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Interaction of Reactive Brilliant Red with Cetylpyridinium and Application to Determination of Cationic Surfactant in Water

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The microsurface adsorption-spectral correction technique and light adsorption ratio variation approach were jointly applied to characterization of the interaction of reactive brilliant red (RBR) with cetylpyridinium chloride (CPC) at pH 3.67. The interaction responded with the Langmuir isothermal adsorption. The saturated binding ratio of RBR to CPC is (1.2 ± 0.1): 1, and the bind constant of the RBR-CPC complex was calculated to be $(1.15 \pm 0.05) \times 10^5$ l/mol. The interaction was applied to the determination of cationic surfactant in water by the light adsorption ratio variation approach with satisfactory results.

Keywords: Reactive brilliant red; Ion-pair attraction; Cetylpyridinium; Spectrophotometry; Determination of cationic surfactants.

INTRODUCTION

Surfactants are extensively used in our daily life as well as a multitude of industrial processes, such as chemical manufacture, oil refining, mineral selection, photosensitive material production, drug synthesis, metallurgy and so on. A surfactant is often essential in many chemical analyses for its solubilization, stabilization and sensitization. Studies of surfactant solutions are still the hot issue in the area of analytical research.[1-5] Several mechanisms like micelle extraction, synergism perturbation,[6] hydrogen bond formation,[7] and asymmetric microenvironment[8] have been applied earlier to study the surfactant activity. The investigation into the interaction between a surfactant and a small molecule or ion is helpful for us to analyze the mechanism of surfactants in washing, emulsification, separation and synergism[9] so as to synthesize new types of efficient detergents.[10] Cetylpyridinium chloride (CPC) as a typical cationic surfactant was used as a standard representative of cationic surfactants.[11] Since 2000, the microsurface adsorption-spectral correction technique (MSASC) has been applied to investigate the interaction of ionic organic compounds with surfactants.[12] It depicts the surfactant micelle as an ionic microparticle to attract the oppositely charged organic compound by ion pair attraction, and the binding often obeys the Langmiur isothermal.[13] Recently, the light adsorption ratio variation approach (LARVA) was advanced,[14] and it improved obviously the analytical sensitivity and accuracy. In this work, it was applied to the determination of cationic surfactants using the interaction of reactive brilliant red (RBR) with CPC at pH 3.67.

PRINCIPLES

Microsurface adsorption-spectral correction technique

In a surfactant (S) solution, the aggregation of S forms an electrostatic global micelle when the concentration of S is greater than the critical micellar concentration (CMC). The electrostatic attraction of a negatively charged ligand (L) occurs on the micellar microsurface until kinetic equilibrium. The electrostatic attraction results in the solubilization of L in S solution. The aggregation of L on S, like on a biomacromolecule,[15] obeys the Langmuir isothermal adsorption. The S-L solution equilibrium occurs as follows (m. s. means microsurface phase.):

$$\begin{array}{lcccc} & N\mathrm{L} & + \quad \mathrm{S(m.s.)} & \longrightarrow & \mathrm{SL}_N\mathrm{(m.s.)} \\ \text{Initial state} & \mathrm{C_{Lo}}\,(A^0_{\lambda 2}) & \mathrm{C_{So}} & & 0 \\ \text{Equilibrium} & \mathrm{C_L} & \sim 0 & & \mathrm{C_{So}}\,(\mathrm{A_c}) \end{array}$$

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where both C_{So} and C_{Lo} are the initial molarities of S and L. C_L is the molarity of excess L in equilibrium. 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, respectively. N is the authentic binding number of L. The interaction of L with S often obeys the Langmuir isotherm equation:

