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Complexation between poly(*N*,*N*-diethylacrylamide) and poly(acrylic acid) in aqueous solution

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Abstract

The complexation between poly(*N*,*N*-diethylacrylamide) (PDEA) and poly(acrylic acid) (PAA) in aqueous solution was studied by viscometric, potentiometric, and fluorescence techniques. It was found that an interpolymer complex formed between the two polymers through hydrogen bonding interactions with the stoichiometry of $r = 0.6$ (r is unit molar ratio of PAA/PDEA), and the complex formation show the dependence on pH values. The phase behaviour studies showed that the lower critical solution temperature of the PDEA–PAA aqueous solution gradually increased with the increasing of r from 0.01 to 0.15, until a soluble system in the whole temperature region was obtained, which remained in the range of $r = 0.15$–0.3. At higher PAA concentrations, when r is above 0.3, the system appeared phase separation, and almost no temperature dependence was observed. Based on these conclusion and structure characteristics of PDEA and PAA, a model containing only short sequences of monomer residues was proposed for the structure of PDEA–PAA complex.

Keywords: Poly(*N*,*N*-diethylacrylamide); Poly(acrylic acid); Phase behaviour; Complexation

1. Introduction

Complexation between synthetic polymers has been extensively investigated [1–8]. Most researches have been to describe the nature of the interaction forces (hydrogen bonding, ionic, hydrophobic interaction), and to determine structural effects (temperature, pH, solvent etc.). During the last few decades, considerable efforts have been devoted to the studies on the association of poly(acrylic acid) (PAA) with nonionic polybase [2,9–13], such as poly(ethylene glycol) (PEG), polyacrylamide (PAM), etc. It has been claimed that such complexation involves “noninterrupted linear sequences of bonds (or noninterrupted ladder structure)” between contiguous monomer residues of the hydrogen bonding donor PAA and the hydrogen bonding acceptor polymers, as shown in Scheme 1 [14]. Either soluble complex or precipitates are formed at room temperature from aqueous mixtures of polybase with PAA, depending on pH [10,15] or ionic strength [16], but they do not present any special temperature sensitivity in the temperature range usually studied. On the other hand, it was recently reported that when poly(vinyl methyl ether) (PVME), a temperature sensitive polymer, which has a lower critical solution temperature (LCST) (about 33 °C), was used as polybase, the complex formed between PVME and PAA by the action of interpolymer hydrogen bonding exhibited a temperature sensitive phase behaviour [17].

PDEA belongs to another kind of temperature sensitive polymer, containing hydrophilic amide groups and hydrophobic vinyl backbone and diethyl side groups. This character leads to the inverse temperature solubility behaviour of aqueous solution of PDEA [18,19]. At low temperatures, the strong hydrogen bonding between the hydrophilic groups and water outweighs the unfavorable free energy related to the exposure of hydrophobic groups to water, leading to good solubility of the

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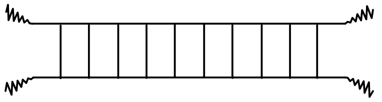


Scheme 1.

polymer in water. When temperature increases, hydrogen bonding weakens, while hydrophobic interactions between hydrophobic side groups strengthen. Above LCST (at 29.8 °C), interactions between hydrophobic groups become dominant, leading to an entropy-driven polymer collapse and phase separation (turning cloudy). This feature is analogous to protein denaturation. Moreover, it is interesting to note that LCST of PDEA aqueous solution is close to the body temperature of homoiothermic animals. Since PDEA is a powerful hydrogen bonding acceptor, it is reasonable to believe that an interpolymer complex (IPC) can form between PDEA and PAA in aqueous solution, and a temperature sensitive phase behaviour could be observed. However, the investigation concerning the interactions and the phase behaviour for PDEA–PAA mixtures in dilute aqueous solution is not available to our knowledge.

