Specific Anion Effect in Water–Nonaqueous Solvent Mixtures: Interplay of the Interactions between Anion, Solvent, and Polymer

6 AUTHORS, INCLUDING:

Tao Wang
University of Science and Technology of China
12 PUBLICATIONS **78** CITATIONS

SEE PROFILE

Ke Lin
Xidian University
21 PUBLICATIONS **193** CITATIONS

SEE PROFILE

Guangming Liu
Nanchang Hangkong University
57 PUBLICATIONS **825** CITATIONS

SEE PROFILE

Guangzhao Zhang
University of Science and Technology of China
**204** PUBLICATIONS **4,086** CITATIONS

SEE PROFILE

Specific Anion Effect in Water−Nonaqueous Solvent Mixtures: Interplay of the Interactions between Anion, Solvent, and Polymer

Lvdan Liu,[†] Tao Wang,[†] Chang Liu,[†] Ke Lin,[†] Guangming Liu,*,[†] and Guangzhao Zhang[‡]

[†]Department of Chemical Physics, Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, 230026, P. R. China

[‡]Faculty of Materials Science and Engineering, South China University of Technology, Guangzhou, 510640, P. R. China

Ⓢ *Supporting Information*

ABSTRACT: Ethanol (EtOH) and dimethylsulfoxide (DMSO) are polar protic and aprotic organic solvents, respectively. In the present work, we have investigated the anion-specific lower critical solution temperature (LCST) and upper critical solution temperature (UCST) behaviors of poly(*N*-isopropylacrylamide) (PNIPAM) in the H_2O−EtOH and H_2O−DMSO mixtures. The turbidity and differential scanning calorimetry studies show that the LCST for the anions follows the Hofmeister series at the molar fraction of EtOH (x_E) or DMSO (x_D) of 6%. At x_E of 26%, the UCST for the anions also follows the Hofmeister series because the dominating interactions for the UCST behavior are similar to that for the LCST behavior in the H_2O−EtOH mixtures. In the H_2O−DMSO mixture at x_D of 70%, an inverted V-shaped anion series is observed for the UCST behavior of PNIPAM. Our studies demonstrate that the specific anion effect on the phase transition behaviors of PNIPAM is influenced not only by the anionic polarization of hydrogen bonding between solvent molecules and PNIPAM but also by the anion adsorption on the PNIPAM chain surface.
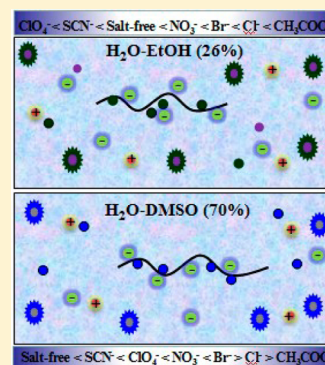
INTRODUCTION

In aqueous solutions, the so-called Hofmeister effect has attracted extensive attention from both theoretical and experimental areas.[1−15] Several models have been proposed to clarify the mechanism of Hofmeister effect in aqueous solutions.[16−18] Specifically, Ninham et al. suggested that the specific ion effect is due to the polarizability of ions and is manifested through the ionic dispersion forces.[16] Kunz et al. suggested that the specific ion effect on ion−surface interactions is significantly influenced by the nature of surfaces.[17] Cremer et al. revealed that both ion−solvent and ion−polymer interactions are responsible for the specific ion effect in macromolecular systems.[18]

In comparison with the extensive studies on the Hofmeister effect in aqueous solutions, only a little attention has been paid to the specific ion effect in organic solvents or water−organic solvent mixtures.[16,19−21] It is suggested that water may not be necessary for the occurrence of the specific ion effect as the Hofmeister phenomena can be observed in pure organic solvents.[20,21] For the water−organic solvent mixtures, nuclear magnetic resonance measurements demonstrated that the anion sequence in terms of the extent of ion pairing in water−ethanol mixtures follows the Hofmeister series.[19] Our previous studies on ion specificity for polymer systems showed that the ordering of ions in water−organic solvent mixtures follows the Hofmeister series but the specific ion effect is amplified with the addition of organic solvents.[22−24]

Actually, the organic solvents used in our previous studies are those that can act as both hydrogen bond donors and acceptors, e.g., methanol, ethanol (EtOH), and ethylene glycol.[22−24]

These kinds of organic solvents are also called polar protic organic solvents.[25−30] In their solvent mixtures with water, the solvent molecules can always form clusters or complexes via hydrogen bonds irrespective of the variation of solvent composition. When the solvent molecules interact with polymers, the polarization of hydrogen bonding by anions can weaken or strengthen the hydrogen bonds between solvent molecules and polymer chains.[18]

One can imagine that the formation of hydrogen bonds in water−organic solvent mixtures would be quite different if the added organic solvents only have hydrogen bond acceptors.[31−36] Dimethylsulfoxide (DMSO) is a widely used polar aprotic organic solvent, which is composed of a strongly polar sulfoxide group and two hydrophobic methyl groups. Thus, it can only act as the hydrogen bond acceptor. In the H_2O−DMSO mixtures, DMSO molecules will form hydrogen bonds with water molecules through the polar sulfoxide groups.[37] At the high molar fraction of DMSO, water molecules will insert into the DMSO clusters assisted by the hydrogen bonding between DMSO and H_2O molecules.[38] Additionally, the polarization of hydrogen bonding by anions would strengthen the interactions between DMSO and polymer as DMSO molecules can merely contribute their hydrogen bond accepting sites to interact with the polymer chains.[18]

In the H_2O−EtOH and H_2O−DMSO mixtures, poly(*N*-isopropylacrylamide) (PNIPAM) has a lower critical solution

temperature (LCST) behavior at the low molar fraction of EtOH (x_E) or DMSO (x_D), whereas PNIPAM exhibits an upper critical solution temperature (UCST) behavior at the relatively high x_E or x_D.[39] Therefore, these phase transition behaviors provide a model system to study the anion specificity in the H_2O−EtOH and H_2O−DMSO mixtures. Since specific anion effect is strongly influenced by the formation of solvent clusters, the polymer−solvent interactions, and the anion−solvent interactions in the water−organic solvent mixtures,[22−24] it is anticipated that the specific anion effect in the H_2O−DMSO mixtures should be different from that in the H_2O−EtOH mixtures.

In the present work, we have investigated the anion-specific LCST and UCST behaviors of PNIPAM in the H_2O−EtOH and H_2O−DMSO mixtures. We find that the anion sequence in terms of the LCST or UCST in the H_2O−EtOH mixtures follows the Hofmeister series. In the H_2O−DMSO mixtures, the anion sequence related to the LCST behavior also follows the Hofmeister series, but an inverted V-shaped anion series is observed for the UCST behavior. We are interested in how the interplay of the interactions between anion, solvent, and polymer will influence the specific anion effect in the water−nonaqueous solvent mixtures.

