Laser Raman spectroscopic study of water in gelatin–surfactant solutions and gels

Abstract A Raman spectroscopic study was carried out on water in gelatin at 4% w/v in gel (25 °C) and sol (40–60 °C) states at various concentrations (0.5, 1, 5, 10 and 15 mM) of anionic surfactant, sodium dodecyl sulfate (SDS). The in-phase collective stretching mode vibration of hydrogen-bonded -OH oscillators, centered around 3250 cm⁻¹ in a tetrahedral network of water molecules, was observed to be significantly affected by temperature and the presence of SDS. According to our observation this may be due to the thinning of the hydration water around the gelatin molecules due to strong thermal agitation. The peak center of the collective bands of water decreased linearly with SDS concentration in the gel state which implied that with the increase in concentration of SDS, the -OH oscillators gradually lost their attachment to gelatin chains and were replaced by SDS molecules. Ultimately this resulted in a thinning of the hydration layer around the gelatin and the oscillation frequency of -OH oscillators moved towards 3250 cm⁻¹ at 1 mM SDS concentration resulting in increased coupling of -OH oscillators to form the tetrahedral network at the critical micelle concentration (cmc) of SDS. The variation in the peak amplitudes and the systematic reversal of their trend about the cmc axis was surprising. At 40 °C the amplitude of the peak at 3250 cm⁻¹ increased drastically due to a possible coil expansion by about 7–8% which accommodated more interstitial water into the pseudonetwork leading to an increase in the number of nearest neighbors and for about 6% increase in the C value. However, at the cmc the peak amplitude was observed to be independent of temperature. Continuous shifting of the peak center and full width at half-maxima towards lower values was observed with increasing SDS concentrations in the gel state.

Key words Raman spectroscopy – -OH stretching – Gelatin – Sodium dodecyl sulfate – Gelation

Introduction

Water is the most significant constituent of living cells and its unique physical and chemical properties have been studied most extensively over the last several decades. The unique feature of the solvation of water has been recognized and it is one of the most studied liquids. The hydrogen bonds (H bonds) which play the most crucial role in many interactions and conformational changes are the focus of attention of many scientists. Water, which is interconnected by weak H bonds forms a tetrahedral network. In the liquid state, two models of water structures have been commonly accepted:
1. Water molecules are connected to neighboring molecules and form a long non-terminating linear chain.

2. Water molecules through intermolecular H bonding form tetrahedral networks [1].

Both models attributed the water structure to the bending and stretching of intermolecular H bonds. The profile of -OH stretching mapped by Raman spectroscopy is known to be useful in providing in-depth understanding of the microscopic thermodynamical environment of macromolecular sols, gels and networks. The properties of water-soluble polymers are largely dependent on the water-polymer interactions. Similarly, the viscoelastic characteristics of polymeric networks and gels depend on the physiochemical properties of the solvent medium. The polymer–solvent interaction decides the structure of gels and networks in a given thermodynamic environment. This interaction provides a distinction between the bulk, interstitial and hydration water. The water manifests itself in deciding the conformations and macroscopic properties of polymers in solutions. The properties of polymers in aqueous solution show different trends due to the interaction with water.

Recently, much attention has been paid to probing the effect of water on polymers such as polyacrylamide, polyethylene glycol, polyacrylic acid, various native proteins and H$_2$O–D$_2$O, H$_2$O$_2$–H$_2$O systems by IR [2–3], NMR [4] and other techniques. However, as molecular vibrations have shorter relaxation times than the rotational arrangements of water molecules, Raman spectroscopy is the most versatile method to study the structure of water in the liquid phase.

The -OH stretching of water has been studied by Giguere and Pigeon-Gosselin [5] and most recently by Hare and Sorensen [6, 7] but the stretching of -OH oscillators in H$_2$O–D$_2$O, H$_2$O$_2$–H$_2$O systems was studied a long time before by Green et al. [8–10]. Although many reports are available on the structure-breaking of water by introducing electrolytes such as KCl, NaCl, etc., the polymer–water system with surfactant as a third component has been sparsely studied notwithstanding the fact that surfactants have the ability to deform the tetrahedral network of the water structure. Reports on chemically cross-linked polymer gels with water as a solvent and on gelatin [11] are readily available, but to our knowledge physical gels with surfactants that form fragile cross-links still remain largely unexplored. Here we have studied the effect of sodium dodecyl sulfate (SDS) on the gelation dynamics of gelatin, which is a biopolymer, using water as a solvent at different temperatures (gel, sol-I and sol-II) tuning the surfactant concentration as an additional parameter.

Gelatin is a polypeptide obtained from denatured collagen comprising all 20 amino acid residues such as glycine, proline, glutamic acid, aspartic acid, lysine and arginine, etc., in different proportions [11]. The lysine and arginine groups comprise about 7.5% of the residues and are positively charged, and these form complexes with the polar head group of anionic surfactants such as SDS. Glutamic and aspartic acid constituting about 12.5% of the residues give the negative nature to the chain. Another 6% of the residues are strongly hydrophobic in nature leaving 58% of the chain to be neutral. In the gel state the individual chains are interlocked with each other by H bonds forming triple helices at junction points, and in the sol state these helices break up to assume random coil conformations. The gelatin concentration for the gelatin used, is typically around 2% w/v [12, 13]. The polar sites of the gelatin chains attract the oppositely polarized site of water molecules and these sites on the chain are screened off from interactions with other -OH oscillators. These water molecules which are attached to the polymer chains are hydration water or associated water and induce a defect in the tetrahedral network of water molecules. The strength of the collective motion is destroyed due to these defects and decreases as $1 - \rho_C^2$, where $\rho_C$ is the mole fraction of positive and negatively charged gelatin residues.

Gelatin in the gel state forms a triple-helix network that can accommodate a huge amount of water. The water molecules in the water pools inside the gel feel reduced effects from surrounding gelatin chains because most of the polar sites are screened off, but their motions are restricted due to the presence of the polymeric network which ultimately produces a deformation in the continuous network structure of the water molecules. This water is termed interstitial water or bound water and that which is totally out of the influence of gelatin chains is called bulk water. Any sort of attachment changes the environment of the -OH oscillators which correspondingly changes the vibrational frequency, peak center, peak amplitude and the collective feature value of the -OH oscillators making it possible for it to be observed by Raman spectroscopy as a shifted Raman band.

**Experimental**

**Materials**

Gelatin was purchased from M/S Loba-Chemie (Indo-Astranal, India) with a sharp molecular weight ($M_w$) distribution ($\approx 10^6$ g mol$^{-1}$). An aqueous solution was prepared by soaking the sample for nearly 45 min at about 55 °C to remove the history effects. The solvent was double-distilled Milli-Q (Millipore, USA) grade water. To prevent bacterial contamination 0.1 mM sodium azide was added. The details of the sample preparation have been discussed by Maity and Bohidar [14]. The SDS used from SISCO Research Laboratories Pvt. Ltd. (Bombay, India) was from batch no. TP/419331. The samples were excited with an argon ion (1 W) laser light source of wavelength 488 nm. The incident light was linearly polarized (using a polarizer) and focused to a spot size of