COMPLEXATION BEHAVIOR OF POLY(ACRYLIC ACID) AND POLY(ETHYLENE OXIDE) IN WATER AND WATER-METHANOL

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Key Words: Complexation, Hydrogen Bonding, Hydrophobic Interaction, Unit Mole Ratio, Stability Constant

ABSTRACT

To investigate the effects of solvent type and temperature on the interpolymer complexation via hydrogen bonding, a study was made on the complex system of poly(acrylic acid) (PAA) and poly(ethylene oxide) (PEO) in two kinds of solvent systems, pure water and water-MeOH (30 wt%) mixed solvent, at various temperatures using the Ubbelohde viscometer, pH-meter, and UV spectrophotometer. The repeating unit mole ratio at the most optimum complexation as confirmed by the reduced viscosity measurement was shifted from [PEO]/[PAA] $\approx$ 1.25:1 to 1.5:1 by the addition of methanol to water. From the UV measurement, the deviation from the "isosbestic point" (where the absorbance of the solution remains constant) has presented another evidence for the solvent effect on complexation. In addition, the analysis of the changes in thermodynamic properties upon complexation as well as the fraction of carboxyls associated with PEO oxygens and the complex stability constant as estimated by potentiomet-

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ric titration at several temperatures reveals that the complex formation in mixed solvent became more unfavorable compared to that in pure solvent at high temperatures above 30°C. This could be explained by considering that in water the hydrophobic interaction as well as the hydrogen bonding may greatly contribute to the stabilization of the polymer complex formed, while in water-methanol the main stabilizing force would be the hydrogen bonding alone.

INTRODUCTION

In general, proton-donating polymers like polycarboxylic acids [e.g., poly(acrylic acid) (PAA) or poly(methacrylic acid) (PMAA)] and proton-accepting polymers such as poly(ethylene oxide) (PEO) or polyvinylpyrrolidone(PVP) typically interact with each other almost stoichiometrically to form a polymer complex via hydrogen (H) bonding preferably in aqueous media [1-3]. Hydrogen bonding complex formation proceeds by the formation of H-bonds between the hydrogen atoms in the non-dissociated -COOH groups of the polyacid and oxygen atoms of the polybase [4-9]. Especially, PEO and PAA of special interest in the present study is known to form a most stable (or strong) complex usually at a repeating unit mole ratio (u.m.r.) of [PEO]/[PAA]=1:1 [4-9]. However, the interpolymer complexation behavior (including the stoichiometric ratio) via H-bonding in solution has been found to be highly sensitive to such factors as pH, temperature, type of solvent (or dielectric constant), polymer concentration, structure and molecular weight of the component polymers, hydrophobic interaction, etc. [6-11]. Thus, most studies have been performed on the polymer complex systems based on H-bonding mainly focusing on the effects of these factors on complexation. Experimental techniques used widely for this purpose are viscosity [3, 4, 6-8, 15, 19], potentiometric titration [6, 11-15], turbidmetry [6], and UV spectroscopy measurements [16-18].

The present study also aims at elucidating mainly the effects of solvent and temperature on the H-bonded complexation. Hence, a comparative study was made on the model complex system of PAA and PEO in two kinds of solvent systems, water (pure solvent) and water-methanol (30% by weight) (mixed solvent), at various temperatures by means of the Ubbelohde viscometer, pH-meter, and UV spectrophotometer. In addition, changes of thermodynamic properties upon complexation as well as the degree of linkage (defined as the ratio of

the bound groups to the total of potentially interacting groups) and the complex stability constant have been estimated from the pH measurement as functions of temperature to investigate the role of hydrophobic interaction in the stabilization of polymer complex formed.

EXPERIMENTAL

Materials

PEO and PAA used in this work were purchased from Aldrich Chemical Co., whose molecular characteristics are given in Table 1 together with the viscosity-average molecular weights (Mv) calculated from the corresponding Mark-Howink equations. For all experimental measurements, triply distilled water and distilled methanol were used as solvents. For the pH control of complex solutions, HCl and NaOH as received from Aldrich Chemical Co. were used in aqueous solution and powder state, respectively.

Measurements

Viscosities on mixed dilute solutions ($C_{PAA} = 0.067$ g/dL) of PAA with PEO added to give required unit mole ratios in water and water-methanol (30 wt%) were measured at 30 ± 0.02 °C with an Ubbelohde-type viscometer. Polymer complex samples for the pH and UV measurements were made by fixing the unit mole ratio at [PEO]/[PAA]=1:1 and changing the pH value from 2 to 12. UV absorption spectra and pH measurements were performed using a

TABLE 1. Molecular Weight Characteristics of PAA and PEO

Sample	Mw[a]	Mv[b]
PAA	450,000	420,000
PEO	600,000	590,000

[a] Data were supplied by Aldrich Chemical Co.

[b] PAA : $[\eta] = 42.2 \times 10^{-3}$ Mv$^{0.62}$ (25 ℃, 2M NaOH aqueous solution)

PEO : $[\eta] = 157 \times 10^{-3}$ Mv$^{0.5}$ (25 ℃, water)

UVicon 860 spectrophotometer and a Cyberscan 2000 pH-meter, respectively, at room temperature under nitrogen atmosphere. The pH titration was carried out with 0.1N HCl and 0.1N NaOH aqueous solutions.

