

Thermally induced sign change of Soret coefficient for dilute and semidilute solutions of poly(*N*-isopropylacrylamide) in ethanol

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We studied the thermal diffusion behavior of poly(*N*-isopropylacrylamide) (PNiPAM) in ethanol in a temperature range from $T = 14.0^\circ\text{C}$ to $T = 40.0^\circ\text{C}$ by means of thermal diffusion forced Rayleigh scattering. The obtained Soret coefficient S_T of PNiPAM was positive for lower temperatures ($T < 34^\circ\text{C}$), while S_T showed a negative value for higher temperatures ($T > 34^\circ\text{C}$). This means PNiPAM molecules move to the cold side for temperatures $T < 34^\circ\text{C}$, whereas they move to the warm side for $T > 34^\circ\text{C}$. This is the first nonaqueous polymeric system for which a sign change with temperature has been observed. We performed static and dynamic light scattering experiments in the same temperature range. The second virial coefficient determined from dilute solutions by static light scattering (SLS) was positive in the comparable temperature range. The results of SLS for the semidilute solution showed a strong repulsion among PNiPAM chains which was enhanced by increasing temperature. These results imply that the observed thermally induced sign change of S_T does not depend on the intermolecular interactions among PNiPAM chains. © 2004 American Institute of Physics. [DOI: 10.1063/1.1803535]

I. INTRODUCTION

Most processes occurring in everyday life have a non-equilibrium nature, which has attracted researchers for many years. Recently, the quantitative understanding of nonequilibrium phenomena has become of interest. For instance, colloidal model systems in external fields are used to understand nonequilibrium phenomena on a microscopic level.¹

One well-known nonequilibrium effect is the Ludwig-Soret effect^{2–4} which describes the formation of a concentration gradient in a multicomponent mixture caused by a temperature gradient. The amplitude of the concentration gradient is characterized by the Soret coefficient S_T , and relates the steady concentration gradient with the steady temperature gradient as follows:

$$\nabla w_1 = -w_1(1-w_1)S_T\nabla T. \quad (1)$$

Here w_1 is the mass fraction and T the temperature. The sign of the Soret coefficient indicates the direction of thermodiffusive motion. That is to say, the component moves to the hot side or the cold side. Although the Soret effect has been known for a long time, a microscopic understanding of the Soret effect in liquid mixtures and polymer solutions is still lacking.⁵

In gas mixtures, the thermal diffusion behavior is well described by the Chapman-Enskog theory. For simple gaseous mixtures, interactions between molecules are dominated by hard sphere repulsion and the heavier component migrates to the cold side.⁶ The tendency of the heavier component to migrate to the cold side is often observed for polymer solutions and colloidal suspensions. However, there are exceptions from the rule of thumb. If specific interactions are present, they greatly influence the thermodiffusive behavior. As early as 1977, Giglio and Vendramini reported that poly(vinyl alcohol) migrates to the warm side in aqueous solution.⁷ Recently, Iacopini and Piazza found lysozyme moving to the region of high temperature.⁸ Debuschewitz and Köhler showed using isotope systems that the sign change is related to the chemical nature of the substances.⁹

In our previous reports, poly(ethylene oxide) (PEO) in the mixed solvent water/ethanol was studied. A sign change of S_T was observed for PEO as a function of water/ethanol composition, i.e., the polymer migrates to the cold side in water-rich compositions ($S_T > 0$), while it moves to the warm side in ethanol-rich range ($S_T < 0$).^{10–13} The sign change at the water-rich side ($w_s \approx 0.82$) is most likely caused by a breakdown of the hydrogen-bond network^{11,14} and is identical for two concentrations of PEO (1 and 5 g/L). Here, w_s means the mass fraction of water for water/ethanol mixture. This result indicates the sign change occurs even in a single chain limit of the polymer for the same solvent composition. In other words, the solvent quality and its interactions with the polymer are the key to an understanding of the sign change behavior of PEO in the mixed solvent.

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These experimental findings could be qualitatively confirmed in a simple lattice chamber model for PEO/water/ethanol. Taking into account the hydrogen bonds and the compressibility of the system, the probability to find the polymer on the warm or the cold side depends on the difference in internal energy.^{11–13} A comparable internal energy argument also works successfully for low molecular weight aqueous mixtures.^{15,16} Nevertheless, this argument is not always sufficient to explain a sign change in all mixtures. Prigogine, Debrouckere, and Amand,¹⁷ argued that for alcoholic mixture, e.g., ethanol/cyclohexane, a free energy argument is needed which accounts for the loss in entropy.

