Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 75 (2007) 664–668
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Interaction between 4-chloro-(2′-hydroxylphenylazo)rhodanine and cetyltrimethyl ammonium bromide

Dan Wu, Gui-Ying Xu*, Xia Xin, Xiao-Rong Cao

Key Laboratory of Colloid and Interface Chemistry (Shandong University), Education Ministry, Jinan 250100, PR China

Received 12 July 2006; received in revised form 19 July 2006; accepted 19 July 2006
Available online 6 September 2006

Abstract

The interaction between 4-chloro-(2′-hydroxylphenylazo)rhodanine (ClHPAR) and cationic surfactant cetyltrimethyl ammonium bromide (CTAB) was investigated by surface tension, absorption spectra, resonance light scattering (RLS) spectra and transmission electron microscopy. It can be concluded from the experimental results that the hydrophobic forces cannot be neglected, even though the electrostatic interaction between ClHPAR and CTAB plays an important role. The RLS spectral behavior of ClHPAR changes in the presence of CTAB. The efficiency and the effectiveness of ClHPAR–CTAB mixture to decrease the surface tension of water are higher than those of any single component, i.e. CTAB and ClHPAR. As one might expect, NaCl and urine have different effects on the interaction between ClHPAR and CTAB and their interaction also depends on pH.

Keywords: Interaction; Cetyltrimethyl ammonium bromide (CTAB); Dye; Surfactant; 4-Chloro-(2′-hydroxylphenylazo)rhodanine (ClHPAR)

1. Introduction

Dye–surfactant interactions are of great importance due to their industrial applications, pertinence to biological process and analytical chemistry [1–3]. For instance, surfactant is often used as a wetting agent, a suspending agent, and a solubilizer for water insoluble dye in various dyeing processes such as textile dyeing, photography and printing ink [4]. Therefore, the interaction between them has been studied quite extensively for many years by different methods including potentiometry, conductometry, voltammetry, tensiometry, etc. [5–14].

Considerable research has confirmed that surfactants can affect the spectra of the solutions of many dyes [15–17], due to aggregation of the dye molecules or dye–surfactant ion pairs and charge transfer between dye and surfactant molecules [18]. This property has been used in spectroscopic determination of metal ions, inorganic substances and biological macromolecules and to improve spectral characteristics of colored systems [19–24]. Hence, it is necessary to probe the mechanism of interaction between the dye and the surfactant.

In our previous work, the aggregation behaviors of sodium bis(2-ethylhexyl)sulfosuccinate and sodium bis(2-ethylhexyl)-phosphate surfactants were studied via the energy transfer between acridine orange and rhodamine B dyes [25]. In this work, surface tension, absorption spectra, resonance light scattering (RLS) spectra and transmission electron microscopy (TEM) techniques were used to investigate the interaction mechanism between 4-chloro-(2′-hydroxylphenylazo)rhodanine (ClHPAR) and cetyltrimethyl ammonium bromide (CTAB). In order to investigate the effect of hydrophobicity of the surfactant upon interaction, tetradecyltrimethyl ammonium bromide (TTAB) and dodecyltrimethyl ammonium bromide (DTAB) were also used. In addition, the effects of pH, NaCl and urea on the interaction between ClHPAR and CTAB are probed.

* Corresponding author. Tel.: +86 531 88365436; fax: +86 531 88564750.
E-mail address: xuguiying@sdu.edu.cn (G.-Y. Xu).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.07.016

2. Experimental

2.1. Apparatus

Absorbance measurements were performed on a Hitachi UV-4100 spectrophotometer, appropriately equipped with 1.0 cm quartz cells.

The RLS spectra were scanned synchronously at the same wavelength of excitation and emission in the range of 300–600 nm by Perkin Elmer LS-55 spectrofluorimeter with a 1.0 cm quartz cell. The excitation and emission slits are 10 and 2.5 nm, respectively.

Surface tension measurements were made on Processor Tensiometer-K12 (Krüss Company, Germany) using the Wilhelmy dipping plate method at 25.0 ± 0.2 °C. The average values of surface tension were obtained by repeating three times.

The morphology and size of products were characterized directly by transmission electron microscopy (JEM100-CXII electron microscope, Japan). Staining was achieved by treating the samples with 1% phosphotungstic acid aqueous solution.

