# Effect of Anions on the Cloud Point Temperature of Aqueous Poly(2-ethyl-2-oxazoline) Solutions

Pınar Tatar Güner[†] and A. Levent Demirel*[,‡]

[†]Materials Science & Engineering Graduate Program and [‡]Chemistry Department, Koç University, Sarıyer, 34450 Istanbul, Turkey

S *Supporting Information*

ABSTRACT: Poly(2-alkyl-2-oxazoline)s have recently gained attention in especially biological applications due to their lower critical solution temperature being close to the body temperature and their biocompatibility. The understanding of how cloud point temperature (T_c) depends on the salt concentration and the molecular mechanisms responsible for such behavior are important to tune T_c as desired by the applications. In this paper, we report the effect of a series of sodium salts on T_c of aqueous poly(2-ethyl-2-oxazoline) (PEOX) solutions by dynamic light scattering. PEOX samples having four different molecular weights were investigated, and the results were compared with those of poly(N-isopropylacrylamide) (PNIPAM), the mostly investigated and used thermoresponsive polymer. Kosmotropic anions decreased T_c linearly while chaotropic anions increased T_c nonlinearly with salt concentration. The contributions of different mechanisms to T_c change have been discussed. Our results indicate that the dominant mechanism is the dehydration of PEOX for divalent kosmotropic anions (CO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$) and direct binding for chaotropic anions (NO_3^-, I^-, ClO_4^-, SCN^-). For the remaining monovalent kosmotropic anions ($H_2PO_4^-$, F^-, Cl^-, Br^-), a combination of dehydration and surface tension mechanisms was in effect. The additional contribution of the surface tension mechanism for the monovalent kosmotropic anions was inferred for different molecular weight PEOX samples and also for PNIPAM. With PEOX molecular weight decreasing from 500 000 to 5000 g/mol, T_c decreased less with salt concentration which was attributed to the contribution of the surface tension mechanism. For PEOX samples, the decrease of T_c with kosmotropic anion concentration was faster compared to PNIPAM due to differences in their chemical structure. Our results show that the molecular mechanisms of interactions between PEOX chains and specific anions can simply be inferred from determination of T_c by a common technique—dynamic light scattering.
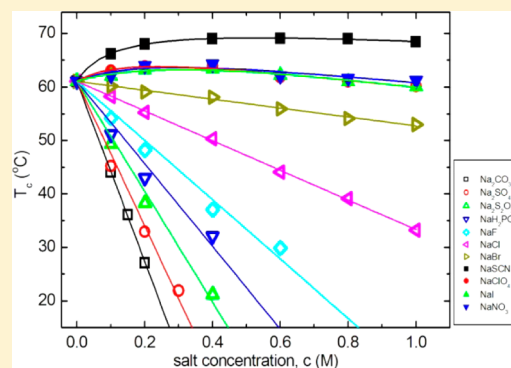
INTRODUCTION

Aqueous solutions of thermoresponsive polymers, such as poly(N-isopropylacrylamide) (PNIPAM) and poly(2-alkyl-2-oxazoline) (PAOX), show lower critical solution temperature (LCST) behavior. They undergo an entropy-driven phase transition from a soluble state to a phase-separated state at a critical temperature (cloud point temperature, T_c) as the temperature is increased. This property has been exploited in various applications such as stimuli responsive gels,[1−3] polymeric sensors,[4] drug delivery,[5] and molecular sensing.[6]

The understanding of how T_c depends on the environmental factors such as salt concentration and the molecular mechanisms responsible for such behavior are important to tune T_c as desired by the applications. Modification of the chemical structure of the polymer has commonly been used to tune T_c. Copolymerization,[7−12] addition of side groups,[13] and modification of end groups[14,15] have been investigated to tune LCST behavior in a large temperature window.