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

where K is the binding constant and γ the molar ratio of L adsorbed to S. With an increase in L molarity, γ approaches the saturated binding number (N). From plots of γ^{-1} vs. C_L^{-1}, N and K can be calculated. C_L and γ are calculated via the following equations:[15]

$$\gamma=\eta\times\frac{C_{Lo}}{C_{So}} \tag{2}$$

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

where

$$\eta=\frac{A_c-A_{\lambda 2}}{A^0_{\lambda 2}}+1 \tag{4}$$

where symbol η represents the effective fraction of L binding on S. $A_{\lambda 2}$ is the absorbance of S-L solution, measured at λ_2 against the reagent blank. A_c is calculated by the relation:[16]

$$A_c=\frac{A_{\lambda 2}-\beta A_{\lambda 1}}{1-\alpha\beta} \tag{5}$$

where

$$\beta=\frac{A^0_{\lambda 2}}{A^0_{\lambda 1}} \tag{6}$$

and

$$\alpha=\frac{A^{SL}_{\lambda 1}}{A^{SL}_{\lambda 2}} \tag{7}$$

Both β and α are the spectral correction constants.[16] $A^0_{\lambda 1}$ and $A_{\lambda 1}$ are the absorbances of L and S-L solutions, measured at λ_1 & λ_2 against water. $A^{SL}_{\lambda 1}$ and $A^{SL}_{\lambda 2}$ are the absorbances of the S-L complex solution without free L, measured at λ_1 & λ_2 against water.

Light-absorption ratio variation approach[14]

The main equations of the LARVA are the following:

$$\Delta A_r=pC_{S0}+q \tag{8}$$

where

$$\Delta A_r=A_r-A_{r0}=\frac{A_{\lambda 2}}{A_{\lambda 1}}-\frac{A^0_{\lambda 2}}{A^0_{\lambda 1}} \tag{9}$$

where ΔA_r is the difference of absorbance ratio. Both p and q are constants derived by regressing the standard series of S solution. In fact, p as the factor of sensitivity is the inverse ratio to C_{L0}.[16] The less that L is added, the higher the analytical sensitivity will become. However, an extremely low amount of L can cause a great measurement error resulting from the noise of the instrument. The addition of L solution resulting in the absorbance between 0.01 and 0.1 is suitable. This method can improve the sensitivity of spectrophotometry and eliminate the background interference of excess L, which is different from the other dual-wavelength methods.[17]

EXPERIMENTAL SECTION

Apparatus and reagents

A Model Lambda 25 (PerkinElmer Instruments, USA) spectrometer, which was connected to a computer with UV Winlab software (version 2.85.04) installed, was used to record the adsorption spectra and absorbances of the reaction solutions. A Model pHS-25 meter (Shanghai Precise Instruments, Shanghai, China) was used to adjust the acidity of the solutions. A water bath (Shanghai Precise Instruments, Shanghai) was used to adjust the temperature of the solutions.

The standard solution of CPC (1.0 mmol/l) was prepared by dissolving CPC (A. R. Shanghai Chemical Reagents) in deionized water. RBR solution (0.5 mmol/l) was prepared by dissolving 0.3076 g of reactive brilliant red X-3B (purity 80%, Shanghai Dye Stuff Factory) in 1000 mL of deionized water. The acetate buffer and ammoniac buffer solutions with pH between 2.25 and 9.62 were used to adjust the pH of solutions. NaCl (2 mol/l) was prepared for adjusting ionic strength of the solution. EDTA (0.1

mol/l) was prepared as the masking agent of metal ions.

Recommended procedures

Aggregation of RBR on CPC: Into a series of 10 mL calibrated colorimetric flasks, a known volume of CPC solution, 1.0 mL of acetate buffer solution and RBR solution from 0 to 0.06 mmol/l were added. The solutions were diluted to 10 mL with deionized water and mixed thoroughly. After 10 min, their absorbances were measured at 503 and 566 nm against a reagent blank treated in the same way without CPC, respectively.

Analysis of samples: Four water samples were analyzed: #1 is from Taihu Lake, #2 is from the Yangzte River, #3 is tap water and #4 is from a local waste pool. 1 mL of the CPC standard solution was added to 100 mL of the samples before coloring. 2 mL of such solutions were then added into a 10 mL calibrated colorimetric flask. The successive operations were carried out according to the above procedures.

