

The role of NaSCN on the equimolar cationic–anionic surfactant mixtures: Evidence from NMR, surface tension and dynamic light scattering

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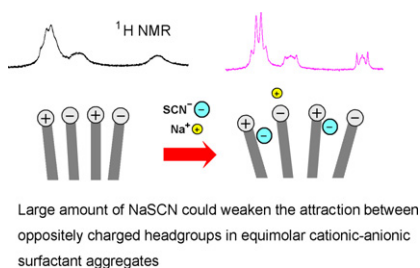
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HIGHLIGHTS

- ▶ Effects of NaSCN on cationic–anionic surfactant mixtures are studied for the first time.
- ▶ NMR directly evidences the weakening of interactions between headgroups by NaSCN.
- ▶ Surface tension and DLS results also support the conclusion made from NMR.

GRAPHICAL ABSTRACT



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ABSTRACT

The effects of different concentrations of sodium thiocyanate (NaSCN) on the homogeneous solution of equimolarly mixed decyltriethylammonium bromide and sodium decylsulfonate ($C_{10}NE-C_{10}SO_3$) were studied by 1H NMR, surface tension and dynamic light scattering (DLS) measurements. For the system of $C_{10}NE-C_{10}SO_3$, the NMR signals were greatly broadened in the micellar concentration region. However, the shape of the NMR peaks for the micellar solutions of $C_{10}NE-C_{10}SO_3$, especially for those protons adjacent to headgroups, recovered to be fine-resolved with the gradual increase of NaSCN concentration. Therefore, the NMR method directly evidenced that the electrostatic attraction between the oppositely charged headgroups in the micellar solution of $C_{10}NE-C_{10}SO_3$ was significantly reduced by NaSCN. The surface tension results showed that both the surface tension at critical micelle concentration (γ_{cmc}) and the minimum molecular area in the surface adsorbed layer (A_{min}) were remarkably increased when NaSCN was added to $C_{10}NE-C_{10}SO_3$. As shown by DLS, the addition of NaSCN could significantly induce the decrease of the aggregate size of $C_{10}NE-C_{10}SO_3$. Both surface tension and DLS results supported the conclusions made by NMR.

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1. Introduction

It is well known that Hofmeister series can be applicable in many cases of the salt effects on proteins, polymers, and surfactants. In a classical Hofmeister series, ions have been ranked from kosmotropes to chaotropes. For

example, the Hofmeister series for anions is $SO_4^{2-} > HPO_4^{2-} > F^- > Cl^- > Br^- > NO_3^- > I^- > ClO_4^- > SCN^-$.

Based on the recently developed mechanism for Hofmeister series, the specificity of ions may be in nature determined by their different adsorption/binding ability to the two-phase interface [1–3] or the interfaces of hydrophobic species or aggregates [4,5]. Moreover, the binding of ions onto surfactant headgroups have been further described in detail, e.g. in a concept of “matching water affinities” by Collins [6]. Therefore, the binding of ions is expected to show influence on the state of headgroups in the

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aggregates of surfactants, however, how to observe such microscopic change is limited by experimental approaches. Surface tension is undoubtedly one, but it is an interfacial measurement upon the surface adsorbed layer and can give only secondhand information of what may happen to the micellar surface. Another conventional way is to detect the morphology change of surfactant aggregates by means of DLS, TEM, rheology, etc., which can indirectly reflect the compactness of headgroups at the aggregate surface according to the packing parameter theory. Based on previous investigations [7–9], SAXS can reflect the swell/shrink of the (ethylene oxide)-based headgroups in the aggregates. However, this aim could only be achieved when the surfactant concentrations are high enough to form liquid–crystalline structure such as hexagonal [7,9], lamellar [9], or discontinuous cubic phase [8]. Measure of zeta-potential could denote the ion adsorption on the particles based on the sign of charge, but the detailed effects of these adsorbed ions upon the headgroups need further elucidation.

The NMR techniques have been proved to be versatile to obtain multi-angle information about a surfactant solution [10,11]. One of the advantages for NMR method is that it can sensitively detect the chemical environment change for each proton in the surfactant molecule, including the protons adjacent to headgroups.

There are strong electrostatic interactions between oppositely charged headgroups in the mixtures of cationic–anionic surfactants [12]. Those equimolar and symmetric ones (i.e. with similar chain length) are expected to be most synergistic. NaSCN is a strong chaotropic salt according to the Hofmeister series. As shown by means of zeta-potential [13], the adsorption of SCN^- is superior to not only cations (Na^+ or Ca^{2+}) but also some anions (Cl^- or NO_3^-) onto the surface of microemulsion droplets stabilized by nonionic surfactant. Therefore, a combination of NaSCN and the equimolar cationic–anionic surfactant mixture might be an attractive model system to show what salt ions could do upon the headgroups who should intensely interact with each other at the aggregate surface. Previous investigations involving the influence of NaSCN on surfactants are mainly focused on nonionic surfactants [7–9,14–17], amphiphilic polymers [18–21], and those oil/water systems containing nonionic surfactants [2,13], where NaSCN has shown significant salting-in effect. However, as the best of our knowledge, the effects of NaSCN on the properties of cationic–anionic surfactant mixtures have not been reported yet.

