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PRODUCTION AND APPLICATION OF THE LANGMUIR AGGREGATES OF EOSINE WITH CETYL TRIMETHYL AMMONIUM BROMIDE

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The procedure of microphase adsorption–spectral correction is applied to the interaction of eosine Y (EO) to the micelles of cetyl trimethyl ammonium bromide (CTAB). The Langmuir aggregation of EO on CTAB occurs owing to microelectrostatic attraction. The results have shown that at pH 3.8, monomeric and micellar aggregates have the structure $EO_5{\cdot}CTAB_2$ and $(EO_5{\cdot}CTAB_2)_{39}$. The adsorption constant of an aggregate is $7.01{\cdot}10^5$, its molar absorption coefficient is $\varepsilon = 8.8{\cdot}10^4$ liters·mole^{-1}·cm^{-1} at 550 nm. Application of the aggregation of EO on CTAB gives satisfactory results for quantitative determination of cation surface-active agents (surfactants).

Keywords: *procedure of microphase adsorption–spectral correction, Langmuir isothermal adsorption, cetyl trimethyl ammonium bromide, eosine Y.*

Introduction. At the present time, highly sensitive determination of trace amounts of a component often requires application of surface-active agents (SAA). The following models were suggested to explain the synergism (i.e., dissolution, stabilization, and increase in sensitivity): micellar extraction [1], perturbation of the synergism [2], formation of a hydrogen bond [3], micellar catalysis [4], asymmetric microenvironment [5], etc. The molecule of a new surfactant usually has a long chain and in an aqueous solution forms various aggregates: spherical, vermicular, tubular, and lamellar [6]. In recent years, a considerable amount of research has been performed to investigate molecular aggregation of surfactants [7, 8]. The understanding of the aggregation of micelles and of their associates with other organic substances, for example, contaminants, is very important for creating efficient surfactants of the new type.

A surfactant always exists in the form of a monomer (Fig. 1a) if its concentration is smaller than the critical concentration of micelle formation (CCM). Conversely, in electrostatic self-association of surfactant molecules (Fig. 1b) globular micelles are formed as soon as the concentration of the surfactant exceeds CCM. The electrostatic attraction of the dye ligand (L) with an oppositely charged monomer or the micelle surface [9] may occur until kinetic equilibrium is attained (Fig. 1). The explanation which was suggested by us earlier [9, 10] for the interaction of a dye probe with a surfactant is not very clear. The present work was carried out to eliminate this drawback. A ligand dissolves in a solution of a surfactant owing to electrostatic interaction. Aggregation of the ligand on the surface of the surfactant forms a monolayer of the type of a biomacromolecule [11, 12]. This aggregation corresponds to the Langmuir adsorption isotherm resulting in the following equilibrium: L (water phase, C_L) $\Leftrightarrow$ SAA-L_N (SAA phase, C_{SAA}). We use the Langmuir isothermal adsorption equation [13]

$$\frac{1}{\gamma} = \frac{1}{N} + \frac{1}{KNC_L}, \tag{1}$$

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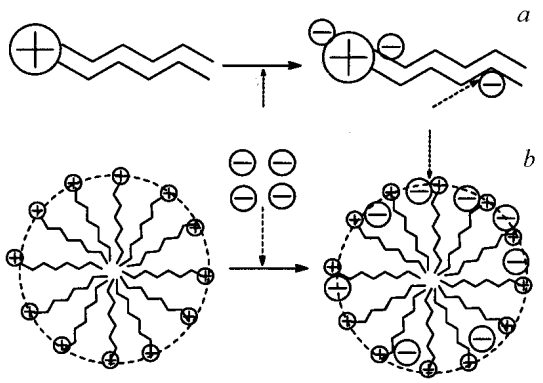


Fig. 1. Aggregation of a ligand on a monomer (a) and SAA micelle (b).

where K is the adsorption constant, C_L is the molar concentration of the ligand excess, and γ is the molar ratio of the ligand adsorbed by the surfactant. As the concentration C_L increases, the quantity γ attains a maximum (N). The dependence $\gamma^{-1}(C_L^{-1})$ is linear, and it yields the values of N and K. Both C_L and γ are calculated from the equations [14]

$$\gamma = \eta \frac{C_{L_0}}{C_{SAA}}, \tag{2}$$

$$C_L = (1 - \eta)\, C_{L_0}, \tag{3}$$

$$\eta = \frac{A_c - \Delta A}{A_0},$$

where C_{SAA} and C_{L_0} are the initial molar concentrations of the surfactant and ligand, η is the effective fraction of the ligand, and A_c, A_0, and ΔA is the true optical density of the SAA-L aggregate, the optical density of the pure reagent (solution of L) with respect to water and of the SAA-L solution with respect to the pure reagent measured directly at the wavelength of the maximum λ_2, respectively. The quantity A_c was calculated from the formula [15]

