Experimental report

22/06/2016

Proposal: **9-10-1399** **Council:** 10/2014

Title: Self Diffusion of Ionic Micelles in Crowded Solution: Effect of Phenyl Ring

Research area: Soft condensed matter

This proposal is a resubmission of 9-10-1341

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Samples:
D_2O
$C_{12}H_{25}SO_4Na$, $C_{12}H_{25}(C_6H_4)SO_3Na$
DTAB, $C_{12}(C_6H_4O_2)TAB$

Instrument	Requested days	Allocated days	From	To
IN16B	4	4	07/07/2015 02/08/2015	10/07/2015 03/08/2015

Abstract:

Dynamical processes in micelles are complex and include multiple relaxation processes on local and global scales which can be studied experimentally via Quasi-elastic Neutron Scattering (QENS) techniques with combination of suitable spectrometers. Even if the structures of sodium dodecyl sulphate (SDS) and sodium dodecyl benzene sulfonate (SDBS) surfactants are very similar, SDBS has peculiar characteristics that derive from the presence of a phenyl group that may change entirely its properties through the formation of pi-stack aggregates. QENS spectra obtained earlier with IN5 spectrometer showed both global as well as internal motions of SDS micelles are faster than SDBS micelles. Molecular dynamics (MD) simulation and picoseconds resolved fluorescence spectroscopic measurement carried out by us indicated faster dynamics in SDS micelles. It is also found that the global and internal motions are strongly correlated. The aim of the proposed experiment is thus to investigate the dynamics using high resolution backscattering spectrometer such that the slower global motion could be observed independently.

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Self Diffusion of Ionic Micelles in Crowded Solution: Effect of Phenyl Ring

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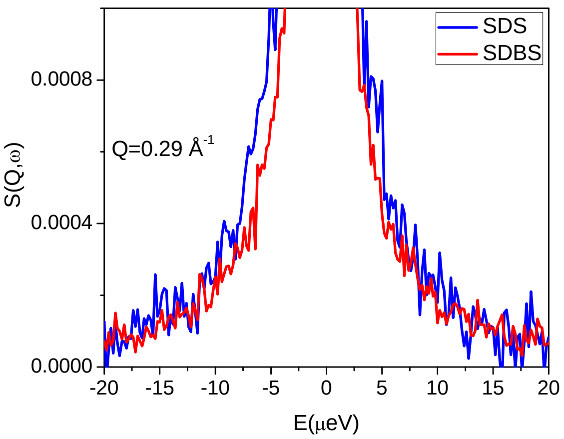
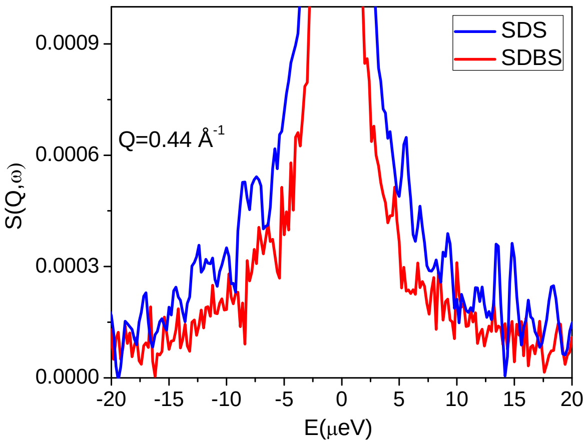
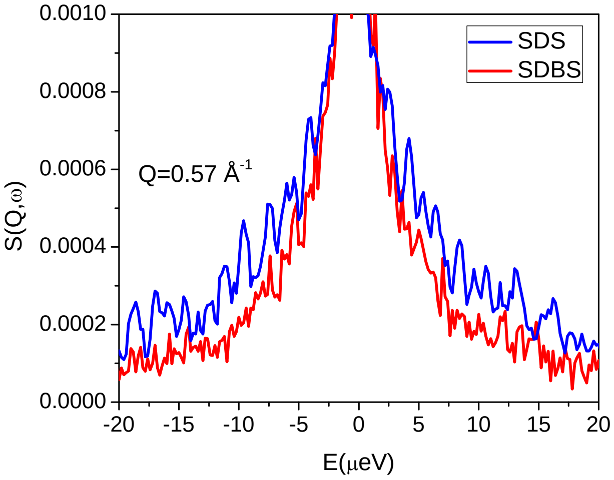
Surfactant molecules are important in a wide variety of processes: commercial (as in detergents, hair color reagents and stain removers), industrial (as in emulsion polymerization), biological (as in molecule transport across cell membranes) and so forth. Their unique properties arise from their amphiphilic nature, i.e., each molecule contains both a hydrophilic and a hydrophobic section. When dissolved in water above a certain concentration (critical micelle concentration) these molecules self-assemble into mesoscopic aggregates, such as micelles, vesicles, and bilayers. Though the structure and macroscopic behavior of micelles has been extensively studied, the fast local dynamics of surfactant molecules in these assemblies and their correlation with microstructure is not investigated in detail. Local dynamics of such assemblies are important in understanding various properties such as the mechanism for releasing solubilized drugs, micellar breaking time, etc.

