Polymer Bulletin 61, 247–255 (2008)
DOI 10.1007/s00289-008-0943-5

Polymer Bulletin

Investigation on thermodynamic parameters and stability of some polyelectrolyte complexes with respect to ionic strength of the medium

B. Vasheghani F. (✉), F. H. Rajabi, M. H. Ahmadi, F. Mashhadi

[1)] Imam Khomeini International University, Faculty of Science, Department of Chemistry,
P.O.Box.: 288, Qazvin: 34149, I.R.Iran
E-mail: bvasheghanif@yahoo.com; Fax: +98 281 3780040

Received: 2 March 2008 / Accepted: 29 April 2008

Summary

The effect of ionic strength of the medium on stability constant and related thermodynamic parameters (e.g. ΔH^0 and ΔS^0) has been studied for a typical polyelectrolyte interpolymer complexes e.g. poly (acrylic acid), poly (ethylene imine) in aqueous solution using various inorganic salts.

Stability constant K, and related thermodynamic parameters have been calculated and compared for interpolymer complex in different complexation medium using Osada's method. The comparative study indicated considerable difference in the values of these parameters which has been explained on the basis of the relative strength of electrostatic interaction in different medium.

Introduction

Molecular interactions play a central role in the functions and structures of biological macromolecules. Synthetic polymers have been widely used as a simple models for biological macromolecules in order to understand the structure-property relationships of the complex natural macromolecules. A knowledge of the structure-property relationship of polymers and the interactions of polymer with other small and large molecules is also essential for the synthesis of polymers tailored for specific applications [1-4]. Water-soluble polymers, in particular, are useful as analogs in underestanding the behaviour of biological macromolecules. Polyelectrolytes are an important class of water-soluble polymers which have been widely studied for their solution behaviour [1-5]. The complexation between oppositely charged polyelectrolytes in solution results in the formation of polyelectrolyte complexes (PECs) which are mainly stabilized by electrostatic interactions. In spite of the comparatively short period of intensive investigation of polyelectrolyte complexes, their outstanding physico-mechanical, dielectric, ion-exchanging and optical properties have roused a great interest in the polymer materials[1-2]. Polyelectrolyte complexes not only have great significance from the biological point of view, but also at present they are widely used in modification of different surfaces[6,7] for preparation of selective membranes[8,9,10], hydrogel capsules[11,12], fibers[13], drugs and enzymes carriers[13,14] biomaterials[15], package films[16] and in purification and enrichment technologies [16].

The polyelectrolyte complex formation is controlled by many factors such as: solvent, ionic strength, temperature, pH, etc…. In additional hydrophobic interactions play an important role in stabilization of synthetic and natural polyelectrolyte complexes [1-5]. Though a considerable amount of work have been reported in the literature regarding the fundamental studies on these types of polymer complexes and their applications, but detailed thermodynamic studies particularly lacking. Keeping this fact in mind since the formation of PECs can be analyzed by electrochemical technique owing to release of counterions [1, 5], we used the potentiometric titration technique and Osad's method [1, 17-21] to evaluate the effect of ionic strength of the medium on stability constants and related thermodynamic parameters [e.g the change in standard free energy (ΔG^0), standard entropy (ΔS^0) and change in standard enthalpy (ΔH^0)] of these type of polycomplexes by using poly(acrylic acid) (PAA) and poly(ethylene imine) (PEI) base.

Experimental

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 [18, 22]. 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 vacuum 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 $[\eta] = KM_{\eta}^{\alpha}$ [23-25]. 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 $\overline{M}_{\eta} = 4.0 \times 10^5$.

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 $\overline{M}_n = 1.5 \times 10^5$.

The inorganic salts (NaCl, KCl, NH_4Cl), of analytical grade, were used as received.

Solvent

Double distilled water was used as the solvent for all the measurements.

Measurement of pH

The pH measurement of aqueous solutions 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 PVP. Complexes did not precipitate at this concentration. The data which obtained from pH measurements at various temperatures are tabulated in Table 1.

