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Langmuir Aggregation of Congo Red on CPC and Its Application

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In this paper, microsurface adsorption-spectral correction technique (MASCT) was used to research the interaction between negatively charged sodium diphenyl diazo-bis-α-naphthylamine-4-sulfonate (Congo Red, CR) and positively charged cetylpyridinium chloride (CPC) in a pH 2.03 BR buffer solution. The experiment results indicate that CR was absorbed on the surface of CPC mainly through electrostatic attraction. This aggregation obeys the Langmuir isothermal adsorption equation. The maximal binding number of CR to CPC was calculated to be 1.2 and the adsorption constant was about 2.03×10^5 L/mol. This CR-CPC binding product is insensitive to a concentrated electrolyte solution, but higher temperature influences this aggregation. By combining this reaction with the absorbance ratio difference (ARD) theory, a new method was established to determine CPC in natural water. The analytical results show that this method is suitable for the determination of trace level CPC in natural water. It is an effective method because no organic hydrophobic solvent and time consuming 2-phase extraction operation are involved. It is the first time that ARD is used for the determination of cationic surfactant, and it will be widely used in future.

Key Words: Congo Red, Microsurface adsorption-spectral correction technique, Absorbance ratio difference, Cetylpyridinium chloride.

Introduction

Cationic surfactants are a kind of chemical products that are widely used in modern industry and daily lives. There will be more and more cationic surfactants consumed in the future.[1] During this process, some of the cationic surfactants are retained in waste water, solid wastes, and industrial waste residues, and then enter the natural environment. They were reported as pollutants[2] for their higher toxicity compared to anionic and nonionic surfactants.[3,4] Therefore, the sensitive methods for the determination of

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cationic surfactants are considerably essential in terms of environment analysis. A number of methods have been continuously proposed in recent years, including high-performance liquid chromatography,[5−6] solid-phase spectrophotometric,[7] capillary electrophoresis,[8] and flow injection analysis.[9−12] Currently, the most frequently used cationic surfactant assay is the solvent extraction spectrophotometric method.[13−15] However, many of the solvents used are harmful to health and 2-phase titration is a time-consuming operation. Some alternative spectrophotometric methods without 2-phase titration have been developed in recent years to detect cationic surfactants.[16−18]

Here, microsurface adsorption-spectral correction technique (MSASC)[16] was used to study the aggregation of CR on CPC. In this study, CR dissolves in water and forms anionic ions; CPC dissolves in water and forms O/W collides with positive charges. Negatively charged CR aggregates on the surfaces of these positively charged collides. This interaction is characterized by a combination of spectral correction[19,20] and Langmuir isothermal adsorption.[21] Through this equation, the maximal binding number of CR to CPC was calculated to be 1.2 and the adsorption constant was calculated to be 2.03 × 10^5 L/mol. The aggregation of CR on CPC is mainly due to the electrostatic attraction. CR-CPC binding product is insensitive to a concentrated electrolyte solution, but higher temperatures influence this aggregation. In addition, by combining this interaction with light adsorption ratio variation approach (LARVA),[22] a new spectrophotometric method was developed to determine the trace level of cationic surfactant in natural water without using organic solvent extraction. This is the first time to use LARVA to detect surfactants. It is an environmentally friendly method to determine cationic surfactants in natural water.

Experimental

Apparatus and reagents

The absorption spectra of CR were recorded with a Perkin-Elmer Model Lambda-25, a computer controlled spectrometer with UV WinLab software (Version 2.85.04). A supersonic wave cleaner, Model KQ318T, (Kunshan Analytical Instruments, China) was used to dissolve CR and CPC in deionized water. The solution pH was measured with a Model pHS-25 acidity meter (Shanghai Precise Sci. Instrum., China). A refrigerator freezer, Model BCD-196, (Meiling Production of Anhui Province, China) was used to store these solutions.

Cetylpyridinium chloride (CPC) was purchased from Shanghai Reagent Company and the 1.0 mmol/L CPC solution was prepared by dissolving 0.1791 g CPC in 500 mL deionized water with the help of supersonic wave cleaner. Congo Red (CR) was purchased from Shanghai Yuanhang Reagent Company and 0.6667 mmol/L CR solution was prepared by dissolving 0.2322 g CR in 500 mL deionized water. Britton-Robinson (BR) buffer solutions were used to adjust the acidity of solution in order to find a proper and highly sensitive condition for this new spectrophotometric system. All other reagents used in this paper were of analytical reagent grade. Deinoized water was used throughout the experiment.