2.2. Reagents

The cationic surfactants, dodecyltrimethyl ammonium bromide (DTAB), tetradecyltrimethyl ammonium bromide (TTAB) and cetyltrimethyl ammonium bromide (CTAB), were obtained from Ameresco and their critical micelle concentrations (CMC) were 15, 3.0, and 0.8 mmol L^{-1} [26], respectively. ClHPAR was purchased from East China Normal University. It has a planar aromatic and heterocyclic structure as is presented in Fig. 1.

NaCl and urine were supplied from Xilong Chemical Factory, Guangdong. Tris–HCl buffer (pH 7.85) was used to control the acidity. Water used in the experiments was triply distilled by a quartz water purification system.

2.3. Procedure

To a test tube, the solutions were added in the following order: buffer solution, an appropriate amount of ClHPAR and cationic surfactant solution. The mixture was diluted to the mark with water and mixed thoroughly. After 10 min, the solution was measured as mentioned above.

3. Results and discussion

3.1. Absorption spectra of mixtures of ClHPAR and cationic surfactants

The absorption spectrum of ClHPAR with and without CTAB at pH 7.85 is shown in Fig. 2. The spectrum of the dye consists of two absorption peaks at 330 and 422 nm. In the presence of CTAB (0.05 mmol L^{-1}, below CMC), the maximum absorption wavelength (λ_{max}) of ClHPAR shifts from 422 to 442 nm and the corresponding absorbance decreases from 0.593 to 0.387. The maximum absorption peak still displays a red shift and the absorbance at this wavelength increases gradually with increasing CTAB concentration. However, there is no remarkable change in the absorption peak at 330 nm, only the absorbance at 330 nm changes.

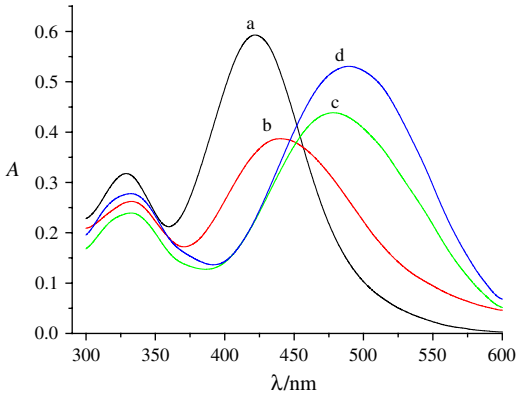

Fig. 2. Absorption spectra of ClHPAR dye (3.0×10^{-5} mol L^{-1}) in the presence of CTAB. Condition: CTAB concentration (a) 0 mmol L^{-1}; (b) 0.05 mmol L^{-1}; (c) 0.3 mmol L^{-1}; and (d) 1.2 mmol L^{-1}.

Fig. 3 shows the effect of CTAB concentration on λ_{max}. Obviously, the values of λ_{max} increase gradually with increasing CTAB concentration (below CMC). This is due to the formation of more ClHPAR–CTAB complexes. The values of λ_{max} become nearly constant as CTAB concentration is well above its CMC, which is attributed to the solubilization of a large amount of dyes in the micelles.

In order to probe the influence of hydrophobicity of the surfactant, the absorption spectra of mixtures of ClHPAR–DTAB and ClHPAR–TTAB were studied synchronously. Some experimental results like absorbance (A), λ_{max}, wavelength shift ($\Delta\lambda$) and electronic transition energy (ΔE) are summarized in Table 1. ΔE is calculated as $\Delta E = hc/(\lambda_{dye-surfactant} - \lambda_{dye-water})$, where h is Planck's constant (6.62×10^{-34} J s), c is the speed of light

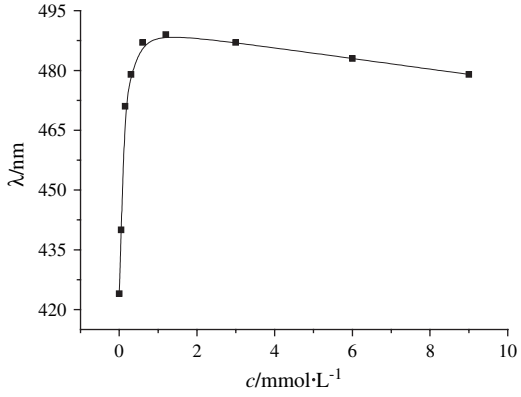

Fig. 3. Effect of CTAB concentration on the maximum wavelength of dye (3.0×10^{-5} mol L^{-1}).