The effective control of the cloud point temperature (T_{cp}, equivalent to LCST, at which the solution turn cloudy) of PDEA aqueous solution should be of great importance, academic, or practical. T_{cp} is affected by many factors [20–22]. It is either decreased in the presence of NaCl, NaOH or increased in the presence of urea. These small molecular weight cosolutes mainly affect the water structure. We think that T_{cp} may be affected by the direct interaction of PDEA with macromolecules through secondary binding forces, such as hydrogen bonding.

On the basis of our previous study [23], we investigate in this work the behaviour of the mixtures of PDEA and PAA in aqueous solution. The viscometric results, together with potentiometric and fluorescence probing data, support the hypothesis of interpolymer hydrogen bonding between PDEA and PAA in dilute aqueous solution. Our work further demonstrate that when PAA concentration is at low level, PDEA–PAA aqueous mixtures exhibit temperature sensitive phase behaviour and T_{cp} of PDEA increase with increasing PAA concentration. Taking into account the steric and kinetic factors, the structure of PDEA–PAA complex should contain relatively few long complexable sequences.

2. Experimental

2.1. Materials

Benzoyl chloride, diethylamine, magnesium sulfate, hydroquinone are A.P. grade and used as received. Acrylic acid is A.P. grade and was distilled under reduced pressure prior to use. 2,2′-azoisobutyronitrile (AIBN) is C.P. grade and was recrystallized from 95% ethanol prior to use. Other regents are A.P. grade and were distilled prior to use.

2.2. Synthesis and characterization of PDEA

PDEA was prepared involving three steps: (1) Acryloyl chloride synthesis: A mixture of 3 moles of acrylic acid, 6 moles of benzoyl chloride and 0.5 g of hydroquinone was distilled through an efficient 25-cm distilling column. The crude product was redistilled through the same column and the fraction boiling at 65–67 °C at about 660 mm Hg was collected. The yield was about 68%. (2) *N*,*N*-diethylacrylamide (DEA) synthesis: Acryloyl chloride and diethylamine were separately dissolved in dichloromethane, then mixed and stirred at 0 °C under nitrogen atmosphere for 4 h. Then the reaction mixture was filtered, washed with water and dried over magnesium sulfate. After the solvent was distilled under vacuum, the crude product was distilled in the presence of hydroquinone at 82 °C under vacuum at 9.4 mm Hg. The yield was about 50%. (3) PDEA synthesis: PDEA was prepared by free radical polymerization. DEA (12.7 g) in methanol (15 ml) was stirred with AIBN (80 mg) under nitrogen atmosphere at 60 °C for 10 h. The crude product was dissolved in acetone and precipitated from hexane. The refined PDEA was dried under vacuum for 24 h and stored in a desiccator. The yield was about 65%. Size exclusion chromatography of a 0.5 wt% solution of PDEA in THF on styrogel column with polystyrene standards and THF as eluent gave an $M_{\mathrm{w}} = 4.31 \times 10^4$, $M_{\mathrm{w}}/M_{\mathrm{n}} = 2.69$. PDEA was characterised by ^{1}H NMR (200 MHz, D_2O, ppm): δ1.0 (CH_3, 6H), δ1.2–2.6 ($-CH_2-CH-$, 3H), δ3.3 (CH_2, 4H).

2.3. Synthesis and characterization of PAA

In a dry reaction flask, appropriate amount of methanol, AIBN, and acrylic acid were mixed. The mixture was allowed to react for 1.5 h at 60 °C under nitrogen protection. To reduce the probability of crosslinking reactions, the initial concentration of acrylic acid was kept below 10% by volume, and conversion was kept below 50%. The polymer was precipitated from diethyl ether and dried under vacuum for 24 h. The viscosity average molecular weight of $M_{\eta} = 5.4 \times 10^4$ g mol^{-1} was estimated for PAA from intrinsic viscosity of the polymer in 2 M NaOH aqueous solution at a constant temperature of 25 °C, using the Mark–Houwink–Sakn-rada (MHS) equation [24,25] $[\eta] = kM_{\eta}^{\alpha}$. The constants k and α in the MHS equation were equal to 42.2×10^{-3} ml g^{-1} and 0.64, respectively. PAA was characterised by

^{1}H NMR (200 MHz, D_2O, ppm): δ1.2–1.9 (–CH_2–, 2H), δ2.2 (–CH–, 1H).

