

Thermal Diffusion of PNiPAM Nano Gel-Particle at the Theta-Temperature

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Thermal diffusion forced Rayleigh scattering (TDFRS) results on thermal diffusion of the nano gel-particle composed of poly(*N*-isopropylacrylamide) (PNiPAM) in water are presented. The Ludwig-Soret effect of the gel-particle was apparently enhanced at the Θ temperature, where the coil to globule transition of the polymer takes place. The result demonstrates that the formation of concentration gradient is intensified at the Θ temperature. This behavior is analogous to the observation of aqueous solution of a linear PNiPAM chain. The anomalous enhancement of Ludwig-Soret effect is considered with taking into account the solvent quality and interactions among solvent molecules and segments.

Key words: Soret coefficient, thermal diffusion, PNiPAM, Θ -temperature, TDFRS

1. INTRODUCTION

In binary fluid mixtures with nonuniform concentration and temperature, the mass flow J_1 of component 1 contains contributions from the concentration and from the temperature gradient [1],

$$J_1 = -\rho D \nabla w - \rho w(1-w) D_T \nabla T, \quad (1)$$

where D is the mutual diffusion coefficient, D_T the thermal diffusion coefficient, ρ the mass density, and w the mass fraction of component 1. In a stationary state, where the diffusion flow J_1 vanishes, the Soret coefficient S_T is given by

$$S_T = \frac{D_T}{D} = -\frac{1}{w(1-w)} \frac{\nabla w}{\nabla T}. \quad (2)$$

The occurrence of a mass flow which is driven by a temperature gradient is termed thermal diffusion or Ludwig-Soret effect [2,3]. The sign of the Soret coefficient indicates the direction of thermodiffusive motion, i.e. the solute molecules move to the hot side or the cold side of the fluid. Although the Soret effect has been known for a long time, the understanding of the Soret effect for liquid mixtures, polymer solutions and colloidal suspensions is still lacking [4].

In a previous report, temperature dependence of the Soret coefficient for the linear chain of PNiPAM (poly(*N*-isopropylacrylamide)) in water was studied in the vicinity of Θ -temperature [5]. The obtained Soret coefficient S_T was always positive in the investigated temperature range ($20 < T / ^\circ\text{C} < 38$), which means polymers migrate to the cold side of the fluid. The magnitude of S_T showed a strong peak at the coil globule

transition temperature ($T = 30.6 ^\circ\text{C}$), which was judged by the second virial coefficient obtained with static light scattering [6]. These observations mean that the concentration gradient is enhanced at the Θ -temperature. It implies that the thermal diffusion of PNiPAM chain is coupled with the contribution of the solvent quality. Furthermore it is supposed that the Soret coefficient is a sensitive indicator of the interactions among solvent molecules and segments. However, the mechanism of enhancement behavior at the Θ -temperature has not been clarified, yet.

Recently, macroscopic PNiPAM gels have been studied extensively. In addition to that system, PNiPAM micro-gel particles have been investigated [7-9], because a short equilibration time of micro-gel particles has an advantage for studying gel properties. Moreover, the study of gel-particles is of great interest for drug delivery systems. Regarding to the thermal diffusion phenomena, investigation of gel-particle is considered as a good model system for studying mechanism of the thermal diffusion behavior of gels. Furthermore, the results of gel-particles can be compared with the results of polymer solutions, where these substances are composed of the same chemical units. This approach is useful for studying the differences between inter- and intra- particle interactions.

In this paper, we tried to evaluate the Soret coefficient for the colloidal suspension of PNiPAM nano gel-particle with the thermal diffusion forced Rayleigh scattering (TDFRS). The tentatively obtained Soret coefficient for gel-particle suspension in the vicinity of the Θ -temperature was compared with the results of the aqueous solution of PNiPAM linear chain.

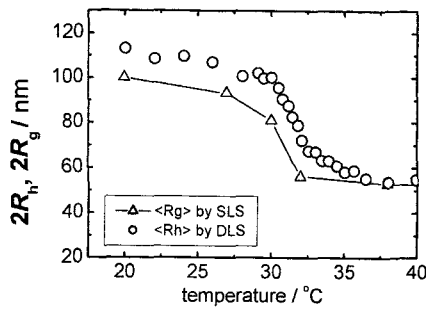


Fig. 1. Radius of gyration R_g and the hydrodynamic radius R_h of gel-particle as a function of temperature obtained by SLS and DLS.