■ EXPERIMENTAL SECTION

Materials. Isopropylacrylamide (NIPAM, Aldrich) was recrystallized three times in a mixture of toluene and hexane (65/35, v/v). 1,4-Dioxane was refluxed over Na and then distilled under vacuum before use. 4,4′-Azobis(isobutyronitrile) (AIBN) was recrystallized three times from ethanol. All the salts (AR grade) were purchased from Sinopharm or Aladdin and used as received. DMSO (99.0%, AR grade) and EtOH (99.7%, AR grade) were purchased from Sinopharm and used as received. The water used was purified by filtration through a Millipore Gradient system after distillation, giving a resistivity of 18.2 MΩ cm. When studying anion specificity, we employed sodium salts so that the influence of cations was constant.

PNIPAM Preparation. Chain-transfer agent cyanoisopropyl dithiobenzoate (CPDB) was synthesized following the previous method.[40] PNIPAM was synthesized by reversible addition−fragmentation chain transfer (RAFT) polymerization in dioxane at 70 °C for ~20 h with CPDB as the chain-transfer agent and AIBN as the initiator. The sample was precipitated three times from tetrahydrofuran (THF) into diethyl ether for purification. The number-average molar mass ($M_n \sim 1.6 \times 10^4$ g mol^{-1}) and the polydispersity index ($M_w/M_n \sim 1.1$) of the sample were measured by gel permeation chromatography (Waters 1515) using monodisperse polystyrene as the calibration standard and THF as the eluent with a flow rate of 1.0 mL min^{-1}.

Cloud Point Measurements. Cloud points were determined by monitoring the turbidity of solutions heated/cooled at a rate of 0.1 °C min^{-1} during the measurements of LCST/UCST using a UNICO 2802PCS UV/visible spectrophotometer with the wavelength set to 500 nm. The temperature of the cell was controlled using a circulating temperature controlled bath with an accuracy of ±0.1 °C and monitored by an electronic thermometer. For measurements below 10 °C, the cell holder was flushed with nitrogen to prevent moisture condensation on the cell surface. The concentration of PNIPAM in the H_2O−EtOH and H_2O−DMSO mixtures was fixed at 5.0 mg mL^{-1}, and the salt concentration was fixed at 0.1 M. In turbidity studies, we chose to use the temperature at

which the transmittance equaled the average of the transmittance values of the high transmittance (low turbidity) and low transmittance (high turbidity) plateaus as the LCST or UCST (Figures S1 and S2, Supporting Information).

Raman Spectra Measurements. In the Raman spectra measurements, a CW laser source (Coherent, Verdi-5W, 532 nm), a monochromator with a 600 grooves/mm grating, and a liquid-nitrogen-cooled CCD detector (Acton Research, Triple-Pro) were used to record the spontaneous Raman spectrum.[41] Liquid samples in a quartz cell (Spectrocell, 10 × 10 mm^2) were excited by the laser. The Raman scattering photons were collected at 180° geometry relative to the incident laser beam with a pair of f = 5 and 20 cm lenses and imaged through a polarization scrambler onto the entrance slit of the monochromator for spectral dispersion. The laser power employed was 0.5 W. The spectral resolution was determined to be ~3.0 cm^{-1}. All the Raman spectra were measured at ~25 °C.

DSC Measurements. The differential scanning calorimetry (DSC) measurements were conducted on a multicell-DSC (TA Instruments) at a heating rate of 1 °C min^{-1}. A reference scan was performed using a solution containing all reagents except PNIPAM. The temperature corresponding to the endothermic peak in the DSC curve was taken as the LCST. The concentration of PNIPAM was fixed at 10.0 mg mL^{-1} so that the measurements were sufficient to yield strong signals and had good accuracy. The salt concentration was fixed at 0.1 M during the DSC measurements.

■ RESULTS AND DISCUSSION

Turbidity Studies. It is known that PNIPAM exhibits a LCST at the low x_E or x_D in the H_2O−EtOH and H_2O−DMSO mixtures.[39] Figure 1 shows the change in LCST as a
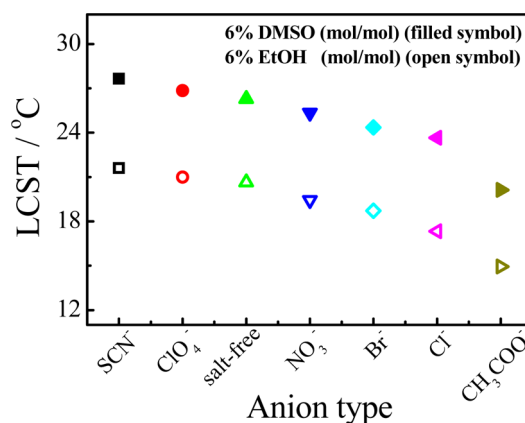
Figure 1. Change in LCST of PNIPAM as a function of anion type in the H_2O−EtOH and H_2O−DMSO mixtures at the molar fraction of EtOH (x_E) or DMSO (x_D) of 6% with Na$^+$ as the common cation, where the polymer concentration is fixed at 5.0 mg mL^{-1} and the salt concentration is fixed at 0.1 M.

function of anion type in the H_2O−EtOH and H_2O−DMSO mixtures at the x_E or x_D of 6%. It can be seen that the LCST in the presence of DMSO is always higher than that in the presence of EtOH for the same anion. As suggested previously, the decrease of LCST induced by the addition of EtOH or DMSO is attributed to the interactions between organic solvent molecules and water molecules.[39,42,43] The added EtOH molecules will form hydrogen bonds with water molecules through the hydroxyl groups. Meanwhile, the hydrophobic

ethyl groups will be hydrated by water molecules accompanied by the formation of ordered hydration shells around the groups.[39,44,45] Thus, the addition of EtOH will disturb the hydration of PNIPAM chains, leading to a decrease in the LCST of PNIPAM.[39]

Likewise, the added DMSO molecules will also form hydrogen bonds with water molecules via the S=O groups. At the same time, the hydrophobic methyl groups are also hydrated by water molecules, resulting in a decrease in the LCST with the addition of DMSO. The difference in the hydrophobic group between EtOH and DMSO is the molecular shape. EtOH has a linear ethyl group, whereas the two methyl groups on DMSO exhibit a more spherical shape. It has been reported that a more spherical hydrophobic group is more miscible with water molecules as a cage structure can be formed by water molecules without a significant distortion of the normal angle between hydrogen bonds of water molecules.[46] That is, the hydration of the linear ethyl group of EtOH may need a larger amount of water molecules compared with the hydration of the two methyl groups of DMSO. Therefore, the addition of 6% EtOH would produce a more significant disturbance to the hydration of PNIPAM than that for the addition of 6% DMSO. As a result, the LCST in the presence of EtOH is always lower than that in the presence of DMSO for the same anion.