Methods

Spectral correction technique for characterization of complex formation:[19,20]

The interaction of CR with CPC(M) is modeled as follows:

	N CR	+CPC	$\rightleftharpoons$	CPC · CR$_\text{N}$
Intiation	$C_0(A^0_{\lambda 1}$ at λ_1 and $A^0_{\lambda 2}$ at $\lambda_2)$	C_{M0}		0
Exuilibrium	$C = C_0 - nC_{M0}C(A^0_{\lambda 1}$ at λ_1 and $A_{\lambda 2}$ at $\lambda_2)$	$C_M \rightarrow 0$		$C_{M0}(A_{c1}$ at λ_1 and A_{c2} at $\lambda_2)$

Figure 1. illustrates the color changes in CR solutions in the presence of CPC. All the parameters are given there, too. The effective fraction (η) of CR binding to CPC and its binding ratio (γ) are calculated by the following equations:

$$\eta = \frac{A_{c2} - A_{\lambda 2}}{A^0_{\lambda 2}} + 1 \tag{1}$$

and

$$\gamma = \eta \times \frac{C_0}{C_{M0}} \tag{2}$$

where

$$A_{c2} = \frac{A_{\lambda 2} - \beta A_{\lambda 1}}{1 - \alpha\beta} \tag{3}$$

$$\alpha = \frac{A^C_{\lambda 1}}{A^C_{\lambda 2}} \tag{4}$$

$$\beta = \frac{A^0_{\lambda 2}}{A^0_{\lambda 1}} \tag{5}$$

where C_{M0} is the initial concentrations of CPC and C_0 is that of CR. In Figure 1, A_{c2} indicates the real absorbance of the CPC-CR complex at wavelengthλ_2. A_{c2} cannot be measured directly. The symbols $A_{\lambda 2}$ and $A_{\lambda 1}$ are the absorbance of the CPC-CR solutions, measured at λ_2 and λ_1 against water, respectively. α and β are the correction constants, which can be calculated by measuring solutions 1 and 2, respectively.

CPC dissolves in water and forms O/W collides with positive charge. Negatively charged CR is absorbed on its surface equally and uniformly via electrostatic attractions. The aggregation of organic molecules on these collides' surface often obeys the Langmuir isothermal adsorption equation:[21]

$$\frac{1}{\gamma} = \frac{1}{N_i} + \frac{1}{KN_iC} \tag{6}$$

where

$$C = (1 - \eta)C_0 \tag{7}$$

where K is an empirical constant relating to the structures of M and L, N_i is the ideal binding number of L. By regression of plots of γ^{-1} vs. C^{-1}, both K and N_i are calculated. The Scatchard equation[23] is similar to Eq. (6). The Langmuir adsorption isotherm may provide a theoretical basis for the Scatchard model.

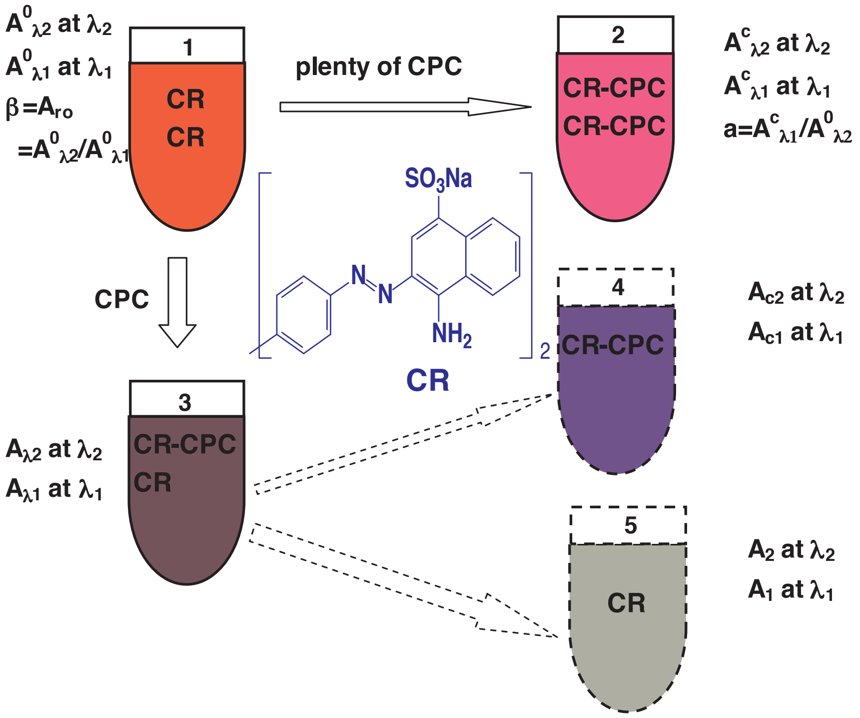

Figure 1. Sketch of the CR-CPC color reaction. 1: CR solution; 2: CPC-CR solution containing excess CPC (free CR approach zero); 3: CPC-CR solution containing micro amounts of CPC. Solution 3 is divided into 4 and 5 (not shown).