RESULTS AND DISCUSSION

Viscosity

Viscometric quantities like the specific (η_{sp}) or intrinsic ($[\eta]$) viscosities have been most frequently used in studies of conformational changes of the component polymers accompanying the complex formation. It is generally known that the complexation between PAA and PEO in dilute aqueous solution via H-bonding brings about a minimum viscosity at a complex stoichiometric u.m.r.(usually [PEO]/[PAA]=1:1) due to the formation of more compact complex molecules compared to the pure state of each complementary polymer.

Figure 1 shows the relationship between the reduced viscosity (η_{sp}/C_{PAA}) for the dilute PAA/PEO complex system ($C_{PAA} = 0.067$ g/dL) and the fraction of PEO added (expressed as [PEO]/[PAA]) in water and water-MeOH (30 wt%) at 30°C. The minimum point of the reduced viscosity (corresponding to the maximum complex formation point) of the mixture solution is observed near [PEO]/[PAA] (in u.m.r.) = 1.25:1 and 1.5:1 in water and water-MeOH medium, respectively. This could be explained as follows :

The PAA/PEO complex formation proceeds via H-bonding between the hydrogen atoms in the non-dissociated -COOH groups of PAA and oxygen atoms in the main chain of PEO, as stated before. So, the existence of certain number of undissociated carboxyl groups is necessary to form a stable complex. Generally, the dissociation behavior of weak carboxylic acids is influenced by the properties (such as dielectric constant) of the medium [19]. For reference, the values of the dielectric constant of water and MeOH at 25°C are reported to be 78.5 and 32.6, respectively. In this regard, the addition of MeOH with the lower dielectric constant to water is expected to cause the dielectric constant of the medium to decrease and hence, the dissociation of carboxylic groups to be weakened, favorably for the complex formation. However, what is more important, the addition of MeOH, a less polar solvent than water, is also expected to disrupt the structure of water molecules and reduce the hydrophobic interaction (between methylene groups of PAA and solvent) responsible for the stabilization of H-bonded polymer complex. Consequently, more numbers of active sites of PEO in the water-MeOH medium will be needed to form a stable complex than in water, leading to a higher stoichiometric ratio.
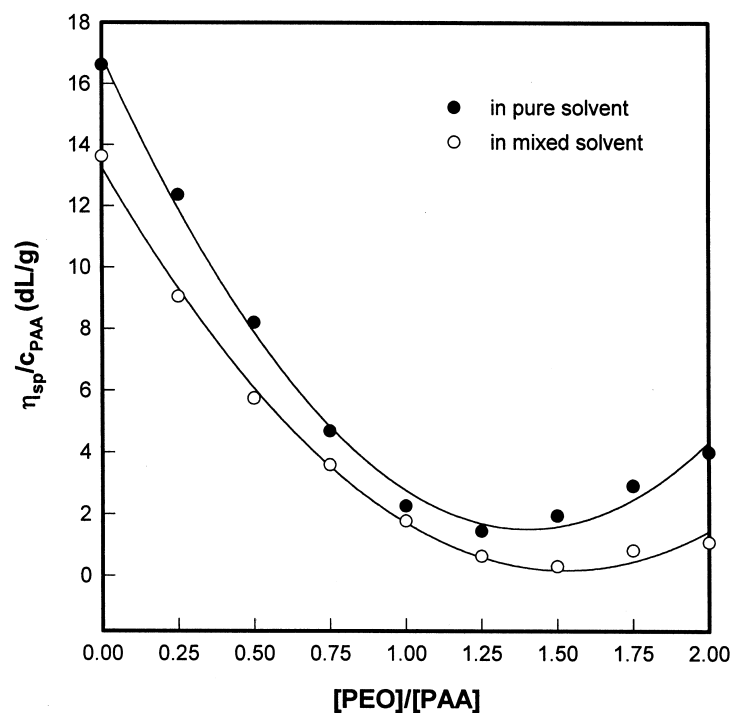
Figure 1. The unit mole ratio ([PEO]/[PAA]) dependence of the reduced viscosity for PAA/PEO complex system (C_{PAA} = 0.067 g/dL) in pure solvent (water) and mixed solvent (water-MeOH, 30 wt%) at 30°C.

The conformational changes of the PAA and PEO component molecules upon complexation were studied by measuring the viscosities of dilute solutions for the homo PAA-pure solvent system, homo PAA-mixed solvent system, PAA/PEO-pure solvent complex system, and PAA/PEO-mixed solvent complex system under varied pH (2 to 12) conditions at 30°C.

