

# Investigation of Surfactant-Stain-Metal Interaction: Naphthochrome Green/Cetyltrimethylammonium Bromide/Rare Earths Ternary Complexation

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**Abstract** : The ternary interaction of naphthochrome green (NCG) with cetyltrimethylammonium bromide (CTAB) and rare earths (REs: Yb, Dy, Er and Eu) has been investigated with the microsurface adsorption-spectral correction technique (MSASC). The aggregation of NCG on CTAB obeys the Langmuir isothermal adsorption. The enrichment of NCG on CTAB and the presence of NaCl sensitize the complexation between REs and NCG. Both the binary aggregate and the ternary complex were characterized in the presence and absence of NaCl at pH 8.30 at 20 and 40°C.

**Key words** : microsurface adsorption-spectral correction technique; Langmuir aggregation; cetyltrimethylammonium bromide; naphthochrome green; rare earths; ternary complex

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## 1 INTRODUCTION

In our daily life and work, surfactants (S) are often widely used because of its especial functions. Investigations on the interaction of S with organic compounds, dye<sup>[1-3]</sup>, suspending solid, oil and other small molecules<sup>[4,5]</sup>, polymers<sup>[6-8]</sup> and biomacromolecules<sup>[9-11]</sup> are important to understanding the mechanism of S, which hold great interests of chemists. The design, preparation and characterization of new efficient surfactants are often reported<sup>[12-14]</sup>. Stain (L) is usually used as a probe reagent in the spectrometric study of S. Understanding the assembly of L on S is helpful not only to investigating the function of S in separation and extraction of an element or a compound<sup>[15,16]</sup> and trace analysis<sup>[17-20]</sup> but also to synthesizing a new-type efficient surfactant and developing its new applications. Some earlier mechanisms<sup>[21,22]</sup> were raised for explaining the synergism, *e.g.*, solubilization, stabilization of surfactant such as micelle extraction, synergism perturbation, electrostatic field aggregate, hydrogen bond formation, micelle catalysis, asymmetric microenvironment and so on. We established the microsurface absorption-spectral correction (MSASC) technique and it was ever applied to a number of the S-L reaction<sup>[23-28]</sup>.

The organic compound, naphthochrome green (NCG) is a kind of anionic stains. It will form monovalent anion in acidic medium, bivalent anion in neutral medium and trivalent anion in basic

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medium. It can be adsorbed on a cationic surfactant, e.g., CTAB by the electrostatic attraction. The ternary interaction of NCG, CTAB and REs has not been studied and applied before and it is investigated in detail in this work.

## 2 EXPERIMENTAL

### 2.1 Apparatus and Reagents

Absorption spectra were recorded on a TU1901 spectrophotometer (PGeneral, Beijing) and independent absorbance was measured on a Model 722 spectrophotometer. DDS-11A conductivity meter (Tianjin Second Analytical Instruments) was used to measure the conductivity together with a DJS-1 conductivity immersion electrode (electrode constant 0.98, Shanghai Tienkuang Devices) in deionized water of less than  $0.5 \mu\text{S}/\text{cm}$ . The pH of the solution was measured with a pH-2C acidity meter (Leici Instruments, Shanghai, China) and a Model 630D pH Pen (Shanghai Ren's Electronics). The temperature was adjusted and remained constant in a Model 116R electrically heated thermostatic bath (Changjiang Test Instruments of Tongjiang, China).