RESULTS AND DISCUSSION

Effect of pH on absorption spectra

The absorption spectra of the CPC-RBR solutions in various pH media are shown in Fig. 1. By comparing the interval between peak and valley, the complexation is the most sensitive at pH 3.67. As a matter of fact, it is easier for RBR with a negative charge to bind with CPC with a positive charge by ion-pair attraction. Nevertheless, RBR may be protonized in strongly acidic solutions to cause the decrease of the reaction sensitivity. As a result, pH 3.67 was used in this work. From curve 2 in Fig. 1, the absorption peak is located at 566 nm (λ_2) and the valley at 503 nm (λ_1). Two such wavelengths were used in the further determination of cationic surfactants.

Characterization of CPC-RBR complex

The variation of the light-absorption ratio, $A_{566\ nm}/A_{503\ nm}$ of the CPC-RBR solution at pH 3.67 is shown as curve 1 in Fig. 1. The ratio approaches minimum and then remains constant at 0.751 ± 0.018 when CPC molarity is more than RBR's. Thus, RBR almost completely reacted with CPC and only a color compound, CPC-RBR complex, existed in the solution. The constant minimum is equal to α. The absorption spectrum of such a solution is shown as curve 1 in Fig. 2. The absorption peak of the CPC-RBR complex is located at 562 nm while that of RBR itself is at 537 nm from curve 2. Thus, the CPC-RBR complex displays only 25 nm of spectral red shift. As a result, the excess RBR affected the light-absorption measurement of the complex at 562 nm. The single wavelength does not fit to the complexation for determination of cationic surfactants. From curve 3, the break point approach[18] was used to estimate the composition ratio of CPC to RBR to be about 0.8:1, which will be further confirmed below. Both η and γ in the CPC-RBR solutions were calculated from Eqs. 2 and

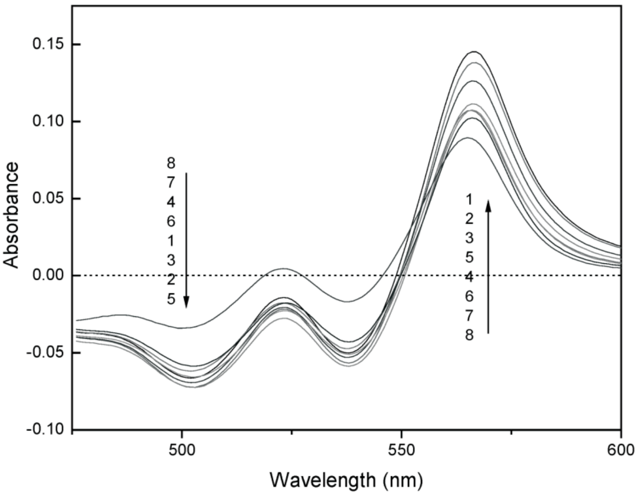

Fig. 1. Effect of pH on the absorption spectra of the CPC-RBR solutions, all of which contained 0.20 μmol of RBR, 0.20 μmol CPC and measured against the reagent blank without CPC: From spectrum (1) to (8) pH 2.94, 3.67, 4.09, 5.05, 6.04, 7.01, 8.17 and 10.63. All solutions were 10.0 mL.

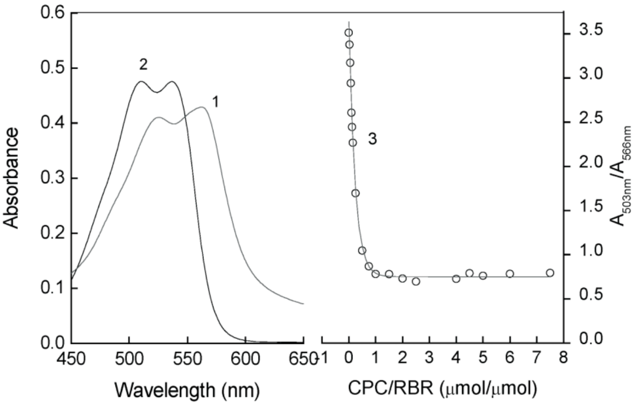

Fig. 2. Formation of the CPC-RBR complex: (1) (2): the absorption spectra of CPC-RBR complex and RBR, respectively both at 0.50 μmol measured against water. (3) variation of $A_{566\ nm}/A_{503\ nm}$. All the solutions were 10.0 mL.

