Chapter Six
Surfactant induced softening in gelatin hydrogels
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6.1 Abstract
Effect of binding of three surfactants, alpha olefin sulfonate (AOS, anionic), Triton-
X100 (TX-100, non-ionic) and cetyl trimethyl ammonium bromide (CTAB, cationic) to the hydrogels of gelatin was studied at room temperature (25°C) by dynamic light scattering and oscillatory rheology with surfactant concentrations (20-100mM) much larger than the critical micellar concentrations (cmc) of these surfactants. The measured intensity auto-correlation function of light scattered from gels revealed the presence of finite heterodyne contribution ≈0.11±0.01 that increased to ≈0.25±0.02 after transition to the soft gel state indicating a softening process for surfactant concentrations exceeding 50mM. The dynamic structure factor S(q,t) of micelle bound gelatin gels revealed two clearly identifiable relaxation modes namely; the fast mode, S(q,t) ∼ exp.(-Dq^2t) for t ≤ 1ms and a stretched exponential mode, S(q,t) ∼ exp.-(t/τc)^β for 1ms ≤ t ≤ 1s. This behavior was universal with β≈ 0.85± 0.04 independent of the surfactant type. The low-frequency (1.5 rad/s) storage modulus G', loss modulus G'' and tanδ behavior revealed a gradual softening of the gel independent of the surfactant type. The exponent (β) fast mode diffusivity (Df) and stretched exponential mode relaxation time were found to be less sensitive to this softening transition.
6.2 Introduction

Gels are a novel state of matter, which have properties like a viscoelastic solid. A number of polymers and polyampholytes can form gels without chemical cross-linking. These are called physical gels, almost all bio-polymeric gels are physical gels [1]. In physical gels like that of gelatin, a three-dimensional interconnected network of polymer chains is formed in the dispersion medium, which is held together by intermolecular hydrogen bonding. The physical gels achieve solution stability through an array of possible secondary forces, like hydrogen bonds, van der Waal forces, dipolar interactions and hydrophobic interactions etc. The fluidity and elasticity of such gels become a matter of time scales of the observations relative to the lability of these interactions, which are amenable to modifications through selective binding to micelles among other possibilities [2]. On the other hand, formation of micelles is a strictly free energy driven process. These are formed of surfactant molecules through self-organization and these interact with polyelectrolytes in a characteristic manner, which are discussed at length in the past though largely for sols [3-6]. The complexation of micelles with a polyampholyte molecule like gelatin, which is an amphoteric polypeptide with a sizable hydrophobic domain, necessitates a closer look. The gel of this biopolymer is known to bind to various types of surfactants modifying the gel state properties rather significantly [7-9]. Gelatin, a polyampholyte obtained from denatured collagen, is a polypeptide and is an ideal case for such studies. It can play host to surfactants that are anionic, cationic or non-ionic because of its unique structure. Aqueous solution properties of gelatin have been well studied and characterized in the past [10,11]. Depending on the process of recovery the gelatin molecules bear different physical characteristics. Type-A gelatin is acid processed, has an isoelectric pH, $pI \approx 9$ whereas the alkali processed type-B gelatin has $pI \approx 5$
The monomeric representation of this polypeptide is \( (\text{Gly-X-Pro})_n \), where X is an amino acid. The detailed chemical composition of this biopolymer is as follows (as per Sigma technical index, pH = 7.0): Glycine constitutes 26\%, alanine and arginine are in 1:1 ratio together constitute \( \approx 19\% \), proline is \( \approx 15\% \), glutamic acid and hydroxyproline are in 1:1 ratio constituting \( \approx 22\% \), aspartic acid \( \approx 6\% \), lysine \( \approx 5\% \), valine, leucine and serine constitute \( \approx 2.0\% \) each, rest 1\% is comprised of isoleucine and threonine etc. Thus the gelatin chain has \( \approx 12\% \) of length that is positively charged (lysine and arginine), \( \approx 16\% \) of length that is negatively charged (aspartic and glutamic acid) and about \( \approx 53\% \) (glycine, proline and hydroxyproline) its chain length is non-ionic leaving about \( \approx 16\% \) of the chain length to be hydrophobic. Thus the positively charged, negatively charged and hydrophobic stretches exist with almost 1:1:1 ratio, which makes this molecule special.

