

***In Situ* Determination of Calcium Carboxymethylcellulose on a Cellulose Film Via Ion Exchange**

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Synopsis

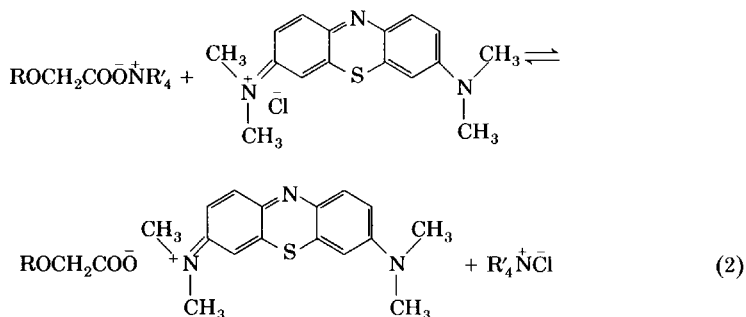
A simple and rapid ion exchange method is presented for the *in situ* determination of calcium carboxymethylcellulose (CaCMC) on a cellulose film. The method is based on the ion-exchange reaction between the calcium ion in CMC and a large quaternary ammonium ion, such as hexadecyltrimethylammonium ion, followed by a second ion exchange reaction in which the quaternary ammonium ion is displaced by 3,9-bisdimethylaminophenazothionium ion. The development of a blue color allows for the determination of the CaCMC distribution on the film by using a scanning densitometer. The reasons that CMC prefers a relatively large quaternary ammonium ion to the divalent calcium ion are suggested. This method is also applicable for the determination of sodium carboxymethylcellulose on a cellulose film where it is only necessary to carry out the second ion-exchange reaction. The minimum detection limit for a CaCMC (degree of substitution is 0.7) coating is at least $1 \mu\text{g}/\text{cm}^2$.

INTRODUCTION

Carboxymethylcellulose (CMC) is one of the few commercially available water-soluble polymers derived from cellulose. It has been widely used as an additive to change surface characteristics at various stages of paper and paperboard manufacture, such as increased oil resistance, decreased porosity, and improved ink printing characteristics. In the food package industry, it is mainly applied to the internal surface of cellulose casing to improve the release characteristics of cellulose film from frankfurters encased and processed. The sodium and calcium salts of carboxymethylcellulose are usually used for such commercial applications. The concentrations of sodium carboxymethylcellulose (NaCMC) may be quantitatively determined by numerous procedures such as an acid-base titrimetric method,¹ a 2,7-dihydroxynaphthalene method,² an anthrone colorimetric method,³ and the uranyl precipitation method.⁴ However, none of these techniques can be used for the *in situ* determination of NaCMC coating on a polymer film. These methods are slow and tedious and require the extraction of NaCMC from the film, thus giving an average value over a relatively large area. In this paper, a procedure is described for determining the location and distribution of a calcium carboxymethylcellulose (CaCMC) coating of a cellulose film by utilizing in the first stage ion-exchange reaction [eq. (1)] between the calcium ion in CMC and

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a large quaternary ammonium ion, followed by a second ion-exchange reaction [eq. (2)], in which the quaternary ammonium ion is displaced by 3,9-bisdimethylaminophenazothionium ion (methylene blue cation):



R, R' and X represent the cellulose structure, alkyl or aryl group, and a halogen atom, respectively. The development of a blue color allows for the *in situ* determination of CaCMC on the film.

EXPERIMENTAL

Materials

CaCMC was prepared by passing an aqueous solution of a Hercules' type 7L NaCMC (degree of substitution is 0.7) four times, through an ion-exchange column packed with Rohm and Haas Amberlite IR120 + calcium cation exchange resin followed by precipitation of the product with ethanol. The precipitate was collected by filtration and washed with 85% ethanol several times. The completion of the displacement of sodium ions in CMC by calcium ions was indicated by the evidence that the calcium content in the product was found to be stoichiometrically equivalent to the carboxymethyl group in the molecule.