Table 1: pH data for complexes at various temperatures

System	Composition of complex (unit mole)	pH								
		20°C	25°C	30°C	35°C	40°C	45°C	50°C	55°C	60°C
	1.0PAA	4.320	4.337	4.355	4.377	4.400	4.425	4.435	4.470	4.470
(I)	1.0PAA +1.0PEI	3.936	4.009	4.082	3.847	3.649	3.155	3.907	3.905	3.913
(II)	1.0PAA +1.0PEI +NaCl	4.908	4.884	4.876	4.902	4.926	4.953	4.976	5.015	5.031
(III)	1.0PAA +1.0PEI +KCl	4.851	4.83	4.825	4.855	4.924	4.891	4.277	4.951	4.97
(IV)	1.0PAA +1.0PEI +NH_4Cl	4.905	4.87	4.89	4.909	4.93	4.947	4.959	4.97	4.952

Result and Discussion

It is known that the complexation between oppositely charged polyelectrolyte in solution results in the formation of polyelectrolyte complexes, which are mainly stabilized by electrostatic interaction. PECs are divided into four subclasses by a combination of strong and weak polyelectrolytes [1-3,5,18-20] and their formation can be analyzed by electrometric titration methods owing to the release of counterions. The complex formation in such systems is controlled by several critical factors such as minimal molecular weight, critical pH of complexation minimal amount of active group sequence, solvent nature, temperature etc… [1-3].

In order to evaluate the influence of ionic strength on the stability constant K and related thermodynamic parameters of PECs, in the present work we consider the stability of poly (acrylic acid) and poly (ethylene imine) (PAA-PEI) complexes as a function of temperature in presence of some low molecular weight inorganic salts. For this purpose several two component interpolymer complexes have been prepared by mixing PAA with stoichiometric quantities of PEI (1:1 unit molar ratio) in pure aqueous medium and in the mediums containing inorganic salts such as NaCl, KCl and NH_4Cl. Since high concentration of the polymer component leads to the suppression of the dissociation of polyelectrolyte components due to the rise in the electrostatic repulsion within inter and interamacromolecules and to the interpenetration of polymer chain, very dilute solution of polymer were prepared (i.e. 10^{-2}). Osada, s method has been chosen for calculation of stability constant K and degree of linkage θ of interpolymer complexes. The degree of linkage θ defined as the ratio of the binding groups to the total number of potentially interacting groups and it is related to stability constant K of the interpolymer complex by the following equation [1-3, 19-20].

$$\theta = 1 - \left([H^+]/[H^+]_0\right)^2 \qquad (1)$$

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

Where C_0 is the initial concentration of polycarboxylic acid [mol/L], $[H^+]$ and $[H^+]_0$ are the proton concentrations in the polymer solution in presence and absence of complementary polymer. The stability of these complexes in different medium at higher temperature is likely to be influenced by the relative strength of electrostatice interaction in them.

The value of θ and K have been determined at several temperature for the complex system in salt free solution and in solutions containing inorganic salt.

It should be noted that, when increasing the ionic strength, the following phenomena are expected to be observed: (1) reduction of electrostatic interactions due to the screening effect of micro salts, (2) acceleration of dissociation of weak polyelectrolytes owing to the decrease of intermolecular electrostatic repulsion, (3) increase of hydrophobicity caused by the contraction of polyelectrolyte chains.

Corresponding plots of Ln K versus reciprocal of temperature for system I to IV are shown in fig. 1.

It can be seen from fig. 1; the complexation system I (i.e PAA-PEI in pure aqueous medium) showed an increase in Ln K with increase in temperature (cf. curve A in fig. 1). However in the case of system II, III and IV there is an initial fall in Ln K with increase in temperature up to 25°C and then there is an increase in Ln K beyond this temperature. This trend could be in view of the fact that in system II-IV addition of

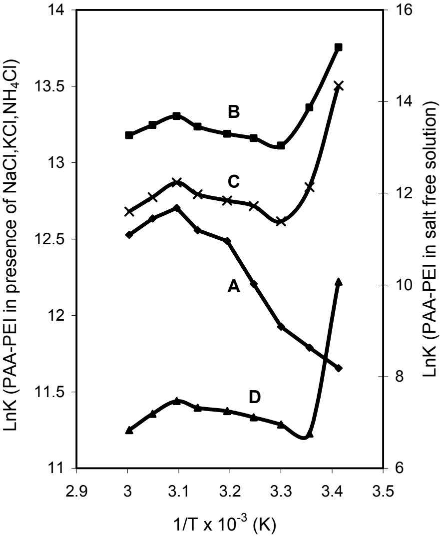

Fig. 1: Relationship of Ln K versus $1/T\times10^{-3}$ for complexation systems: I (A), II (B), III (C) and IV (D).

the salts increase the ionic strength of the solutions and cause partial dissociation of PAA. This results some preliminary interaction between carboxylic groups of the acid and positive ions of the salts. With increase in temperature these interaction become less significant. As can be seen from figure 1, for all these systems (i.e II-IV) beyond 25°C as a result of strong electrostatic interactions K will increase with increase in temperature up to 50°C.

