Experimental Report

24/06/2014

Proposal: **9-13-480** **Council:** 10/2012

Title: Dynamics in Cationic Micelles: Effect due to location of Phenyl Ring

This proposal is a new proposal

Research Area: Soft condensed matter

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Samples: C1H23O(C6H4)ON(CH3)3Br + D2O

Instrument	Req. Days	All. Days	From	To
IN6	0	4	12/07/2013	16/07/2013

Abstract:

Surfactants have unique properties base from their amphiphilic nature, i.e., each molecule contains both a hydrophilic and a hydrophobic section and are important in a wide variety of processes: commercial, industrial and biological. The possibility of structural variations and their implications on the micellar behavior is at the core of current research in this area. Understanding and correlating the effect of subtle structural variations on the properties of aqueous surfactant solutions is far from complete. With that view, a series of isomeric cationic surfactants bearing a long alkyl chain that carries a 1,4-phenylene unit and a trimethyl ammonium head group is synthesized. The location of the phenyl ring within the alkyl tail is varied in an effort to understand its influence on the amphiphilic properties of the surfactants. Interest here is the effect of aromatic pi-pi interactions and the location of the aromatic ring, on the segmental dynamics of the surfactant in it’s micellar form. The aim of the proposed experiment is to carry out a systematic study of the internal dynamics in phenyl ring bearing cationic surfactants as a function of its location along the alkyl chain.

Dynamics in Cationic Micelles: Effect due to Location of Phenyl Ring

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Amphiphilic molecules e.g. surfactants, lipids, etc. are of great interest owing a number of applications in pharmaceutical, medical, food science, material synthesis and so forth. By tailoring the molecular architecture and the interaction between the surfactants, discrete micellar structures of a specific size, shape and order can be created. The structural variations and their implications on the micellar behavior is at the core of current research in this area. Dynamical landscape in ionic micelles has been obtained by us in details [1-3]. More specific structural studies have examined the role of branching within the hydrophobic tail and their location and the effect of unsaturation within the hydrophobic tail group, heteroatom inclusion within the hydrophobic tail, head group structure and so forth. Recently, a series of cationic surfactants with the unique feature in which the alkyl tail carries a 1,4-dioxyphenylene unit whose position is varied from the tail end to the head group are synthesized and effect of the location of phenyl ring on the structure and macroscopic behavior of micelles formed by these surfactants have been studied [4]. However, the effect towards dynamics of these assemblies and their correlation with microstructure is yet to be understood. In case of Sodium Dodecyl Sulfate (SDS; $C_{12}H_{25}SO_4Na$)) and Sodium Dodecyl Benzene Solfonate (SDBS; $C_{12}H_{25}C_6H_4SO_3Na$) based micellar systems, we have investigated the effect of additional phenyl group located near the head group, on the dynamics of ionic micelles [5]. It is found that due to presence of phenyl group, segmental motion of alkyl chain gets hindered. It is of interest to carry out a systematic study of the local dynamics in phenyl ring bearing surfactant as a function of its location along the alkyl chain and understand how the segmental dynamics of micelles gets modified with respect to the location of the aromatic ring. This is important since local dynamics of such assemblies are directly related to various properties such as the mechanism in releasing the solubilized drugs, micellar breaking time, etc.

Quasielastic neutron scattering (QENS) experiments have been carried out on 0.3 M cationic micelles based on a series of isomers namely I1, I3, I4 and I5 ($C_{12}(C_6H_4O_2)$ trimethylammonium bromide) in which location of phenyl ring varies along the alkyl chain (Fig. 1) using the time of flight spectrometer IN6 at the Institute Laue Langvin, Gernoble, France. QENS data are also taken for Cetyltrimethylammonium bromide (CTAB or C_{16}TAB) where no 1,4 dioxyphenylene unit exists in the alkyl chain as shown in Fig. 1. Aim of the experiment was to investigate the role of 1,4 dioxyphenylene unit in the alkyl chain and its effect on the segmental dynamics of the micelle. IN6 was operated with the incident neutron wavelength 5.12

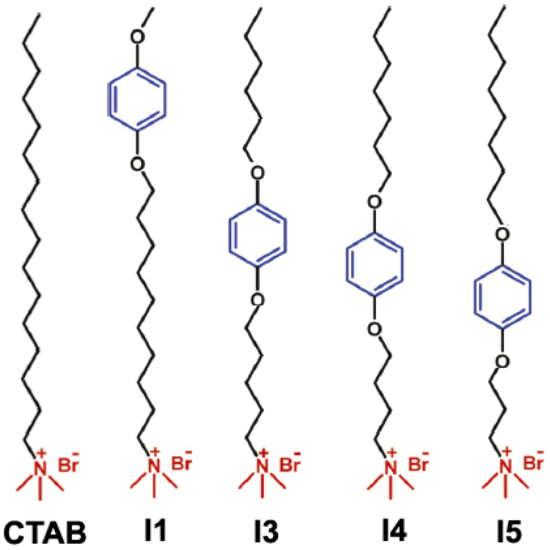

Fig. 1 Structure of surfactant molecules bearing 1,4 dioxyphenylene unit at different locations.

