

Effect of Alkali Metal Halides on the Upper Critical Solution Temperature of Poly(*N*-acetylacrylamide) in Ethanol-Water System

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An upper critical solution temperature (UCST) of poly(*N*-acetylacrylamide) is changeable with adding a variety of cations and anions. The interpolymer complex, which is formed due to hydrogen bonding between acetylamide groups in the polymer molecules, is responsible for the UCST behavior of the polymer. The addition of cations or anions in the polymer solution made the UCST decreasing. The UCST is 38.5, 17, or 14.5°C in the mixture of 30 wt% ethanol and 70 wt% of 1.0 M KF, KCl, or KBr in aqueous solution, respectively. The UCST change shows a linear relation against the salt concentration. There is a close relationship between the UCST change and the dynamic hydration number (n_{DHN}) of each anion. The additive anion or cation is possible to affect in the polymer solution to form or break the hydrogen bonds between the acetylamide groups in the polymer molecules.

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Poly(*N*-isopropylacrylamide) (PNIPAAm) gels are classified in a thermo-shrinking type of volume phase transition, which comes out at a lower critical solution temperature (LCST) of the polymer.¹⁻³ The LCST is changeable when electrolytes or nonelectrolytes are added into the gel.⁴⁻⁸ It has been reported that the presence of additives influences on the situation of the hydrated water around the polymer chains in the gel. The collapse of water clusters around the polymers is considered to be responsible for the LCST change. One of the authors has reported the effects of additive alkali metal halides on the kinetics of gel deswelling and on the LCST of the macroporous poly(NIPAAm) gel.^{9,10} In the case of the salts, the LCST change has been investigated in connection with the salting-out effect, which is closely related with the Hofmeister's series.

A thermo-swelling type of gel turns into a transition state at an upper critical solution temperature (UCST). As compared with the LCST gels, few UCST gels have been applied to the intelligent gel systems. The polymer molecules in most of UCST gels include both proton-donor and proton-acceptor groups.¹¹⁻¹⁴ Accordingly, association or dissociation of hydrogen bonding between polymer chains has been discussed in connection with the UCST behavior of the polymer: The hydrogen bonding is scissored at the UCST by heating the mixture, which composes the interpolymer complex dissolving in the solvent.

It was expected that the additive cations or anions might influence on the formation of the interpolymer complex of poly(*N*-acetylacrylamide) (PNAAm). It is worthwhile to discuss the relationship between the hydrogen bonding of acetylamide groups and the soluble-insoluble change of the polymers in the solution.

Uedaira et al. defined the dynamic hydration number (n_{DHN}) of cations or anions as following,^{16,17}

$$n_{\text{DHN}} = n_{\text{h}} (\tau^{\text{h}} / \tau^0 - 1), \quad (1)$$

where n_{h} , τ^{h} , and τ^0 are the coordination number of the ion, the rotational correlation times of water molecules around the ion, and those of pure water. The value of n_{DHN} means the dynamic state of the water molecules in the hydration sphere around the ion relative to the bulk water formed by the same number of water molecules as the sphere.¹⁶ The dynamic state of water molecules is related with the magnitude of interaction between the ions and the water molecules. The dynamic hydration number is explained in the connection with the structure-forming or -breaking properties of the ions. Additive ions are expected to affect the formation of hydrogen bonding between polymer chains and to change the UCST.

In this report, PNAAm as one of the representative UCST polymers will be studied concerning the interpolymer complex.¹⁵ Because, effects of the additives on the thermal properties of PNAAm are not investigated well so far, despite that the UCST polymers can be expected for a variety of thermosensitive devices. Therefore, thermal properties of PNAAm are investigated in connection with the hydrogen bonding between amide groups of the polymers in the mixtures of ethanol and aqueous alkali metal halide. The UCST change of the PNAAm is discussed concerning the hydrated properties of additive cations or anions. Consequently, the UCST change of PNAAm will be discussed with respect to n_{DHN} .

