Ludwig−Soret Effect of Poly(*N*-isopropylacrylamide): Temperature Dependence Study in Monohydric Alcohols

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ABSTRACT: We report the experimental results of the Ludwig−Soret effect for poly(*N*-isopropylacrylamide) (PNiPAM) in alcohols measured in the temperature range from 20 to 45 °C by means of thermal diffusion forced Rayleigh scattering (TDFRS). Alcohols, used in this study as solvent, are monohydric alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and *tert*-butanol). In the studied temperature range, PNiPAM in methanol shows a positive Soret coefficient, whereas PNiPAM has a negative Soret coefficient in larger alcohols, i.e., 1-propanol, 2-propanol, 1-butanol, and *tert*-butanol. In ethanol the temperature dependence of the Soret coefficient of PNiPAM shows a sign change from positive to negative with increasing temperature at $T = 34$ °C. The temperature dependence of the Soret coefficients for these alcohol solutions is discussed in terms of cohesive energies such as the Hildebrand solubility parameter. It is indicated that the balance between the hydrogen-bonding capability and the hydrophobic association plays a dominant role for the sign change in the Soret coefficient and the thermal diffusion coefficient of PNiPAM.

I. Introduction

Thermosensitive polymers and gels have been studied extensively due to their high application potential, such as drug delivery, soft actuator, and reactors.[1−3] One of the most frequently investigated systems is the biocompatible polymer poly(*N*-isopropylacrylamide) (PNiPAM). In dilute aqueous solutions, linear PNiPAM exhibits a thermoreversible transition at a Θ-temperature of ~31 °C.[4−9] Gels composed of cross-linked PNiPAM chains show a discontinuous volume phase transition with changing temperature, pH, salt content, or solvent composition.[10−15] The thermodynamic equilibrium state has been investigated extensively by numerous methods.

Recently, the thermal diffusion phenomenon also called Ludwig−Soret effect was studied for aqueous solutions of PNiPAM in the vicinity of the coil−globule transition temperature.[16] The Ludwig−Soret effect leads to a net mass flux and builds up a concentration gradient, when a temperature gradient across a fluid mixture is applied.[17,18] Phenomenologically, the mass flow $\mathbf{J_1}$ of component 1 is expressed as[19]

$$\mathbf{J_1} = -\rho D \nabla w_1 - \rho w_1(1 - w_1) D_T \nabla T \qquad (1)$$

Here, ρ is the density of the solution, D the translational mass diffusion coefficient, D_T the thermal diffusion coefficient, w_1 the mass fraction of component 1, and T the temperature. In the steady state the flux vanishes ($\mathbf{J_1} = 0$), and steady temperature and concentration gradients are formed. Thus, the Soret coefficient S_T of component 1 is expressed as

$$S_T \equiv \frac{D_T}{D} = -\frac{1}{w_1(1 - w_1)} \frac{\nabla w_1}{\nabla T} \qquad (2)$$

The sign of S_T indicates the direction of the flux of component 1.[20] There are several detailed and systematic studies of the Ludwig−Soret effect for organic polymer systems covering scaling behavior, concentration dependence, and preferential solvation effects in mixed solvents.[21−26] While the Soret coefficient of organic polymers is typically positive, S_T of water-soluble polymers often shows a sign change with temperature or solvent composition. Piazza et al. reported that a aqueous lysozyme solution shows a sign change of S_T as a function of temperature and salt content.[27] A sign change of S_T was also observed for poly(ethylene oxide) (PEO) in water/ethanol mixtures[28,29] and dextran in water with and without urea.[30] A sign change of S_T is no unique feature for aqueous polymer solutions and has been observed for other systems, such as colloidal suspensions,[31−33] surfactant solutions,[34,35] and solvent mixtures.[36,37] Usually, the mechanism leading to a sign change is system dependent, although, for several aqueous mixtures with and without solutes such as polymers and colloids, the sign change concentration is almost system independent and strongly correlated with the breakdown of the hydrogen-bond network.[38] Also, the temperature dependence of S_T for a large class of macromolecules and colloids in water shows a distinctive universal characteristic.[39]