Stock standard solution of CTAB (10.00 mmol/L) was prepared by dissolving cetyltrimethylammonium bromide (CTAB) (Shanghai Chemical Reagents) in de-ionized water and then the CTAB solution (2.00 mmol/L) was prepared daily by diluting the stock solution. Stock NCG solution (1.00 mg/ml) was prepared by dissolving 1.00 g naphthochrome green (C. I. 44530, content 70%, Koch-Light Laboratories, Colnbrock Berks, England) in 500 ml deionized water. This solution contained 2.77 mmol/L NCG and its diluted solution containing 0.200 mg/ml (0.277 mmol/L) NCG was prepared daily. The CTAB-NCG adsorption aggregate solution was prepared by dissolving 0.100 g NCG in 500 ml 10.0 mmol/L CTAB containing 5 ml buffer solution of pH 8.3. In this solution, the large aggregate, 0.138 mmol/L  $\text{NCG}_2\text{-CTAB}_{80}$  (80: micellar aggregation number) was formed. Standard stock REs solutions [Yb, Dy, Er and Eu, all 10.0 mmol/L] were prepared by dissolving their oxides in 10 ml HCl solution (1+1) and then their 1.00 mmol/L work solutions were prepared daily by diluting the above solutions with deionized water. The acetate and ammonium buffer solutions between pH 3 and 11.0 were prepared to adjust the acidity of the solution. 2.0 mol/L NaCl was used to adjust the ionic strength of the aqueous solutions and sensitize the complexation between REs and NCG.

### 2.2 General Procedures

Interaction of CTAB with NCG: Into a 25 ml calibrated flask were added 1.00 ml of 1.00 mmol/L CTAB, 2.5 ml of pH 8.30 buffer solution and an appropriate volume of the NCG solution. The mixture was diluted with deionized water to 25 ml and mixed thoroughly. After 5 min, the absorbances were measured at 571 and 688 nm with 1 cm cell against a reagent blank treated in the same way without CTAB, and then  $A_c$ ,  $\gamma$  and  $C_L$  were calculated.

Interaction of CTAB-NCG with REs: 1.00  $\mu\text{mol}$  of a RE was added into a 25 ml buffer solution flask containing 2.5 ml of pH 8.30, 10 ml of 2.0 mol/L NaCl and a known volume of the CTAB-NCG aggregate solution. After 20 min, the absorbances were measured at 518 and 620 nm against a reagent blank treated in the same way without RE and then  $A_c$ ,  $\gamma$  and  $C_L$  were calculated.

### 3 RESULTS AND DISCUSSION

#### 3.1 Spectral Analysis

The absorption spectra of the NCG, CTAB–NCG and CTAB–NCG–Yb (Yb as a representative of REs) solutions of pH 8.30 are shown in Fig.1. From Curve 1, it can be seen that the peak of the NCG solution is located at 580 nm. From Curve 2, we observe that the absorption spectral peak of the CTAB–NCG aggregate is located at 605 nm. So the spectral red shift of the CTAB–NCG aggregate is only 25 nm. This is attributed to the fact that the electrostatic attraction is often less than the chemical bond connection and it causes only little interaction against NCG color functional group. From the relative spectrum 3, the peak and valley of the CTAB–NCG solution against NCG are located at 688 and 571 nm. Therefore, the two wavelengths were used in the study of the binary complex. From Curves 1 and 2, the correction coefficients were calculated to be  $\beta=0.026$  and  $\alpha=1.01$ . Therefore, the real absorbance of the CTAB–NCG aggregate is calculated by  $A_c=1.03(\Delta A-0.026\Delta A')$ .

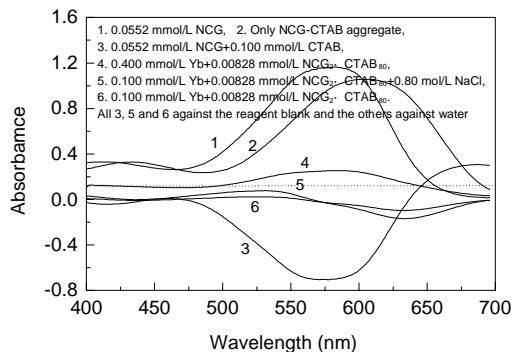


Fig.1 Absorption spectra of NCG, NCG–CTAB and RE–NCG–CTAB solutions at pH 8.30

From Curve 4, the peak of the CTAB–NCG–RE aggregates is located at 550 nm. So the spectral violet shift of the CTAB–NCG–RE product is 45 nm. However, from the relative spectra 5 and 6, the peak and valley of the CTAB–NCG–RE solution against the CTAB–NCG aggregate are located at 518 and 620 nm. Therefore, the two wavelengths were used in studying the ternary complex. From Curves 2 and 4, the correction coefficients were calculated to be  $\beta=0.385$  and  $\alpha=0.750$  in NaCl absence and  $\beta=0.466$  and  $\alpha=0.60$  in 0.80 mol/L NaCl medium. Therefore, the real absorbance of the CTAB–NCG–RE complex is calculated by  $A_c=1.41(\Delta A-0.385\Delta A')$  in NaCl absence and  $A_c=1.39(\Delta A-0.466\Delta A')$  in 0.80 mol/L NaCl medium.