In contrast to dilute polymer solutions, a few studies of thermal diffusion were reported in the range of semidilute polymer solutions. These studies focused on scaling properties¹⁸ and the effect on the glass transition^{19,20} of polystyrene in a good solvent. The effect of strong interactions among colloids upon the addition of a surfactant was reported and the measurements indicated that the interparticle interaction of colloids affect the thermal diffusion.²¹ Recently, a reversal of the thermal diffusion process was predicted for dense colloidal suspensions where the temperature dependence of interparticle interactions between colloids lead to a sign change of thermal diffusion coefficient.^{22,23} It is unclear whether this interparticle argument for the sign change of S_T can be adapted to concentrated solutions of strongly interacting polymer molecules. So far, there are no reports which deal with the sign change behavior of polymer solutions of interacting polymers in nondilute polymer solutions.

In this study, we report the thermal diffusion behavior of poly(*N*-isopropylacrylamide) (PNiPAM). PNiPAM single chains and gels have been studied extensively because of both scientific interest and industrial application purposes. For example, PNiPAM solutions show responses to the change of environmental parameters such as temperature, pH, ionic strength, solvent composition, and so on.^{24–30} It has been observed that PNiPAM aqueous solutions show a coil-globule transition which is induced by detachment of water molecules with increasing temperature.^{25,31–33} It has also been shown that the coil-globule transition is induced by changing the composition of mixed solvent, water/alcohol.²⁶ In this work we concentrated on the systematic study of PNiPAM in the good solvent, ethanol for which no coil-globule transition has been observed. As in the case of PEO, we expect an interesting thermal diffusion behavior as a function of temperature and/or solvent composition for PNiPAM. PNiPAM in comparison with PEO has the big advantage that pure binary mixtures PNiPAM/water and PNiPAM/ethanol can be studied individually, while PEO in pure ethanol could not be studied. In order to understand the complicated behavior of the ternary systems a systematic study of the binary mixtures is probably essential.

We present experimental TDFRS (thermal diffusion forced Rayleigh scattering) data of the Soret coefficient for the binary system of PNiPAM/ethanol as a function of temperature. The investigated concentrations of PNiPAM are in the dilute and the semidilute region which are confirmed by light scattering experiments. We find the thermally induced

sign change of Soret coefficient of PNiPAM/ethanol for both concentration regimes.

II. EXPERIMENT

A. Sample preparation

PNiPAM was polymerized from *N*-isopropylacrylamide (Aldrich) (0.18 M) in benzene (160 ml) with 2,2'-azo-bis(isobutyronitrile) (1.8 mM) as an initiator. The solution was degassed three times and polymerized at 56 °C for 20 h by stirring under an argon atmosphere. In this study, all solvents were high performance liquid chromatography grade and were used as received. The fractionation of this product was carried out by a phase separation technique in acetone/*n*-hexane mixture at room temperature.³¹ The fractionation procedure was repeated several times and one fraction was used in this study. The weight-averaged molecular weight was determined to be $M_w = 3.04 \times 10^6$ g/mol by static light scattering. A polydispersity index was determined by GPC (gel permeation chromatography) using DMF (dimethyl formamide) as eluent and calibrated by polystyrene as $M_w/M_n = 1.2$.

Ethanol (Fluka) was used without further purification. The water content of a freshly opened bottle of ethanol was determined to be 0.11 vol % by Karl Fisher titration. For 0.54 g/L and 1.00 g/L PNiPAM dissolved in ethanol, the water content increased to 0.13 vol % and 0.20 vol %, respectively. The measurements indicate that the PNiPAM is hydrated even though it had been dried for 24 h under vacuum prior to preparing the solutions. It is also possible that some water traces came in during the sample preparation procedure.

For the TDFRS measurements four different concentrations of PNiPAM/ethanol (0.2, 1.0, 2.0, and 5.0 g/L) were prepared with a spurious amount of the dye, quinizarin (Aldrich). The solution was filtered directly into the optical quartz cell with 0.2 mm path length (Hellma) through 0.22 or 0.45 μ m teflon membrane filters (Millipore).