PNIPAM, LCST of ∼32 °C, has been the mostly investigated and used thermoresponsive polymer in applications. Poly(2-isopropyl-2-oxazoline) (PIPOX), LCST of ∼37 °C, is a structural isomer of PNIPAM and has recently gained attention in biological applications due to its LCST being close to the

body temperature and its biocompatibility.[16,17] The thermoresponsive properties of the other members of PAOX have also been thoroughly investigated.[18−22] Aqueous poly(2-ethyl-2-oxazoline) (PEOX) solutions has LCST of ∼61 °C. CH_3COO^- and SCN^- anions were shown to affect T_c of aqueous PEOX solutions and the self-assembly kinetics of PEOX above T_c.[23] Although CH_3COO^- anions decreased T_c and SCN^- anions increased T_c, they both enhanced the self-assembly kinetics compared to that in pure water. The effect of a series of lithium and sodium salts on T_c of aqueous PAOX having ethyl, propyl, and isopropyl side chains has previously been reported.[24] The anion effects were concluded to depend significantly on the hydrophilicity of the polymer chains but not on the molecular architecture.

The presence of ions in the solution has long been known to influence the macromolecule−solvent interactions and thus the LCST behavior.[25] The effectiveness of ions in stabilizing (or destabilizing) biopolymers or synthetic polymers in aqueous solutions follows a trend, known as Hofmeister series after

Franz Hofmeister's work on the relative ability of ions to influence protein stability in aqueous solutions in the 19th century.[25,26] The anions result in more pronounced effects compared to cations.[27] The 11 anions investigated in this study are listed below in typical order of their effectiveness to decrease solubility of polymers: CO_3^{2-} > SO_4^{2-} > $S_2O_3^{2-}$ > $H_2PO_4^-$ > F^- > Cl^- > Br^- ≈ NO_3^- > I^- > ClO_4^- > SCN^-.

The hydration strength of the anions in the series decreases from left to right. More strongly hydrated anions to the left of Br^- decrease the solubility of polymers and are known as kosmotropes. The anions to the right of Br^- increase the solubility of polymers and are known as chaotropes. Recent investigations have shown that direct ion–macromolecule interactions are responsible for the observed effects rather than the indirect influence of ions on the macromolecules through water structure modification.[28,29] Molecular-level mechanisms are still to be understood.[30,31]

Three different mechanisms have been introduced for the interaction of anions with PNIPAM in aqueous solutions:[31] (i) Dehydration mechanism: interaction of anions with the water molecules hydrogen bonded to the polymer (hydration water), dehydrating it, and decreasing its solubility (decreasing T_c of aqueous polymer solutions). (ii) Surface tension mechanism: increase in the surface tension of solution resulting in an increase in free energy of especially alkyl/water interface and decreasing solubility of polymer. (iii) Direct binding mechanism: direct binding of anions to the polymer and increasing its solubility.

In this paper, we report the effect of a series of sodium salts on T_c of aqueous PEOX solutions and interpret the results in terms of the above mechanisms introduced for PNIPAM.[31] Similar to aqueous PNIPAM solutions, our results for PEOX indicate that the dominant mechanism is the dehydration of PEOX chains for divalent kosmotropic anions (CO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$) and direct binding for chaotropic anions (NO_3^-, I^-, ClO_4^-, SCN^-). For the remaining monovalent kosmotropic anions ($H_2PO_4^-$, F^-, Cl^-, Br^-), a combination of dehydration and surface tension mechanisms was in effect. The additional contribution of the surface tension mechanism has been inferred for different molecular weight PEOX samples and for PNIPAM. With PEOX molecular weight decreasing from 500 000 to 5000 g/mol, T_c decreased less with salt concentration which was attributed to the contribution of the surface tension mechanism. For PEOX samples, the decrease of T_c with kosmotropic anion concentration was faster compared to PNIPAM due to differences in their chemical structure.

