Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics
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Supporting Information for: "Critical solution behavior of poly(N-isopropyl acrylamide) in ionic liquid/water mixtures" by Purnendu K. Nayak, Adam P. Hathorne, and Harry Bermudez

Experimental Section

Poly(N-isopropylacrylamide) (PNIPAM) was obtained from Polymer Source, Inc. with number-average molecular weights $M_n = 10.3$ kg/mol and 32 kg/mol having polydispersity indices of 1.12 and 1.5, respectively. Ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) ($\geq 98\%$ purity, $\leq 0.5\%$ water) and 1-butyl-3-methylimidazolium acetate ([BMIM][OAc]) ($\geq 95\%$ purity, $\leq 2.0\%$ water) were obtained from Sigma-Aldrich and used after drying under reduced pressure for 72 h at 65 °C. The dried IL samples were analysed for water content by Karl Fischer titration and was found to contain $< 0.2\%$ water for [BMIM][BF_4] and $< 0.1\%$ water for [BMIM][OAc]. X-ray photoelectron spectroscopy (XPS) was used to confirm the elemental composition and purity [1]: no trace metals or otherwise unexpected atomic peaks were found. Reverse-osmosis purified water was used for all sample preparations.

Samples for cloud point measurements were prepared by measuring the required mass into a 5 mL glass vial followed by addition of required volume of reverse-osmosis water and vortexed for 15 sec. The sample was then allowed to stand for 15 min followed by addition of the appropriate amount of IL and further subjected to vortexing. The final sample was let to stand for at least 3 h to equilibrate before measurements were performed.

Cloud point temperatures were primarily determined by visual observation [2–4]. A glass vial containing the PNIPAM solution and properly secured with Teflon-coated screw cap was placed on an analog dry block heater. The temperature was read by a thermometer inserted into one of the block heater apertures. The temperature was increased manually in approximately 5°C intervals and allowed to equilibrate for at least 5 min. The heater had dual temperature control for control over two ranges: low range up to approximately 55°C, and high range from 55 to 130°C. The sample was observed intermittently for change in solution turbidity and the cloud point was recorded as the temperature at which the sample began to show the initial signs of becoming translucent or hazy.

Independent confirmation of the visually determined cloud point data was obtained for selected samples by turbidimetry. Briefly, absorbance measurements were obtained on a Spectramax M5 Multi-Mode Microplate reader. All sample solutions consisted of 200 μL aliquots in 96-well flat-bottom polystyrene microplates. The microplate lids were sealed with Parafilm to minimize loss of volume. Absorbance measurements were recorded at a wavelength of 500 nm starting from room temperature to 60°C. Temperature was manually ramped with a step increase of 2.5°C and at each temperature was equilibrated for 5 min and subjected to shaking for 15 s before measurement runs were performed. All data were normalized by the maximum and minimum values, and cloud points are determined from the initial break points in the resulting absorbance versus temperature curves.

Solvatochromic analysis was performed by monitoring the λ_{max} of Reichardt's dye, 4-nitroaniline (**I**), and N,N-dimethyl-4-nitroaniline (**II**), at room temperature with a SpectraMax M5 Fluorescence Spectrophotometer. All dyes were obtained from Sigma-Aldrich. The 4-nitroaniline was recrystallized from ethanol.