B. Methods

The experimental setup of TDFRS has been described in detail elsewhere.³⁴ In brief, the interference grating was written by an argon-ion laser operating at the wavelength of $\lambda = 488$ nm. The grating was read by a He-Ne laser at $\lambda = 632.8$ 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. The TDFRS measurements were carried out in a temperature range from 14.0 to 40.0 °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 ($\partial n / \partial w_1$) and the temperature ($\partial n / \partial T$) have to be determined separately. The quantities ($\partial n / \partial T$) and ($\partial n / \partial w_1$) of PNiPAM/ethanol were measured by means of a scanning Michelson interferometer operating at a wavelength of 632.8 nm.³⁵ The analysis procedure is explained elsewhere.^{10,11,34}

Static and dynamic light scattering was carried out in the angular range $25^\circ < \theta < 150^\circ$. Kr-ions laser was used as the light source (wavelength $\lambda = 647.1$ nm). ALV-5000E correlator was used to measure the correlation function of scat-

tered light in the dynamic light scattering (DLS) experiment. A cylindrical cell having an inner diameter of 18 mm was placed in a thermostated bath, the temperature of which was controlled with an uncertainty of 0.02 °C. The sample solution was filtered directly into the cylindrical cell through 0.22 μm teflon membrane filter (Millipore). The sample solutions were kept at desired temperature for at least 2 h to ensure equilibrium before starting data acquisition.

III. WORKING EQUATIONS

A. TDFRS

Thermodiffusion in a binary mixture is described by the flux \mathbf{J}_1 of one of the components in response to a temperature and concentration gradient as⁴

$$\mathbf{J}_1 = -\rho D \nabla w_1 - \rho w_1 (1 - w_1) D_T \nabla T, \quad (2)$$

where D is the translational mass diffusion coefficient, D_T the thermal diffusion coefficient, and ρ the total mass density. In a steady state with the presence of a temperature gradient at a constant pressure \mathbf{J}_1 goes to zero giving Eq. (1). The Soret coefficient S_T of component 1 is the ratio of thermal and mutual diffusion coefficients i.e.,

$$S_T = \frac{D_T}{D}. \quad (3)$$

In the TDFRS experiment, the heterodyne signal intensity of the read out laser is proportional to the amplitude of the refractive index gradient $\Delta n(T, w_1)$ (Ref. 36),

$$\Delta n(T, w_1) = \left(\frac{\partial n}{\partial T} \right) \Delta T + \left(\frac{\partial n}{\partial w_1} \right) \Delta w_1. \quad (4)$$

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

$$\zeta_{\text{het}}(t) = 1 + \left(\frac{\partial n}{\partial T} \right)^{-1} \left(\frac{\partial n}{\partial w_1} \right) S_T w_1 (1 - w_1) (1 - e^{-q^2 D t}). \quad (5)$$

B. SLS and DLS

The absolute Rayleigh ratio R , the excess intensity of scattered light corrected with the instrument constant, is expressed as

$$\frac{Kc}{R(q)} = \frac{1}{M_w P(q)} + 2A_2 c, \quad (6)$$

where K is the optical constant ($K = 1.33 \times 10^{-7} \text{ cm}^2 \text{ g}^{-2} \text{ mol}$). c , A_2 , and $P(q)$ are the concentration of polymer in g cm^{-3} , second virial coefficient, and particle scattering factor, respectively. q is the wave vector, $q = (4\pi n/\lambda_0) \sin(\theta/2)$. $P(q)$ depends on the dimension of polymer and is related to the radius of gyration R_g as

$$\frac{1}{P(q)} = 1 - \frac{1}{3} q^2 \langle R_g^2 \rangle + \dots \quad (7)$$

The autocorrelation function of the scattered light intensity $g^{(2)}(q, t)$ is related to the normalized field correlation function $g^{(1)}(q, t)$ by

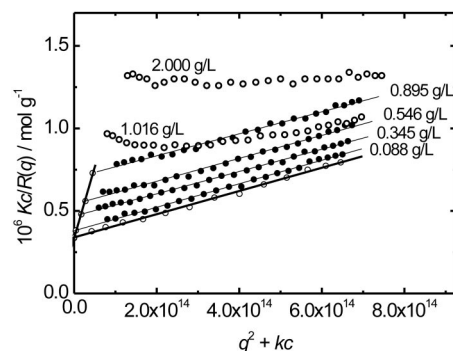


FIG. 1. Typical Zimm plot of PNIPAM/ethanol at 40.0 °C.

