

Electronic Supplementary Information

Ion Specificity of Macromolecules in Crowded Environments

Wangqin Song, Lvdan Liu, and Guangming Liu*

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

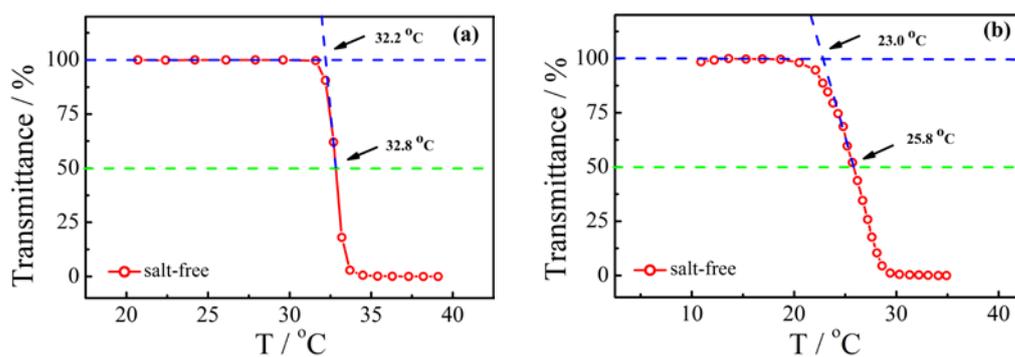
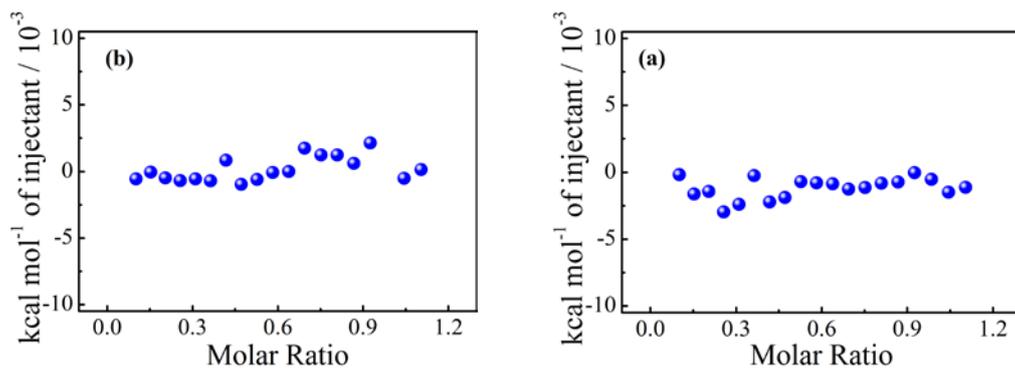
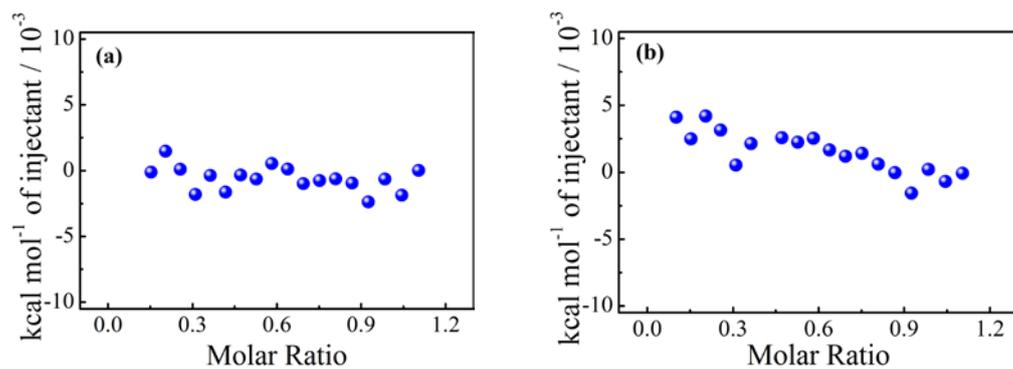


Figure S1. Temperature dependence of transmittance of PNIPAM in the salt-free solutions. (a) Dilute solution. (b) Dextran solution with a concentration of 250 mg mL⁻¹. Here, the PNIPAM concentration is fixed at 1.0 mg mL⁻¹.