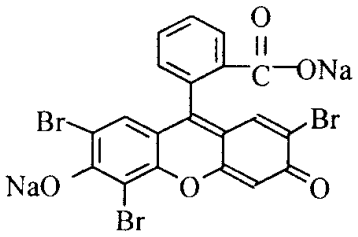
$$A_c = \frac{\Delta A - \beta \Delta A'}{1 - \alpha\beta},$$

where $\Delta A'$ is the optical density of the SAA-L solution measured at the wavelength of the minimum λ_1 and α and β are the coefficients of correction which can be calculated by means of direct measurement of SAA-L_N and L [14–16]. The molar coefficient of extinction (the real $\varepsilon_r^{\lambda_2}$ rather than the apparent one $\varepsilon_a^{\lambda_2}$) of the micellar aggregate at the wavelength λ_2 can be directly calculated as

$$\varepsilon_r^{\lambda_2} = \frac{mNA_c}{\delta\gamma C_{SAA}},$$

where δ is the thickness of the cell (cm) and m is the number of SAA molecules that form a micelle.

In the present work, we investigated aggregation of eosine Y (EO)



on a cation SAA, namely, cetyl trimethyl ammonium bromide (CTAB). In an aqueous solution, eosine forms anions which can be attracted by the surface of CTAB. The aggregation is sensitive to the high ionic strength of the solution and is selective in the presence of Na_2EDTA,* ethylenediamine, and potassium sodium tartrate. The investigation confirms the assumption on the microelectrostatic field of the SAA micelle. The results showed that at pH 3.8 the ratio of the binding of EO with CTAB is 2.5:1 and the equilibrium constant $K_{CTAB\cdot EO} = 7.01\cdot10^5$.

EXPERIMENTAL

Equipment and Reagents. The absorption spectra were recorded on a TU1901 spectrophotometer (PGeneral, Peking, China). The conductivity was measured by a DDS-11A conductometer (Trianjin 2nd Analytical Instruments, China), which, together with a DIS-1 immersion electrode (the electrode constant is 0.98, Shanghai Tienkuang Devices, China), for deionized water gives a value less than 0.3 $(\mu\Omega\cdot cm)^{-1}$; the pH of the solution was measured by a pH-2C acidity meter (Leici Instruments, Shanghai, China) and by a 630D pH meter (Shanghai Ren's Electric, China). The temperature was controlled and maintained constant with the aid of an electrically heated 116R thermostated temperature bath (Changjiang Test Instruments of Tongjiang, China).

A standard 1-mmole/liter solution of CTAB was prepared by dissolving CTAB (Shanghai Chemical Reagents, China) in deionized water: a 1-mmole/liter solution of eosine was obtained by dissolving 0.814 g EO (the content of eosine is 85%, Shanghai Third Reagents, China) in 1000 ml of deionized water. To control the pH of solutions, Britton–Robinson buffer solutions (pH 1.80–8.69) were prepared. To mask the ions of foreign metals in the samples used, a masking reagent was prepared by mixing the following solutions: 100 ml of 5% Na_2EDTA, 100 ml of 2% ethylene diamine, and 100 ml of 5% potassium-sodium tartrate.

Technique. The corresponding working solution of CTAB, 2.5 ml of the buffer solution, and 1 ml of the solution of eosine were put into a volumetric flask. The volume of the mixture was brought up to the mark by adding deionized water, and the solution was carefully mixed. All the measurements were made at 550 and 510 nm relative to the standard prepared similarly, but without CTAB.