For a diluted solution of PNiPAM in water it is found that the temperature dependence of S_T of PNiPAM shows an apparent peak at the Θ-temperature.[16] It implies that the magnitude of the concentration gradient becomes large at the Θ-temperature. According to the nature of the coil−globule transition of PNiPAM, it is expected that interactions among the segments and solvent molecules play an important role for the thermal diffusion behavior. The experimental results also show that the sign of S_T is always positive in the measured temperature range which implies that the PNiPAM molecules migrate to the cold side of the fluid. In contrast to the aqueous PNiPAM solution, S_T of PNiPAM in ethanol shows a sign change from positive to negative at 34 °C with increasing temperature.[40] This means PNiPAM migrates to the hot side of the fluid at high temperatures ($T > 34$ °C). It should be mentioned that the sign change temperature is identical for both diluted and semidiluted solutions. These observations indicate that the thermally induced sign change for polymer solutions is strongly coupled with the choice of solvent and depends on the solvation properties, but not so much on the polymer−polymer interactions. In order to understand the mechanisms of the

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Ludwig−Soret effect of PNiPAM, we varied the solvent quality systematically.

For PNiPAM solutions, the balance between hydrophilic and hydrophobic interactions is a key feature to understand properties of the system. Good solvent candidates for PNiPAM with a strong capability to form hydrogen bonds are alcohols. Furthermore, the alcohols can be varied systematically by increasing the chain length and using isomers. In this study we present thermal diffusion forced Rayleigh scattering (TDFRS) measurements for PNiPAM in monohydric alcohols such as methanol, ethanol, 1-propanol, and 1-butanol. Structural isomers of 1-propanol and 1-butanol, i.e., 2-propanol and *tert*-butanol, were also investigated.

II. Experimental Section

Materials. Alcohols used in this study are HPLC analytical grades (purity >99.9, only for *tert*-butanol purity >99.5) purchased from Sigma-Aldrich or Fluka, and we used freshly opened bottles without further purification. PNiPAM was polymerized from *N*-isopropylacrylamide in benzene with an initiator 2,2′-azobis-(isobutyronitrile), and the product was fractionated several times by a phase separation technique in acetone/*n*-hexane mixture.[4,40] One fraction was used in this study which has the weight-averaged molecular weight $M_w = 1.2 \times 10^6$ g/mol with a polydispersity M_w/M_n of 1.26 obtained from GPC. Before preparing the sample solutions PNiPAM was kept under vacuum at least 24 h for drying. In this study the solutions of 10.0 g/L PNiPAM in alcohols were prepared with a small amount of the dye, quinizarin. For measurements the solution was filtered directly into the optical quartz cell with 0.2 mm path length (Hellma) through 0.22 or 0.45 μm Teflon membrane filters (Millipore).

TDFRS Experiments. The experimental details of TDFRS have been described elsewhere.[35] The normalized heterodyne signal intensity, $\zeta_{\mathrm{het}}(t)$, to the thermal signal is related to the Soret coefficient S_T and diffusion coefficient D as follows:[41]

$$\zeta_{\mathrm{het}}(t) = 1 + \left(\frac{\partial n}{\partial T}\right)^{-1}\left(\frac{\partial n}{\partial w_1}\right) S_T w_1 (1 - w_1)(1 - \mathrm{e}^{-q^2 D t}) \qquad (3)$$

Here, t is the time, n the index of refraction, and q the wavenumber. The contrast factors, refractive index increments with respect to the temperature and the weight fraction, $(\partial n/\partial T)$ and $(\partial n/\partial w_1)$, should be determined individually.[42] The TDFRS measurements were carried out in the temperature range from 20 to 45 °C, where the temperature of the sample cell was controlled by circulating water from a thermostat with an uncertainty of 0.02 °C.