As far as studying relaxations in pure gelatin gels is concerned, dynamic light scattering (DLS) has been routinely used in the past in the testing and refinement of predictions from scaling theory pertaining to relaxations phenomena in gels [13-18]. Statistical analysis of DLS data obtained from gelatin gels has seen plenty of divergence in the past. Some indicative reports are discussed in the following. Amis et al [14] and Borsali et al [15] observed a single relaxation mode, which was interpreted as the gel mode relaxation. Time-resolved DLS studies of Okamoto et al [13] revealed a single mode relaxation in the gel state too. The corresponding gel mode diffusivity was \( \approx 5 \times 10^{-7} \text{ cm}^2\text{s}^{-1} \). Two-mode relaxations comprising a fast mode (diffusivity \( D_f \approx 10^{-7} \text{ cm}^2\text{s}^{-1} \)) and a slow mode (diffusivity \( D_s \approx 10^{-8} \text{ cm}^2\text{s}^{-1} \)) were reported by Cho et al [19], Oikawa et al [20] and Sharma et al [21]. Three-mode relaxations in gel phase was observed by Ren et al [16] and Maity et al [22], which comprised three types of
relaxation processes; the diffusive fast mode followed by a power law relaxation behavior in an intermediate time domain and a stretched exponential decay at longer time scales. Brown et al [17] and Ren et al [18] illustrated that the contention of self-diffusion giving a raise in slow mode relaxation was incorrect. The situation is further clouded by the fact that scattering signal from gels contains finite heterodyne contribution [23]. In addition the gel state keeps evolving with time (making the system non-ergodic) to minimize free energy which immediately makes the derivation of $S(q,t)$ from measured intensity correlation function non-trivial (Siegert relation remains invalid here) [23]. Many works reported in the literature did not take this into account in their data treatment. Secondly, there seems to be over reliance on the relaxation time distribution analysis, which is obtained through inverse Laplace transformation of the measured correlation function. Since this is a numerical procedure involving statistical routines this can often produce ghost modes in the relaxation time spectrum even for small fluctuations in the baseline of the data. This is clearly shown by Okamoto et al [13].

Structural properties of gels can be altered through binding with micelles among others. Interaction of gelatin solutions to micelles has been studied in the past and some reports on binding of gelatin molecules to surfactants at low a concentration has been reported [24-28]. On the other hand, systematic rheological measurements to explore micelle bound gels at high surfactant concentrations have been few and far between in the literature though surfactant induced thickening of gelatin solutions has been reported [28]. Two questions are pertinent here. Is the relaxation behavior observed in micelle bound gelatin gels universal? And, is the micelle bound gel structurally different from a normal gel? In this work, we have studied the binding of
three different types of surfactants to this biopolymer in an attempt to address the questions raised. In an earlier work [24], we studied the binding of surfactants to gelatin in the dilute solution phase of the biopolymer (0.5% w/v) which is being extended to the gel state (5% w/v) with non obvious conclusions and observation of surfactant induced phase transition of the gel to a structural liquid-like phase. Again, at low surfactant concentrations (≤ 50mM) these gels do not undergo any such transition [22].

The DLS experiments were mostly carried out at a fixed scattering angle of 90° though for elucidation of q-independence of diffusivity (fast mode) some representative experiments were performed with varying scattering angles. The issue of non-ergodic scattering from gels does cause concern at smaller scattering volumes. In our experiments, we did not focus the laser beam onto the sample deliberately to maintain a larger scattering volume, thus ensuring ergodicity in all DLS measurements.

The normalized intensity correlation function, \( g_2(q, t) \), obtained from the gel state scattering can be related to the structure factor, \( S(q, t) \), as [21, 23]

\[
g_2(q, t) = 1 + \beta' \left[ 2X(1-X) S(q, t) + X^2 |S(q, t)|^2 \right] \tag{6.1}
\]

where \( \beta' \) is the coherence area factor having a maximum value of 1 and defines the signal-to-noise ratio in experiments. The parameter \( X \) (0 ≤ X ≤ 1) defines the amount of heterodyne contribution present in the correlation data. Eq. (6.1) accounts for the heterodyne contribution buried in the measured data in a measurable way. Both \( \beta' \) and \( X \) are measurable parameters. The measured intensity auto-correlation data was analyzed exactly following the description given in refs. [21, 23]. For the gels, we
found $X \approx 0.11 \pm 0.01$, independent of the sample. Thus the pre-factor of the linear term in $S(q, t)$ in Eq. (6.1) is close to 20 times larger than the quadratic second term. This gave

$$S(q, t) = \frac{[g_2(q, t) - 1]}{[2\beta X(1-X)]}$$

(6.2)

For surfactant concentration $\approx 75$ mM the value of heterodyne parameter increased to $X \approx 0.25 \pm 0.02$ (see Figure 6.1). The pre-factor of the first term in Eq. (6.1) is still $\approx 10$ times larger than the same of the quadratic term. This justified usage of Eq. (6.2) for all our data. Any error thus accrued is absorbed as experimental error in subsequent data analysis.

