ARTICLE

Cu(II), Ni(II) Complexation with Acid Alizarine Blue B in the Presence of Cetyltrimethylammonium Bromide

Rong Shen[a,b], Hong-Wen Gao[c], Han-Qing Yu[b*]

a. Department of Chemical Engineering, Anhui Vocational and Technical College, Hefei 230051, China;
b. Department of Chemistry, University of Science and Technology of China, Hefei 230026, China;
c. Key Laboratory of Yangtze Water Environment of Ministry of Education, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China

The coordination reactions of Cu(II) and Ni(II) with acid alizarine blue B (AABB) in the presence of cetyltrimethylammonium bromide (CTAB) micelle were investigated using the microsurface adsorption-spectral correction technique (MSASC). The aggregation of AABB on CTAB followed the Langmuir isothermal adsorption law. The enrichment of AABB on CTAB sensitized the complexation between Cu(II) or Ni(II) and AABB. The binding ratio of AABB to CTAB was 1:2.5, and monomeric aggregate, $AABB_2CTAB_5$, was formed with an adsorption constant of 5.95×10^5 at 20 °C or 2.48×10^5 at 40 °C. In the ternary complexation, the ratio of AABB:Cu and AABB:Ni were 1:1 and 1:2.5, respectively. Two types of aggregates, $Cu_2\cdot AABB_2\cdot CTAB_{80}$ and $Ni_5\cdot AABB_2\cdot CTAB_{80}$, were formed.

Key words: Microsurface adsorption-spectral correction technique, Langmuir aggregation, Acid alizarine blue B, Cetyltrimethylammonium bromide, Ternary complex

I. INTRODUCTION

Surfactants (S) are very useful in trace analysis and element separation because of their synergism, e.g. solubilization, stabilization and sensitization [1,2]. The preparation and characterization of new and efficient surfactants are under extensive investigation [3-5]. Dye ligand (L) is often used as a probe in spectrometric study of surfactants. Understanding of the assembly of L on S is helpful to investigate the mechanisms of S in separation and extraction of elements/compounds, in trace analysis, and in synthesizing new-type surfactants and expanding their applications. Some mechanisms have been proposed to explain the synergism of surfactant such as micelle extraction [6], synergism perturbation [7], hydrogen bond formation [8], micelle catalysis [9], and asymmetric microenvironment [10].

We established a microsurface adsorption-spectral correction (MSASC) technique, which was different from other dual-wavelength spectrophotometric methods in operation. This method can eliminate the absorption interference of free ligands and consequently can reveal the real absorbance of complex, providing a helpful experimental strategy for studying the interaction of L with S and that of metal ions (M) with S-L aggregate [11]. In this work, the coordination reactions of Cu(II) and Ni(II) with acid alizarine blue B (AABB) in the presence of cetyltrimethylammonium

bromide (CTAB) micelle were investigated in details using the MSASC.

II. PRINCIPLES

In S solution, the aggregation of S forms big electrostatic global micelles when the concentration of S is higher than their critical micelle concentration (CMC). The electrostatic force drives L to the surface of the micelles until kinetic equilibrium is reached. The enrichment of L on S microsurface results in a rapid and easy complexation with M added later. In other words, S micelle provides the complexation between M and L with a catalytic reaction field. The monolayer aggregation of L on S similar to that of biomacromolecules was observed [12,13]. The aggregation obeys the Langmuir isothermal adsorption law. The schematic equilibrium is as follows: L(aqueous phase, C_L)$\Longleftrightarrow$$SL_N$(S micro surface phase, C_S)

The Langmuir equation is:

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

where K is the equilibrium constant, C_L is the molarity of the excess L and γ is the molar ratio of the effective adsorption of L to S. With increasing L concentration, γ approaches a maximal binding number N. C_L and γ can be calculated by the relations:

$$\gamma = \eta \frac{C_{L0}}{C_S} \tag{2}$$

$$C_L = (1-\eta)C_{L0} \tag{3}$$

*Author to whom correspondence should be addressed. E-mail: hqyu@ustc.edu.cn

     178

$$\eta = \frac{A_C - \Delta A}{A_0} \qquad (4)$$

where C_S and C_{L0} are the initial molarities of S and L, respectively. η is the effective fraction of L. A_C is the real absorbance of the S-L product. A_0 is the absorbance of the L with water as a reference, and ΔA is the absorbance of the S-L solution with reagent blank as the reference solution, which can be directly measured at the peak wavelength λ_2. A_c was calculated by means of [12,13]:

