The Influence of Different Ions on the Phase Separation of Poly (Vinyl Alcohol) and Poly (Sodium 4-Styrene Sulphonate) in Aqueous Solution

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Summary: In aqueous solution the phase separation behavior of mixture of PVA-PSSNa has been studied. The critical concentration at which macroscopic phase separation occur is 1.0 mol/L. The cloud point curve is typically of (lower critical solution temperature) LCST type. The driving force responsible for shifting the LCST is hydrogen bonding and hydrophobic interaction of the macromolecules. When both the polymers have close molecular weight the polymer hetero-association increases which in turn decreases the intramolecular interaction within PVA chains. Addition of Hofmeister series of salts enhances the formation of complex between PVA-PSSNa which in turn decreases the LCST of mixture of polymers. The decrease of the LCST is in the order Na_2SO_4 < NaF < NaCl < $NaClO_3$ < NaNO3 < NaBr < NaSCN which is opposite to classical Hofmeister series. Chaotropic anions favour the formation of complex more than kosmotropic anions this is because chaotropes have low surface tension values as compared to kosmotropes which lead to strengthening of hydrophobic interaction and enhances the complex formation which in turn shift the LCST toward lower temperature.

Key words: Poly (vinyl alcohol), Poly (Sodium 4-Styrene Sulphonate), LCST, phase separation and Hofmeister series.

Introduction

Polymer-polymer compatibility has gained much interest by many researchers. To meet new requirements in material properties blending of polymers with good compatibility is considered to be the most suitable method. Among which, the tailored chemical structure is very important particularly for preparation of ion exchange membrane [1]. A blend of aqueous solution of different polymer seldom attains perfect miscibility. In general, a negative change in free energy is required for the the miscibility of polymer blend [2]. In order to meet new requirements in material properties blending of polymer with good compatibility is known to be a very convenient method. In polymer blends component can be completely miscible, partially miscible or non miscible. Upper critical solution temperature (UCST) phenomenon is observed for partially miscible blend whereas, upper order-disorder transition (UODT) is observed in corresponding block copolymer which is caused by unfavorable energies [3]. Another type of phase separation phenomenon beyond those typical phase separation behavior is called as lower critical solution temperature (LCST) observed in some polymer blends or lower disorder-order transition (LDOT) in the corresponding block copolymers [4-6]. Specific interactions such as hydrogen bonding, van der Waals forces and electrostatic interactions are responsible for the compatability of two polymers. The miscibility of PVA with another polymer is due to cross- hydrogen bond interactions. For completely and partially associative polymers such interactions are very important [7, 8].

The most important parameters governing phase separation are temperature, concentration of the polymer, pH and ionic strength [9-11]. The LCST of the mixture of PVA and PSSNa is strongly affected by the presence of Hofmeister series of anions. Although, more than one century the Hofmeister series has been extensively investigated to explain the mechanism how ions affect the different aspects of polymer properties in aqueous solution [12]. A typical Hofmeister series is CO_3^{2-} > SO_4^{2-} > $S_2O_3^{2-}$ > $H_2PO_4^{2-}$ > F^- > Cl^- > Br^- > NO_3^- > I^- > ClO_4^- > SCN^-.The ions on the left side of chloride ion is known as “kosmotropic” ions whereas ions on the right side are known as “chaotropic” ions. According to Hofmeister series “kosmotropic” ions which are strongly hydrated anions effectively salt out polymers from aqueous solution whereas, “chaotropic” ions which are weakly hydrated shows salt in effect. In the past a lot of work has been done in understanding the ordering of series and mechanism involved [13, 14]. Previously, it was believed that these ions can affect the bulk water structure which in turn affects the hydrophobic- hydrophilic transition of proteins in aqueous solution. Recently, it is believed that ions