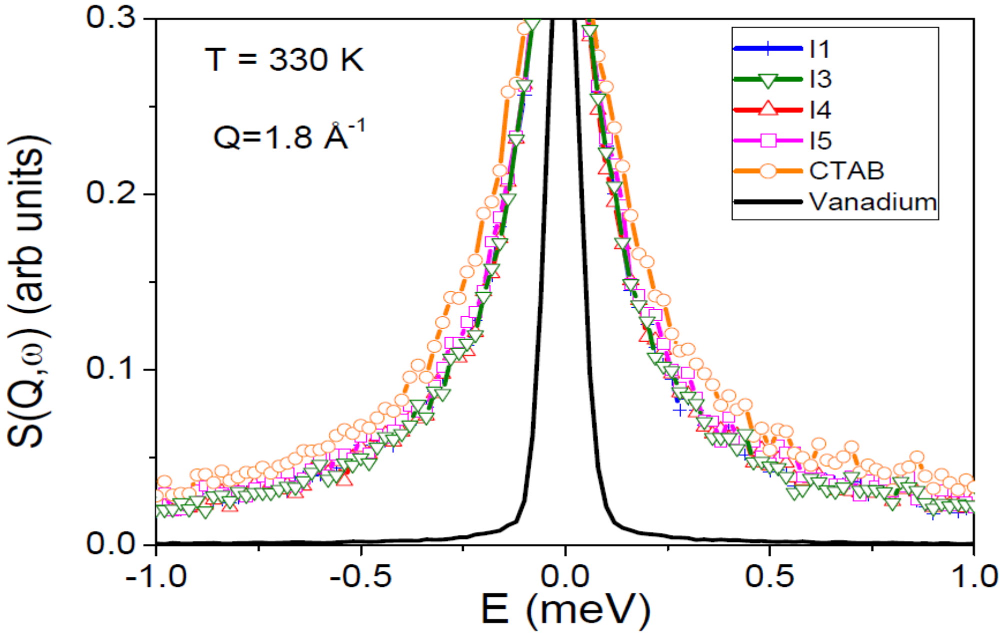

Fig. 2 Typical quasielastic spectra obtained for I1, I3, I4, I5 and CTAB micelles at 1.8 Å^{-1} at 330 K. Instrumental resolution is also shown for comparison.

Å providing an energy resolution of $\Delta E \sim 90$ μeV (full width at half-maximum, FWHM). QENS measurements were carried out on at three different temperatures 300, 315 and 330 K in the wave-vector transfer (Q) range 0.3-1.7 Å^{-1}. Data were collected for pure D_2O also at each temperature to estimate the contribution of the solvent. For neutron scattering measurements, samples were placed in an annular aluminum can with an internal spacing of 0.3 mm to minimize multiple scattering and have reasonable measuring statistics. Scattering functions, S(Q,ω), for the micelles alone are obtained by subtracting the contribution of solvent from the spectra of the micellar solution. Subtracted QENS spectra for the isomer series along with CTAB are shown in Fig. 2 at 330 K at Q=1.8 Å^{-1}. The instrumental resolution, as measured using standard vanadium sample, is also shown for comparison. The spectra are normalised to the peak intensities of vanadium. have exactly same molecular formula and the It is found that the dynamics of the isomer series of surfactants bearing 1,4 dioxyphenylene unit are not much different (Fig. 2). However, when compared with CTAB micelle which does not have any phenyl ring, a significant difference in the dynamics is observed. It is found that due to presence of 1,4 dioxyphenylene unit in $C_{12}(C_6H_4O_2)$TAB series, the dynamical behavior is constrained compared to C_{16}TAB. Similar effect due the presence of phenyl ring was found in case of SDS and SDBS. However, location of 1,4 dioxyphenylene unit in different isomers seems not to have much effect on the dynamics of the micelle. Detailed data analysis is in progress.

References

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