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Soret Coefficient of Poly(*N*-isopropylacrylamide)/Water in the Vicinity of Coil−Globule Transition Temperature

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According to thermodynamics of polymer solutions, polymers show conformational changes depending on the solvent quality. A transition of single polymer chain induced by the solvent quality change, known as a coil−globule transition, has been extensively studied because of their importance in not only polymer physics but also application aspects for the collapse of a gel network, the folding of a protein, and so on.[1−6]

Poly(*N*-isopropylacrylamide) (PNiPAM) chain in water has a Θ temperature at 30.6 °C, where the second virial coefficient is zero, and shows the coil−globule transition by heating. Indeed, there are many reports studying PNiPAM solutions by scattering methods,[7−10] fluorescence,[11] electronic paramagnetic resonance,[12] IR spectroscopy,[13,14] and calorimetry.[15,16] A considerable amount of work on PNiPAM solutions is collected in a review.[17] However, thermal diffusion phenomena, also called the Ludwig−Soret effect, have not been studied with taking into account the coil−globule transition in the vicinity of the Θ temperature.

The Ludwig−Soret effect accounts for a mass flux, $\mathbf{J}_1$, in a mixture which is induced by a temperature and a concentration gradient.[18−21] Under a steady temperature gradient a steady concentration gradient is built up, where the flux vanishes ($\mathbf{J}_1 = 0$). The Soret coefficient, S_T, is expressed as

$$S_T \equiv \frac{D_T}{D} = -\frac{1}{c_1(1-c_1)}\frac{\nabla c_1}{\nabla T} \qquad (1)$$

where D is the translational mass diffusion coefficient, D_T the thermal diffusion coefficient, c_1 the mass fraction of component 1, and T the temperature.

The sign of S_T indicates whether component 1 migrates to the warm side or the cold side of the fluid.[22] If the system is dominated by short-range interactions, the thermal diffusion behavior can be attributed to single particle and collective contributions.[23] There are several detailed and systematic studies of thermal diffusion phenomena of organic polymer systems covering scaling behavior, concentration effects, and preferential solvation effects in mixed solvents.[24−29] In contrast to those organic systems, there are only few studies for aqueous polymer solutions.

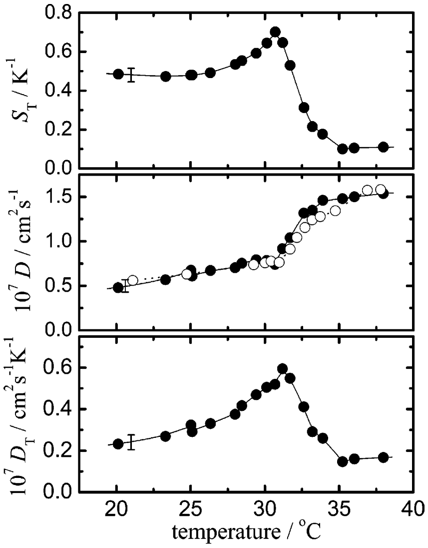

Figure 1. Temperature dependencies of Soret coefficient S_T, translational diffusion coefficient D, and thermal diffusion coefficient D_T of 1.0 g/L PNiPAM in water obtained by TDFRS (closed circles). The diffusion coefficients shown by the open circles were the results of dynamic light scattering. Lines are drawn to guide eye.

Observations of the Ludwig−Soret effect in the vicinity of coil−globule transition of PNiPAM/water will illuminate the importance of segment−segment and segment−solvent interactions. These key features can be varied experimentally according to the consequence of coil−globule transition of PNiPAM. This approach will lead to deeper understanding of thermal diffusion behavior of aqueous polymer systems as well as provide new insight into the solution properties of PNiPAM in a thermodynamically nonequilibrium state.

PNiPAM was purified by a fractionation method.[8] One fraction was used in this study which had the weight-averaged molecular weight $M_w = 3.0 \times 10^6$ g/mol with a polydispersity M_w/M_n of 1.20. Details of sample preparation and characterizations are described elsewhere.[30] Water was deionized by a Milli-Q system. In this study 1.0 g/L PNiPAM in water was prepared with a tiny amount of the dye, Basantol Yellow 215.[31]

The experimental details of thermal diffusion forced Rayleigh scattering (TDFRS) have been described elsewhere.[32] The normalized heterodyne signal intensity, $\zeta_{het}(t)$, to the thermal signal is related to the Soret coefficient S_T and diffusion coefficient D as follows:

$$\zeta_{het}(t) = 1 + \left(\frac{\partial n}{\partial T}\right)_{p,c_1}^{-1}\left(\frac{\partial n}{\partial c_1}\right)_{p,T} S_T c_1(1-c_1)(1-e^{-q^2Dt}) \qquad (2)$$

Here, t is the time, n the index of refraction, and q the wavenumber. The contrast factors $(\partial n/\partial T)$ and $(\partial n/\partial c_1)$ should be determined separately.[33] The TDFRS measurements were carried out in the temperature range from 20 to 38 °C, where the temperature of the sample cell was controlled by circulating water from a thermostat with an uncertainty of 0.02 °C. The wavenumber in the present study was $q = 4600$ cm^{-1}.