Figure 2 shows the relationship between the reduced viscosity ((η_{sp}/C_{PAA}, C_{PAA} = 0.067 g/dL) of homo PAA and PAA/PEO (1:1 by u.m.r.) complex solutions and the value of pH in water and water-MeOH solvent systems, respectively, at 30°C. At lower pH (pH 3.5-5.5), the PAA/PEO complex system is found to have the lower (reduced) viscosity than the homo PAA system for pure solvent, probably for the same reason as discussed in Figure 1, the tendency being less obvious for mixed solvent with lower dielectric constant. In addition, the pure solvent system appears to exhibit the higher viscosity than the mixed solvent system for homo PAA solution, but about the same viscosity as the mixed
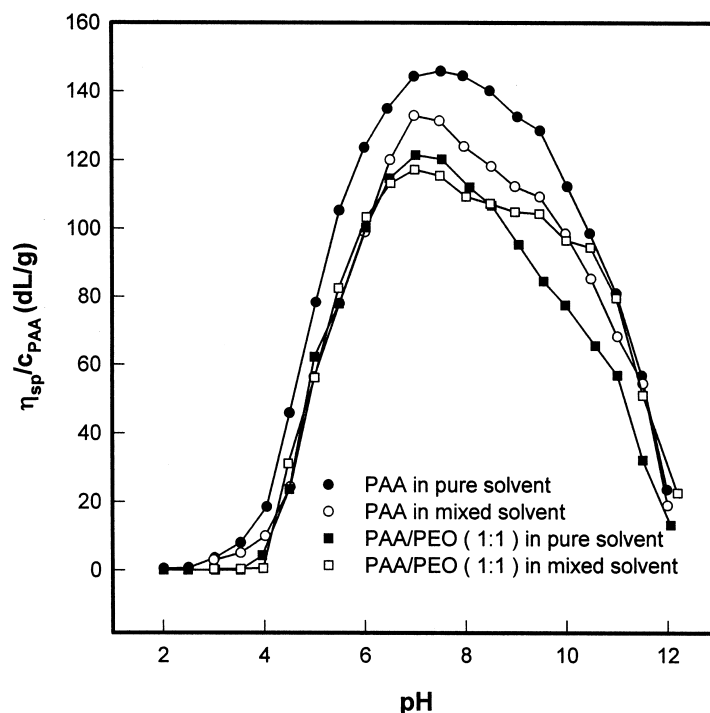
Figure 2. Relationship between the reduced viscosity of PAA and 1:1 unit mole ratio PAA/PEO complex solutions (C_{PAA} = 0.067 g/dL) and pH in water and water-MeOH (30 wt%) at 30°C.

solvent system for PAA/PEO complex solution. For homo PAA solution, in particular, it could also be explained as the depression of dissociation of -COOH groups attached to a PAA chain by the addition of MeOH to water, leading to weakened mutual repulsion of -COO⁻ ions, and hence smaller hydrodynamic volume and viscosity. With further increase in pH, on the other hand, all the curves in Figure 2 show a common tendency of the reduced viscosity to increase up to about pH 7 and then decrease with increasing pH, keeping similar trends to a lower pH region. This could be explained as follows:

The first increase in reduced viscosity with pH may be ascribed to the increased hydrodynamic volume of polymer chains to the mutual repulsion of -COO⁻ ions attached to a dissociated PAA chain caused by the increase in pH [20]. And the decrease in reduced viscosity with further increase in pH above ca. 7 seems to be attributable to the fact that the dissociation of carboxylic groups of PAA becomes saturated at higher pH and further the increase in ion pairs formed between -COO⁻ and Na⁺ caused by the still added base (NaOH) will bring about the decrease in

mutual repulsion of -COO⁻ ions, yielding a smaller hydrodynamic volume, and hence decreased (reduced) viscosity.

Potentiometric Titration

Generally, the complex formation between polyacids and polybases via H-bonding in aqueous media is strongly dependent on pH of the medium, which will affect the charge density of the component polymers, and their molecular conformations responsible for the interpolymer complexation. As noted previously, the complexation between PEO and PAA via H-bonds is produced only by carboxyl groups in the undissociated state. Thus, dissociated carboxyl groups in mixed polymer solutions at a certain pH are influenced by the complexation and become undissociated by the extraction (or recapturing) of protons from the solution into the domain of polymer chains, leading to an increase in pH of the medium [8].

Hence, Figure 3 shows the dissociation behavior of PAA and PAA/PEO in water and water-MeOH upon titration with HCl and NaOH aqueous solution. A closer inspection of the titration curves shows that in the case of homo PAA
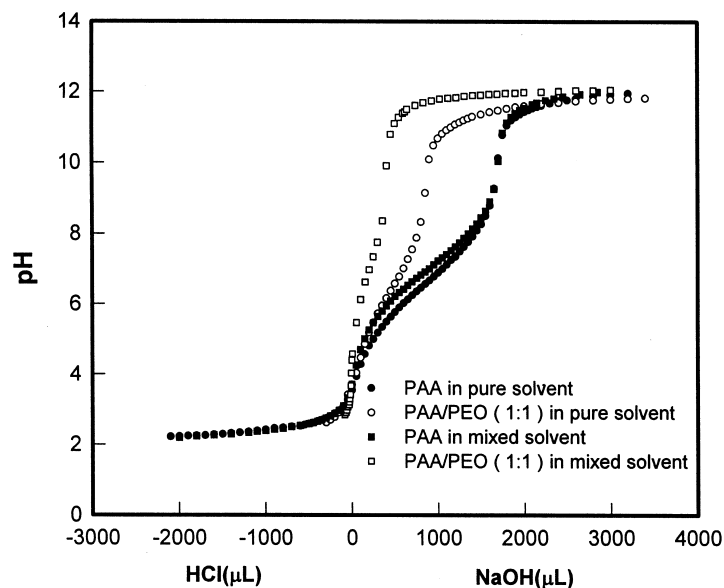
Figure 3. Potentiometric titration curves for PAA and PAA/PEO (1:1) complex solutions (C_{PAA} = 0.067 g/dL) in water and water-MeOH (30 wt%) at room temperature.