While we rejected the effective diameter values (calculated from cumulant analysis), the $S(q,t)$ data was fitted to NNLS, CONTIN and two-exponential fitting subroutines to evaluate the Laplace inversion of the correlation function data [29]. Reproducible and robust results were obtained from NNLS (non-negatively constrained least squares [29]) fitting only. CONTIN analysis failed to yield statistically consistent results from sample to sample while the two-exponential model often gave delta-function like distribution to the relaxation time spectrum. The relaxation time distributions thus obtained are shown in Figures 6.2. In order to avoid over dependence on the Laplace inversion method, independently, unsuccessful attempt was made to fit the structure factor data to a single exponential and also to a three-relaxation mode model with the intermediate mode being a power-law mode. This gave credence to the applicability of a two-mode relaxation process to the $S(q,t)$ data. Having confirmed this all $S(q,t)$ were least-squares fitted to the functional form

$$S(q, t) = A \exp(-D_f q^2 t) + (1-A) \exp[-(t/t_c)^\beta]$$

(6.3)
Where, the fast (diffusivity $=D_f$) and slow modes (relaxation time $=\tau_c$) follow exponential and stretched exponential relaxation respectively. Here $A$ and $\beta$ are independent of $q$ but not $\tau_c$. However, the $q$ dependence of slow mode relaxation time was not explored in the present experiments. The correlation data was analyzed through user defined least-squares fitting routines of Sigma Plot software (SPSS, USA). The $S(q,t)$ data was split as follows:

$$S(q,t) = \begin{cases} 
\exp(-D_f q^2 t); & t \leq 1\text{ms} \quad \text{fast mode} \\
\exp(-t/\tau_c\beta); & 1\text{ms} \leq t \leq 1\text{s} \quad \text{slow mode}
\end{cases}$$

These relaxation domains will be discussed in details in the next section.

![Graph showing the evolution of the heterodyne parameter, X, as a function of surfactant concentration measured at 25°C. Gelatin concentration was 5% (w/v). Notice that variation in X was independent of surfactant type.](image)
Figure 6.2: Relaxation time distribution obtained from the Laplace inversion of the measured intensity correlation function via NNLS statistical analysis for various concentrations of AOS. The gelatin concentration was 5% by weight. Notice that the structure factor contained two relaxation modes differing in relaxation time by a decade approximately.

6.3 Results and Discussions

It has been presumed in this analysis that addition of surfactant did not alter the osmotic pressure of the surfactant-free gel. Gels have frozen heterogeneities that work as local oscillators and give finite heterodyne contribution to the detected scattered intensity. This is reflected in the X parameter introduced in Eq.(6.1). Our
measurements gave $X = 0.11 \pm 0.01$ independent of surfactant type or concentration (Figure 6.1). As the surfactant concentration was increased beyond 50mM the $X$ parameter recorded a two-fold increase ($X = 0.25 \pm 0.02$). It has been shown earlier [21, 23] that as a gel melts and a sol state evolves $X$ slowly recovers its limiting value 1 (full homodyne). It may be argued that the enhanced scattering due to micelles immobilized on the time-scale of the DLS experiments contribute to higher value of $X$ at surfactant concentrations $> 50$ mM. That would not of itself be indicative of a softening process. At higher surfactant concentrations it is possible that the density of intra-molecular hydrogen bonding between gelatin molecules (that helps in forming triple helices) reduces because of steric hindrance offered by these micelles that are present in abundance close to the vicinity of gelatin molecules. Recall that the concentration of +vely charged: -vely charged: hydrophobic segments present on gelatin backbone (at neutral pH) is in the ratio $= 1:1:1$. So, regardless of the surface charge state of the micelles the propensity of hydrogen bonds will reduce as surfactant concentration is increased. The triple helices are the (mechanically active) stress bearing units of the network implying direct correlation between loss of density of triple helices to same in network rigidity. Thus increase in the value of the $X$ parameter can be construed as equivalent of a softening process.