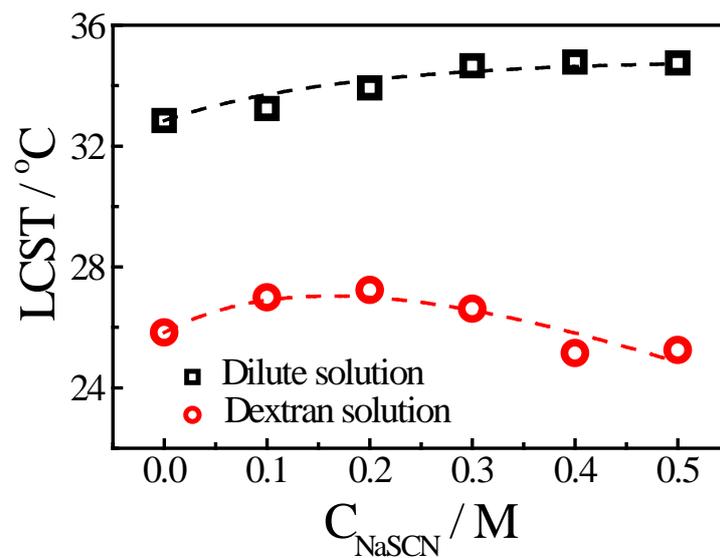
In Fig. S1, the LCST can be defined either as the intersection of two straight lines drawn through the transmittance versus temperature curves during the initial stage of phase transition of PNIPAM or as the temperature corresponding to 50% of the transmittance. In comparison with the dilute solution, the relatively slow decrease in transmittance with temperature in the crowded environment indicates the slower aggregation of PNIPAM chains. This is understandable because the rate of diffusion of macromolecules is reduced in crowded conditions.^{S1, S2}



Figures S2. (a) ITC titration data derived from the integrated heats of the exothermic peaks for the titration of NaCl solution into dextran solution. (b) ITC titration data derived from the integrated heats of the exothermic peaks for the titration of CH₃COONa solution into dextran solution.



Figures S3. (a) ITC titration data derived from the integrated heats of the exothermic peaks for the titration of NaCl solution into PEG solution. (b) ITC titration data derived from the integrated heats of the exothermic peaks for the titration of CH₃COONa solution into PEG solution.



Figures S4. Change in LCST of PNIPAM as a function of NaSCN concentration (C_{NaSCN}) in dilute solution and in the solution with a dextran concentration of 250 mg mL⁻¹. Here, the PNIPAM concentration is fixed at 1.0 mg mL⁻¹ and the dashed lines are curves fits to the experimental data with Eq. 1 as shown in main text. The fitting results are listed in Table S1.

Table S1. Fitted values for c , B_{max} , and K_A obtained from Fig. S4.

	c (°C / M)	B_{max} (°C)	K_A (M ⁻¹)
NaSCN	-1.5	4.4	3.0
NaSCN + dextran	-16.6	12.7	2.7

In Table S1, K_A in the dilute solution is larger than that in the crowded environment of dextran. Thus, it is expected that the B_{max} in the dilute solution should be also larger than that in the crowded environment of dextran because a stronger binding of SCN⁻ on PNIPAM surface would generate a stronger salting-in effect. However, the fitting results show that the B_{max} in the dilute solution is much smaller than that in the crowded environment of dextran, which obviously violate the common sense that the salting-in effect is in proportion to the binding of chaotropic anions on the PNIPAM surface. In other words, the Eq. 1 as shown in main text is not suitable for the current system of PNIPAM in crowded environments.

References

- S1. R. Metzler, J.-H. Jeon, A. G. Cherstvy and E. Barkai, *Phys. Chem. Chem. Phys.*, 2014, **16**, 24128-24164.
- S2. I. Pastor, E. Vilaseca, S. Madurga, J. Lluís Garcés, M. Cascante and F. Mas, *J. Phys. Chem. B*, 2011, **115**, 1115-1121.