solution in both water and water-methanol, the contents of NaOH needed to reach the equivalent point (near pH 7) are about 1,800 $\mu\ell$ while in the case of PAA/PEO complex solution in both water and water-methanol, the contents of NaOH needed are about 900 $\mu\ell$ and 500 $\mu\ell$, respectively. This could be understood by considering that the complex formation between PAA and PEO via H-bonds may suppress the dissociation of carboxyl groups attached to a PAA chain and that the addition of methanol in water may also cause the dissociation of carboxyl groups to a decrease as a result of the decrease in dielectric constant of the medium, as pointed out before.

UV Spectra

UV spectra of monocarboxylic acid and its salt are generally known to have two main bands ascribed to COOH and COO⁻. The UV spectra of PAA also have two main bands ascribed to COOH $\eta\rightarrow\pi^*$ and to COO⁻ $\pi\rightarrow\pi^*$. Since the absorbance of the band of $\eta\rightarrow\pi^*$ decreases while that of $\pi\rightarrow\pi^*$ increases with pH as shown in Figure 4(a), a clear "isosbestic point" (where the absorbance of the solution remains constant) appears as a result at $\lambda = 223$ nm over a whole range of pH. The existence of an isosbestic point for the homo PAA solution in water suggests only two kinds of species, COOH and COO⁻. The UV spectra of PAA also show the deviation from the isosbestic point only in the region above pH = 12. From this fact, we could suggest that the formation of -COO⁻Na⁺, which is caused by interaction between dissociated Na⁺ from excess NaOH and -COO⁻ of PAA, brings about the deviation from the isosbestic point.

Comparing the deviation point of the homo PAA system with that of the PAA/PEO (1:1 by u.m.r.) complex system, as given in Figure 4(b), the PAA/PEO complex is found to have the deviation point at the lower pH. This may result from the fact that the formation of complex between PEO and PAA via H-bonds decreases the dissociation of carboxyl groups attached to PAA chains in aqueous solution, as stated before.

Figure 4(c) and Figure 4(d) show the pH dependence of UV spectra for homo PAA and PAA/PEO complex solutions in water-MeOH (30 wt%). From the comparison of Figures 4(a)-4(d), we can notice that in the case of homo PAA solution there seems little difference in the deviation points between water and water-MeOH solvent systems. In the case of PAA/PEO complex solution, however, the deviation points for water and water-MeOH turn out to be about 11.5 and 10.0, respectively. This could be explained by considering the fact that the addition of MeOH into water suppresses the dissociation of weak PAA polyacid, as noted previously.
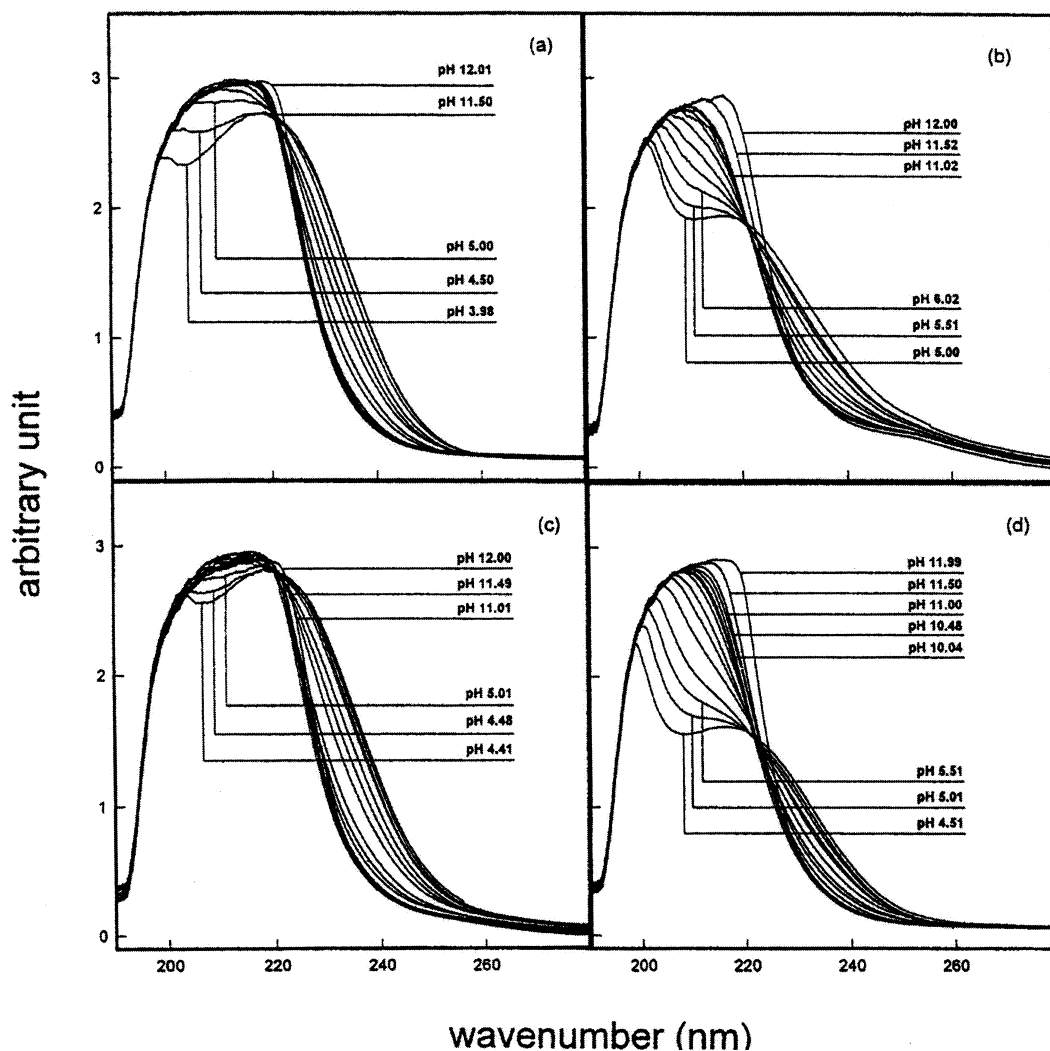
Figure 4. UV spectra of PAA and PAA/PEO (1:1) complex solutions (C_{PAA} = 0.067 g/dL) at various pH conditions in water and water-MeOH (30 wt%) at room temperature: (a) PAA in water; (b) PAA/PEO (1:1) in water; (c) PAA in water-MeOH (30 wt%); (d) PAA/PEO (1:1) in water-MeOH (30 wt%).