2.4. Sample preparation

Polymer solutions were prepared from their stock solutions. The concentrations of the stock solutions for PDEA, PAA1, and PAA2 were 2%, 0.457%, and 0.0457% (w/v), respectively.

For complexation measurements, the samples of various r (unit molar ratio of PAA to PDEA) were prepared in a similar manner. In a typical procedure, for the preparation of the mixture of $r = 0.6$, 1 ml of PDEA stock solution was diluted to about 8 ml by adding de-ionization water, followed by the addition of 1.5 ml PAA1 stock solution under shaking. Then the solution was diluted to 10 ml with de-ionization water. For samples of $r < 0.3$, stock solution of PAA2 was used instead of that of PAA1. In the case of measurement of pH dependent reduced viscosity (Fig. 3), PDEA stock solution was diluted using de-ionization water and various amount of NaOH solution.

For fluorescence measurements, the probe pyrene was initially dissolved in diethyl ether to obtain a stock solution of known concentration (≈10^{-3} mol l^{-1}). This solution was diluted to 10^{-5} mol l^{-1} just before use. One ml of the probe solution (10^{-5} mol l^{-1}) was injected into a 10 ml volumetric flask. The ether was evaporated at room temperature. Subsequently, a polymer sample as above was prepared in the volumetric flask. The mixture was sonicated for 20 min, and then left at room temperature for a day.

For all samples, the concentration of PDEA was fixed at 0.2% (w/v).

2.5. Measurements of complexation between PDEA and PAA

2.5.1. Turbidity measurements

Turbidity measurements were conducted with a Shimadzu UV/VIS spectrophotometer UV-240 equipped with a temperature controlled cell holder. The transmittance of a light beam at a fixed wavelength of 500 nm was measured.

2.5.2. Potentiometric measurements

Potentiometric measurements were carried out at 25 °C with pHS-10C pH meter.

2.5.3. Viscosity measurements

Viscosity measurements were carried out in a water-bath, thermostated at 25 ± 0.1 °C, using Ubbelohde viscometer.

2.5.4. Fluorescence measurements

Fluorescence measurements were conducted with a Shimadzu spectroflurophotometer RF-540 at 25 °C. Pyrene was employed as a micropolarity sensitive probe. Final concentration of pyrene was 1.0×10^{-6} mol l^{-1}. An excitation wavelength of 336 nm was used.

3. Results and discussion

3.1. Complexation between PDEA and PAA

Since polymer–polymer complexation in solution is always accompanied by the contraction or collapse of the component polymer coils, which result in viscosity decrease, turbidity or even precipitation, measurement of the viscosity variation with composition has been commonly used as a basis for the estimation of the complex composition [26]. Fig. 1 shows the variation of the reduced viscosity, η_{red}, of the PDEA–PAA aqueous solution versus the unit molar ratio r (= [PAA]/[PDEA]) at 25 °C. This behaviour is typical of system forming polymer complex. As long as r is lower than 0.04, η_{red} of the polymer mixtures present a smooth variation on r, indicating no apparent specific interaction of the polymer coils in the solution. While r increases further, the viscosity decreases till mixed unit molar ratio is equal to 0.6. In these cases, both hydrogen bonding and additional hydrophobic interactions contributed to the compact structure of the complex. The total hydrodynamic volume of complexed chains is smaller than the hydrodynamic volume of the free chains. The increase of viscosity after $r = 0.6$ is due to the presence of free PAA chains. Many studies [27] showed that the minimum in viscosity was related to the largest degree of complexation in complexable system. In this case, the minimum in viscosity observed at about $r = 0.6$ corresponds to a

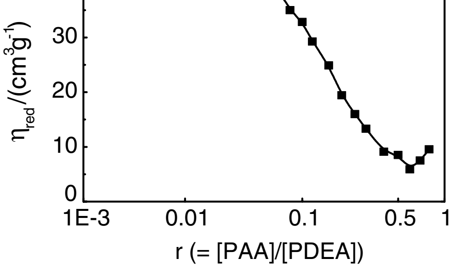


Fig. 1. Unit mole ratio (r) of PAA to PDEA dependence of reduced viscosity (η_{red}) in aqueous solution (PDEA concentration is 0.2 wt%, 25 °C).