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only affect the closest hydration shells and the water structure is not affected by the salt ions. In case of thermal responsive polymer the Hofmeister series can be explained on the basis of direct interaction of these anions with macromolecules and its immediate nearby hydration shell [15]. Another proposed mechanism is simple hydrogen-bonding hydration of different polymer polar groups. The electron pair donicity, and acceptability of water molecules through ionic hydration are also one of the factor for the destabilization of hydrogen bonding hydration to polymers [16]. Zaslavsk *et al.* studied the concentration effects of inorganic salts on phase separation of two non ionic polymers. They reported that addition of salt cause alteration of the polymer water interaction due to direct ion-polymer binding and the polymer configurational changes [17]. Kaji *et al* reported that the critical concentration where phase separation occurs decrease with increasing amount of salt in the mixture of PVSNa and PSSNa [18]. Mbareck *et al* [19] studied interpolymer association between poly (vinyl alchol) PVA and poly (sodium styrene sulfonate) (PSSNa) in aqueous solution. However, to our knowledge, the detailed investigations of the effect of Hofmeister series of anions on the phase separation of mixture of polymer are still not available.

In this research work we will show that the blend of aqueous solution of Poly (vinyl alcohol) PVA and Poly (Sodium 4-Styrene Sulphonate) PSSNa having similar molecular weight is a promising system to exhibit LCST type behavior. Addition of salt and variation of concentration and ratio of both the polymers alter the LCST value. In the presence of salts the mixture of PVA and PSSNa displayed Anti-Hofmeister property. PVA is chosen because it is well known for its interesting behavior and its versatile applications [20]. The hydroxyl group of PVA can act as both the hydrogen bond donor and the acceptor. Polymers with both the hydrogen bond acceptor and donor chemical groups like poly (acrylic acid) or poly (styrene sulfonate) were reported to be compatible with PVA [21]. Poly(styrene sulfonate) : poly(3,4-ethylenedioxy-thiophene) is one of the well known conducting polymer for industrial application[22-23]. The drawback of this system is that it is brittle and hence difficult to form into free standing films [24]. Many researchers used blend of PVA and PSSNa for electrical conductivities application [25]. The aim of the research work is to improve the interaction between PVA and PSSNa which may lead to stronger conductive material. It will also improve our knowledge concerning about the effect of variation of concentration of mixture of polymers, proportion of both the polymers and Hofmeister series of anions on phase separation of the aqueous solutions of PVA/PSSNa having the similar molecular weight and chain length.

Results and Discussion

In a mixture of polymer water ternary system phase separation is known to occur when the total concentration (C_t) of the two polymers is not less than 1mol/L within the studied temperature range which is shown in Fig 1. The Figure displays the transmittance curves of mixture of polymers with different total molar concentration when heating the solutions. The critical concentration at which macroscopic phase separation occur is 1.0 mol/L and the phase separation is quite sharp when the concentration of the mixture of polymers is 1.5 mol/L. We further continue our studies by using this concentration. At higher temperature phase separation is accompanied by the formation of precipitates.

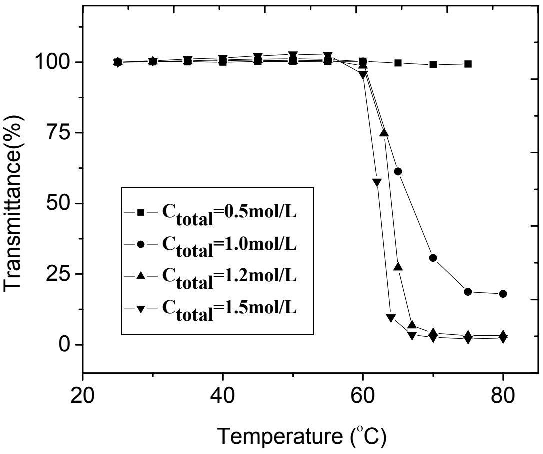

Fig. 1: Plots of transmittance of light as a function of temperature for different equi-molar mixtures of PVA and PSSNa.