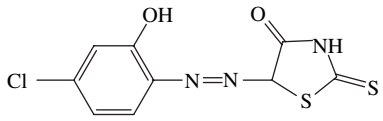

Fig. 1. The chemical structure of ClHPAR.

Table 1
Values of A, λ_{max}, ΔE and concentration of different surfactants in dye solution

Surfactant type	Concentration/ mmol L^{-1}	λ_{max}/nm	$\Delta\lambda$/nm	A	$\Delta E \times 10^{20}$/J
Without surfactant		422		0.593	
CTAB	0.05	442	20	0.387	−2.13
	0.3	478	56	0.438	−5.51
	1.2	488	66	0.530	−6.36
	3.0	487	65	0.525	−6.28
TTAB	0.05	433	11	0.295	−1.19
	0.2	442	20	0.310	−2.13
	1.0	464	42	0.381	−4.26
	3.0	474	52	0.461	−5.16
	6.0	474	52	0.450	−5.16
DTAB	0.05	424	2	0.258	−0.22
	2.0	436	14	0.348	−1.51
	3.0	445	23	0.363	−2.43
	8.0	456	38	0.414	−3.51
	20	460	38	0.554	−3.89

(3×10^{10} cm s^{-1}) and ΔE is the energy of excitation between two energy levels. From the more negative value of ΔE, it can be judged that the process of ClHPAR solubilization in the micelles of CTAB is easier than that in the micelles of TTAB and DTAB. This law is in agreement with that in the literature [27]. By comparing with TTAB and DTAB, it is found that the maximum red shift of ClHPAR is observed in the presence of CTAB (from 422 to 488 nm), suggesting the interaction between ClHPAR and CTAB is the strongest. It is well-known that they have the same electrostatic forces because CTAB, TTAB and DTAB possess identical head group. But the difference is only of hydrophobic tails. It is observed from the red shift of λ_{max} that the longer the hydrophobic tail, the stronger the interaction, indicating hydrophobic interaction is important likewise. It is this reason why CTAB is often used as a medium for enhancing the stability, the sensitivity and the solubility of the studied system in analytical chemistry. Hence, CTAB–ClHPAR system is chosen for the study.

3.2. Effect of pH on the absorption spectra of ClHPAR–CTAB systems

Values of A, λ_{max}, ΔE and concentration of CTAB in dye solution at different pH are shown in Table 2. It may be seen that pH affects the spectral behaviors of ClHPAR and ClHPAR–CTAB. Whether CTAB concentration is 0.05 mmol L^{-1} (below CMC) or 1.2 mmol L^{-1} (above CMC), the order of λ_{max} shift is as follows: pH 6.95 < pH 7.85 ≅ pH 8.56 ≅ pH 9.34. The order of λ_{max} shift and the more negative value of ΔE imply that the interaction between ClHPAR and CTAB in alkaline solution is stronger than that in weak acidic solution. The reason is that ClHPAR dissociates more easily in alkaline solution that formed negatively charged dye, in favor of the interaction between ClHPAR and CTAB through the electrostatic forces.

Table 2
Values of A, λ_{max}, ΔE and concentration of CTAB in dye solution at different pH

pH	CTAB concentration/ mmol L^{-1}	λ_{max}/nm	$\Delta\lambda$/nm	A	$\Delta E \times 10^{20}$/J
6.95	0	421		0.641	
	0.05	434	13	0.446	−1.41
	1.2	458	37	0.572	−3.81
7.85	0	422		0.593	
	0.05	442	20	0.387	−2.13
	1.2	488	66	0.530	−6.36
8.56	0	436		0.488	
	0.05	456	20	0.369	−2.00
	1.2	503	67	0.539	−6.07
9.34	0	428		0.522	
	0.05	448	20	0.384	−2.07
	1.2	498	70	0.523	−6.52

3.3. Effect of additives on the absorption spectra of ClHPAR–CTAB systems

Fig. 4 presents the influence of NaCl and urine at various concentrations on the interaction of ClHPAR with CTAB. It can be seen that NaCl and urine have different effects on the interaction: the absorbance of ClHPAR–CTAB at 478 nm increases with increasing NaCl concentration, and on the contrary, that of ClHPAR–CTAB decreases in the presence of urine. As has been already pointed out that the addition of NaCl usually causes a decrease in the CMC for the ionic surfactant, whereas urine causes an increase in the CMC of the surfactant [28,29], the following explanation is proposed for the observed behavior: the addition of NaCl may help to produce larger and more micelles and make the dye pass from the water into the micelles, and urine tends to weaken the formation of CTAB micelles, leading to the decrease of the solubilization of dyes in the micelles.

