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Ion Pair [NaCMC-CAPB] Complex Formed *via* Interaction of Carboxymethylcellulose Sodium Salt (NaCMC) with Cocamidopropyl Betaine (CAPB)

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Polyelectrolyte complexes (PECs) based on oppositely charged polyelectrolytes-surfactants have gained great attention for their various potential applications such as membranes for filtration or in fuel cells, and flocculants for water purification. In this manuscript, a complex formed by carboxymethylcellulose sodium salt polyelectrolyte and cocamidopropyl betaine surfactant was studied. Conductimetry, potentiometry, viscometry and FTIR methods were used to study the structure and properties of this complex. The results showed that the complex was formed by ionic binding and hydrophobic aggregates. The measurements confirmed the interactions between the different functional groups in both components. Also, the characteristic concentrations of the NaCMC-CAPB complex such as critical aggregation concentration (CAC) and saturation concentration (X_2) were calculated using the conductivity plots. The presence of charges on the complex indicated water solubility in a wide concentration range of polyelectrolyte and surfactant. In addition, the effect of surfactant on reduced viscosity of polyelectrolyte solutions was discussed.

Keywords: Carboxymethylcellulose sodium salt, Cocamidopropyl betaine, Interaction, Complex, Characteristic concentrations

INTRODUCTION

Polymer-surfactant mixtures are extensively used in a wide range of domestic, industrial, and technological applications, which include food staffs, paints, drug delivery systems, coating fluids, laundry products, and cosmetics [1]. In such applications, polymers in aqueous solution are used as viscosity modifiers, stabilizers, and deposition aids [1].

Interactions between polymers and surfactants in aqueous solutions have been an attractive topic in colloid and polymer science [2-6]. The desired properties of polymer solutions can be obtained by adding suitable types and amounts of surfactant [7,8].

When surfactant concentration exceeds its critical aggregation concentration (CAC), the surfactants and oppositely charged polyelectrolyte mixtures start forming aggregates [9-12]; this aggregation depends on the properties of the surfactant and polyelectrolyte [9-12]. Formation of polyelectrolyte-surfactant complex originates from electrostatic bonding [13], and is further stabilized by the hydrophobic interactions of surfactant tails [13]. The properties of polyelectrolyte-surfactant complex are highly related to the charge density and backbone rigidity of the polymer, the chain length and concentration of surfactant, and the ionic strength and pH of the solutions. These solutions present also interesting surface properties since polyelectrolyte-surfactant of opposite charge complexes make thick surface layers, which provide great practical applications in colloidal stabilization, strengthening of foam, and emulsions surfaces [14]. Surfactant is amphiphilic molecule contains hydrophilic groups or "tails" and hydrophobic groups or "heads [15-19]. Due to their

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properties, surfactants have been extensively investigated [15-19] for their use in wide applications.

Zwitterionic surfactants are good wetting agents and can be classified to high, moderate or low foaming surfactants [20]. Probably the most important class of amphoteric surfactants is amidopropyl betaines, in particular cocamidopropyl betaine (CAPB) [20,21].

CAPB is synthesized from the reaction between coconut oil (coconut fatty acid obtained from hydrolyzing of coconut oil) and 3,3-dimethylamine propylamine (DMAPA) in an aqueous solution [22,23]. In this process, the cocamidopropyl dimethylamine is formed as an intermediate product [22,23]. Cocamidopropyl betaine is mostly used as a cosmetic ingredient or a detergent [20,23]. It is used in cosmetics and personal hygiene products, mainly in rinse-off products such as shampoos. It is also used in roll-on deodorants, in the preparations for the treatment of acne, in conditioners, in eye make-up products, and germ-killing drugs [23-26]. The state of ionization of CAPB changes with pH [27,28]. In an acidic medium (pH less than 3.4), the nitrogen atom is protonated and the molecule behaves like a cationic surfactant, and carboxylic acid is not ionized. At medium and high pH, the strength of both positive and negative charges get equal; this indicates that the CAPB is present in the zwitterionic form [27-29]. Betaines are often favored over other surfactants due to its low irritative effect on the skin and mucous membranes; this makes it especially beneficial for the use in personal care products [28].

