

# Solubilization of octane in cationic surfactant–anionic polymer complexes: Effect of ionic strength



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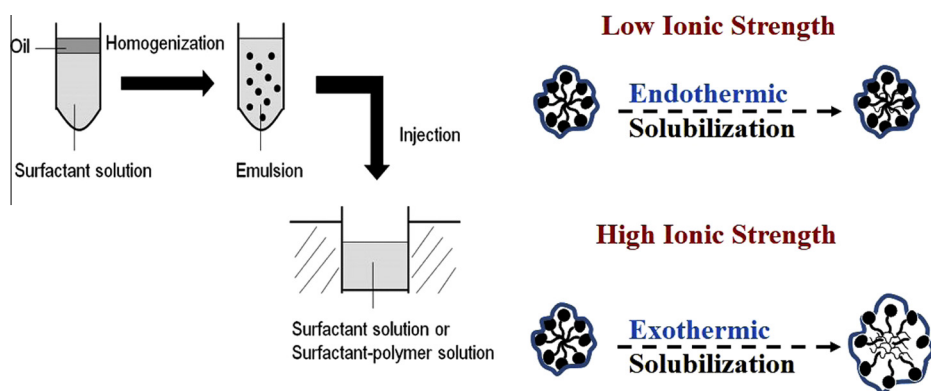
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## GRAPHICAL ABSTRACT



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## ABSTRACT

Polymers may alter the ability of oppositely charged surfactant micelles to solubilize hydrophobic molecules depending on surfactant–polymer interactions. This study was conducted to investigate the effect of ionic strength on the solubilization thermodynamics of an octane oil-in-water emulsion in mixtures of an anionic polymer (carboxymethyl cellulose) and cationic cetyltrimethylammonium bromide (CTAB) surfactant micelles using isothermal titration calorimetry (ITC). Results indicated that the CTAB binding capacity of carboxymethyl cellulose increased with increasing NaCl concentrations up to 100 mM, and the thermodynamic behavior of octane solubilization in CTAB micelles, either in the absence or presence of polymer, was found to have a strong dependence on ionic strength. The increasing ionic strength caused the solubilization in CTAB micelles to be less endothermic or even exothermic, but increased the solubilization capacity. Based on the phase separation model, the solubilization was suggested to be driven by enthalpy. It is indicated that increasing ionic strength gave rise to a larger Gibbs energy decrease but a smaller unfavorable entropy increase for octane solubilization in cationic surfactant micelles.

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## 1. Introduction

Surfactant–polymer interactions have been of a great interest to a large number of researches [1]. In particular, the interactions between polymers and surfactants having opposite charges have been studied, since they have shown to be of importance in forming microcapsules to be used in a wide range of industrial applications [2]. Often, addition of polymers to oppositely charged surfactant micelles may lead to the formation of surfactant–polymer complexes with improved functionalities [3,4]. For example, electrostatic complexes formed by cationic–nonionic mixed surfactant micelles (lauric arginate/Tween 20) and an anionic biopolymer (pectin) have been shown to be able to resist freeze–thaw and cooling–heating cycles, as well as changes in pH and/or ionic strength [4].

When surfactant molecules are mixed with a solution of oppositely charged polymer molecules, a number of different structures may be formed depending on the nature of the surfactant–polymer interactions [1]. These interactions may favor or oppose binding of the polymer depending on the type of interactions, e.g. electrostatic, van der Waals interactions, or hydrogen bonding, as well as various entropic effects [5]. The change in micellar structure may in turn alter the ability of micelles to solubilize hydrophobic compounds.

To date, little research has been carried out to investigate the effect of polymers on the solubilization of hydrocarbons in micelles. It was reported [6,7] that the aggregation number of anionic micelles interacted with a cationic polymer was lower than that of micelles, and the binding results gave rise to a larger Gibbs energy decrease for oil solubilization than that for micelles of single-surfactant systems. It was then found [8,9] that the larger energy decrease was ascribed to the higher hydrophobicity of the oppositely charged surfactant–polymer aggregates and a configurational reorganization of the polymer chains. Recently [10] we studied the solubilization of an octane oil-in-water emulsion mixed with carboxymethyl cellulose and anionic, nonionic and cationic surfactant micelles, and found that the addition of anionic carboxymethyl cellulose accelerated octane solubilization in cationic micelles, but did not affect the solubilization behavior of micelles that were nonionic and anionic. The thermodynamic behavior investigations [11] by isothermal titration calorimetry (ITC) showed that the solubilization capacity of cationic micelles or mixed cationic/nonionic micelles was enhanced while that of nonionic or anionic micelles was decreased. Further studies [12] suggested that with increasing concentrations of the anionic polymer and with increasing temperatures, the solubilization capacity of the cationic micelles increased.

