationic surfactant, 1.2 mL of 1.00 mmol/L IC was added. Both γ and C_L of each solution were calculated. Their relationship is shown in Figure 7. Due to the linear plots γ^{-1} vs. C_L^{-1} , the adsorption of IC on CTAB obeys the Langmuir isothermal adsorption. From the intercept, the maximal binding number of IC on CTAB is calculated to be $N=1$. Therefore, the monomer complex IC·CTAB is formed. We estimated that the large micellar complex, $(\text{IC}\cdot\text{CTAB})_n$, is formed only when the concentration of CTAB is more than its CMC at 0.96 mmol/L and sufficient IC exists in the solution. From the linear slope, the binding constant of complex IC·CTAB was calculated to be $K = 2.20 \times 10^5 \text{ L}\cdot\text{mol}^{-1}$. For the determination of the binding constant of a complex, the MSASC technique has special advantages in operation and principle by comparing with the classical method, such as the Pesavento model,¹⁵ continuous variations.¹⁶

In addition, η of IC in the solutions, as shown in Figure 8,

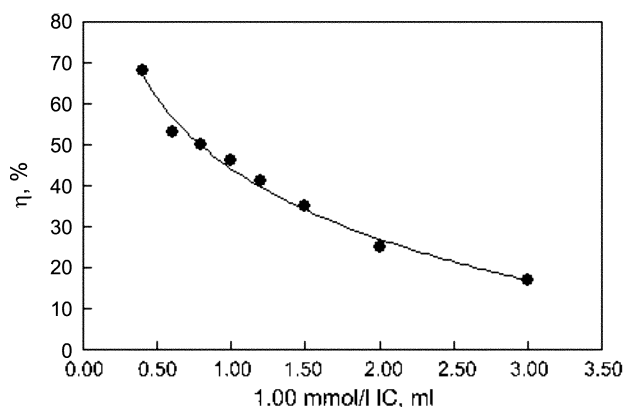


Figure 8. Change of η with IC where the solutions contained 0.500 μmol CTAB/25 mL.

η is only 40% with the addition of 1.2 mL of 1.00 mmol/L IC. The free IC in equilibrium approaches 60%. Therefore, so much free IC no doubt seriously affects the measurement of real absorbance of the complex. The real (not apparent) molar absorptivity of the micellar complex was calculated to be $\epsilon_{\text{IC}\cdot\text{CTAB}}^{560 \text{ nm}} = 8.58 \times 10^5 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.

Determination of cationic surfactants.

Calibration graph and precision: The standard series of CTAB solutions was prepared and measured, using 1.2 mL of 1.00 mmol/L IC. The calibration graph is shown in Figure 9. A_c points (\bullet sign) are more linear than the measurement points (Δ sign) and curve 2 has a much higher slope than that of curve 1. Therefore, the spectral correction technique has higher sensitivity and better accuracy than single wavelength spectrophotometry. Three times the standard deviation (SD) of fifteen replicated determinations of the reagent blanks was used to calculate the detection limit of cationic surfactant to be 1.0 $\mu\text{g}/\text{mL}$. Six replicated determinations of 0.500 μmol of standard CTAB revealed the average concentration was $0.511 \pm 0.010 \mu\text{mol}$ and the relative standard deviation (RSD) was 2.0%.

Effect of foreign ions: By adding the masking reagent to

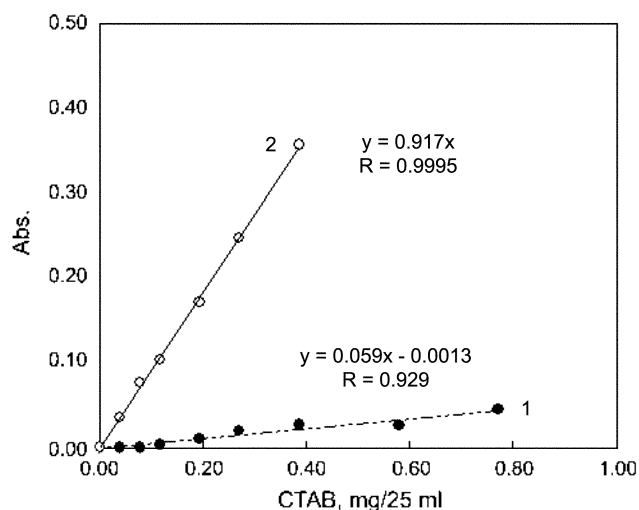


Figure 9. Standard curves for the determination of cationic surfactant: 1- ΔA measured at 560 nm and 2- A_c .

Table 1. Determination of cationic surfactant in wastewater

Sample No.	Added	CTAB, Found (mg)
1#	15 mL of the sample	0.031 ± 0.0017 RSD: 5.3%
	0.100 mg of CTAB + 15 mL of the sample	0.136 ± 0.007 Rec.: 105%
2#	5.00 mL of the sample	0.016 ± 0.001 RSD: 6.2%
	0.200 mg of CTAB + 5 mL of the sample	0.206 ± 0.006 Rec.: 95.0%

the procedure, the influence of foreign ions and substances was investigated. None of the following ions and compounds affected the direct determination of 0.500 μmol of CTAB (less than 10% error): 1 mg of K^+ , Ca^{2+} , F^- , SO_4^{2-} , Ac^- , NO_3^- , Mg^{2+} , 0.5 mg of NH_4^+ , I^- , PO_4^{3-} , $\text{C}_2\text{O}_4^{2-}$, glucose, amino acid, acetone, ethanol, SDS; 0.2 mg of Al(III), Ba(II), Mn(II), Zn(II), Pb(II); 0.1 mg of Cu(II), Ni(II), Co(II), Cd(II), Fe(III), Be(II) and 0.05 mg of Hg(II).

Conclusions

The determination of cationic surfactant in wastewater was made and the results are summarized in Table 1. The recovery of CTAB is between 95.0 and 105%, and the RSD is less than 6.2%.

The MSASC technique provides a very useful experimental strategy for the study of the physico-chemical interaction

among molecules. This work and some earlier systems^{8,9,17} all indicate the binding of L with S originating from an electrostatic attraction between S and an oppositely charged L not from a chemical bond. This provides a new way to analyze why surfactants can be used extensively in many industries and applications common to daily life. Though the IC-CTAB binding reaction is applied to only the macro analysis of cationic surfactant, its simplicity and accuracy may remind us of and point the way toward new and sensitive spectrophotometric methods for trace analysis.

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