(i) **Fast mode relaxation**

A typical set of relaxation time distribution data is presented for AOS in Figure 6.2. This has been achieved through Laplace inversion of the measured intensity correlation data following NNLS statistical subroutine. The data clearly reveals the presence of two relaxation modes; one fast with mean relaxation time in milliseconds
and another slow mode with same in tens of milliseconds. The fast mode portion of S(q,t) data were fitted by taking the average value of S(q,t) of those channels where the fast mode almost decayed to a constant value, and this was used as the base line (t~1ms). The S(q,t) data were fitted to S(q,t) ~ exp.(-Γ(q)t) ~ exp.(-Dq^2t), where a single exponential fitting was found to be adequate. The Γ(q) values were found to be consistently linear with q^2 (data not shown) proving that this mode was diffusive. This allowed the diffusion coefficient of the fast mode to be deduced from Dr = Γ(q)/q^2.

Figures 6.3-6.5 depict the dependence of fast mode diffusivity on surfactant concentration for various surfactants. The fast mode distribution remains relatively independent of AOS concentration (Figure 6.3). The corresponding fast mode diffusivity value was Dr ~ (0.11±0.01) x 10^{-7} cm^2/s for AOS independent of surfactant concentration. In case of TX-100 this increased smoothly from (0.40±0.03) x 10^{-7} cm^2/s at 25mM to (0.50±0.03) x 10^{-7} cm^2/s at 100mM of surfactant concentration (Figure 6.4). The corresponding variation in Dr was from (0.10±0.01) x 10^{-7} cm^2/s to (0.16±0.02) x 10^{-7} cm^2/s for CTAB (Figure 6.5). For surfactant free gel Dr ~ (0.09±0.01) x 10^{-7} cm^2/s which compares rather well with the same for low surfactant containing gels where the surfactants were ionic. On the other hand gels containing TX-100 surfactant did exhibit significant increase in values of fast mode diffusivity indicating profound hydrophobic interactions. The increase in the fast mode diffusivity is ascribed to corresponding change in mesh size (ξ), which is discussed in the following.

It is worthwhile to ponder over the origin of this mode. If one derives an equivalent correlation length (ξ) corresponding to, say Dr ~ 0.1 x 10^{-7} cm^2/s using solvent viscosity η_0 = 1cP from Stokes-Einstein relation Dr = k_B T/(6πη_0ξ), where k_B is
Boltzmann's constant \( k \) and \( T \) is absolute temperature, one gets a value for \( \xi \) of the order of \(-200\) nm. This is comparable to the size of the triple-helices present in gelatin gels [30]. This implies that at low concentration of surfactants (<50mM), the micelles-bound gel network is comprised of sub-units each of which is a triple helix. However, this contention does not preclude the presence of other networks comprising smaller correlation lengths. As the surfactant concentration exceeds 50mM, the order of magnitude of \( \xi \) remains same. This was the case for both the ionic surfactants. For the non-ionic surfactant, TX-100, the mesh size was \( \xi \approx 50\)nm at 25mM and 40nm at concentrations higher than this. Unlike ionic surfactants, TX-100 binding to gelatin molecules is largely hydrophobic in nature. It is interesting to note that though triple helices are present in the TX-100 bound gel system the dynamics is governed by the smaller networks unlike in ionic surfactant case. This is an anomaly that eludes an exact explanation at present.

Figure 6.3: Isochronal plots of storage and loss modulii (\( G' \) and \( G'' \)), dynamic viscosity \( \eta^* \) and gel mode diffusivity \( D_\ell \) as function of concentration of anionic surfactant AOS deduced at \( 25^\circ C \). The gel concentration was fixed at 5% (w/v) in water. Notice the change in slope close to AOS concentration \( \approx 55\)mM, which signals the micelle induced softening of the gel network and its transformation to a soft gel. The smooth lines are guide to eye only.
Figure 6.4: Isochronal plots of storage and loss modulii (G' and G''), dynamic viscosity |η*| and gel mode diffusivity Dr as function of concentration of cationic surfactant TX-100 deduced at 25°C. The gel concentration was fixed at 5% (w/v) in water. Notice the change in slope close to TX-100 concentration ≈55mM, which signals the micelle induced softening of the gel network and its transformation to a soft gel. The smooth lines are guide to eye only.