3.4. The resonance light scattering properties of ClHPAR–CTAB systems

The RLS spectra of ClHPAR with CTAB concentration increasing at pH 7.85 are displayed in Fig. 5. It can be seen that

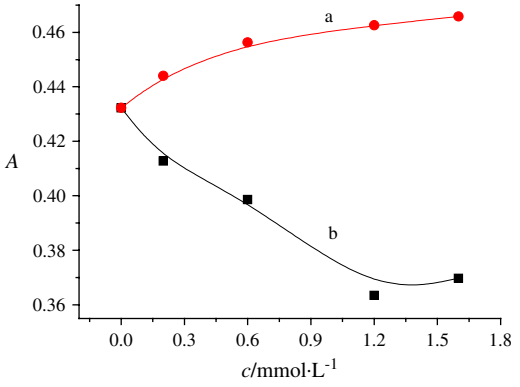

Fig. 4. Effect of additive concentration on the absorbance of CTAB (0.3 mmol L^{-1})–dye (3.0×10^{-5} mol L^{-1}): (a) NaCl and (b) urea.

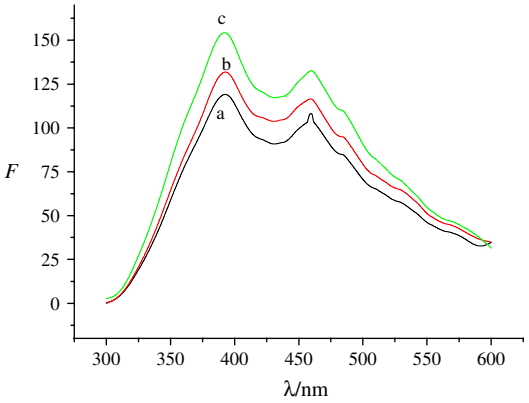

Fig. 5. The RLS spectra of ClHPAR dye (2.0×10^{-6} mol L^{-1}) in the presence of CTAB. Condition: CTAB concentration (a) 0 mmol L^{-1}; (b) 0.003 mmol L^{-1}; and (c) 0.025 mmol L^{-1}.

there are two obvious RLS peaks for the ClHPAR at 392 and 459 nm, which are located at the wavelength of their minimum absorption (see Fig. 2). The intensity of the RLS signal of ClHPAR increases in the presence of CTAB. And the intensity of the RLS signal, located at 392 nm, is the strongest. According to RLS theory [30,31], the formation of larger particles of ClHPAR–CTAB complex is the reason for the increase of the RLS intensity.

In order to verify the size of the particles, TEM image was measured. Fig. 6 shows the morphologies and sizes of ClHPAR and ClHPAR–CTAB complex. It may be seen that the particle size of ClHPAR–CTAB complex (Fig. 6b and c) is larger than that of ClHPAR (Fig. 6a), exhibiting that the I_{RLS} of ClHPAR–CTAB complex is stronger than that of ClHPAR. Based on the size of the particle, the order of the I_{RLS} is as follows: c > b > a, which is consistent with the results of Fig. 5.

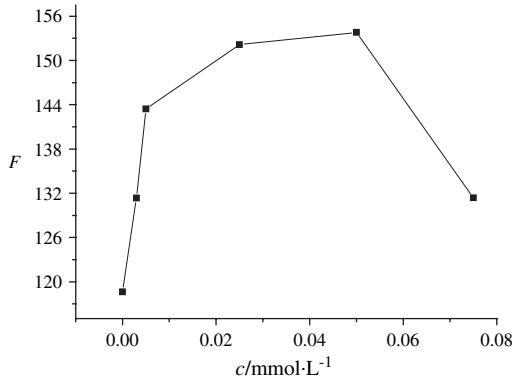

Fig. 7. Effect of CTAB concentration on the intensity of dye (2.0×10^{-6} mol L^{-1}).