Development of the absorbance ratio difference method (ARD)

The equations of absorbance ratio difference method are established to determine trace level of CPC. From the color reaction between CPC and CR as shown in Figure 1:

$$A_{\lambda 1} = A_1 + A_{C1}$$

and

$$\begin{aligned}
A_{\lambda 2} &= A_2 + A_{C2} \\
A_r &= \frac{A_{\lambda 2}}{A_{\lambda 1}} = \frac{A_2 + A_{C2}}{A_1 + A_{C1}} = \frac{\delta C_L \varepsilon_{\lambda 2} + \delta C_{M_0} \varepsilon'_{\lambda 2}}{\delta C_L \varepsilon_{\lambda 1} + \delta C_{M_0} \varepsilon'_{\lambda 1}} \\
A_{r0} &= \frac{A^0_{\lambda 2}}{A^0_{\lambda 1}} = \frac{\delta C_{L0} \varepsilon_{\lambda 2}}{\delta C_{L0} \varepsilon_{\lambda 1}} \\
\Delta A_r &= A_r - A_{r0} = \frac{C_L \varepsilon_{\lambda 2} + C_{M_0} \varepsilon'_{\lambda 2}}{C_L \varepsilon_{\lambda 1} + C_{M_0} \varepsilon'_{\lambda 1}} - \frac{\varepsilon_{\lambda 2}}{\varepsilon_{\lambda 1}} \\
&= \frac{(\varepsilon_{\lambda 1} \varepsilon'_{\lambda 2} - \varepsilon_{\lambda 2} \varepsilon'_{\lambda 1}) C_{M0}}{(C_{L0} - nC_{M0})(\varepsilon_{\lambda 1})^2 + C_{M0} \varepsilon'_{\lambda 1} \varepsilon_{\lambda 1}} \\
\Delta A_r^{-1} &= \frac{C_{L0} (\varepsilon_{\lambda 1})^2}{\varepsilon'_{\lambda 2} \varepsilon_{\lambda 1} - \varepsilon'_{\lambda 1} \varepsilon_{\lambda 2}} \cdot C_{M0}^{-1} + \frac{\varepsilon_{\lambda 1} (\varepsilon'_{\lambda 1} - n \varepsilon_{\lambda 1})}{\varepsilon'_{\lambda 2} \varepsilon_{\lambda 1} - \varepsilon'_{\lambda 1} \varepsilon_{\lambda 2}} \\
\Delta A_r^{-1} &= p' C_{M0}^{-1} + q' \qquad (8)
\end{aligned}$$

where $p' = \dfrac{C_{L0}(\varepsilon_{\lambda1})^2}{\varepsilon'_{\lambda2}\varepsilon_{\lambda1} - \varepsilon'_{\lambda1}\varepsilon_{\lambda2}}$ and $q' = \dfrac{\varepsilon_{\lambda1}(\varepsilon'_{\lambda1} - n\varepsilon_{\lambda1})}{\varepsilon'_{\lambda2}\varepsilon_{\lambda1} - \varepsilon'_{\lambda1}\varepsilon_{\lambda2}}$.

The symbols $\varepsilon_{\lambda1}$, $\varepsilon_{\lambda2}$, $\varepsilon_{\lambda1}'$, and $\varepsilon_{\lambda2}'$ are the molar absorptivities of CR and CPC-CR complex at λ_1 and λ_2. Plot ΔA_r^{-1} vs. $C_{M_0}^{-1}$ is linear in a wide range of CPC concentration, and C_{M0} can be calculated from Eq. (8). ΔA_r is the absorbance ratio difference of the solution; p' and q' are constants when λ_1, λ_2, and the reaction condition are selected. The factor of sensitivity p' is proportional to CR concentration (C_{L0}), while ΔA_r^{-1}vs. $C_{M_0}^{-1}$ is linear. Therefore, higher analytical sensitivity is obtained with less addition of CR. However, too low value of CR can cause an obvious error of measurement because of the instrument background noise. This equation is suitable for the determination of cationic surfactant with higher sensitivity.