Carboxymethylcellulose is an anionic, water-soluble cellulose derivative [30]. It is used in many different applications, such as drilling fluid industry, paper industry, food products, pharmaceuticals, wastewater treatment, and storage energy production [31]. NaCMC is a highly charged anionic polyelectrolyte with carboxylic acid groups. It is the product of reaction between cellulose with sodium hydroxide and chloroacetic acid [32].

The polymer chain of NaCMC in solution is partly in a helical conformation; this considerably influences the rheological behavior of NaCMC in aqueous solution. Although NaCMC is used extensively in the formulation of drilling fluids, there are few reports on their rheological or adsorption properties [33]. NaCMC contains -OH and -COOH groups in its chemical structure, fulfilling an important criterion to work as a corrosion inhibitor [34]. The use of NaCMC as an inhibitor is particularly important because of its low cost, water solubility, non-toxicity, and environmentally friendly properties [34].

In recent years, hydrophobic ion pairing has been the most useful strategy for transforming charged hydrophilic molecules into hydrophobic complexes [35]; it is also the process of formation of ionic interactions between a charged hydrophilic molecule and an opposite counterion [36,37]. The ion pair can be formed by electrostatic, hydrophobic or charge transfer interactions [38]; it is formed by the temporary electrostatic attraction force between a positive ion and a negative [38]. In this study, the interactions between NaCMC polyelectrolyte and CAPB surfactant in aqueous solutions are studied using conductivity, potentiometry and viscometry techniques.

EXPERIMENTAL

Products

Carboxymethylcellulose sodium salt (NaCMC) (from PROLABO) was designated by the degree of carboxymethylation (DS) values included between (0.82-0.95) given by PROLABO. Its average macromolecular weight is estimated at 316405 g mol^{-1} using viscometry technique.

The cocamidopropyl betaine is a fatty acid amidoalkyl betaine. It is a light yellowish liquid, amphoteric (Active ingredient: 30%, Water content: 65%, Sodium chloride: 5%, pH value (original product): 5, Density (20 °C): 1.05 g cm^{-3}).