Thermodynamic Characteristics

The characteristics of polymers are governed not only by the chemical structure of the individual polymer chains but also by the formation of polymer aggregates. Polymers are therefore characterized by both first order and higher

order structural features, such as configuration and conformation of polymer chains. It has been known that the polymer-polymer interaction is much stronger in water than in organic solvents by the hydrophobic effect [5, 21]. Hence, we investigated the importance of the hydrophobic influence on the stability of the PAA/PEO complexation both in pure water and in water-methanol mixed solvent.

At the complexation, two types of equilibria could usually be considered. Firstly, that associated with intermolecular hydrogen bonding and secondly, intramolecular dissociation of the PAA. For weak acids (such as PAA) with a degree of dissociation α, a dissociation constant K_α and concentration C, the dissociation constant K_α can be expressed as :

$$K_\alpha = \left(\frac{[H^+][A^-]}{[HA]} \right) = \frac{(C\alpha)^2}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \tag{1}$$

From Equation 1, the degree of dissociation can be approximated for weak acids (where $1 - \alpha \fallingdotseq 1$) as :

$$\alpha = \left(\frac{K_\alpha}{C} \right)^{1/2} \tag{2}$$

And from the definition of α, we have

$$\alpha = \frac{[H^+]}{C} \tag{3}$$

Thus, from the Equations 1-3, the concentration of $[H+]$ can be given as:

$$[H^+] = \left(K_\alpha \times C \right)^{1/2} \tag{4}$$

In the case of dilute solution, this relationship is considered to be valid for the PAA both in the presence and the absence of PEO acting as a proton acceptor. Hence, expressing the free (undissociated) carboxyl concentrations by C and C_o, and the proton concentrations by $[H^+]$ and $[H^+]_o$ for these two cases, the fraction of carboxyls associated (or complexed) with oxygens of PEO can be expressed as:

$$\theta = \frac{(C_o - C)}{C_o} = 1 - \frac{C}{C_o}$$

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

(5)

The stability (or equilibrium) constant, K, of the PAA/PEO complex can then be represented as:

$$K = \left(\frac{[\text{complex}]}{[\text{PAA}][\text{PEO}]}\right) = \frac{C_o \theta}{C_o^2 (1 - \theta)^2}$$

(6)

Therefore, we could determine (though approximately) θ and K for the H-bonded complex system by measuring the concentration of the hydrogen ion of the complex solution at a given temperature. Also, the stability constant K is related to the standard-free-energy change upon complexation by the well-known relation:

$$\Delta G^o = -RT\ln K$$

(7)

In addition, the stability constant and its temperature dependence can be used to calculate standard-enthalpy changes and standard-entropy changes using the following equations:

$$\frac{d(\ln K)}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H^o}{R}$$

(8)

and

$$\Delta S^o = -\frac{(\Delta G^o - \Delta H^o)}{T}$$

(9)