Fig. 2 shows the transmittance of polymers mixture as a function of temperature having different PVA and PSSNa molar ratio and total concentration is 1.5mol/L. When the molar ratio of PVA is 9, then no change in transmittance is observed within the studied temperature range

In equimolar mixture (molar 5:5) of PVA/PSSNa, the LCST of the solution is minimum as compared to other molar ratio of PSSNa (7 and 9). However, with the increase in molar concentration of PSSNa, the value of LCST increases. This is due to the fact that the PSSNa component in the mixture is hydrophilic in nature and with the increase in the PSSNa content, the hydrophilicity of the overall system increases, which is responsible for higher value of the LCST of the mixture. When both the polymers have close molecular weight the polymer hetero-association increases which in turn decreases the intramolecular interaction within PVA chains. The compatibility between PVA/PSSNa is due to hydrogen bonding between OH and SO_3 of the polymers. In the absence of salt, phase separation is accompanied by the formation of precipitates which is due to polymer-polymer complex formation. Both PVA and PSSNa are hydrated by water molecules. With the increase in temperature, the structure of water is interrupted and therefore hinders the ability of PVA and PSSNa to form hydrogen bond with water. Hydrogen bonding occurs at lower temperature with the increase in temperature, it get weaken and as a result hydrophobic interaction between the polymers get stronger. The effect of temperature is more pronounced on PVA as compared to PSSNa as PVA is more hydrophobic whereas, PSSNa become partial hydrophobic and partial hydrophilic. The driving force responsible for shifting the LCST is hydrogen bonding and hydrophobic interaction of the macromolecules

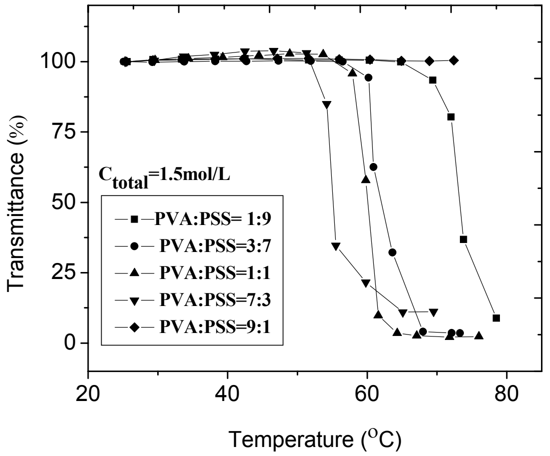

Fig. 2: Plots of transmittance as a function of temperature for PVA/PSSNa mixture where C_{total} = 1.5 mol/L.

Fig. 3 shows the transmittance of PVA/PSSNa mixture (molar ratio 1:9) as a function of temperature at C_{total} = 1.5 mol/L in the presence of different salts having ionic strength I = 0.2mol/L. Addition of Hofmeister series of salts enhances the formation of complex between PVA and PSSNa which in turn decreases the LCST of the polymer mixture. The "salting out" effect is found in all the salt solutions used in the present studies. In the presence of salt, the thermodynamic quality of the solvent becomes poor which leads to the strengthening of hydrophobic interaction. The LCST of mixture decreases in the following order i.e. $Na_2SO_4 < NaF < NaCl < NaClO_3 < NaNO_3 < NaBr <$ NaSCN, which is opposite to the classical Hofmeister series. Addition of salt to PVA/PSSNa mixture favors the aggregation of polymer-polymer complex which result in phase separation. Many authors have reported that the appearance of precipitate or the increase of mixture turbidity is a sign of compatibility deterioration [26, 27]. In case of NaSCN, the LCST is minimum, which enhances the formation of complex. The SCN^- bound itself to the more hydrophobic part i.e. benzene ring in the mixture and as a result electron pair donicity ability increases which favor the hydrogen bonding between PVA and PSSNa and thus enhances the formation of complex. The other chaotropic anions behave in the similar way. Kosmotropes, which are typical "salting out" anions, are not as effective as chaotropic anions for complex formation so the value of LCST is greater as compared to chaotropic anions.