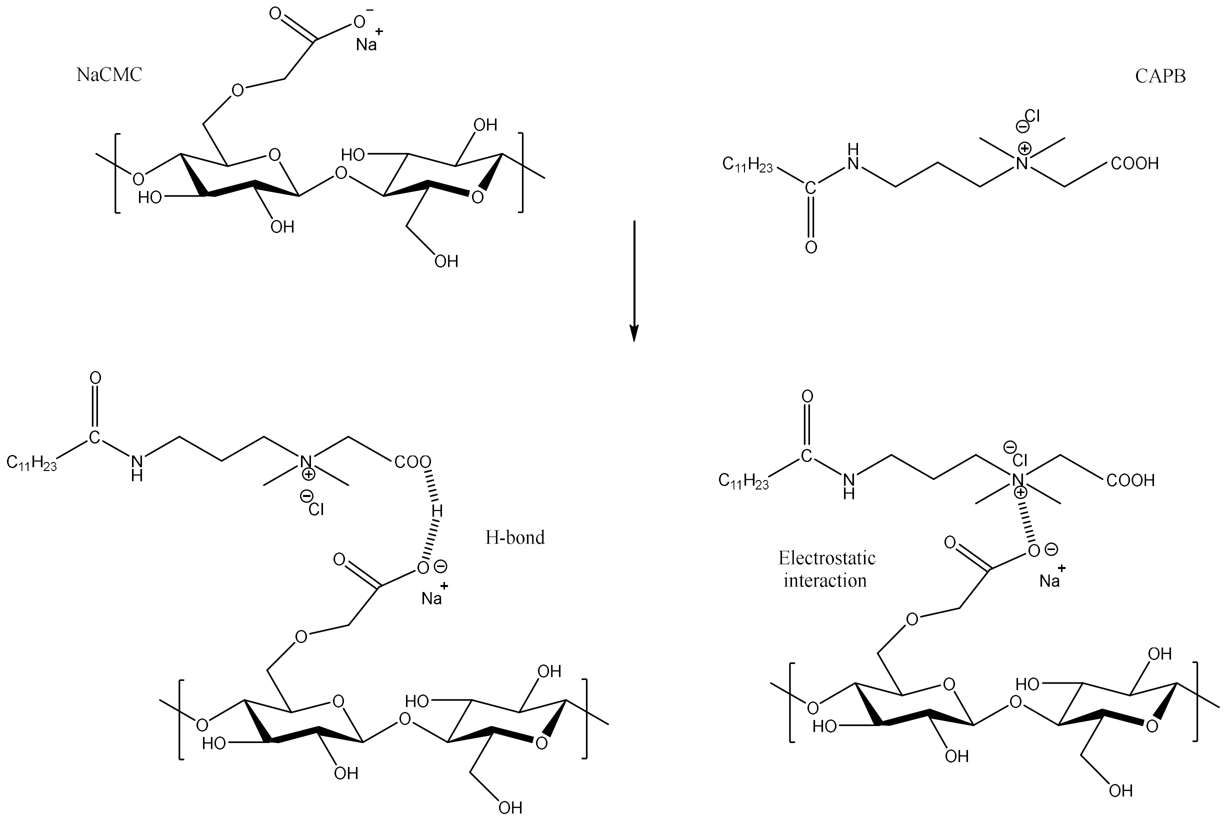
Apparatus

Conductivity was measured using a CDM 210 conductimeter (Radiometer, Meter Lab). Potentiometric measurements were carried out using an OHAUS type pH meter at a temperature of 25 °C. Viscosity was measured with a capillary standard Ubbelohde viscometer at 25.0 ± 0.1°C.

Reagents

Preparation of carboxymethylcellulose sodium salt solutions. To obtain a concentration of 10^{-3} g ml^{-1}, 1 g of NaCMC was dissolved in 1 l of distilled water with stirring for 72 h to ensure the total solubility of the polymer.

Preparation of cocamidopropyl betaine solutions. Cocamidopropyl betaine is available as a viscous pale yellow



Scheme 1. Preparation of NaCMC-CAPB complex

solution; its molar mass is 342.524 g mol^{-1}. Cocamidopropyl betaine and distilled water were used to prepare solutions of different concentrations.

Preparation of mixed NaCMC-CAPB solutions. For FTIR, viscosity and conductivity measurements, in a water bath thermostatically controlled at 25 ± 0.1 °C, with stirring, the reaction of mixture was prepared by addition of surfactant solution (pH = 4,86) per ml to 50 ml of NaCMC solution (pH = 6,75) placed in a beaker.

To understand the behavior of mixture solutions during complexation, we considered two possibilities of functions interaction between NaCMC and CAPB, as shown in Scheme 1. The NaCMC-CAPB complex is formed by electrostatic interaction and hydrogen bonding.

RESULTS AND DISCUSSION

Conductivity Study of Cocamidopropyl Betaine Surfactant in Water

Zwitterionic surfactants are surface active molecules that contain positive and negative charges in the head group. The critical micelle concentration of pure surfactant CAPB was obtained by conductometric measurements [20], and it was in good agreement with the literature values [39,40]. It should be noted that the cmc of CAPB has been determined by other researchers with different values [23,25,41,42].

Figure 1 shows the conductivity variation of CAPB surfactant versus its concentration in aqueous solution at 25 °C. The linear increase in conductivity with two different slopes is the reason for the increase in surfactant concentration. The intersection between two slopes of the curve represents the critical micelle concentration value, thus it's equal to (0.99 × 10^{-3} g ml^{-1}). The first slope was higher than the second slope; the concentrations lower than the value of cmc corresponds to the formation of the free micelles of CAPB. This micellization process was rapid. The conductivity increased linearly again beyond the cmc, but this increase was slight compared to the first regime, which is due to the decrease in the number of charge carriers. This can be explained by the fact that after the value of cmc, condensation counterions are formed on the micelles.