EXPERIMENTAL SECTION

Materials and Methods. Two of the poly(2-ethyl-2-oxazoline) (PEOX) samples (MW ~ 500 000 and 50 000 g/mol) and poly(N-isopropylacrylamide (MW ~ 22 000 g/mol) were purchased from Aldrich. The other two PEOX samples (MW ~ 200 000 and 5000 g/mol) were purchased from Alfa Aesar. All commercial polymers used had broad molar mass distributions (PDI ~ 3–4). It is well-known that the molar mass influences T_c (T_c is lower ~4–5 °C for PEOX molar mass 500 000 g/mol compared to that of 5000 g/mol at 1 mg/mL concentration). The effect of anions on T_c was in most cases much larger than 4–5 °C within the investigated range of salt concentrations (up to 1 M). Analytical grade sodium salts were purchased from Merck. Solutions were prepared by deionized water (18.0 MΩ). For all solutions, polymer (PEOX or PNIPAM) concentration was kept constant at 1 mg/mL. The

effect of 11 sodium salts was investigated: Na_2CO_3, Na_2SO_4, $Na_2S_2O_3$, NaH_2PO_4, NaF, $NaCl$, $NaBr$, $NaNO_3$, NaI, $NaClO_4$, and $NaSCN$. The salt concentrations were varied between 0 and 1 M.

The cloud point T_c of aqueous solutions was determined by dynamic light scattering (DLS) measurements using a Malvern Zetasizer Nano S instrument at 632.8 nm wavelength and 173° scattering angle. The temperature was increased from room temperature up to 70 °C with 1 °C steps. The solutions were equilibrated at each temperature at least 3 min. Ten measurements of hydrodynamic size, each having 3 runs with 10 s duration time, were averaged at each temperature.

RESULTS AND DISCUSSION

Effect of Anions on T_c of PEOX-500K solutions. Figure 1 shows the hydrodynamic size measured by DLS in aqueous
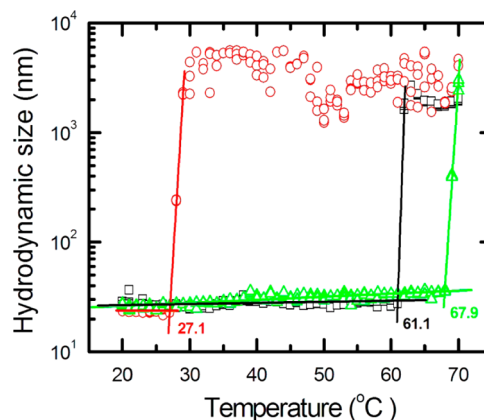

Figure 1. Hydrodynamic size as measured by DLS in 1 mg/mL aqueous PEOX-500K solutions: in pure water (squares), in 0.2 M Na_2CO_3 solution (circles), and in 0.2 M NaSCN solution (triangles).

PEOX-500K solutions as a function of temperature. PEOX concentration was kept constant at 1 mg/mL for all the solutions examined. T_c was defined as the temperature at which the hydrodynamic size increased suddenly from ~25 nm to several micrometers due to phase separation. T_c of PEOX-500K solutions in water was 61.1 °C. For PEOX-500K solutions in 0.2 M Na_2CO_3(aq), CO_3^{2-} being the most effective kosmotropic anion, T_c decreased significantly to 27.1 °C. In 0.2 M NaSCN(aq), SCN^- being the most effective chaotropic anion, T_c increased slightly to 67.9 °C. At the same salt concentration, T_c of PEOX solutions containing other sodium salts was between that of CO_3^{2-} and SCN^- containing solutions (Figure 2).

Figure 2 shows the effect of a series of 11 sodium salts on the T_c of aqueous PEOX-500K solutions. In the presence of kosmotropic anions, T_c decreased linearly with the salt concentration. The solid lines for the data of kosmotropic anions in Figure 2 (open symbols) represent the linear fits to $T_c(c) = T_c^° + sc$. The fitting parameters are shown in Table 1. The constant $T_c^° = 61.1$ °C is the T_c of PEOX-500K solution in pure water, and c is the salt concentration. The slope of the linear decrease s changed with the anion type in the order of CO_3^{2-} > SO_4^{2-} > $S_2O_3^{2-}$ > $H_2PO_4^-$ > F^- > Cl^- > Br^-, which followed the order in the Hofmeister series of anions.