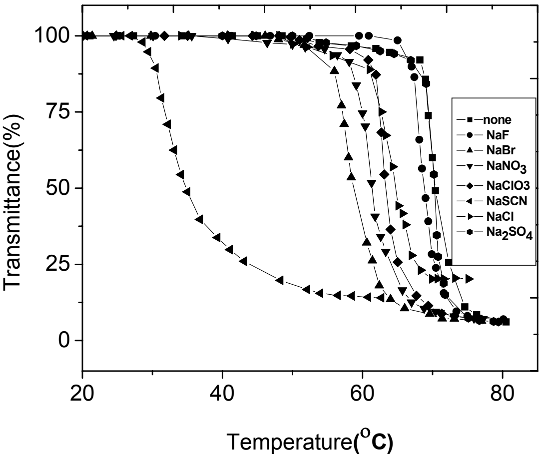

Fig. 3: Plots of transmittance as a function of temperature for PVA/PSSNa (molar ratio 1:9) in the presence of different salts having ionic strength I= 0.2 mol/L where C_{total}=1.5mol/L.

Fig. 4 and 5 show the transmittance of light for PVA/PSSNa mixture as a function of temperature (molar ratios 3:7, 5:5) at C_{total} = 1.5 mol/L in the presence of different salts having ionic strength I = 0.2mol/L. The LCST decreases in the same way as described in the Fig. 3.

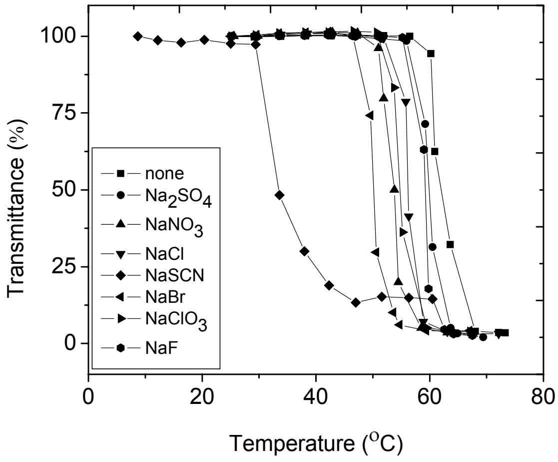

Fig. 4: Plots of transmittance as a function of temperature for PVA/PSSNa mixture (molar ratio 3:7) in the presence of different salts having ionic strength I = 0.2mol/L where C_{total} = 1.5 mol/L.

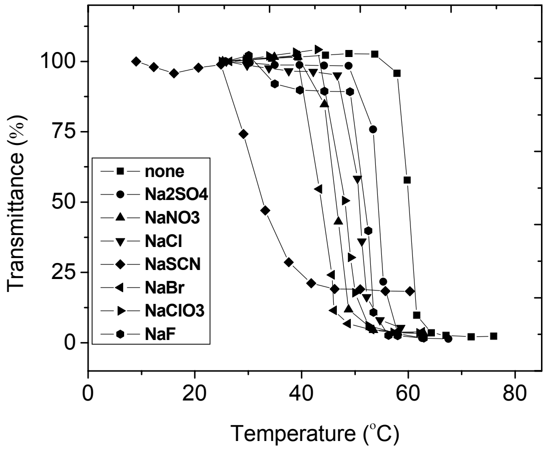

Fig. 5: Plots of transmittance as a function of temperature for PVA/PSSNa mixture (molar ratio 5:5) in the presence of different salts having ionic strength I = 0.2mol/L where C_{total} = 1.5mol/L.

Fig. 6 shows the transmittance of light for the PVA/PSSNa mixture (molar ratio of 7:3) at C_{total} = 1.5 mol/L in the presence of different salts having ionic strength I = 0.2mol/L as a function of temperature. The effectiveness of the anionic species for reducing the LCST is in the following order Na_2SO_4 < NaF < NaCl < $NaClO_3$ < $NaNO_3$ < NaBr < NaSCN. The trend of decreasing the LCST follow the same trend when the PVA content is less or equal to PSSNa content.

