The association effect of quaternary ammonium salt on carboxymethyl cellulose and its analytical applications

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ABSTRACT

Sodium carboxymethyl cellulose (CMC) has been extensively used in petroleum, geology, common household chemicals, food, medicine and other industries, owing to its excellent water-soluble, emulsifying, water retention and film forming properties. It is known as ‘industrial monosodium glutamate’. However, the research of the test method on CMC is far behind the research of its actual application value. This study showed that, weak acid or weak basic medium, the carboxyl groups dissociated from CMC, existing as a big negative ion, which can form ion-association complexes with some quaternary ammonium cations through electrostatic and hydrophobic interactions. The absorption spectrum changes and Triton-X100 can increase the sensitivity of the system. The maximum absorption wavelengths are, respectively, about 256 nm for dodecyl trimethyl ammonium bromide (LTAB), 244 nm for tetradecyltrimethyl ammonium bromide (TTAB) and 240 nm for cetyltrimethyl ammonium bromide (CTAB) with CMC. The reactions show very high sensitivities and the maximum molar absorption coefficients are $1.10 \times 10^4 \text{ L/(mol·cm)}$ for LTAB system, $1.24 \times 10^6 \text{ L/(mol·cm)}$ for TTAB system and $1.78 \times 10^6 \text{ L/(mol·cm)}$ for CTAB system. This method is simple and rapid, and can be applied for the spectrophotometric determination of trace CMC in the supernatant of centrifuged drilling mud.

Key words | carboxymethyl cellulose, drilling mud, quaternary ammonium salt, ultraviolet spectrophotometry

INTRODUCTION

Carboxymethyl cellulose (CMC) is a kind of derivative of natural cellulose with an ether structure, and the carboxyl in the molecular chain can form salt. The most common is its sodium salt, namely sodium CMC, which is called CMC customarily (Lu et al. 1996; Nie et al. 2004). CMC sodium salt is usually used extensively, in order to increase its solubility in water. There are many dissociable carboxymethyls in its large polymer matrix. Therefore, they can exist as big anions with more negative charge in aqueous solution. CMC is used extensively in industry because of its excellent adhesion, promotion, thickening, emulsion, sustained release and film forming properties (Zhan 1997; Yang et al. 2002; Tan & Liu 2009). Thus, CMC is one of the most important water-soluble cellulose derivatives. There is less research and fewer methods on the determination of CMC at present, which is far from meeting the need of industrial analysis. There are several methods to determine the content of trace CMC, such as the naphthol method (Ranjbar & Fresenius 1988), anthrone method (Halliwell et al. 1983), phenol method (Kong et al. 2006), scattering method (Liu et al. 2005a, b), fluorescence quenching technique (Liu et al. 2006), gel permeation chromatography (Yomota et al. 1984) and nuclear magnetic resonance method (Hall & Wooten 1998). CMC was found to have a fading effect on acridine dyes, and the method to analyze CMC has been successfully established (Liu et al. 2005a, b). Quantitative determination methods for CMC are very seldom currently used. Precipitation titration is applied to determine large amounts of CMC, and anthrone spectrophotometric methods are applied to determine slight and trace amounts of CMC (Halliwell et al. 1983). Both those two methods have good accuracy and reproducibility; however, the process is tedious and sensitivity is low. The study of a quantitative determination method for CMC falls far behind its practical application. Therefore, it is of great significance to further research the chemical properties and develop an analysis method for CMC.
Quaternary ammonium salt is a kind of cationic surfactant, possessing good water solubility. It can dissolve in alkaline and acidic medium and is stable. Owing to the slight toxicity, low irritation, low corrosivity, strong surface activity, bactericidal properties and low price of quaternary ammonium salt, it is used widely in household chemicals, material science, energy industry and fine chemical industry (Guo et al. 2002; Yang et al. 2003). It is also used in photometric analysis because of its micellar solubilization to a complex system of metal ions and dyes (Cao et al. 1999; Qin et al. 2007). Recently, quaternary ammonium salt was widely used to quantitatively determine metals in water. Wen et al. (2014) studied the flotation separation behavior of Cu$^{2+}$ with potassium iodide–ascorbic acid–tetradecyltrimethyl ammonium bromide system. The proposed method has been applied to the flotation separation of trace Cu(II) in various environmental water samples with a recovery of 97–104%; Song et al. (2010) set up a sensitive, simple and new resonance light scattering method to determine trace amounts of Bi(III) in the environment based on the ternary ion-association complex particles of Bi(III)–alizarin red-s–cetyltrimethyl ammonium bromide (CTAB); Shen & Zou (2015) established a novel method to determine trace Cr(III) by kinetic spectrophotometry with CTAB as sensitizer and phenanthroline as activator; Wen et al. (2009) showed that [AuCl$_4$]$^{-}$ reacted with CTAB to form a yellow CTMAB–AuCl$_4$ associated complex and proposed a method for measurement of trace gold in waste samples without preseparation. The analytical results were in good accordance with those of the flame atomic absorption spectrometry method (Wen et al. 2009); Chen et al. (2000) established a determination method for trace aluminum in drinking water by spectrophotometry based on the sensitizing effect of CTAB, and the detection limit was 0.008 mg/L; Ma et al. (2007) studied the flotation of gold(III) in a solution of potassium iodide and CTAB, which was a non-toxic, simple, rapid and economic method to separate and enrich gold; Zhong (2006) studied the resonance light scattering spectrum of a Cu-KI-CTAB system or Ag-KI-CTAB system in subacidity medium with a simple fluorophotometer and established a determination method for trace Cu(II) or Ag(I) in wastewater, and the detection limits were all 0.005 μg/mL; Yu et al. (2006) established a determination method for Mn(II) by spectrophotometry based on the sensitizing effect of CTAB, and the detection limit was 6.38 × 10$^{-8}$ g/L. The method was successfully used to determine Mn(II) in tea and the soaked tea water.