$$g^{(2)}(q, t) = B(1 + \beta |g^{(1)}(q, t)|^2), \quad (8)$$

where B and β are the base line and a constant relating to the coherence of detection, respectively. The measured correlation functions were analyzed by the cumulant method to obtain the average decay rates $\bar{\Gamma}$,

$$\ln |g^{(1)}(t)| = -\bar{\Gamma}t + \frac{\mu_2}{2!}t^2 - \frac{\mu_3}{3!}t^3 + \dots, \quad (9)$$

where μ_i is the i th cumulant and $\mu_2/\bar{\Gamma}^2$ gives the normalized dispersion of distribution of $\bar{\Gamma}$. If the fluctuation of the scattering light intensity is due to the translational diffusion of the polymer chains, the decay rate has the form

$$\bar{\Gamma}/q^2 = D_0(1 + k_d c + \dots). \quad (10)$$

Here D_0 is the translational diffusion coefficient at infinite dilution and k_d is a constant for the effect of polymer concentration. The hydrodynamic radius R_h is related to D_0 by the Stokes-Einstein equation, $R_h = k_B T / (6\pi\eta D_0)$, where k_B is Boltzmann's constant and η denotes the solvent viscosity.

IV. RESULTS AND DISCUSSION

A. Characteristics of PNIPAM deduced by light scattering

To the best of our knowledge, no systematic light scattering experiments have been performed on linear PNIPAM/ethanol. In order to characterize the PNIPAM/ethanol solutions, we performed SLS and DLS measurements in the same temperature range ($15^\circ\text{C} < T < 40^\circ\text{C}$) as the following TDFRS experiments. Molecular parameters such as molecular weight M_w , radius of gyration R_g , hydrodynamic radius R_h , and the second virial coefficient A_2 are important to characterize structure and interactions of the system. The previously mentioned system quantities are necessary to interpret the thermal diffusion data. Figure 1 shows a typical example of a Zimm plot for PNIPAM/ethanol. The angular dependence of the scattered light intensity shows a good linear relation below the concentration of 0.895 g/L, whereas for solutions of higher concentration, the plot shows an upward curvature at low angles. The quantities M_w , A_2 , and R_g were determined using low concentration samples ($c < 0.895 \text{ g/L}$) by standard extrapolating procedures and are listed in Table I. The second virial coefficient A_2 is positive for all temperatures. This indicates that ethanol is a good

TABLE I. Temperature dependence of characteristic parameters for PNIPAM/ethanol. The parameters were obtained by SLS and DLS using the concentrations of PNIPAM solution below 0.895 g/L.

T (°C)	$10^{-6}M_w$ (/g mol ⁻¹)	10^4A_2 (/cm ³ mol g ⁻²)	$\langle R_g^2 \rangle_z^{1/2}$ (/nm)	$10^8\langle D_0 \rangle_z$ (/cm ² s ⁻¹)	$\langle R_h^{-1} \rangle_z^{-1}$ (/nm)	$\langle R_g \rangle / \langle R_h \rangle$	k_d (/cm ³ g ⁻¹)	μ_2 / Γ^2
15.0	3.17	2.10	85.3	3.42	47.0	1.81	81.7	0.30
20.0	3.02	2.08	79.9	3.78	47.3	1.69	121	0.13
25.0	3.07	2.01	80.1	4.19	47.6	1.69	111	0.15
30.0	2.95	2.06	78.0	4.70	47.0	1.66	91.2	0.11
35.0	3.04	2.11	80.6	5.22	46.9	1.72	96.1	0.14
40.0	2.96	2.16	78.9	5.74	47.0	1.68	140	0.12

solvent in the entire temperature range investigated. The overlapping concentration $c^* [= 3M_w / (4\pi N_A R_g^3)]$ is temperature independent and is calculated as 2.3 g/L from the averaged values M_w and R_g . Here N_A is Avogadro's number. The calculated overlap concentration lies above the concentration for which deviations from the linear behavior are observed, but due to the fact that the dilute/semidilute transition is not sharp the agreement is reasonable. Analyses of DLS data were also carried out using only the low concentration samples. The diffusion constant $\langle D_0 \rangle$ increased with increasing temperature which is comparable to the solvent viscosity change. The hydrodynamic radius $\langle R_h \rangle$ does not show a temperature dependence. The value of $\langle R_g \rangle / \langle R_h \rangle$ is ≈ 1.7 , which is typical for flexible coils in a good solvent.

