Critical solution behavior of poly(N-isopropyl acrylamide) in ionic liquid–water mixtures†

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The wide diversity of room-temperature ionic liquids (ILs) presents opportunities for studying, and controlling, polymer phase behavior. We have examined the phase behavior of poly(N-isopropyl acrylamide) (PNIPAM) in imidazolium ILs and their mixtures with water. We find there is a strong influence of the IL anion; specifically, the tetrafluoroborate anion yields a complex phase diagram with both LCST and UCST-type regimes. PNIPAM is generally miscible at intermediate IL–water compositions, although this range depends on the polymer molecular weight. Solvatochromatic characterization of both neat and mixed solvents reveals a key role for the interplay between PNIPAM-IL hydrogen-bonding and ion-pairing within the IL. These results demonstrate that appropriate selection of ILs should allow for increased control over polymer phase behavior.

Due to their low volatility and high thermal stability, room-temperature ionic liquids (ILs) have demonstrated potential utility for a broad range of applications, including as reaction[1,2] or separation media.[3,4] Although the influence of ILs on self-assembly phenomena and polymer phase behavior has only begun to emerge in the last few years,[5–8] ILs potentially allow for new approaches to tune macromolecular phase behavior, and therefore merit exploration.

PNIPAM has well known inverse phase behavior in water, characterized by a lower critical solution temperature (LCST) of ≈ 32 °C.[9] The diverse and tunable solvent properties of ILs have recently motivated re-examination of PNIPAM phase behavior. Ueki and Watanabe[7] first reported that PNIPAM showed upper critical solution temperature (UCST) behavior when dissolved in the hydrophobic IL 1-ethyl-3-methylimidazolium bis(trifluoromethyl) sulfonylamide ([EMIM][TFSA]). Such results immediately suggested

to us the possibility of complex phase behavior for PNIPAM at intermediate compositions of IL–water mixtures. Because [EMIM][TFSA] is immiscible with water, we instead selected anions (acetate [OAc]$^-$, thiocyanate [SCN]$^-$, and tetrafluoroborate [BF$_4$]$^-$) that result in hydrophilic ILs which are fully miscible with water. The cation was chosen to be the relatively common 1-butyl-3-methylimidazolium [BMIM]$^+$.

For all the IL–water solvent mixtures that we examined, PNIPAM displayed LCST-type behavior in the water-rich regime (Fig. 1). Such effects have been seen with mixtures of molecular solvents and water[10,11] and also with inorganic salts in water.[12] In contrast to the above works that were restricted to the water-rich regime, the phase behavior in the IL-rich regime depends much more strongly on the nature of the IL anion. In neat [BMIM][OAc] we find that PNIPAM is completely soluble in the temperature range studied (Fig. 1a). Similar behavior is observed for neat [BMIM][SCN] (data not shown). On the other hand, in neat [BMIM][BF$_4$], PNIPAM is only soluble *above* 85 °C. At lower temperatures in neat [BMIM][BF$_4$], PNIPAM appears as an insoluble dispersed phase (Fig. 1b). Thus in [BMIM][BF$_4$]–water mixtures, the phase behavior of PNIPAM depends in a complex
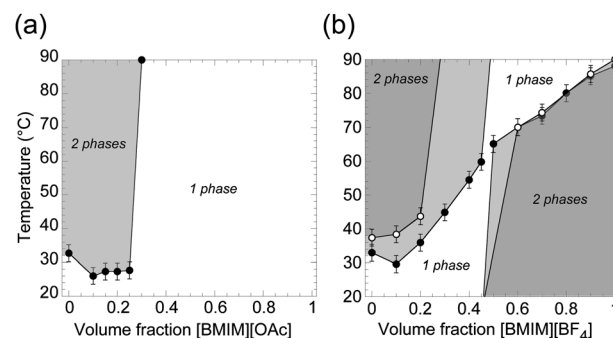
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Fig. 1 Cloud point T_{cp} versus solvent composition phase diagrams for PNIPAM in IL–water mixtures, at constant polymer concentration ϕ_p. (a) $M_n = 32$ kg mol^{-1}, $\phi_p = 0.13$ wt% (filled circles) in [BMIM][OAc]–water. (b) $M_n = 10.3$ kg mol^{-1}, $\phi_p = 0.21$ wt% (open circles) and $M_n = 32$ kg mol^{-1}, $\phi_p = 0.13$ wt% (filled circles) in [BMIM][BF$_4$]–water.
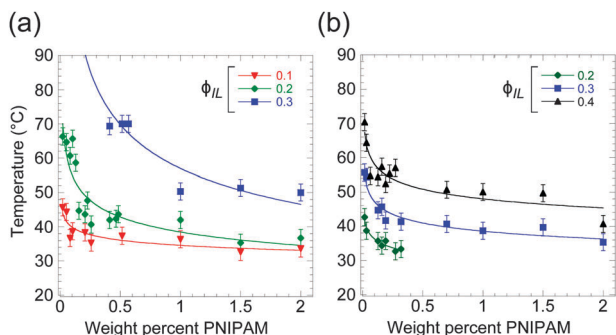
Fig. 2 Cloud point T_{cp} versus polymer concentration phase diagrams for PNI-PAM in [BMIM][BF$_4$]–water mixtures, at the constant IL volume fractions ϕ_{IL} denoted in the inset. (a) $M_n = 10.3$ kg mol^{-1}. (b) $M_n = 32$ kg mol^{-1}.