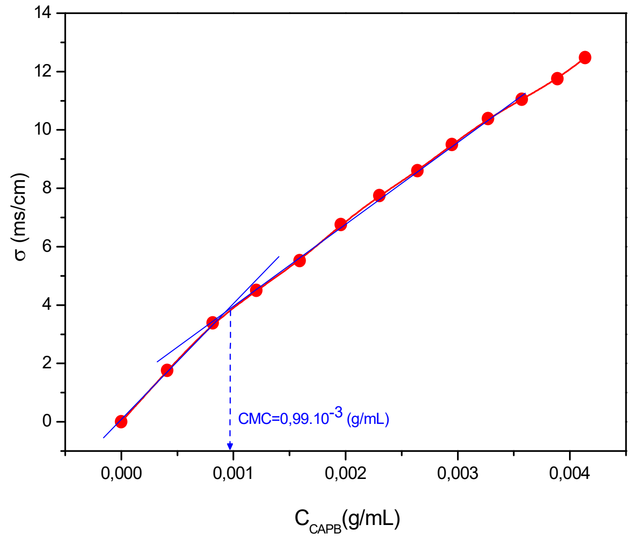


Fig. 1. Conductivity variation of the CAPB as a function of its concentration at 25 °C.

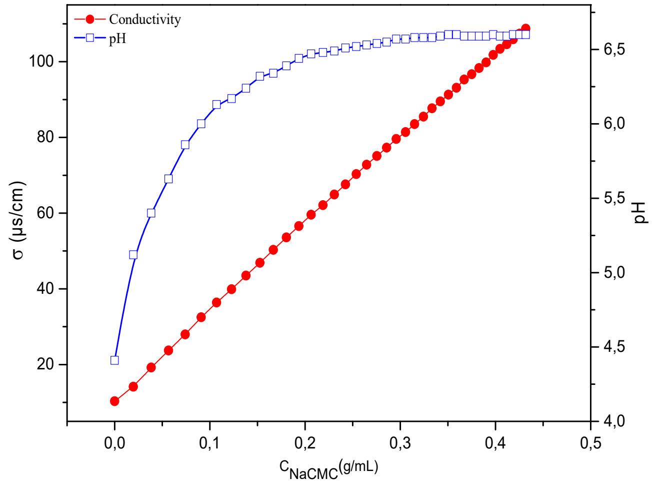


Fig. 2. Conductivity and pH variations of polymer NaCMC as a function of its concentration at 25 °C.

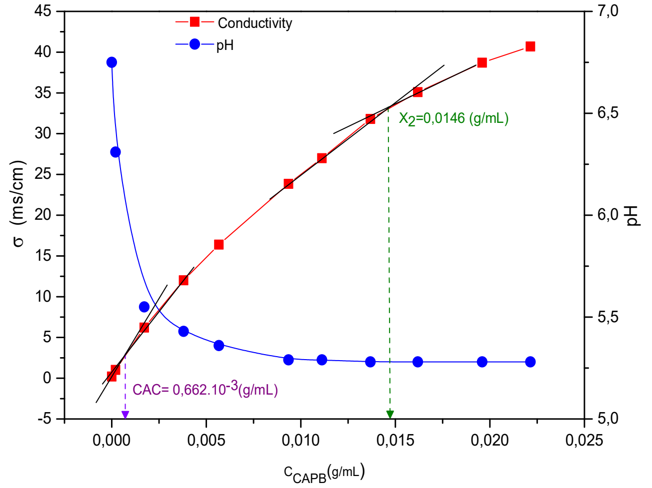


Fig. 3. Conductivity and pH variations of the NaCMC-CAPB mixture according to CAPB concentration at 25 °C and NaCMC 10^{-3} g ml^{-1}.