Two different mechanisms may contribute to the linear decrease of T_c with salt concentration:[31] dehydration of the polymer chains and increase in the surface tension of solution.
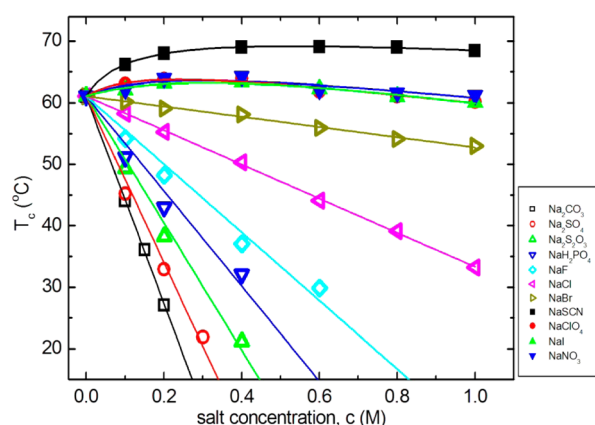
Figure 2. Change of T_c of 1 mg/mL aqueous PEOX-500K solutions with the concentration of various sodium salts. For seven kosmotropic anions, the solid lines are linear fits to the data (open symbols). For four chaotropic anions, the solid lines are fits to the data (filled symbols) as discussed in the text.

Table 1. Fitting Parameters for T_c vs c Curves of PEOX-500K Data in Figure 2

anion	T_c° (°C)	slope, s (°C/M)	A (°C)	K (M^{-1})
CO_3^{2-}	61.1	−169.0		
SO_4^{2-}	61.1	−135.7		
$S_2O_3^{2-}$	61.1	−103.4		
$H_2PO_4^-$	61.1	−77.2		
F^-	61.1	−55.5		
Cl^-	61.1	−27.8		
Br^-	61.1	−8.3		
NO_3^-	61.1	−7.2	8.6	4.0
I^-	61.1	−10.1	13.0	2.2
ClO_4^-	61.1	−7.6	7.5	6.3
SCN^-	61.1	−3.5	12.3	8.0

The anions interacting with water molecules hydrogen bonded to the polymer chain change the electron distribution in the bonds, resulting in the breakage of the hydrogen bond and removal of the hydration water. Surface tension of salt solutions is also known to increase linearly with salt concentration.[32] This increases the free energy of the alkyl/water interface of dissolved polymer chains and favors aggregation (phase separation) to minimize total interfacial area.

In the presence of chaotropic anions, T_c increased non-linearly with the salt concentration. The initial increase was followed by decrease at larger salt concentrations. At constant salt concentration, the observed shift in T_c was larger for SCN^- compared to other three chaotropic anions which showed similar effect: $ClO_4^- \approx I^- \approx NO_3^-$. The solid lines for the chaotropic anions are fits to the following expression:[31] $T_c(c) = T_c^{\circ} + sc + A[Kc/(1 + Kc)]$. The fitting parameters are shown in Table 1.

The first two terms $T_c^{\circ} + sc$ model the same two mechanisms (dehydration and surface tension mechanisms) discussed above for the kosmotropic anions. The third term is the Langmuir adsorption isotherm and models the direct binding of the chaotropic anions to the polymer. K is the binding constant, and A represents the maximum shift in T_c due to direct ion binding. The direct binding of anions to the polymer chains increases the solubility of the polymer and causes T_c to increase with salt concentration toward a plateau value determined by A. However, at larger salt concentrations, the linear term dominates and T_c goes over a peak and decreases.

Correlation of Slope s with Hydration Entropy of Anions, $\Delta S_{hydration}$, and Surface Tension Increment of Anions, $\Delta\sigma$. To understand the contributions of dehydration and surface tension mechanisms for the anions investigated, the slope s was plotted in Figure 3 as a function of hydration entropy of the anions,[33] $\Delta S_{hydration}$ (Figure 3a), and as a function of the surface tension increments of the anions,[31,32] $\Delta\sigma$ (Figure 3b). Table 2 shows $\Delta S_{hydration}$ and $\Delta\sigma$ values of the anions used in Figure 3.