manner on the combination of temperature and IL volume fraction ϕ_{IL}.

Fig. 2 shows the dependence of the cloud point T_{cp} on PNIPAM molecular weight and concentration in the water-rich regime for [BMIM][BF$_4$]–water mixtures. The effect of molecular weight is to decrease T_{cp}, which agrees with the trend for the critical temperature T_c as predicted from a modified Flory–Huggins solution theory where the interaction parameter χ increases with temperature.[13] There is some controversy regarding the relationship between M_n and T_{cp}, with some papers[14,15] reporting an inverse correlation (as herein) and others[16,17] reporting a direct correlation. These discrepancies can be attributed to factors including, but not limited to, end-group hydrophobicity, stereochemistry, and polydispersity. The data of Fig. 2 is consistent with a relatively moderate hydro-phobicity of polymer chain ends, and should become less pronounced as M_n increases.

The observed trend in T_{cp} over the concentration range studied also agrees with a Flory–Huggins-type prediction of an initial decrease of T_c with polymer concentration. We emphasize that the "critical solution temperature" (e.g., LCST or UCST) can only be identified from the binodal line of the entire phase diagram,[13,18] which is here approximated by each of the cloud point curves in Fig. 2. This approximation is validated by reversible behavior upon heating/cooling near the phase boundary (Fig. S1†), as well as selected turbidimetry measurements (Fig. S2†). We also note that all polymer con-centrations examined are substantially below their overlap values $\phi_p^* \approx N^{-4/5}$, if we conservatively assume good solvent conditions.[13]

It is apparent from Fig. 2 that increasing IL content increases T_{cp}. However, this trend does not continue indefinitely. The effect of IL content on PNIPAM phase behavior is more clearly depicted as in Fig. 1. From this perspective, it is seen that PNIPAM is generally soluble at intermediate IL–water compositions. Interestingly, for [BMIM][BF$_4$]–water, the width of this solubility "window" decreases with increasing molecular weight (Fig. 1b), suggesting an eventual convergence of the two insoluble regimes. Further investigation of this effect is currently underway in our laboratory, and we should mention here that others have observed multi-phase behavior in imidazolium IL–alcohol mixtures.[19,20] In contrast to PNIPAM phase

behavior here, Smith et al. found that silica microparticles remain colloidally stable in both neat ethylammonium nitrate (EAN) and water, but not for their mixtures.[21] Thus ILs and their mixtures with water should provide many future opportunities for unique manipulation of colloidal and interfacial assembly.

To provide a more detailed description of the changes in the solvent environment as a function of composition, solvatochromic characterization was performed in the absence of PNIPAM. Values of hydrogen-bond donor (HBD) acidity α and hydrogen-bond acceptor (HBA) basicity β were determined according to:[22]

$$\beta = (1.035\nu_{II}^{max} - \nu_I^{max} + 2.64)/2.8 \qquad (1)$$

$$\alpha = 1.964E_N^T - 0.885\pi^* + 0.228 \qquad (2)$$

where **I** refers to 4-nitroaniline and **II** refers to N,N-dimethyl-4-nitroaniline. Values of polarizability π^* and polarity E_T^N were calculated from

$$\pi^* = (\nu_{II}^{max} - 27.52)/(-3.182) \qquad (3)$$

$$E_N^T = 882.44/\lambda^{max} - 0.948 \qquad (4)$$

where E_T^N values were obtained using Reichardt's dye.

Previous reports have emphasized the important role of the IL anion and its basicity in determining polymer solubility.[23] Solvatochromatic characterization of ILs has revealed that the IL anion is primarily responsible for the HBA basicity β,[24] and therefore we sought to use this approach to better understand the phase behavior of PNIPAM in IL–water mixtures. It can be seen that neat [BMIM][OAc] has the highest β value of the ILs studied (Fig. 3a), indicating that [OAc]$^-$ has the strongest interactions with PNIPAM. This observation is rationalized by the structure of the anions (Fig. 3a, right); [OAc]$^-$ has the greatest maximum surface charge and largest dipole moment, as compared to [SCN]$^-$ and [BF$_4$]$^-$.[25] Similarly, because [BF$_4$]$^-$ has the largest volume, smallest maximum surface charge, and no dipole moment,[25] we expect it to have the weakest interactions with PNIPAM.