Quaternary ammonium salt was found to be a stable and easy to obtain cationic surfactant, and has been widely used to determine metal ions in water; nevertheless, there are few reports on determining CMC by using ultraviolet (UV) spectrophotometry. This is because almost all reactions are based on the association and sensitization of metal ion. However, quaternary ammonium salt, as a cationic surfactant, should be investigated as to whether it can be used to determine the content of CMC in water. Therefore, the current paper took CMC as a study object, systematically studied the interaction between quaternary ammonium salt with different carbon chain lengths and CMC, and investigated the stability and the absorption spectrum of the association complex of quaternary ammonium salt and CMC. The quaternary ammonium salt included dodecyl trimethyl ammonium bromides (LTABs), tetradecyltrimethyl ammonium bromide (TTAB), CTAB and octadecyltrimethyl ammonium bromide (OTAB). The current paper studied the effects of some factors, such as acidity of solution, non-ionic surfactant, reaction time, reaction temperature and coexisting substances, on the association compounds. UV spectra of CMC were obtained, which can be used to determine CMC in petroleum drilling waste mud.

**EXPERIMENTAL**

**Instruments and materials**

UV-visible spectrophotometer model UV-2450 was purchased from Shimadzu Co. (Tianjin, China). Digital pH meter model DELTA320 was purchased from Mettler Toledo Company (Shanghai, China). Thermostatic water bath kettle was purchased from Beijing Changyuan equipment factory (Beijing, China). TGL20M desktop high-speed refrigerated centrifuge was purchased from Kaida Scientific Instruments Co., Ltd (Hunan, China).

CMC was purchased from Shanghai Chemical Reagent Co., Ltd (Shanghai, China). Quaternary ammonium salts LTAB, TTAB, CTAB and OTAB were purchased from Sigma Company (Japan Sigma). Triton-X100 (CP (chemically pure)) and OP-10 emulsifier (CP) were purchased from Shanghai Hengyuan Biological Technology Co., Ltd (Shanghai, China). Tween-20 (CP) was purchased from Xi’an Chemical Reagent Plant (Xi’an, China). The other chemicals were all analytically pure, and redistilled water was used in all experiments.

**Experimental method**

A certain amount of CMC solution, 1.0 mL Britton–Robinson (BR) buffer solution, 2.0 mL quaternary ammonium solution,
2.0 mL non-ionic surfactant were added into a drying colorimetric tube and the mixture was diluted with redistilled water to 10.0 mL. At room temperature, after 20 min reaction, taking the blank solution without CMC as reference, the absorbance at optimal absorption wavelength was measured using a UV spectrophotometer.

