Supporting Information

Effect of Water Structure on Gelation of Agar in Glycerol Solutions and Phase Diagram of Agar Organogels

Shilpi Boral and H.B. Bohidar*
Polymer and Biophysics Laboratory, School of Physical Sciences
Jawaharlal Nehru University, New Delhi-110 067, India.

1. Raman plots:

   Deconvolution of Raman spectra obtained from 10% glycerol solution, 0.02% agar in 10% glycerol solution (sol phase) and 0.3% agar in 10% glycerol (gel phase) are shown in Fig. S1. In every spectrum, the frequency band from 3050 to 3600 cm^{-1} was fitted to three-peak Lorentzian function that resolved the O-H stretching peaks located at 3200 cm^{-1}, 3310 cm^{-1} and 3460 cm^{-1}. These peaks represent the ice-like water structure (fully structured), liquid-like water structure (partially structured) and amorphous water structure (free water) respectively. The spectral analysis was robust that made us believe that the peaks in question were resolvable through sufficient statistical accuracy (χ^2 >0.97) as can be seen from Fig. S1.

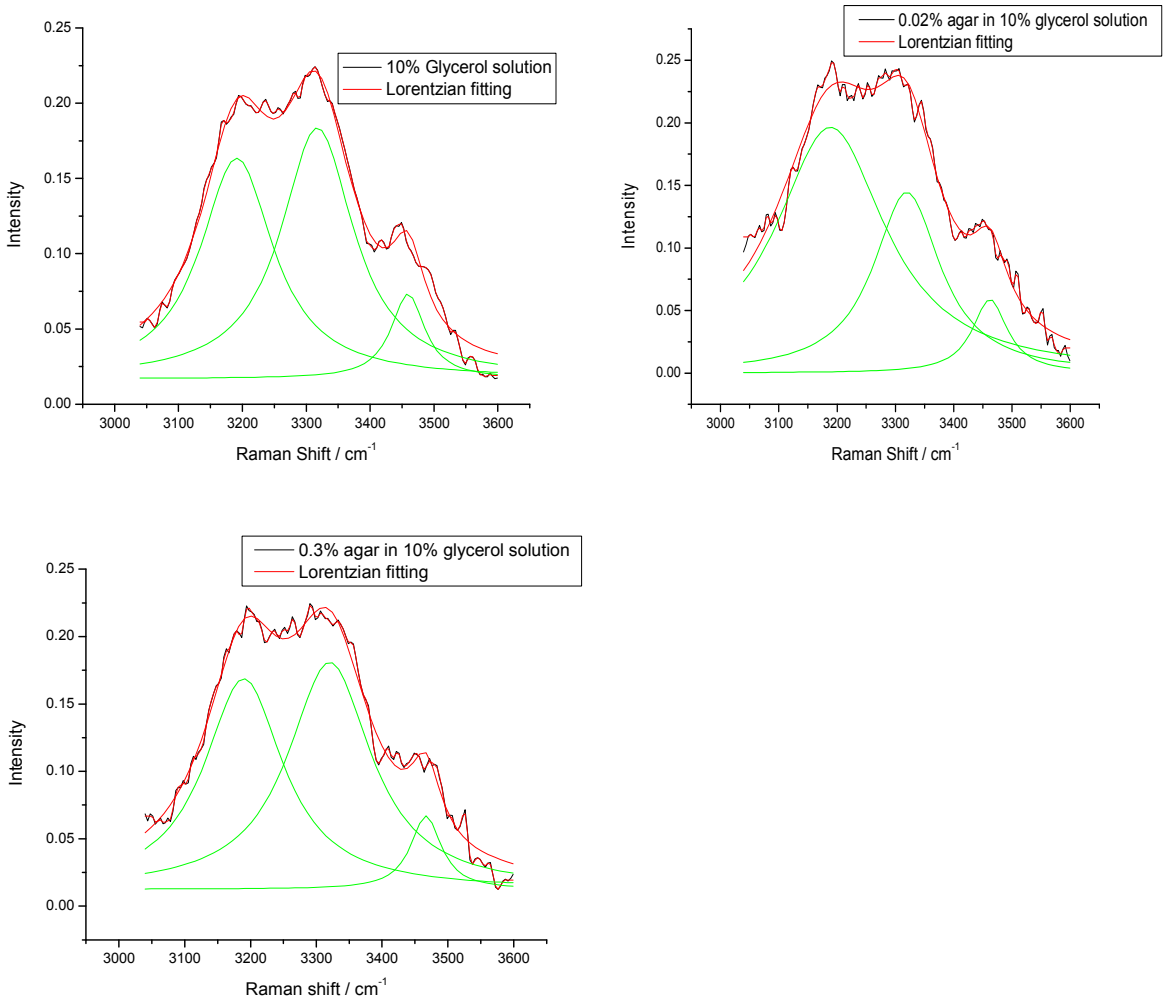
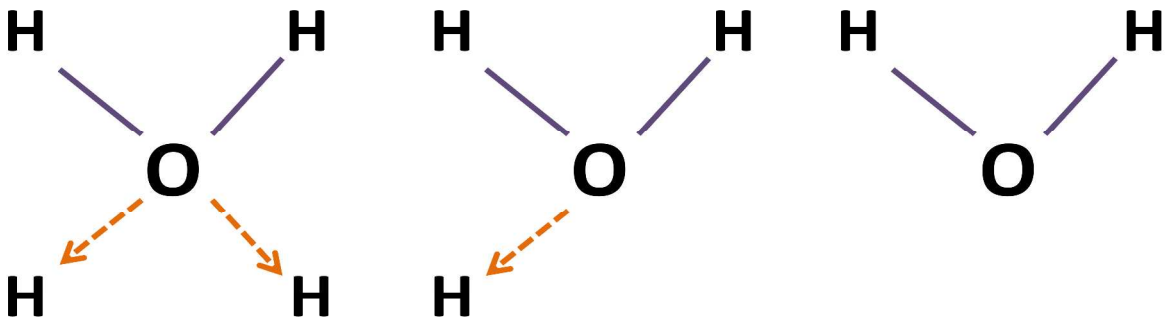