$$A_C = \frac{\Delta A - \beta \Delta A'}{1 - \alpha\beta} \qquad (5)$$

where $\Delta A'$ is the absorbance of the S-L solution measured at the valley wavelength λ_1. Usually, α and β are the correction constants and they are calculated by measuring SL_N and L solutions. In addition, the molar absorptivity (real $\varepsilon_\gamma{}^{\lambda_2}$, not apparent $\varepsilon_\alpha{}^{\lambda_2}$) of the adsorption product SL_N at λ_2 is also directly calculated using the equation:

$$\varepsilon_\gamma{}^{\lambda_2} = \frac{NA_C}{\delta\gamma C_S} \qquad (6)$$

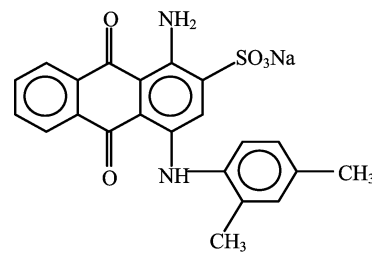where δ is the cell thickness (cm).

III. EXPERIMENTAL

A. Apparatus and reagents

Absorption spectra were recorded by a spectrophotometer (TU1901, PGeneral, Beijing) and independent absorbance was measured using another spectrophotometer (Model 722, Shanghai 3rd Analytical Instrument). The pH of the solution was measured with an acidity meter (pH S-2C, Leici Instruments, Shanghai). The temperature was controlled by an electrically heated thermostatic bath (Model 116R, Changjiang Test Instruments of Tongjiang). Surface tension was measured using a surface tension apparatus (A DSA 10 MK 2 Drop Shape Analysis System, Germany).

All reagents were of analytical grade. Stock standard solution of CTAB (10.00 mmol/L) was prepared by dissolving CTAB (Shanghai Chemical Reagents) in deionized water and the CTAB solution (1.00 mmol/L) was prepared daily by diluting the stock solution. Solution of AABB (0.180 mmol/L) (Chroma, Schmid GMBH & Co.) was prepared in deionized water. The CTAB-AABB adsorption aggregate solution was prepared with 10 mL buffer solution of pH 9.1 in 1 L deionized water. In this solution, the large aggregate, 0.180 mmol/L AABB$_2\cdot$CTAB$_{80}$ was formed. Cu(II) 0.312 mmol/L and Ni(II) 0.341 mmol/L work solutions were prepared by diluting the 1 g/L Cu (II) and 500 mg/L Ni (II) (GSB07-1260-2000, Institute for Reference Materials of SEPA) solutions with deionized water. The acetate, phosphate and ammonium buffer solutions between pH 3.0 and 11.0 were used to adjust the acidity of the solution. NaCl solution of 2.0 mol/L was used to adjust

the ionic strength of the aqueous solutions. AABB is a kind of anionic dyes. Its structure is given below:

Acid alizarine blue B (AABB)

It is sensitive to bind on CTAB and then to complex with M.

B. Experimental procedures

Interaction of CTAB with AABB: 1 mL of 1.00 mmol/L CTAB and 2.5 mL pH 9.1 buffer were added into a 25 mL calibrated flask with an appropriate volume of the AABB solution. The mixture was diluted with deionized water to 25 mL. The absorbance was measured at 586 and 633 nm with 1 cm cell with the AABB as the reference, and A_C of the binary adsorption aggregate was calculated.

Interaction of CTAB-AABB with metals: 0.312 μmol Cu(II) or 0.341 μmol Ni(II) was added into a 25 mL solution flask containing 2.5 mL pH 9.1 buffer and an appropriate volume of the CTAB-AABB aggregate solution (0.180 mmol/L). The absorbance was measured at 563 and 481 nm, respectively, with the CTAB-AABB aggregate as a reference and A_C of the ternary complex was calculated.