Thus, from the pH measurement for the H-bonded complex system at a given temperature we can, in principle, estimate the degree of linkage θ (defined as the ratio of the bound groups to the total of potentially interacting carboxylic
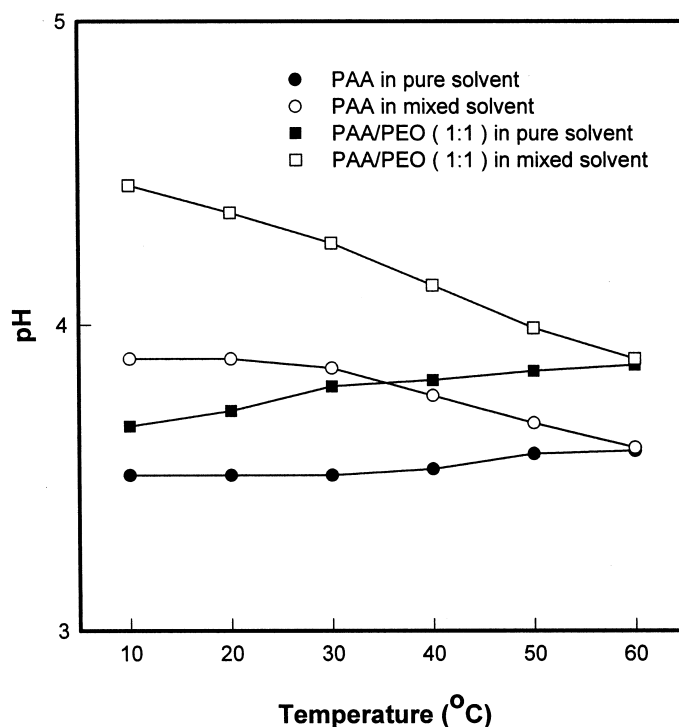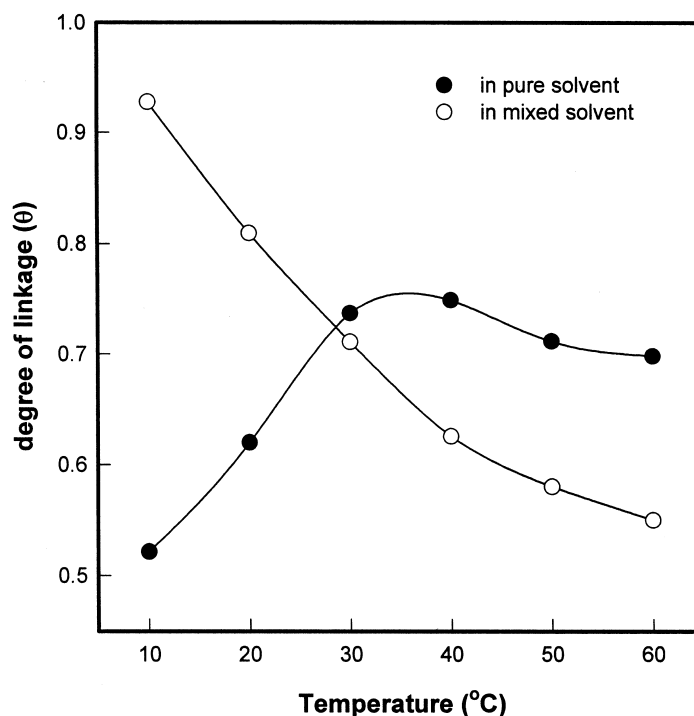
Figure 5.   Temperature dependence of pH for PAA and PAA/PEO (1:1) complex solutions (C_{PAA} = 0.067 g/dL) in water and water-MeOH (30 wt%).

groups), the stability constant K, and changes in standard thermodynamic state functions (such as the Gibbs free energy, enthalpy and entropy) associated with the complex formation.

Figure 5 shows the temperature dependence of pH values for PAA and PAA/PEO(1:1) complex solutions in water and water-MeOH (30 wt%). In pure water, the PAA and PAA/PEO complex systems show that the pH value slowly increases with increasing temperature. But in water-methanol mixed solvent, the PAA and PAA/PEO complex systems show that the pH value slowly decreases with increasing temperature.

The temperature dependence of the degree of linkage (θ) for the PAA/PEO(1:1) complex in water and water-methanol is shown in Figure 6. In water, θ increases rapidly with temperature in the range of 10 to 30°C. Over 30°C, θ seems to become independent of temperature. In water-methanol, however, continuously decreases with temperature. This behavior could be explained

Figure 6.   Temperature dependence of degree of linkage (θ) for 1:1 PAA/PEO complex solution (C_{PAA} = 0.067 g/dL) in water and water-MeOH (30 wt%).

by considering the hydrophobic effect concerned. That is, in water-MeOH mixed solvent the main stabilizing force upon complexation is the hydrogen bonding (unfavorable interaction at higher temperatures) only due to the lack of hydrophobic interaction (rather increasing with increasing temperature), thereby causing θ to decrease with increasing temperature. The temperature dependence of the stability constant (*ln K)* for the 1:1 (by u.m.r.) PAA/PEO complex solution in water and water-MeOH (30 wt%) shown in Figure 7 exhibits the same tendency as that in Figure 6.