A similar specific anion effect on the LCST behavior is observed in the H_2O−EtOH and H_2O−DMSO mixtures at x_E and x_D of 6%. The LCST decreases following the order SCN^- > ClO_4^- > salt-free > NO_3^- > Br^- > Cl^- > CH_3COO^-, which is consistent with the classical Hofmeister series.[3−5,47−49] Here, SCN^- and ClO_4^- exhibit a salting-in effect, but other anions exhibit a salting-out effect in comparison with the salt-free solution. Clearly, the specific anion effect on the LCST behavior of PNIPAM observed in Figure 1 is similar to that in water.[18,22] This is understandable because the solubility of PNIPAM in the H_2O−EtOH and H_2O−DMSO mixtures at x_E or x_D of 6% is still dominated by the interactions between water, anion, and PNIPAM. Here, the anion specificity can be explained by the following: (i) the polarization of hydrogen bonding between H_2O and PNIPAM by anions[18] and (ii) the adsorption of chaotropic anions on the PNIPAM chain surface.[50] As reported previously, the anionic polarization of hydrogen bonding between H_2O and PNIPAM will lead to a decrease in the solubility of PNIPAM by weakening the interactions of water molecules with the carbonyl oxygen and amide nitrogen.[18] Thus, the LCST should decrease following the series SCN^- > ClO_4^- > NO_3^- > Br^- > Cl^- > CH_3COO^- as the capability of the anions to polarize the hydrogen bonds increases from SCN^- to CH_3COO^- along the series.[18]

On the other hand, the chaotropic anions can also adsorb onto the PNIPAM chain surface via dispersion interactions, which is correlated with the polarizability of anions.[50] The anions can more strongly adsorb onto the PNIPAM chain surface following the order Cl^- < Br^- < NO_3^- < ClO_4^- < SCN^- as the polarizability of the anions increases from Cl^- to SCN^- along this series.[51] The adsorption of anions on the chain surface will enhance the solubility of PNIPAM through the charge−dipole interactions between the adsorbed anions and the water molecules and reduce the extent of PNIPAM aggregation due to the electrostatic repulsion between the negatively charged polymer chains. Therefore, the anion adsorption will also cause the LCST to decrease following the series SCN^- > ClO_4^- > NO_3^- > Br^- > Cl^-. That is, the

anion adsorption on the PNIPAM chain surface and the anionic polarization of hydrogen bonding between H_2O and PNIPAM have a similar effect on the ordering of anion series in terms of the LCST. Consequently, the LCST decreases following the series from chaotropic to kosmotropic anion at x_E or x_D of 6% in the solvent mixtures.

It is known that PNIPAM also exhibits an UCST behavior in the H_2O−EtOH mixtures at x_E around 26%. UCST is a critical temperature above which polymer becomes soluble and below which polymer turns insoluble.[39,52−55] Therefore, a lower UCST is indicative of a higher solubility. In Figure 2, the UCST
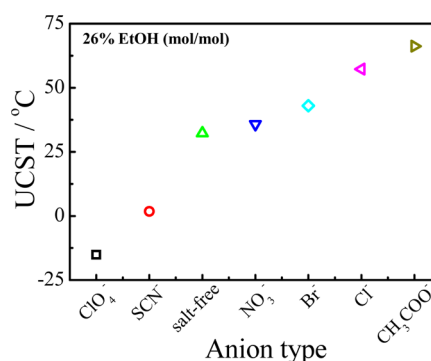
Figure 2. Change in UCST of PNIPAM as a function of anion type in the H_2O−EtOH mixture at the molar fraction of EtOH (x_E) of 26% with Na^+ as the common cation, where the polymer concentration is fixed at 5.0 mg mL^{-1} and the salt concentration is fixed at 0.1 M.

of PNIPAM increases following the order ClO_4^- < SCN^- < salt-free < NO_3^- < Br^- < Cl^- < CH_3COO^-, which is also consistent with the Hofmeister series. The lower UCST for SCN^- and ClO_4^- compared with that for the salt-free solution suggests that these two types of anions lead to a salting-in effect. In contrast, other anions exhibit a salting-out effect with the higher UCST than that for the salt-free solution.

In the H_2O−DMSO mixtures, PNIPAM also exhibits an UCST behavior at x_D around 70%.[39] Interestingly, Figure 3 shows that all the anions have a salting-out effect compared with that for the salt-free solution, as reflected by the fact that PNIPAM exhibits higher UCSTs in the presence of the anions than that for the salt-free solution. Moreover, the anion
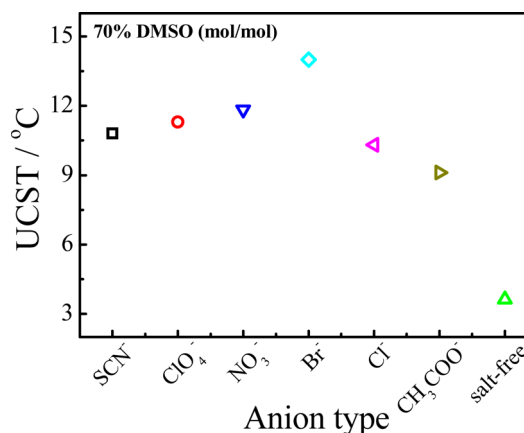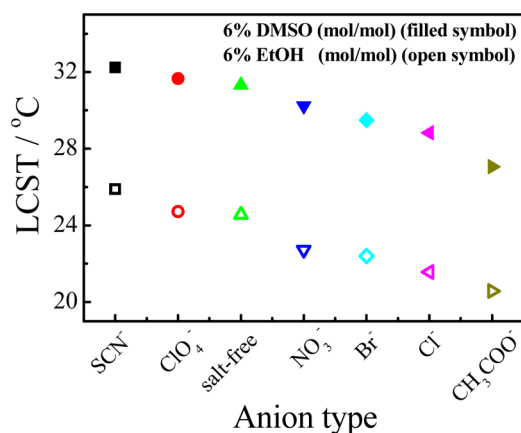
Figure 3. Change in UCST of PNIPAM as a function of anion type in the H_2O−DMSO mixture at the molar fraction of DMSO (x_D) of 70% with Na^+ as the common cation, where the polymer concentration is fixed at 5.0 mg mL^{-1} and the salt concentration is fixed at 0.1 M.

sequence related to the UCST follows an inverted V-shaped series $SCN^- < ClO_4^- < NO_3^- < Br^- > Cl^- > CH_3COO^-$, which is different from the results in Figures 1 and 2.

