Temperature Dependence of Soret Coefficient in Aqueous and Nonaqueous Solutions of Pullulan

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We present experimental results of the temperature dependence of the Ludwig-Soret effect for pullulan solutions. The Soret coefficients of 5.0 g L^{-1} pullulan in water and in dimethyl sulfoxide (DMSO) were determined in the experimental temperature range between 20.0 and 50.0 °C by means of thermal diffusion Forced Rayleigh scattering (TDFRS). The sign of the Soret coefficient of pullulan in water is negative at room temperature, which indicates that the pullulan molecules migrate to the warm side of the fluid. The Soret coefficient of pullulan increases steeply with increase of the solution temperature and shows a sign change from negative to positive at 41.7 °C. The positive sign of the Soret coefficient means the pullulan molecules move to the cold side. In contrast to the aqueous solution, the solution of pullulan in DMSO shows a very weak temperature dependence of the Soret coefficient and has always a positive sign. In addition to the TDFRS experiments, we also performed light scattering (LS) experiments for the pullulan solutions under homogeneous temperature condition in a temperature range between 20.0 and 55.0 °C. The thermodynamic properties of pullulan solutions obtained by LS show no pronounced correlation with the thermal diffusion behavior of pullulan. These results indicate the existence of a special role of interactions due to solvation on the temperature dependence of the thermal diffusion behavior of polysaccharide solutions.

Introduction

The Ludwig-Soret effect, also known as thermal diffusion, describes the transport of mass induced by a temperature gradient.[1–3] For polymer solutions, under a stationary temperature gradient, the macromolecules migrate to the cold or the warm side of the fluid and form a concentration gradient. The magnitude of the Soret coefficient of polymers is much larger than that of the mixtures composed of small molecules. This fact provides a practical application of polymer separation, for example, thermal field-flow fractionation (thFFF), which has been applied for characterization of polymer solutions.[4–6] Although the Ludwig-Soret effect of fluid mixtures has been studied for a long time since the exploring works of Ludwig and Soret, the understanding of the molecular mechanisms of the phenomena remains unclear. For complex systems such as polymer solutions and colloidal suspensions, there is no complete theory to predict the direction of the solute molecules in a temperature gradient.[7,8] Only specific aspects as the interaction contribution or charge effects in highly diluted solutions of colloidal dispersions have been considered so far.[9–14]

The Ludwig-Soret effect for a binary fluid mixture is described by the flux $\mathbf{J_1}$ of component 1 contains contributions of the concentration and the temperature gradient as follows[15]

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

Here, ρ is the density of solution, D is the translational mass diffusion coefficient, D_T is the thermal diffusion coefficient, w is the mass fraction of component 1, and T is the temperature.

In a steady state where the mass flow vanishes ($\mathbf{J_1} = 0$), the concentration gradient is given by

$$\nabla w = -S_T w(1-w)\nabla T \qquad (2)$$

where $S_T = D_T/D$ is the Soret coefficient. The sign of the Soret coefficient indicates the direction of the flux of component 1. The positive sign of S_T means that the component 1 migrates to the cold side. In general for organic polymer solutions, the polymers due to their heavier mass and larger size compared to the solvent molecules move to the cold side.[16–19]

The temperature dependence of the Soret coefficient and thermal diffusion coefficient for polymer solution is system dependent. Theoretically it has been predicted that the temperature dependence of the thermal diffusion coefficient is proportional to $1/T^2$,[20–22] however, the experimental data show a more complicated temperature dependence. For polystyrene [PS] solutions, the temperature dependence of S_T has been studied by Brimhall et al.[23] with thFFF experiment. They showed that the thermal diffusion coefficient is proportional to the temperature. Mes et al. discussed the temperature dependence of the thermal diffusion coefficient of PS solutions taking into account the thermodynamic interaction parameter χ of the Flory–Huggins equation.[24] They found a slight increase of the Soret coefficient as function of temperature. Under poor solvent conditions close to a critical temperature the Soret coefficient diverges due to the critical slowing down, but D_T remains constant.[7,25,26] For aqueous solutions of polymers the Soret coefficient shows often a complicated temperature dependence. The Soret coefficient of poly(ethylenoxide) [PEO] changes sign from negative to positive with increasing temperature for ethanol/water mixtures with a high ethanol content, while S_T is always positive for PEO in pure water.[27–30] A similar temperature dependence of the Soret coefficient has been observed for polysaccharide in