2. EXPERIMENT

Linear PNiPAM chain was polymerized from *N*-isopropylacrylamide (NiPAM) with an initiator, then the product was fractionated several times. The procedure was described in ref. 10 in detail.

PNiPAM nano gel-particles were synthesized by an emulsion polymerization. The pregel solution, NiPAM (552mM), *N,N'*-methylenebisacrylamide (4.32mM), SDS (18.2 mM), and ammonium persulfate (1.096 mM) in water was degassed, then stirred at 70 °C for 3 hrs under nitrogen atmosphere. The reaction was terminated with adding methanol, and the obtained gel-particle suspension was dialyzed extensively. The procedure was described elsewhere [7,8].

Static and dynamic light scattering (SLS and DLS) measurements were carried out to determine the particle size by means of a homemade spectrometer with ALV-5000 correlator [11]. An Ar-ion laser operated at the wavelength 488 nm was used as the light source.

Thermal diffusion forced Rayleigh scattering (TDFRS) was used for determination of Soret coefficient. The experimental setup of TDFRS has been described elsewhere [12]. In brief, the interference grating was written by an Ar-ion laser with 488 nm. The grating was read by a He-Ne laser with 632.8 nm. The intensity of the diffracted beam was measured by a photomultiplier. A mirror mounted on a piezocrystal was used for phase shift and stabilization to obtain the heterodyne signal.

In the TDFRS experiment, the heterodyne signal intensity of the read out laser is proportional to the amplitude of the refractive index gradient $\Delta n(T,w)$ [Ref. 9],

$$\Delta n(T,w) = \left(\frac{\partial n}{\partial T} \right)_{P,w} \Delta T + \left(\frac{\partial n}{\partial w} \right)_{P,T} \Delta w \quad (3)$$

The normalized total intensity $\zeta_{\text{het}}(t)$ to the thermal signal is related to the Soret coefficient as

$$\zeta_{\text{het}}(t) = 1 + \left(\frac{\partial n}{\partial T} \right)_{P,w}^{-1} \left(\frac{\partial n}{\partial w} \right)_{P,T} S_T w (1-w) (1 - e^{-\Gamma t}) \quad (4)$$

where Γ is decay rate which has the relation with diffusion coefficient D as $D = \Gamma/q^2$. q is the wave vector ($q = (4\pi n/\lambda)\sin(\theta/2)$).

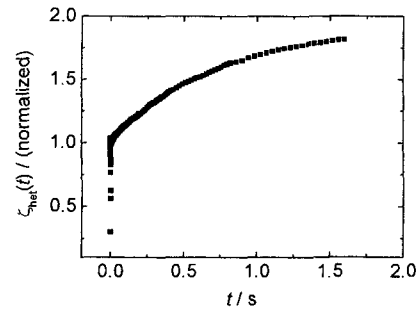


Fig. 2. Typical example of TDFRS signal for the PNiPAM gel-particles suspended in water (1.0 g/L) at 20.0 °C.

The TDFRS measurements were carried out in a temperature range from 20.0 to 38.0 °C. The temperature of the sample cell was thermostatically controlled by circulating water with an uncertainty of 0.02 °C. Refractive index increments with respect to the mass fraction ($\partial n/\partial w$) and the temperature ($\partial n/\partial T$) have to be determined separately. The quantities ($\partial n/\partial T$) and ($\partial n/\partial w$) of the samples were measured by means of a scanning Michelson interferometer operating at a wavelength of 632.8 nm. The analysis procedure was described elsewhere [10].

3. RESULTS AND DISCUSSION

In order to clarify the temperature dependence of dimension for the gel-particle, we carried out the light scattering measurements. Figure 1 shows the radius of gyration R_g and the hydrodynamic radius R_h of gel-particle suspended in water as a function of temperature. At lower temperatures, the gel-particle swells well in water, whereas for high temperatures the dimension of gel-particle becomes smaller. A steep shrink of the particle starts at Θ -temperature of the PNiPAM aqueous solution. In comparison with the volume change behavior of a PNiPAM bulk gel, which shows a discontinuous transition, the gel-particle showed a rather continuous transition behavior. The difference of the shrinking behavior could be associated with the difference of homogeneity of the network structure between the bulk gel and the gel-particle [7]. It means that the nano size gel-particle has a better homogenous network in comparison with the bulk gel. We will focus on the thermal diffusion behavior for this gel-particle, and the obtained Soret coefficient will be compared with the result of the linear PNiPAM chain.