DSC and Raman Spectroscopy Studies. We have also investigated the phase transition behaviors of PNIPAM in the $H_2O-EtOH$ and $H_2O-DMSO$ mixtures by using DSC in the presence of different anions. Figure 4 shows that the LCST in

Figure 4. Change in LCST of PNIPAM as a function of anion type in the $H_2O-EtOH$ and $H_2O-DMSO$ mixtures at the molar fraction of EtOH (x_E) or DMSO (x_D) of 6% with Na^+ as the common cation obtained from the DSC measurements, where the polymer concentration is fixed at 10.0 mg mL^{-1} and the salt concentration is fixed at 0.1 M.
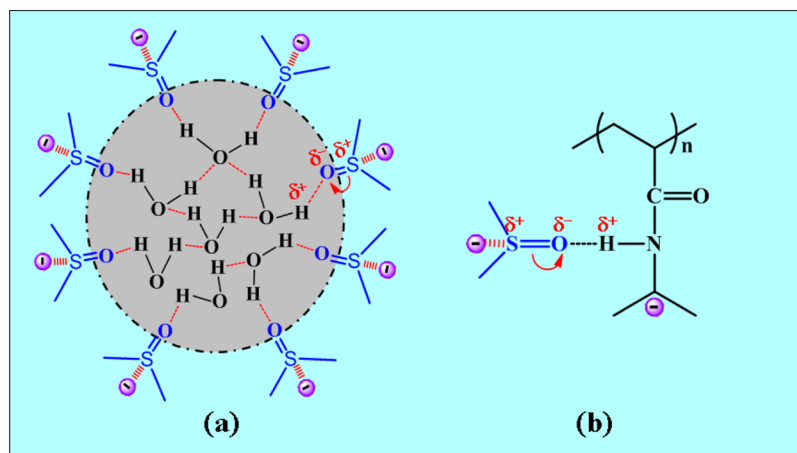
the $H_2O-EtOH$ and $H_2O-DMSO$ mixtures decreases following the series $SCN^- > ClO_4^- >$ salt-free $> NO_3^- > Br^- > Cl^- > CH_3COO^-$, which is consistent with the observation in Figure 1. Also, the LCST in the presence of DMSO is always higher than that in the presence of EtOH for the same anion. Again, the anion specificity observed here can be explained by the cooperative effect of the anion adsorption on the PNIPAM chain surface and the anionic polarization of hydrogen bonding between H_2O and PNIPAM.[18,50] It is suggested that endothermic peaks in the heating process are due to the heat required to break the hydrogen bonds between PNIPAM and

solvents.[56] The enthalpy change (ΔH) in the presence of different anions during the phase transition can be obtained from the integration of the endothermic peaks (Figure S3, Supporting Information). In Supporting Information Figure S3, the ΔH is independent of the anion type in the $H_2O-EtOH$ and $H_2O-DMSO$ mixtures, suggesting that the specific anion effect on the LCST behavior may be dominated by entropy change.[22,57,58] Similar to the previous study,[59] the UCST phase transition of PNIPAM in the $H_2O-EtOH$ and $H_2O-DMSO$ mixtures cannot be detected in the DSC measurements, but the reason still remains unclear.

Considering that the specific anion effect on the phase transition behavior of PNIPAM is also strongly influenced by the hydrogen bonding between the solvent molecules in the solvent mixtures,[22,23] we have measured the Raman spectra of the $H_2O-EtOH$ and $H_2O-DMSO$ mixtures (Figures S4–S7, Supporting Information). Supporting Information Figure S4 indicates that the solvent molecules form the firmest hydrogen bond network at the x_E of 26%. At the low x_E, the LCST of PNIPAM is determined by the competition between the decrease in enthalpy and the decrease in entropy during the hydration of PNIPAM chains.[39] The addition of EtOH to water in the range of x_E between 0% and 26% results in a decrease in LCST because the formation of firm hydrogen bond network induced by the hydrophobic hydration of EtOH molecules disturbs the hydration of PNIPAM chains. At x_E of 26%, the PNIPAM chains are insoluble even at a very low temperature due to the formation of firmest hydrogen bond network. Nevertheless, the water molecules would escape from the hydration shell of EtOH molecules with the increasing temperature as a higher temperature would strengthen the entropy contribution to the change of free energy; that is, a dehydration of EtOH molecules would occur at a higher temperature.

Once the hydration shells around the EtOH molecules are broken, the free EtOH molecules are allowed to interact with polymer chains via the hydrophobic interactions.[39] Meanwhile, the free H_2O molecules will be available in solvating the PNIPAM chains, and the polymer becomes soluble in the solvent mixture again. This might be the reason why the UCST behavior of PNIPAM occurs at x_E around 26%. Thus, the

Scheme 1. Interactions between Anions, Solvent Molecules, and PNIPAM Chains[a]

[a](a) The formation of H_2O/DMSO cluster and the stabilization of the cluster via the polarization of hydrogen bonding between DMSO and H_2O by anions. (b) The polarization of hydrogen bonding between DMSO and PNIPAM by anions and the direct adsorption of anions onto the PNIPAM chain surface.

solubility of PNIPAM at x_E of 26% in the presence of different anions is still dominated by the interactions between anion, water, and PNIPAM, which is similar to that for the LCST behavior at the x_E of 6%. In other words, specific anion effect on the UCST behavior in the $H_2O-EtOH$ mixture can also be interpreted by the cooperative effect of the anion adsorption on the PNIPAM chain surface and the anionic polarization of hydrogen bonding between PNIPAM and water. This is why the anion specificity observed for the UCST behavior is similar to that for the LCST behavior in the $H_2O-EtOH$ mixtures.

Supporting Information Figures S5 and S6 indicate that the $H_2O-DMSO$ mixture at x_D of 70% is composed of free DMSO molecules and $H_2O/DMSO$ clusters. For the latter, the water molecules are expected to be surrounded by the DMSO molecules with the DMSO molecules as the hydrogen bond acceptors (Scheme 1). It is reasonable that the solubility of PNIPAM should be dominated by the solvation of PNIPAM chains by DMSO molecules in the $H_2O-DMSO$ mixture at x_D of 70%. As x_D changes from 100% to 70%, the formation of $H_2O/DMSO$ clusters induced by the addition of H_2O will disturb the solvation of PNIPAM chains, leading PNIPAM to be insoluble at the low temperature. As the temperature increases to a certain value, DMSO and H_2O molecules would be released out from the clusters since the formation of $H_2O/DMSO$ cluster has negative changes in both enthalpy and entropy. The released DMSO molecules will enhance the solubility of PNIPAM via solvating the chains. This might be the reason why the UCST behavior is observed at x_D around 70%. Since the added anions may enhance the stability of the clusters by polarizing the hydrogen bonds between DMSO and H_2O molecules (Scheme 1), all the anions would exhibit a salting-out effect compared with the salt-free solution (Figure 3).