The focus of this study was to evaluate the effect of ionic strength on the thermodynamic behaviors of octane solubilization in cationic surfactant–anionic polymer complexes. By using the ITC technique, we investigated both the nature of the surfactant–polymer interactions (Fig. 1a), and the solubilization of octane in micelles (Fig. 1b).

## 2. Materials and methods

### 2.1. Materials

Octane (anhydrous,  $\geq 99\%$ ), cetyltrimethylammonium bromide (CTAB) ( $\geq 99\%$ ) and sodium chloride (NaCl) ( $\geq 99\%$ ) were purchased from Sigma Aldrich (St. Louis, MO, USA). Carboxymethyl cellulose (GRINDSTED Cellulose gum BEV 010 NG, Material 623947, Batch L987) was provided by Danisco (Copenhagen, Denmark). All materials were used without further purifications. Double distilled water was used throughout the study.

### 2.2. Solution preparation

CTAB and carboxymethyl cellulose solutions were prepared by dispersing them in double distilled water, and 0.1 mM, 1 mM, 10 mM, and 100 mM NaCl solutions, respectively. The surfactant–polymer complex solutions were prepared by mixing equal volumes of CTAB solution with carboxymethyl cellulose solutions and stirred overnight at 37 °C prior to use. Concentrations of surfactant in solutions were chosen such that critical micelle concentrations (CMC) were always exceeded. The CMC for CTAB in water at 25 °C is 0.03 wt% [13].

### 2.3. Emulsion preparation

The emulsion preparation was conducted as previously reported [10]. Briefly, a coarse pre-emulsion was prepared by homogenizing 10 wt% octane and 90 wt% aqueous surfactant solution (0.2 wt% in water or NaCl solutions) at room temperature using a high shear blender (Standard Unit, IKA Werk GmbH, Berlin, Germany). The coarse emulsion was then homogenized for 3 min at 50% power using an ultrasonicator (UW 2200, Bandelin Sonoplus, Germany) to manufacture a finely dispersed emulsion for solubilization. Octane was chosen for its rapid solubilization kinetic [14]. The freshly prepared oil-in-water emulsion was used immediately after manufacture for the solubilization studies.

### 2.4. Isothermal titration calorimetry

An isothermal titration calorimeter (Nano ITC 2G, TA Instruments, MA, USA) was used to assess the thermodynamics of (i) the surfactant–polymer interactions (Fig. 1a), and (ii) the solubilization of an octane emulsion in surfactant and surfactant–polymer solutions (Fig. 1b) at 37 °C in various NaCl solutions, respectively.

For the surfactant–polymer interactions, fifty aliquots of 5  $\mu\text{L}$  of 0.3 wt% CTAB solution were injected sequentially into a 996  $\mu\text{L}$  titration cell initially containing either water or NaCl solutions, or respective 0.0025 wt% carboxymethyl cellulose solutions [15]. For the solubilization measurements, fifty aliquots of 5  $\mu\text{L}$  of the octane-in-water emulsion (10 wt% octane, 0.2 wt% surfactant in water or NaCl solutions) were injected sequentially into a 996  $\mu\text{L}$  titration cell initially containing either 0.2 wt% CTAB or 0.2 wt% CTAB–0.02 wt% carboxymethyl cellulose in water or NaCl solutions [11]. The initial baseline prior to the first injection and the final baseline after last injection were recorded for 1000 s. The time intervals between successive injections were 300 s. Solutions in the titration cell were stirred at a rate of 315 rpm during all experiments. All solutions were degassed for 30 min prior to all measurements. All samples were freshly prepared prior to ITC measurements. All measurements were done in duplicates.

For the surfactant–polymer interactions, the dependence of the enthalpy change ( $\Delta H$ ) per injection on the surfactant concentration (wt%) was calculated by integration of the heat flow versus time, and the difference in the enthalpy change ( $\Delta\Delta H$ ) versus surfactant concentration was calculated by subtracting enthalpy changes in the absence and presence of carboxymethyl cellulose to analyze the effect of carboxymethyl cellulose on the CMC of surfactant. For the solubilization measurements, the dependence of the enthalpy change ( $\Delta H$ ) per injection on the solubilization concentration (mg of octane/g surfactant) was calculated by integration of the heat flow versus time data. The heat ( $\Delta H_{\text{Total}}$ ) generated during the octane solubilization in either CTAB or CTAB–carboxymethyl cellulose solution was determined by calculating the area of exothermic and endothermic peaks per injection. The oil solubilization capacity (mg of octane/g surfactant) was calculated by plotting the enthalpy versus the oil concentration.

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