The temperature dependence of ΔG^{o} for the 1:1 PAA/PEO complex system in water and water-MeOH is shown in Figure 8. From this figure we can notice that in water, ΔG^{o} decreases with temperature in the range of 10 to 40°C. Over 40°C, ΔG^{o} is independent of the temperature. In water-methanol, however, ΔG^{o} increases with temperature. Meanwhile, $-\Delta G^{o}$ is said to be a measure of the driving force for the complexation. At temperatures above 30°C, $-\Delta G^{o}$ seems to
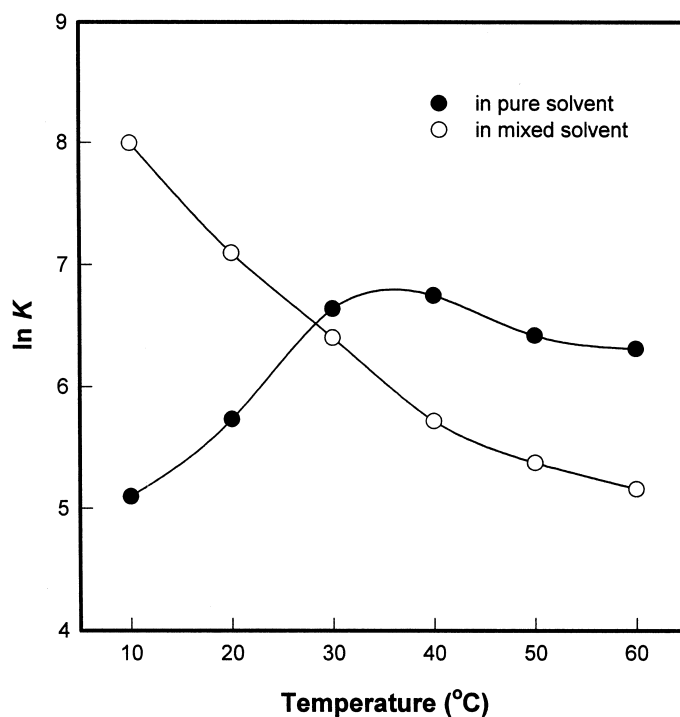
Figure 7. Temperature dependence of complex stability constant (ln K) for 1:1 PAA/PEO complex solution ($C_{PAA} = 0.067$ g/dL) in water and water-MeOH (30 wt%).

be greater for water than for water-methanol, suggesting that the complex formation in mixed solvent becomes unstable with increasing temperature. This could also be explained in terms of the hydrophobic effect involved, as mentioned above.

The temperature dependences of ΔH^o and ΔS^o for the 1:1 PAA/PEO complex solutions in water and water-MeOH are shown in Figure 9 and Figure 10, respectively. The standard-enthalpy changes (ΔH^o) in water are found to be positive up to 40°C, while in water-methanol they are negative for the whole temperature range covered. This is in agreement with the fact that positive values of ΔH^o are characteristic of hydrophobic interaction. The standard-entropy changes (ΔS^o) in water have positive values, which also indicates the presence of hydrophobic interaction, whilst in water-methanol ΔS^o have negative values, again indicating that they have no (or negligible) hydrophobic interaction associ-
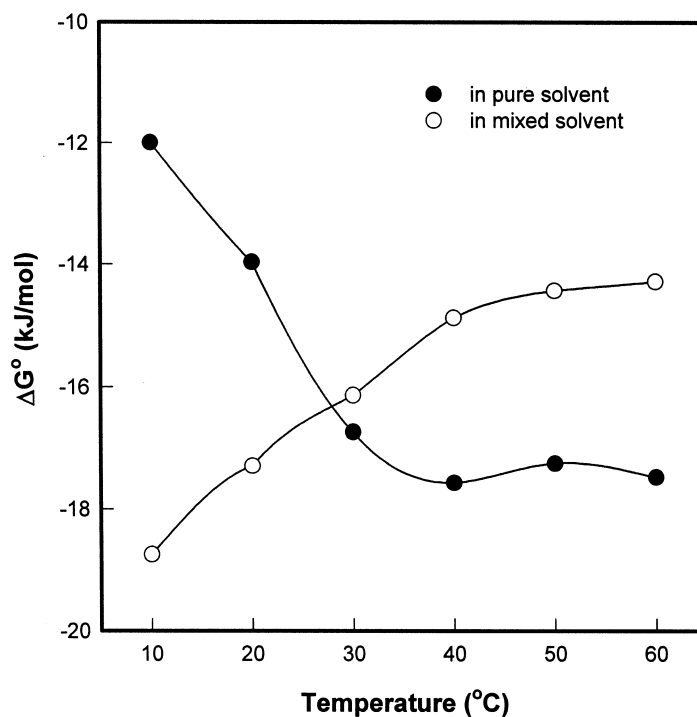
Figure 8. Temperature dependence of Gibbs free energy change upon complexation (ΔG^o) for 1:1 PAA/PEO complex solution (C_{PAA} = 0.067 g/dL) in water and water-MeOH (30 wt%).

ated with the complexation. The results of and together with those of θ, K and ΔG^o are all consistent in showing that the addition of MeOH to water reduces the hydrophobic interaction responsible for the stabilization of H-bonded polymer complex, thereby causing the formation of polycomplex between PAA and PEO more unfavorable at higher temperatures.