IV. RESULTS AND DISCUSSION

A. Spectral analysis

The absorption spectra of the solutions of AABB, CTAB-AABB and CTAB-AABB-Cu (Cu as a representative of M) at pH 9.1 are shown in Fig.1. The peak of the AABB was located at 570 nm whereas that of the CTAB-AABB aggregate was at 580 nm. Namely, there was a red shift of 10 nm in the spectrum of CTAB-AABB aggregate, which might be attributed to the fact that the electrostatic attraction is much weaker than the chemical bonding. The peak and valley of the CTAB-AABB solution with AABB as the reference are located at 586 and 633 nm as shown in curve 3. Thus, the two wavelengths were used in the study of the binary complex. The ratio of A_{481}/A_{563} of ternary complex decreased markedly with the increase of M molarity at the initial stage and then approached constants. It means that M has complexed completely with the AABB binding on CTAB micelle. So the spectrum of this solution originated from the

absorbance of CTAB-AABB-M ternary complex, which was shown in curve 6. The peak and valley of the Cu-CTAB-AABB solution with the CTAB-AABB aggregate as the reference are located at 563 and 481 nm. Therefore, these two wavelengths were used in study of the ternary complex. From curves 1 and 2, the correction coefficients were calculated as $\alpha= 0.104$ and $\beta=1.28$ (AABB-CTAB), respectively. In the same way, the correction coefficients were calculated to be $\alpha=0.255$, $\beta=1.176$ (AABB-CTAB-Cu) and $\alpha=0.490$, $\beta=1.073$ (AABB-CTAB-Ni), respectively, from curves 4 and 5.
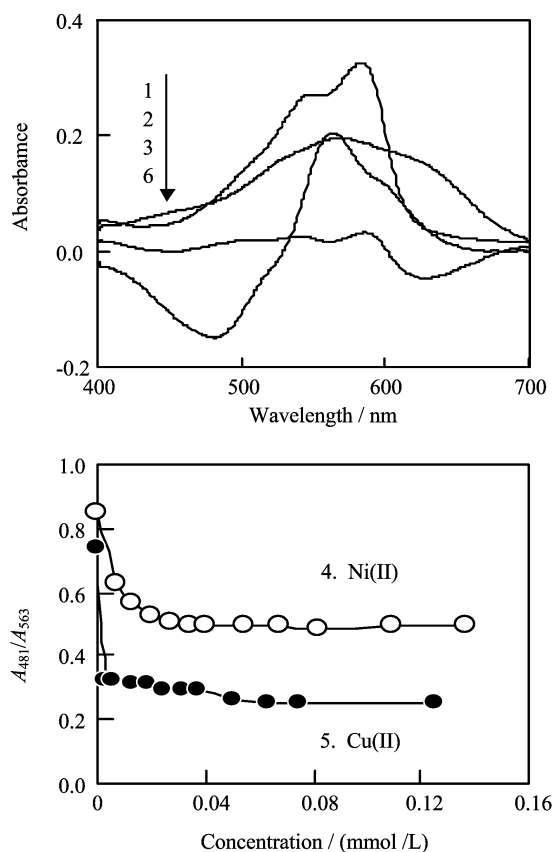

FIG. 1 Absorption spectra of AABB, AABB-CTAB and AABB-CTAB-Cu (top). A_{481}/A_{563} of AABB-CTAB-M at pH 9.1 (low). Curves 1, 2, 4 and 5 all measured against water, curves 3 and 6 measured against the reagent blanks.
1. 0.180 mmol/L AABB;
2. 0.180 mmol/L AABB+10.0 mmol/L CTAB;
3. 0.180 mmol/L $AABB_2 \cdot CTAB_{80}$;
4. 0.180 mmol/L $AABB_2 \cdot CTAB_{80}$+Ni(II);
5. 0.180 mmol/L $AABB_2 \cdot CTAB_{80}$+Cu(II);
6. 0.180 mmol/L $AABB_2 \cdot CTAB_{80}$+0.126 mmol/L Cu(II).

B. Interaction between CTAB and AABB

As illustrated in Fig.2, the inflexion of surface tension curve appeared at the valley of the curve of A_{633}/A_{586}, indicating that AABB bound most CTAB at this point [14,15]. AABB was excessive before the point, and CTAB integrated AABB gradually with the increase

