If one assumes scale invariance of aggregate distribution, Eqs. 5.14 and 5.15 reduce to

\[ I_s \sim <m> \]  \hspace{1cm} (5.16)

\[ R_h \sim <m>^{1/d_f} \]  \hspace{1cm} (5.17)

leading to \( R_h \sim <I_s>^{1/d_f} \), consequently a plot of log \( R_h \) against \( I_s \) should yield the fractal dimension of the cluster, which was not observed in our case implying absence of such scale invariance in aggregate size distribution. The polydispersity parameter \((P)\) deduced from the normalized second moment [16] of the correlation function, showed a remarkable decrease with time (see Figure 5.8) implying larger aggregates were selectively formed at the cost of smaller ones alike what was seen on the substrates. The temporal dependence exhibited, \( P \sim t^{-0.2} \). During the association process, the highly polydisperse aggregates are driven towards a close to monodisperse solution. DLA processes are known to produce smaller aggregates formed rapidly with wide particle size distribution. In contrast RCA aggregates grow slowly into large clusters and exhibit low polydispersity in size distribution. The fractal dimension observed in the bulk \((d_f \text{ in } 3-d \approx 2.6\pm0.2)\) is close to that of the DLA whereas the polydispersity feature and aggregate size growth mimics that of a RCA process, which appears anomalous.

The physical mechanism of aggregation in the bulk can be visualized as follows. Gelatin is not soluble in alcohols whereas water is a good solvent. As ethanol is added to water, the water molecules will preferentially bind to the alcohol molecules through hydrogen bonding (we will see it more explicitly in the rheology section) and the resultant binary mixture becomes a marginal solvent for gelatin molecules. Secondly, the dielectric constant \((\varepsilon)\) decreases [19] significantly facilitating stronger electrostatic interactions between charged segments (both intra and inter) of gelatin molecules. The strength of electrostatic interactions between two oppositely charged particles increases as \( \varepsilon^{-3/2} \) at a given temperature as per the Debye-Hückel theory [20]. Since, the solution pH was close to the iso-electric point of gelatin, there is no net charge on the polypeptide. Nonetheless, as mentioned already, the chemical structure of this biopolymer indicates almost 1:1 positive and negatively charged patches on this linear random coil molecule. These overlap as the chain contracts due to the decrease in the Flory-Huggin’s solute-solvent interaction [21] brought in by the presence of ethanol resulting in bringing charged segments to each other’s vicinity through electrostatic interactions yielding chain collapse.
5.2.3 Rheology of the solution

Structure evolutions (disintegration and reformation of structures) are not instantaneous, which gives rise to thixotropy. There are several model methods to evaluate thixotropy parameter for a given complex fluid. The rheology data was fitted to Herschel-Bulkley, Cross, Power law and Carreau models [22] but the model that provided the best data fitting was Cross model, defined as:

\[
\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (c \gamma)^d}
\]

where \( \eta_0 \) and \( \eta_\infty \) indicate zero and infinite shear rate viscosities, \( c \) is consistency coefficient and \( d \) is rate index. However, the Cross and Herschel-Bulkley models gave identical thixotropy values. The software provided by T.A. Instruments, UK was used for all the data analysis reported here.

Figure 5.9: Variation of solution thixotropy as function of ethanol concentration for aqueous solutions with and without gelatin. Notice that presence of ethanol increases the solution thixotropy significantly.
Figure 5.10: Variation of solution viscosity at infinite frequency as function of ethanol concentration for aqueous solutions with and without gelatin. Notice that presence of ethanol increases the solution thixotropy significantly and close to ethanol concentration =45±2% v/v there is a dip in the viscosity value. This is the region where fractal aggregates are formed on hydrophilic substrates.

Figure 5.11: Comparison of solution viscosity at infinite frequency as function of ethanol concentration for aqueous gelatin solutions. Notice that solution thixotropy rises close to ethanol concentration =45±2% (v/v) where there is a dip in the viscosity value. This is the region where fractal aggregates are formed on hydrophilic substrates.
The thixotropy evaluated from shear stress versus shear strain data is plotted as function of ethanol concentration in Figure 5.9, which reveals shear thinning or pseudoplastic fluid features. The thixotropy of the ethanol-water binary mixture decreases with increased ethanol concentration and reaches a minimum at an ethanol concentration $\approx 45\pm3\%$ (v/v). Beyond this, the thixotropy value rises again. When gelatin was added as a third component the thixotropy fell by typically 20% of its value compared to that of ethanol-water binary mixture value. Regardless, the minimum was still located at an ethanol concentration $\approx 45\pm3\%$ (v/v). The infinite viscosity versus shear rate plot is given in Figure 5.10 for various ethanol concentrations, which again exhibits pseudoplasticity. Shear thinning, which is the essential feature of many complex fluids is clearly seen here and this arises from the elongation of the structures along the direction of the shear. The $\eta_\infty$ of the ethanol-water binary mixture increases with increased ethanol concentration and reaches a maximum at an ethanol concentration $\approx 45\pm3\%$ (v/v). Beyond this, the $\eta_\infty$ value falls.

