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Aggregation of Sodium Dodecyl Sulfonate in Poly-ethylene Glycol Aqueous Solutions Studied by Two-dimensional Nuclear Overhauser Enhancement Spectroscopy

Xiao Wen FANG[1], Hong Chang GAO[1], Shi Zhen MAO[1], Sui ZHAO[2], Jia Yong YU[2], You Ru DU[1]*

[1]State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071
[2]Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100101

Abstract: Two-dimensional nuclear overhauser enhancement (2D NOESY) measurements show that sodium dodecyl sulfonate SDSN molecules co-aggregate with poly-ethylene glycol PEG in their aqueous solution at a concentration range of SDSN between the so-called co-aggregation concentration (cac) and the normal critical micellar concentration (cmc). SDSN micelles are formed when the cmc of SDSN is reached with PEG uniformly distributed in the interior.

Keywords: 2D NOESY, sodium dodecyl sulfonate, poly-ethylene glycol, aggregation.

Introduction

The investigation of the interaction between sodium dodecyl sulfate (SDS) and poly-ethylene glycol (PEG) in aqueous solutions has received considerable attention. Jones reported the observation in which two discontinuities instead of one appeared in the surface tension curve when SDS was added to a PEG solution of fixed concentration[1]. The first discontinuity was attributed to the beginning of SDS to bind with PEG, defined as cac, and the second to the beginning of the formation of self-aggregated SDS micelles when PEG was completely exhausted, defined as c_2. Hou *et al*. has found similar phenomenon for the mixture of sodium dodecyl sulfonate SDSN and PEG aqueous solution[2]. They also attributed the first discontinuity as the start of co-aggregation of SDSN with PEG although direct evidence has not been provided. It is evident that the turning points at the so-called cac on the surface tension and the conductivity curves only give the information of the concentration of the free SDSN monomers, which starts to become lower than the total concentration of SDSN. In short, a part of the SDSN molecules is in an aggregation state. This does not imply that the SDSN molecules should be combined with PEG, they can also be self-aggregated. Furthermore, Hou *et al.*[2] postulated a necklace model for the co-aggregation formed from SDSN and PEG according to very small variations of the ^{13}C chemical shifts. It is well known that two-dimensional nuclear overhauser enhancement (2D NOESY) experiment is an

* E-mail: lfshen@wipm.whcnc.ac.cn

effective method for studying the three dimensional structure of macromolecules due to have long motional correlation time. Cross signals in a 2D NOESY spectrum rely on the cross relaxation of longitudinal magnetization during the mixing time. One can extract valuable information about inter-nucleus distances (less than 5 Å) from the existence of the cross peaks. In order to obtain further insight into the interaction between PEG and SDSN in aqueous solutions, the 2D NOESY experiment shows the vicinity of protons of different kinds of molecules[3].

Experimental

Sodium dodecyl sulfonate (SDSN) was of chemically pure grade from the Yongjia Fine Chimical Plant of China, and the poly-ethylene glycol-4000 was the chromatographic pure product of the Shanghai Chemical Plant of China. Its molecular weight is 4000 D. D_2O of 99.6 % deuterated was produced by Beijing Chemical Factory, used without any further purification . The 2D NOESY measurements were performed on a Bruker ARX-500 with a ^1H frequency of 500.13 MHz at 40°C. 32 accumulations were collected generally. D_2O was used as solvent in order to weaken the water signal. Meanwhile, presaturation method was used to further suppress the proton signal of the solvent. The 2D NOESY experiments were performed with the standard three pulses sequence[4]. When the concentration of PEG is fixed in 2 g/L, the cac and cmc of SDSN are 7 mmol/L and 9.7 mmol/L, respectively[2]. For observing the dynamic behaviors of molecules in the different concentration ranges solutions, two kinds of solutions with concentration 7.5 mmol/L and 50 mmol/L were prepared. Mixing time of 1.5 s was chosen for the system at a concentration of 7.5 mmol/L of SDSN, and the mixing time of 1.4 s was used for the solution of 50 mmol/L of SDSN, with the addition of 2 g of PEG per liter in both cases.