Conductivity and Potentiometric Study of NaCMC in Water

Figure 2 shows the potentiometry and conductivity variations of the NaCMC polymer versus its concentrations at 25 °C. The conductivity varied linearly with the concentration of NaCMC. It can be explained by the increase in $-COO^-$ charge during the addition of NaCMC.

For potentiometry curve, we obtained a considerable increase in the pH values with an increase in the NaCMC concentration. After reaching pH = 6.5, the pH values became stable, which can be explained by the saturation in $-COO^-$ anions.

Conductometric and Potentiometric Study of the NaCMC-CAPB Mixture

Figure 3 represents the conductivity and pH variations of the NaCMC-CAPB mixture versus CAPB's concentration considering a fixed NaCMC concentration equal to 10^{-3} g ml^{-1} at 25 °C. The conductivity curve contains two breaks, in which the first represents the critical aggregation concentration (CAC = $0{,}662 \times 10^{-3}$ g ml^{-1}), or formation of the aggregates between the surfactant CAPB and the NaCMC polymer. The second break corresponds to the saturation of the polymer by the surfactant, it is known as (X_2 = 0, 0146 g ml^{-1}). Consequently, the interaction of NaCMC with CAPB differs at lower and higher concentrations of the cmc [19].

The increase in conductivity of the mixture can be explained in terms of higher mobility of the CAPB bound to the polymer. The carboxylate groups ($-COO^-$) of NaCMC formed complex with cationic sites ($-N^+$) of CAPB (electrostatic interaction). After reaching the CAC, there was an obvious decrease in the slope caused by the reduction of the mobility of the free ions of surfactant in solution, which were hampered before the formation of aggregates bound to the polymer.

In aqueous solutions, the carboxylic functionals containing in the polymer and the surfactant may be considered as weak acid, so its dissociation is no longer total. It means that in the solution, there are carboxylic groups (-COOH) and carboxylate groups ($-COO^-$); this gives the possibility of hydrogen bond formation.

On the other hand, for low concentration of surfactant, the pH decreased rapidly with an increase in surfactant concentrations caused by the increase of H proton in the solution; this can be explained by deprotonation of the carboxylic groups in the polymer and surfactant. However, some of the carboxylates groups of polymer and surfactant were protonated in the presence of H protons, due to their weak basic character. During complexation, the acid-base reaction caused the transfer of hydrogen between the functional groups of the polyelectrolyte and the surfactant, which can explain the pH stability. The H-bond was formed between the hydrogen donor (-COOH) of polymer and the hydrogen acceptor ($-COO^-$) of surfactant. The H-bond was also formed between the hydrogen donor of surfactant and the hydrogen acceptor of polymer, as shown in Scheme 2.

Viscosimetric Study of CAPB

Figure 4 represents the reduced viscosity change of CAPB as a function of its concentrations. A break with a slope of (0.98×10^{-3} g ml^{-1}) was observed; this break represents the critical micelle concentration, which confirms the conductivity results. Before reaching this concentration, the viscosity decreased with the concentration of CAPB. After cmc value, its reduced viscosity increased with an increase in concentration. Indeed, for concentration values greater than (0.0024 g ml^{-1}), the increase in viscosity is very important. This can be explained by electrostatic effects, leading to modification of the form of micelles at these concentrations.