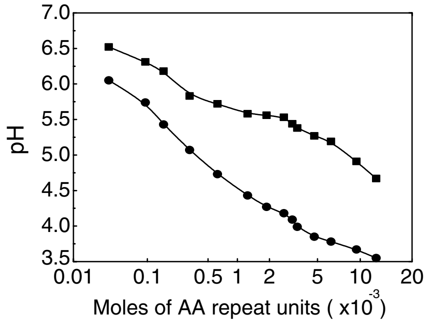


Fig. 2. PAA concentration dependence of pH for pure PAA (●) and PAA–PDEA–H_2O system (■) (PDEA concentration is 0.2 wt%, 25 °C).

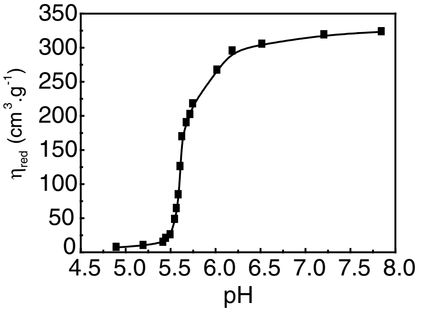


Fig. 3. pH dependence of reduced viscosity (η_{red}) for PAA–PDEA–H_2O system of $r = 0.6$ (concentration of PDEA and PAA are 0.2, 0.068 wt%, respectively, 25 °C).

PDEA/PAA unit molar ratio equal to about 1.67, relating to the stoichiometry of the IPC formed.

The presence of PDEA–PAA complex is further proved by the potentiometric results, as shown in Fig. 2. At low PAA concentration (low r) and relatively high pH values, deviation of the pH between the PDEA–PAA mixtures and the pure PAA is relatively little, which indicates the absence of strong interaction between the two polymers. As the PAA concentration increases, we observe a deviation of the pH for the PDEA–PAA mixtures to higher values as compared with the pH of the pure PAA aqueous solutions. This increase in pH is consistent with the formation of strong hydrogen bonding IPC between PAA and PDEA. The IPC between PDEA and PAA, attributed to hydrogen bonding interaction, could be briefly described by the equation

$$\mathrm{PAA} + \mathrm{PDEA} \rightleftharpoons \mathrm{IPC{-}H}_n \tag{1}$$

where IPC–H_n is a hydrogen bonding IPC and n is the number of carboxylic hydrogens which are related to the polymerisation degree of PAA and are involved in the hydrogen bonding interaction with the amide of PDEA. The complex formed, being a weak polyacid, is expected to partially dissociate according to the equilibrium,

$$\mathrm{IPC{-}H}_n \rightleftharpoons \mathrm{IPC{-}H}_{n-k}^{-k} + k\mathrm{H}^+ \tag{2}$$

where $k \ll n$. IPC–H_{n-k}^{-k} is a hydrogen bonding IPC with the dissociation of amounts of carboxylic acid groups, k is the number of carboxylic sites related to the dissociation of carboxylic acid groups. The complex formed induces a displacement of the PAA dissociation equilibrium to the undissociated form, resulting in a decrease of the H^+ concentration of PDEA–PAA mixtures as compared to the H^+ concentration of the pure PAA solution.

To investigate the effect of pH on the IPC, reduced viscosity of mixed solution at $r = 0.6$ was measured at various pH values. The results are shown in Fig. 3. When the pH of the mixed solution is lower than 5.5, the reduced viscosity does not show much increase, suggesting that the IPC is hardly affected. When the pH reaches 5.5, within a narrow range pH from 5.5 to 6.0, the reduced viscosity increases almost vertically from 20 to above 260 cm^3 g^{-1}, reflecting an abrupt transition to highly expanded states. Further rising of pH from 6.0 lead to only small increase of the reduced viscosity.