The linear relation of scattered light intensity for $c < 0.895$ g/L ensures that the solutions are in the dilute concentration range. On the other hand, the upward curvature at the concentration of 1.0 g/L indicates the appearance of an excluded volume effect or a strong repulsion among polymer chains that can be explained with the decrease of the scattered light intensity due to the interference of scattered light from different chains. Since the curvature appears approaching the overlapping concentration, the upward curvature could be a result of repulsions between polymer chains. The higher concentration sample (2.0 g/L) as shown in Fig. 1 exhibits a very weak angular dependence. These observed effects are probably due to the substantial overlapping and the enhancement of repulsion interactions.

This kind of upward curvature at low scattering angles was observed for polyelectrolytes and copolymers where the long range interactions result in the anomalous angular dependence.^{37,38} A similar behavior for the scattering intensity was observed with non-ionic polymers.^{39,40} The structural isomer of PNIPAM, poly(*N*-n-propylacrylamide) also showed the upswing in the curve for water/2-propanol, where the long range repulsions arise from the solvation shell composed of the selective solvation between propanol and polymer chain.⁴⁰ For PNIPAM/ethanol, the origin of the long range intermolecular interactions could be related to the hydrophilic and hydrophobic nature of isopropylacrylamide groups and the formation of hydrogen bonds. In this context, we will also discuss in the following section the influence of traces of water on the system behavior.

The temperature dependence of the normalized scattering intensity $R(q)^{-1}/R(0)^{-1}$ for 1.0 g/L solution is shown in Fig. 2. Here, $R(0)^{-1}$ is the inverse intensity at $q=0$ determined by the extrapolation using the linear range (higher

angles). The plot at 20 °C shows a flat range at low scattering vectors. In comparison, the scattering intensities at higher temperatures show a peak at low q values. Additionally, at the higher q vectors the slope of the intensity in dependence of q^2 decreases with increasing temperature. This result indicates that the repulsive interaction is stronger at higher temperatures. Although these interactions between PNIPAM chains observed by SLS measurements are not completely understood and the transition from dilute to semidilute is not sharp in general, it can be presumed that the concentration above 1.0 g/l belong to the semidilute range where intermolecular interactions become more important.

B. Thermal diffusion of PNIPAM

TDFRS measurements were carried out using the dilute sample (0.2 g/L) and the semidiluted concentrations (1.0, 2.0, and 5.0 g/L). Figure 3 shows a typical normalized heterodyne signal as a function of time after the intensity grating has been switched on at time $t=0$ obtained for 1.0 g/L solution. The rapid increase of $\zeta_{\text{het}}(t)$ is the establishment of the temperature modulation on the time scale of micro seconds. It is observed that the concentration part of the $\zeta_{\text{het}}(t)$ signal increases with time for lower temperatures. This implies that the polymer moves to the cold side. In contrast, for higher temperatures the signal decreases with time therefore the PNIPAM molecules move to the warm side. The Soret coefficient S_T and the mutual diffusion coefficient D shown in Figs. 4 and 5 were obtained using a nonlinear least-squares fit to Eq. (5) with the measured contrast factors, $(\partial n / \partial T)$ and $(\partial n / \partial w_1)$. The variation of $(\partial n / \partial T)$ with concentration is displayed in Fig. 6. In the investigated tempera-

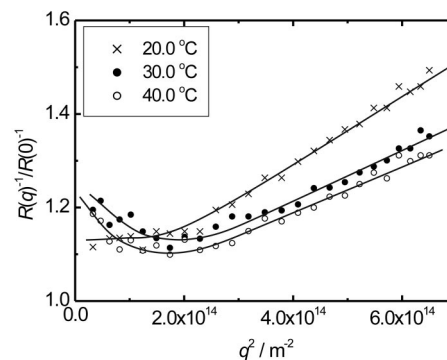


FIG. 2. Temperature dependence of normalized scattering intensity for 1.0 g/L PNIPAM/ethanol. The lines are drawn to guide eyes.

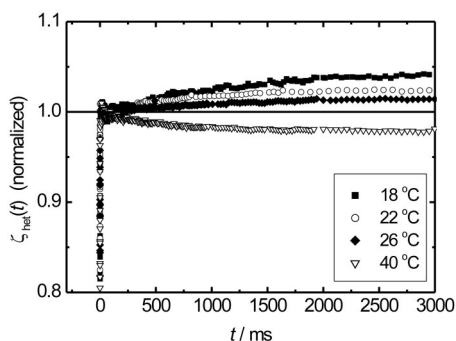


FIG. 3. Typical normalized TDFRS signals of 1.0 g/L PNiPAM at different temperatures.

ture and concentration range, the refractive index increment with respect to the mass fraction ($\partial n/\partial w_1$) did not show any systematic variation. An average value of $(\partial n/\partial w_1)=0.110 \pm 0.001$ was used, which was calculated using six different temperatures in the range between 15 and 35 °C.