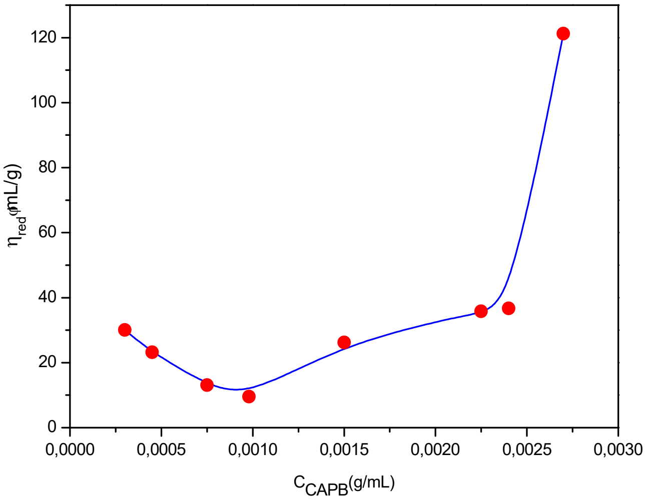
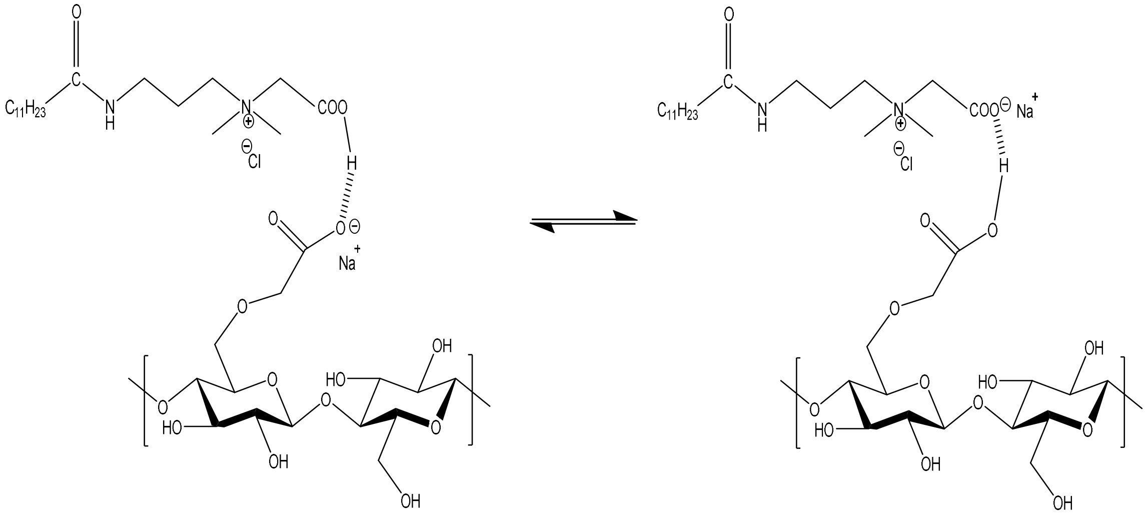


Fig. 4. Reduced viscosity variation of the CAPB as a function of its concentrations at 25 °C.



Scheme 2. H bond interactions in NaCMC-CAPB complex

Viscosimetric Study of NaCMC

Figure 5 shows the reduced viscosity variation of NaCMC solutions as a function of its concentrations at 25 °C in absence of salt. The reduced viscosity of NaCMC increased with a decrease in the polymer concentrations. Because of the electrostatic repulsion that makes the polymer chains very extensive, the reduced viscosity decreased with an increase in polymer concentration. NaCMC polymer represents a typical polyelectrolyte behavior. On the other hand, in presence of NaCl, the reduced viscosity of NaCMC increased lineally with its concentrations. Indeed, the presence of salt reduces the viscosity of polyelectrolyte. The intrinsic viscosity of the NaCMC polymer was determined by extrapolation to zero polymer concentration; a value of 561.65 ml g^{-1} was obtained. The value of the intrinsic viscosity thus determined, making it possible to reach the viscometric average macromolecular mass of the NaCMC polyelectrolyte from the Mark-Houwink equation.