#### 3.2 Analysis on Interaction of CTAB with NCG

By comparing Curves 2 with 1 shown in Fig.2, the flexion of Curve 2 always appears at the valley of Curve 1. It indicates that NCG just binds most CTAB at this point. NCG is always excessive before the point and CTAB becomes excessive after the point. From Curve 2, we also find that the surface tension decreases rapidly when CTAB is over the flexion point. Thus, more and more CTAB free in solution begins to appear and this causes the rapid decrease of the surface tension of the solution. From Curve 2, we still observe that the addition of the ammonium buffer solution decreases obviously the CMC of CTAB from 0.96 mmol/L to about 0.32 mmol/L. From Curves 1 and 2 in Fig.2(a)~(c), the valley of Curve 1 is located at the constant molar ratio of CTAB to NCG at 2:1. This indicates each NCG can bind 2 CTAB at most.

From Curves 1 and 2 in Fig.2(d), we find that the ratio,  $A_{620}/A_{518}$  decreases with the increase in Yb molarity and then approach constants at 0.75 in the absence of NaCl and 0.60 in 0.80 mol/L

NaCl medium. This means that enough Yb has complexed the complete NCG binding on CTAB micelle. So, the spectrum of this solution represents that of the CTAB–NCG–RE ternary complex and  $\alpha$  was calculated from it, which was drawn as Curve 4 in Fig.1.

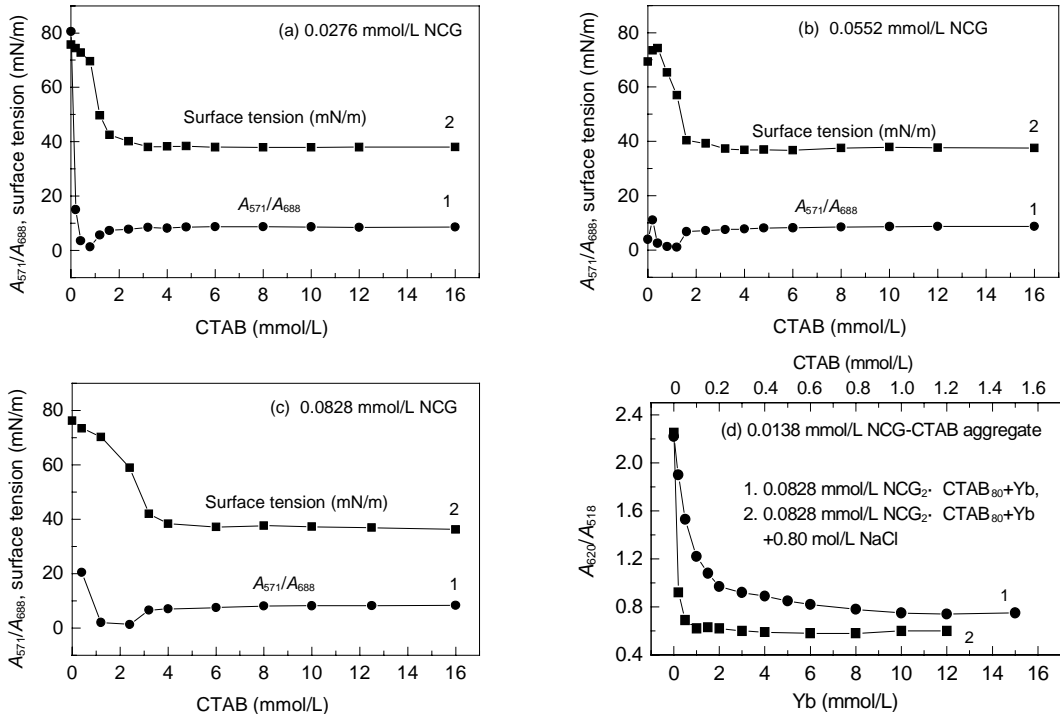


Fig.2 Effect of CTAB on  $A_{571}/A_{688}$ ,  $A_{620}/A_{518}$  (d) and surface tension