4 and their variations are shown in Fig. 3A. The equilibrium concentration of RBR approaches zero if the initial RBR is less than 0.01 mmol/l, which is attributed to the fact that RBR is much less than CPC. From curve 2, γ of RBR to CPC increases with an increase of RBR molarity and then approaches a constant at 1.2 ± 0.1. This indicated that the binding of RBR onto CPC reached a saturation. Such a constant maximum should respond to *N* of RBR, which is consistent with the result obtained above by the break point.[18]

From curve 2 of Fig. 3, η of RBR is less than 60% when RBR is more than 0.04 mmol/l. This indicates that over 40% RBR remained free in the solution. Certainly, it interfered in the measurement of light absorption of the complex. Therefore, the LARVA was applied to the determination of cationic surfactants instead of single wavelength spectrophotometry in this work.

Plots γ^{-1} vs C_L^{-1} was fitted by Langmuir isothermal adsorption (Fig. 3B). The interaction of RBR with CPC corresponded to such an adsorption model. From the intercept, *N* of RBR was calculated to be 1.2 ± 0.1 which responds to the above data. From the line slope, *K* was calculated to be $(1.15 \pm 0.05) \times 10^5$ l/mol.

Effects of ionic strength and temperature

To investigate the effect of ionic strength on the aggregation of RBR on CPC, NaCl was added into the RBR-CPC solutions, and its effect on γ is shown as curve 1 in Fig. 4. γ almost remains constant and has no obvious change with increasing ionic strength. The binding of RBR to CPC is strong enough to impact the electrolyte. The effect of temperature on γ is shown as curve 2 in Fig. 4. γ decreases obviously when the temperature is over 30 °C. The destruction of electrostatic attraction among molecules in a high temperature may cause this phenomenon.[10,12]

Application of LARVA

Calibration graphs and limit of detection (LOD) of CPC

Four series of standard solutions containing CPC between 0 and 0.1 mmol/l were prepared and 0.30, 0.40 and 0.50 mL of 0.50 mmol/l RBR were added, respectively. The absorbances of each solution were measured at 566 and 503 nm, and ΔA_r was calculated by Eq. 9. The regression equations are given in Table 1. The LOD of CPC, defined

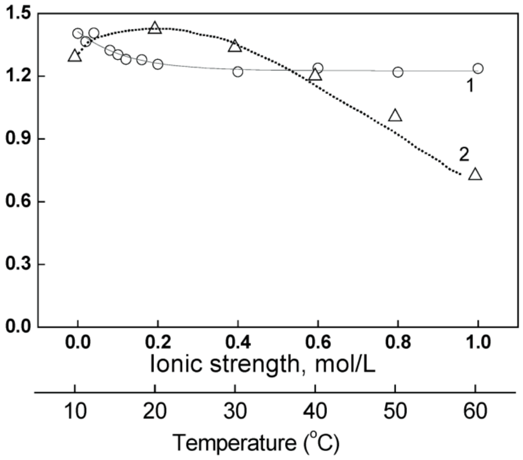

Fig. 4. Effects of the ionic strength and temperature on γ of the solutions containing 0.2 μmol RBR and 0.1 μmol CPC. All the solutions were 10.0 mL (circle: ionic strength (1), triangle: temperature (2)).