As mentioned above for weak polyelectrolyte like PAA, addition of salts lead to the charge screening effects, which also favors compaction of macromolecules. Hence, the enhancement in complexation ability of these polymeric pairs can be explained by additional stabilization of PECs by hydrophobic interaction caused by deterioration of thermodynamic quality of the solvent in the presence of salt. It can also be seen that the K for system II is more as a result of stronger electrostatic interaction between PAA-PEI in presence of Na^+ as compared to K^+ and NH_4^+. It should be noted that the inorganic salts can be arranged in the following series: NaCl> KCl> NH_4Cl by their ability to cause the dissociation of PAA [27-29]. These results are confirmed by the literature data, which reported that the binding ability of Na^+ to PAA is higher than that of K^+ [27-29].

In system IV (i.e in presence of NH_4Cl) due to following reaction $\boldsymbol{NH_4^+ \rightarrow NH_3 + H^+}$ an increase of H^+ concentration in the medium results in less dissociation of PAA, hence weaker electrostatic interaction is occurred. It can be seen in system I there is a continuous increase of K with temperature. However, because of the slow disintegration of the complex, the value of K for all systems (I-IV) decreases at 50°C.

The thermodynamic parameters [e.g. change in standard enthalpy (ΔH^0) and entropy (ΔS^0)] can be calculated from temperature dependence of the stability constant K by the thermodynamic equation [1-3, 19-20]:

$$\Delta G^0 = -RTLnK \tag{3}$$

$$\mathrm{d(LnK)/d(1/T) = -\Delta H^0/R} \tag{4}$$

$$\Delta S^0 = -(\Delta G^0 - \Delta H^0)/T \tag{5}$$

Where R is the molar gas constant and ΔG^0 is the change in standard free energy.

The plots of ΔH^0 vs T and ΔS^0 vs T for PAA-PEI complexes in systems I-IV are depicted in figures 2 and 3 respectively.

The net enthalpy change ΔH^0 and overall change in entropy ΔS^0 during interpolymer complex formation consist of three basic steps e.g. (1) desolvation, (2) complex formation as a result of electrostatic interaction and (3) conformational changes involving complex formation. Therefore, the overall change in ΔH^0 and ΔS^0 are the sum of these contributions [19-21, 24]. Since the contribution to each step will be different values for ΔH^0 and ΔS^0 are understandable. On comparing ΔH^0 vs T and ΔS^0 vs T curves for all complex system in pure aqueous and in water salt mixture (i.e. I-IV) three distinct maxima can be seen for each system at 32.5°C, 45°C and 55°C respectively.

The maxima values for all systems are tabulated in table 2. It can be seen from table 2 that $\Delta H^0{}_{(max.)1}$, $\Delta H^0{}_{(max.)2}$ and $\Delta H^0{}_{(max.)3}$ values follow different trends in complexation system I to IV.

The $\Delta H^0{}_{(max.)1}$ values were found to be in the following order;

I > IV > III > II

Table 2: The maximum values of ΔH^0 and ΔS^0 observed for various system

System	Composition of complex (unit mole)	Maxima observed in ΔH^0 (K cal. mol^{-1})			Maxima observed in ΔS^0 (cal. deg^{-1}. mol^{-1})		
		(max)1	(max)2	(max)3	(max)1	(max)2	(max)3
(I)	1.0PAA+1.0PEI	35.24	18.18	23.5	135.44	84.44	109.3
(II)	1.0PAA+1.0PEI+NaCl	10.9	45.4	11.9	51.95	135.5	67.4
(III)	1.0PAA +1.0PEI+KCl	14.35	36.6	16.1	64.4	118.5	83.4
(IV)	1.0PAA +1.0PEI+NH_4Cl	18.2	30	20	79.6	102	97.8

This trend is in accordance with the influence of inorganic salts on polymer – solvent interaction. It can be seen this maxima as a result of desolvation at 32.5°C is much higher for system I as compared to other system (i.e. in absence of inorganic salt). It is known that the presence of salt in aqueous solution will reduce the polymer – solvent interaction. Figure 2 shows NaCl caused more deterioration of thermodynamic quality of the solvent which results less polymer – solvent interaction as compared to KCl and NH_4Cl.