A typical commercial cellulose casing is generally a 1–1.5 mil thick tubing made from regenerated cellulose. In order to adapt to rapid processing on automatic machinery, the tubing is usually shirred into an accordion-pleated form referred to as a "shirred strand." A sample of a commercial clear cellulose casing internally coated with CaCMC was used in the experiment.

Methylene blue, lithium chloride, sodium chloride, potassium chloride, ammonium chloride, tetramethylammonium chloride, tetraethylammonium chloride, tetrabutylammonium chloride, 1-hexadecylpyridinium chloride, and hexadecyltrimethylammonium chloride were purchased from Sargent-Welch Scientific Co. and used without further purification.

Method

A strand of shirred cellulose casing was deshirred by hand and cut into sections 20–50 cm in length. One end of the tubing was closed by tying a knot. The cellulose tubing was then filled with 0.5% 1-hexadecylpyridinium chloride

or hexadecyltrimethyl ammonium chloride in 50% methanol. After 2 min, the solution was replaced with a 0.5% methylene blue in 75% methanol. Five seconds later, the methylene blue solution was poured out, and the inside of the tubing was thoroughly washed with methanol to remove excess reagents. The tubing was cut open and allowed to air-dry. After undergoing two sequential ion exchanges, colorless CaCMC was converted into methylene blue CMC. The characteristic blue color developed has maximum absorbance at 668 nm. The CMC distribution of the film was visually examined and spectrophotometrically scanned at 600 nm using a Beckman Model R-112 scanning densitometer. A cellulose casing without CMC coating was subjected to the same ion-exchange reactions under the same conditions and used as a blank for the background correction.

In order to estimate the minimum detection limit, 10 μL of a standard solution (e.g., 0.01%) of the synthetic CaCMC in 50% methanol was evenly applied to a 1-cm² cellulose film by means of a 10 μL syringe. The sample was allowed to air-dry and then subjected to the ion-exchange reactions using the same solutions for the same periods of time at room temperature. The absorbance of the developed color was determined with a Beckman Acta MIV Spectrophotometer at 600 nm.

RESULTS AND DISCUSSION

Figure 1 shows a typical photograph of a commercial cellulose casing after undergoing two sequential ion exchanges. It reveals an uneven CaCMC distribution throughout the cellulose surface. An interesting feature of this photograph is that CaCMC is rich on the folded lines resulting from shirring. This suggests that a CMC solution was applied to the casing during shirring. The variation of the CaCMC coating parallel to the long axis of the casing can be clearly seen on the CaCMC distribution curves recorded with a Beckman Model R-112 scanning densitometer at 600 nm as shown in Figure 2. Since the densitometer was not calibrated to measure the absolute absorbance, the full scale of the absorbance on the curves could be anywhere below 1 absorbance unit.

Nevertheless, a quantitative analysis of the casing for the CMC distribution can be achieved by establishing the absorptivity of methylene blue-CMC (MB-CMC) in the solid state, determining the selectivity coefficients for ion exchange reactions, and using a scanning densitometer which is capable of measuring the absolute absorbance. A blank correction is needed for a quantitative analysis because of the presence of a small number of carboxyl groups in natural cellulose. The absorptivity of MB-CMC in the solid state can be obtained by the following steps: (1) Dissolve a known quantity of methylene blue in a solution of a polymer which is free of carboxyl groups and transparent in the visible range. Then a film is cast on a release paper with a doctors knife. (2) Measure the thickness of the dry film containing methylene blue with a microinterferometer and determine the density of the film. (3) Measure the absorbance of the film at a selected wavelength with a spectrophotometer. (4) Calculate the absorptivity of methylene blue in the solid state using the absorbance, density, and the thickness of the film, as well as the ratio of methylene blue/polymer. (5) Determine the degree of substitution of