Figure 1 shows typical TDFRS signals for 10.0 g/L PNiPAM in three alcohols (methanol, ethanol, and 1-propanol). Different symbols refer to the different experimental temperatures. The rapid increase of normalized heterodyne signal $\zeta_{\mathrm{het}}(t)$ corresponds to the establishment of the temperature gradient on the time scale of microseconds after the intensity grating has been switched on at time $t = 0$. At later times, the slower increasing or decreasing part of the signal indicates the establishment of the concentration gradient in the time scale of seconds. S_T and D are simultaneously determined from the concentration signal of $\zeta_{\mathrm{het}}(t)$ using a least-square fit to eq 3.

III. Results and Discussion

Temperature Dependence. Typical TDFRS signals for 10.0 g/L PNiPAM in three alcohols as a function of temperature are shown in Figure 1. In methanol the concentration signal of $\zeta_{\mathrm{het}}(t)$ always increases with time, whereas $\zeta_{\mathrm{het}}(t)$ decreases with time for 1-propanol in the measured temperature range. For the ethanol solution, the signal changes its direction from upward to downward with increasing temperature. The turnaround of the signal corresponds to the sign change of Soret and thermal diffusion coefficients which will be described below. As a general trend, the amplitude of the concentration part of $\zeta_{\mathrm{het}}(t)$ decreases with increasing temperature and with increasing number of carbon atoms in the alcohols. The residuals between the experimental data and the fitted curve are displayed in Figure 2. The residuals are small (less than 1%) and show no systematic deviations.

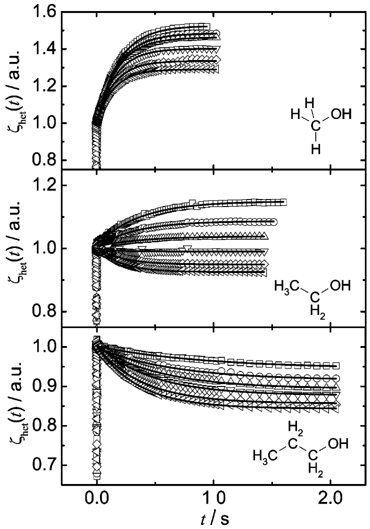

Figure 1. Typical examples of the normalized TDFRS signal for solutions 10.0 g/L PNiPAM in different alcohols. The alcohols are methanol, ethanol, and 1-propanol. Different symbols refer to the experimental temperatures as T/°C = 20 (□), 25 (○), 30 (△), 35 (▽), 40 (◇), and 45 (tilted △). The solid lines refer to a fit according to eq 3.

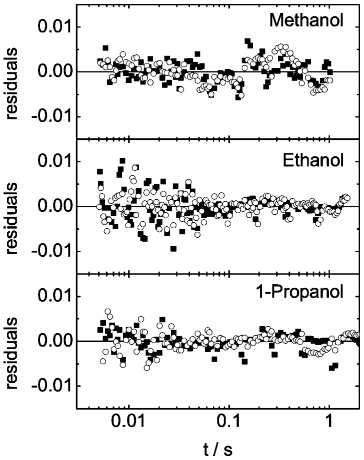

Figure 2. Residuals of the experimental TDFRS signal and the fitted curve according to eq 3 for PNiPAM in methanol, ethanol, and 1-propanol at 25 °C (■) and 45 °C (○).

