

Effect of surfactants on polyvinyl alcohol-borax hydrogel: Rheology and thermal aspects

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Addition of the surfactant, sodium dodecyl sulphate well below the critical micelle concentration facilitates cross-linked networks in the polyvinyl alcohol-borax hydrogel, while at a concentration higher than the CMC, surfactant micelles start destabilizing the cross-linking in the gel network. The PVA-borax hydrogel shows an increased elastic behavior, in particular at lower SDS concentration and Maxwellian fluid behaviour at lower concentration of both SDS and TX-100. Inclusion of SDS in the hydrogel also significantly lowers the gel-sol transition temperature.

Keywords: Surfactants, Gel network, Crosslinking, PVA-borax hydrogels, Rheology, Swelling ratio, Sol-gel transition, Surfactants

Polyvinyl alcohol (PVA), a biodegradable water soluble synthetic semicrystalline polymer, acquires special attention because of its delicate properties and wide range of applications as fibre (vinylon), film, in the paper industry, in textile sizing, as a modifier of thermosetting resins, in plywood manufacture, as pressure sensitive adhesives, emulsifier, etc.¹ PVA can form hydrogel by different methods like chemical cross-linker, -irradiation, etc. having various applications including soft tissue replacement, articular cartilage, articular cartilage, artificial skin, wound dressing, drug delivery system, artificial muscles, actuators, etc.² Aqueous PVA-solution can also form hydrogel when subjected to several rounds of freezing-thawing cycles.

The cross-linking of polyvinyl alcohol (PVA) through hydroxyl groups with borax is believed to form aqueous PVA-borate complex or hydrogels³ and undergoes phase change, i.e. sometimes a clear-opaque transition, with increasing boric acid concentration.⁴ Shibayama *et al.*⁵ have observed reentrant behavior of PVA-borate gel at higher borate concentration. Robb *et al.*⁶ also observed that PVA-

borate-gel does not show critical power behavior of frequency dependency of storage and loss modulus at certain ranges of PVA, i.e., 2–6.6 wt% and sodium borate, i.e., 0.5–3.74 wt%, which is different from those reported in literature for most of the chemically cross-linked gels. Hydrophobically modified water soluble polymers may organize into viscoelastic hydrogels indicating the presence of the so-called rubbery plateau in the rheogram.⁷ Under applied oscillatory shear, there exists a certain range of applied frequency (ω) over which the material behaves more like elastic solid (having large storage modulus) than a viscous fluid (having large loss modulus). Generally, for a hydrogel, elastic (storage) modulus has been found to exceed the viscous modulus. The PVA-borax-water system was observed to show a weak gel behavior at temperatures below 30 °C and there is a sol-gel transition around 40 °C (ref. 8). Addition of surfactant can modify behaviors like viscosity, viscoelastic properties, phase transition temperature, etc., of water soluble polymers or the synthesized polymer gels thereof.⁹ The increase in viscosity has been attributed to the expansion of the polymer coils as well as the increased intermolecular interactions between the polymer and the surfactant molecules. Decrease in drastic changes in the phase transition has been observed to depend upon the chemical structure of the surfactant, i.e., hydrophobic chain length and hydrophilic head group.¹⁰

Till date, the study on the effect of surfactant on PVA-borax gel system has not been reported nor attempted. It is, therefore, considered worthwhile to investigate the effect of surfactants, viz., sodium decyl sulphate (SDS) (anionic) and TX-100 (non-ionic) on the behavior of polyvinyl alcohol (PVA)-borax gel.

Experimental

PVA (15,000) was procured from Fluka. Analytical reagent (AR) grade sample of Sodium Dodecyl sulfate (SDS) with purity greater than 99% and borax (disodium tetraborate) were obtained from Loba Chemie, Bombay, while nonionic surfactant, TX-100, $[\text{CH}_3\text{-C}(\text{CH}_3)_2\text{-CH}_2\text{-C}(\text{CH}_3)_2\text{-C}_6\text{H}_5\text{-O}(\text{CH}_2\text{-CH}_2\text{-O})_x\text{-H}]$, where x is 9.5 on an average] was obtained from

Sigma. The SDS sample was purified following standard procedure.¹¹ It was re-crystallized several times from hot methanol, refluxed in diethyl ether nearly for 72 hours through Soxhlet extractor and finally dried under vacuum.