$\Delta H^0_{(max.)1}$ for various salts is shown to be in following order:

$NH^+_4 > K^+ > Na^+$

The second maxima value, $\Delta H^0{}_{(max.)2}$ is observed at 45°C for the four systems (e.g. I-IV) indicates the following trend (cf. fig. 2 and table 2)

II > III > IV > I

This maxima attributed to relative strength of electrostatic interactions and indicate presence of inorganic salts in the medium dissociate PAA more and results stronger electrostatic interaction between PAA and PEI as compared to pure aqueous medium.

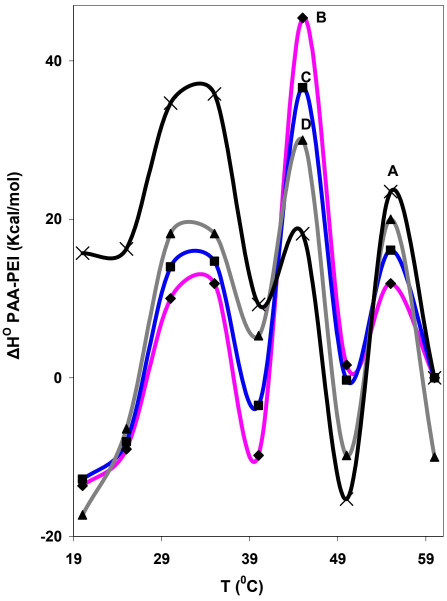

Fig. 2: Temperature dependence of standard enthalpy changes ΔH^0 for complexation systems: I (A), II (B), III (C) and IV (D).

Moreover, hydrophobic interactions are likely to reinforce the electrostatic interaction more in presence of inorganic salts.

It can also be seen that in presence of Na^+ the electrostatic interaction between PAA-PEI is stronger than in the case of K^+ and NH^+_4.

The third and final maxima, $\Delta H^0_{(max.)3}$ observed at 55°C indicates the following trend

I > IV > III > II

This may be attributed to abrupt conformational change which is likely to contribute to overall change in ΔH^0. The minima which is observed before this maxima at 50°C indicates disintegration of the PEC complex. As a result of disintegration of the PEC at this temperature the entropy of the solution will increase. The new arrangement (configuration) of the released component in the solution, in order to obtain a more stable arrangement will result in conformational change.

This is understandable at higher temperature weaker interactions get more destabilized. Hence as a result of lower stability constant of the PEC, more dissociation of the complex and conformational change is expected. In presence of salts the disintegration of PEC and conformational change at higher temperature are in following order

$NH^+_4 > K^+ > Na^+$

The three maxima observed in ΔS^0 vs T plots (cf. fig. 3) for the four complexation systems, also indicated similar trend as in ΔH^0 vs T curves (cf. compare fig. 2 with fig. 3).

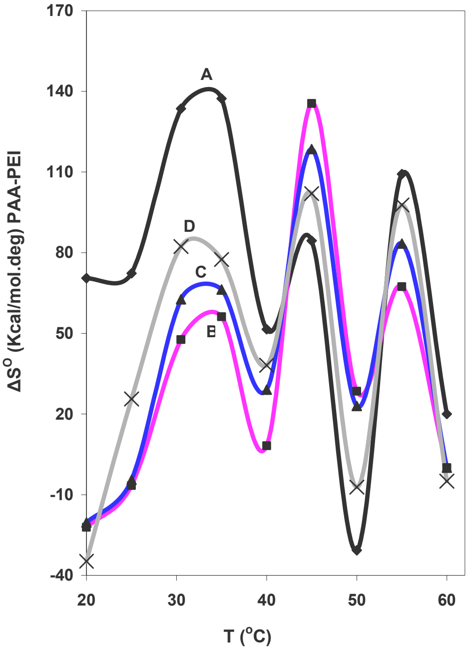

Fig. 3: Temperature dependence of standard entropy changes ΔS^0 for complexation systems: I (A), II (B), III (C) and IV (D).

The overall change in entropy (ΔS^0) at different temperature is obviously related to: (a) desolvation, (b) complex formation by electrostatic interactions and (c) conformational change of the complexes as a result of destabilization of interaction forces within reacting polymer at different temperature [19-21, 24]. Therefore, on the basis of arguments put forward earlier, and due to the presence of different inorganic salt and their effect on ionic strength of the medium and their ability to dissociate PAA, one can justify the relative values of $\Delta S^0_{(max.)1}$, $\Delta S^0_{(max.)2}$ and $\Delta S^0_{(max.)3}$ for the complexation systems I to IV.