The slope s did not show any dependence either on $\Delta S_{hydration}$ (Figure 3a) or on $\Delta\sigma$ (Figure 3b) of the chaotropic anions (filled circles). This indicates that direct ion binding to PEOX chains, possibly through the amide dipole, was the dominant mechanism for chaotropic anions. For ClO_4^-, I^-, and NO_3^- anions, slightly more negative slopes (steeper decrease of T_c with c) together with smaller A and K values compared to those for SCN^- caused T_c to peak at $c \sim 0.25$ M and decrease beyond it.

For kosmotropic anions, the slope s increased gradually and almost linearly with $\Delta S_{hydration}$. The solid line in Figure 3a is, however, not a linear fit to the data but drawn as a lower bound going through data points of CO_3^{2-}, SO_4^{2-}, Cl^-, and Br^- such
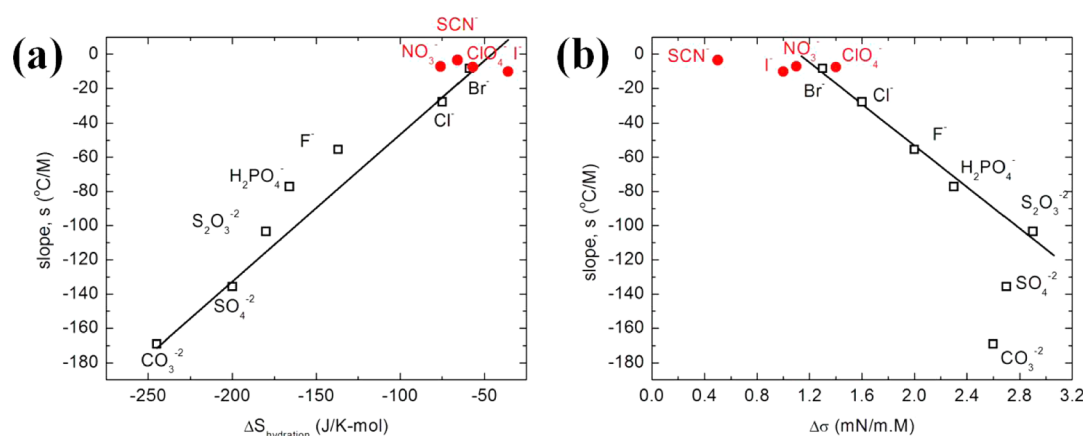

Figure 3. Plot of slope s as determined by fits to the data of Figure 2 as a function of (a) $\Delta S_{hydration}$ of anions and (b) the surface tension increment of the anions, $\Delta\sigma$: kosmotropic anions (open squares); chaotropic anions (filled circles).

Table 2. $\Delta S_{hydration}$ and $\Delta\sigma$ Values of Anions Used for Analysis

anion	$\Delta S_{hydration}{}^a$ (J/(K mol))	$\Delta\sigma^b$ (mN/(m M))	anion	$\Delta S_{hydration}{}^a$ (J/(K mol))	$\Delta\sigma^b$ (mN/(m M))
CO_3^{2-}	−245	2.6	Br^-	−59	1.3
SO_4^{2-}	−200	2.7	NO_3^-	−76	1.1
$S_2O_3^{2-}$	−180	2.9	I^-	−36	1
$H_2PO_4^-$	−166	2.3	ClO_4^-	−57	1.4
F^-	−137	2.0	SCN^-	−66	0.5
Cl^-	−75	1.6			

^{a}Reference 33. ^{b}References 31 and 32.

that the data points corresponding to $S_2O_3^{2-}$, $H_2PO_4^-$, and F^- stay above this lower bound. These are the anions for which the slope s showed a positive correlation with $\Delta\sigma$ (more negative slope with increasing $\Delta\sigma$) in Figure 3b. The solid line in Figure 3b is linear fit to the data points of $S_2O_3^{2-}$, $H_2PO_4^-$, F^-, Cl^-, and Br^-.