A stock solution of 7.5% (w/v) PVA polymer was prepared by dissolving the polymer in doubly distilled water. The dissolution was carried out by standing the solutions for about 48 h at 25 °C to remove air bubble. A mixture containing 10 mL of 7.5% (w/v) PVA solution and 3 mL of 3% (w/v) borax solution was prepared with constant stirring. The mixture was briefly warmed and kept overnight after which a uniform simple PVA-borax gel was obtained.

Rheological measurements of PVA-borax gels, both in absence and presence of a surfactant were made on a stress controlled AR500 rheometer (TA Instruments, UK).¹² The instrument was equipped with a Peltier system in the range -10 to 99 °C for standard mode and from -20 to 180 °C in the extended mode. The Peltier plate on which the sample was kept has a temperature stability of ± 0.1 °C. The measuring geometry employed in the study was a 20 mm parallel plate arrangement. An equilibration time of 30 min was allowed before taking the measurement for each sample. Measurements were made in the dynamic oscillation mode at 25 °C temperature with appropriate inertial corrections in the angular frequency range 0-100 rad/s.

The swelling ratios of PVA gels were measured gravimetrically in the temperature ranges from 15-60 °C. The hydrogel samples were incubated in deionized water at a constant temperature for at least 12 hours. By recording the weight of a cut piece of the gel before and after ageing, the swelling ratio, S_w , was calculated from the following formula^{1,13}, $S_w = (W_s - W_d)/W_d$, where W_s is the weight of gel after ageing and W_d is the dry weight of the hydrogel.

The sol-gel transition of the polymer gel was measured by ball-drop method.¹⁴ A known amount of the gel was taken in a glass vial of about 10 mm in radius. A stainless steel ball of about 200 mg weight was placed on the top of the gel (all gels prepared were capable of supporting a steel ball). The vial containing the gel was supported externally at a constant temperature and time taken for the ball while crossing between two predetermined marks on the vial was recorded using a stop watch. The experiments of ball dropping were performed at least twice or until there is good reproducibility between the readings.

Results and discussion

In the rheograms, elastic modulus (or storage modulus) represented by G' and viscous modulus (or loss modulus) represented by G'' have been plotted as a function of ω /(rad/s).¹⁵⁻¹⁷ G'' represents a measure of dissipated or lost (as heat) per cycle of sinusoidal deformation, an indication of liquid or viscous behavior. G' on the other hand, is generally taken as a measure of the energy stored in the material and recovered from it per cycle, or, in other words an indication of the solid or elastic character of the material under test. The elastic property of the sample dominates in the region where the G' is greater than G'' while the behavior of the sample is more liquid-like when G'' is greater than G' .¹⁸ The point where the G'' curve intersects with G' curve has been interpreted as an estimation of the relaxation time and is represented by ' τ '.¹⁶

The oscillating rheogram of PVA-borax gels both in absence and presence of a surfactant (SDS or TX-100) at 25 °C are shown in Fig. 1. The surfactants used in this study are SDS and TX-100. SDS is an anionic surfactant having 12 carbon tails attached to the hydrophilic sulphate group, while TX-100 is a nonionic surfactant having hydrophilic polyethylene oxide chain (on average of 9.5 ethylene oxide unit). Anionic surfactants are relatively low cost and employed in most surfactant based formulations and detergents as compared to their nonionic counterparts. The interaction between surfactants and water soluble nonionic polymer are much stronger with anionic-like SDS as compared to nonionic surfactants like TX-100.¹⁰ From the rheogram of PVA-borax gel shown in Fig. 1, it is observed that the dominant elastic nature starts showing around a ' ω ' value of 13. This means that up to a frequency of 13 rad/s G'' is observed to be greater than G' , but beyond this frequency G' starts increases and becomes larger than G'' . This behavior indicates that PVA-borax system expresses its gel-like nature and possesses elastic character beyond this frequency and below this frequency, the viscous character predominates. The presence of either SDS (as monomer) or TX-100 in the PVA-borax system does not change the value of ω at 13 where G' curves starts increasing more than G'' curve to show the gel-like nature of the system. However the presence of SDS micelles tends to inhibit the attainment of elastic nature of the PVA-borax system, since the G' curve intersect the G'' curve only at around ω at ~ 20 (Fig. 1c). The presence