RESULTS AND DISCUSSION

Absorption Spectra. We carried out the reaction of adsorption between EO and CTAB. The absorption spectra of the solutions of EO and EO–CTAB are shown in Fig. 2. It is seen that the spectral maximum of the product (curve 1) is located at 540 nm and that of EO (curve 2) at 520 nm. The maximum is shifted to the red region by 20 nm. The absorption spectrum of the EO–CTAB solution relative to the reagent (EO) (curve 3) has a maximum at 550 nm and a minimum at 510 nm. Therefore, we used these two wavelengths to ensure the least measurement error. We have found that the coefficient of correction β increases smoothly on increase in the concentration of EO (Fig. 3), especially after the addition of 1.2 ml of a 1-mmole/liter solution of EO. Consequently, the molecules of EO in a solution can form dimers or polymers [17, 18], especially if the concentration of EO exceeds 0.05 mole/liter. It is seen from Fig. 4 that the coefficient of correction α remains constant (0.813) at a concentration of CTAB 10 times exceeding that of EO. We assume that this solution no longer contains free EO, and we use it to measure the spectrum only of the product, as shown in Fig. 2.

*EDTA is the abbreviation for ethylendiamine tetraacetate.

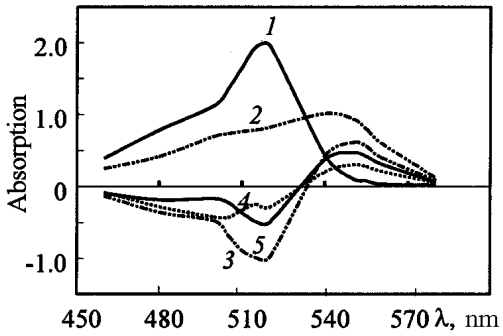
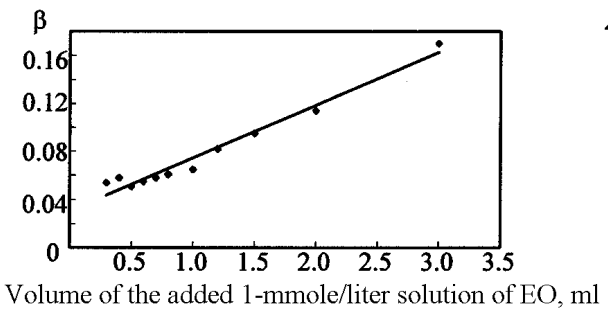


Fig. 2. Absorption spectra of EO and of its solutions with CTAB: 1) solution of EO (1 μmole) at pH 3.8; 2) EO (1 μmole)–CTAB (6 μmole) solution (not containing free EO) at pH 3.8; 3–5) EO (1 μmole)–CTAB (0.5 μmole) solution at pH 3.8, 5.72, and 3.20, respectively; spectra 1 and 2 are recorded relative to water and 3–5 relative to a pure reagent.



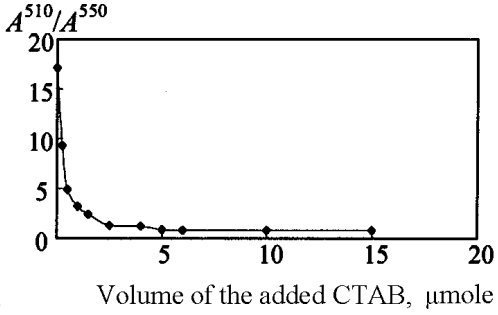


Fig. 3. Change in β at different concentrations of EO.

Fig. 4. Dependence of the optical density ratio of the EO (1 μmole)–CTAB solution measured at 510 and 550 nm at pH 3.8 on the CTAB concentration.

Effect of pH on the Adsorption of EO. The effect of pH on the absorption spectra of the CTAB–EO solutions is depicted in Fig. 5. The reaction is sensitive in the range of pH 3.20–5.72. In this range, the EO^- anion can be formed, which can easily and closely be attracted by the electrostatic field of the micelle. In the present work we used a buffer solution with pH 3.8.

Effect of Temperature and Time on the Adsorption of EO. The molar ratio of EO to CTAB at different temperatures is shown in Fig. 6. The ratio remains almost constant at T = 10–40°C but decreases rapidly at a temperature above 40°C. This shows that interaction of EO and CTAB agrees exactly with the general notion of surface adsorption.

At a temperature of 10°C the effect of the reaction duration on γ shows that the reaction is fast and γ remains constant for 1 h. In the present work, measurements were made for 30 min.