It is well known that for the hydrogen bond complex formed between poly(carboxylic acid) and a proton acceptor polymer, there was a critical state of dissociation, above which no hydrogen-bonding complex was formed [3]. Partial ionization converts some carboxyl groups to dissociated carboxylate groups which are incapable of hydrogen-bonding formation. Complexation can occur only when the polyacid is neutralized below a certain ionization degree [2]. The increase in pH of the system will raise the degree of dissociation. When the pH reaches the critical pH value, the undissociated acid sequences become too short to form the complex. This critical pH value is characteristic of the system with definite composition and has been used as a criterion for the ability to form IPC for systems that are composed of poly(carboxylic acid)s and nonionic polymers [15,28–35]. In our case, the critical pH value is about 5.7, which is higher than that (5.0) for the complexation of PAA with poly(acrylamide) (PAM) [30,31] suggesting that PDEA–PAA has stronger complex-forming ability.

In order to obtain detailed structural information of the complex, fluorescence measurements were carried out. The fluorescence spectrum of a pyrene probe offers a simple and convenient means of sensing the molecules's local environment. In particular, the ratio of the intensities of the first over the third vibronic bands of pyrene, I_1/I_3, provides a measure of the polarity of the medium [36–38]. Fig. 4 shows the variation of I_1/I_3 of pyrene in PDEA–PAA aqueous solution versus r (I_1 at 373.0 nm and I_3 at 383.9 nm). As r becomes higher than 0.006, the I_1/I_3 ratio starts to decrease, from an initial level of 1.79 to 1.59, indicating an increase in the hydrophobicity of the polymer mixture as compared with

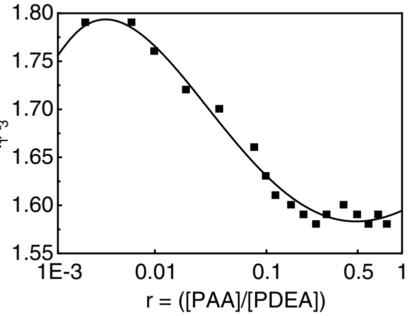
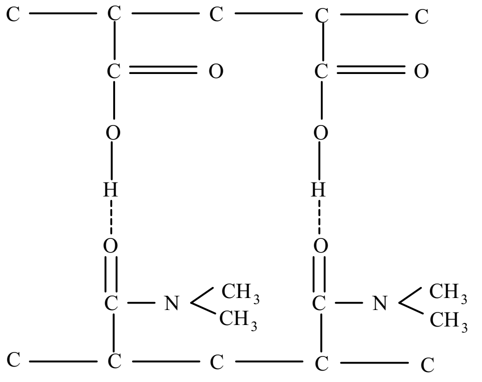


Fig. 4. Unit mole ratio (r) of PAA to PDEA dependence of ratio (I_1/I_3) of the fluorescence vibronic peaks of pyrene for PAA–PDEA–pyrene–H_2O system (PDEA concentration is 0.2 wt%. $\lambda_{ex} = 336.0$ nm, $\lambda_{I_1} = 373.0$ nm, $\lambda_{I_3} = 383.9$ nm, 25 °C).

the pure PDEA solution (I_1/I_3 is 1.67). This behaviour is due to the formation of a complex with a compact structure, which is considered to be caused by the shrinkage of the polymer chains. The electrostatic repulsion is weakened by complex formation and at the same time hydrophilic groups on the component polymer chains are effectively shielded and consequently the hydrophobicity of polymer chains becomes larger. The main force for stabilization of the polycomplex in an aqueous environment, as suggested earlier, is the hydrophobic effect. When PAA and PDEA solutions are mixed, the hydrophilic amide and carboxyl groups are "locked" through hydrogen bonding, in agreement with the result of viscometry, resulting in a shrinkage of the PDEA chain that should favour the formation of small hydrophobic clusters through the aggregation of the side ethyl groups.

