

*Full Length Research Paper*

# Equilibrium and related thermodynamic studies of a hydrogen bonded multicomponent complex in mixed solvents

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Accepted 2 November, 2011

**An interesting multicomponent complex has been prepared by incorporating a non – ionic homopolymer (e.g., Poly(Vinyl Pyrrolidone) PVP) on a typical copolymer (e.g., Methacrylic Acid/Acryl Amide MA/AAm). Stability constants and related thermodynamic parameters (e.g., Free energy change  $\Delta F^\circ$ , Enthalpy change  $\Delta H^\circ$  and Entropy change  $\Delta S^\circ$ ) have been determined. Interpretations have been sought in terms of secondary binding forces like hydrogen bonding, Van der Waals interactions and hydrophobic interactions. Hydrophobic interactions get significantly diminished in higher concentration of organic solvents (e.g., methanol) thus affecting the stability of the complex.**

**Key words:** Non-ionic homopolymer, copolymer, stability constants hydrophobic interactions, stability constants, thermodynamic parameters.

## INTRODUCTION

Interactions between polymers in solution may lead to the formation of the polycomplexes. These noncovalent interactions play key roles in many natural processes leading to the inter-macromolecular assemblies. One of the most important forces responsible for self-assembly is hydrogen bonding, which also plays an important role in the self-assembly of synthetic polymers in aqueous solutions (Papisov and Litmanovich, 1989; Bekturov and Bimendina, 1981; Tsuchida and Abe 1982; Chatterjee et al., 1994; Sharma and Chhabra 2005, Brostow et al., 2010; Mark, 1990). These unique entities have potential applications in technology (e.g., membrane and separation technology) and medicine (e.g. drug delivery formulations). As interactions between the polymers affect their physicochemical properties and chemical properties, their study is of considerable interest. A typical polyelectrolyte e.g., poly (methacrylic acid) interacts with complementary homopolymers (e.g., PVP) through secondary binding forces, for instance hydrogen

bonding, ion dipole interactions etc. (Papisov, and Litmanovich, 1989; Sharma et al., 2009, 2010a, b). The presence of certain alien groups (e.g., AAm) on the PMA chain influences its reactivity. The reactivity of these groups when present in the copolymer matrix is rendered to the neighboring group effect (Chatterjee et al., 1994, 1984). It disrupts the stereoregularity of the macromolecular matrix thus affecting its complexation ability. It may also reduce the sequence of active units in the copolymer chain below the critical chain length. Further, the nature of the solvent is expected to influence these interactions (Sharma et al., 2009, 2010a, b). The role of the hydrophobic interactions on the stability of these complexes is well known. It is therefore expected that the complex would be relatively less stable in the organic solvents due to diminishing hydrophobic effect. Mixtures of water and methanol provide different configurational environment to the interacting macromolecules which may ultimately affect their complexation ability. The different secondary binding forces are expected to be influenced differently in the presence of organic solvent as a function of temperature. Keeping all these facts in mind, we have carried out equilibrium and related thermodynamic studies of a typical copolymer (MA/AAm)

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and non ionic homopolymer e.g., PVP interaction in different solvent mixtures. This is an interesting system as both the interacting groups involve only hydrogen bonding. Osada's procedure has been followed to carry out the thermodynamic studies of the interpolymer complex (Osada and Sato, 1976, Osada, 1979).

## EXPERIMENTAL

### Methacrylic acid – acrylamide copolymer MA/AAm

The random copolymer was prepared by known methods and characterized (Chatterjee et al., 1982). It contained 0.56 mol. of MA and 0.44 mol. of AAm units, respectively.

### Poly (Vinyl Pyrrolidone) (PVP)

PVP was supplied by Fluka, Switzerland. The polymer was characterized by viscosity measurements and its weight average molecular weight ( $M_w$ ) was found to be  $2.4 \times 10^4$  g/mol (Chatterjee et al., 1995).

Double distilled water and analytical grade methanol were used for all the experimental measurements.