Figure 4 shows the Soret coefficient of PNiPAM as a function of temperature. For all concentrations the Soret coefficient of PNiPAM decreases with increasing temperature. Tendentiously the magnitude of the Soret coefficient increases with decreasing concentration, but this effect is not very pronounced in the investigated concentration range. For all samples the sign change of the Soret coefficient occurs around 34 °C. Within the error bars no systematic deviation of the sign change temperature can be observed. Here, the error is one standard deviation. The highest uncertainty was found for the lowest concentration of 0.2 g/L, where the amplitude of the concentration signal is small because of the low concentration. Approaching to the sign change temperature the situation becomes even worse due to the small value of S_T . The positive S_T at $T < 34$ °C means the PNiPAM molecules migrate to the cold side, whereas the negative S_T at $T > 34$ °C corresponds to the migration of PNiPAM molecules to the warm side. For several complex systems, such as a protein in water⁸ or a polymer in a water/ethanol mixture,¹⁴ a sign change in the thermodiffusive behavior with temperature has been observed. In these systems the

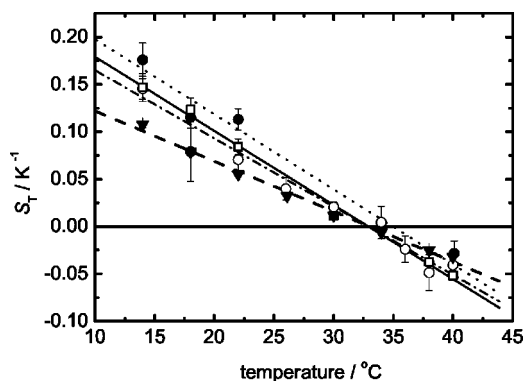


FIG. 4. Temperature dependence of Soret coefficient S_T of PNiPAM/ethanol. The concentrations are 0.2 g/L (●), 1.0 g/L (○), 2.0 g/L (□), and 5.0 g/L (▼). The lines represent the linear regression line of the data points for the various concentration 0.2 g/L (dotted), 1.0 g/L (dash-dotted), 2.0 g/L (solid), and 5.0 g/L (dashed).

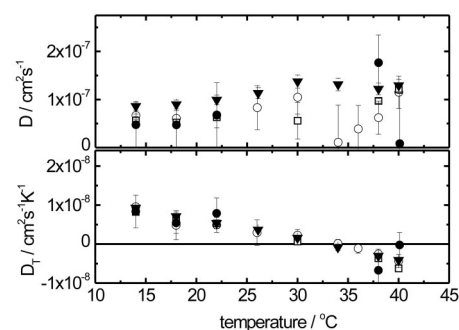


FIG. 5. Temperature dependence of translational diffusion coefficient D and thermal diffusion coefficient D_T of 0.2 g/L (●), 1.0 g/L (○), 2.0 g/L (□), and 5.0 g/L (▼) PNiPAM/ethanol.

Soret coefficient of the polymers increased with increasing temperature, while in the current study the Soret coefficient decreases with temperature. One difference of the PNiPAM system compared to the previous systems is the choice of the solvent. The present system was studied in ethanol while all other systems contained water as the majority component.

Figure 5 shows the translational diffusion and the thermal diffusion coefficient of PNiPAM solutions as a function of temperature. The slight increase of D with temperature is not very pronounced and can be fully understood by the temperature dependence of the solvent viscosity. A discontinuity of D with temperature was observed between 34 and 36 °C for 1.0 g/L sample, where the sign change of S_T and D_T occurred. Since the heterodyne signal $\zeta_{het}(t)$ has no amplitude at the sign change temperature, the diffusion coefficient D can not be evaluated [cf. Eq. (5)]. Therefore it is difficult to evaluate the diffusion coefficient D near the sign change point, because of the small amplitude of $\zeta_{het}(t)$, and we will not discuss further the behavior of D .