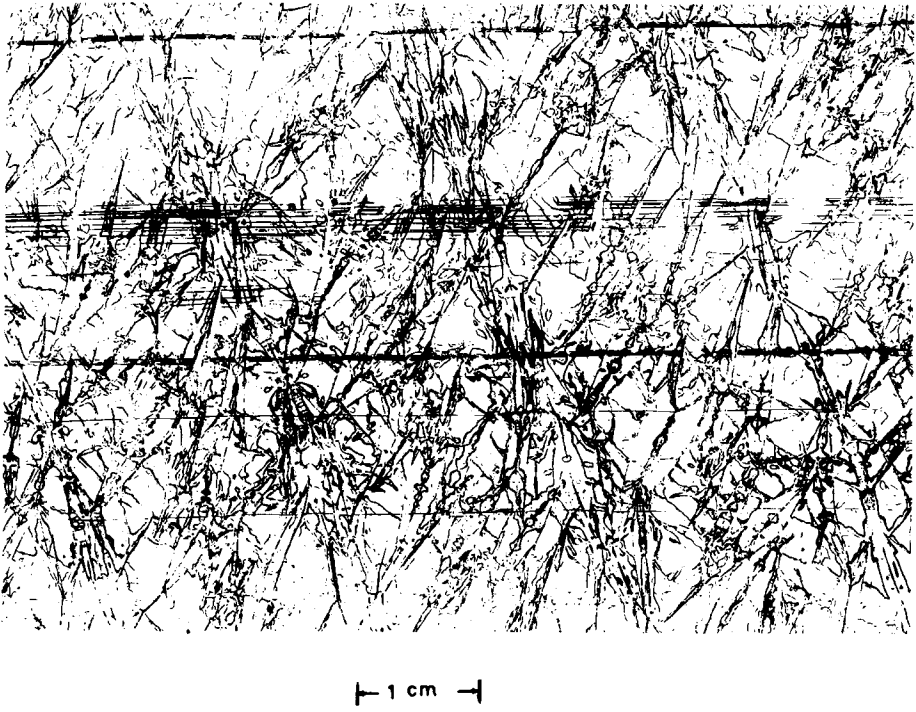


Fig. 1. Commercial cellulose casing coated with CaCMC after undergoing two sequential ion exchanges.

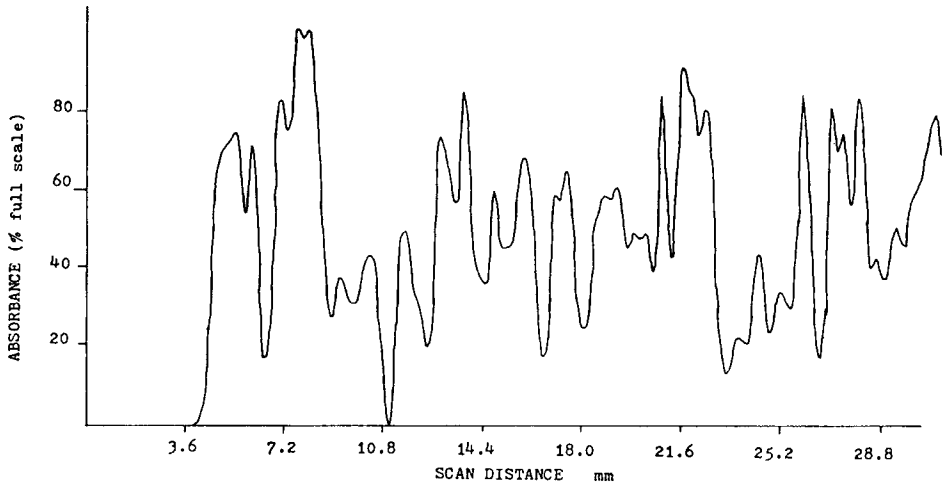


Fig. 2. CaCMC distribution curve for a commercial cellulose casing. The curve was obtained by scanning the casing along the long-axis at 600 nm with a Beckman Model R-112 scanning densitometer.

the CMC being analyzed and calculate the absorptivity of MB-CMC assuming that the molar absorptivity of methylene blue is independent of the type of counter ion.

