Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Vasheghani, F. B. , Rajabi, F. H. and Ahmadi, M. H.(2007) 'Thermodynamic Study of Multi-Component Polymer Complexes of Varying Composition in a Mixed Solvent', Journal of Macromolecular Science, Part A, 44: 1, 113 — 118

To link to this Article: DOI: 10.1080/10601320601044674

URL: http://dx.doi.org/10.1080/10601320601044674

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2007) **44**, 113–118

ISSN: 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320601044674

Thermodynamic Study of Multi-Component Polymer Complexes of Varying Composition in a Mixed Solvent

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Received January, 2006, Accepted May, 2006

Multi-component complexes of varying composition have been prepared from poly acrylic acid, polyelectrolyte and non-ionic polymer in a water-methanol mixture. The stability constant and related thermodynamic parameters of these complexes in a solvent mixture of water-CH_3OH were determined at several temperatures. The entropy (ΔS^0) and enthalpy (ΔH^0) changes of the systems with temperature have been interpreted in terms of destabilization of the various interacting forces involved in complex formation. Some of the observations have been attributed to the change in the degree of solvation of the component polymers, reduced hydrophobic interactions and dielectric constant of the medium.

Keywords: multi-component; polymer complexes; mixed solvent; thermodynamic study

1 Introduction

Intermacromolecular interactions have attracted considerable attention in past decades because of the unique properties of the products of these reactions-interpolymer complexes (IPC). Many articles have been devoted to various aspects of IPC including several reviews and monographs (1–22).

However, most of the information available on intermacromolecular complexes is qualitative in nature because of the lack of a suitable theory to interpret the experimental observations (5, 23). Moreover, very little information is available regarding the formation and stability of multi-component intermacromolecular complexes. In our recent publications, a stepwise destabilization of two and three-component interpolymer complexes in aqueous medium has been reported (24–26). It is well known that the complex formation between poly carboxylic acids and non-ionic proton accepting polymers is characterized by several critical phenomena such as minimal molecular weight, critical pH of complexation, minimal content of active components etc. (27–31).

Keeping this in mind, some three component intermacromolecular complexes of various composition have been prepared by interacting poly acrylic acid (PAA) with poly ethylene imine (PEI) and poly vinyl pyrrolidone (PVP) in a mixed solvent (i.e., water-methanol mixture). These systems are interesting in view of the fact that, the specific contribution from different interaction forces (e.g. electrostatic, hydrogen bonding and ion-dipole interactions) will depend on the composition of the intermacromolecular complexes. In aqueous medium, the stabilization of complexes is mainly through hydrophobic interactions (1–5, 32, 33). In organic solvents, one can expect considerable weakening of hydrophobic interactions, and hence, stability constant and thermodynamic parameters (e.g. change in entropy ΔS° and enthalpy ΔH°) of the interpolymer complexes are most likely to be affected in such media (2–6, 34). However, the solvent effect is considered to be one of the most important controlling factors during interpolymer complexation, because some solvents can interact with polymer via hydrogen bonds (2, 34–38). Thus complex formation can be regarded as a three-component system involving a proton donating polymer, a proton accepting polymer, and a solvent. In less polar solvents like methanol, ethanol, DMSO, the interaction due to poly carboxylic acid (e.g. PAA) and solvent is considerable, thereby reducing its interaction with other polymer. Therefore, in a mixed solvent like water-methanol mixture, the extent of ionization of poly carboxylic acid will depend on the composition of the medium.

Though considerable data are available in the literature regarding the role of solvent on interpolymer complexation, there seems to be no mention on stability and related thermodynamic parameters of multi-component complexes of poly acrylic acid, poly ethylene imine and poly vinyl pyrrolidone in water-methanol mixture. The main aim of this investigation was to find out the role of dielectric constant and

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reduced hydrophobic interactions on the stability and thermodynamic parameters of interpolymer complexes.

2 Experimental

2.1 *Poly(acrylic acid) (PAA)*

Purified acrylic acid (distilled twice *in vacuo*, b. p. 63°C, 12 mmHg) was polymerized with benzoyl peroxide as an initiator in a moist dioxane-methanol mixture (25, 26). The polymerization time was 2.5 h in nitrogen at 50°C. The reaction mixture was dissolved in methanol and reprecipitated twice with ethyl acetate. The polymer was dried to constant weight *in vacuo* at 110°C. The viscosity average molecular weight of the polymer was calculated from intrinsic viscosity of polymer in 2 M NaOH aqueous solution at a constant temperature of 25°C using the Mark-Houwink equation $[\eta] = KM_{\eta}^{\alpha}$ (33–39). The constant K and α in the above equation were equal to 42.2×10^{-3} ml g^{-1} and 0.64, respectively. The viscosity average molecular weight $\overline{M_{\eta}} = 4.0 \times 10^{5}$.