**The preparation of solution**

The CMC standard solution was prepared by weighing exactly 0.2500 g CMC and transferring it into 150 mL distilled water under temperatures of 30–50 °C, and then it was intensively mixed and transferred into a 250 mL volumetric flask. The stock solution was ready with a concentration of 1.0 g/L. The stock solution was diluted to 100 mg/L as a working solution.

BR buffer solution was prepared by mixing 0.04 mol/L of three acids (H₃PO₄, H₃BO₄ and HAc) and 0.02 mol/L NaOH solution in a certain proportion with variation of pH, and the pH value was adjusted using a digital pH meter model DELTA320.

**RESULTS AND DISCUSSION**

**Absorption spectra**

The absorption spectra for CMC, CMC + quaternary ammonium, and CMC + quaternary ammonium + non-ionic surfactant are shown in Figure 1, respectively. There was no absorption peak at 190–800 nm when CMC exists alone. The results of the experiment showed that the maximum absorption peak was less than 190 nm in the UV region when CMC exists alone, and the UV spectrophotometer could not determine the absorbency. The absorption peak’s position of the system CMC + quaternary ammonium salt was related to the quaternary ammonium salt. The maximum absorption peaks were at 209 nm, 215 nm and 207 nm accordingly, when LTAB, TTAB and CTAB were added, respectively. The order of absorption value from largest to smallest was ΔACTAB > ΔATTAB > ΔALTAB. The reason for producing the absorption peak is that CMC anionic polymer reacts with quaternary ammonium salt to form an ion-association complex, which leads to the redshift of absorption peaks of CMC, and the absorption peaks appear in the UV-detectable area of the instrument. There was no absorption peak within the range of 190–800 nm for the CMC + OTAB system. The reason may be that the carbon chain is too long, the hydrophobic interaction is too strong, and the shielding effect of the folded chain structure on CMC is too strong, leading to the decrease of absorbance. The stronger redshift occurred in the CMC + quaternary ammonium + non-ionic surfactant system. After adding non-ionic surfactant, the maximum absorption peak of the system produced further redshift, and the absorbance value increased. Comparing Figure 1(a) and 1(b), the maximum absorption peak redshifted by 33 nm after adding Triton-X100 in CMC + CTAB system, and the absorbance value increased by 40%.

![Figure 1](https://iwaponline.com/wst/article-pdf/72/6/837/466151/wst072060837.pdf)

**Figure 1** | Absorption spectra. (a) a. 50 mg/L CMC; b. 50 mg/L CMC + 2 mg/L LTAB; c. 50 mg/L CMC + 5 mg/L TTAB; d. 50 mg/L CMC + 1 mg/L CTAB; e. 50 mg/L CMC + 2 mg/L OTAB; BR: pH = 5.00, 1.0 mL. (b) a. 50 mg/L CMC; b. 50 mg/L CMC + 1 mg/L CTAB + 1% OP emulsifier; c. 50 mg/L CMC + 1 mg/L CTAB + 0.5‰ Triton-X100; d. 50 mg/L CMC + 1 mg/L CTAB + 1% Tween-20; e. 50 mg/L CMC + 1 mg/L CTAB + 1% OP emulsifier; f. 50 mg/L CMC + 1 mg/L CTAB + 1% Tween-20.
The choice of quaternary ammonium

CMC is a type of ion-association complex. It may change the original features of the absorption spectra when reacting with cationic quaternary ammonium and forming an ion-association complex (Liu et al. 2006). Therefore, carbon-chain quaternary ammonium salts with different lengths were chosen to research association with CMC. The results showed that both the TTAB system and CTAB system have higher absorption peak, and the peaks were completely stable. Although the LTAB system also had an absorption peak, its value was very small. No absorption peak occurred in the reaction of any concentration of OTAB and CMC. The further research on the dosage of TTAB and CTAB showed that the absorbance reached the maximum and was stable when the dosage of TTAB was 1.5–3.0 mL, and the concentration of TTAB was 2.0 g/L. When the dosage of TTAB was less than 1.5 mL, the association was incomplete and the absorbance was relatively low. Therefore the suitable amount of TTAB was 2.0 mL. The absorbance reached the maximum and was stable when the dosage of CTAB was 0.5–2.0 mL, and the concentration of CTAB was 1.0 g/L. The suitable amount of CTAB was 1.0 mL. In addition, it was shown that CMC reacted with cationic quaternary ammonium to form ion-association complex, and the spectra feature of cationic quaternary ammonium hardly changed. When the concentration of CMC was bigger, the absorption peak was blueshifted 3–6 nm. As shown in Figure 2(a) and 2(b), the absorbance at the largest absorption wavelength increased with the increase of the CMC concentration.