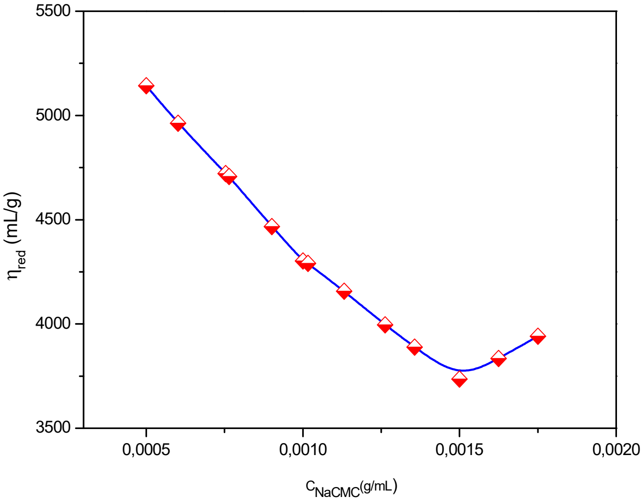


Fig. 5. Reduced viscosity variation of NaCMC solutions as a function of its concentration at 25 °C in absence of NaCl.

Viscosimetric Study of NaCMC-CAPB Mixture at 25 °C

Figure 6 shows the reduced viscosity variation of NaCMC-CAPB mixture versus the CAPB concentration. For low concentrations of CAPB, the reduced viscosity rapidly decreases with an increase in the surfactant concentration. This can be explained by the strong interactions between the anionic sites of polymer and the cationic sites of surfactant caused by electrostatic interactions. A slight increase of reduced viscosity was observed at high surfactant concentrations. It is explained by the repulsion of negative charges of zwiterionic surfactant.

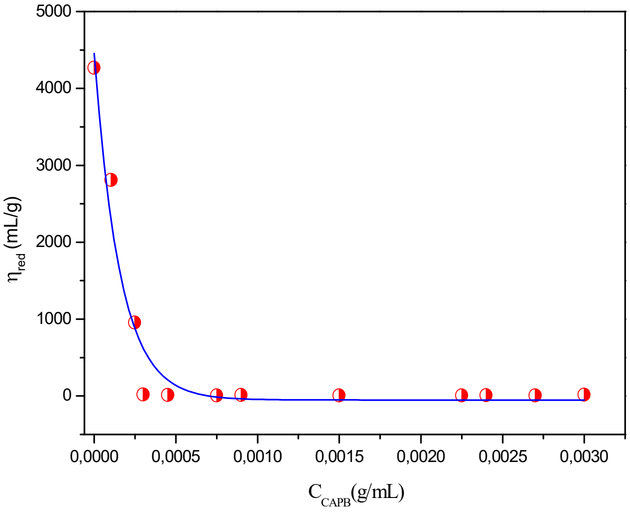


Fig. 6. Reduced viscosity variation of the NaCMC- CAPB mixture according to CAPB concentrations at 25 °C and NaCMC 10^{-3} g ml^{-1}.

FTIR Spectra of NaCMC, CAPB and NaCMC-CAPB

The infrared spectrum in the range of 4500-400 cm^{-1} was used to confirm the ion association properties of the interaction between carboxymethylcellulose and cocamidopropyl betaine, and to identify the resulting ion association. The FTIR spectra of NaCMC, CAPB and the complex (NaCMC-CAPB) are shown in Figs. 7 (a, b and c), respectively; they are in accordance with the literature [33].

The Table 1 gathers the assignment of the absorption bands in the FTIR spectra. The FTIR spectrum of the cocamidopropyl betaine molecule (Fig. 7b) was characterized by the following bonds: Absorption bonds at 2929 and 2854 cm^{-1} corresponds to valent and deformed vibrations of the CH methyl groups. Peaks at around 1000-1350 cm^{-1} are due to valent bonds of C-N groups. Fluctuation bonds at 3040-3700 cm^{-1} are related to N-H groups. The absorption band of the C=O group was obtained at a

Table 1. Assignment of Absorption Bands in the FTIR Spectra

Wave number ν (cm^{-1})			Attribution	Nature
NaCMC	CAPB	NaCMC-CAPB		
3430	3435	3436	O-H (NaCMC)	Elongation (Stretching)
			N-H (CAPB)	
2923	2929	2924	C-H	Elongation
	2854	2854	C-H	Elongation
	2099	2096		
1629	1633	1633	C=O (NaCMC)	Elongation
			C=O (CAPB)	
1384	1399	1384	CH_2 (CAPB)	
			C-O (NaCMC)	Elongation