The pH measurements of aqueous solutions of the polymer or complex were carried out in a water jacketed cell with "PTA" digital pH meter, using combination electrode. The temperature of the sample solution was controlled by circulating thermostatically controlled water.

The pH was measured at copolymer concentration of  $5 \times 10^{-3}$  um/L in absence and presence of stoichiometric concentration of PVP. Complexes did not precipitate at these concentrations.

## RESULTS AND DISCUSSION

The secondary binding forces leading to the formation of inter polymer complexes (IPCs) include Coulombic, hydrogen-bonding, van der Waals, charge transfer and hydrophobic interactions. However hydrophobic interactions are caused by rearrangement of water molecules rather than by direct cohesive forces between the macromolecules. The aqueous solutions of IPCs receive strong hydrophobic effects as compared to mixed solvents (Jiang et al., 1999). Solvent thus plays a very significant role in the polymer – polymer interactions (Chatterjee et al., 1994; Sharma et al., 2009, 2010a, b) and sometimes even affects the stoichiometries of the resulting interpolymer complexes. This is particularly true in view of the fact that hydrophobic interactions will be considerably reduced in the presence of organic solvents like methanol (Sharma et al., 2009, 2010a, b). Organic solvents reduce the stability of interpolymer complexes involving hydrogen bonded units and the related thermodynamic parameters ( $\Delta H^0$  and  $\Delta S^0$ ). In other words, the higher the concentration of the solvent, lower will be the stability of the interpolymer complex. Keeping this object in mind, we have studied the following interpolymer complex in mixed solvents of water and methanol of different compositions.

### Complex A: 1 um MA/AAm + 1 um PVP

Here um refers to unit mole, molar unit for polymers. This system has been studied in three solvent mixtures, including

S1: 90% Water + 10% Methanol

S2: 80% Water + 20% Methanol

S3: 70% Water + 30% Methanol

The nature of the interacting forces between the two comonomers units (e.g., Methacrylic acid MA and ACRYL amide AAm with poly(vinyl pyrrolidone) PVP are different; one would therefore expect them to get affected differently upon decreasing the hydrophobic interactions (e.g., (a) MA-VP and (b) AAm-VP). For instance in (a) hydrogen bonding interactions are involved, whereas in (b) weak electrostatic and hydrogen bonding interactions are involved respectively. Determination of stability constant and related thermodynamic parameters ( $\Delta H^0$  and  $\Delta S^0$ ) for this three component complex may possibly help in understanding the role of hydrophobic interactions in the polyelectrolyte complexes. Degrees of association ( $\Theta$ ) and stability constants ( $K$ ) of the complexes (1 to 3) at different temperatures have been calculated using Osada's procedure (Osada and Sato, 1976; Osada 1979). The degree of association ( $\Theta$ ) may be defined as the ratio of binding groups and is related to the stability constants by the following equations:

$$\Theta = 1 - \left( \frac{[\text{H}^+]}{[\text{H}^+]_0} \right)^2$$

$$K = \frac{\Theta}{C_0(1 - \Theta)^2}$$

where  $K$  is the stability constant of the corresponding complex (the units of  $K$  in this case is L/um that is,  $\text{conc}^{-1}$ ) and  $T$  is the temperature in degree Kelvin. The related thermodynamic parameters (e.g.,  $\Delta H^0$ ,  $\Delta S^0$ ) have also been calculated using the following equations:

$$d \ln K / d(1/T) = -\Delta H^0 / R$$

$$\Delta F^0 = -RT \ln K$$

$$\Delta S^0 = -(\Delta F^0 - \Delta H^0) / T$$

where  $\Delta H^0$  is the enthalpy change,  $\Delta S^0$  is the entropy and  $\Delta F^0$  is the free energy change during the complex formation.  $R$  is the universal gas constant.