Procedures

Interaction between CR and CPC. All studies were carried out in 10.0 mL calibrated flasks. Into each flask, 1.0 mL of pH 2.03 buffer solution and known amount of CPC and CR solution were added. The solution was diluted to 10.0 mL with deionized water and mixed well. After reacting for 5 min, the absorbances $A_{\lambda2}^0$, $A_{\lambda1}^0$ of the CR solution and $A_{\lambda2}$, $A_{\lambda1}$ of the CR-CPC solutions were measured at 590 nm (λ_2) and 469nm (λ_1) against water, respectively. According to Eqs. 1-3, A_{c2}, η and γ were calculated.

Determination of CPC. Waste water sample was pretreated with 0.45 μm filter membrane. Then 1.0 mL pH 2.03 BR buffer solution, 0.6 mL 0.6667mmol/L CR and appropriate value of water sample (after pretreatment) were added into the flask. The solutions were diluted to 10.0 mL with deionized water and mixed well. After reacting 5 min, the absorbances (A_{590nm} and A_{469nm}) of the reaction solution were measured at 469 nm and 590 nm against water. $A_r = A_{469nm}/A_{590nm}$. Therefore,

$$\Delta A_r = A_r - A_r^0 = \frac{A_{469nm}}{A_{590nm}} - \frac{A_{469nm}^0}{A_{590nm}^0} \tag{9}$$

where A_{590nm}^0 and A_{469nm}^0 are the absorbances of reagent blank (CR) against water. Finally, the CPC concentration in the sample was calculated from plots ΔA_r^{-1} vs. C_{M0}^{-1}.

Results and Discussion

pH dependence and spectral analysis

The absorption spectra of CR-CPC complexes were measured at various pH buffer solutions as shown in Figure 2. The intervals between positive peak and negative trough increase in acid media. This means that acidic medium is favorable for the interaction of CPC and CR. CPC forms cationic ions in acidic medium. CR forms anion with the existence of $-SO_3^-$ groups. Lower pH is favored for the electrostatic interaction between CPC and CR. However, there are -N=N- and $-NH_2$ groups in CR and they will be protonized in a much lower pH buffer solution. The protonizing of these groups is not favorable for this interaction. Therefore, there is an optimal pH for obtaining a maximal binding number of CR to CPC. pH 2.03 optimizes the formation of complexes between CR and CPC. The working wavelengths were 469 and 590 nm in a subsequent work.

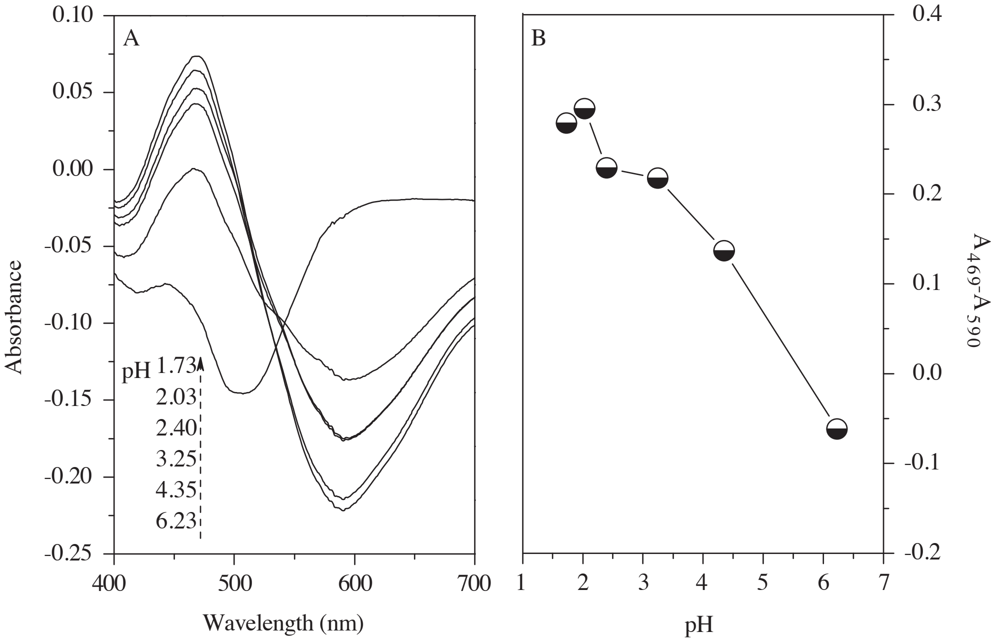

Figure 2. (a) Variation of the absorption spectra of the CPC-CR solutions with different pH. The solutions contained 0.0333 mmol/L CR and 0.1 mmol/L CPC at pH 1.73, 2.03, 2.40, 3.25, 4.35, and 6.23, respectively. All the absorption spectra were measured against the reagent blank. (b) The difference between A_{469} and A_{590} of above spectra at different pH values.