Results and Discussion

The assignment of SDSN protons is shown in **Scheme 1**. And the contour plots of 2D NOESY experiments of 7.5 mmol/L and 50 mmol/L SDSN are shown in **Figures 1** and **2**, respectively. In **Figure 1**, four cross peaks between PEG and SDSN protons and twelve cross peaks between the protons of SDSN themselves were observed. In **Figure 2**, ten cross peaks between PEG and SDSN and eighteen cross peaks between protons of SDSN themselves were observed. These cross peaks are enclosed in squares with labeling.

The cross peaks between PEG proton and S-1, S-2 protons of SDSN molecules could be found in **Figure 1**. This obviously shows that the PEG protons are relatively close to the SDSN protons (less than 5 Å in space). This is a favorable environment for the combination of SDSN with the PEG molecules so we can conclude that SDSN molecules combined with PEG in the aqueous solution at a concentration range from the so-called co-aggregation concentration (cac) to the normal critical micellar concentration (cmc) of SDSN. Synchronously the presence of the cross peaks among the protons of SDSN indicates the self-aggregation of SDSN molecules in this solution. For a single molecule S-1 should be more than 5 Å apart from S-4, whereas the cross peak between

S-1 and S-4 is significant in **Figure 1** showing that the distance between S-1 and S-4 is less than 5 Å. This dipolar interaction should originate from the inter-molecular effect, *i.e*. the hydrocarbon chains of SDSN are closely packed, and self-aggregation occurred.

Figure 2 shows the contour plot of the 2D NOESY experiment for the mixed solution at a concentration of 50 mmol/L of SDSN. The cross-peaks between PEG proton and all SDSN protons, respectively, appeared. Besides, compared with **Figure 1** more cross-peaks with higher intensity between the SDSN protons appeared. These experimental results show that with the increase of the concentration of SDSN, micellization of SDSN is significantly enhanced with more closely packed hydrocarbon chains. The appearance of cross peaks between PEG proton and all the protons of SDSN, respectively, implies that PEG molecules are uniformly involved in the hydrophobic micellar core of the SDSN micelles.

Scheme 1 The molecular formula of SDSN and its proton labeling

$$\mathbf{SO_3\text{-}CH_2CH_2CH_2(CH_2)_8CH_3}$$

S-1 S-2 S-3 S-4 S-5

Figure 1 Contour plot of 2D ^1H-^1H NOESY experiment with SDSN 7.5 mmol/L and mixing time of 1.5 s

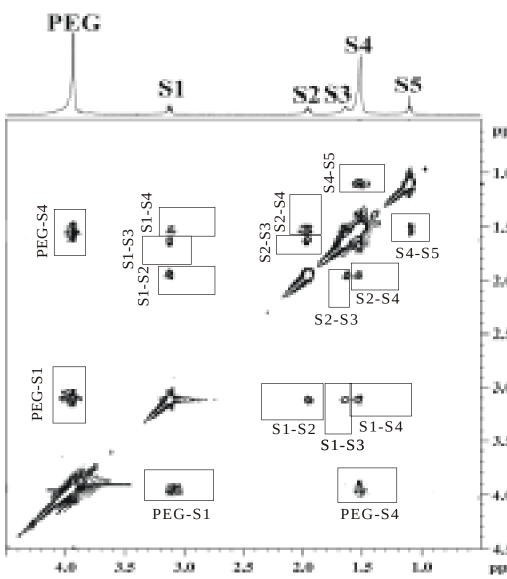
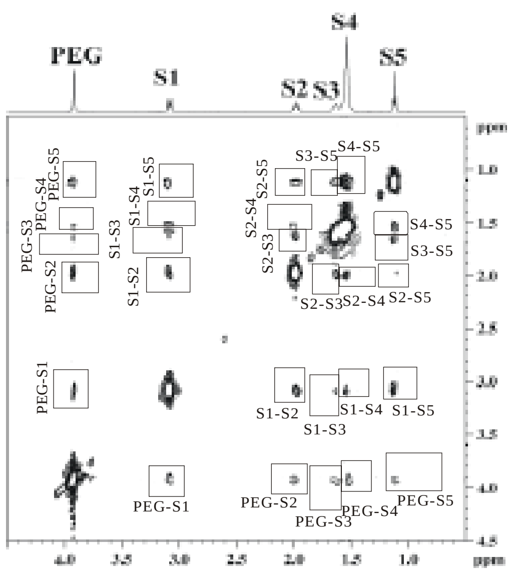


Figure 2 Contour plot of 2D ^1H-^1H NOESY experiment with SDSN 50 mmol/L and mixing time of 1.4 s



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