



# Interaction between cationic surfactant of 1-methyl-3-tetradecylimidazolium bromide and anionic polymer of sodium polystyrene sulfonate

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## ABSTRACT

The interaction between long-chain imidazolium ionic liquid ( $C_{14}mimBr$ ) and anionic polyelectrolyte of sodium polystyrene sulfonate (NaPSS) has been studied using surface tension, isothermal titration microcalorimetry (ITC), dynamic light scattering (DLS) and conductance methods. The result shows that the surface tension plots have a pronounced hump in the surface tension at surfactant concentrations below the critical micelle concentration (*cmc*) of the surfactant. The cooperative adsorption of surfactant and polymer on the surface ( $PS_s$ ) and the formation of polymer/surfactant aggregate in bulk solution ( $PS_M$ ) provide a rational explanation about it. The formation of surfactant/polymer complexes is affected by the concentration of the surfactant or NaPSS, which is also ascertained by ITC and DLS measurements. Further, the thermodynamic parameters are derived from calorimetric titration and conductance curves, and the effects of polymer concentration and temperature on the parameters are evaluated in detail.

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## 1. Introduction

The formation of polymer and surfactant complexes in aqueous solution and the manipulation of surfactant adsorption by polymers have been an active research area for a number of years, and a number of comprehensive reviews exist [1–3]. It remains an area of much current interest because of the widespread applications in this area, such as fabric conditioners, hair shampoos, detergents, foams, emulsions, and mineral recovery [4–6]. For the more weakly nonionic polymer–ionic surfactant systems the interacting mechanisms are relatively well understood [7,8]. Thus, much of the recent focus has been on the strongly interacting mixtures of polyelectrolytes and ionic surfactants of opposite charge due to their complexities and widespread applications [9–11].

For these strongly interacting systems, the primary nature of the interaction is electrostatic, but specific and hydrophobic interaction between the polymer backbones and the alkyl tail of the surfactants are also important. Both of the electrostatic and the hydrophobic interactions drive the self-assembly of surfactant

molecules to form ordered structures inside the polymer/surfactant complexes. Although many researches unravel the binding mechanisms on the basis of some specific systems, the binding behaviors have not been observed very clearly. For one polymer/surfactant system with a new polymer or surfactant, it is difficult to obtain a precise forecast of the binding behavior, especially the corresponding thermodynamic parameters. Therefore, in this paper the binding behavior of one cationic surfactant to an anionic polymer is studied over a large surfactant concentration range.

In our previous studies, the interactions between imidazolium surfactants and sodium carboxymethylcellulose (NaCMC) or copolymers were reported [12–14]. It was found that the binding behaviors of surfactant to NaCMC are affected greatly by the alkyl chain length of the surfactant, and the ITC titration curve of 1-methyl-3-tetradecylimidazolium bromide ( $C_{14}mimBr$ ) and NaCMC aqueous solution is very interesting and representative. Thus we choose the system of another anionic polyelectrolyte (NaPSS) and  $C_{14}mimBr$  to continue the research work in this field. The surfactant, one surface-active IL, has attracted more attention due to its extensively application in the colloid and interface field [15–18]. The polyelectrolyte was also extensively used because of its variety of applications, such as flocculation, personal care products, drug (kayexalate) and so on [19–26]. Hence the primary motivation

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of this study reported here is to investigate and understand the consequence of the relative strength of the interaction between NaPSS and C<sub>14</sub>mimBr. A variety of methods have been widely used, including surface tension, isothermal titration calorimetry, conductance and light scattering, to determine the effects of polymer concentration, surfactant concentration and temperature on NaPSS/C<sub>14</sub>mimBr interaction. In order to avoid the precipitate, the polymer concentration used is relatively small. It is believed that the elucidation of the binding behavior may facilitate better understanding of the mechanism of polymer/surfactant systems and will benefit future uses.

## 2. Experimental

### 2.1. Materials

1-Methyl-3-tetradecylimidazolium bromide (C<sub>14</sub>mimBr) was synthesized and purified in our laboratory according to previous report [27]. The purity of C<sub>14</sub>mimBr were checked by <sup>1</sup>HNMR spectroscopy in CDCl<sub>3</sub>. Sodium polystyrene sulfonate (NaPSS) was purchased from Alfa and used without further purification. The polymer was fully sulfonated (i.e. 100% of the segments were charged), and the average molecular weight (*M<sub>w</sub>*) of NaPSS was 3.0 × 10<sup>5</sup> g/mol. Triply distilled water was used for preparation of aqueous solutions.

### 2.2. Surface tension measurement

The surface tension measurements were made on a Model JYW-200B surface tensiometer (China, ±0.1 mN/m) using the du Noüy ring method. Temperature was controlled at 293.15, 298.15, 303.15, 308.15 and 313.15 K using a super constant temperature trough (China, ±0.1 K). The surface tension was determined using a single-measurement method. After each measurement, immerse the ring in sodium dodecyl sulfate cleaning solution and then rinse with distilled water. The solutions were kept in sample cells for 30 min until the surface tension did not change with time. The average values of equilibrium surface tension were measured at least twice until the values were reproducible.