CONCLUSION

The results obtained in this work can be summarized as follows:

The characteristics of polymer complex formation via hydrogen-bonding between PAA and PEO at dilute aqueous solution are significantly dependent on the properties of solvent, as confirmed by the measurements of viscosity, pH and
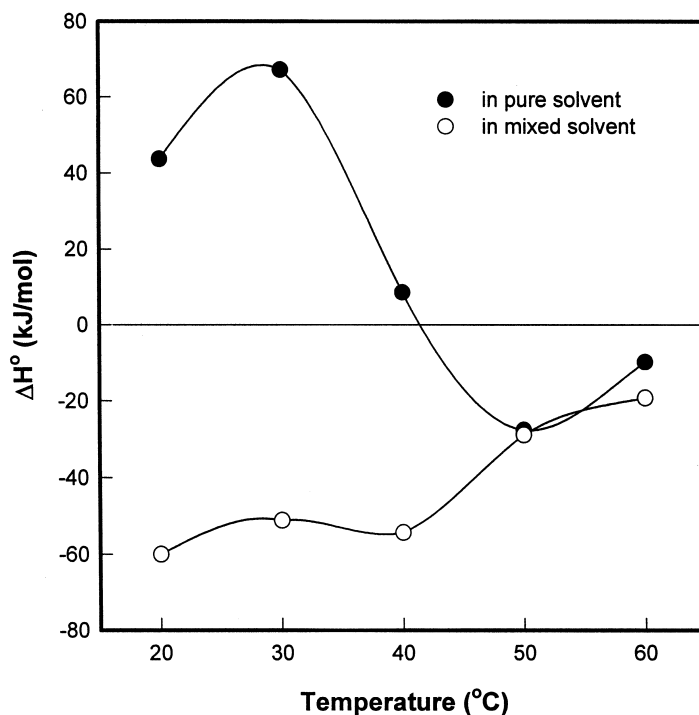
Figure 9. Temperature dependence of enthalphy change upon complexation (ΔH^o) for 1:1 PAA/PEO complex solution (C_{PAA} = 0.067 g/dL) in water and water-MeOH (30 wt%).

UV absorption spectra. The addition of methanol to water caused to decrease the dielectric constant of the medium, and hence the dissociation of the -COOH groups, and to disrupt the structure of water molecules and therefore reduce the hydrophobic interaction between -CH$_2$- of PAA and solvent. The viscosity measurement showed that the maximum complex formation point was shifted from [PEO]/[PAA] (in u.m.r.)≈1.25:1 in water to 1.5:1 in water-MeOH (30 wt%). From the UV measurement, the deviation from the isosbestic point indicated the solvent effect again. Thermodynamic characteristics such as the fraction of carboxyls associated with PEO oxygens, the complex stability constant, and changes in Gibbs free energy, enthalpy and entropy upon complexation have been estimated from the pH measurement as a function of temperature, all yielding consistent results. In particular, standard enthalpy and entropy changes were positive (ΔH^o >0, ΔS_o >0) in water at temperatures up to 40°C while in water-MeOH they were negative over the whole temperature covered. These findings
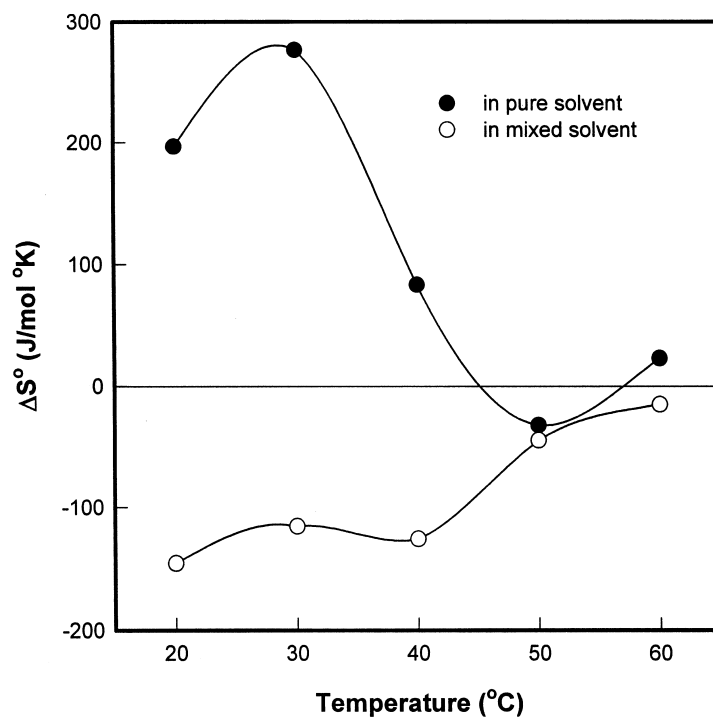
Figure 10.   Temperature dependence of entropy change upon complexation (ΔH^{o}) for 1:1 PAA/PEO complex solution (C_{PAA} = 0.067 g/dL) in water and water-MeOH (30 wt%).

may suggest that the complex formation in mixed solvent is exclusively due to H-bonding between PAA and PEO unlike that in pure water possessing the hydrophobic interaction as well responsible for the stabilization of polycomplex formed.

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