Figure 6.5: Isochronal plots of storage and loss modulii (G' and G''), dynamic viscosity |η*| and gel mode diffusivity Dr as function of concentration of non-ionic surfactant CTAB deduced at 25°C. The gel concentration was fixed at 5% (w/v) in water. Notice the change in slope close to CTAB concentration ≈55mM, which signals the micelle induced softening of the gel network and its transformation to a soft gel. The smooth lines are guide to eye only.
(ii) Slow mode relaxations

The slow mode relaxations were present in all gel samples (see representative data for AOS in Figure 6.2). For times $1 \text{ms} > t > 1 \text{s}$, the measured dynamic structure factor $S(q,t)$ exhibited stretched exponential behavior represented by

$$S(q,t) \sim \exp \left( -\frac{t}{\tau_s} \right)^\beta$$

(6.5)

with the slow mode decay time constant $\tau_s$ given by

$$\tau_s = \frac{\tau_c}{\beta} \frac{\Gamma(1/\beta)}{}$$

(6.6)

where $\beta$ is the stretching exponent and describes the width of the distribution of relaxation times and $\Gamma(1/\beta)$ is the gamma function. Stretched exponential mode of data fitting to the entire set of samples yielded $\beta = 0.85 \pm 0.04$ invariant of concentration and the surfactant type (Figure 6.6). The relaxation time $\tau_s$ decreased smoothly by $\approx 100\%$ with increase in surfactant concentration independent of ionic nature of surfactants whereas for TX-100 samples this change was minimal.

The origin of stretched exponential regimes has been attributed as anomalous Gaussian diffusions in the past [31]. The slow mode diffusivity seen in gels often referred to as anomalous diffusion has not found a satisfactory explanation yet though such behaviour has been observed systematically in many DLS experiments. The origin of stretched exponential has been attributed to the inter mode coupling effects prevailing in constrained or interacting systems [32]. In the semi-empirical
approximation, the coupling model allows dynamic constraints to come into play at long time scales and it manifests itself in giving rise to fractional decay of dynamic structure factor, $S(q,t)$, though this does not identify the specificity of the mechanism of interactions responsible for coupling. However, this description has been very effective in describing complex relaxations [32]. In this work, Ngai and Rendell [32] have clearly shown that anomalous diffusion in disordered fractal-like systems can be adequately described through this model. In another treatment, the slow mode has been ascribed to the motion of clusters of polymer strands inside the crowded gel network [33].

It can be qualitatively argued that a pure gelatin gel is more solid-like because of the presence of strong excluded volume interactions, which will make the viscous relaxations difficult because of topological constraints and hence, would reveal a slower relaxation. On the contrary, in a gel that is devoid of such interactions and topological constraints will permit rapid viscous relaxation of the network (we call it a softening process). So when a gel undergoes softening the network relaxation time will decrease, which has been observed in these studies, though not appreciably (Figure 6.6). We shall not discuss this any further with the comment that possibly a hierarchically constrained dynamics where the relaxation time at any stage depends on its precedent in a constrained way would provide an adequate description of the observed relaxations in stretched exponential regime.
Figure 6.6: Plots of the scaling exponent \( \beta \) (closed symbols) and slow mode relaxation time \( \tau_s \) (open symbols) as function of concentration of surfactants deduced at 25°C. The gel concentration was fixed at 5% (w/v) in water. Notice the smooth change in slope of \( \tau_s \) close to surfactant concentration \( \approx 55 \text{mM} \), which signals the micelle induced softening of the gel network and its transformation to a soft gel. The scaling exponent remained invariant of this transition. The smooth lines are guide to eye only.

(iii) Rheological studies

Some representative values of measured frequency dependent storage and loss modulii are plotted in Figure 6.7 performed on a typical surfactant AOS bound to gelatin gel. The low frequency (1.5 rad/s) values of \( G' \), \( G'' \) and the associated dynamic viscosity \( \eta* \) =\([G'^2(\omega)+G''^2(\omega)]^{0.5}/\omega \) values are plotted together for comparison in Figures 6.3-6.5. An approach to model visco-elastic systems with a distribution in relaxation times is through assigning a power-law dependence to the stress relaxation modulus \( G(t) \), and is given as [34]

\[
G(t) \sim t^\Delta
\]  

(6.7)

In the oscillation mode \( G(t) \) or its frequency dependent equivalent \( G(\omega) \) break down to \( G'(\omega) \) and \( G''(\omega) \) with
\[ G'(\omega) \text{ and } G''(\omega) \sim \omega^{\Delta} \] 

(6.8)