Figure 2 shows typical signal of TDFRS experiment for the gel-particles suspended in water. The rapid increase of $\zeta_{\text{het}}(t)$ is the establishment of the temperature modulation on the time scale of micro seconds. In the later time, the slow increase of signal intensity corresponds to the migration of gel-particle by thermal diffusion (formation of concentration gradient). The Soret coefficients are obtained by a least squares fit using Eq. 4 and plotted in Fig. 3 with filled circles.

As shown in Fig. 3 the Soret coefficient of gel-particle is always positive in the measured temperature range which corresponds to that the particles migrate to the cold side of the fluid. The S_T

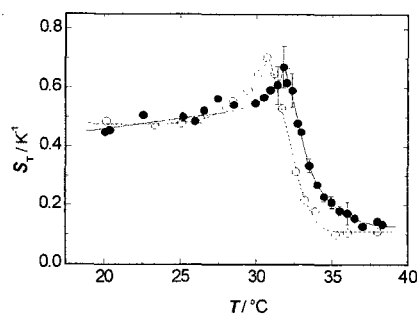


Fig. 3. Temperature dependence of Soret coefficients obtained from 1.0 g/L gel-particles in water (●) and from 1.0 g/L linear chain of PNiPAM in water (○).

shows an apparent peak at 31.8 °C with a steep decrease at higher temperature side. The result means that the magnitude of the concentration gradient is enhanced at around the temperature. The steep decrease of S_T is result of the shrinking of the gel-particle which corresponds to a large mutual diffusion coefficient giving a small Soret coefficient, cf. Eq. (2). The S_T of the linear PNiPAM chain in water is also shown in Fig. 3 which is obtained from Ref. 5. The peak temperature of linear chain is 30.7 °C which agrees well with the Θ -temperature of linear PNiPAM in water. The behavior of temperature dependence of S_T of gel-particle is quit similar with that of linear polymer chain, although the peak temperature of the gel-particle is higher than the linear chain. The difference of the peak temperature is 1.1 °C.

The enhancement of the concentration gradient at Θ -temperature is considered as follows. It is known for the linear PNiPAM chain in water that the coil-globule transition is taken place by heating where the second virial coefficient is zero at 30.6 °C. The polymer has a better solubility in colder water as can be judged by temperature dependence of the second virial coefficient [6], where the segment-solvent contact is favored. The direction of thermodiffusive motion of PNiPAM molecules in water is always toward the cold side, corresponding to the positive sign of S_T . The thermodiffusive motion by the Ludwig-Soret effect has the same direction with the better solubility side of the polymer, i.e., cold side. These facts indicate that 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 fact could be associated with the enhancement of Soret coefficient and which tends to be pronounced approaching the Θ -temperature.

As shown in Fig. 3 the entire behavior of S_T is similar between the gel-particle and linear chain. It indicates that the origin of thermal diffusion for these systems is equivalent, i.e. the thermal diffusion behavior is dominated by the thermodynamic properties of PNiPAM in water. The reason of the slight shift of peak position to higher temperature can be expected that the existence of the cross-linking in gel-particles modifies the properties of thermal responses. The other consideration is the difference of inter-particle

interactions in these systems. For colloidal systems Dhont reported theoretical aspects of thermal diffusion where he showed the contribution of inter-particle interaction plays a key role for thermal diffusion [13]. However for a linear PNiPAM solution, it has not been observed any special contributions of inter-molecular interactions for thermal diffusion behavior [10]. Therefore the observed shift of the peak position of S_T might be result of the inter-particle interactions of gel-particles. To confirm these points further studies are necessary with taking into account some parameters, such as the density of polymer network, the particle size, the concentration of particles and so on.

As a conclusion, we investigated thermal diffusion behavior of the PNiPAM nano gel-particle dispersed in water by means of TDFRS. The tentative experimental results showed that the entire behavior of S_T of gel-particles as a function of temperature is identical with that of the linear PNiPAM chain in water. This observation indicates that the origin of the thermal diffusion for these systems depends on the chemical structure of the system. In other words, the thermal diffusion is dominated by the effect of interfaces among segments and solvent molecules. The contribution of the cross-linking in the gel-particles is not well clarified at this stage. However, the slight shift of S_T towards higher temperature side may be related with the factor of the crosslinking structure of the gel or the inter-particle interactions. Nevertheless, it is indicated that these systems used in this study are good candidate to study the inter-particle interactions and microscopic mechanisms of Ludwig-Soret effect, since the systems composed of the same chemical species can be used for comparison. These points will be reported in detail in the future.

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