1D17

Gelation of Aqueous Surfactant Solutions Examined by Raman Spectroscopy

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Introduction

Beyond a critical concentration, surfactant (e.g. cetyltrimethylammonium bromide) molecules aggregate into micelles, vesicle etc. in aqueous solution. The shape of the assembled structure depends on the S/m ratio (S – surface area of the aggregate and m- number of molecules per aggregate). Interplay of several intermolecular forces, such as, repulsive interaction between ionic head groups, van der Waal's interaction between the hydrophobic chains, selective hydration of the ionic head group etc. controls the aggregation behavior. Interestingly, addition of small organic molecules (e.g. Na-salicylate, NaSA) induces further aggregation of these micellar aggregates into worm-like micelle (fibrils)[1] and eventually results in the gelation of the aqueous solution. This behavior is not easily explained by the geometrical argument proposed to explain the shape of surfactant aggregates in solution.[2] A specific intermolecular interaction is believed to be responsible for the gelation of surfactant solution but the true nature of this interaction remains unclear. We have used Raman spectroscopy to probe the behavior of a gelator, Na-salicylate, in the CTAB-gel and to understand the specific intermolecular interaction that leads to gelation.

Experiment

In a typical experiment we prepared the gel samples by mixing 20 mM cetyltrimethylammonium bromide (CTAB), 20 mM Na-salicylate and water. The water composition was varied from 20 to 500 weight percent. The samples were maintained at 40°C for two to five days to equilibrate and ensure homogeneity. Photograph of a gel-sample is given in Figure 1. Raman spectra were recorded with a He-Ne laser (632.8 nm, 30 mW) using a Raman microscope (Olympus microscope and spectrometer from Tokyo Instruments) equipped with a 100X oil immersion objective. In a typical acquisition, sample was exposed for 10 min and 5 cycles were averaged.

Figure 1: Transparent CTAB gel.

Results and Discussion

The present investigation of CTAB gel was initiated to probe the intermolecular interaction and to understand the nature of gelator in the material. CTAB aqueous solution transforms to a gel upon addition of NaSA. The ionic interaction between the head groups of CTAB and NaSA has been predicted as the reason for the gelation of the surfactant solution. In order to test this hypothesis we have attempted to prepare gel with salicylic acid (SA) instead of NaSA. In our study, specific Raman bands for SA and NaSA have been identified, which are used as Raman signatures to address the nature of the gelator. The pKa of SA is 2.9 and in neutral water SA should exist as carboxylate, which is a requisite for the gel formation if ionic

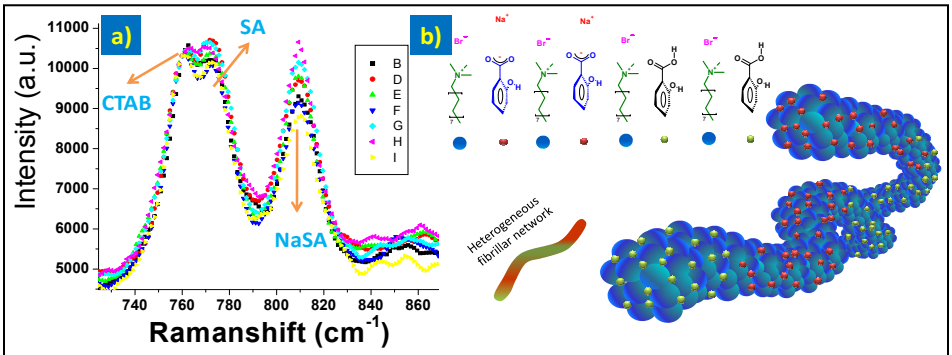

Figure 2. a) Raman spectra of the gel. Relative intensity of these bands indicates the spatial distribution of constituents in the gel b) A pictorial depiction of distribution of different components in the fibrillar network in the gel.

interaction is responsible for it. As expected, addition of the acid form (SA) also induced gelation of CTAB solution. However, the Raman spectrum of SA-CTAB gel had features different from the Raman spectrum of the NaSA-CTAB gel. Detailed analysis revealed that SA remains in the carboxylic acid form in spite of the neutral pH of water. Such a behavior is unexpected from the acid base chemistry. Moreover, this result disproves the hither to believed ionic interaction mechanism of gelation.

Raman image recorded for the gel prepared with a mixture of NaSA and SA indicated that their distribution is not homogeneous within the gel. Self segregation of SA and NaSA along the self assembled fibrils of CTAB (see the introduction) in the gel could be a possible reason (Figure 2). We believe that the difference in hydration of SA and NaSA drives their self segregation.

Our findings pose the question, "*what interaction causes gelation?*" A new Raman band was observed in the low wavenumber region (~160 cm^{-1}) of the Raman spectrum of the gel, which was absent in the Raman spectrum of solid SA. Our study has revealed that this mode has a large contribution from aromatic ring vibrations. The nature of the carboxylic group minimally affects the position of this mode. Moreover, the position of this mode shows a considerable shift and change in bandwidth in the gel compared to its position and bandwidth in the aqueous solution. Similarly, a considerable shift the vibrational mode of trimethylammonium was also observed in gel. Hence it is possible that the aromatic pi interaction between the head group and the benzene ring of SA (or NaSA) is the intermolecular interaction that leads to gelation. To substantiate our hypothesis we found that simple benzene molecule also formed of transparent gel type material.

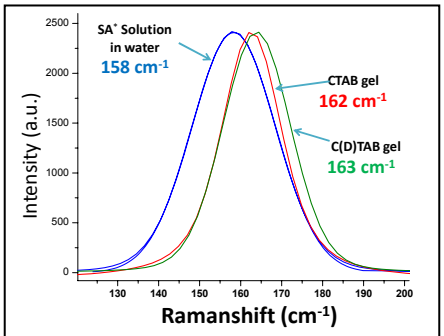

Figure 3. Raman band in the low wavenumber region is shown in the figure.

References

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