Effect of the acidity of solution on the reaction

The research demonstrates that the absorbance of ion-association complex will be influenced, to a certain extent, by the change in pH. The acidity has a great influence on the absorbance of the ion-association complex. When the acidity of the solution is too high, it could promote ion-association complex dissociation, thus reducing the stability of the complex and causing the absorbance to decrease. However, when the acidity is lower the solution may turn turbid. This may be due to ion-association complex degeneration in the acidic environment. Therefore, this paper selected the BR buffer solution with different pH (1.0–8.5) to determine the effect of pH on the absorbance as shown in Figure 3, and the results showed that pH and the dosage of buffer solution had nothing to do with the absorbance of LTAB system. When pH was from 4.0 to 7.0 and the dosage of buffer solution was from 0.5 to 1.5 mL, the absorbance reached the maximum and remained stable in TTAB system. Therefore, the suitable pH is 5.0 and the dosage of buffer solution is 1.0 mL. In CTAB system, when pH was from 1.0 to 8.5 and the dosage of buffer solution was from 0.5 to 3.0 mL, the absorbance had slight change. Moreover, the absorbance in CTAB system was bigger than that in TTAB system with the same concentration of CMC. The ion-association complex formed by CMC and CTAB was more stable, and it cannot be affected easily by environmental factors. In the experiment, 1.0 mL buffer solution with pH 7.0 was added into CTAB system.

![Figure 2](https://iwaponline.com/wst/article-pdf/72/6/837/466151/wst072060837.pdf)
Choice of the non-ionic surfactant and its effects on the reaction

The negative charge of CMC and the positive charge of cationic quaternary ammonium neutralized when the ion-association complex formed. Meanwhile, CMC was covered by a hydrophobic aryl group, which gave the ion-association complex high hydrophobicity. This could gradually precipitate out without the non-ionic surfactant and would lead to the decrease of the sensitivity and stability of the UV spectrophotometry. However, the ion-association complex could remain stable in the solution with addition of the non-ionic surfactant. Therefore, the effects of the non-ionic surfactant (including Triton-X100, Tween-20 and OP emulsifier) with different concentration on the reaction were investigated. CTAB system was taken as an example in the experiment. The absorbance of CTAB system with Triton-X100 increased significantly from 0.96 to 1.39. The absorbance of the system with Tween-20 increased from 0.96 to 1.09, and the effect was not significant. A small amount of OP emulsifier made the absorbance greatly reduce, resulting in the absorption peak disappearing. Further study proved that the suitable amount of Triton-X100 was 1.0 mL with a concentration of 5.0 g/L.

Effect of time on the reaction

The association reaction is a continuous process. The absorbance is likely to change with the increase of time. In order to study the effect of stability on association reaction time, the effect of the reaction time (1–240 min) on the absorbance was investigated in the TTAB-CMC-Triton-X100 system and CTAB-CMC-Triton-X100 system, by measuring the absorbance and observing its change. The research showed that all of the absorbencies of both systems increased gradually up to 10 min, and the absorbance tended to be stable after 10 min. After 120 min, the absorbance of TTB-CMC-Triton-X100 system decreased gradually. After 180 min, the absorbance of CTAB-CMC-Triton-X100 system had a slight decrease. The research demonstrated that both of the systems had a quick and stable reaction. Therefore, in the experiment, the absorbance was determined after 20 min.

Effect of temperature on the reaction

The effect of the reaction temperature (15–60 °C) on the absorbance was investigated. The absorbance of TTAB-CMC-Triton-X100 system reached the maximum and tended to be stable at 15–40 °C. However, when the temperature was higher than 40 °C, the absorbance decreased significantly. The absorbance of CTAB-CMC-Triton-X100 system was stable and there was no change at 15–30 °C. When the temperature was higher than 30 °C, the absorbance significantly decreased. The research showed that the reaction speeded up with the increase of temperature, and the strength of UV spectrophotometry increased. Nevertheless, the stability decreased. Therefore, the suitable temperature ranges of the TTAB-CMC-Triton-X100 system and CTAB-CMC-Triton-X100 system were, respectively, 15–40 °C and 15–30 °C. Therefore, in the experiment, the absorbance was determined under normal conditions.