### 2.3. Electric conductivity measurement

The conductivity measurements were carried out with a TOA conductivity meter Model using a DJS-1C Pt electrode (the electrode constant was 1.05 calibrated by 0.01 mol/L KCl aqueous solution). The temperature was controlled at 293.15, 298.15, 303.15, 308.15 and 313.15 K using a thermostated water-circulating bath (China, ±0.1 K). The sample solution was stabilized for several days before the conductance of one solution was measured. When the conductance of the solution was measured, the electrode should be kept in the solution for a few minutes to ensure the values of conductance unchangeable. The solution was unstirred in the process of measurement. The conductivity curves were corrected by subtracting the conductivity of the water solution, and the conductivities of the distilled water are 2.00, 2.12, 2.35, 2.59 and 2.73 μs cm<sup>-1</sup> at the temperatures of 293.15, 298.15, 303.15, 308.15 and 313.15 K separately in one group of measurements. The uncertainty of the measurements was within ±2%.

### 2.4. Dynamic light scattering (DLS)

Measurements were carried out at 298.15 ± 0.1 K with an LLS spectrometer (Zetasizer Nano ZS, Malvern Instruments, UK), which employs a multi-τ digital time correlator (ALV-5000). Light of λ = 632.8 nm from a solid-state He-Ne laser (22 mW) was used as the incident beam. The measurement was conducted at a

scattering angle of 90°. All solutions made freshly were filtered through a 0.45 μm membrane filter of hydrophilic PVDF before measurements. The correlation function of scattering data was analyzed via the CONTIN method to obtain the distribution of diffusion coefficients (*D*) of the solutes. The apparent hydrodynamic radius (*R<sub>h</sub>*) was deduced from *D* by the Stokes-Einstein equation  $R_h = kT/6\pi\eta D$ , where *k* is the Boltzmann constant, *T* is the absolute temperature, and *η* is the solvent viscosity, respectively.

### 2.5. Isothermal titration microcalorimetry (ITC)

Microcalorimetry was performed on a nano-watt isothermal titration microcalorimeter (Thermometric 2277, Sweden), controlled by Digitam 4.1 software. Experiments were performed in a 1 mL stainless steel sample cell controlled at a temperature of 298.15 ± 0.01 K. The cell was initially loaded with 0.5 mL water or NaPSS solution. Concentrated C<sub>14</sub>mimBr and NaPSS solution was injected into the cell consecutively using a 500 μL Hamilton syringe controlled by a Thermometric 612 Lund pump. The polymer concentration in the syringe maintained a constant with the cell. The interval between two injections was 45 min, which was sufficiently long for the signal to return to the baseline. The sample solution was stirred at 50 rpm with a gold propeller in the cell. All experiments were repeated twice to achieve the reproducibility within ±2%.

## 3. Results and discussion

### 3.1. Effect of NaPSS concentration on the C<sub>14</sub>mimBr-NaPSS interaction

#### 3.1.1. Surface tension

The surface tension for the C<sub>14</sub>mimBr and NaPSS aqueous solution at 298.15 K is measured for a range of different polymer concentrations. For each polymer concentration, the surface tension is determined over a broad surfactant concentration range, extended from just above the five times of *cmc* of the pure surfactant to below the concentration of hundredth of *cmc* at which the surface tension changes sharply toward that of pure water. The surface tension at the very dilute surfactant concentrations is difficult to measure with accuracy. In this region, it is difficult to establish the surfactant adsorb equilibrium at the air/aqueous interface, so the uncertainty in the measurements of surface tension is estimated to be 0.3 mN m<sup>-1</sup>.

The plots of surface tension against the logarithm of the C<sub>14</sub>mimBr concentration at a fixed NaPSS concentration of 0.005, 0.01, 0.025, and 0.05 g/L for the C<sub>14</sub>mimBr/NaPSS mixture are shown in Fig. 1. For pure C<sub>14</sub>mimBr solution, the surface tension shows the expected behavior, with an abrupt change in the slope at the critical surfactant concentration (*cmc*). While the addition of NaPSS results a marked change at a low surfactant concentration and a hump at an intermediate concentration of surfactant in the surface tension curve. As the polymer concentration decreases, the onset of the hump shifts to lower surfactant concentration and the height of the hump increases. This general pattern of the plots is similar to that observed previously for the C<sub>16</sub>TAB/NaPSS and SDS/PDMAAC systems [19,20]. Taylor et al. had rationalized these surface tension profiles using three different polymer-surfactant aggregates. The enlightenment and reference of these explanations allow us to obtain the more reasonable deduction to the adsorption pattern of the C<sub>14</sub>mimBr/NaPSS system.

Initially, the surface tension is not affected basically by the addition of polymer at the very low surfactant concentration. It is supposed that the cationic headgroups of surfactant monomers might bind to the negatively charged groups along the polymer

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