It may be concluded that polyelectrolyte complexes formed as a result of electrostatic interaction between PAA-PEI is influenced by the presence of specific types of inorganic salts.

The effect of inorganic salts on polyelectrolyte complexes is determined by the action of two factors: 1) increase in ionic strength of the solution leads to better dissociation of PAA, 2) addition of inorganic salts deteriorates the thermodynamic quality of the solvent with respect to polymers and leads to strengthening of hydrophobic interactions both of these factors favor the PEC complexation. The contribution of each is reflected in the temperature dependence of K and other related thermodynamic parameters. The information obtained in this investigation can be used for the predication of solubility behavior of polymeric materials based on IPC in the media of different ionic strength.

References

1. Bekturov E A, Bimendina L A (1981) Adv Polym Sci 41: 99.
2. Tsuchida E, Abe K (1982) Adv Polym Sci 45: 1.
3. Jiang M, Li M, Xiang M, Zhou H (1999) Adv Polym Sci 146: 121.
4. Huipeny Z, Weixin L, Guang Y, Qun C (2005) European Polymer Journal 41: 2354-59.
5. Khutoryanskiy V V, Nurkeeva Z S, Mun G A, Sergaziyev A D, Ryskalieva Z, Rosiak J M (2003) European Polymer Journal 39: 761-66.
6. Kramer G, Buchhammer H M, Lunkwitz K (1997) J Appl Polym Sci 65: 41-50.
7. Petzold G, Berwald S, Buchhammer H M (2000) Macromol Mater Eng 279: 10-8.
8. Karakane H, Tsuyumoto M, Maeda Y, Honda Z (1991) J Appl Polym Sci 72: 3229-39.
9. Nam S Y, Lee Y M (1997) J Member Sci 135: 161-71.
10. Prafula C, Narendra N D, Neelotpal S S (2007) Polymer Bulletin 58: 489-494.
11. Kono K, Ohno T, Kumei T, Takagishi T (1996) J Appl Polym Sci 59: 687-93.
12. Yamamoto H, Senoo Y (2000) Macromol Chem Phys 201: 84-92.
13. Peniche C, Elvira C, San R (1998) Journal Polymer 39: 6549-54.
14. Kabanov V A (1994) Vysokomol Soedin 36: 183-97.
15. Barbani N, Lazzeri L, Cristallini C, Cascone M G, Polacco G, Pizzirani G (1999) J Appl Polym Sci 72: 971-6.
16. Torres J A, Dewitt M, Savent V (1997) Biopolymers Utilizing Nature's Advanced Materials. ACS Symposium Series 723, 248-81 (Chapter 17].
17. Osada Y (1979) J Polym Sci Polym Chem 17: 3478.
18. Vasheghani F B, Rajabi F H, Ahmadi M H (2007) Journal of Macromolecular Science Pure and Applied Chemistry 44: 113-118.
19. Chatterjee S K, Vasheghani F B, Rajabi F H, Chatterjee N, Polymer 33(15): 3308.
20. Vasheghani F B, Rajabi F H, Ahmadi M H (2007) Polymer Bulletin 58: 553-63.
21. Chatterjee S K, Misra N (1997) J Polym Comm 38: 1985.
22. Chatterjee S K, Chatterjee N, Khan M, Gosh S (1990) J Polym Comm 32(7): 220
23. Levy G B, Frank H P (1955) Polymer Science 17: 247.
24. Vasheghani F B, Rajabi F H, Ahmadi M H, Nouhi S (2005) Polymer Bulletin 55: 437-45.

25. Yan R X, Chen Z X, Song Z W, Bao Q N (1989) Water Soluble Polymers. Beijing: Chemical Industry Press, p. 145.
26. Fengling B, Mingzhu L (2003) European Polymer Journal 39: 1867-1879
27. Nurkeeva Z S, Mun G A, Khutoryanskiy V V, Bitekenova A B, Dubolazov A V, Esirkegenova S Z (2003) The European Physical Journal E10: 65-68.
28. Shuping J, Mingzhu L, Shilan C, Yong C (2005) European Polymer Journal 41: 2406-413.
29. Mun G A, Nurkeeva Z S, Khutoryanskiy V V, Sarybayeva G S, Dubolazov A V (2003) European Polymer Journal 39:1687-9.