The thermal diffusion coefficient D_T was determined by Eq. (3) using the values of S_T and D . As in the case of the Soret coefficient we observed a decrease with temperature and the sign change around 34 °C. As shown in Fig. 5, D_T is independent of concentration in the investigated range indicating that with respect to the thermal diffusion behavior all solutions seem to belong to the dilute regime. The weaker concentration dependence of D_T might be explained if one

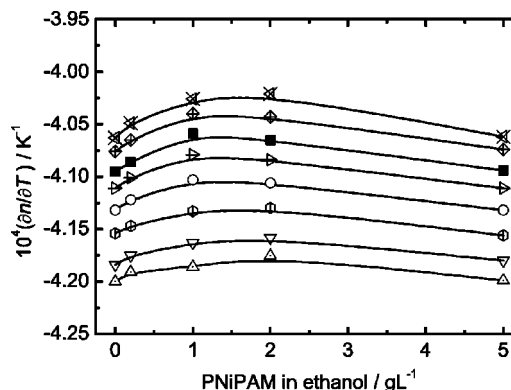


FIG. 6. Concentration and temperature dependencies of $(\partial n/\partial T)$ for PNiPAM/ethanol. The different symbols correspond to the temperatures at 14, 18, 22, 26, 30, 34, 38, and 40.0 °C from the top to the bottom.

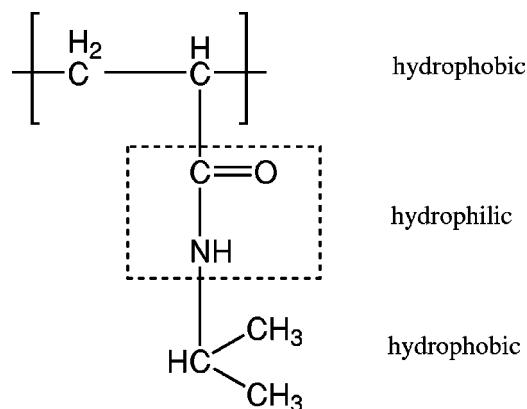


FIG. 7. Chemical structure of PNIPAM indicating hydrophobic and hydrophilic regions.

draws an analogy to hard spheres. For this case the concentration dependence of $D_T = D_{T,0}[1 - 0.35c + \dots]$ is by a factor 4 weaker than for $D = D_0[1 + 1.45c + \dots]$.²³ A similar trend might be expected for Gaussian chains. We can conclude that in the investigated concentration range the sign change of the system is mainly caused by single particle effects.

The mechanism underlying the thermal diffusion process with ethanol as the major component may be different from systems with water as the major component. For low molecular weight mixtures, there is a difference in the behavior between mixtures containing water and alcoholic mixtures without water. For instance, in aqueous mixtures the sign change of the Soret coefficient can be qualitatively explained by an energy argument.^{15,16} In contrast, sign changes in alcoholic mixtures without water require the consideration of entropic effects.¹⁷ Presently, there is no microscopic understanding of the sign change in the thermal diffusion behavior. Often sign changes occur when the solvent quality becomes poorer, but this explanation can be ruled out because the second virial coefficient remains constant in the investigated temperature range. Preliminary measurements of PNIPAM/water show only a sharp drop of the Soret coefficient at the coil-globule transition temperature, but no sign change.⁴¹ These observations indicate that the nature of sign change is not necessarily connected to a worsening of the solvent quality.

In analogy to previous papers on the sign change of the Soret coefficient of PEO in dilute solutions, it is suggested that the sign change is mainly driven by structural changes in the vicinity of the macromolecule and not so much by polymer-polymer interactions. We expect that interactions via hydrogen bonding play a dominant role in the thermal diffusion behavior, although the situation might be more complicated due to the complex structure of the PNIPAM polymer. We tried to introduce this complicated hydrophilic/hydrophobic balance within the PNIPAM in a schematic sketch (Fig. 7). In a simplified way one might identify hydrophobic and hydrophilic *region* consisting of small chemical subgroups. This scheme might cover some aspects although in practice the situation is often more complicated. For instance, the solubility of poly

(*N*-isopropylmethacrylamide) in water is better than the PNIPAM in water.⁴² On the other hand, poly(*N*-*n*-propylacrylamide) is less soluble in water.⁴³ These facts indicate that the solution properties of PNIPAM are significantly affected by a solvation and a competition between hydrophobic and hydrophilic interactions. And these interactions will be certainly temperature dependent. In the PEO/ethanol/water system some qualitative agreement with a lattice model calculation taking into account the special interaction of hydrogen bonding between polymer and solvent could be achieved.^{11–14} In the present case of the PNIPAM/ethanol system, a similar approach might work if one considers the chemically different units of the PNIPAM segment. Nevertheless, it is expected that the sign change in PNIPAM/ethanol might be explained in a similar lattice framework.