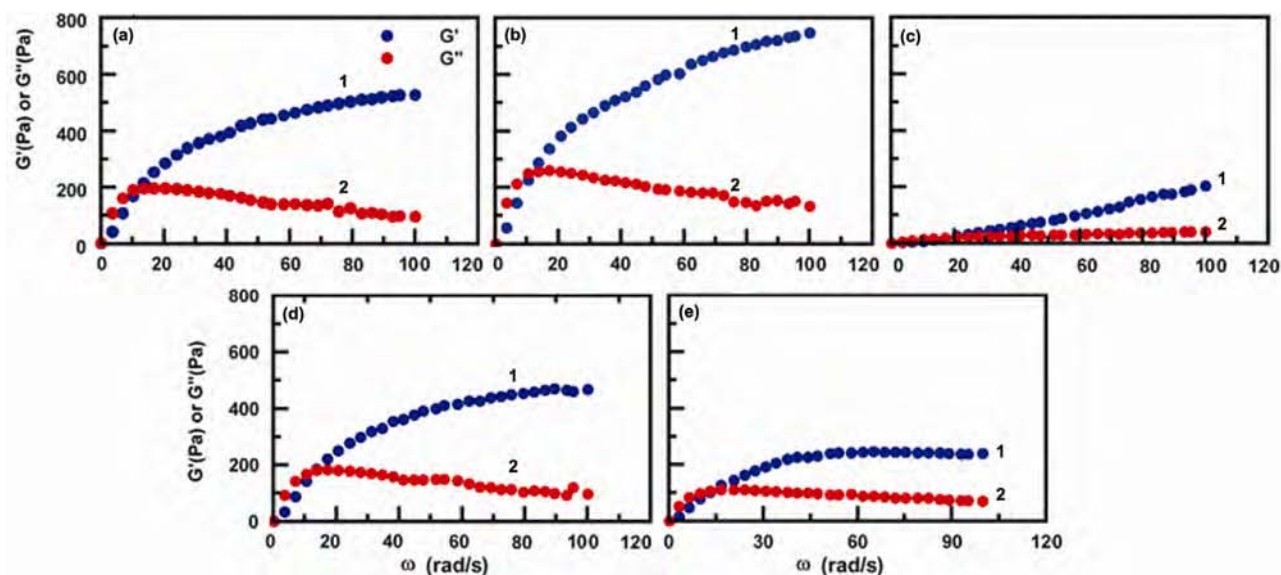
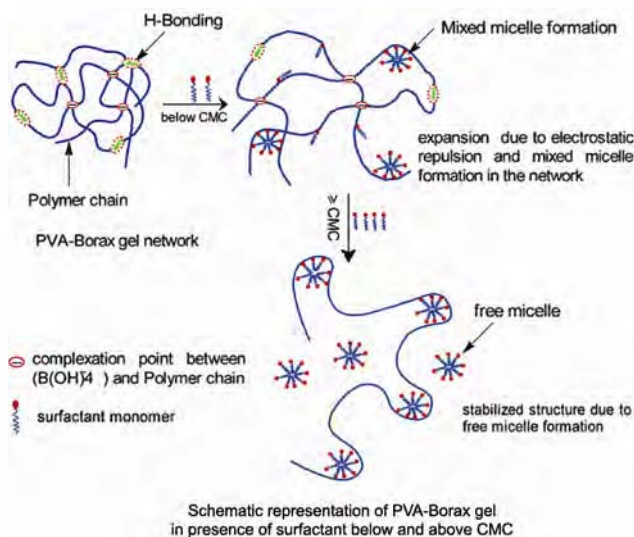


Fig. 1 – Plot of G' (curve 1) and G'' (curve 2) vs ω (rad/s) of (a) PVA-borax gel alone, and, PVA-borax gel in presence of SDS. [(b) 4 mM; (c) 12 mM] and TX-100 [(d) 0.1 mM; (e) 0.5 mM] at 25 °C.