Figure S1: Raman spectra of glycerol solution, agar organosol and agar organogel recorded at room temperature and their Lorentzian three-component deconvolution.

2. Hydrogen Bond model

We propose a hydration model and hypothesize that the specific hydration of oxygen atoms by available hydrogen atoms in the system dictates the area of various Raman bands. In this model, the total number of H-atoms, H_T means the sum of all the H-atoms attached to O-atoms of both water and glycerol molecules ($H_T = H_W + H_G$). But the H-atoms attached to C-atoms in glycerol are excluded while calculating H_G. In the systems where agar was added, the H-atoms (H_A of agar) were used for calculation which are

found in –OH groups. In case of agar organo solutions and gels, the number of H_A was negligible in comparison to H_G and H_W values. Specifically, when the O-atom (irrespective of whether it belongs to water molecule or glycerol molecule) has all the 4 bonds (including the covalent and H-bonds) engaged with 4 H-atoms, we describe it as fully structured, when 3 bonds are engaged with 3 different H-atoms, it is partially structured and when only 2 bonds are engaged with 2 H-atoms, we refer to it as free water molecule. Thus the ice-like structure can only be contributed if the O-atom belongs to water molecule. Suppose the O-atom belongs to glycerol molecule, it contributes to liquid-like or free water depending on the number of H-atoms attached to it through covalent and H-bond. Figure S2 describes the concept of our proposed Hydrogen bond model.



A:ice-like structure B: liquid-like structure C: amorphous structure

Figure S2. Differentiation between Oxygen-hydrogen bonding where O represents O_W and the H-bonds can be formed with either H_W or H_G atoms. A, B and C will contribute to different water structures. Similar conjugation of O_G atoms with H_W or H_G atoms is possible.

The approach adopted to estimate hydrogen bond active atoms was quite simple. The number of individual hydrogen bond active H and O atoms in the solvents was determined from their concentration. It was assumed that all these atoms form hydrogen bonds ignoring any steric restriction. Number of atoms in a given liquid of molecular weight, M and density, ρ, having

volume v is, $n = (\rho v/M)N_A$, N_A being the Avogadro number. If this liquid is water, we have 2n number of H-atoms balanced by n number of O-atoms. For glycerol, we have 3n number of H-atoms balanced by 3n number of O-atoms. All these are H-bond active atoms.

3. Hydrodynamic Radius

   The agar sols of 0.02% (w/v) in the binary solvent of water-glycerol mixture were projected to light scattering experiments and the effective hydrodynamic radius was calculated for various glycerol concentration in the solution. Figure S3 depicts the increase in R_h with increase in glycerol concentration.

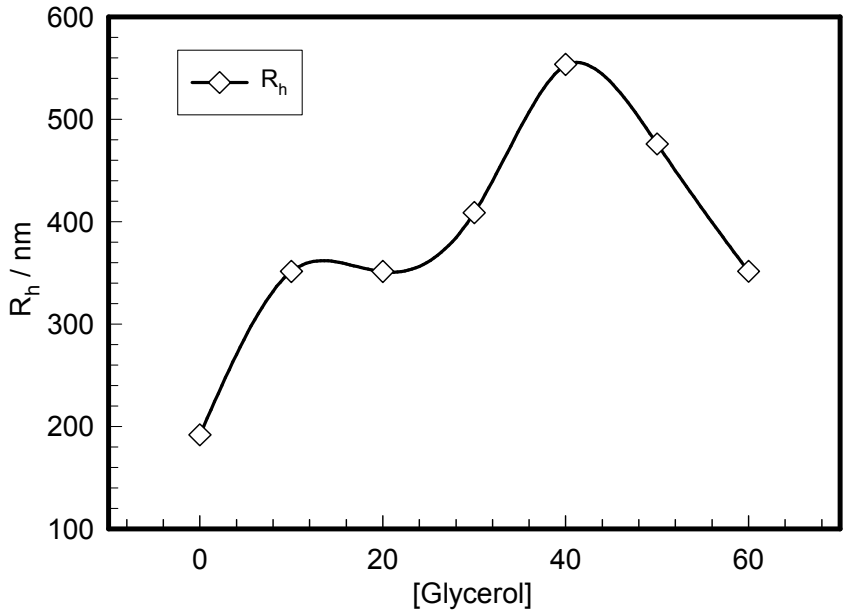


Figure S3: Plot of hydrodynamic radius with glycerol concentration. its clear from the plot that the size of agar particles increases almost 3 times with increase of glycerol concentration from 0% to 40% (v/v).