of CTAB: At the point, AABB was aggregated thoroughly by CTAB and the ratio of A_{633}/A_{586} approached to a minimum: CTAB became excessive after the point. From the curve of surface tension, we also found that the surface tension decreased rapidly when CTAB was over the inflexion. Thus, more and more CTAB free in the solution began to appear, which caused the rapid decrease of surface tension of the solution. Meanwhile, the ratio of A_{633}/A_{586} increased slightly since the self-aggregation of CTAB might become stronger with increasing CTAB. The valley of A_{633}/A_{586} curve is located at the molar ratio of CTAB to AABB at 2.5:1, suggesting that each AABB can bind 2.5 molecules of CTAB at most.
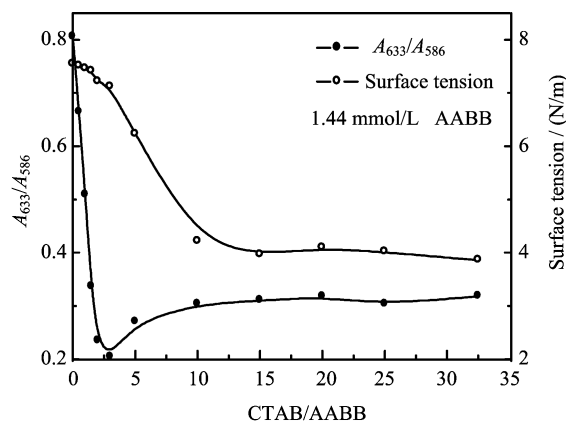

FIG. 2 Effect of CTAB dosage on A_{633}/A_{586} and surface tension.

C. Effects of pH, ionic strength and temperature

The absorbance of binary aggregate measured at 586 and 633 nm and that of the ternary solutions measured at 563 and 481 nm at various pH, are shown in Fig.3 and Fig.4, respectively. Comparing the two curves in each figure, a maximum absorbance difference in binary aggregate was observed at pH 9.1, while that in ternary complex was given at pH 10.6. These results
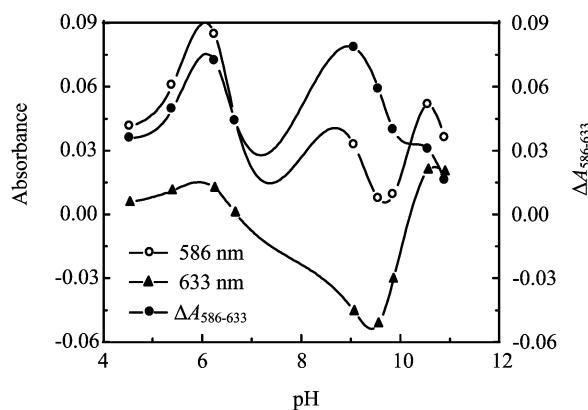

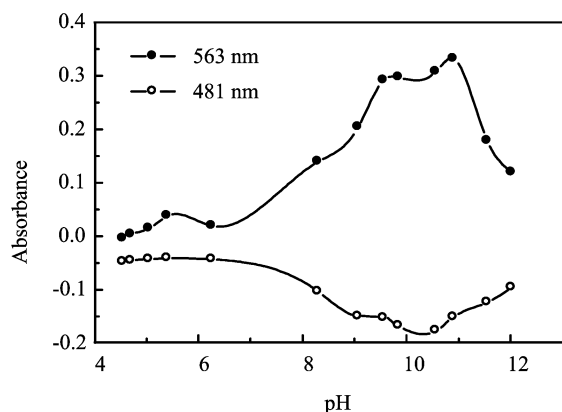FIG. 3 Effect of pH on absorbance of the AABB-CTAB solution

FIG. 4 Effect of pH on absorbance of the AABB-CTAB-Cu solution.

increase of temperature could accelerate the desorption of AABB from CTAB. However the adsorption ratio of AABB to CTAB remains almost constant in curve 2. The reason might be that as CTAB was excessive, the desorbed AABB from CTAB microsurface would bind rapidly on another free CTAB molecule. The effect of temperature on the adsorption ratio of AABB to Cu and Ni are shown in curve 3 and 4, too. The adsorption ratio of AABB to Cu and Ni decreased about 15%-20% as temperature increased from 20 to 60 °C. It was because that the M-L connection depended on the coordination bond, not the electrostatic attraction. Consequently, the M-L connection was much stronger than the S-L connection. A high temperature was often possible to break off the S-L connection, but not easily to destroy the M-L connection.

indicate that the binary aggregate was most sensitive around pH 9.1, and that the ternary complex was more sensitive in stronger basic medium. However, $Cu(OH)_2$ and $Ni(OH)_2$ could be formed easily in stronger basic medium because of hydrolysis of M, thus interfering the ternary complexation. Therefore, buffer solution of pH 9.1 was used in this study.