The Soret coefficient S_T and the translational diffusion coefficient D of PNiPAM were obtained by a least-squares fit to eq 3. The thermal diffusion coefficient D_T was calculated using eq 2. The obtained values are shown in Figure 3. In methanol the magnitude of S_T and D_T of PNiPAM decrease with increasing temperature, and the signs of them are always positive in the measured temperature range. The positive sign means that the PNiPAM molecules migrate to the cold side of the fluid, which is a typical observation for polymer solutions under good solvent conditions. For larger alcohols, i.e., 1-propanol, 2-propanol, 1-butanol, and *tert*-butanol, in contrast to methanol, the sign is always negative. The negative sign means the PNiPAM molecule moves to the warm side of the fluid, which is often observed under poor solvent conditions.[28,43−45] In those larger alcohols except for *tert*-butanol the magnitude of S_T of

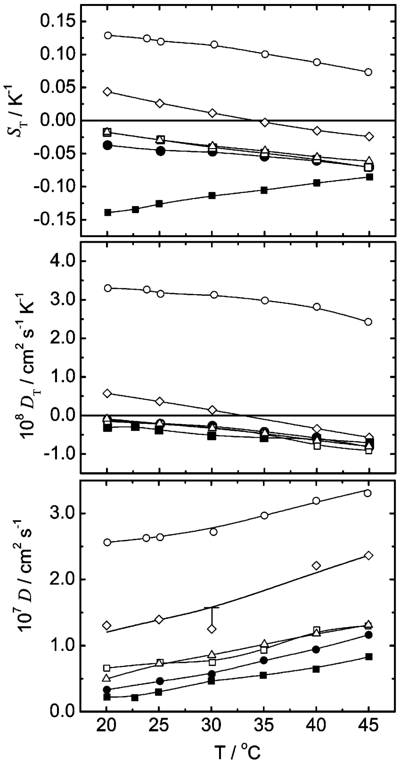

Figure 3. Temperature dependence of the Soret coefficient S_T, the thermal diffusion coefficient D_T, and the translational diffusion coefficient D of 10.0 g/L PNiPAM in alcohols. The alcohols as solvents are methanol (○), ethanol (◇), 1-propanol (△), 1-butanol (□), 2-propanol (●), and *tert*-butanol (■). Lines are drawn to guide eye. The large uncertainty in D near the sign change temperature $T^{\pm}$ is indicated by an error bar.

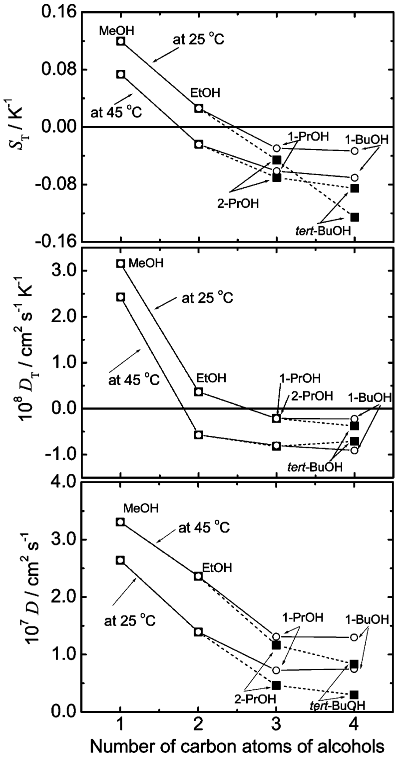

Figure 4. S_T, D_T, and D of PNiPAM plotted against the number of carbon atoms of solvent at 25 and 45 °C. The solid lines with open circles indicate the alcohols composed of linear alkyl chain, while the dashed lines with filled squares represent the alcohols with branched alkyl chain, which refers to secondary and tertiary alcohols.

PNiPAM is almost the same for all temperatures and decreases with temperature. Only for *tert*-butanol, the S_T shows an increasing behavior, although the temperature dependence of D_T for *tert*-butanol is similar to the 1-propanol, 2-propanol, and 1-butanol solutions, as shown in Figure 3. In the ethanol solution, the sign change is observed which agrees well with the previous publication.[40] The translational diffusion coefficient D of PNiPAM increases with increasing temperature. Here, a large deviation of the diffusion coefficient D in the ethanol solution arises from the small amplitude of $\zeta_{\mathrm{het}}(t)$ near the sign change temperature; i.e., the amplitude diminishes at the sign change temperature where the concentration gradient becomes zero. The entire behavior of D is reasonable if the temperature dependence of the viscosity of the alcohols is considered.