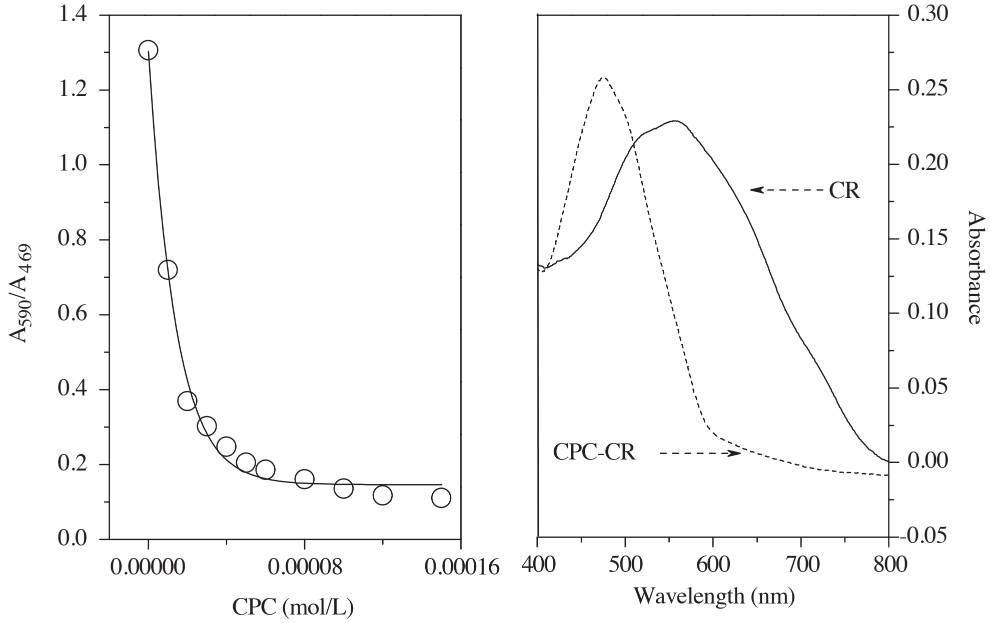

Figure 3. Variation of the absorbance ratio (A_{590} / A_{469}) of the CPC-CR solution (A) at pH 2.03. A, the solutions contained 0.0333 mmol/L CR. With the increase of CPC's concentration, the absorbance ratio decreased and at last it reached equilibrium and remained unchanged. 3b. The spectra of CR (0.0333 mmol/L CR) and CR-CPC solution (0.0333 mmol/L CR and 0.1 mmol/L CPC).

Characterization of complex formation

In order to obtain α, the absorbance ratios of the CR-CPC solutions were measured at 469 and 590 nm, respectively. The A_{590nm}/A_{469nm} ratio of CPC-CR solutions decreased with increased CPC. Then it approached to a constant with the addition of 60.0 μmol/L CPC. This means that more and more CR molecules bind to the CPC, and there is almost no free CR in solutions. As a result, $\alpha = 0.1462$ for the CR-CPC complex. β is the A_{469nm}/A_{590nm} ratio in the absence of CPC. In addition, the gross maximal binding number of CR to CPC was predicted to be approximately 1.1 by the molar ratio method.[24] The exact value will be calculated below.

Figure 4 shows the variation of γ for CR in various CPC solutions. γ always increases with more addition of CR. More and more CR molecules bind to the CPC. From curve A, γ approaches to a maximal constant at about 1.2 when 40 μmol/L CR is added. This indicates that the binding of CR to CPC reaches saturation. With the addition of more CR, the fraction of excess CR increases, but γ does not increase correspondingly. C for each solution is calculated from Eq. (7). γ^{-1} vs. C^{-1} plot is shown in Figure 4(b). It shows good linear relationships, which indicates that the binding of CR to CPC collides obeys the Langmuir adsorption isotherm. Through Eq. (6), the ideal binding number (N_i) of CR to CPC collides was calculated to be 1.58, which is bigger than 1.2 because steric effects were not considered. And the binding constant (K) was calculated to be 2.03 × 10^5 L/mol.