In this work, we tried to study whether there is any effect of NaSCN upon the strong electrostatic interactions between oppositely charged headgroups by means of NMR. The equimolar mixture of decyltriethylammonium bromide and sodium decylsulfonate ($\text{C}_{10}\text{NE}-\text{C}_{10}\text{SO}_3$) was chosen since our previous studies showed that it could remain homogeneous at high concentration of surfactants [22,23] and even in the presence of high concentration of NaCl, NaBr, and NaI [24]. Our lab have also previously investigated (i) the effects of sodium halides on surface tension [25]; (ii) the effects of alkali metal halides on the viscosity and aggregate size [24] and (iii) the aqueous two phases induced by NaF, Na_2SO_4 , and Na_3PO_4 [26] in the equimolar $\text{C}_{10}\text{NE}-\text{C}_{10}\text{SO}_3$ mixtures. These previous results under the condition of high concentrations of salts are shown to be consistent with Hofmeister series. In the present work, NMR was tried for the systems of $\text{C}_{10}\text{NE}-\text{C}_{10}\text{SO}_3$ with the addition of NaSCN. Surprisingly, we found that NMR could directly “see” the weakening of the electrostatic interactions between the oppositely charged headgroups with the addition of NaSCN.

2. Experimental

2.1. Materials

Decyltriethylammonium bromide (C_{10}NE) and sodium decylsulfonate (C_{10}SO_3) were prepared by the procedure described in

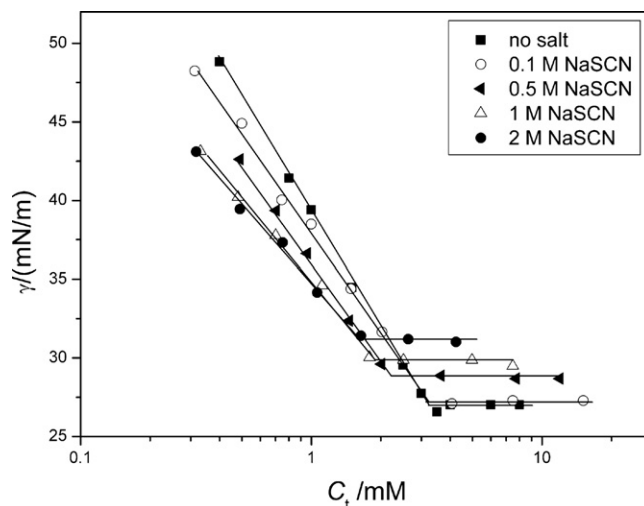


Fig. 1. The plots of surface tension (γ) vs. the total concentration of surfactants (C_t) for the equimolar mixtures of $\text{C}_{10}\text{NE}-\text{C}_{10}\text{SO}_3$ in the presence of constant concentration of NaSCN (0, 0.1 M, 0.5 M, 1 M and 2 M NaSCN, respectively).

our previous paper [23]. NaSCN was a product of ACROS organics ($\geq 98.0\%$, ACS reagent). Because the crystal of NaSCN is hygroscopic, it was dried before use by heating in a vacuum oven for 48 h. D_2O (99.8 atom% D, ACROS) was used as received.

2.2. Methods

The surface tension was measured by drop volume method [27] at $(25.0 \pm 0.1)^\circ\text{C}$. Deionized water was used to prepare solutions. The densities of aqueous solutions of 0.1 M, 0.5 M, 1 M and 2 M NaSCN were measured by densimeter, respectively, which were used to correct the density coefficients in the measure of surface tension for those surfactant solutions with the same concentrations of NaSCN.

The ^1H NMR experiments were performed on a Varian Mercury Plus 300 spectrometer (^1H : 300.21 MHz) with D_2O as solvent at 25°C . All the proton chemical shifts were referenced to an external blank solvent of D_2O by its residual peak ($\delta_{\text{HDO}} = 4.700$ ppm), with field frequency kept locked and those samples under investigation were successively measured thereafter.

Dynamic light scattering (DLS) measurements were performed on a spectrometer of standard design (ALV-5000/E/WIN Multiple Tau Digital Correlator) and a Spectra-Physics 2017 200 mW Ar laser (514.5 nm wavelength) at 25°C . All solutions were filtered through a $0.2\ \mu\text{m}$ ArcoDisk filter into the cylindrical scattering cells before light scattering measurements. The scattering angle was 90° and the intensity autocorrelation functions were analyzed using the CONTIN program.

3. Results

3.1. Surface tension results for the equimolar $\text{C}_{10}\text{NE}-\text{C}_{10}\text{SO}_3$ mixtures with the addition of NaSCN

Surface tension studies were performed first to obtain preliminary information for the equimolar mixtures of decyltriethylammonium bromide and sodium decylsulfonate ($\text{C}_{10}\text{NE}-\text{C}_{10}\text{SO}_3$) with the addition of NaSCN. Fig. 1 shows the variation of surface tension (γ) with the total concentration of surfactants (C_t) for $\text{C}_{10}\text{NE}-\text{C}_{10}\text{SO}_3$ in the absence and presence of NaSCN. The critical micelle concentration (cmc) and the surface tension at cmc (γ_{cmc}) for each system obtained from Fig. 1 are listed in Table 1. According to the derived Gibbs adsorption equation both for equimolar

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