of SDS monomers increases the elasticity of the gels (Fig. 1b), while there is a remarkable decrease in the elastic modulus due to the presence of SDS micelles (Fig. 1c). These observations suggest that surfactant, when present well below their CMC values (as monomer) of the surfactant (SDS), facilitates the cross-linking network of the PVA gels (Scheme 1). This can be explained on the basis that PVA-borax behaves as weak gel having cross-linking network due to the PVA-borax complexation and intermolecular hydrogen bonding.¹⁹ The PVA polymer chains in the gel network possess polyelectrolyte character carrying negative charge due to borate ion ($\text{B}(\text{OH})_4^-$) during complexation. A schematic model of PVA-borax gel network in presence of surfactant is presented in Scheme 1. In presence of SDS monomer, i.e., below CMC, destabilization occurs due to electrostatic repulsion between negative charges of the polymer chains and SDS monomers leading to the expansion and mixed micelle formation, thereby initiating destabilization in the gel network and hence the shear modulus is increased. But at a higher concentration (beyond the CMC), the surfactant micelles apparently start destabilizing the cross linking in the gel network, therefore resulting in decrease in the shear modulus. Such destabilizing effect is also observed in case of the PVA-borax gel in presence of TX-100 (Fig. 1(d & e)), since the presence of TX-100 starts decreasing the elastic modulus even at its lower concentration and the effect is significant at higher



Scheme 1

concentration, i.e., at 0.5 mM. However, relevant literature for comparison could not found.

The presence of a maximum in the G'' curve (loss modulus) along with a plateau in G' curve in the rheogram of PVA-borax gels in 4 mM SDS or 0.1 mM TX-100 in the lower frequency region after crossing relaxation time (Fig. 1b & d) suggests the possibility of the gel system behaving like a Maxwellian fluid.¹⁶ Behavior of this type indicates an energy loss process due to backbone configuration changes which diminishes at higher frequency.¹⁷ In order to have a better understanding of the Maxwellian fluidity, a plot of G'' against G' , which is

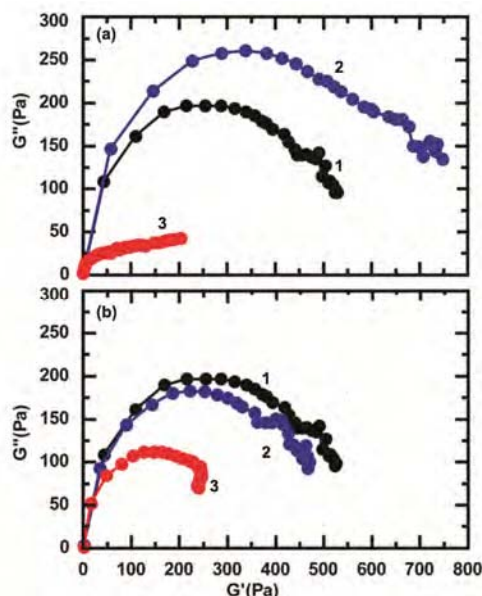


Fig. 2 – Cole-Cole plot of PVA-borax gel in presence of (a) SDS [1, 0 mM, 2, 4 mM, 3, 12 mM], and, TX-100 [1, 0 mM, 2, 0.1 mM, 3, 0.5 mM] at 25 °C.

commonly known as Cole-Cole plot²⁰, for the PVA-borax gels are presented in Fig. 2. For a perfect Maxwellian model, the shape of the plot should be semi-circular.¹⁶ The present results for PVA-borax gels with or without a surfactant did not yield any regular semicircles in the G'' vs G' plots. However, shapes of circular arc pattern are observed up to a certain G' value of the PVA-borax gel and also for the gel in presence of monomers of TX-100 or SDS. This result suggests a strong inter chain coupling or interaction through the adsorbed surfactant, which is in agreement with our earlier observation.

From a number of trial runs on the gels, it was found that the optimum period of incubation for maximum swelling/deswelling of the gels from dry network was observed to be about two hours unlike those of PNIPA gels, which required about 5 days for equilibration.²¹ All the gels under investigation were incubated for more than two hours at a constant weight. As the temperature increased, the gels showed shrinkage, both in size and weight.