Effect of the Concentration of EO and of the Adsorption Ratio. The absorption of the EO–CTAB solution was measured when the volume of the added 1-mmole/liter solution of EO was changed from 0.3 to 1.2 ml (i.e., only 0.2 μmole of EO was added). The values of γ and C_L for each solution were calculated from Eqs. (1)–(3). It is found that the dependence $\gamma^{-1}(C_L^{-1})$ is linear (Fig. 7), i.e., interaction between EO and the micelles of CTAB agrees exactly with the adsorption of the Langmuir monolayer. The following regression equation was obtained: $\gamma^{-1} = (0.571 \cdot 10^{-6}) \cdot C_L^{-1} + 0.404$ (the linear coefficient of correlation R = 0.995). The binding ratio N has a value of 2.5. Consequently, the formula of the monomer product is $EO_5 \cdot CTAB_2$ and that of the micellar one is $(EO_5 \cdot CTAB_2)_{39}$ if the

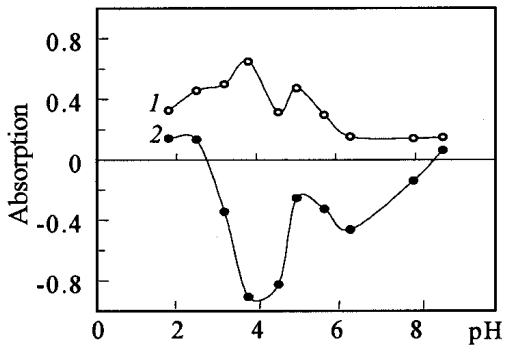


Fig. 5. Effect of pH on the optical densities of the solution containing 1.0 μmole of EO and 0.5 μmole of CTAB measured at 550 (1) and 510 nm (2).

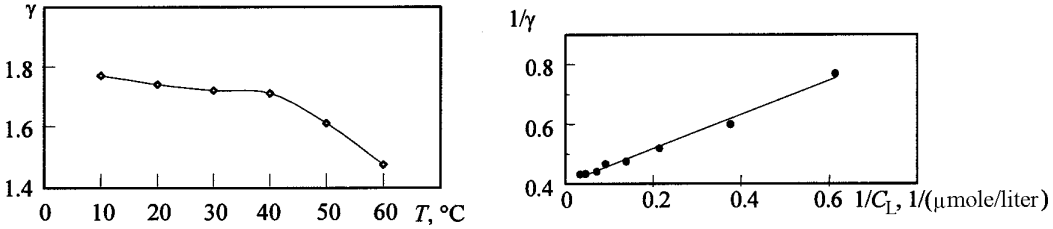


Fig. 6. The temperature dependence of γ for the EO (1 μmole)–CTAB (0.5 μmole) solution.

Fig. 7. The dependence of γ^{-1} on C_L^{-1}.

concentration of CTAB exceeds the critical concentration of micelle formation. The adsorption constant $K = 7.01 \cdot 10^5$ was calculated from the slope of the straight line obtained. As regards implementation and theory, the method of spectral correction has special advantages in determination of the binding ratio and equilibrium constant over such classical methods as the Scatchard model [19], the model of molar ratios [20], continuous variations [21], and the model of equilibrium motion [22].

To select the appropriate working additive of 1-mmole/liter solution of EO, in the quantitative determination of the cation SAA solutions were measured which contained 0.5 μmole CTAB and different concentrations of EO. The changes in absorption are shown in Fig. 8. It is seen that the true optical densities attain a maximum on addition of more than 1.2 ml of 1-mole/liter solution of EO. In the present work we added 2 ml of EO. Figure 9 additionally shows an effective fraction of EO of 68% on the above-indicated addition. The fraction of free EO is 32%. Consequently, free EO exerts its influence on measurements of the optical density of the product. The calculated value of the true molar coefficient of extinction of the monomer product $EO_5 \cdot CTAB_2$ at 550 nm is $\varepsilon = 8.8 \cdot 10^4$ liters·mole^{-1}·cm^{-1}.

Application of Adsorption for Quantitative Determination. A standard series of prepared solutions of CTAB containing 2 ml of EO solution was measured at pH 3.8. The curves of this series are shown in Fig. 10. It is found that the calculated values of A_c (light circles) better lie on a straight line than the measured ones (dark circles), and curve 2 has a greater slope than curve 1 in the range of concentrations of CTAB 0–0.2 mg. Thus, the technique of spectral correction is more sensitive and more accurate than the ordinary spectrophotometry. To determine CTAB quantitatively, we used the following regression equation for A_c: $y = 5.57x - 0.001$ (the linear coefficient of correlation is 0.9994). The detection limit for a 25-ml measuring flask was calculated to be equal to 5 μg and the relative standard deviation for a standard solution was 2.5%.