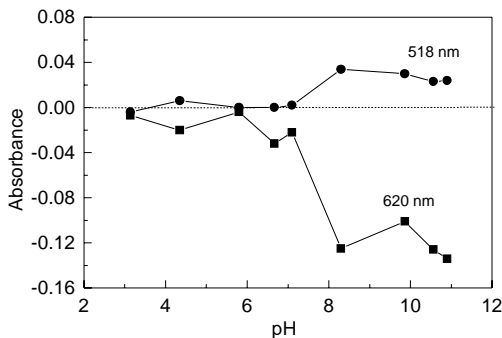


Fig.3 Effect of pH on absorbance of the solution measured

### 3.3 Effect of pH on CTAB–NCG–RE Aggregate

By varying pH of the ternary solutions containing 0.00828 mmol/L  $\text{NCG}_2 \cdot \text{CTAB}_{80}$  and 0.100 mmol/L Yb at pH 8.30, the absorbances measured at 518 and 620 nm are shown in Fig.3. By comparing the absorbance difference between the two curves, we observe that pH 8.30 gives a maximum. It indicates the ternary complexation is most sensitive among them. Therefore, pH 8.30 buffer solution was used in this study.

### 3.4 Effect of Ionic Strength and Temperature

In order to investigate the effect of ionic strength on the binding of NCG on CTAB, 2.0 mol/L NaCl was added and the result is shown in Fig.4. From Curve (a)–1,  $\gamma$  decreases with the increase of ionic strength between 0 and 1.25 mol/L. This is attributed to the fact that much more  $\text{Cl}^-$  occupied CTAB microsurface to weaken the binding of NCG. From Curve (a)–2,  $\gamma$  remains constant. This is because CTAB is more excessive and free in the solution and the desorption of NCG from a CTAB

molecule will bind rapidly on another free CTAB molecule. From Curve (a)–3, we see that  $\gamma$  of NCG to Yb in the presence of CTAB increases with the increase of ionic strength and remains a maximum when it is over 0.45 mol/L. So, NaCl sensitizes the ternary complexation. In this study, 0.80 mol/L NaCl was used in the ternary reaction solution and it increases the sensitivity over 1.5 times that in the absence of NaCl.