Figure 1 shows the temperature dependence of the Soret coefficient S_T, diffusion coefficient D, and thermal diffusion coefficient D_T for 1.0 g/L PNiPAM in water. The error bar is one standard deviation. The S_T remains

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almost constant below 25 °C and has a maximum at 30.7 °C with a steep decrease and a plateau at higher temperatures. The diffusion coefficient turns upward at 30.7 °C with increasing temperature. These significant points agreed well with the Θ temperature (30.6 °C) reported elsewhere.[8,34] The diffusion coefficients shown by open circles were the results of dynamic light scattering (DLS). The sharp increase of D in the poor solvent (above the Θ temperature) corresponds to the formation of a compact conformation of polymer chains. The hydrodynamic radius (R_h) changes from 39.4 nm (21.1 °C) to 21.2 nm (37.8 °C), which is evaluated using the Stokes−Einstein equation. The magnitude of the diffusion coefficient at 20 °C is in good agreement with previous studies and shows a similar temperature dependence through the coil−globule transition.[8,34,35] The thermal diffusion coefficient has a shape similar to S_T, although the D_T shows an apparent increase with increasing temperature in the good solvent side and the temperature of the largest D_T was 31.2 °C. Even though the temperatures at maximum S_T and D_T differ slightly, the temperature dependence of S_T and D_T shows peaks at close to the Θ temperature of PNiPAM in water.

The positive S_T of PNiPAM indicates that polymers migrate to the cold side of the fluid under the temperature gradient (typical for polymer solutions). The peak of S_T means that the concentration gradient is enhanced approaching the Θ temperature. The steep decrease of S_T above the Θ temperature could be associated with the transition to the globular state, where the conformation of polymer and relating interactions among segments and solvents are drastically changed by heating. The enhancement of the S_T near the Θ temperature is considered by taking into account the solvent quality as follows.

The direction of thermodiffusive motion of PNiPAM molecules in water is always toward cold side, corresponding to the positive sign of S_T. The polymer has a better solubility in colder water as can be judged by temperature dependence of the second virial coefficient.[8] The thermodiffusive motion by the Ludwig−Soret effect has the same direction with the better solubility side of the polymer. These facts indicate the magnitude of the concentration gradient induced by the Ludwig−Soret effect should have a tendency to be enlarged by the better solubility of polymer in the cold side. This could be the origin of the enhancement of Soret coefficient which tends to be pronounced approaching the Θ temperature.

In previous reports, we studied the ternary system of poly(ethylene oxide) in the mixed solvent water/ethanol and found a sign change of S_T with changing the solvent compositions. The polymer moves to the cold side in high water compositions ($S_T > 0$), while it migrates to hot side in low water compositions ($S_T < 0$).[31,36,37] The sign of S_T was also changed by varying the temperature in a certain composition range of solvent mixture, although in pure water the S_T of PEO was positive. A calculation of lattice chamber model for this system showed that hydrogen bonding plays a key role in describing the sign change behavior of the polymer.[31,37,38] In a recent study of PNiPAM/ethanol, we found that the S_T and D_T monotonically decreased with increasing temperature. The sign change of S_T and D_T takes place at 34 °C, where ethanol was a good solvent and the chain dimension remains almost constant at all temperature measured by static and dynamic light scattering (15−40 °C). Additionally, the sign change temperatures are identical for both dilute and semidilute solutions of PNiPAM/ethanol.[30] In this work, we observe the formation of a compact conformation together with the rapid decrease of the Soret coefficient in the poor solvent, while the sign remains positive. These results indicate the sign change behavior is relating to specific interactions between chain segments and solvent molecules. According to the consequence of the coil−globule transition of PNiPAM/water, segment−solvent interactions are favored at low temperatures where polymer chains are solvated with water molecules. In the poor solvent the segment−segment and the water−water contacts are favored due to a liberation of water molecules, and the chain shrinks to a compact structure. This picture for dilute solution of PNiPAM provides that the thermal diffusion behavior strongly depends on the interface at segments and solvents.

In conclusion, the behaviors of S_T and D_T for PNiPAM/water are susceptible to short-range associations, such as the segment−segment and segment−solvent interactions and relating chain dimensions where the unperturbed chain showed the largest response against the field of temperature gradient. Although as discussed in the previous report the effect of a tiny amount of water should be taken into account to interpret thermally induced sign change of S_T for PNiPAM/ethanol, in the present study using water as a solvent the structure of the segment and water via hydrogen bonding is not the same as PNiPAM in ethanol. To clarify the effect of solvent association in detail, we need to study the ternary system of PNiPAM/water/ethanol, where the local structures and a preferential solvation as well as a co-nonsolvency effect should be considered.

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