The corresponding plots of  $\ln K$  Vs  $1/T$  and related thermodynamic parameters (e.g.,  $\Delta H^0$  and  $\Delta S^0$ ) for the aforementioned complexation system in three solvent mixtures are depicted in Figures 1 to and 3, respectively. The units of  $1/T$  would be  $K^{-1}$ . As expected, the two media

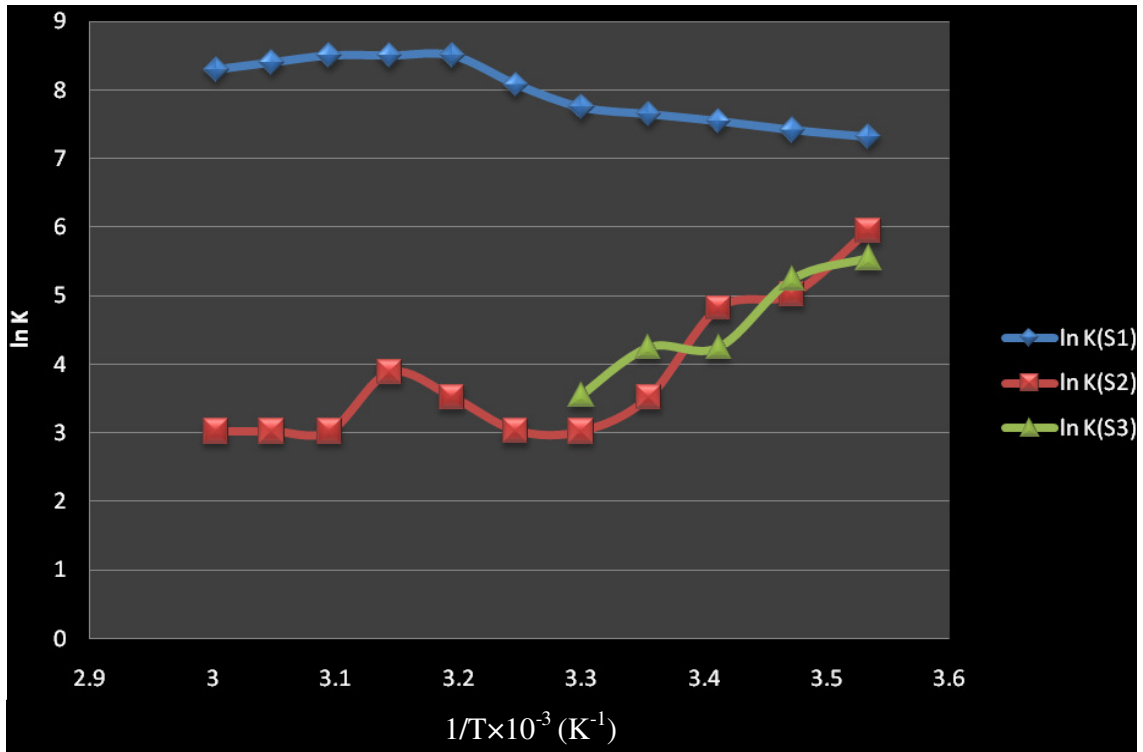


Figure 1. Variation of  $\ln K$  with  $1/T$  for complexation system MA-AAm/PVP in solvent systems S1 and S2, S3.