Previous and this measurement show that a change of the thermal diffusion behavior is not necessarily correlated with a structural change of the polymer. This observation was also made for the system PEO/ethanol/water. For very low water contents the chains collapsed and start to expand when the water content is increased to 20 wt %.¹⁰ In this concentration range the negative Soret coefficient of PEO in ethanol/water decreases moderately unaffected by the change of the chain dimensions. On the other hand, the chain dimensions remain constant at a water content around 80 wt % where the Soret coefficient of PEO in ethanol/water changes sign and becomes positive.¹⁴ It might be expected that local structural changes which can lead to a sign change of the Soret coefficient do not necessarily affect the solubility and structural parameters of the polymer. The Soret coefficient of PNIPAM in water decreases only sharply at the coil-globule temperature but does not change sign.⁴¹ One can speculate that the thermal diffusion behavior is probably more influenced by changes in local heat transport properties induced due to local structural changes.

Another consideration is the effect of the minute amount of water in PNIPAM/ethanol. As shown in the Experiment, it is in practice difficult to prepare water-free PNIPAM/ethanol solutions. Therefore, it is desired to study PNIPAM/ethanol/water mixtures to observe how the addition of water will influence the thermal diffusion behavior for both dilute and semidilute solutions. This point is currently being examined and will be reported at a later date.⁴¹ Although in this study the water content in the solution is very low, an estimation indicates that even for the high concentration of 5 g/L the number of water molecules is in the same order of magnitude as the number of repeating units present in the solution. This might lead to a selective solvation of water with PNIPAM, which could have a significant effect on the local heat transport properties in the system. And as in the case of the PNIPAM/water system we might expect a detachment of the water molecules at the coil-globule transition temperature of 31 °C. Due to the fact that the transition temperature is close to the sign change temperature of 34 °C we might expect a similar mechanism. These observations indicate that the thermal diffusion could be affected by the temperature dependencies of the selective solvation and the competition of hy-

dophobic and hydrophilic interactions among polymer repeating units and solvent molecules.

V. CONCLUSIONS

The light scattering data indicate that we are in the semidilute regime and that there are interactions between the polymer chains. On the other hand, the thermal diffusion data do not show any significant dependence on the concentration which might be due to a similar weaker concentration dependence of the thermal diffusion as known for hard spheres.²³ For instance, the sign change in the thermal diffusion behavior occurs for all concentrations more or less at the same temperature. We can not confirm any concentration dependence as suggested by Dhont for interacting colloidal particles.²³ Therefore, we assume that the observed sign change is mainly attributed to a single particle effect or the interaction of the polymer with the solvent.

The temperature dependence of the Soret coefficient is opposite to the aqueous systems which have been investigated. This means that the Soret coefficient becomes negative at high temperatures and is positive at low temperatures. In literature it has been suggested that the simple energetic explanation in water systems needs to be expanded by an entropic contribution for alcoholic systems. Nevertheless, unavoidable traces of water might also influence the behavior of the systems. Even for the highest PNIPAM concentration the number of water molecules is of the same order of magnitude as the number of segments present in the solution. Therefore, it is possible that water although only present in a very low concentration needs to be considered to explain the behavior.

We suggest the following mechanism, based on the model explaining the coil-globule transition in aqueous mixtures. Here one assumes that the detachment of water occurs at a certain temperature which is likely around the transition temperature. If water molecules are liberated from the macromolecule, a local structure change of solvent in the vicinity of the chain takes place. From the previous experiments we know that the interface between the polymer and the solvent is important and has a strong effect for thermal diffusion behavior. A structural change among the segments and solvents, for instance, leads to a sign change in the case of PEO. In the case of PNIPAM/ethanol, light scattering measurements indicate that such a structural change influences the local heat transport properties but is not so sensitive for structural parameters as the radius of gyration and the hydrodynamic radius for PNIPAM/ethanol at homogenous temperatures. On the other hand, if we assume the liberation of water molecules with increasing temperature, this might lead to a similar structural change, which can then result in a change of the thermal diffusion behavior. In order to check this hypothesis we need to investigate the effects of addition of water to the present system and its temperature dependencies.

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