The swelling behavior of PVA-borax gels in presence of SDS or TX-100 is presented in Fig. 3. It is obvious from these figures that the swelling behaviour of PVA-borax gels is conspicuous by the absence of any discontinuity. The PVA-borax gels showed a gradual decrease in the swelling with temperature. The smaller value of the swelling ratio at higher temperature within the investigated temperature range

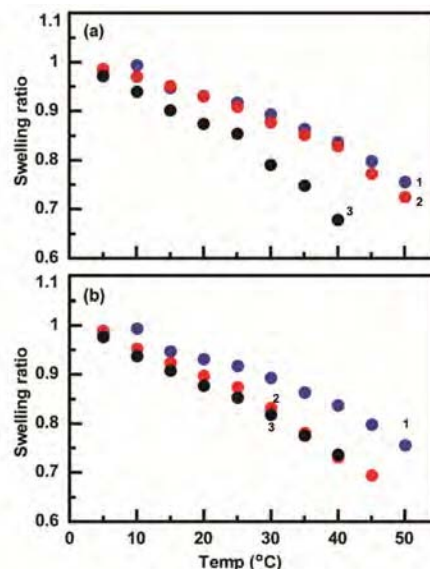


Fig. 3 – Swelling ratio curve showing temperature dependence of PVA-borax gel in presence of (a) SDS [1, 0 mM, 2, 3 mM, 3, 11 mM], and, (b) TX-100 [1, 0 mM, 2, 0.1 mM, 3, 0.5 mM].

is due to the hydrophobic interaction between the surfactant tails and the hydrophobic groups in the gel, which then becomes the dominant character resulting in significant shrinkage of the gel network.²² This hydrophobic interaction is the driving force for the surfactant-gel interaction. At lower temperature the water inside the gel network is highly structured or ordered as a result of hydrogen bonding between water and hydrophilic groups of the polymer. As the temperature increased this structured water is released and the interaction between the hydrophobic groups of the polymer prevailed thus causing shrinkage of the gel. As the hydrophobic interaction occurs inside the gel network, the solvent molecules in the gel network are drawn out of the network which results in the shrinkage of the gel and hence, a smaller value of the swelling ratio at higher temperature.²³ Presence of either SDS or TX-100 led to further decrease in the swelling ratio and the effect is more pronounced in the case of SDS as compared to TX-100. Though there is a decrease in swelling ratio in the presence of TX-100, the values are very close to one another and are not very distinct even at different surfactant concentration, i.e., 0.1 mM and 0.5 mM. The presence of SDS shows a wider variation of the swelling ratio of the PVA-borax gel as compared to TX-100, since swelling ratio of the gel at 3 mM is more, while the decrease in the swelling ratio is quite prominent in the case of the gel at 11 mM SDS (Fig. 3(a)). From Fig. 3(b), it is observed that there is little impact on

the swelling behavior in the case of TX-100 containing PVA-borax gel, which corroborates the greater affinity of the anionic surfactant to form mixed micelles in the gels due to preferential uptake of the surfactant by the gels.²⁴ This behavior also suggests that while SDS micelles or TX-100 surfactant preferably lead to dissociating the cross-linking of the polymer chain resulting in the lost of the gel-like nature of the PVA-borax system the monomer of SDS apparently facilitates the cross-linking of the network. When the surfactant head groups are ionic, the otherwise neutral gel is converted to a polyelectrolyte gel, which introduces additional osmotic pressure. Swelling ratio less than unity implies that there is no significant change in the cross-linking network of the PVA gel during the experiment although the solvent penetrates and swells the cross-linked PVA gel network.²⁵ while measuring the swelling ratio, it was also observed that PVA-borax gel is soluble in hot water and hence the observed behavior may reflect a continuous collapse of the PVA gels with temperature. Consequently, the transition temperature of the PVA-borax gels could not be determined precisely by swelling ratio method as in the case of PNIPA gels. It was, therefore, considered reasonable to determine the sol-gel transition temperature for the PVA gels by ball drop technique as an additional support. The sol-gel transition curves for the PVA-borax gels in presence of SDS and TX-100 are in agreement with the findings from swelling ratio studies. The PVA-borax gel was observed to melt at around 25-30 °C. Addition of a surfactant, i.e., either SDS beyond CMC or TX-100 was found to soften the gels and the effect was more pronounced in the case of SDS as compared to TX-100 since it takes less time to soften even at lower temperature. This corroborates our earlier observations from swelling ratio.