The hydrogen bonds between PNIPAM and DMSO are mainly formed by the N–H and S=O groups. Therefore, the anions will also strengthen the hydrogen bonds between PNIPAM and DMSO via the polarization of hydrogen bonding (Scheme 1). If an anion can more effectively polarize the hydrogen bonds, it will give rise to a higher solubility of PNIPAM. Thus, the UCST of PNIPAM should decrease following the series $SCN^- > ClO_4^- > NO_3^- > Br^- > Cl^- > CH_3COO^-$ because the capability of the anions to polarize the hydrogen bonds increases from SCN^- to CH_3COO^- along the series,[18] which is inconsistent with the inverted V-shaped series observed in Figure 3.

Actually, the chaotropic anions can also adsorb onto the PNIPAM chain surface via dispersion interactions (Scheme 1).[18,60-65] The chaotropic anion with a larger polarizability is expected to adsorb on the chain surface more strongly.[61,64,65] Thus, the anions can more strongly adsorb onto the PNIPAM chain surface following the order $Cl^- < Br^- < NO_3^- < ClO_4^- < SCN^-$ as the polarizability of the anions increases from Cl^- to SCN^- along this series.[51] The adsorption of anions on the chain surface would enhance the solubility of PNIPAM through the charge–dipole interactions between the adsorbed anions and the DMSO molecules and reduce the extent of PNIPAM aggregation due to the electrostatic repulsion between negatively charged polymer chains.[50] Consequently, the UCST should decrease following the series $Cl^- < Br^- < NO_3^- < ClO_4^- < SCN^-$. Therefore, the anion adsorption on the PNIPAM chain surface and the anionic polarization of hydrogen bonding between DMSO and PNIPAM have an opposing effect on the ordering of anion series in terms of the

UCST. As a result, the competitive effect between the polarization of hydrogen bonding and the anion adsorption leads to the occurrence of the inverted V-shaped anion series for the UCST behavior of PNIPAM in the $H_2O-DMSO$ mixture.

Salt Concentration Dependence of UCST. Figure 5 shows the change in UCST of PNIPAM as a function of salt
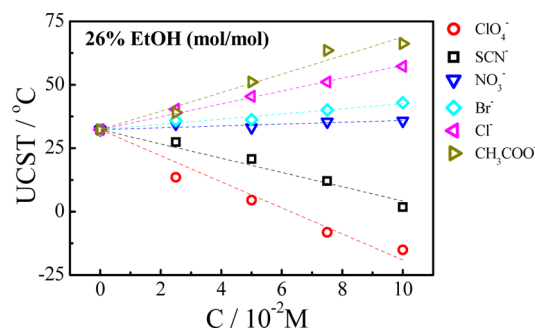
Figure 5. Change in UCST of PNIPAM as a function of salt concentration (C) for the anions in the $H_2O-EtOH$ mixture at x_E of 26% with Na^+ as the common cation, where the polymer concentration is fixed at 5.0 mg mL^{-1}.

concentration (C) in the presence of different anions in the $H_2O-EtOH$ mixture at x_E of 26%. The UCST for ClO_4^- and SCN^- linearly decreases with the salt concentration, whereas the UCST for other anions linearly increases with the salt concentration. Namely, the specific anion effect becomes more obvious with the increasing salt concentration. It is suggested that the slope (s) for the plot between salt concentration and phase transition temperature of macromolecules may correlate with the anion–solvent and anion–polymer interactions.[18,60,66] For example, the strength of the anionic polarization of hydrogen bonding and the anion adsorption may increase with the salt concentration, which would lead the UCST to increase or decrease with the salt concentration with different slopes for the different anions. The more strongly hydrated anion with a lower hydration entropy (ΔS_{hydr}) can more effectively polarize the water molecules to weaken their interactions with the PNIPAM chains, leading to a lower solubility of PNIPAM.[18] On the other hand, the anion with a larger polarizability (α) is expected to adsorb on the PNIPAM chain surface more strongly via dispersion interactions, resulting in a higher solubility of PNIPAM.[50] For the anion-specific UCST behavior of PNIPAM in the $H_2O-EtOH$ mixture, we suggest that the anion adsorption on PNIPAM chain surface and the anionic polarization of hydrogen bonding between H_2O and PNIPAM have a similar effect on the ordering of anion series. That is, either of them will cause the UCST to increase following the order $ClO_4^- < SCN^- < NO_3^- < Br^- < Cl^- < CH_3COO^-$ at x_E of 26%. If this suggestion is right, s should correlate with ΔS_{hydr} and α for the anions.

Figure 6a shows the plot of s as a function of ΔS_{hydr} for the anions in the $H_2O-EtOH$ mixture at x_E of 26%. Clearly, s is correlated with ΔS_{hydr} for the anions with the exception of CH_3COO^-, indicating that the specific anion effect on the UCST behavior in the $H_2O-EtOH$ mixture is correlated with the capability of the anions to polarize the hydrogen bonds between PNIPAM chains and water molecules. The deviation of CH_3COO^- is probably because the hydration of this anion is influenced not only by the charge–dipole interactions but also

10940

dx.doi.org/10.1021/jp406215c | J. Phys. Chem. B 2013, 117, 10936–10943
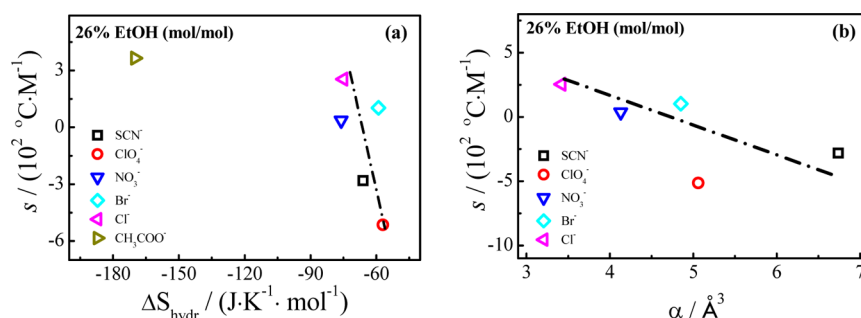
Figure 6. Plot of slope (*s*) as obtained from Figure 5 as functions of hydration entropy (ΔS_{hydr}) and polarizability (α) of the anions in the H_2O–EtOH mixture at x_E of 26% with Na^+ as the common cation. (a) The correlation between *s* and ΔS_{hydr} for the anions. (b) The correlation between *s* and α for the chaotropic anions. Here, the values of hydration entropy are obtained from ref 67, and the polarizability data are taken from ref 51.

by the hydrogen bonding interactions between the $C=O$ group of CH_3COO^- and the OH group of water molecules. Interestingly, *s* is also correlated with α for the chaotropic anions (Figure 6b), suggesting that the anion specificity is also correlated with the anion adsorption on the PNIPAM chain surface via dispersion interactions. The results in Figure 6 further confirm that the anion-specific UCST behavior at x_E of 26% is induced by the cooperative effect of the anion adsorption on the PNIPAM chain surface and the anionic polarization of hydrogen bonding between H_2O and PNIPAM.