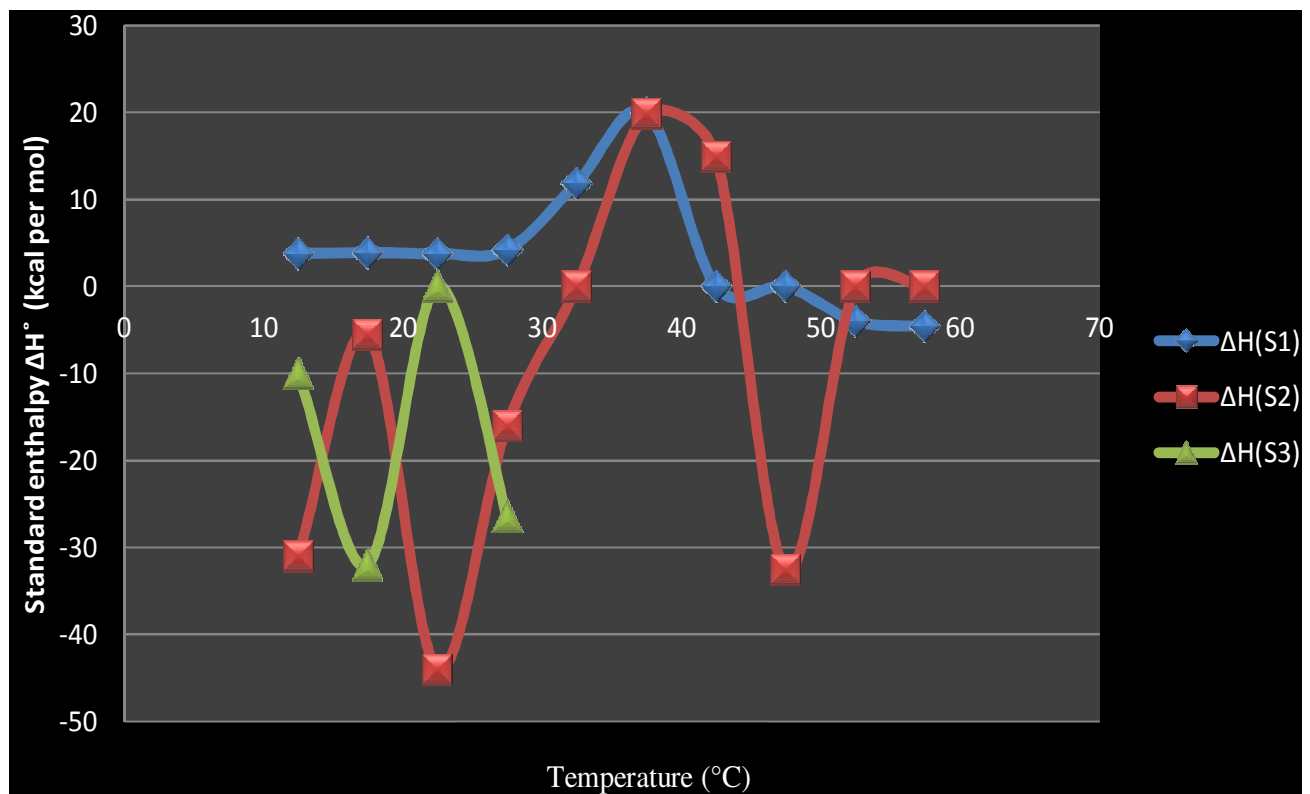
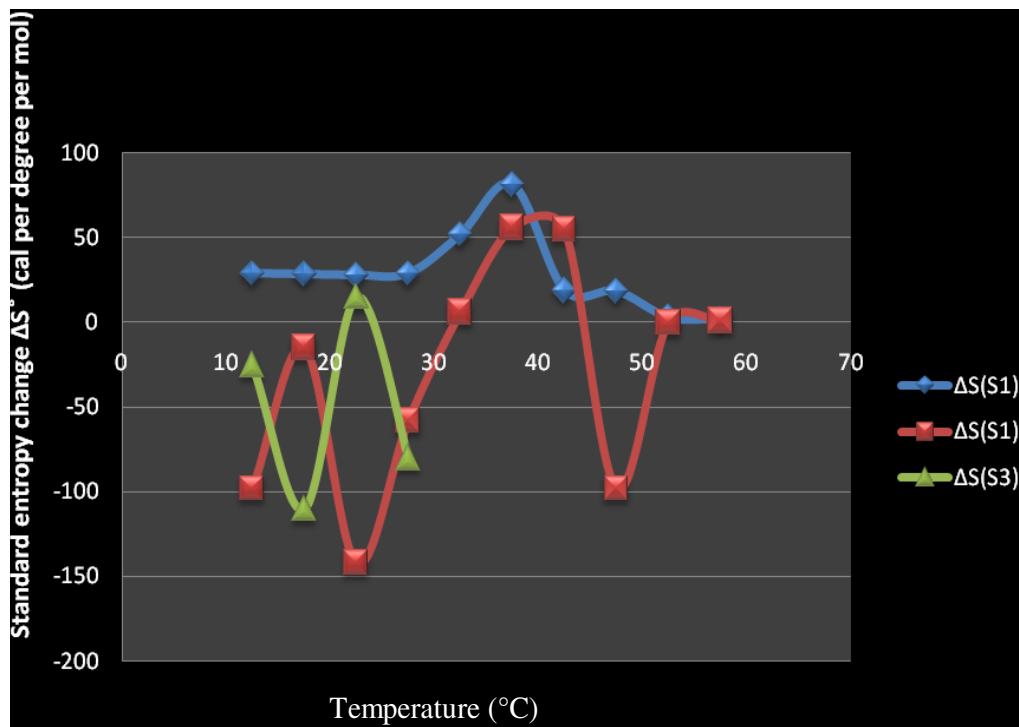