2.2 *Poly(ethylene imines) (PEI)*

PEI was supplied by BDH Chemical Ltd (Poole, UK) in the form of a 50% viscous aqueous solution, with number average molecular weight $\overline{M_{n}} = 1.5 \times 10^{5}$.

2.3 *Poly(vinyl pyrrolidone) (PVP)*

PVP was supplied by Fluka Switzerland in the form of a white crystalline powder. The weight average molecular weight ($\overline{M_{w}}$) of the polymer was calculated from viscosity measurements using the following equation:

$$[\eta] = 6.76 \times 10^{-2} M^{0.55} \text{ (in aqueous medium at } 25^{\circ}\text{C)} \quad (1)$$

where $[\eta]$ is intrinsic viscosity and $\overline{M_{\eta}} = 2.4 \times 10^{4}$ (g/mol) (26, 33).

2.4 *Solvent*

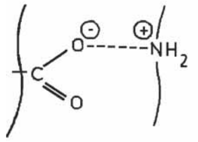
Double distilled water and analytical grade methanol (CH_3OH) were used for the mixed solvent for all the measurements.

2.5 *Measurement of pH*

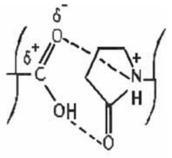
The pH measurement of aqueous solution of the polymer or complex was carried out in a water jacketed cell by ATI ORION pH meter (model 525A), using a combination electrode (ORION pH Triode 91–57) with auto calibration for buffers 1.68, 4.01, 7.00, 10.01 and 12.46 within a range of ±0.001 pH units. Two points standard calibration was performed at the beginning of each day measurements and also with one standard every 2 h to compensate for possible electrode drift. In all experiments the temperature was thermostatically controlled within ±0.05°C by circulating water through jacketed glass cell, and the sample solution was continuously stirred using a magnetic stirrer. The pH was measured at a polymer concentration of 1×10^{-3} mol · L^{-1} in the absence and presence of stoichiometric concentration of PEI and PVP. Complexes did not precipitate at this concentration. In every system, the amount of PAA was kept constant as the amount of PEI and PVP was varied during each experiment. Five measurements performed for each system at a particular temperature and data which are obtained from pH measurements at various temperatures are tabulated in Table 1.

3 Results and Discussion

The complexation of poly acrylic acid (PAA) with poly ethylene imine (PEI) effectively involves the interactions between carboxylic units of PAA with amino groups of PEI through electrostatic interactions (1–5, 23–26). Whereas complex formation of PAA with PVP is attributed to hydrogen bonding and ion dipole interactions, as is shown below.



PAA-PEI



PAA-PVP

Keeping this in mind, in the present investigation, several three component interpolymer complexes have been prepared by mixing PAA with stoichiometric quantities of PEI and PVP in a mixed solvent containing 10% methanol + 90% water.

II) 1.0 unit mole PAA + 0.8 unit mole PEI
+ 0.2 unit mole PVP
III) 1.0 unit mole PAA + 0.6 unit mole PEI
+ 0.4 unit mole PVP
IV) 1.0 unit mole PAA + 0.4 unit mole PEI
+ 0.6 unit mole PVP
V) 1.0 unit mole PAA + 0.2 unit mole PEI
+ 0.8 unit mole PVP

The relative proportion of interacting forces, e. g. electrostatic, hydrogen bonding and ion-dipole interactions in each of these three component complexes (e.g. II to V) will depend on the actual composition of the complex (1–5, 13, 14, 26). One would expect it to be reflected on stability constant (***K***) and related thermodynamic parameters (e.g. ΔH° and ΔS°) of this complexes.