Effect of Alcohols. In order to elucidate the effect of solvent species on the Ludwig−Soret effect of PNiPAM, S_T, D_T, and D are plotted against the number of carbon atoms of alcohol and shown in Figure 4. Alcohol solutions are divided into two series to examine the structural isomer effect which is indicated by the symbol and the line type. The solid lines with open circles indicate the alcohols composed of linear alkyl chain, while the dashed lines with filled squares represent the alcohols with branched alkyl chain, which refer to the secondary and tertiary alcohols. For methanol and ethanol the square and circle symbols are overlapping each other. Two temperatures (25 and 45 °C) are selected and shown in Figure 4. It clearly shows that the sign change behavior of PNiPAM depends on the particular alcohol. Both S_T and D_T decrease with increasing number of carbon atoms for both temperatures and change their sign with temperature in the ethanol solution. At 25 °C for the branched alcohols the S_T decreases almost linearly as shown by the dashed line, while for the series of linear alcohols we observe a curvature. While the values of S_T for 1-propanol and 2-propanol are similar for all temperatures, the values for 1-butanol and *tert*-butanol differ largely from each other at 25 °C. The structural change of the alcohols affects the thermal diffusion behavior much more at lower temperatures, and the difference is more pronounced for larger alcohols. As can be seen in the plot of D_T, the effect of the structural isomer is not expressive in comparison with the S_T. This behavior will be discussed further in terms of Hildebrand solubility parameters as described below. The diffusion coefficient D decreases with increasing number of carbon atoms of alcohols and is larger at higher temperature. For larger alcohols we observe a similar spread of the value of D as in the case of the S_T. The behavior is reasonable since the viscosity of the alcohols is smaller at high temperatures, and the viscosity of *tert*-butanol is larger than for 1-butanol.

The obtained Soret and thermal diffusion coefficient are compared with a parameter of cohesive energy density, which is also referred as the Hildebrand solubility parameter. The Hildebrand parameter represents a thermodynamic property of materials which implies the enthalpy change on mixing or the energy associated with the net attractive interactions of the material. For polar and hydrogen-bonding substances, the Hildebrand solubility parameter δ_t is practically expressed with the sum of three components as

$$\delta_t^{\,2} = \delta_d^{\,2} + \delta_p^{\,2} + \delta_h^{\,2} \qquad (4)$$

Here, δ_d, δ_p, and δ_h are the dispersion, the polar, and the hydrogen-bonding term, respectively. These parameters, in general, describe the solvent abilities of liquids which are based on a variety of chemical and physical properties. Unfortunately, these values show differences depending on determination methods.[46−48] The relationship between thermal diffusion

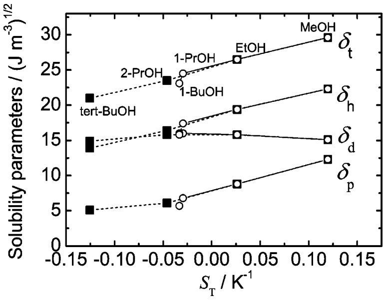

Figure 5. Soret coefficient of 10.0 g/L PNiPAM in alcohols obtained at 25 °C compared with solubility parameters of alcohols. Lines and symbols have the same meaning as in Figure 4.

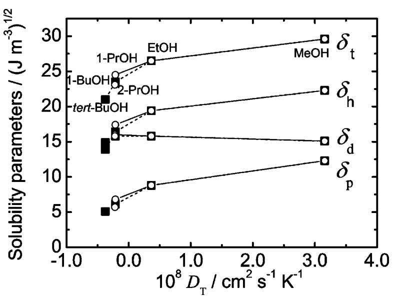

Figure 6. Thermal diffusion coefficient of 10.0 g/L PNiPAM in alcohols obtained at 25 °C compared with solubility parameters of alcohols. Lines and symbols have the same meaning as in Figure 4.