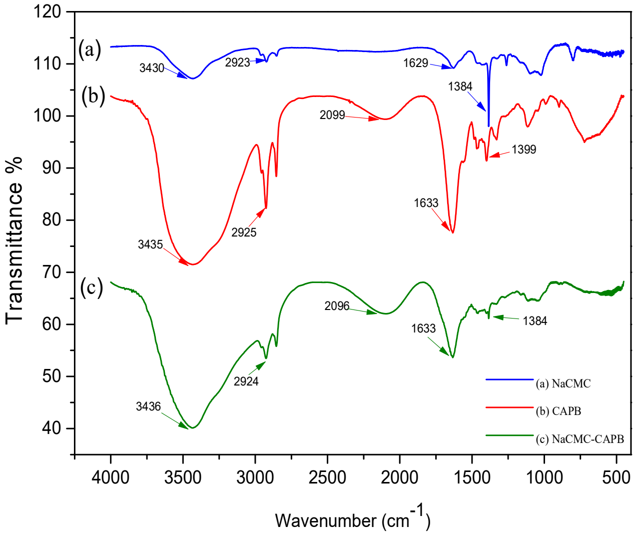


Fig. 7. FTIR spectra of NaCMC, CAPB and NaCMC-CAPB.

frequency of 1625 cm^{-1}. The peak at 1399 cm^{-1} was assigned to valent and deformed vibrations of methylene groups.

For FTIR spectrum of carboxymethylcellulose (Fig. 7a), the characteristic peaks related to the $-COO^-$ group were observed at 1629 cm^{-1}. A bond appeared at 3430 cm^{-1} correspons to the variations in the valence of OH. A strong peak at 1384 cm^{-1} is attributed to the C-O bonds. The peak at 2923 cm^{-1} may be related to the CH methyl groups.

The infrared spectrum of the NaCMC-CAPB complex (Fig. 7c) showed the characteristic bands of NaCMC and CAPB. For NaCMC, the characteristic peak of OH was at 3436 cm^{-1}, and that of CH methyl groups were at 2854 and 2923 cm^{-1}. There were also the absorption bonds of cocamidopropyl betaine. These are the absorption bands according to the spectrum: NH group in the range of 3040-3700 cm^{-1}, C=O in the range of 1500-1700 cm^{-1}, the amide bonds in the range of 1040-1180 cm^{-1}, the latter group can react with the carboxyl group of NaCMC, which can be confirmed by the reduction intensity of its peak. The presence of the characteristic bands of NaCMC and CAPB in the FTIR spectrum of the complex confirms the associative nature of the interaction between carboxymethyl cellulose and cocamidopropyl betaine.

CONCLUSIONS

The complex based on NaCMC polymer and CAPB surfactant was studied by conductimetry, potentiometry and FTIR methods. The presence of charges in the NaCMC/CAPB complex explains water solubility in a wide concentration range of polyelectrolyte and surfactant.

The analysis of CAC and cmc of surfactant indicated the existence of strong electrostatic and hydrophobic interactions between CAPB surfactant and oppositely charged NaCMC. The results showed that for low concentrations of CAPB, the reduced viscosity rapidly decreased with an increase in the surfactant concentration. This can be explained by the strong interactions between the anionic sites of polymer and the cationic sites of surfactant caused by electrostatic interactions. For high surfactant concentrations, a slight increase in reduced viscosity was observed, caused by the repulsion of surfactant charges. Consequently, the interaction is different for $C_{CAPB} <$ cmc and $C_{CAPB} >$ cmc.

The presence of the characteristic bands of NaCMC and CAPB in the FTIR spectrum of the complex confirmed the associative nature of the interaction between carboxymethyl cellulose and cocamidopropyl betaine.

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