CO_3^{2-} and SO_4^{2-} anions showed slight negative correlation with σ. Nearly the same $\Delta\sigma$ for CO_3^{2-} and SO_4^{2-} anions, 2.6 and 2.7 mN/(m M), respectively, but significantly different slopes s, indicates that dehydration of the PEOX chains resulting from interaction of the anions with hydration water was the dominant mechanism in decreasing T_c within the experimentally investigated ranges of salt concentration and temperature (Figure 2). On the other side of the kosmotropic anion series, the slopes s corresponding to Cl^- and Br^- anions depended on the combination of both dehydration and surface tension mechanisms. By drawing a lower bound line between these two limits, we argue that the deviation from the lower bound in the direction of less negative slope (less steep decrease in T_c with c) for $S_2O_3^{2-}$, $H_2PO_4^-$, and F^- is the additional contribution of the surface energy mechanism.

A two-step phase transition was observed for aqueous PNIPAM solutions at higher kosmotropic anion concentrations using a temperature gradient microfluidic apparatus.[31] The crossover salt concentration from single step to two-step transition increased in the order $CO_3^{2-} > SO_4^{2-} > S_2O_3^{2-} > H_2PO_4^- > F^-$, and crossover was not observed up to 1 M for other anions. Slope s for single-step transition and for the first transition after crossover correlated well with $\Delta S_{hydration}$. Slope s for the second transition after crossover was less negative (less steep) and correlated well with $\Delta\sigma$. Note that dehydration mechanism decreased T_c faster with salt concentration than the surface tension mechanism. In the case of combination of the two mechanisms, the slope s gets less negative as the contribution of surface tension mechanism increases.

For 1 mg/mL aqueous PEOX-500K solutions, any two-step transition could not be detected by DLS within the experimental ranges of our measurements: salt concentration ~0–1 M and T_c ~ 20–70 °C. Assuming that the relative contributions of dehydration and surface tension mechanisms changed with the anion type similar to the shift of crossover from single-step to two-step transition in PNIPAM solutions,[31] we argue that the additional contribution of the surface tension mechanism shifts the data points corresponding to $S_2O_3^{2-}$, $H_2PO_4^-$, and F^- anions above the lower bound line. Similar behavior has also been observed with different molecular weight PEOX samples and with PNIPAM (Figure 4).

Comparison with Different Molecular Weight PEOX Samples and with PNIPAM. Figure 4 shows the plot of slope s as a function of $\Delta S_{hydration}$ for PEOX-5K ($\triangledown$), PEOX-50K ($\triangle$), PEOX-200K ($\bigcirc$), PEOX-500K ($\square$), and PNIPAM-22K ($\Diamond$) (see Figures S1–S4, respectively, in the Supporting
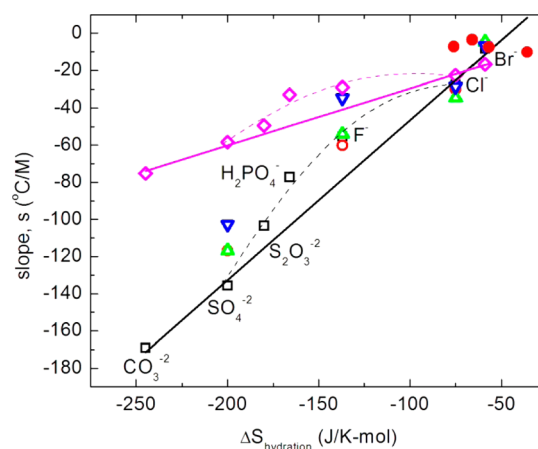

Figure 4. Plot of slope s as a function of $\Delta S_{hydration}$ of anions for different molecular weight PEOX samples (PEOX-500K ($\square$), PEOX-200K ($\bigcirc$), PEOX-50K ($\triangle$), PEOX-5K ($\triangledown$), and PNIPAM-22K ($\Diamond$)). The solid lines are the lower bounds for PEOX-500K and PNIPAM-22K data. The dashed lines represent the deviations from the lower bound and were drawn to guide the eye.