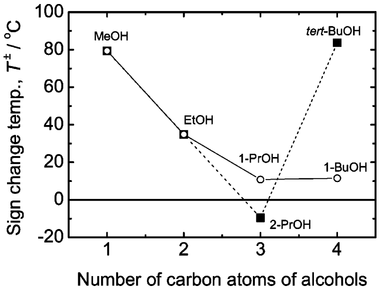

Figure 7. Sign change temperature $T^{\pm}$ of S_T and D_T plotted against the number of carbon atoms of alcohols. The symbols and lines have the same meaning as in Figure 4.

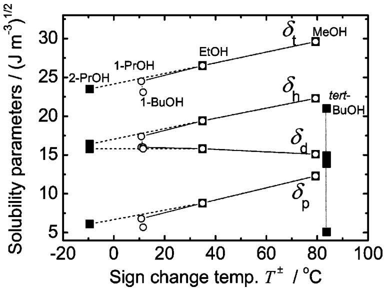

Figure 8. Sign change temperature $T^{\pm}$ plotted against Hildebrand solubility parameters. The symbols and lines have the same meaning as in Figure 4.

phenomena and the total Hildebrand solubility parameters of solvent was argued previously.[49−51] A correlation between the Soret coefficient and the cohesive energy or Hildebrand parameter is quite intuitive and has been carried out in the past.[49,50,52] It is reasonable to expect that a large difference of the Hildebrand parameters between the two components of fluid, which implies a low compatibility leads to a larger Soret coefficient. In the other words, if two components are not compatible, it is easier to drive them apart by applying a temperature gradient.

Figure 5 shows the Soret coefficient of PNiPAM in alcohols determined at 25 °C, compared with the Hildebrand solubility parameters of alcohols, which are obtained from the novel literature.[47,48] For instance, the Soret coefficient of PNiPAM in methanol was obtained as $S_T = 0.12$ K^{-1} and is presented at the abscissa, while each component of the Hildebrand solubility parameter of methanol is plotted at the ordinate. The lines and symbols have the same meaning as in Figure 4. The solubility parameters show a trend that shorter alcohols have larger values of δ_t, δ_h, and δ_p, while the δ_d is almost constant. For the studied alcohols the hydrogen-bonding term δ_h dominates the total solubility parameter. The δ_t increases almost linearly with increasing the Soret coefficient of PNiPAM throughout negative to positive S_T; i.e., larger values of S_T are obtained for the alcohol solution having a stronger net attractive interactions and stronger hydrogen-bonding capability. It is confirmed from the constant values of the dispersion term δ_d that the dispersion component is not related to the sign change behavior of S_T directly. It is interesting to mention that the S_T shows a linear relation against the total Hildebrand solubility parameter δ_t and hydrogen-bonding component δ_h in both linear and branched alcohols. In contrast to the linear relation between S_T and the Hildebrand solubility parameters, the plot of S_T vs the number of carbon atoms (Figure 4) shows large deviations between the linear and the branched alcohols. In the case for the D_T plotted against the Hildebrand solubility parameters as shown in Figure 6, the values of D_T of linear and branched alcohol solutions are lying on the curves of each component of the Hildebrand parameter. As mentioned previously, the complicated hydrophilic and hydrophobic nature of the functional group of PNiPAM is strongly related to the thermal properties. Therefore, it is expected that the sign change behavior of PNiPAM is related to the valence between δ_p, δ_h, and δ_d of alcohols. In the case of water, δ_t and δ_h are reported as 47.8 and 42.3 (J/m^3)$^{1/2}$, respectively, which are much larger than the values of methanol, whereas δ_d is 16.0 similar to alcohols and δ_p is 4.1 below *tert*-butanol. The S_T of PNiPAM in water does not show any sign change and is always positive in the similar temperature range, although the value of S_T is enhanced at the Θ-temperature and diminished at higher temperatures due to the coil−globule transition.[16] These results indicate that the dominant interactions via hydrogen bonds of water, by itself, do not lead to the negative S_T of PNiPAM in water. Therefore, it is expected that the coupling of hydrophobic interactions with hydrogen bonding is necessary to induce the sign change of S_T for PNiPAM.