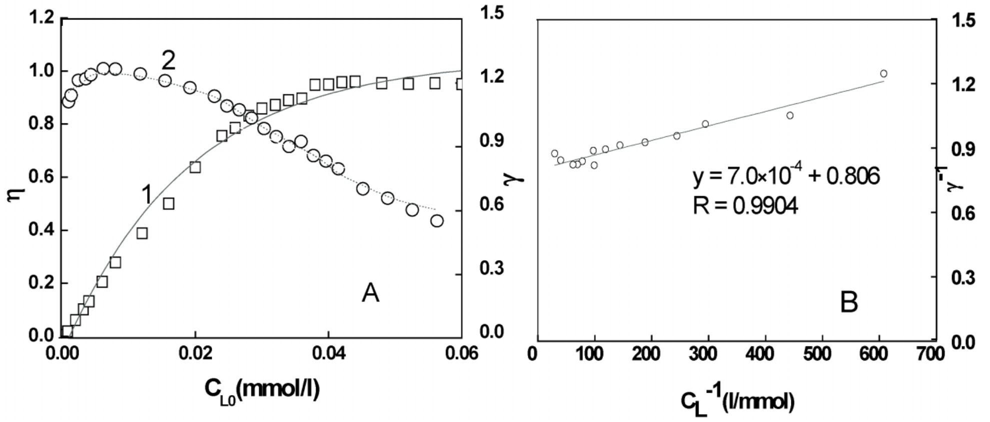

Fig. 3. A: Variation of η and γ: (1) η of RBR. (2) γ of the binding RBR to CPC. B: Variation of γ^{-1} with the C_L^{-1}, the reciprocal of the intercept is the ideal binding number (*Ni*) of RBR on CPC. All the solutions contained 0.1 μmol of CPC and RBR from 0.5 μmol to 75 μmol at pH 3.67. All the solutions were 10.0 mL.

Table 1. Regression equations and limit of detection of CPC

Line	CPC (mol/l)	RBR (mol/l)	ΔA_r vs C_M	p	R[1)]	σ[2)]	LOD[3)] (ng/mL)
1	0-10	15	$\Delta A_r = 0.0810C_{CPC}-0.0141$	0.0810	0.9914	0.001114	15.1
2	0-12	20	$\Delta A_r = 0.0673C_{CPC}-0.0225$	0.0673	0.9943	0.000906	15.0
3	0-15	25	$\Delta A_r = 0.0554C_{CPC}-0.0197$	0.0554	0.9921	0.00078	15.7

[1)] Linear correlation coefficient.

[2)] Standard deviation of 10 repetitive reagent blanks.

[3)] LOD of CPC in 10 mL of flask was calculated by LOD = $3\sigma/p$ (p: line slope).

as 3 times the standard deviation (σ) of 10 replicated blanks, was calculated and is given in Table 1 as well. Series 2 has the least σ and the lowest LOD, so it was chosen as the working equation.

Effect of foreign ions

By adding the masking reagent EDTA to the solutions, the influence of foreign ions was investigated and the result is given in Table 2. None of the following ions and compounds affected the direct determination of 0.500 μmol of CPC (less than 5% error): 1 mg of K^+, Ca^{2+}, NO_3^-, Mg^{2+}, SO_4^{2-}, 0.2 mg of PO_4^{3-}, NH_4^+, $C_2O_4^{2-}$, 0.1 mg of Fe^{2+}, Zn^{2+}, Ba^{2+}, Al^{3+}, Mn^{2+}, Cu^{2+}, 0.01 mg of Fe^{3+} and 0.05 mg of SDS. Therefore, the recommended method is selective and suitable for analysis of water.

Analysis of water samples

As a test of the method, cationic surfactants in four water samples were determined and the results are listed in Table 3. The recovery rates of CPC are between 98.6 and 100% with the relative standard deviation (RSD) less than 2.57%. Thus, the recommended method is accurate and precise.

CONCLUSION

Like in some earlier studies,[19] RBR anion can bind to CPC by ion-pair attraction and the interaction of RBR with CPC is the most sensitive at pH 3.67. The aggregation of RBR on CPC has been characterized by MSASC. The maximal binding number of RBR is 1.2 ± 0.1 and the binding constant is $(1.15 \pm 0.05) \times 10^5$ l/mol. Such an interaction has been applied successfully to the determination of cationic surfactants in water by LARVA with the recovery of CPC between 98.6 and 100% and the RSD less than 2.57%.