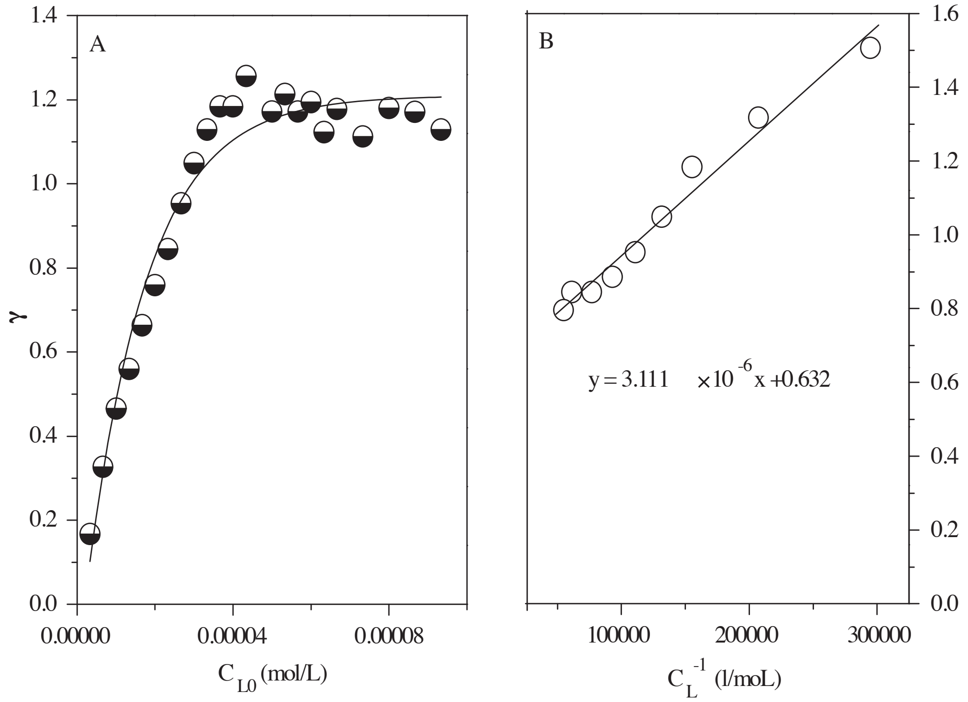

Figure 4. (a). Variation of γ with initial CR concentration in 0.02 mmol/L CPC at pH 2.03. (b). Plots of γ^{-1} vs. C^{-1} for these solutions.

Effects of electrolytes and temperature

NaCl was added to CR-CPC solutions to investigate the effects of electrolytes on the electrostatic interactions. The results were given in Figure 5(a). With increasing NaCl concentration, γ for CR slightly decreases and then does not change when the concentration of NaCl is higher than 0.4 mol/L. Negatively charged CR binds to CPC collides mainly through electrostatic attraction. Higher concentration electrolyte slightly influences the charges on the surface of collides, therefore it has a little effect on the γ of CR to CPC.

The effect of the temperature on the γ of CR to CPC is also shown in Figure 5(b). The experimental results indicate that γ decreases with the increase of temperature. Higher temperature causes CR's desorption from CPC. This is in accordance with the objective nature of a surface adsorption.[25]