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water.[31] The Soret coefficient of dextran shows a negative value at room temperature while it is positive at higher temperatures. The addition of urea to the aqueous solution of dextran leads to an increase of S_T and the temperature dependent slope decreases, thus, the sign change temperature shifts to lower temperatures. The reason is probably that the addition of urea destroys the hydrogen bonding network.[31] Thermally induced sign changes of the Soret coefficient can also be found in the other biological polymers, proteins, and DNA.[32−34]

Poly(*N*-isopropylacrylamide) [PNiPAM] is one of the water-soluble polymers, which has been studied systematically in water and in monoalcohols.[35−37] PNiPAM in water has a Θ-temperature at 30.6 °C. At lower temperatures, water is a good solvent, while it becomes a poor solvent above the Θ-temperature. The temperature dependence of S_T shows a strong enhancement at the Θ-temperature, but the sign of S_T is always positive.[36] While for PNiPAM in alcohol solutions, S_T of PNiPAM decreases with temperature and changes the sign from positive to negative.[35,37] Here, it should be noted that the system of PNiPAM in alcohols is so far the only system, with a negative slope for the temperature dependence of S_T. All aqueous solutions mentioned above, that is, PEO, dextran, lysozyme, and DNA show a positive slope. This behavior indicates that the interactions among the polymer molecules and solvents have a key role for thermal diffusion.

Recently, the temperature dependence of the thermal diffusion behavior has been extensively studied for biopolymers, DNA, protein, and polysaccharide, which show a sign change of the Soret coefficient as function of temperature. Duhr et al. studied DNA in solution and found a sign change of S_T around 2 °C.[34] Iacopini et al. reported the Soret effect for lysozyme solutions which show a sign change of S_T from negative to positive with increasing temperature.[32,33,38] Sugaya et al. reported a sign change for dextran in water.[31] It is interesting to study the relationships between physiological functions and thermal diffusion of biological polymers, because the biopolymers play their functions under complex conditions subjected to various fields. However, the number of studies of the Ludwig-Soret effect for biological polymers are limited.

In this study, we will report the experimental study of the Ludwig-Soret effect for solutions of pullulan, which is one of the standard samples of polysaccharide. It is composed of α-D-(1→6)-linked maltotriose. To study the contribution of the hydrogen bonding on Ludwig-Soret effect of pullulan, water, and dimethyl sulfoxide [DMSO] were used as solvent. DMSO is a polar aprotic solvent that does not form hydrogen bonds. Pullulan and dextran, both of them are composed of glucose as basic constituent, but have different glycosidic bonds on their chains. Therefore, it might give some insight into the contribution of hydrogen bonds to the thermal diffusion behavior. Additionally, we studied the solution properties of pullulan under homogeneous temperature condition by light scattering (LS), which yields fundamental properties such as the mass and size of the polymers and the thermodynamic parameters of the solutions.

Experimental Section

Materials. Pullulan (Hayashibara Co., PF20) was purified three times by a methanol precipitation from the aqueous solutions. The molar mass of pullulan was measured in water by static LS and we obtained $M_w = 440$ kg/mol. Distilled and deionized water was prepared by a Milli-Q system. DMSO of an analytical grade was used as solvent without further purification. For the thermal diffusion forced Rayleigh scattering (TDFRS) measurements 5.0 g L^{-1} pullulan in water and in DMSO
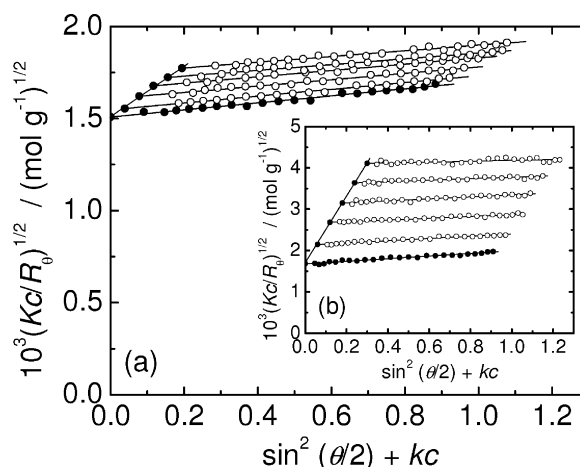

Figure 1. Typical results of LS experiments. Berry plot for pullulan in water (a) and pullulan in DMSO (b) measured at 25.0 °C.

were prepared. To achieve a sufficient absorption of the laser light we added a small amount of the dye, Basantol Yellow (BASF) or quinizarin (Sigma-Aldrich).