The HBD acidity α will reflect interactions of the IL cation, primarily the C^2 proton of the imidazolium ring, with either the IL anion or the amide oxygens of PNIPAM (Fig. 3b, right). Because the interaction of [BMIM]$^+$ with both water and PNIPAM is presumably constant across all the systems, the magnitude of α provides a relative measure of the strength of ion-pairing.[26] First consider neat [BMIM][OAc]: here β is large while α has a low value similar to that of [C$_n$M$_2$IM] ILs (which are substantially less capable as hydrogen-bond donors due to replacement of the most acidic C^2 proton with a methyl group[24]). This low α value suggests strong ion-pairing within [BMIM][OAc] (Fig. 3b, right). By contrast, for [BMIM][BF$_4$], the α value is quite large (≈ 0.7), and suggests weak IL ion-pairing. Unfortunately, the strength of the hydrogen-bonding between [BMIM]$^+$ and the PNIPAM amide group cannot be directly determined from α values, although it is expected to be constant for all the ILs examined.

It is also instructive to examine the results for water: it has the lowest β value and the highest α value. Such a combination suggests that water's primary interaction with PNIPAM is as a
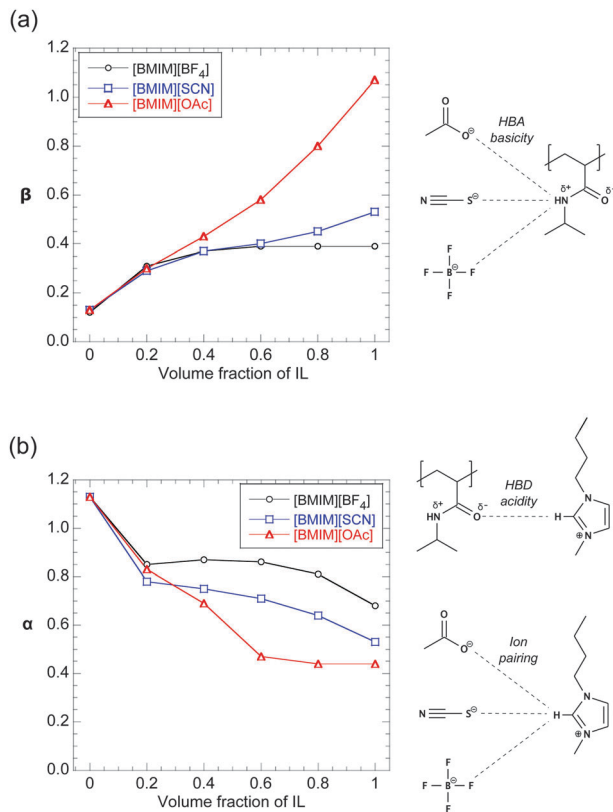
Fig. 3 Change in (a) HBA basicity β and (b) HBD acidity α with composition for [BMIM][BF$_4$]–water (circles), [BMIM][SCN]–water (squares), and [BMIM][OAc]–water (triangles). To the right of each plot, a schematic of possible interactions is shown.

hydrogen-bond donor, which might be anticipated intuitively. However, LCST-type behavior requires not only attractive interactions ($\Delta H_m < 0$) but also the formation of an ordered solvation shell ($\Delta S_m < 0$).[18,23] Indeed, the phase diagram of PNIPAM in water can be accurately described by invoking cooperative hydrogen-bonding.[27]

In neat [BMIM][OAc], PNIPAM is soluble over the entire temperature range studied. The dominant effect is therefore the [OAc]$^-$–amide interaction, manifested in large β values. This interaction is sufficiently attractive ($\Delta H_m < 0$), that we observe solubility over a large temperature range. However, depending on the sign of ΔS_m, there remains the possibility of LCST-type behavior at temperatures beyond 100 °C, as observed for other polymer–IL systems.[28,29]

In neat [BMIM][BF$_4$], the low β values reflect much weaker [BF$_4$]$^-$–amide interactions. The relatively low strength of ion-pairing within this IL would favor hydrogen-bonding between [BMIM]$^+$ and PNIPAM, but must be reconciled with the observed UCST-type behavior ($\Delta H_m > 0$, $\Delta S_m > 0$). We therefore conclude that the interactions between [BMIM][BF$_4$] and PNI-PAM must be quite weak (possibly due to competition between [BMIM]$^+$ and [BF$_4$]$^-$ for the polymer, as suggested for other polymer–IL systems[23,30]), or even be repulsive, such that $\Delta H_m > 0$. UCST-type behavior also requires the lack of an ordered solvation shell ($\Delta S_m > 0$), which is quite common. While [BMIM][SCN]

appears intermediate to [BMIM][OAc] and [BMIM][BF$_4$] in its solvatochromatic properties, it displays behavior more similar to [BMIM][OAc], suggesting that [SCN]$^-$–amide interactions are sufficiently strong (*i.e.*, β values are sufficiently large).