In the H_2O–DMSO mixture at x_D of 70%, UCST linearly increases with the increasing salt concentration for all the anions, indicating that the salting-out effect becomes more obvious with the salt concentration (Figure 7). Meanwhile, the
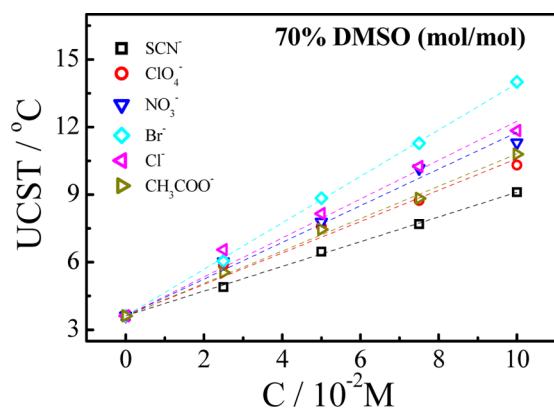
Figure 7. Change in UCST of PNIPAM as a function of salt concentration (*C*) for the anions in the H_2O–DMSO mixture at x_D of 70% with Na^+ as the common cation, where the polymer concentration is fixed at 5.0 mg mL^{-1}.

specific anion effect is also amplified with the salt concentration. The correlation of *s* with α for the anions is shown in Figure 8. Here, *s* is uncorrelated with α for the anions at x_D of 70%, suggesting that the specific anion effect on the UCST behavior of PNIPAM in the H_2O–DMSO mixture is not solely determined by the anion adsorption on the PNIPAM chain surface. This is understandable because the effect of anionic polarization of hydrogen bonding between DMSO and PNIPAM on the ordering of anion series is opposite to that generated by the anion adsorption on PNIPAM chain surface. In other words, the inverted V-shaped anion series for the UCST behavior in the H_2O–DMSO mixture is induced by the competitive effect between the anionic polarization of hydrogen bonding and the adsorption of chaotropic anions (Figure 3).
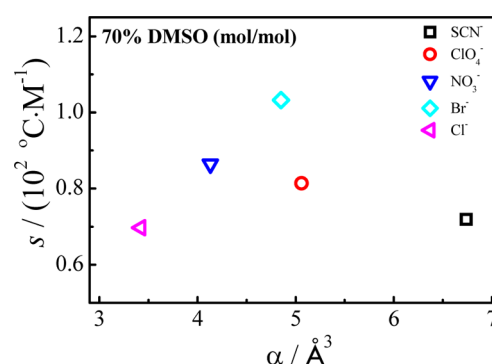
Figure 8. Plot of slope (*s*) as obtained from Figure 7 as a function of polarizability (α) of the anions in the H_2O–DMSO mixture at x_D of 70% with Na^+ as the common cation. Here, the polarizability data are taken from ref 51

■ CONCLUSION

Our studies show that the anion adsorption on the PNIPAM chain surface and the anionic polarization of hydrogen bonding between H_2O and PNIPAM have a similar effect on the ordering of anion series in terms of the LCST in the H_2O–EtOH and H_2O–DMSO mixtures. Accordingly, the LCST decreases following the series from chaotropic to kosmotropic anion. At x_E of 26%, the dominating interactions for the UCST behavior are similar to that for the LCST behavior, and the UCST increases following the series from chaotropic to kosmotropic anion. At x_D of 70%, the anion adsorption on the PNIPAM chain surface and the anionic polarization of hydrogen bonding between DMSO and PNIPAM have an opposing effect on the ordering of anion series in terms of the UCST. As a result, an inverted V-shaped anion series is observed for the UCST behavior in the H_2O–DMSO mixture. Our studies reveal that the combined effect of the anion adsorption on polymer surface and the anionic polarization of hydrogen bonding between solvent molecules and polymer plays a crucial role in the determination of anion specificity of macromolecules in water–nonaqueous solvent mixtures.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Additional data of the temperature dependence of transmittance, the DSC measurements, and the Raman spectroscopy measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: gml@ustc.edu.cn.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Hofmeister, F. Zur Lehre von der Wirkung der Salze (About the Science of the Effect of Salts). *Arch. Exp. Pathol. Pharmakol.* **1888**, *24*, 247−260.

(2) Parsegian, V. A. Solvation: Hopes for Hofmeister. *Nature* **1995**, *378*, 335−336.

(3) Collins, K. D.; Washabaugh, M. W. The Hofmeister Effect and the Behavior of Water at Interfaces. *Q. Rev. Biophys.* **1985**, *18*, 323−422.

(4) Kunz, W.; Lo Nostro, P.; Ninham, B. W. Hofmeister Phenomena. *Curr. Opin. Colloid Interface Sci.* **2004**, *9*, 1−18.

(5) Cacace, M. G.; Landau, E. M.; Ramsden, J. J. The Hofmeister Series: Salt and Solvent Effects on Interfacial Phenomena. *Q. Rev. Biophys.* **1997**, *30*, 241−277.

(6) Lo Nostro, P.; Fratoni, L. U.; Ninham, B. W.; Baglioni, P. Water Absorbency by Wool Fibers: Hofmeister Effect. *Biomacromolecules* **2002**, *3*, 1217−1224.

(7) Boström, M.; Williams, D. R. M.; Stewart, P. R.; Ninham, B. W. Hofmeister Effects in Membrane Biology: The Role of Ionic Dispersion Potentials. *Phys. Rev. E* **2003**, *68*, 041902.

(8) Boström, M.; Williams, D. R. M.; Ninham, B. W. Special Ion Effects: Why the Properties of Lysozyme in Salt Solutions Follow a Hofmeister Series. *Biophys. J.* **2003**, *85*, 686−694.

(9) Baldwin, R. L. How Hofmeister Ion Interactions Affect Protein Stability. *Biophys. J.* **1996**, *71*, 2056−2063.

(10) Boström, M.; Williams, D. R. M.; Ninham, B. W. Specific Ion Effects: Why DLVO Theory Fails for Biology and Colloid Systems. *Phys. Rev. Lett.* **2001**, *87*, 168103.

(11) Debeljuh, N. J.; Sutti, A.; Barrow, C. J.; Byrne, N. Phase Transition of Poly(N-isopropylacrylamide) in Aqueous Protic Ionic Liquids: Kosmotropic versus Chaotropic Anions and Their Interaction with Water. *J. Phys. Chem. B* **2013**, *117*, 8430−8435.

(12) Deniz, V.; Parsons, D. F. Effect of Nonelectrostatic Ion Interactions on Surface Forces Involving Ion Adsorption Equilibria. *J. Phys. Chem. C* **2013**, *117*, 16416−16428.

(13) Du, H, B.; Wickramasinghe, S. R.; Qian, X, H. Specificity in Cationic Interaction with Poly(N-isopropylacrylamide). *J. Phys. Chem. B* **2013**, *117*, 5090−5101.