Table 2. Effect of foreign ions on ΔA_r of the solutions containing 0.1 μmol CPC

No.	Foreign ion	Added, μg/10 mL	ΔA_r	Error, %
1	CPC	35.80	0.6363	
2	K^+	1000	0.6456	1.47
3	Ca^{2+}	1000	0.6399	0.56
4	NO_3^-	1000	0.6399	0.56
5	Mg^{2+}	1000	0.6607	3.84
6	SO_4^{2-}	1000	0.6607	3.84
7	PO_4^-	200	0.6598	3.69
8	NH_4^+	200	0.6456	1.46
9	$C_2O_4^{2-}$	200	0.6454	1.44
10	Fe^{2+}	100	0.6286	-1.20
11	Zn^{2+}	100	0.6680	4.99
12	Ba^{2+}	100	0.6354	-0.14
13	Al^{3+}	100	0.6589	3.55
14	Mn^{2+}	100	0.6663	4.71
15	Cu^{2+}	100	0.6497	2.10
16	Fe^{3+}	10	0.6516	2.40
17	SDS	50	0.6382	0.47

Error = $(\Delta A_r^{No.x}-\Delta A_r^{No.1})/\Delta A_r^{No.1} \times 100$ (× is from 2 to 17).

Table 3. Determination of cationic surfactant (CS) in natural water

Sample from	CPC added, (ng/10 mL)	CS found, (μg/l)	RSD (%)	Recovery (%)
Yangtze River	0	16.8[a]	2.27	
	358	52.2[b]		98.8
Taihu Lake	0	17.9[a]	2.57	
	358	53.2[b]		98.6
Tap Water	0	19.0[a]	1.95	
	358	54.5[b]		99.1
Wastewater	0	20.2[a]	4.54	
	358	56.0[b]		100.0

[a] Average of 4 replicate determinations.

[b] Average of 3 replicate determinations.

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REFERENCES

1. Singh, D. K.; Sahu, A. *J. Chin. Chem. Soc*. **2005**, *52*, 247.
2. Knaebel, A.; Oda, R. *Langmuir* **2000**, *16*, 2489.
3. Urata, K., Takaishi, N. J. *Surf. Deterg*. **2001**, *4*, 191.
4. Oda, R.; Huc, I.; Candau, S. J. *Chem. Commun*. **1997**, 2105.
5. Sehgal, P.; Doe, H.; Bakshi, M. S. *J. Surf. Deterg*. **2002**, *5*, 123.
6. Ci, Y. X.; Yang, M. M. *Chin. Sci. Bull*. **1983**, *16*, 980.
7. Zheng, Y. X.; Li, L. D.; Sun, S. Q. Chin. *J. Chem. Reagents*. **1984**, *6*, 273.
8. Qi, W. B.; Zhu, L. Z. *Chem. J.Chin. Univ*. **1986**, *7*, 407.
9. Sovilj, V.; Petrovic, L. et al. *Colloid. Surface. A*. **2007**, *298*, 94.
10. Zhai, S. R.; Gong, Y. J. et al. *J. Chin. Chem. Soc*. **2004**, *51*, 49.
11. Wang, W. K. *J. Chin. Chem. Soc*. **2006**, *53*, 583.
12. Wang, H. Y.; Gao, H. W.; Zhao, J. F. *Bull. Korean Chem. Soc.* **2003**, *24*, 1444.
13. Zhang, Y. L.; Pei, X. M.; Liu, X. H. *J. Chin. Chem. Soc*. **2005**, *52*, 885.
14. Gao, H. W.; Xia, S. Q. et al. *Water Res*. **2004**, *38*, 1642.
15. Langmuir, I. *J. Am. Chem. Soc*. **1918**, *40*, 1361.
16. Gao, H. W. *Bull. Korean Chem. Soc.* **2002**, *23*, 943.
17. Liu, S. D.; Yang, Z. *Chin. J. Pharmaceuticals.* **1995**, *26*, 231.
18. Gao, H. W.; Hu, Z. J.; Zhao, J. F. *Chem Phys Lett.* **2003**, *376*, 251.
19. Yu, J. F.; Jia, J. P.; Ma, Z. F. *J. Chin. Chem. Soc*. **2004**, *51*, 1319.