Dynamical processes in micelles are complex and include multiple relaxation processes on local and global scales. We have carried out measurements on anionic as well as cationic micelles in a wide dynamical range using various instruments to elucidate various dynamical processes that could present in these molecular self assemblies. Combining the data obtained from TOF spectrometers IN5, IN6 at ILL, Focus at PSI and backscattering spectrometer IRIS at ISIS facility, we have obtained detailed dynamical landscape in different ionic micellar systems [1-6] and vesicles [7]. SDS and SDBS are two surfactants having very similar structures, however the global dynamics are found to be very different, which is not understood [5]. It was thought that the effect could be an artifact of the deconvolution of different dynamical components. We have carried out QENS measurements on micelles based on these two surfactants using IN16B. It was expected that the fast internal motion would not be seen within the energy window of IN16B, but the global motion being a slower will be observed without ambiguity.

Figure 1 shows the data after the contribution from the solvent (D_2O) and empty can are removed. It is clear that the global dynamics in SDS is faster than SDBS.







This confirms that global dynamics is indeed slower in SDBS than SDS [5]. It was also found in our MD simulation studies that this is due to the hydration effect [6]. The interior of SDBS is devoid of water due to the presence of the phenyl ring. Our recent optical studies have also showed that SDBS is more compact than SDS and extracted dynamics of hydration slower water motion at the less flexible SDBS compared to SDS micelles [8].

[1] V. K. Sharma, Gunjan Verma, S. Gautam, P. A. Hassan, S. Mitra and R. Mukhopadhyay, *J. Phys. Chem. B* 114 (2010) 17049.

[2] S. Mitra, V. K. Sharma, V. G. Sakai, J. Peter Embs and R. Mukhopadhyay, *J. Phys. Chem B*, 115 (2011) 9732.

[3] V.K. Sharma, S. Mitra, V.G. Sakai, P.A. Hassan, J. Peter Embs and R. Mukhopadhyay, *Soft Matter*, **8 (2012) 3151**

[4] V. K. Sharma, S. Mitra, V.G. Sakai and R. Mukhopadhyay, *J. Phys. Chem. B* 116 (2012) 9007

[5] V. K. Sharma, S. Mitra, M. Johnson and R. Mukhopadhyay, *J. Phys. Chem.* B 117 (2013) 6250.

[6] B. Aoun, V.K. Sharma, E. Pellegrini, S. Mitra, M. Johnson and R. Mukhopadhyay, *J. Phys. Chem.* B, 119 (2015) 5079

[7] S. Mitra, V.K. Sharma, V. Garcia Sakai, A. Orecchini, T. Seydel, M. Johnson, and R. Mukhopadhyay, J. Phys. Chem. B, **120**, 3777 (2016).

[8] S. Choudhury, PK Mondal, V.K. Sharma, S. Mitra, V. Garcia Sakai, R. Mukhopadhyay and S.K. Pal, J. Phys. Chem. B 119 (2015) 10849