(14) Siretanu, I.; Chapel, J.-P.; Bastos-González, D.; Drummond, C. Ions-Induced Nanostructuration: Effect of Specific Ionic Adsorption on Hydrophobic Polymer Surfaces. *J. Phys. Chem. B* **2013**, *117*, 6814−6822.

(15) Tomé, L. I. N.; Pinho, S. P.; Jorge, M.; Gomes, J. R. B.; Coutinho, J. A. P. Salting-in with a Salting-out Agent: Explaining the Cation Specific Effects on the Aqueous Solubility of Amino Acids. *J. Phys. Chem. B* **2013**, *117*, 6116−6128.

(16) Ninham, B. W.; Lo Nostro, P. *Molecular Forces and Self Assembly in Colloid, Nano Sciences and Biology*; Cambridge University Press: London, U.K., 2010.

(17) Kunz, W. *Specific Ion Effects*; World Scientific Publishing Company: River Edge, NJ, 2010.

(18) Zhang, Y. J.; Furyk, S.; Bergbreiter, D. E.; Cremer, P. S. Specific Ion Effects on the Water Solubility of Macromolecules: PNIPAM and the Hofmeister Series. *J. Am. Chem. Soc.* **2005**, *127*, 14505−14510.

(19) Hallberg, F.; Furó, I.; Stilbs, P. Ion Pairing in Ethanol/Water Solution Probed by Electrophoretic and Diffusion NMR. *J. Am. Chem. Soc.* **2009**, *131*, 13900−13901.

(20) Bilaničová, D.; Salis, A.; Ninham, B. W.; Monduzzi, M. Specific Anion Effects on Enzymatic Activity in Nonaqueous Media. *J. Phys. Chem. B* **2008**, *112*, 12066−12072.

(21) Peruzzi, N.; Ninham, B. W.; Lo Nostro, P.; Baglioni, P. Hofmeister Phenomena in Nonaqueous Media: The Solubility of Electrolytes in Ethylene Carbonate. *J. Phys. Chem. B* **2012**, *116*, 14398−14405.

(22) Wang, T.; Liu, G. M.; Zhang, G. Z.; Craig, V. S. J. Insights into Ion Specificity in Water−Methanol Mixtures via the Reentrant Behavior of Polymer. *Langmuir* **2012**, *28*, 1893−1899.

(23) Liu, L. D.; Wang, T.; Liu, C.; Lin, K.; Ding, Y. W.; Liu, G. M.; Zhang, G. Z. Mechanistic Insights into Amplification of Specific Ion Effect in Water−Nonaqueous Solvent Mixtures. *J. Phys. Chem. B* **2013**, *117*, 2535−2544.

(24) Long, Y. C.; Wang, T.; Liu, L. D.; Liu, G. M.; Zhang, G. Z. Ion Specificity at a Low Salt Concentration in Water−Methanol Mixtures Exemplified by a Growth of Polyelectrolyte Multilayer. *Langmuir* **2013**, *29*, 3645−3653.

(25) Smithrud, D. B.; Diederich, F. Strength of Molecular Complexation of Apolar Solutes in Water and in Organic Solvents Is Predictable by Linear Free Energy Relationships: A General Model for Solvation Effects on Apolar Binding. *J. Am. Chem. Soc.* **1990**, *112*, 339−343.

(26) Chang, T. L.; Cheung, H. C. Solvent Effects on the Photoisomerization Rates of the Zwitterionic and the Cationic Forms of Rhodamine B in Protic Solvents. *J. Phys. Chem.* **1992**, *96*, 4874−4878.

(27) Kamlet, M. J.; Taft, R. W. Solvatochromic Comparison Method.1. β-Scale of Solvent Hydrogen-Bond Acceptor (HBA) Basicities. *J. Am. Chem. Soc.* **1976**, *98*, 377−383.

(28) Taft, R. W.; Kamlet, M. J. Solvatochromic Comparison Method.2. α-Scale of Solvent Hydrogen-Bond Donor (HBD) Acidities. *J. Am. Chem. Soc.* **1976**, *98*, 2886−2894.

(29) Marcus, Y. The Effectivity of Solvents as Electron Pair Donors. *J. Solution Chem.* **1984**, *13*, 599−624.

(30) Guàrdia, E.; Martí, J.; Padró, J. A.; Saiz, L.; Komolkin, A. V. Dynamics in Hydrogen Bonded Liquids: Water and Alcohols. *J. Mol. Liq.* **2002**, *96−7*, 3−17.

(31) Sastry, M. I. S.; Singh, S. Self-Association of Dimethylsulfoxide and Its Dipolar Interactions with Water Raman Spectral Studies. *J. Raman Spectrosc.* **1984**, *15*, 80−85.

(32) Ahmed, M. K.; Ali, S.; Wojcik, E. The C−O Stretching Infrared Band as a Probe of Hydrogen Bonding in Ethanol−Water and Methanol−Water Mixtures. *Spectrosc. Lett.* **2012**, *45*, 420−423.

(33) Nose, A.; Hojo, M. Hydrogen Bonding of Water−Ethanol in Alcoholic Beverages. *J. Biosci. Bioeng.* **2006**, *102*, 269−280.

(34) Yang, D. P.; Wang, H. P. Effects of Hydrogen Bonding on the Transition Properties of Ethanol−Water Clusters: A TD-DFT Study. *J. Cluster Sci.* **2013**, *24*, 485−495.

(35) Abe, N.; Ito, M. Effects of Hydrogen-Bonding on the Raman Intensities of Methanol, Ethanol and Water. *J. Raman Spectrosc.* **1978**, *7*, 161−167.

(36) Luzar, A.; Stefan, J. Dielectric Behavior of DMSO−Water Mixtures. A Hydrogen-Bonding Model. *J. Mol. Liq.* **1990**, *46*, 221−238.

(37) Noack, K.; Kiefer, J.; Leipertz, A. Concentration-Dependent Hydrogen-Bonding Effects on the Dimethyl Sulfoxide Vibrational Structure in the Presence of Water, Methanol, and Ethanol. *ChemPhysChem* **2010**, *11*, 630−637.

(38) Bertoluzza, A.; Bonora, S.; Battaglia, M. A.; Monti, P. Raman and Infrared Study on the Effects of Dimethylsulfoxide (DMSO) on Water Structure. *J. Raman Spectrosc.* **1979**, *8*, 231−235.

(39) Costa, R. O. R.; Freitas, R. F. S. Phase Behavior of Poly(N-isopropylacrylamide) in Binary Aqueous Solutions. *Polymer* **2002**, *43*, 5879−5885.

10942

dx.doi.org/10.1021/jp406215c | *J. Phys. Chem. B* 2013, 117, 10936−10943

(40) Perrier, S.; Barner-Kowollik, C.; Quinn, J. F.; Vana, P.; Davis, T. P. Origin of Inhibition Effects in the Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization of Methyl Acrylate. *Macromolecules* **2002**, *35*, 8300−8306.