Information for the change of T_c with the salt concentration, c). The solid line going through data points of CO_3^{2-}, SO_4^{2-}, Cl^-, and Br^- is the lower bound line for PEOX-500K (same as that in Figure 3a). For smaller molecular weight PEOX samples, the data points of Cl^- and Br^- also fell on this line. But, the data points of other kosmotropic anions were all above this line. A horizontal shift in data points to the left of solid line is clearly apparent as one goes from Cl^- to F^-.

Similar to PEOX-500K, the additional contribution of surface tension mechanism was observed for lower molecular weight PEOX solutions as well. Slight molecular weight dependence in the direction of less negative slopes with decreasing molecular weight of PEOX is apparent in Figure 4. This dependence is expected for the surface tension mechanism as smaller molecules will result in larger total area of alkyl/water interface and more enhanced interfacial energy contribution with increasing salt concentration. The enhanced influence of polar end groups is also expected to be responsible for the observed molecular weight dependence.

The data of PNIPAM-22K ($\Diamond$) in Figure 4 also showed similar behavior. The solid line is the lower bound line for PNIPAM and goes through the data points of CO_3^{2-}, SO_4^{2-}, Cl^-, and Br^-. The data points of $S_2O_3^{2-}$, $H_2PO_4^-$, and F^- were above the line because of the additional contribution of the surface tension mechanism as discussed before for PEOX. PNIPAM showed weaker dependence on $\Delta S_{hydration}$ compared to PEOX samples due to differences in their chemical structures. PEOX is more hydrophilic, and thus the dehydrated collapsed state will contain more water compared to that of PNIPAM. PNIPAM can act as both H-bond donor and

acceptor while PEOX can only act as acceptor. Therefore, PNIPAM can make more hydrogen bonds with water per monomer compared to PEOX and thus requires more ions for dehydration.

■ CONCLUSIONS

The specific anion effects on T_c of aqueous PEOX solutions have been investigated by DLS measurements. The measurements were done by using a series of 11 sodium salts on four different molecular weight PEOX samples and for comparison on PNIPAM. The change in T_c followed the trend in Hofmeister anion series. The correlation of the results with the hydration entropy of anions, $\Delta S_{hydration}$, and the surface tension increment of anions, $\Delta\sigma$, helped to identify the contribution of different mechanisms in T_c change.

Kosmotropic anions decreased T_c linearly while chaotropic anions increased T_c nonlinearly with salt concentration. For chaotropic anions (NO_3^-, I^-, ClO_4^-, SCN^-) direct binding of anions to polymer chains was the dominant mechanism. For divalent kosmotropic anions (CO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$) the dominant mechanism was the dehydration of PEOX chains. For monovalent kosmotropic anions ($H_2PO_4^-$, F^-, Cl^-, Br^-) a combination of dehydration and surface tension mechanisms was responsible for the change of T_c. The additional contribution of the surface tension mechanism for the monovalent kosmotropic anions was inferred for different molecular weight PEOX samples and also for PNIPAM. With PEOX molecular weight decreasing from 500 000 to 5000 g/mol, T_c decreased less with salt concentration, which was attributed to the contribution of the surface tension mechanism. For PEOX samples, the decrease of T_c with kosmotropic anion concentration was faster compared to PNIPAM due to differences in their chemical structure.

The results show that the molecular mechanisms of interactions between PEOX chains and specific anions can simply be inferred from determination of T_c by a common technique—dynamic light scattering. The understanding of how T_c of aqueous PEOX solutions depends on the salt concentration and the molecular mechanisms responsible for such behavior are important to tune T_c as desired by the applications. As such, the results are expected to contribute to biological applications of PEOX which have been gaining attention due to its biocompatibility.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Effect of anions on T_c of aqueous PEOX-5K, PEOX-50K, PEOX-200K, and PNIPAM-22K solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail ldemirel@ku.edu.tr; Ph +90 212 3381350; Fax +90 212 3381559.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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