Standard curve

Under the optimal conditions, different concentrations of CMC reacted with LTAB, TTAB and CTAB, respectively. Triton-X100 was added into each system for solubilization. The absorbances were determined at maximum absorption wavelength, and calibration curves were drawn. Table 1 shows the linear range, correlation coefficient of calibration curve (γ), molar absorptivity (ε) and detection limit. The molar absorptivities were $1.10 \times 10^4$ L/(mol·cm) for LTAB system at 256 nm, $1.24 \times 10^6$ L/(mol·cm) for TTAB system at 244 nm and $1.78 \times 10^6$ L/(mol·cm) for CTAB system at 240 nm. The research results showed that CTAB system had a higher sensitivity; therefore, the paper took CTAB system as an example to study the selectivity of the method and analytical application of CMC.
Effect of coexisting substances on the reaction

The effect of coexisting substances on the absorbance for CTAB system was investigated. When the concentration of CMC was 50 mg/L and the relative error was ±5%, the following multiple coexistence substances did not interfere with the determination (numbers in brackets refer to the concentration multiplier, i.e. Na⁺ concentration was 1,500 greater than CMC concentration): K⁺, Na⁺ (1,500), NH₄⁺, Mg²⁺, H₂PO₄⁻ (150), Ca²⁺, Zn²⁺, Cu²⁺, Mn²⁺ (40), Fe³⁺ (25), NO₃⁻/C₀ (20), HCO₃⁻/C₀ (200), aminoacetic acid (180), sucrose, urea (80), 1,3-dimethylurea (24), glucose (20), dextrin (10), soluble starch (8) and humic acid (2). DL-Aspartic acid could interfere with the determination when it was 1.5 times the content of CMC. Consequently, the amino acids should be separated before the determination if the samples to be analyzed contain amino acids.

Sample analysis

Waste drilling mud was collected from three well sites (162#, 164# and 528#) as the test sample; the sites are in the mining area of northern Shaanxi Province in Changqing oilfield. A certain amount of drilling mud was centrifuged in a TGL20M desktop high-speed refrigerated centrifuge; the centrifugal time was 10 min and the speed was 6000 rev/min. The supernatant was carefully transferred to a 10.0 mL colorimetric tube to determine the content of CMC by means of the current determining method. The results are listed in Table 2. We found the recovery of the method was 91.0–103.0% and its relative standard deviation (RSD) was 2.1–3.2% from the analysis results of the sample in Table 2. The results show the method is reliable and applicable.

CONCLUSION

Some quaternary ammonium cations and CMC could form ion-association complexes by electrostatic and hydrophobic interactions in weak acid or weak basic medium, with Triton-X100 increasing the sensitivity of the system. Therefore, a method was established to determine CMC through quaternary ammonium salt and Triton-X100. The method is simple and fast, and shows very high sensitivities, good accuracy and reproducibility. It can be applied for the spectrophotometric determination of trace CMC in the supernatant of centrifuged drilling mud.

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REFERENCES


Table 1 | Related parameters for the calibration graphs and the sensitivities of the methods

<table>
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<tr>
<th>System</th>
<th>λ (nm)</th>
<th>Regression equation</th>
<th>Linear range (mg/L)</th>
<th>Correlation coefficient γ (n = 5)</th>
<th>Molar absorptivity ε (L/(mol·cm))</th>
<th>Detection limit (mg/L)</th>
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<td>LTAB</td>
<td>256</td>
<td>ΔA = 0.00001C + 0.057</td>
<td>50–150</td>
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<td>0.9883</td>
<td>1.24 × 10⁶</td>
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<tr>
<td>CTAB</td>
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<td>1.8–75</td>
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Table 2 | Determination results of CMC in the supernatant of the drilling mud

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<th>Sample</th>
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<th>Added CMC (mg/L)</th>
<th>Found CMC (mg/L)</th>
<th>Recovery (%)</th>
<th>RSD (%)</th>
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