(41) Yu, Y. Q.; Lin, K.; Zhou, X. G.; Wang, H.; Liu, S. L.; Ma, X. X. New C−H Stretching Vibrational Spectral Features in the Raman Spectra of Gaseous and Liquid Ethanol. *J. Phys. Chem. C* **2007**, *111*, 8971−8978.

(42) Schild, H. G.; Muthukumar, M.; Tirrell, D. A. Cononsolvency in Mixed Aqueous Solutions of Poly(*N*-isopropylacrylamide). *Macromolecules* **1991**, *24*, 948−952.

(43) Mukae, K.; Sakurai, M.; Sawamura, S.; Makino, K.; Kim, S. W.; Ueda, I.; Shirahama, K. Swelling of Poly(*N*-isopropylacrylamide) Gels in Water−Alcohol (C1−C4) Mixed Solvents. *J. Phys. Chem.* **1993**, *97*, 737−741.

(44) Franks, F.; Ives, D. J. G. Structural Properties of Alcohol−Water Mixtures. *Q. Rev. Biophys.* **1966**, *20*, 1−44.

(45) Onori, G.; Santucci, A. Dynamical and Structural Properties of Water/Alcohol Mixtures. *J. Mol. Liq.* **1996**, *69*, 161−181.

(46) Hayashi, H.; Nishikawa, K.; Iijima, T. Small-Angle X-Ray Scattering Study of Fluctuations in 1-Propanol−Water and 2-Propanol−Water Systems. *J. Phys. Chem.* **1990**, *94*, 8334−8338.

(47) Bauduin, P.; Renoncourt, A.; Touraud, D.; Kunz, W.; Ninham, B. W. Hofmeister Effect on Enzymatic Catalysis and Colloidal Structures. *Curr. Opin. Colloid Interface Sci.* **2004**, *9*, 43−47.

(48) Kunz, W.; Henle, J.; Ninham, B. W. "Zur Lehre von der Wirkung der Salze" (About the Science of the Effect of Salts): Franz Hofmeister's Historical Papers. *Curr. Opin. Colloid Interface Sci.* **2004**, *9*, 19−37.

(49) Kunz, W. Specific Ion Effects in Colloidal and Biological Systems. *Curr. Opin. Colloid Interface Sci.* **2010**, *15*, 34−39.

(50) Boström, M.; Parsons, D. F.; Salis, A.; Ninham, B. W.; Monduzzi, M. Possible Origin of the Inverse and Direct Hofmeister Series for Lysozyme at Low and High Salt Concentrations. *Langmuir* **2011**, *27*, 9504−9511.

(51) Marcus, Y. *Ion Properties*; Marcel Dekker: New York, 1997.

(52) Yamauchi, H.; Maeda, Y. LCST and UCST Behavior of Poly(*N*-isopropylacrylamide) in DMSO/Water Mixed Solvents Studied by IR and Micro-Raman Spectroscopy. *J. Phys. Chem. B* **2007**, *111*, 12964−12968.

(53) Pagonis, K.; Bokias, G. Upper Critical Solution Temperature-Type Cononsolvency of Poly(*N,N*-dimethylacrylamide) in Water−Organic Solvent Mixtures. *Polymer* **2004**, *45*, 2149−2153.

(54) Roth, P. J.; Davis, T. P.; Lowe, A. B. Comparison between the LCST and UCST Transitions of Double Thermoresponsive Diblock Copolymers: Insights into the Behavior of POEGMA in Alcohols. *Macromolecules* **2012**, *45*, 3221−3230.

(55) Asai, H.; Fujii, K.; Ueki, T.; Sawamura, S.; Nakamura, Y.; Kitazawa, Y.; Watanabe, M.; Han, Y. S.; Kim, T. H.; Shibayama, M. Structural Study on the UCST-Type Phase Separation of Poly(*N*-isopropylacrylamide) in Ionic Liquid. *Macromolecules* **2013**, *46*, 1101−1106.

(56) Heskins, M.; Guillet, J. E. Solution Properties of Poly(*N*-isopropylacrylamide). *J. Macromol. Sci., Chem.* **1968**, *2*, 1441−1455.

(57) Shechter, I.; Ramon, O.; Portnaya, I.; Paz, Y.; Livney, Y. D. Microcalorimetric Study of the Effects of a Chaotropic Salt, KSCN, on the Lower Critical Solution Temperature (LCST) of Aqueous Poly(*N*-isopropylacrylamide) (PNIPA) Solutions. *Macromolecules* **2010**, *43*, 480−487.

(58) Livney, Y. D.; Portnaya, I.; Faupin, B.; Ramon, O.; Cohen, Y.; Cogan, U.; Mizrahi, S. Interactions between Inorganic Salts and Polyacrylamide Aqueous Solutions and Gels. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 508−519.

(59) Maeda, Y.; Mochiduki, H.; Ikeda, I. Hydration Changes during Thermosensitive Association of a Block Copolymer Consisting of LCST and UCST Blocks. *Macromol. Rapid Commun.* **2004**, *25*, 1330−1334.

(60) Zhang, Y. J.; Cremer, P. S. The Inverse and Direct Hofmeister Series for Lysozyme. *Proc. Natl. Acad. Sci.* **2009**, *106*, 15249−15253.

(61) Lund, M.; Jungwirth, P.; Woodward, C. E. Ion Specific Protein Assembly and Hydrophobic Surface Forces. *Phys. Rev. Lett.* **2008**, *100*, 258105.

(62) Lund, M.; Vrbka, L.; Jungwirth, P. Specific Ion Binding to Nonpolar Surface Patches of Proteins. *J. Am. Chem. Soc.* **2008**, *130*, 11582−11583.

(63) Parsons, D. F.; Ninham, B. W. Charge Reversal of Surfaces in Divalent Electrolytes: The Role of Ionic Dispersion Interactions. *Langmuir* **2010**, *26*, 6430−6436.

(64) Chen, F. G.; Li, C. L.; Wang, X. Y.; Liu, G. M.; Zhang, G. Z. pH and Ion-Species Sensitive Fluorescence Properties of Star Polyelectrolytes Containing a Triphenylene Core. *Soft Matter* **2012**, *8*, 6364−6370.

(65) Parsons, D. F.; Ninham, B. W. Importance of Accurate Dynamic Polarizabilities for the Ionic Dispersion Interactions of Alkali Halides. *Langmuir* **2010**, *26*, 1816−1823.

(66) Güner, P. T.; Demirel, A. L. Effect of Anions on the Cloud Point Temperature of Aqueous Poly(2-ethyl-2-oxazoline) Solutions. *J. Phys. Chem. B* **2012**, *116*, 14510−14514.

(67) Marcus, Y.; Loewenschuss, A. Standard Entropies of Hydration of Ions. *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **1984**, *81*, 81−135.