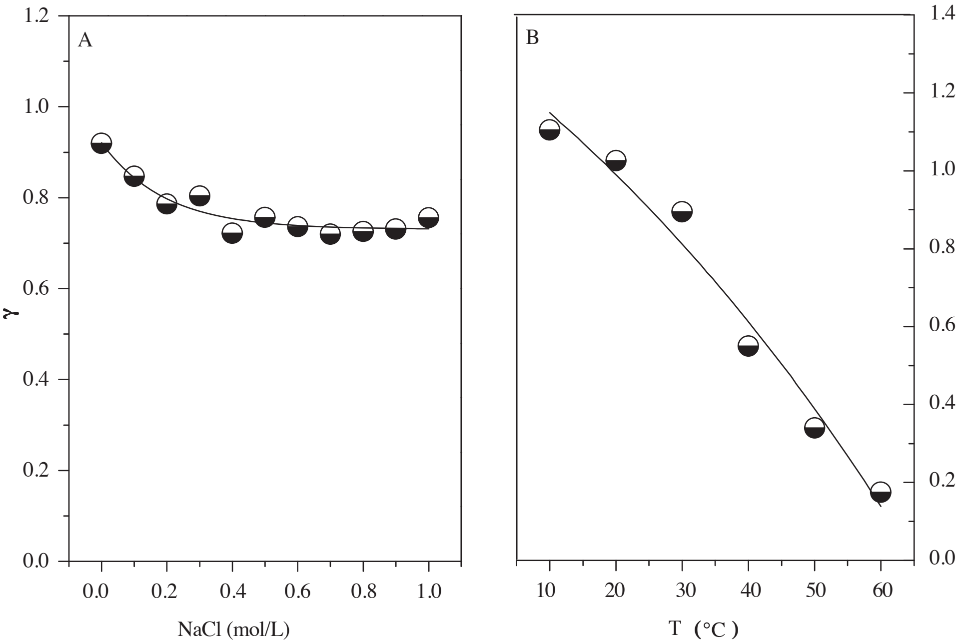

Figure 5. Effects of electrolyte concentration (a) and temperature (b) on γ. The solutions contained 0.0266 mmol/L CR and 0.02 mmol/L CPC.

Determination of CPC in natural water

Here CR is used as a new probe to detect CPC with absorbance ratio difference method (ARD). As shown in Eq. (8), the factor of sensitivity, $p'$is proportional to CR concentration (C_{L0}), while ΔA_r^{-1} vs. $C_{M_0}^{-1}$ is linear. Therefore, less addition of CR was favorable to improve the method's sensitivity. However, too low CR value can cause an obvious error of measurement because of instrument background noise. So it is necessary to define the volume CR in our experiment. Here, 3 standard series of CPC were prepared, as shown in Figure 6 and Table 1. CR changes from 0.1 mmol/L to 0.5 mmol/L, and then the slope coefficient of standard curve changes from 5.8598 L/mol to 19.498 L/mol. ΔA_r^{-1} vs. $C_{M_0}^{-1}$ is linear, so higher analytical sensitivity can be obtained at a lower concentration of CR. This is compatible with ARD theory. On the other side, the increase in instrument background noise at a lower concentration CR influences the detection of CPC. Considering these 2 aspects, a suitable concentration of CR should be selected for the lowest LOD of CPC. In this experiment, 0.3 mmol/L was selected as the most appropriate condition for its lowest LOD.

Effect of foreign substances. The experimental results in Figure 7 indicated that none of the following species influences the direct determination of 0.015 μol/L CPC (error less than 5%): 460 mg/L Na^+, 710 mg/L Cl^-, 20.0 mg/L Al^{3+}, 5.0 mg/L NH_4^+, 10.0 mg/L Ba^{2+}, 0.5 mg/L Cu^{2+}, 10.0 mg/L Ca^{2+}, 10.0 mg/L Mg^{2+}, 4.0 mg/L Zn^{2+}, 30.0 mg/L NO_3^-, 10.0 mg/L PO_4^{3-}, 20.0 mg/L SO_4^{2-}, 2.2 mg/L Fe^{2+} , 0.5 mg/L Fe^{3+}, and 120 mg/L urea. We also found that some organic compounds did not influence the detection of CPC, such as 0.7 mg/L SDBS, 1.2 mg/L BSA, and 4.0 mg/L DNA. In fact, their concentrations in the practical samples were low. Therefore, they did not influence the determination of CPC. The recommended method is highly selective. It is fit for the analysis of cationic surfactants in natural water.

Table 1. The linear regression equations and LOD of SDBS at pH 2.03.

CPC (mg/L)	CR (mmol/L)	Regression Equation	R^1	LOD^2 (mg/L)
0-3.5801	0.013	$\Delta A_r^{-1}=5.8598C_{M0}^{-1}-1.4971$	0.9987	0.1661
0-10.7430	0.040	$\Delta A_r^{-1}=11.160C_{M0}^{-1}$- 0.8186	0.9993	0.0833
0-17.9005	0.120	$\Delta A_r^{-1}=19.498C_{M0}^{-1}$- 0.6524	0.9987	0.1734

[1]Linear correlation coefficient; [2]LOD of CPC in 10 mL of flask was calculated by LOD=$3\sigma/k$