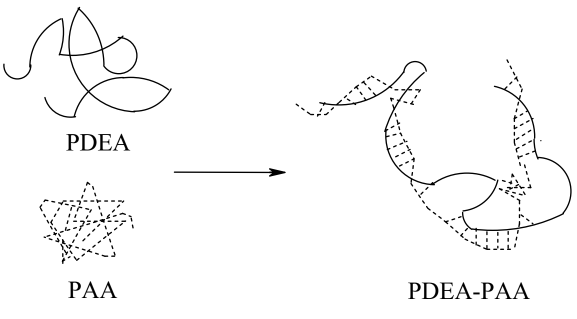


Scheme 2.

From a thermodynamic point of view, the formation of one noncovalent bond (hydrogen bonding, electrostatic) between two macromolecular species in solution is quite improbable, while the formation of a large number of such bonds leads to a thermodynamically stable complex. For this reason, a model of "noninterrupted sequences of bonds" between contiguous monomer residues was proposed, the structure can be represented in Scheme 1 [14]. As far as we know, among the experimental methods used at present, there is none that can give a direct proof of the existence of such uninterrupted sequences. Moreover, experimental results showed that even in the case of homopolymer couples, the complexation is not perfect, a fraction of the interactive monomers is not involved in the complex. In our case, taking into account of steric and kinetic factors, the model seems unrealistic. In a previous paper by Morawetz and Wang [39], which deal with the complexation of PAA and poly(N,N-dimethylacrylamide-co-acrylamide) (PDAA), it was pointed out that the single 16-membered ring formed by two consecutive residues of PAA hydrogen bonding to two consecutive residues of PDAA as shown in Scheme 2 is improbable due to the steric effect of the N-methyl groups. To assume a long sequence of such rings condensed with each other seems utterly fantastic. In our case, the steric effect of ethyl group is even more profound, so we think that the stable complexes may be formed with polymers containing relatively few long sequences of monomer residues. It is generally believed that a critical chain length is needed to form stable complex, and the critical chain length (the shortest length for acid sequences to format complex), which depends on the affinity between the two complementary groups, would decrease as the interaction strength increases. PDEA is a disubstituted amide, and as a strong proton acceptor, can be compared to poly(N-vinylpyrrolidone) (PVP). So the critical chain length of PDEA must be small enough, similar to the critical chain length of PVP (about 13). Based on the conclusion, we proposed a zipping model for the structure of PDEA–PAA complex shown in the Scheme 3.

3.2. Phase behaviour of PDEA in the presence of PAA

Fig. 5 shows the variation of the transmittance of 0.2 wt% PDEA in the presence of PAA at various unit



Scheme 3.

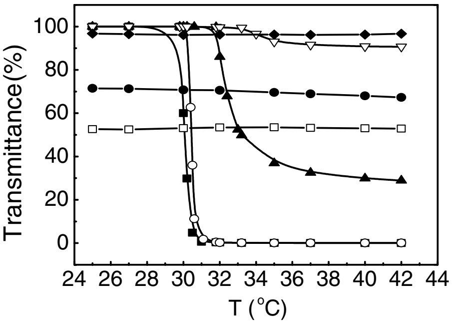


Fig. 5. Temperature dependence of transmittance percentage at different unit mole ratio (r) of PAA to PDEA in aqueous solution (■: PDEA concentration is 0.2 wt%, no PAA; ○: $r = 0.04$; ▲: $r = 0.1$; ▽: $r = 0.15$; ◆: $r = 0.3$; ●: $r = 0.6$; □: $r = 0.8$).