For the sake of discussion, we shall express the exponents of \( G' \) and \( G'' \) as \( \Delta' \) and \( \Delta'' \) respectively. Owing to instrumental limitations the frequency range scanned was limited which did not permit exploration of detailed fundamental structure of the gel network. Thus the discussion of rheological data is largely qualitative. For a thermally reversible gel probed on a time-scale much shorter than the network rearrangement time, one expects linear viscoelastic behaviour implying \( G'' \sim \omega \), which was not observed in our studies as revealed in Figure 6.7 (b). The low frequency slopes of \( G'(\omega) \sim \omega^{\Delta'} \) was found to have a value \( \Delta' \approx 0.15 \) for low surfactant concentrations (<50 mM) that increased to \( \approx 0.36 \) (Figure 6.8). A low exponent signifies solid-like behaviour of the material and an increase in this indicates transition to a less solid-like state. This combined with the tan\( \delta \) plot clearly implies the transition of the micelles bound gel (at surfactant concentrations <50mM) to a softened gel state (for surfactant concentrations >50mM). For a Maxwell visco-elastic substance the exponents \( \Delta' \) and \( \Delta'' \) are exactly 2 and 1 respectively in the low frequency domain of experiments [35]. For all the surfactants similar observations were made. Experimental data for pure gelatin samples has shown that the power law exponent assumed values in the range 0.6-0.8. Our measurements for pure gelatin sample gave \( \Delta' \approx \Delta'' \approx 0.8 \).

Rouse's theory [36] of visco-elastic relaxation with the assumption of no hydrodynamic interaction between the motions of sub-molecular junctions, corresponding to the free-draining limit is characterized by an average friction felt by a sub-molecular unit (crosslink). The internal viscosity arising from intra-molecular friction is neglected in this analysis [33]. Blizard's ladder network model captures the Rouse's prescription and postulates that the storage and shear modulii exhibit
exponents $\Delta \approx 0.5$ at high frequency (visco-elastic response) and $\Delta' \approx 2$ and $\Delta'' \approx 1$ at low frequency (liquid like response) [37].

The deviations from predicted values grow larger as the solvent component is increased and this also reveals the failure of Rouse's concept of attributing an average friction coefficient to the cross-links (sub-molecules). The failure is due to the fact that at shorter time scales which reflect modes of motions with short-range configurational changes corresponding to the rearrangement within a sub-molecule which is beyond the scope of Rouse's model. The exact description of shorter time scale features calls for a more detailed picture of the local motions of polymer segments. It can be argued that the micelle-bound gel system will be rich in short-time scale dynamics, which the Blizard's model fails to capture. Hence, the observation of small slopes is not surprising. Further extension of this model to the other extreme of un-crosslinked solutions reveals (at low frequency) the following scaling relations [37]

$$G' \sim \omega^0 \text{ and } G'' \sim \omega^1$$

(solid like) \hspace{2cm} (6.9)

The rheology data (Figure 6.9) indicate qualitative agreement with the essential features imbibed in Eq. (6.9). When a gel represented by Blizard's ladder model is fully melted to a sol state the value of $\Delta$ which had a very small value for a gel increases to 2 for $G'$ and increases to 1 for $G''$. Figure 6.9 reveals that the exponent for $G''$ increases from 0.15 (surfactant concentration <55 mM) to 0.36 (surfactant concentration > 55 mM) indicating softening in Blizard's model. Here $G'$ increases from 0.17 to 0.25 for the above mentioned surfactant concentrations. Regardless, it
supports the conclusions drawn earlier and reiterates that one definitely has a
softening from gel to another phase that still has a significant storage modulus. This
state has been speculated to be a soft gel state due its high G' value. The data for G'
could not be obtained at smaller frequency values because of instrumental limitations,
which did not permit evaluation of an anticipated terminal response G_e. Nevertheless,
at least a 10-fold decrease in the value of G_e with increasing surfactant concentration
was observed (Figures 6.3-6.5) at the lowest ω.