Figure 2. Temperature dependence of standard enthalpy change ( $\Delta H^\circ$ ) for the complexation system MA-AAm/PVP in solvent systems S1, S2 and S3.



**Figure 3.** Temperature dependence of standard entropy change ( $\Delta S^\circ$ ) for the complexation system MA-AAm/PVP in solvent systems S1, S2 and S3.

S1 and S2 showed a very interesting trend (Figure 1). An increase in stability with increase in temperature was observed in the medium containing lower concentration of the organic solvent, that is, S1 which can be explained due to the persistent hydrophobic interactions. The case was reverse in case of S2 as here the stability reduced due to higher amount of organic solvent. This can be interpreted in terms of diminishing hydrophobic interactions in S2 as compared to S1. However in S3, containing 30% methanol and almost no contribution from hydrophobicity, measurements could not be completed beyond 30°C due to precipitation of the complex. Of course, a steady fall in  $\ln K$  was observed from 10 to 30°C.

The corresponding plots of  $\Delta H$  vs T and  $\Delta S$  vs T in the three media are presented in Figures 2 and 3. Each of the curve in the three media showed two maxima in  $\Delta H$ , which may be designated as  $\Delta H_1$  and  $\Delta H_2$ . The values of  $\Delta H_1$  and  $\Delta H_2$  for the complexation system also indicated an identical trend, that is,

$$\Delta H_{S1} > \Delta H_{S2} > \Delta H_{S3}$$

The extent of hydrogen bonding in different interacting groups in different media would be very different. This obviously indicated that the solvent medium influences desolvation, complexation by secondary binding forces and conformational change of the complexation system as is reflected in the absolute values of the overall

enthalpy ( $\Delta H_M$ ) (Chatterjee et al., 1985, 1992, 1993a, b) in different media. All these individual enthalpy changes will be markedly different in each of the solvent media (e.g., S1, S2 and S3) and thus the difference in the absolute values of  $\Delta H_M$  could be justified. Similar trend in  $\Delta S^\circ$  could be explained on identical lines. The thermodynamic characteristics are in complete accordance with the temperature dependence of the complex (Chatterjee et al., 1994; Sharma et al., 2009, 2010a, b; Jiang et al., 1999).

## Conclusions

It may be concluded that the presence of higher percentage of organic solvent in medium reduces the stability of the complexes, due to weakening of hydrophobic interactions.

The related thermodynamic parameters (e.g.,  $\Delta H^\circ$ ,  $\Delta S^\circ$ ) of the complexes are thus likely to be influenced in the presence of organic solvents (Chatterjee et al., 1995; Sharma et al., 2010a, b; Sharma and Chhabra, 2005). The investigation on complexation in non-aqueous media is relatively new, receiving special attention lately and thus allowing significant information about these complexes (Jiang, 1999).

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