On addition of a masking reagent, the following substances and compounds do not influence direct determination of 0.1 mg of CTAB (the error is less than 10%): 1 mg Ca^{2+}, F^-, SO_4^{2-}, Ac^-, Mg^{2+}, 0.5 mg NH_4^+, I^-, PO_4^{3-},

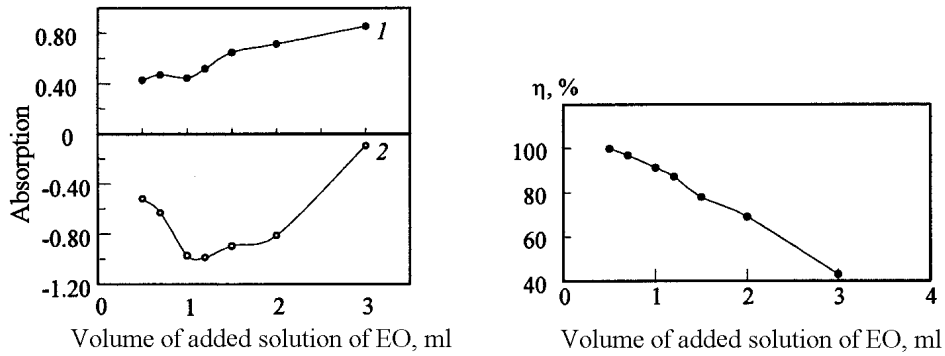


Fig. 8. The effect of the addition of 1 mmole/liter of the EO solution on the optical densities of the solutions containing 0.5 μmole of CTAB at pH 3.8 and measured at 550 (1) and 510 nm (2) relative to a pure reagent.

Fig. 9. The effect of addition of a 1-mmole/liter solution of EO on the effective fraction (the solution contains 0.5 μmole of CTAB).

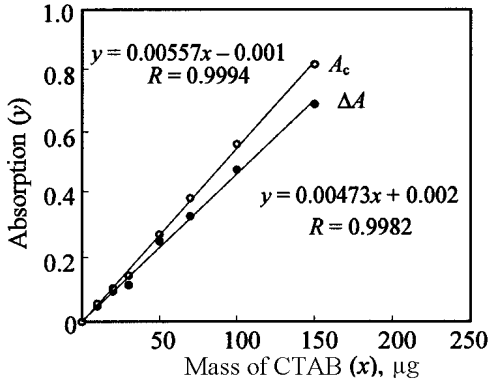


Fig. 10. Standard curves for determining a cation SAA at pH 3.8.

$C_2O_4^{2-}$, glucose, amino acids, acetone, ethanol; 0.1 mg Al(III), Ba(II), Mn(II), triton x-100, sodium dodecyl benzene sulfonate, 0.02 μg Cu(II), Ni(II), Co(II), Cd(II), Fe(III), Fe(II), Zn(II), Pb(II), and 0.01 mg Hg(II).

The measurements were carried out for two samples: sample 1 was taken from the Huanhe river and sample 2 from a local sewer pipe. The results of determining the cation SAA in the samples and on the detectability of the CTAB standard are presented in Table 1. The calculations show that in samples 1 and 2 there are 1.86 and 3.50 mg/liter cation SAA, respectively. The mean detectability is 98.2–106%, and the relative standard deviation (RSD) is less than 7.5%.

Conclusions. Investigation of the reaction between EO and CTAB confirms the notion of multialyer adsorption of EO molecules on CTAB. Though the technique of microphase adsorption — spectral correction cannot provide greater sensitivity than other methods, e.g., Rayleigh scattering of light, it satisfies the accuracy and correctness criteria and offers additional advantages, which are simplicity and convenience. To our mind, the classical method may also play an important part in studying the mechanism of micelle synergism.

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TABLE 1. Determination of Cation SAA in Samples with EO as a Reagent at pH 3.8

Sample	Added	Determined (mg)
Water of Huanhe river	10 ml of the sample	0.0189 0.0208 0.0176 0.0188 0.0169 mean: 0.0186 ± 0.0014 RSD: 7.5%
	0.02 mg of standard CTAB + 10 ml of the sample	0.0381 0.0398 0.0368 mean: 0.0382 ± 0.0016 detectability: 98.2%
Sewer water	5 ml of the sample	0.0153 0.0180 0.0183 0.0187 0.0172 mean: 0.0175 ± 0.001 RSD: 6.1%
	0.1 mg of standard CTAB + 5 ml of the sample	0.0291 0.0270 0.0281 mean: 0.0281 ± 0.0010 detectability: 106%

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