When gelatin was added as a third component the $\eta_\infty$ increased by typically 50% of its value compared to that of ethanol-water binary mixture value. Regardless, the maximum was still located at an ethanol concentration $\approx 45\pm3\%$ (v/v). The rate index parameter $d$ that defines the sharpness of viscosity change typically varied in the narrow range 0.6-0.8 for all the solutions regardless of the presence of gelatin (for pure water $d \approx 0.75$). The consistency coefficient $c$ on the other hand remained close to 3.5 for solutions (which is the pure water value) with gelatin whereas for water-ethanol mixtures the same was an order of magnitude larger. This implies that the presence of ethanol does change viscoelastic nature of the solution rather significantly. The infinite shear rate viscosity ($\eta_\infty$) was found to be very sensitive to ethanol concentration and this is shown in Figure 5.11 along with the corresponding thixotropy values. Note that close to ethanol concentration $\approx 45\pm2\%$ (v/v), thixotropy shows a minimum whereas $\eta_\infty$ shows a maxima. We could not get reproducible zero shear rate viscosity ($\eta_0$) values. Since, gelatin molecules are several orders of magnitude larger in size than ethanol molecules energetically hydrogen bonding between ethanol and water will be more favourable. This results in the formation of hydrogen bonded ethanol-water clusters that support thixotropic behaviour. It is plausible that at this specific concentration of ethanol, the stoichiometric condition for maximum
hydrogen bonding between alcohol and water molecules is achieved. The observed thixotropy reflects the disintegration and reformation of such hydrogen-bonded ethanol-water structures.

5.3 Conclusions

It has been shown that the binary liquid mixture of ethanol and water exhibit maximum hydrogen bonding at ethanol concentration = 45±2% (v/v) which is supported by thixotropic and viscosity data. This provides the appropriate thermodynamic environment for the gelatin molecules to form self-assembled clusters of fractal dimension ≈ 2.6 in the bulk (3-d) and 1.7 on surfaces (2-d). We have proposed a RSA model for surface aggregation of gelatin because of the following reasons. Exposing a surface to a polymer solution (polydispersity assumed) containing adsorbable polymer molecules and aggregates creates an instantaneous non-equilibrium situation. Thermodynamically, the larger particles have a higher surface affinity because they make more surface contact per molecule. Since, the free energy of hydration is also negative larger particles on the surface are preferred. However, due to their higher diffusion coefficients smaller particles will reach the surface first and there will be a propensity of these initially on the substrate. Once these reach the surface there is kinetic rearrangement of the particles to minimize the total surface free energy of the adsorbed solution layer. At equilibrium the smaller particles are desorbed and coalesce into the larger particles to minimize free energy of hydration. In the present case, the selective evaporation of ethanol does expedite this process and various micro-structures evolve with time. The size polydispersity imparts randomness to the whole process, which is a necessary condition of RSA. Above constitutes a generalized description of RSA model [5, 6] and this is exactly what was observed in our 2-d experiments. Specifically, the fractal aggregates formed on hydrophilic surfaces followed random sequential adsorption kinetics with the initial particle size distribution given by a power law. These aggregates followed a sequence of morphological time dependent changes, driven by selective but slow evaporation of ethanol, to yield several types of self-organized aggregates. Surface tension does play a role here, which needs to be explored.
The aggregation in the bulk of the solution appears to be an anomalous process and could be explained through Smoluchowski aggregation model albeit qualitatively. It gives a DLA type fractal dimension to the cluster but shows extremely low polydispersity, which in fact is a signature of a slowly growing RCA aggregate. The coherent picture that emerges is: (i) at this specific alcohol-water mixture, the hydrogen bonding between the two liquids is at its maximum; (ii) since such a solvent is a marginal one for gelatin, which is a linear random coil polymer, the charged segments of this polyampholyte overlap due to electrostatic attractions leading to contraction of the chain. This can be both inter or intra molecular, which results in the formation of fractal aggregates. In the bulk this produced aggregates of narrow particle size distribution; (iii) morphological evolution of aggregates on hydrophilic surfaces owe their origin to selective evaporation of ethanol that leads to solvation instability of the gelatin molecules and the concomitant optimization of sharing of available solvent.
5.4 References