In the present study, PVA-borax gel shows significant elastic behaviour and Maxwellian fluid behaviour to some extent at lower surfactant concentrations of SDS and TX-100. Inclusion of SDS in PVA-borax gel significantly lowers the gel-sol temperature. SDS appears to have a greater affinity towards PVA-borax gel than TX-100.

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References

- Gohil J M, Bhattacharya A & Ray P, *J Polym Res*, 13 (2006) 161.
- Mansur H S, Sadahira C M, Souza A N & Mansur A A P, *Mater Sci Eng C*, 28 (2008) 539; Zhao X, Kim J, Cezar C A, Huebsch N, Lee K, Bouhadird K & Mooney D J, *Proc Natl Acad Sci USA*, 108 (2011) 67; Wu J, Gong X, Fan Y & Xia H, *Soft Matter*, 7 (2011) 6205.
- Lin H L, Yu T L & Cheng C H, *Colloid Polym Sci*, 278 (2000) 187; Leiber L, Pezron E & Pinacus P A, *Polymers*, 29 (1988) 1105.
- Kurokawa H, Shibayama M, Ishimaru T, Nomura S & Wu W L, *Polymers*, 33 (1992) 2182.
- Shibayama M, Takeshi T & Nomura S, *Macromolecules* 27 (1994) 5350.
- Robb I D & Smeulders J B A F, *Polymers* 38 (1997) 2165.
- Lin H-L, Liu W-H, Shen K-S, Yu T L & Cheng C H, *J Polym Res*, 10 (2003) 171.
- Dualeh A J & Steiner C A, *Macromolecules*, 23, (1990) 251; Murase Y, Onda T, Tsuji K & Tanak T, *Macromolecules*, 32 (1999) 8589.
- Yang Y, Schulz D & Steiner C A, *Langmuir*, 15 (1999) 4335.
- Bakshi M S & Sachar S, *Colloid Polym Sci*, 283 (2005) 671; Kaura A & Bakshi M S, *Colloid Surf A*, 244 (2004) 45; Benrraous M, Bales B & Zana R, *J Colloid Interface Sci*, 267 (2003) 519
- Fendler J F & Fendler E J, *Catalysis in Micellar and Macromolecular System*, (Academic Press, New York) 1975.
- Santinath S, Aswal V K & Bohidar H B, *Int J Biol Macromol*, 41 (2007) 30.
- Wang C H, Li Y & Hu Z, *Macromolecules*, 30 (1997) 4727; Nonaka T, Yoda T & Kurihara S, *J Polym Sci Part A: Polym Chem*, 36 (1998) 3097; Mounir A, Darwish N & Shehata A, *J Appl Polym Sci*, 91 (2004) 3921; Thomas J, Lowman A & Marcolongo M, *J Biomed Mater Res*, 67A (2003) 1329; Lowman A M, Dziubla T D, Bures P & Peppas N A, *Adv Chem Eng*, 29 (2004) 75.
- Tan H M, Moet A, Hiltner A & Baer E, *Polym J*, 12 (1980) 335.
- Carlsson A, Karlström G & Lindman B, *Colloids Surf*, 47 (1990) 147.
- Deguchi S, Kroda K, Akiyoshi K, Lindman B & Sunamoto J, *Colloid Surf A*, 147 (1999) 203.
- Goddard E D & Leung P S, *Colloids Surf*, 65 (1992) 211.
- Fuchs T, Richtering W, Burchard W, Kajiwarra K & Kitamura S, *Polym Gel Networks*, 5 (1998) 541.
- Lin H-Li, Liu Y-F, Yua T L, Liu W-H, Rwei S-P, *Polymer* 46 (2005) 5541.
- Cole K S & Cole R H, *J Chem Phys*, 9 (1941) 341.
- Marsano E, Bianchi E & Visacardi A, *Polymer*, 45 (2004) 157.
- Zhang X-Z, Yang Y-Y, Wang F-J & Chung T-S, *Langmuir*, 18 (2002) 2013.
- Yoshida M, Asano M, Omichi H, Kimimura W, Kumakura M & Katachi R, *Macromolecules*, 30 (1997) 2795.
- Yoshida M, Asano M, Omichi H, Kamimura W, Kumakura M & Katakai R, *Macromolecules*, 30 (1997) 2795.
- Park J-S, Park J-W, Ruckenstein E, *J Appl Polym Sci*, 82 (2001) 1816.