In order to investigate the effect of ionic strength on the binding of AABB and CTAB, 2.0 mol/L NaCl solution was added at various dosages. The adsorption ratio of AABB to CTAB decreased slowly with the increase of ionic strength. This was attributed to the fact that a large amount of Cl^- occupied the surface of CTAB to weaken the binding of AABB.

The adsorption ratio of AABB to CTAB and that of AABB to Cu and Ni at various temperature are shown in Fig.5. As shown in curve 1, the adsorption ratio of AABB to CTAB decreased with increasing temperature over 40 °C, and the value of the adsorption ratio decreased by about 28% with an increase of 10 °C in temperature. This was attributed to the fact that the
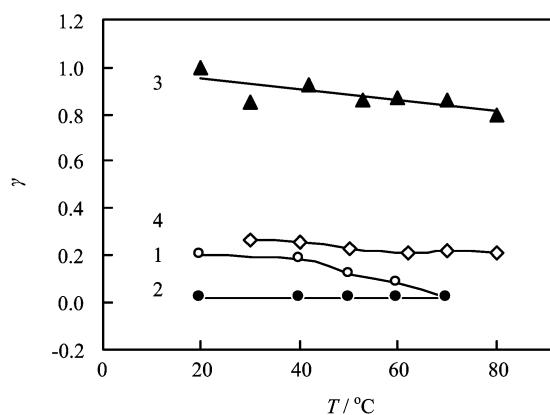
D. Characterization of binary aggregate and ternary complexes

By varying the AABB concentration in solutions containing 0.02 mmol/L CTAB at pH 9.1 and temperature at 20 or 40 °C, the relationship of γ^{-1} and $C_L{}^{-1}$ are shown in Fig.6. Both of the correlation coefficients were high, indicating that the aggregation of AABB on CTAB obeys the Langmuir isothermal adsorption. The binding ratio of AABB to CTAB is 0.4 at 20 °C and 0.2 at 40 °C, respectively. The maximal binding number of L decreased with the increase of temperature. The reason has been given above. The binding ratio, adsorption constant K and the real (not apparent) molar absorptivity ($\varepsilon_\gamma{}^{586}$) of the aggregates are listed in Table I. The monomer aggregate, $AABB_2 \cdot CTAB_5$ was formed at 20 °C, while $AABB \cdot CTAB_5$ was formed at 40 °C. The large micelle aggregates, $(AABB_2 \cdot CTAB_5)_{16}$ (at 20 °C) and $(AABB \cdot CTAB_5)_{16}$ (at 40 °C) would be formed when AABB was enough.

FIG. 5 Effect of temperature on the adsorption ratio.
1. 0.180 μmol AABB+1.0 μmol CTAB;
2. 0.450 μmol AABB+20 μmol CTAB;
3. 0.450 μmol $AABB_2 \cdot CTAB_{80}$+0.156 μmol Cu^{2+};
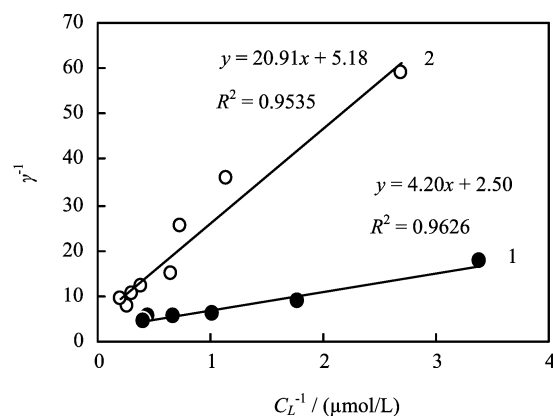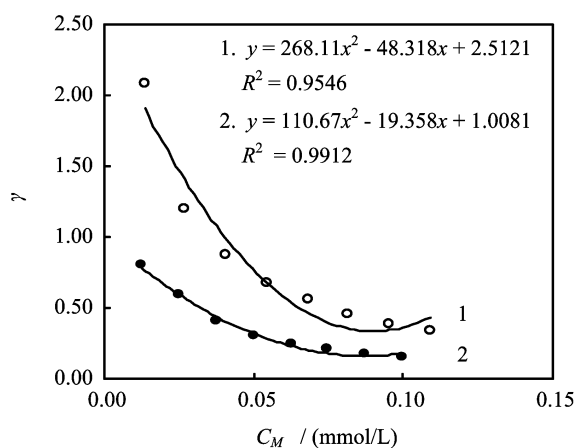4. 0.360 μmol $AABB_2 \cdot CTAB_{80}$+1.705 μmol Ni^{2+}.