Photographs of transition behaviors

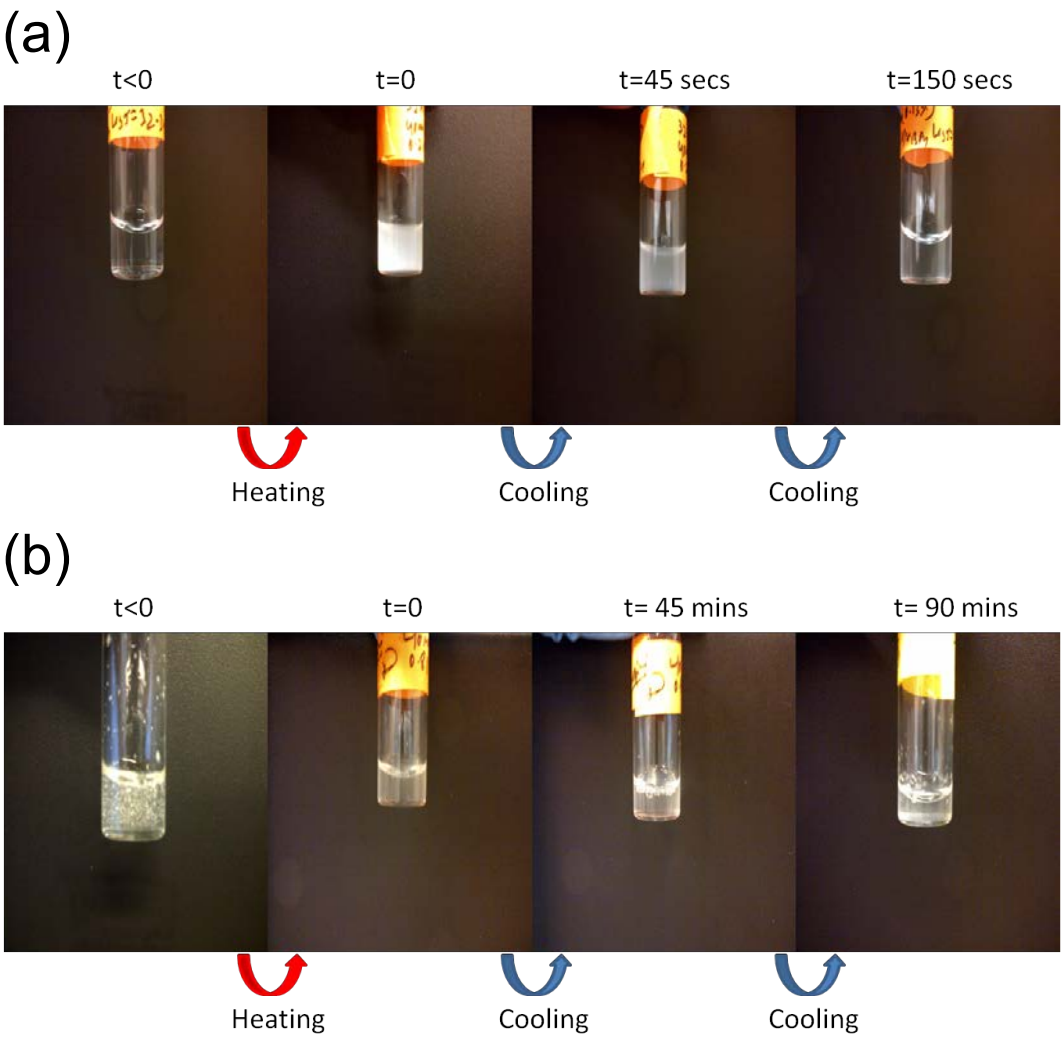

Figure S1: Time-sequence photographs of PNIPAM ($M_n = 32$ kDa, $\phi_p = 0.13$ wt%) in [BMIM][BF_4]/water mixtures. (a) For IL volume fraction $\phi_{IL} = 0.2$ showing the reversibility of the LCST-type transition behavior. From left to right: ($t < 0$) sample is held at 30°C; ($t = 0$) sample becomes turbid at 35°C; ($t = 45$ sec) sample upon cooling towards room temperature; ($t = 150$ sec) further cooling towards room temperature. (b) For IL volume fraction $\phi_{IL} = 0.2$ showing the reversibility of the UCST-type transition behavior. From left to right: ($t < 0$) sample is held at room temperature; ($t = 0$) sample becomes clear at 80°C; ($t = 45$ min) sample upon cooling towards room temperature; ($t = 150$ min) further cooling towards room temperature.

Turbidimetry measurements

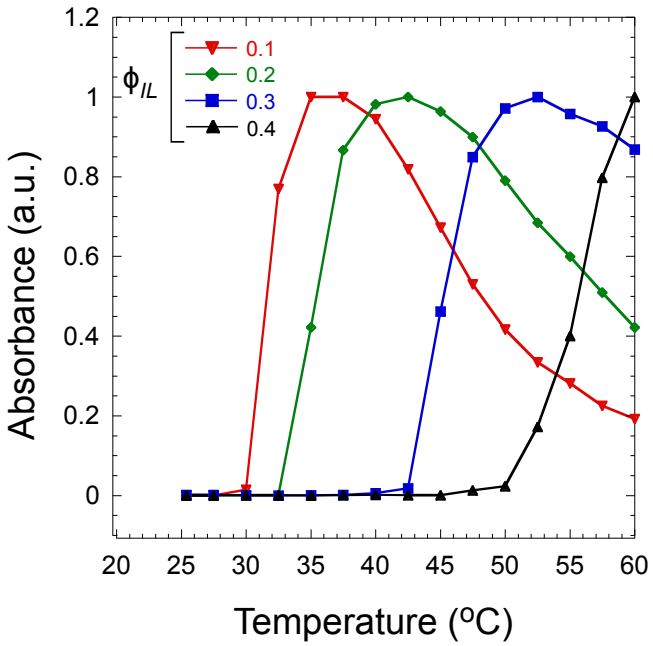

Figure S2: Absorbance versus temperature measurements of PNIPAM ($M_n = 32$ kDa, $\phi_p = 0.13$ wt%) in [BMIM][BF_4]/water mixtures. The data sets represent IL volume fractions ϕ_{IL} ranging from 0.1 to 0.4.

References

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