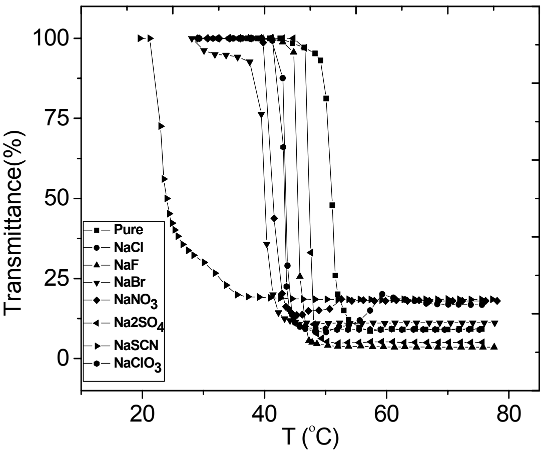

Fig. 6: Plots of transmittance as a function of temperature for PVA/PSSNa (molar ratio 7:3) in the presence of different salts having ionic strength I = 0.2mol/L where C_{total}= 1.5 mol/L.

Fig. 7 shows the transmittance of light for mixture of PVA/PSSNa (molar ratio 9:1) at C_{total} = 1.5 mol/L in the presence of different salts having ionic strength I = 0.2mol/L as a function of temperature. A mixture of PVA and PSSNa does not exhibit LCST in pure water when the PVA content is 9. The possible explanation is that the LCST in the water is beyond the temperature range we studied. The mixture exhibit LCST when different salts are added and the effectiveness of the anionic species for reducing the LCST is in the order i.e. Na_2SO_4 < $NaNO_3$ < NaBr < $NaClO_3$ < NaCl < NaF < NaSCN. The order is opposite to "lyotropic series" or Hofmeister series of the anions. This is due to the fact that the addition of Hofmeister series of anions increases the interaction between PVA and PSSNa. SCN^- ion has low surface tension value as compared to SO_4^{2-} as shown in Fig. 8 so in the case of SCN^- the interaction between PVA and PSSNa are stronger as compared to water. In other words we can say that addition of SCN^- anion to the PVA/PSSNa mixture increases the hydrophobic interaction between the polymers and hinders their ability to form hydrogen bond with water. That's why SCN^- shifts the LCST toward lower temperature as compared to kosmotropic anions. Fig. 8 is just used for the comparison of surface tension values for kosmotropic and chaotropic anions. Fig. 9 show LCST of PVA/PSSNa mixture for comparison at C_{total} = 1.5 mol/L in the presence of different salts having ionic strength I = 0.2mol/L and at different molar ratios of PVA and PSSNa.

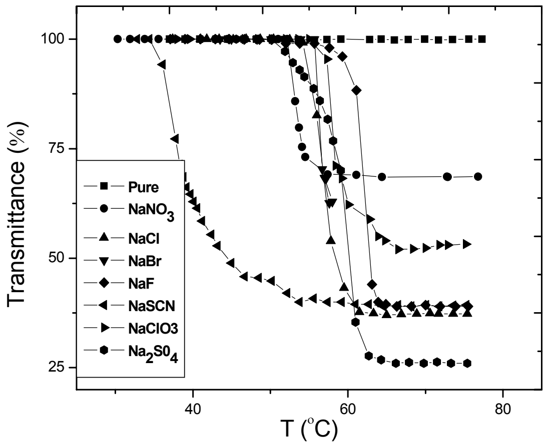

Fig. 7: Plots of transmittance as a function of temperature for PVA/PSSNa mixture (molar ratio 9:1) in the presence of different salts having ionic strength I = 0.2mol/L where C_{total} = 1.5 mol/ L.