Sign Change Behavior. As shown in Figure 3, a thermally induced sign change was observed only for the ethanol solution. Although for the other systems the sign change was not observed in the experimental temperature range, the sign change temperatures $T^{\pm}$ are linearly extrapolated. Figure 7 shows the sign change temperature $T^{\pm}$ as a function of the number of carbons in the alcohol. $T^{\pm}$decreases with increasing number of carbon atoms in the alcohols, except for *tert*-butanol. It indicates that the mechanism which leads to the sign change is different for *tert*-butanol compared to the other solutions. Indeed, the temperature dependence of S_T for *tert*-butanol shows an opposite slope, although D_T shows almost identical values with two propanols and 1-butanol, as shown in Figure 3. When the sign change temperature is plotted against the Hildebrand solubility parameters, it shows good linear dependence for both linear and branched alcohols, except for *tert*-butanol, which is shown in Figure 8. The apparent difference in *tert*-butanol solution could be related to its structural hindrance of hydroxide group in surrounding methyl groups of the tertiary alcohol, which might have different association mechanism with PNiPAM segments. It is, again, indicated that the coupling of hydrophobic interactions with hydrogen-bonding capability plays a key role for sign change behavior as well as thermal diffusion phenomena for the solutions of PNiPAM in alcohols.

In the recent years a sign change of S_T of polymers in pure solvents and solvent mixtures has been observed several times, when the solvent quality had been changed by varying either the temperature or the solvent composition.[27−30] The observation that the solvent quality plays a key role agrees with lattice calculations[44] and a recent simulation for a polymer represented by a generic bead−spring model.[45] Both studies showed that a better solvent quality causes a higher affinity for polymers to the cold side. Semenov and Schimpf developed a model based on a temperature-dependent osmotic pressure gradient. They predict a sign change of S_T in dependence of the Hamaker constants for the solute and the solvent.[54] Mes et al. related the thermal diffusion coefficient D_T of polystyrene in several solvents to the temperature dependence of the interaction parameter χ of the Flory−Huggins lattice theory, the concentration, and the mobility.[51] They calculated the temperature dependence of the enthalpic contribution of χ by estimating χ from the total Hildebrand solubility parameter. This approach lead to a qualitative agreement with the experimental data. It would be interesting to check whether their concept could also be applied to other polymers such as PNiPAM. This will be done in the future.

IV. Conclusions

The Ludwig−Soret effect of PNiPAM in monohydric alcohols is studied in the temperature range between 20 and 45 °C. For the methanol solution, the sign of S_T and D_T is positive, while for the solutions of 1-propanol, 2-propanol, 1-butanol, and *tert*-butanol the sign is negative. The negative sign of S_T and D_T corresponds to that PNiPAM molecules migrate to the hot side of the fluid. At room temperature the effect of structural isomer in butanol is significant for the Soret coefficient, which indicates the existing of different mechanism for thermal diffusion between 1-butanol and *tert*-butanol. Indeed, the temperature dependence of S_T shows opposite slope in the *tert*-butanol solution in comparison with other alcohols investigated in this study. The sign change temperature of S_T has a good correlation with the Hildebrand solubility parameters, except for *tert*-butanol. It is expected from the Hildebrand solubility parameters on the variation of alcohol species that the balance of hydrogen-bonding capability with hydrophobic interactions is associated with the thermal diffusion behavior of PNiPAM, and a modification of these interactions leads to a sign change of S_T for PNiPAM in alcohols.

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