Experimental

Materials *N*-Acetylacrylamide (NAAm) was prepared by the condensation reaction between acrylamide and *N,N*-dimethylacetamide dimethyl acetal.¹⁵ The yield of NAAm for two step synthesis was 40%. All other chemicals were of guaranteed grade or the best commercially available.

Polymer preparation Aqueous NAAm solution was bubbled with nitrogen gas to remove the dissolved oxygen. Polymerization of NAAm was carried out by adding ammonium peroxodisulfate as the initiator at 5°C. After the

reaction, the polymer solution was dialyzed in distilled water and then freeze-dried.

Measurement of the optical transmittance PNAcAam was dissolved in the mixture of 30 wt% ethanol and 70 wt% of 0 - 1.0 M (1 M = 1 mol dm⁻³) alkali metal halide in aqueous solutions (KF, KCl, KBr, LiCl, NaCl, and CsCl). The optical transmittance of 0.2 wt% PNAcAam solution was measured at 500 nm using UV-VIS spectrophotometer (UV-2400PC, Shimadzu). The temperature of the cell can be controlled by the water-flowing system using Uni-cool UC-55N (Tokyo Rikakikai). The temperature was determined by a thermocouple inserted into the polymer solution of the cell. The polymer solution was stirred during measurement to avoid the precipitation of the insoluble polymer complex separated from the solution using an electromagnet controlled by a function generator (FG-273, Kenwood) and a galvanostat (HA-211, Hokuto Denko). The change of the optical transmittance was recorded with temperature due to heating up and cooling down (0.1 °C/min).

Determination of the UCST The optical transmittances of the soluble (45°C) and the insoluble (5°C) polymer solution were measured. This difference of the optical transmittance was defined as the maximum change of the optical transmittance (ΔT_r). The UCST as the critical temperature was determined at the temperature where the transmittance got to 100% of ΔT_r .

The UCST change (ΔT) is defined according to Eq.(2), where T_c is the UCST of the PNAcAam in the mixtures prepared by the variety of salt solutions and T_0 (=36.5°C) is that in 30 wt% ethanol and 70% water not containing alkali metal halide.

$$\Delta T = T_c - T_0 \quad (2)$$

Results and discussion

The UCST properties of PNAcAam PNAcAam (molecular weight 85,000) was dissolved in the mixtures of 30 wt% ethanol and 70 wt% of 0.2 - 1.0 M KBr in aqueous solutions. Temperature dependence of the optical transmittance was determined at 500 nm (Fig. 1). The each cloudy solution turns transparent with increasing the temperature. No hysteresis of the transmittance profile was observed in the process of heating up and cooling down (data not shown).

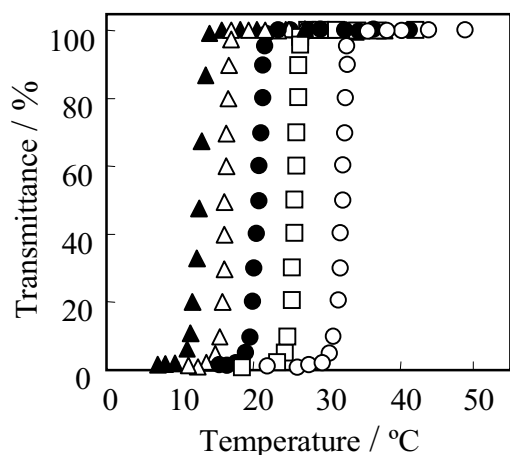


Fig. 1 Effect of temperature on the optical transmittance of the PNAcAam in the mixture of 30 wt% ethanol and 70 wt% of 0.2 M (○), 0.4 M (□), 0.6 M (●), 0.8 M (△), and 1.0 M (▲) KBr solution. Transmittance was measured at 500 nm with heating the mixture.