Such an observation is further strengthened when one looks at the low frequency
(ω=1.5 rad/s) features of G', G'' and |η*| shown in Figures 6.3-6.5 which are quite
revealing. One consistently observes smooth decrease in the values of both the
moduli and the dynamic viscosity close to surfactant concentration alike a softening
transition. The dynamic viscosity essentially captures the combined effect of both G'
and G'' as far as the evolution of a more liquid-like phase from a solid-like gel is
concerned as in the present case. The effective viscosity of a spherical particle
diffusing inside a polymer matrix (gel) would have a value that is orders of magnitude
larger as the particle size is varied from nanometers to few hundred nanometers as
easily can be seen from Stokes' law. Kuhn has argued that the increase in the effective
viscosity with size of the diffusing particle is analogous to the increase in dynamic
viscosity with decreasing frequency [35, 36]. Because such a situation mirrors the
configurational rearrangement correlated over increasingly large length scales. The
dynamic viscosity data is shown in Figure. 6.9a agrees with the Kuhn argument rather
well. The values of |η*| show increase with decrease in the angular frequency
implying that presence of micelles inside the gelatin network does induce
configurational rearrangement that is transient (possibly) in nature (Figure 6.9a).
Correspondingly, the $\tan\delta = G''(\omega)/G'(\omega)$ would systematically increase at a given frequency, if the Kuhn contention were valid. This was indeed clearly observed as seen from the data in Figure 6.9b.

Figure 6.7(a): Plots of storage modulus ($G'$) as function of frequency for various concentrations of anionic surfactant AOS deduced at 25°C. The gel concentration was fixed at 5% (w/v) in water. Notice the sharp decrease in magnitude of $G'$ between AOS concentration ~50mM and 75mM, which signals the micelle induced softening of the gel network and its transformation to a soft gel. See text for details.

Figure 6.7(b): Plots of loss modulus ($G''$) as function of frequency for various concentrations of anionic surfactant AOS deduced at 25°C. The gel concentration was fixed at 5% (w/v) in water. Notice the sharp decrease in magnitude of $G''$ between AOS concentration ~50mM and 75mM, which signals the micelle induced softening of the gel network and its transformation to a soft gel. See text for details.
Figure 6.8: Plots of low frequency exponents of storage and loss modulii (G’ \sim \omega^A and 
G'' \sim \omega^{A''}) , and tan \delta as function of concentration of anionic surfactant AOS deduced at 
25^\circ C. The gel concentration was fixed at 5% (w/v) in water. Notice the change in 
slopes close to AOS concentration \approx 55mM, which signals the micelle induced 
softening of the gel network and its transformation to a soft gel. The smooth lines are 
guide to eye only. The inset shows the percentage loss in rigidity as function of AOS 
concentration. See text for details

(iv) Structure of the micelle-bound gel phase

Theory of rubber elasticity extended to networks (physical cross-links) predicts that 
the magnitude of G’ at low and moderate frequency is directly related to the density 
of mechanically active and reversible physical cross-links [33]. The effective volume 
occupied by the network in the continuous medium is given by G''. Let us develop a 
coherent picture from the data. Figures 6.3-6.5 indicate that, typically at the cross-
over surfactant concentration \approx 55mM there is a gradual transition to a high 
configurational entropic state that has lower dynamic viscosity, and low storage and 
loss modulii. Figure 6.6 implies a smooth reduction in the slow mode relaxation time 
(\tau_x). The exponents of G’ and G’’ show increase in their values beyond this cross-over 
surfactant concentration coincident with the sharp increase in the value of tan \delta, 
which is clearly shown in Figures 6.9(a, b). All these collectively indicate that beyond 
the cross-over concentration the micelle-bound gel phase gains significantly in 
fluidity which was denied earlier to the gel network due to the presence of a rigid
triple-helical intertwined network of a much lower entropic state. This is alike a softening process except that gel-micelle interactions play the role of temperature. It is possible to conjecture the following. When the surfactant added gelatin sol is cooled from 50°C to room temperature there is a competition between gelation and micellization phenomena. Since, gelation involves formation of triple helices and subsequent reorganization is a slow process [39] whereas micellization being a free energy driven process is faster. Thus it is reasonable to argue that micellization occurs first which is followed by binding of the free micelles to gelatin chains (recall that it has positive, negative and hydrophobic binding sites). In this process some chains get bound preferentially and can still be part of the triple helical structure, which is a precursor to gelation. For these molecules the micelles act as junction points (crosslinks) and a network structure evolves. Simultaneously, the segments of gelatin chains that are free of any binding go on to form a triple helix based physical gel. So, the final structure is a hybrid of the normal gel that is topologically interlinked to a micelle-bridged gel. Such a gel will be weaker than a normal gel having a propensity of triple-helices, which is manifested in the significant increase in the value of $G''$ (Figure 6.7b). Depending on the concentration of surfactants one of these two processes dominates. The micellar-bridged gel is known to be a transient gel and manifests itself at higher surfactant concentrations. Crosslinks formed by the micelles act as transient junctions with these junctions being in equilibrium between disruption and re-formation. The lifetime of these crosslinks defines the time scale over which this reorganization occurs. Below the cross-over concentration the physical gel of gelatin prevails. The data presented in this work substantiates such a model. One ignores the presence of mechanically inactive sub-molecules in this analysis and the functionality of the micelle remains vague.
Figure 6.9(a): Plots of dynamic viscosity ($|\eta^*|$) as function of frequency for various concentrations of anionic surfactant AOS measured at 25°C. The gel concentration was fixed at 5% (w/v) in water. Notice the sharp decrease in magnitude of $|\eta^*|$ between AOS concentration =50mM and 75mM, which signals the micelle induced softening of the gel network and its transformation to a soft gel. The low frequency values of this parameter are shown for the three surfactants in Figures. 6.3-6.5. See text for details.