In the absence of interferences, the estimated minimum detection limit for CaCMC (degree of substitution is 0.7) coating on a cellulose film by this method was at least $1 \mu\text{g}/\text{cm}^2$.

Three alkali and six quaternary ammonium ions were evaluated for the ion-exchange reaction on CaCMC cation exchanger [eq. (1)], under the conditions described in the experimental section, and the results are presented in Table I. As expected, the CMC prefers the divalent calcium ion over the monovalent alkali ions. This is consistent with one of the general selectivity rules that "the ion exchange prefers the counter ion of higher valence."⁵ This may be partly due to the relatively low solubility of calcium carboxylate. The former phenomenon may be explained using the Donnan potential and electrostatic effect, while the latter may be rationalized using the Le Chatelier principle.

Table I also shows that only the quaternary ammonium ions larger than 1-hexadecylpyridinium ion undergo an ion exchange reaction with CaCMC. From the C—C, C—N, and C—H bond lengths, the calculated ionic size of 1-hexadecylpyridinium ion is approximately 19.5 Å. The fact that CMC prefers a large quaternary ammonium ion to the calcium ion may be attributed to the Van der Waal interaction between the organic counterion and the ion exchanger. It follows one of the selectivity rules that the ion exchanger prefers counterions with organic groups that are similar in structure to the components of the matrix of the ion exchanger. Generally, the strength of the Van der Waal forces increase as the size of the organic counterion increases while the rates of exchange decrease with increasing ionic size. This may explain why smaller quaternary ammonium ions fail to displace the calcium ion on CMC because of the selectivity factor rather than a slow exchange rate. It may be that Coulombic forces play a more important role than Van der Waal forces in determining the affinity of the cation to CMC when

TABLE I
Results of the Exchange of Quaternary Ammonium Ions
and Alkali Ions for Calcium Ion on CMC

Counterion	Approximate ionic size (Å)	Result
Lithium	3.4 ^a	Negative
Sodium	2.76 ^a	Negative
Potassium	2.32 ^a	Negative
Ammonium	2.4 ^{a, b}	Negative
Tetramethylammonium	4.6 ^b	Negative
Tetraethylammonium	7.2 ^b	Negative
Tetrabutylammonium	10.5	Negative
1-Hexadecylpyridinium	19.5	Positive
Hexadecyltrimethylammonium	> 20	Positive

^a Hydrated radii.

^b From Kressman and Kitchener.⁶

the ion is small. The role is reversed when the ion is large. This behavior is consistent with the finding of Kressman and Kitchener⁶ for a cation exchange system involving a synthetic phenolsulfonate resin.

With regard to the exchange reaction between the quaternary ammonium CMC and methylene blue cation [eq. (2)], the predominant force is probably the electrostatic attraction since the electrostatic force is proportional to the ionic charge and inversely proportional to the square of the distance between the charges. CMC prefers the smaller methylene blue cation to the larger quaternary ammonium ion. The full development of a blue color after this reaction is completed within a few seconds, indicating that the exchange is rapid.

It is interesting to note that the methylene blue cation will displace a monovalent sodium ion directly on NaCMC cation exchanger. This is not the case for the CaCMC. This may be the result of electrostatic effect and solubility characteristics. It has been mentioned earlier that the ion exchanger tends to prefer the counterions of higher valence and the ion which forms stronger bonds with the fixed ionic groups of the ion exchanger. It is thought that the ion exchange between CaCMC and methylene blue is dictated by Coulombic forces and the solubility factor, whereas the reaction between NaCMC and methylene blue is controlled by the Van der Waals forces. Hence, the determination of the CaCMC distribution needs a two-stage ion exchange procedure, while the evaluation of NaCMC distribution requires only a one-step ion exchange.

In summary, an ion exchange method has been described for the *in situ* determination of CaCMC distribution on a cellulose film. It can be performed on a sample as small as 0.5×1 cm and may be used as a rapid analytical method to maintain the product quality as well as to evaluate the efficiency of various coating techniques.

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