The results in Fig. 7 reveal that the I_{RLS} of ClHPAR increases as CTAB concentration (below 0.025 mmol L^{-1}) increases, and reaches a maximum at 0.025–0.05 mmol L^{-1} CTAB, then decreases with increasing CTAB concentration.

3.5. Surface tension

In order to further investigate the interaction mechanism between the dye and the surfactant, the surface tension was measured. ClHPAR has high surface tension and its value of the aqueous solution is in the range of 72–65 mN m^{-1} as the concentration is between 1.0×10^{-5} and 5.0×10^{-3} mol L^{-1}. The surface tension isotherms of CTAB and CTAB–ClHPAR mixed solutions are displayed in Fig. 8. Generally, the critical micelle concentration and lowest surface tension (γ_{CMC}) are used to estimate the surface activity of material. The former is entitled the efficiency to decrease the surface tension of the solvent, and the latter is entitled

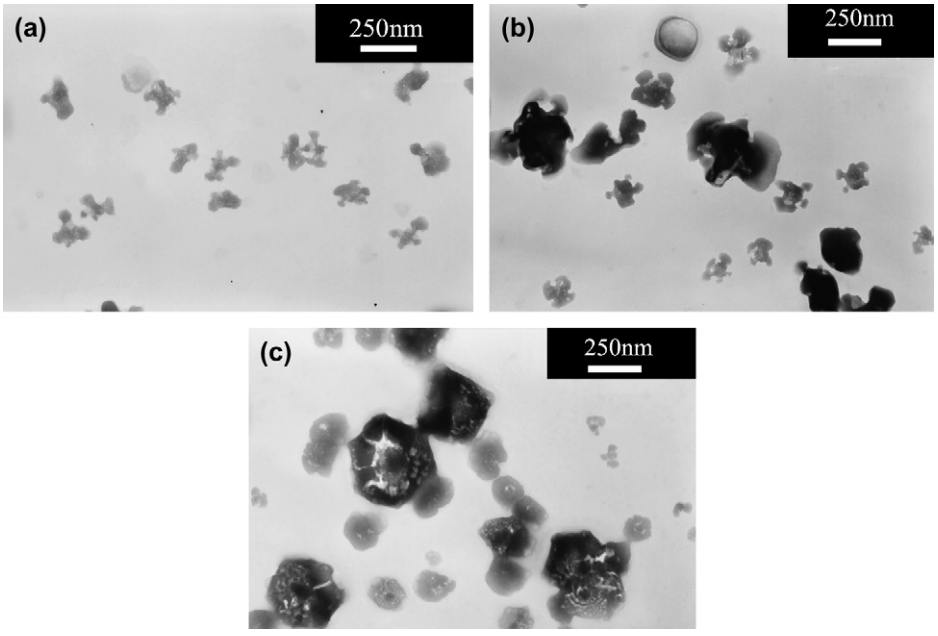

Fig. 6. TEM images of ClHPAR–CTAB and ClHPAR. (a) Dye: 2.0×10^{-6} mol L^{-1}; (b) dye (2.0×10^{-6} mol L^{-1}) + CTAB (0.003 mmol L^{-1}); and (c) dye (2.0×10^{-6} mol L^{-1}) + CTAB (0.025 mmol L^{-1}).

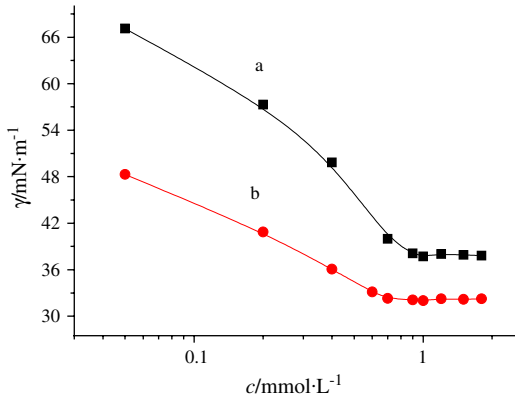

Fig. 8. Surface tension as a function of CTAB concentration: (a) CTAB and (b) CTAB + ClHPAR (concentration ratio 2:1).

the effectiveness to decrease the surface tension of the solvent [32]. It can be seen clearly that CTAB–ClHPAR system has lower γ_{CMC} value and CMC, implying the efficiency and the effectiveness of CTAB–ClHPAR system to decrease the surface tension of water are higher than those of both CTAB and ClHPAR. It is inferred that there is strong intermolecular interaction between ClHPAR and CTAB.