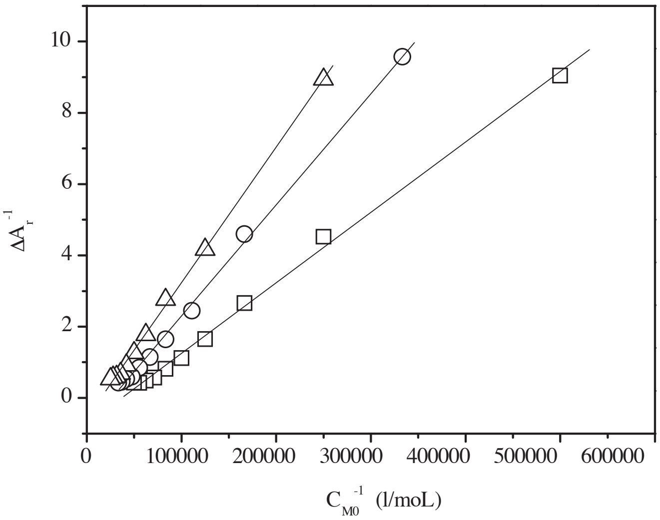

Figure 6. Variation of CPC's standard curve at different concentrations of CR in pH 2.03 BR buffer solution. From 1 to 3, the concentrations of CR were 0.013 mmol/L, 0.040 mmol/L, and 0.120mmol/L, respectively.

Examples for Analysis of Samples. Waste water samples were pretreated with 0.45 μm filter membrane. The cationic surfactants in the samples were measured according to the procedures described in "Procedures". Three water samples were detected. The analytical results are given in Table 2. As the experimental results shown, CPC in natural water can be detected by this method with good results. With the addition of standard CPC, the recovery is 98.73%, 96.58%, and 99.23%, respectively. In this method, it is not necessary to use an organic hydrophobic solvent. There is no 2-phase extraction operation in this method. It is an environmentally friendly method with higher efficiency to determine CPC in natural water.

Conclusions

In this paper a new developer system CR-CPC was found for detection of cationic surfactants in natural water. In a pH 2.03 BR buffer solution CPC forms micelles with positive charges on their surface. Negatively

Table 2. Determination of CPC with this method at pH 2.03.

sample	standard CPC[1] mg	Found mg/L[2]	Recorvery (%)[3]
Taihu	0.0000	0.7294	
	0.0214	2.8502	98.73
Changjiang	0.0000	0.6327	
	0.0214	2.7074	96.58
Sanhaowu	0.0000	0.5899	
	0.0214	2.7215	99.23

[1] into 10mL flask; [2,3] the average of 3 duplicate experiment results

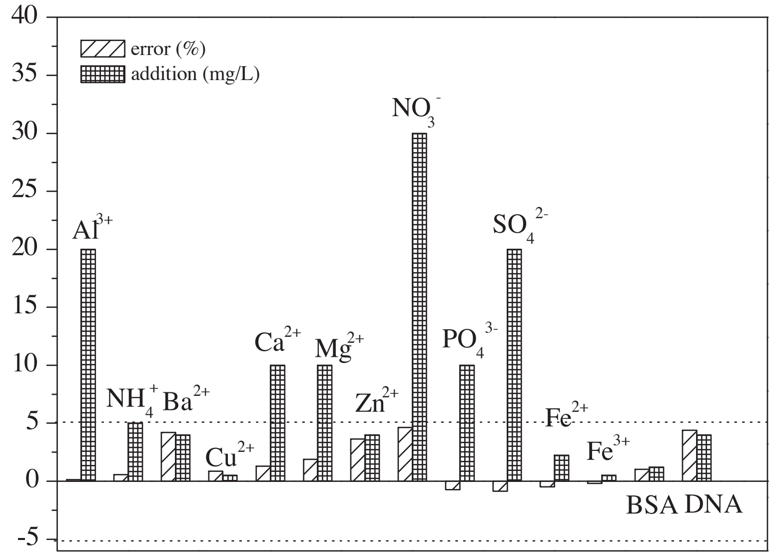

Figure 7. The effect of foreign substances on the determination of 0.015 mmol/L CPC with 0.040 mmol/L CR at pH 2.03.

charged CR absorbs on the surface of these micelles through electrostatic interaction. The aggregation of CR on CPC obeys the Langmuir isothermal adsorption equation. The maximal binding number of CR to CPC was calculated to be 1.2. The adsorption constant was about 2.03×10^5 L/mol. This CR-CPC complex was insensitive to a concentrated electrolyte solution. However, higher temperature influences this aggregation. Through combination the reaction with absorbance ratio difference theory, a new method was established to determine CPC in natural water with higher sensitivity and selectivity. There are no organic hydrophobic solvents and time consuming 2-phase extraction operation in this method. In an addition, by controlling the CR concentration, a better standard curve can be obtained with higher sensitivity. This is very important for the detection of waste water with lower concentration cationic surfactant. It is the first time that ARD is used for the determination of cationic surfactant and would be widely used in the future.

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