Table 1. pH Data for PAA and PAA-PEI-PVP complex systems in water-methanol mixture at various temperature

System	Composition of complex (unit mole)	pH							RSD
		20°C	30°C	40°C	45°C	50°C	55°C	60°C	
I	1.0 PAA	5.080	5.070	5.082	5.110	5.141	5.240	5.270	0.006
II	1.0 PAA + 0.8 PEI + 0.2 PVP	5.430	5.467	5.641	5.744	5.744	5.955	6.014	0.007
III	1.0 PAA + 0.6 PEI + 0.4 PVP	5.557	5.415	5.570	5.695	5.725	5.713	5.805	0.009
IV	1.0 PAA + 0.4 PEI + 0.6 PVP	5.160	5.200	5.182	5.300	5.242	5.300	5.398	0.007
V	1.0 PAA + 0.2 PEI + 0.8 PVP	5.185	5.158	5.160	5.174	5.220	5.272	5.342	0.009

We have determined the stability constant (***K***), degree of linkage (***θ***), and other related thermodynamic parameters (e.g. ΔH° and ΔS°) for the complexation systems (II–V) by using Osada's method (2, 25, 26, 40). The method involves determination of degree of linkage (***θ***), which is defined as the ratio of binding groups to the total number of potentially interacting groups. The stability constant (***K***) is related to ***θ*** by:

$$\theta = 1 - ([H^+]/[H_0^+])^2 \tag{2}$$

$$\mathrm{K} = \frac{\theta}{\mathrm{C}_0(1-\theta)^2} \tag{3}$$

Where C_0 is the initial concentration of poly carboxylic acid ($\mathrm{mol \cdot L^{-1}}$) and $[H^+]$ and $[H^+]_0$ are proton concentration in the poly carboxylic acid solution in the presence and absence of proton accepting polymer, respectively. The values of ***θ*** for the complexes systems studied are given in Table 2.

The corresponding plots of Ln***K*** vs. reciprocal of temperature are shown in Figure 1.

It can be seen from Table 2 and Figure 1 that the relative stability of system II is much greater compared to the other systems. This is in view of the fact that system II has a relatively higher proportion of electrostatic interaction compared to the other systems. At elevated temperature, ***K*** of the system II increases due to reinforced hydrophobic interactions, whereas coulomb forces are only slightly affected. However, at ≈50°C, ***K*** decreases possibly due to the slow disintegration of the complex. It is shown that beyond 50°C, ***K*** for all complex systems abruptly falls after the initial increase with temperature, whereas the fall in plots of Ln***K*** vs. 1/T for the same systems when we studied them in pure aqueous medium, beyond 50°C was gradual. This behavior is expected, because in the presence of methanol, hydrophobic interactions are considerably reduced (2, 33). This in fact, is reflected on the absolute value of ***K*** beyond this temperature. In system III, IV and V the relative proportions of hydrogen bonding and ion-dipole interactions are large due to the presence of a higher proportion of PVP in these complexes. Since temperature has a pronounced influence on hydrogen bonding complexes ***K*** for these complexes has been found to be relatively small. However, the effect of hydrophobic interaction is likely to stabilize the hydrogen bond containing complex more than the polyelectrolyte complex (2, 32), and will partly compensate for the temperature effect.

The thermodynamic Parameters (e.g. ΔH° and ΔS°) can be calculated from the temperature dependence of stability constant (***K***) of the complexes, by using the following relationships (2, 24–26, 31, 40).

$$\Delta G^0 = -RTLnK \tag{4}$$

$$d(LnK)/d(1/T) = -\Delta H^0/R \tag{5}$$

$$\Delta S^0 = -(\Delta G^0 - \Delta H^0)/T \tag{6}$$

Where ΔG° is the change in standard free energy and (R) is the molar gas constant.

The standard enthalpy and entropy change for complexation system (II to V) have been calculated on the basis of the above equations at several temperature and the corresponding plots are depicted in Figures 2–3. The complexation systems showed two maxima for ΔH° and ΔS° for all systems at 40°C and 55°C. It is evident from Figures 2 and 3 that the first maxima values ($\Delta H_{(max.)1}$ and $\Delta S_{(max.)1}$) are in

Table 2. Degree of the linkage of complexes at various temperatures

System	Composition of complex (unit mole)	Degree of linkage (θ)						
		20°C	30°C	40°C	45°C	50°C	55°C	60°C
II	1.0 PAA + 0.8 PEI + 0.2 PVP	0.799	0.840	0.923	0.946	0.937	0.962	0.967
III	1.0 PAA + 0.6 PEI + 0.4 PVP	0.889	0.796	0.893	0.932	0.932	0.905	0.915
IV	1.0 PAA + 0.4 PEI + 0.6 PVP	0.310	0.450	0.367	0.370	0.373	0.243	0.449
V	1.0 PAA + 0.2 PEI + 0.8 PVP	0.385	0.334	0.297	0.258	0.302	0.139	0.286