FIG. 6 The relationship of γ^{-1} and $C_L{}^{-1}$. 1. 20 °C; 2. 40 °C.

The adsorption ratio γ of M-AABB-CTAB solutions at various Cu(II) or Ni(II) concentrations were also measured. Plots of C_M $vs.$ γ are shown in Fig.7. The

TABLE I The binding constants of the AABB-CTAB aggregate at pH 9.1

$T/^\circ C$	N	$K \times 10^5$	$\varepsilon^{586} \times 10^4$ /(L/mol·cm)
20	0.4	5.95	3.73
40	0.2	2.48	1.50

adsorption ratio γ of M to AABB decreased with the increase of M concentration. Therefore, the maximal binding number N of each ternary complex could be obtained from the intercepts of two curves. Cu(II) could form 1:1 and Ni(II) could form 2.5:1 complexes to AABB. Thus, ternary complexs $Cu_2 \cdot AABB_2 \cdot CTAB_{80}$ and $Ni_5 \cdot AABB_2 \cdot CTAB_{80}$ would be formed. The ε_γ^{481} was 7.28×10^4 L/mol·cm for $Cu_2 \cdot AABB_2 \cdot CTAB_{80}$, and 6.38×10^4 L/mol·cm for $Ni_5 \cdot AABB_2 \cdot CTAB_{80}$. The interaction of M with AABB occurring on CTAB micelle could be regarded as an adsorption interaction. The adsorption force came from the coordination bond, not the electrostatic attraction.

FIG. 7 The relationship of C_M and γ. 1. AABB-CTAB-Ni; 2. AABB-CTAB-Cu.

V. CONCLUSIONS

The interaction between AABB and CTAB confirmed the Langmuir isothermal adsorption of a stain on ionic surfactant due to electrostatic attraction. The enrichment of a dye ligand on micelle accelerated its coordination with a metal ion. In other words, S micelle provided a catalysis field to sensitize the complexation between M and L. The MSASC technique qualitatively explained the synergism of S in aqueous medium such as solubilization, sensitization and stabilization, and provided a useful experimental approach for studying a binary aggregate or a ternary complexation. The technique would play an important role in studying the interaction among molecules.

[1] W. B. Qi and L. Z. Zhu, Chin. J. Instrum. Anal. **5**, 1 (1986).
[2] N. Ishibashi and K. Kina, Anal. Lett. **5**, 637 (1972).
[3] D. Dinino, Y. Talmon, H. Levy, *et al.* Science **269**, 1420 (1995).
[4] D. Dinino, Y. Talmon and R. Zana, Langmuir **11**, 1448 (1995).
[5] R. Zana and Y. Talmon, Nature **362**, 2293 (1993).
[6] H. Nishida, Bunseki Kagaku **26**, 271 (1977).
[7] Y. X. Ci and M. M. Yang, Chin. Sci. Bull. **16**, 980 (1983).
[8] Y. X. Zheng, L. D. Li and S. Q. Sun, Chin. J. Chem. Reagents. **6**, 273 (1984).
[9] B. Savvins, P. K. Chernova and L. I. M. Kudpatseva, Zh. Anal. Khim. **33**, 2127 (1978).
[10] W. B. Qi and L. Z. Zhu, Chem. J. Chin. Univ. **7**, 407 (1986).
[11] H. W. Gao, Y. Q. Zi and Y. C. Li, Acta. Phys. Chim. Sin. **18**, 540 (2002).
[12] H. W. Gao, Y. C. Li and J. Jiang, Chin. J. Chem. Phys. **14**, 737 (2001).
[13] H. W. Gao, J. R. Wu and R. Shen, Chin. J. Chem. **22**, 798 (2004).
[14] H. W. Gao, R. Shen and Y. L. Zhang, Russ. J. Phys. Chem. **78**, 1149 (2004).
[15] L. X. Zheng, R. Shen and H. W. Gao, Chin. J. Pro. Eng. **3**, 401 (2003).