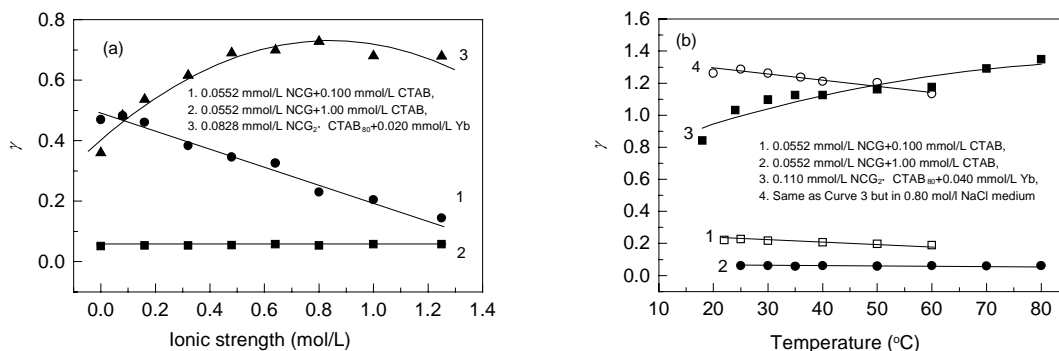


Fig.4 Effect of ionic strength (a) and temperature (b) on  $\gamma$

At various temperatures,  $\gamma$  of NCG to CTAB and that of NCG to Yb are shown in Fig.4, too. From Curve (b)–1,  $\gamma$  of NCG to CTAB decreases slowly with the increase of temperature. NCG decreases by about 8% with an increase of 20°C. This is attributed to the fact the increase of temperature accelerated the desorption of NCG from CTAB. This obeys the common nature of surface adsorption. From Curve (b)–2,  $\gamma$  remains constant. This is because CTAB is more excessive and free in the solution and the desorption of NCG from CTAB microsurface will bind rapidly on another free CTAB molecule. From curve (b)–3, the increase of temperature accelerates the complete coordination of NCG with Yb and results in an increase of  $\gamma$ . From Curve (b)–4,  $\gamma$  decreases only slightly. It is possible for higher temperature to affect the sensitization of NaCl.

### 3.5 Effect of Time on Formation of Ternary Complex

The ternary solutions containing 0.0138 mmol/L NCG<sub>2</sub>-CTAB<sub>80</sub> and 0.020 mmol/L Yb were measured at pH 8.30 and at 20 and 30°C at various reaction time and  $\gamma$  of each is shown in Fig.5. We observe that the ternary complexation becomes rapid with the increase of temperature. By comparing Curve 1 with 3, the reaction is complete at 20°C over 80 min but in only 40 min at 30°C. In the same way, the reaction is complete in 0.80 mol/L NaCl medium at 20°C in 30 min but only 20 min at 30°C. So, the presence of NaCl and the increase of temperature both accelerate the complexation, but the former also increases the sensitivity for over 1.5 times. Therefore, the ternary reaction was measured in 40 min in the absence of NaCl and 20 min in 0.80 mol/L NaCl.

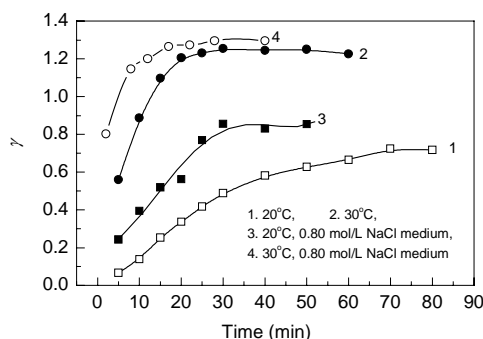


Fig.5 Effect of time on  $\gamma$

### 3.6 Characterization of Binary Aggregate and Ternary Complexes

By varying NCG molarity in the solutions containing 0.060 mmol/L CTAB at pH 8.30 and at 20, 30 and 60°C, both  $\gamma$  and  $C_L$  of each solution were calculated and all plots of  $\gamma^{-1}$  vs.  $C_L^{-1}$  are linear. So the adsorption of NCG on CTAB obeys the Langmuir isothermal adsorption. The binding ratio of CTAB to NCG is 2.0, 2.16 and 2.60. The binding ratio, adsorption constant ( $K$ ) and the real (not apparent) molar absorptivity ( $\epsilon_r^{688 \text{ nm}}$ ) of the aggregates were calculated as shown in Table 1. The large micellar aggregate, NCG<sub>40</sub>·CTAB<sub>80</sub> will be formed at 20°C when NCG has enough high concentration with CTAB over 0.32 mmol/L. The binding number of L decreases with the increase of temperature. In characterization of the S–L complexation, the spectral correction technique has special advantages in operation and principle over the classical methods such as the Scatchard model<sup>[29]</sup>, molar ratios and others.

**Table 1 The binding constants of the CTAB–NCG aggregate at pH 8.30**

Temperature (°C)	$\gamma$ =CTAB:NCG	$K (\times 10^5)$	$\epsilon_r^{688 \text{ nm}} [\times 10^5 \text{ L}/(\text{mol}\cdot\text{cm})]$
20	2:1	3.33	7.83
30	2:1 + 3:1 <sup>1)</sup>	4.47	7.56
60	2:1 + 3:1 <sup>1)</sup>	1.21	5.52

Note: 1) Mixture of both aggregates of NCG·CTAB<sub>2</sub> and NCG·CTAB<sub>3</sub>.