We believe the interplay of hydrogen-bonding can possibly explain the trends in α and β values. Based on the fact that β never increases with the addition of water (Fig. 3a), water must be a weak base and not readily accept protons from PNIPAM. As water is introduced into [BMIM][OAc] ($\phi_{IL} > 0.6$), the dominant effect is [OAc]$^-$ accepting protons from water. This interaction largely explains why α remains nearly constant and why β decreases. At higher water contents ($\phi_{IL} < 0.6$), water donates protons to PNIPAM, causing α to increase. By contrast, as water is introduced into [BMIM][BF$_4$] ($\phi_{IL} > 0.6$), it acts as an acid, donating protons to PNIPAM and increasing α values. Because both water and [BF$_4$]$^-$ are weak bases, β stays relatively constant. At intermediate water content ($\phi_{IL} \approx 0.2$–0.6), [BF$_4$]$^-$ begins to accept protons from water, which causes α to plateau and β to decrease. In this case, the donation of protons from water to PNIPAM is only clear at the highest water contents ($\phi_{IL} < 0.2$). Curiously, the LCST-type phase boundaries for both [BMIM][OAc] and [BMIM][BF$_4$] (Fig. 1) correspond to $\beta \leq 0.35$ (Fig. 3a), suggesting a critical role for IL anion basicity. Unfortunately, no such correlation is obvious for the UCST-type boundaries.

In the water-rich regimes, $\phi_{IL} < 0.3$, there is almost no difference in either α or β values among the various ILs (Fig. 3), as might be expected. Since water is in abundance, LCST-type behavior for PNIPAM is expected and observed (Fig. 1). Differences of T_{cp} in the water-rich regime are explained by the Hofmeister effect that is well known for inorganic salts in water. Work by Cremer *et al.*[12] has established that specific interactions of inorganic anions with PNIPAM determine the polymer's solubility, with [SCN]$^-$ known to be a strong chaotrope. It is natural to generalize these findings to organic anions, and in fact [OAc]$^-$ is a strong kosmotrope while [BF$_4$]$^-$ is a weak kosmotrope.[31] Indeed, the changes in cloud point ΔT_{cp} agree quite well with the Hofmeister series (Fig. 4). As further support of the above, Reddy *et al.*[32] showed that when small amounts of 1-benzyl-3-methylimidazolium tetrafluoroborate
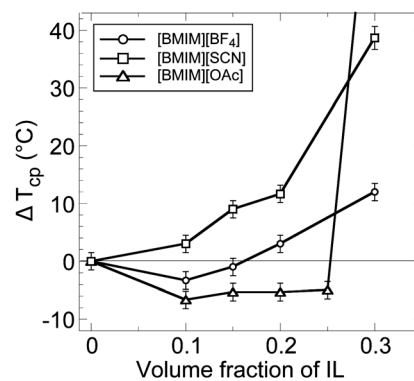

Fig. 4 Change in cloud point ΔT_{cp} as a function of IL volume fraction for PNIPAM with M_n = 32 kg mol^{-1} at ϕ_p = 0.13 wt%.

([BzMIM][BF$_4$]) are added to water, a depression of PNIPAM's LCST-type behavior occurs.

Finally, we wish to comment that a valine elastin-like polypeptide in [BMIM][BF$_4$]–water mixtures displays LCST-type phase behavior similar to that of PNIPAM (data not shown). Such a result is not completely unexpected, given the chemical similarity between valine elastin-like polypeptides and PNIPAM. We also note that poly(ethylene oxide), which is primarily a hydrogen-bond acceptor, has been shown to display LCST-type behavior at temperatures exceeding 100 °C in [EMIM][BF$_4$], [BMIM][BF$_4$], and their mixtures.[28,29] Although it remains the subject of more thorough study, our results here and works by the Watanabe group[23,30,33] indicate that the interplay of hydrogen-bond donating and accepting abilities between polymers and IL ions appears to be key in determining solubility behavior (*i.e.*, [OAc]$^-$ *versus* [BF$_4$]$^-$). Looking to the future, careful consideration of chemical interactions should allow for increased control of polymer phase behavior by selection of the appropriate ionic liquid.

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