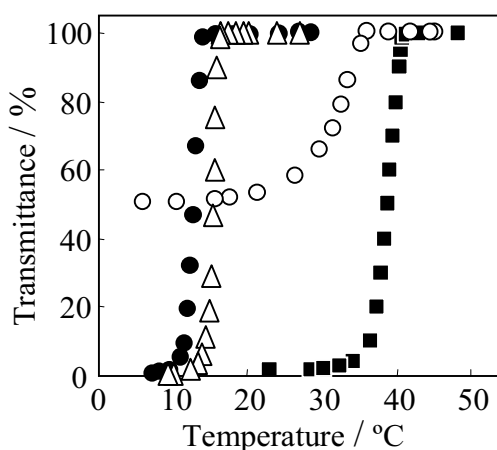


Fig. 2 Salt dependency on the optical transmittance of the PNAcAam in the mixture of 30 wt% ethanol and 70wt% of water (○), 1.0 M KF (■), 1.0 M KCl (△), and 1.0 M KBr (●) solution. Transmittance was measured at 500 nm with heating the mixture.

It is plausible that the interpolymer complex is insoluble in the mixture and the optical transmittance decreases. This means that the dissociation of the interpolymer complex is responsible for the transmittance change. The interpolymer complex is formed due to self-association between acetylamide groups, which is possible to serve as both proton-donor and -acceptor in polymer molecules. The formation of hydrogen bonds comes out at low temperature. Because the mixture is cloudy at lower temperature. On the other hand, the hydrogen bonds are broken and in turn the polymers are hydrated by heating. It is deduced, therefore, that the UCST is related with the change of polymer solubility due to the dissociation of the hydrogen bonds between the acetylamide groups.

PNAcAam is soluble in water and insoluble in ethanol between 5 and 50°C (data not shown). The solubility change of PNAcAam in various mixture of water and ethanol may be involved with the UCST properties of the polymer. Assuming that the affinity of ethanol molecules to PNAcAam is weaker than that of water molecules, the formation of the cluster composed of ethanol and water may be connected with the solubility of PNAcAam. A hypothesis was reported with respect to the relationship between the chemical potential change of water and the LCST change of PNIPAAm in the presence of low molecular additives.¹⁸⁻²⁰ Kawasaki et al. supposed in their report that decrement of the chemical potential of water by any means destabilizes the hydration on PNIPAAm chains.²⁰ The addition of ethanol brings about the destabilization of the hydration around the PNAcAam chains. Accordingly, it is considered that addition of ethanol makes the chemical potential of water decreasing.

The UCST's in the mixtures prepared from 0.2 and 1.0 M KBr are 33 and 14.5°C, respectively. As shown in Fig. 1, the UCST decreased with increasing the KBr concentration. This result indicates that addition of KBr makes the interpolymer complex soluble caused by breaking the hydrogen bonds.

Effect of the anions on the UCST Fig. 2 shows the anion dependency on the optical transmittance of the PNAcAam. The big change of optical transmittance was observed in the small change of temperature, when potassium halide was added in the mixture. The UCST's measured for KF, KCl, and KBr are 38.5, 17, and 14.5°C, respectively. The anions of Cl⁻ and Br⁻ are known to exhibit the structure-breaking properties on water cluster.¹⁷ Therefore, it is explained that the hydrated water to polymers may dissociate due to the salting-out effect of anions,

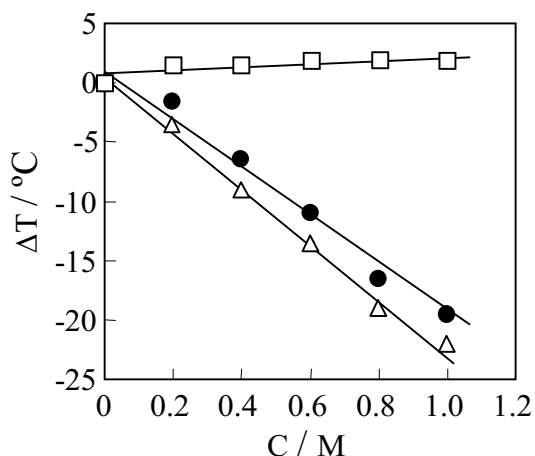


Fig. 3 Relationship between the UCST change (ΔT) of PNAAm and the salt concentration. ΔT was determined from the measurement of the optical transmittance at 500 nm in 30 wt% ethanol and 70 wt% of 1.0 M KF (\square), KCl (\bullet), and KBr (\triangle) solution.