4. Conclusions

In the presence of CTAB, the spectral behaviors including the absorption spectra and resonance light scattering spectra of ClHPAR are changed. In alkaline solution, ClHPAR dissociates more easily and interacts with CTAB more strongly than that in weak acidic solution. ClHPAR–CTAB mixture has higher surface activity than each of them. ClHPAR interacts with cationic surfactants via the electrostatic forces and hydrophobic forces and the order of the interaction is as follows: CTAB > TTAB > DTAB.

Acknowledgements

The authors gratefully acknowledge the financial support from the Key Project (2004BA313B20) and the Natural Science Foundation (20573067) of China.

References

[1] Barni E, Savarino P, Viscardi G. Acc Chem Res 1991;24:98.
[2] Garcia MED, Sanz-Medel A. Dye–surfactant interactions: a review. Talanta 1986;33:255.
[3] Tanford C. The hydrophobic effect: formation of micelles and biological membranes. New York: Wiley-Interscience; 1980.
[4] Navarro A, Sanz F. J Colloid Interface Sci 2001;237:1.
[5] Bilski P, Holt RN, Chignell CF. J Photochem Photobiol A 1997;110:67.
[6] Yang J. J Colloid Interface Sci 2004;274:237.
[7] Biswas S, Bhattacharya SC, Sen PK, Moulik SP. J Photochem Photobiol A 1999;123:121.
[8] Simončič B, Špan J. Dyes Pigments 2000;46:1.
[9] Bračko S, Špan J. Dyes Pigments 2001;50:77.
[10] Pereira RV, Gehlen MH. Spectrochim Acta Part A 2005;61:2926.
[11] Shannigrahi M, Bagchi S. J Photochem Photobiol A 2004;168:133.
[12] Bhowmik BB, Ganguly P. Spectrochim Acta Part A 1997;2005:61.
[13] Sidorowicz A, Mora C, Jabłonk S, Poła A, Modrzycka T, Mosiadz D, et al. J Mol Struct 2005;744–747:711.
[14] Göktürk S, Tuncay M. Spectrochim Acta Part A 1857;2003:59.
[15] Colichman E. J Am Chem Soc 1951;73:3385.
[16] Rosendorfova J, Cermakova L. Talanta 1980;27:705.
[17] Khamisa M, Bulosb B, Jumeanc F, Manassraa A, Dakiky M. Dyes Pigments 2005;66:179.
[18] Rohatgi-Mukherjee KK, Chaudhuri R, Bhowmik BB. J Colloid Interface Sci 1985;106:45.
[19] Benamor M, Belhamel K, Draa MT. J Pharmaceut Biomed Anal 2000;23:1033.
[20] Winkler W, Arenhövel-Pacula A. Talanta 2000;53:277.
[21] Fiedler HD, Westrup JL, Souza AJ, Pavei AD, Chagas CU, Nome F. Talanta 2004;64:190.
[22] Šandor M, Geistmann F, Schuster M. Anal Chim Acta 1999;388:19.
[23] Du B, Wu D, Wei Q, Duan CH, Li Y. Instrum Sci Technol 2005;33:715.
[24] Wei Q, Wu D, Du B, Li ZJ, Huo YQ. J Food Compos Anal 2006;19:76.
[25] Luan YX, Xu GY, Li YM, Sun CX, Song SE, Liu J. Dyes Pigments 2005;67:223.
[26] Karukstis KK, Savin DA, Loftus CT, D'Angelo ND. J Colloid Interface Sci 1998;203:157.
[27] Awan MA, Shah SS. Colloids Surf A 1997;122:97.
[28] Acharya KR, Bhattacharya SC, Moulik SP. J Mol Liq 2000;87:85.
[29] Lucassen-Reynders EH. Physical chemistry of surfactant action. New York: Marcel Dekker Inc.; 1981.
[30] Yao G, Li KA, Tong SY. Anal Chim Acta 1999;398:319.
[31] Anglister J, Steinberg IZ. Chem Phys Lett 1979;65:50.
[32] Rosen MJ, Zhu BY. J Colloid Interface Sci 1984;99:427.