molar ratios of PAA to PDEA as a function of temperature. The 0.2 wt% PDEA pure aqueous solution starts to turn cloudy at the cloud point temperature 29.8 °C and reaches its maximum turbidity within 1 °C. In the presence of PAA, as long as r remains low, 0.01–0.15, a gradual displacement of the turbidity curves to higher temperatures is observed, while the level of the maximum turbidity decreases. When r is higher than 0.3, the solutions become turbid irrespective of the temperature, while the turbidity level increases with r. Moreover, the ternary systems remain visually homogeneous in the whole temperature region studied at intermediate r values, ranging from 0.17 to 0.3. In Fig. 6, the cloud point temperature T_{cp}, in this instance defined as the onset of the turbidity curves presented in Fig. 5, is plotted against r. The plots are limited to the low r region, 0–0.15, where a temperature sensitive phase behaviour is observed. T_{cp} is 29.8 °C for the pure PDEA aqueous solution and increases gradually as r increases. Similar phenomenon was also found in the system of PVME and PAA aqueous solution as reported by Staikes and Karayanni [17]. These results can be rationalized considering that solubility behaviour of the IPC formed should vary between the charged (soluble) and the uncharged (unsoluble) form as shown in Eq. (2). At low PAA concentrations, when $r = 0.01$–0.15, the cloud point temperature increase of the ternary systems, could be attributed to the charge of the weakly dissociated polyacid associated with the PDEA chains through hydrogen bonding interactions. By increasing r, the IPC is enriched in dissociated carboxylic acid groups, so that it becomes visually soluble at any temperature. As r increases further (>0.3), however, the solution starts becoming more and more turbid. This behaviour should be due to a displacement of equilibrium (2) to the left. The presence of an excess of PAA provides the solution with H^+ and the uncharged form of the IPC should now prevail.

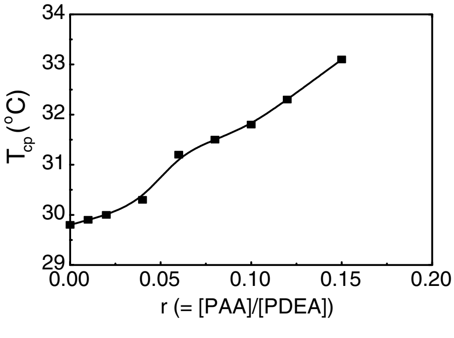


Fig. 6. Unit mole ratio (r) of PAA to PDEA dependence of cloud point temperature (T_{cp}) in aqueous solution (PDEA concentration is 0.2 wt%).

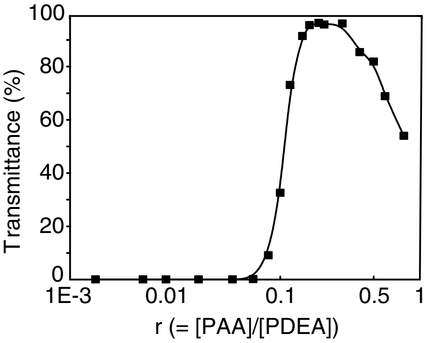


Fig. 7. Unit mole ratio (r) of PAA to PDEA dependence of transmittance percentage in aqueous solution ($\lambda = 500$ nm, 37 °C).

An alternative way to monitor the phase behaviour of these systems is by measuring the turbidity at a fixed temperature higher than the cloud point of the pure PDEA solution as a function of r. The results, measured at 37 °C, are presented in Fig. 7. As r is lower than 0.06, the transmittance remains almost constant. While at higher r values it increases abruptly, indicating a apparent interaction between PDEA and PAA. The solution become almost clear at about $r = 0.17$. While $r > 0.3$, the solution become progressively turbid again. This turbidity is almost independent of temperature and increases with the increasing PAA concentration. This phase behaviour is in conformity with the Eq. (2).

4. Conclusions

Viscometric, potentiometric, and fluorescence studies showed that interpolymer complexation between PDEA and PAA were both pH and unit molar ratio of PAA to PDEA dependent and a conformational change occurred when 0.2 wt% PDEA is mixed with different concentration PAA in aqueous solution. The complexation occurs most efficiently at a unit molar ratio of about $r = 0.6$, suggesting that only some of the segments of PDEA have taken part in the complexation. The critical pH value to form complexation was about 5.7 at $r = 0.6$. The change of the phase behaviour of the system with the variation of r was observed, a phenomenon which can be accounted for by the variation in the degree of complexation between PDEA and PAA and the degree of dissociation of the formed complex. Considering all these conclusions and structure characteristics of PDEA and PAA, we proposed a zipple model for the structure of PDEA–PAA complex.

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