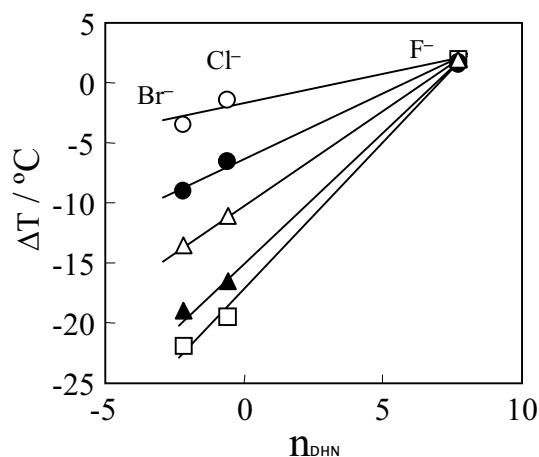


Fig. 4 Relationship between the UCST change (ΔT) of PNAAm and the dynamic hydration number (n_{DHN}) of the anion added in the mixture. ΔT was determined from the measurement of the optical transmittance at 500 nm in 30 wt% ethanol and 70 wt% of potassium halide in aqueous solutions. The concentrations of each anion were 1.0 (\square), 0.8 M (\blacktriangle), 0.6 M (\triangle), 0.4 M (\bullet), and 0.2 M (\circ). The values of n_{DHN} were cited from the paper described by Uedaira et al.¹⁷ The n_{DHN} 's for F^- , Cl^- , and Br^- are 7.7, -0.56, and -2.22, respectively.

which bring about the aggregation of polymer molecules as the insoluble interpolymer complex.⁹

The relationship between the anion concentration and the UCST change (ΔT) was surveyed as shown in Fig. 3. The nearly linear relationship was observed for each anion used. ΔT decreased with increasing the concentration of Cl^- and Br^- ($\Delta T < 0$), except that ΔT was nearly constant irrespective of the concentration of F^- ($\Delta T \approx 0-2$). The polymer complex is insoluble at the highest temperature (38.5°C) in the presence of F^- . F^- is considered to be a strong structure-forming anion, while Cl^- and Br^- are the structure-breaking anions. It seems that the hydrogen bonds between acetylamine groups in the polymer complex is more stable in the presence of F^- than Cl^- and Br^- .

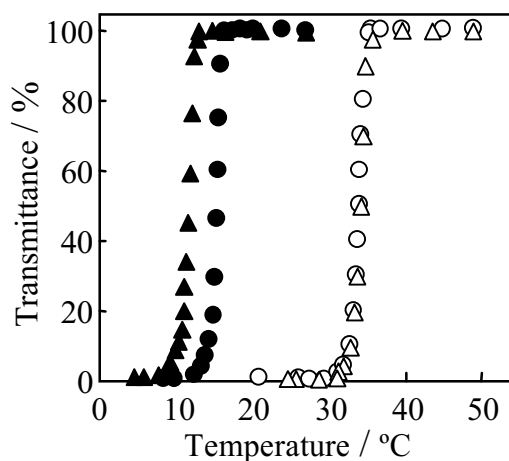


Fig. 5 Effect of additive cations on the optical transmittance of the PNAAm in the mixture of 30 wt% ethanol and 70 wt% of 1.0 M NaCl (\blacktriangle), 1.0 M KCl (\bullet), 0.2 M NaCl (\triangle), and 0.2 M KCl (\circ) solution. Transmittance was measured at 500 nm with heating the mixture.