By varying the addition of 0.138 mmol/L NCG<sub>2</sub>·CTAB<sub>80</sub>, the REs(Yb, Dy, Er and Eu)–NCG–CTAB solutions were measured at 20 and 40°C.  $\gamma$  of NCG to RE in the presence of CTAB and the effective fraction( $\eta$ ) of NCG were calculated. Plots of  $\gamma^{-1}$  vs.  $C_L^{-1}$  are linear. Therefore, the coordination of Eu with NCG occurring on CTAB micelle can be regarded as an adsorption interaction, the adsorption force comes from the coordinate bond, but not the electrostatic attraction. The complex ratio( $\gamma$ ) and equilibrium constant( $K$ ) of each ternary complex were calculated from the linear incepts and slopes and are given in Table 2. We found that both the incept and slope always become little in the presence of NaCl. This also indicates the sensitization action of NaCl. The four kinds of REs will form 1:3, 1:4 and 1:5 complexes with NCG. In addition, all  $\epsilon_r^{518 \text{ nm}}$  of the ternary micellar aggregates were calculated as given in Table 2.

**Table 2 The binding constants of the NCG–REs complexes on CTAB micelle at pH 8.30**

Temp. (°C)	NaCl (mol/L)	RE	$\gamma$ =NCG:RE	$K (\times 10^5)$	$\epsilon_r^{688 \text{ nm}} [\times 10^5 \text{ L}/(\text{mol}\cdot\text{cm})]$					
					1st	2nd	3rd	4th	5th	
20	0	Yb	3:1	1.67	0.976	1.95	2.93			
		Dy	5:1	0.346	0.980	1.96	2.94	3.92	4.90	
		Er	3:1	1.93	1.04	2.08	3.12			
		Eu	4:1	0.453	1.16	2.32	3.48	4.64		
	0.80	Yb	4:1	9.32	1.04	2.08	3.12	4.16		
		Dy	5:1	1.22	1.00	2.00	3.00	4.00	5.00	
		Er	4:1	3.37	1.04	2.08	3.12	4.16		
		Eu	4:1	0.535	1.12	2.24	3.36	4.48		
40	0	Yb	5:1	2.25	1.04	2.08	3.12	4.16	5.20	
		Dy	5:1	0.989	1.09	2.18	3.27	4.36	5.45	
		Er	4:1	2.37	1.04	2.08	3.12	4.16		
		Eu	5:1	0.356	1.03	2.06	3.09	4.12	5.15	
	0.80	Yb	4:1	13.6	1.16	2.32	3.48	4.64		
		Dy	5:1	1.82	1.09	2.18	3.27	4.36	5.45	
		Er	4:1	2.71	1.07	2.14	3.21	4.28		
		Eu	4:1	1.19	1.04	2.08	3.12	4.16		

## 4 CONCLUSION

The investigation on the interaction of NCG with CTAB confirms the Langmuir isothermal adsorption of a stain on ionic surfactant because of the electrostatic attraction. Just the enrichment of a stain ligand on micelle accelerates its coordination with a metal ion. The MSASC technique provides a very helpful experimental approach for studying a binary or ternary complexation and will play an important role in studying the interaction among molecules.

### SYMBOLS:

$A_{518}$	Absorbance measured at 518 nm against water	$\alpha$	Correction constant of a L–S spectrum
$A_{620}$	Absorbance measured at 620 nm against water	$\beta$	Correction constant of a L spectrum
$A_c$	Real absorbance	$\gamma$	Binding ratio
$C_L$	Molarity of excess of L	$\epsilon_r^{688 \text{ nm}}$	Real molar absorptivity at 688 nm
$C_{L0}$	Initial molar concentration of L	$\epsilon_r^{518 \text{ nm}}$	Real molar absorptivity at 518 nm
$K$	Equilibrium constant	$\Delta A$	Absorbance measured at peak wavelength against a reagent blank
$N$	Maximal binding number	$\Delta A'$	Absorbance measured at valley wavelength against a reagent blank

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