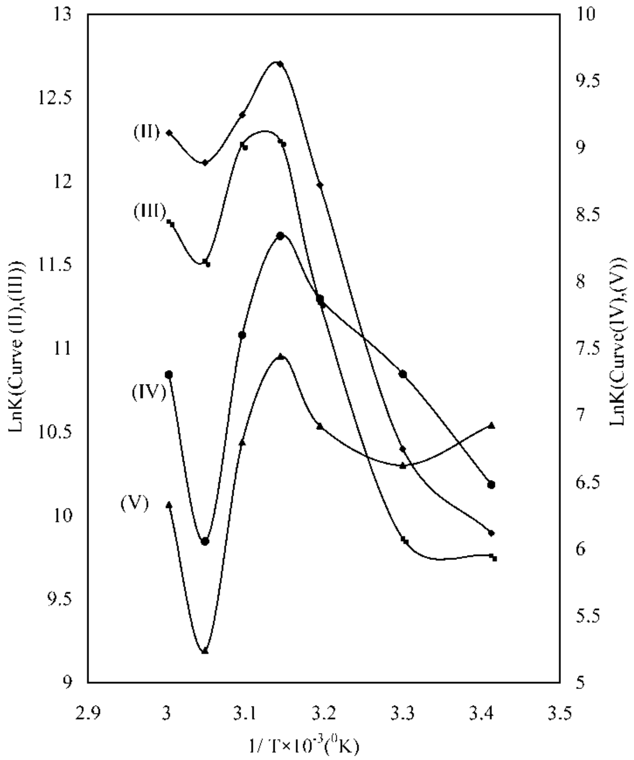


Fig. 1. Relationship of Ln K vs. 1/ T for complexation system: (II), (III), (IV), (V).

the following order:

III > II > IV > V

However the second maxima values ($\Delta H_{(\max.)2}$ and $\Delta S_{(\max.)2}$) for system II-V follow a different trend:

V > IV > III > II

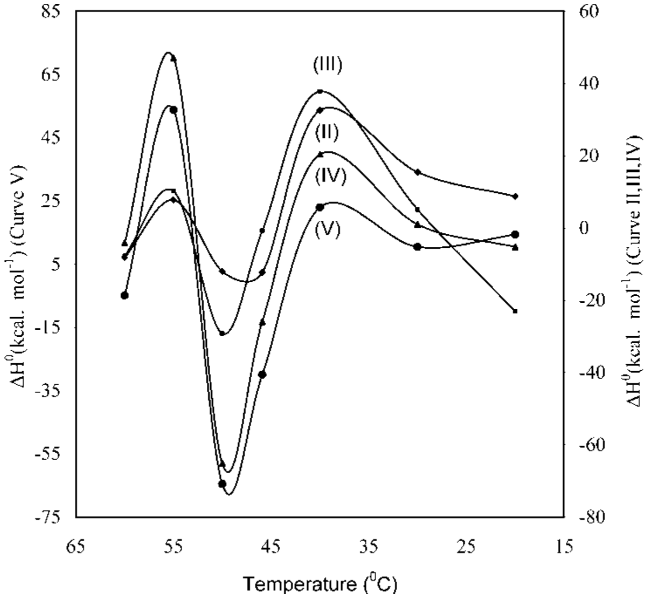


Fig. 2. Temperature dependence of standard enthalpy changes ΔH° for complexation system: (II), (III), (IV), (V).