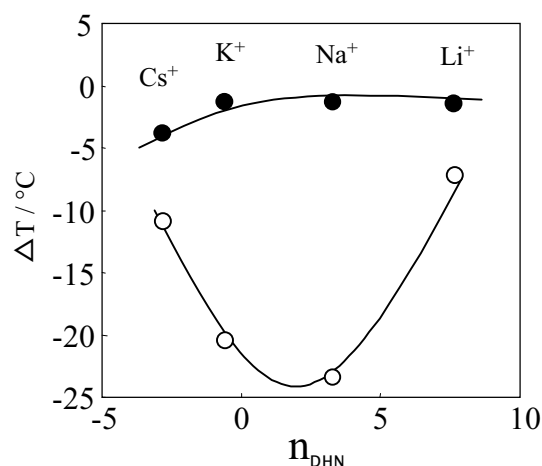


Fig. 6 Relationship between the UCST change (ΔT) of PNAAm and the dynamic hydration number (n_{DHN}) of the cation added in the mixture. ΔT was determined from the measurement of the optical transmittance at 500 nm in 30 wt% ethanol and 70 wt% of alkali metal chloride in aqueous solutions. The concentrations of cations were 1.0 (\circ), and 0.2 M (\bullet). The values of n_{DHN} were cited from the paper described by Uedaira et al.¹⁷ The n_{DHN} 's for Li^+ , Na^+ , K^+ and Cs^+ are 7.7, 3.3, -0.56, and -2.78, respectively.

The UCST decrease in the presence of the anions was studied from the viewpoint of the hydration of the anions. Figure 4 shows the plots of ΔT against the dynamic hydration number (n_{DHN}) of each anion added with various concentration of the alkali metal halides.^{16,17} The n_{DHN} for F^- shows positive, which means F^- behaves as the structure-forming anion. On the contrary, the n_{DHN} 's for Cl^- and Br^- are -0.56 and -2.22, respectively. Since the n_{DHN} 's for Cl^- and Br^- are negative, these anions are classified into the structure-breaking anions. Figure 4 shows a linear relationship between n_{DHN} and ΔT in every concentration of anions. This result indicates that the additive anions interact with the hydrated water molecules around the PNAAm, and change the situation of the polymer hydration and that of hydrogen bonding between acetylamine groups.

Effect of the cations on the UCST Effects of additive cations on the UCST of PNAcAAM were surveyed using LiCl, NaCl, KCl, and CsCl. Figure 5 shows the representative results of the transmittance-temperature relationship on NaCl and KCl. No difference was observed in the case of the 0.2 M solutions in the profiles between Na⁺ and K⁺. However, the cation dependence appeared obviously with 1.0 M NaCl and KCl. Both salts used made the UCST decreasing from 36.5°C to around 10°C and ΔT_r expanding from around 50 to 100%. These results demonstrate that the UCST is controlled under the effects of both anions and cations. The plots of ΔT in 1.0 M or 0.2 M alkali metal chloride solution against n_{DHN} are shown in Fig. 6. As compared with Fig. 4, the plots for cations do not fall on a straight line. Li⁺ and Na⁺, of which n_{DHN} are positive, are considered to be the structure-forming cations. On the contrary, the structure-breaking ions of K⁺ and Cs⁺ have the negative n_{DHN} . The UCST's of PNAcAAM are higher in 0.2 M than in 1.0 M alkali metal chloride solutions. The salting-out effect may not be neglected. It is plausible that cations may interact with the hydrated water molecules around PNAcAAM in the same way as anions.

As conclusion, the fact that the UCST of PNAcAAM is controlled by addition of the alkali metal halide in ethanol-water system was discussed in connection with (1) the relationship between the UCST change (ΔT) and the dynamic hydration number (n_{DHN}) of anions and cations, and (2) the effect of additive anions or cations on the hydrogen bonds between acetylamide groups of PNAcAAM chains.

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