Figure 6.9(b): Plots of tanδ as function of frequency for various concentrations of anionic surfactant AOS measured at 25°C. The gel concentration was fixed at 5% (w/v) in water. Notice the increase in magnitude of tanδ with AOS concentration, which implies the micelle, induced softening of the gel and its transformation to a soft gel. The low frequency values of this parameter are shown for the three surfactants in Figure 6.8. See text for details.
6.4 Conclusion

It has been shown clearly that bonding of micelles significantly changes the structural properties of gelatin hydrogels in a gradual manner. A physically distinguishable surfactant concentration \( \approx 55 \text{mM} \) defines the cross-over point. Below this concentration the hydrogen bonded triple-helix physical network is in abundance. The formation of transient micellar bridges ensues even at 25mM of surfactant concentration but there is still a propensity of triple helices inside the gel structure to give it considerable rigidity. Beyond the cross-over concentration the density of micellar crosslinks increase exponentially and a softening-like behaviour of the gel phase is encountered. It has been mentioned earlier that the storage modulus \( G' \) is a measure of crosslink density. Since the rigidity of the gel owes its origin to the existence of intermolecular hydrogen bonds between peptide linkages of adjacent helix units, the loss of rigidity \( (G') \) can be attributed to the loss of these linkages, which in turn manifests as the gain in micelle-bridged linkages. From Figure 6.7a, it is possible to estimate this loss of rigidity as a function of surfactant concentration with the definition that \( \Delta G' = (G'_0 - G'_s)/G'_0 \), \( (\omega \approx 1.5 \text{ rad./s}) \) where \( G'_0 \) and \( G'_s \) are storage modulii of pure gelatin gel and micelle-bound gel respectively. \( \Delta G' \) reduced by 45%, 65%, 90% and 92% when AOS concentration was 25mM, 50mM, 75mM and 100mM respectively implying a proportionate loss in density of triple-helix based crosslinks. For CTAB these reductions were 62%, 70%, 73% and 80% while for the non-ionic surfactant TX-100 these were 60%, 65%, 70% and 80% respectively (see Figure 6.8 inset). The cross-over concentration refers to surfactant concentrations that induce softening of more than 70% (typically chosen as \( 100/\sqrt{2} \approx 70\% \) ) of rigid crosslinks. These are immediately
replaced by micelles-bridged crosslinks though not in one to one ratio. In fact, though micelle induced softening starts at surfactant concentrations as low as 25mM the intensity of this is really felt only when about 70% of the original crosslinks are destroyed and replaced by transient ones, which occurs at surfactant concentration ≈55mM. The simultaneous shift in the relaxation times could indicate monitoring unequal responses in $G'$ and $G''$ data, which would consequently have bearing on the reported $|\eta^*|$ and tanδ values. This we visualize as the major problem associated with our rheological data. Regardless, the DLS and rheology data together do imply a structural change inside the gel closely associated with increasing surfactant concentration.

The universality seen in the various parameters like exponents $\beta$ and heterodyne parameter $X$ were remarkable. The rheology data supported the light scattering results and were found to be more sensitive to the softening process. The credit for exhibiting the universal relaxation and softening behaviour goes to the biopolymer gelatin, which can bind to anionic, cationic and non-ionic surfactants with almost same affinity due to its unique structure. In a recent work, a master curve for elasticity was established for gelatin samples extracted from biodiversity sources and the data interpreted within the framework of percolation theory [40].

6.5 References