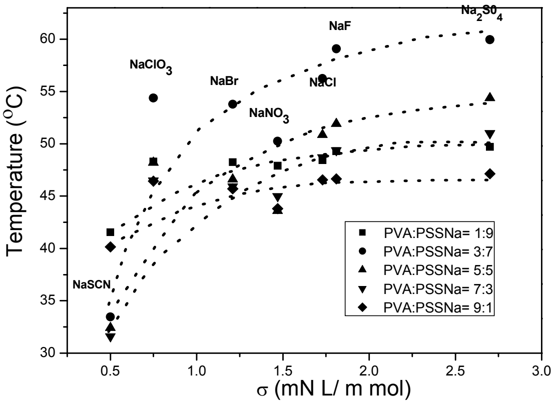

Fig. 8: Plots of LCST as a function surface tension increment of anions for different Hofmeister anions. The surface tension increments were obtained from reference [28].

Experimental

Materials

Poly (Sodium 4-Styrene Sulphonate) (PSSNa) (M_w =7.0 × 10^4) and Poly (vinyl alcohol) PVA (M_w = 6.1 × 10^4) were purchased from Aldrich and used as received. PVA and PSSNa solutions were prepared separately dissolving polymer in deionized water and heating PVA under reflux, with stirring, at 80 ° C for 1 day (1.5 mol/L). Afterwards, the PVA and PSSNa solutions were cooled at room temperature. The two solutions were mixed in defined proportions to obtain a value of 0.5 mol/L, 1.0 mol/L, 1.2 mol/L and 1.5 mol/L as the total polymer repeat unit concentration. The inorganic salts used were of analytical grade. The ionic strength of salt solutions were fixed at I= 0.2 mol/L. All the solutions were made using Millipore water.

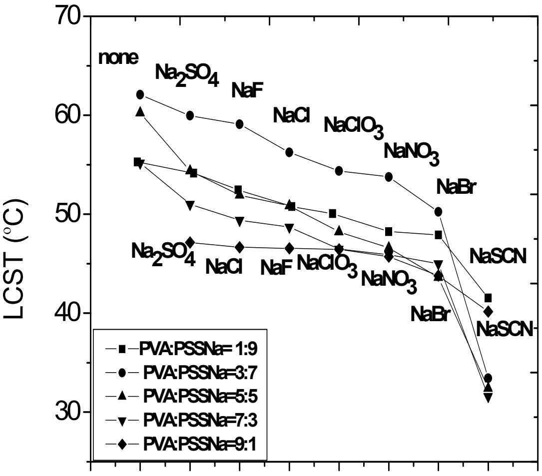

Fig. 9: Plot of LCST of mixture of PVA/PSSNa in the presence of different salt having ionic strength I = 0.2mol/L where C_{total} = 1. 5 mol/L.

Cloud point Measurements

Cloud points were determined by measuring the change in turbidity of solutions heated at a rate of 0.1 ºC/min**.** UNICO 2802PCS UV/visible spectrophotometer at a wavelength 500 nm was used for turbidity measurements. For the cloud point measurements in the presence of different ratios of PVA to PSSNa the total polymer concentration was fixed at 1.5 mol/L and the ionic strength of salts were fixed at 0.2 mol/L. The temperature of the cell was controlled using a circulating bath with an accuracy of ± 0.1 ºC and monitored by an electronic thermometer. We defined the LCST the temperature at which the transmitted light reaches the average value of transmittance between the highest one (< LCST) and the lowest one (> LCST), so that we can easily and accurately obtain the critical phase transition temperatures and compare them under different conditions.

Conclusions

In PVA-PSSNa-water ternary system phase separation occurs when the total concentration (C_t) of the two polymers is not less than 1mol/L within the studied temperature range. With the increase of temperature the solvation of PVA and PSSNa decreases which in turn strengthen the intermacromolecular interactions between polymers. The increase of intermacromolecular interactions between PVA and PSSNa leads to formation of stronger conductive material. Addition of Hofmeister series of salts favours the formation of complex between PVA-PSSNa which in turn decreases the LCST of mixture of polymers. The decrease of the LCST of mixture of polymers is opposite to Hofmeister series. Chaotropic anions are more effective in the formation of complex as compared to kosmotropes so that is why the chaotropic anions shift the LCST toward lower temperature.

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