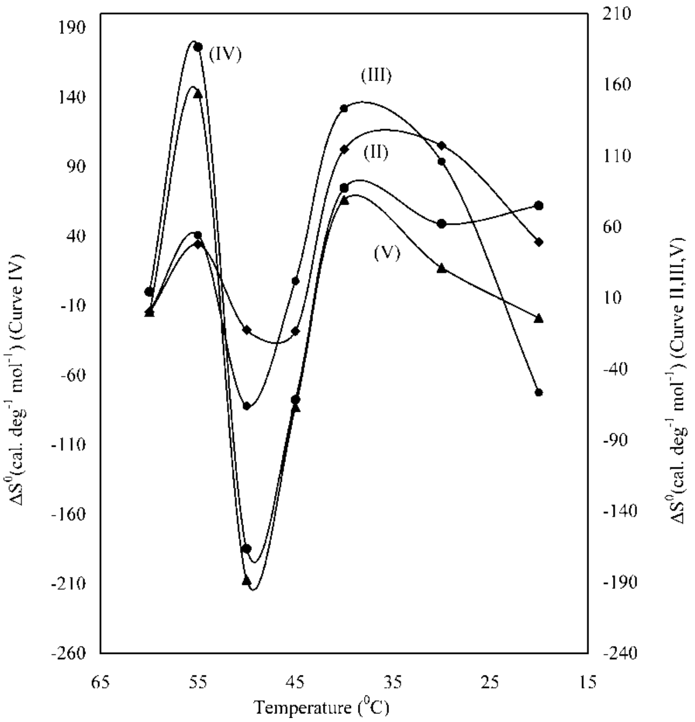


Fig. 3. Temperature dependence of standard entropy changes ΔS° for complexation system: (II), (III), (IV), (V).

The maxima values of the four systems are tabulated in Table 3.

In system III, larger amount of PVP as compared to system II result larger value of $\Delta H_{(\max.)1}$ up to 40°C. This is due to the fact that hydrophobic interactions also reinforce hydrogen bonding in addition to strong electrostatic interactions of PEI. In system II, larger proportion of PEI as compared to IV, make the complex system II more stable, since electrostatic interactions are not much effected by temperature. However, around 40°C, all this interactions get destabilized and an abrupt fall in ΔH° has been observed (cf. Figure 2). The second maxima value $\Delta H_{(\max.)2}$ at 55°C for all complex systems may be attributed to the relative amount of hydrogen bonding interactions, which get destabilized at higher temperature and result an abrupt rise in ΔH° (cf. Figure 2). This behavior is due to abrupt conformational change, which is likely to contribute to overall change in ΔH°. Since system V has more hydrogen bonding, the height of the maxima is more in these system followed by IV and III. In fact, the absolute value of $\Delta H_{(\max.)2}$ for all systems are proportional to the amount of PVP units in the complexes.

Therefore at a higher temperature, the contribution due to conformational change towards ΔH° will be more because the net enthalpy change (ΔH_M) during interpolymer complex formation consist of three basic steps e.g. desolvation (ΔH_1), complex formation by electrostatic, ion-dipole or hydrogen bonding interaction (ΔH_2) and conformational changes involving complex formation (ΔH_3). Therefore,

Table 3. The maxima values of ΔH^0 and ΔS^0 observed for various systems

System	Composition of complexes (Unit mole)	Maxima observed in ΔH^0 (K cal $\cdot$ mol^{-1})		Maxima observed in ΔS^0 (cal $\cdot$ deg^{-1} $\cdot$ mol^{-1})	
		$\Delta H_{(max.)1}$	$\Delta H_{(max.)2}$	$\Delta S_{(max.)1}$	$\Delta S_{(max.)2}$
(II)	1.0 PAA+ 0.8 PEI + 0.2 PVP	28.412	7.754	114.573	47.703
(III)	1.0 PAA + 0.6 PEI + 0.4 PVP	37.836	10.268	143.286	54.199
(IV)	1.0 PAA + 0.4 PEI + 0.6 PVP	20.406	47.102	78.947	154.017
(V)	1.0 PAA + 0.2 PEI + 0.8 PVP	18.444	53.753	74.566	175.913

ΔH_M is the sum of these contributions (2–5, 26):

$$\Delta H_M = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Since the contribution to each step will be different for the various systems, different values for ΔH_M are understandable.

The two maxima which are observed in ΔS° vs. T plots (cf. Figure 3) for all complexation systems (II–IV), also indicated a similar trend as in ΔH° vs. T plots (cf. compare Figure 2 with Figure 3).

This is understandable, because the overall change in entropy ΔS° at different temperature is obviously related to: (a) desolvation, (b) complex formation by electrostatic, hydrogen bonding, and (c) configurational change of the complexes as a result of destabilization of interaction forces within reacting pairs at different temperature (2–6, 26). Therefore, on the basis of arguments put forward earlier, and due to presence of different proportions of various reacting unit pairs in the respective complexes, one can justify the relative values of $\Delta S_{(max.)1}$ and $\Delta S_{(max.)2}$ for complexation system II–V.

4 Conclusions

In conclusion, it can be said that in the presence of methanol in the medium, the stability constant of the interpolymer complex decreases due to negligible hydrophobic interactions as well as a higher degree of solvation of the component polymer. In the presence of organic solvent in the medium, the values of ΔH° and ΔS° during complexation are entirely different from those observed in aqueous medium (41). This could possibly be attributed to strong interactions between component polymers and solvent, dielectric constant of medium, and higher degree of solvation.

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