Methods. The experimental setup of TDFRS has been described in detail elsewhere.[39] In brief, the optical grating is written by the interference of two beams of the argon ion laser (λ = 488 nm). The interference grating is read out by a He−Ne laser (λ = 632.8 nm). The intensity of the diffracted beam was measured by a photomultiplier. A mirror mounted on a piezocrystal was used for phase shifting and stabilization to obtain the heterodyne signal. The TDFRS measurements were carried out in the temperature range from 20 to 50 °C. The temperature of the sample cell was controlled by circulating water from a thermostat bath with an uncertainty of 0. 01 °C. The sample solutions were filtered directly into the optical quartz cell with 0.2 mm path length through 0.22 μm membrane filter.

Light scattering (LS) experiments were carried out in an angular range of 25° < θ < 150°. A He−Ne laser with a wavelength of λ = 632.8 nm was used as light source. The correlation function of scattered light $g^{(2)}(t)$ was obtained with an ALV-6000E correlator. The measurements were carried out in a temperature range from 20 to 55 °C. The temperature of the sample cell was controlled by a circulating water bath with an uncertainty of 0. 02 °C. All samples were kept at the measurement temperature for at least one hour to ensure thermal equilibrium before starting the data acquisition. The concentrations of pullulan in water were prepared in the range of 0.49 to 2.43 g L^{-1} and for pullulan in DMSO were prepared in the range of 2.00 to 9.99 g L^{-1}.

The refractive index increments with respect to the mass fraction (∂n/∂w) and to the temperature (∂n/∂T) need to be determined for evaluation of S_T and D_T in the TDFRS experiment. Here, w denotes the mass fraction of the polymer in solvents. To analyze the static LS experiment, the derivative of the refractive index with concentration (∂n/∂c) is typically used. The concentration c in g cm^{-3} can be recalculated from the mass fraction w. The refractive index increments (∂n/∂T) and (∂n/∂w) of pullulan in water and in DMSO were measured with a scanning Michelson interferometer operating at a wavelength of 632.8 nm.[40] The value of (∂n/∂T) was obtained from interference signals in the temperature range of ±0.5 °C around the desired temperature.

Results and Discussion

Laser Light Scattering. To characterize the solution properties of pullulan in water and in DMSO, we performed static and dynamic LS measurements in a temperature range of 20 < T_e/°C < 55 (pullulan in water) and 20 < T_e/°C < 40 (pullulan in DMSO). The refractive index increments with respect to the concentration for pullulan in water and in DMSO were obtained
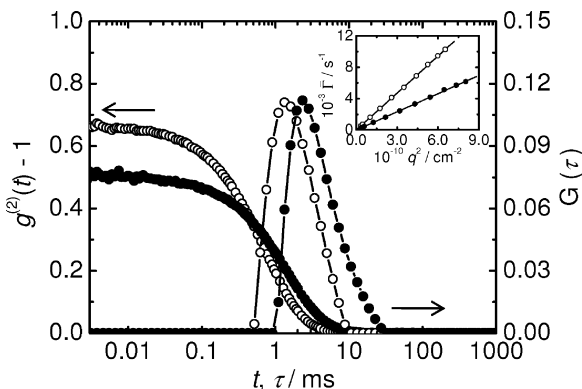
Figure 2. Typical correlation function of scattered light $g^{(2)}(t)$ and the distribution function $G(\tau)$ obtained by DLS for 5.0 g/L pullulan in water (○) and in DMSO (●) at $T_e = 25.0$ °C and $q = 30°$. The inset shows the average decay rate $\bar{\Gamma}$ as a function of scattering vector q^2.
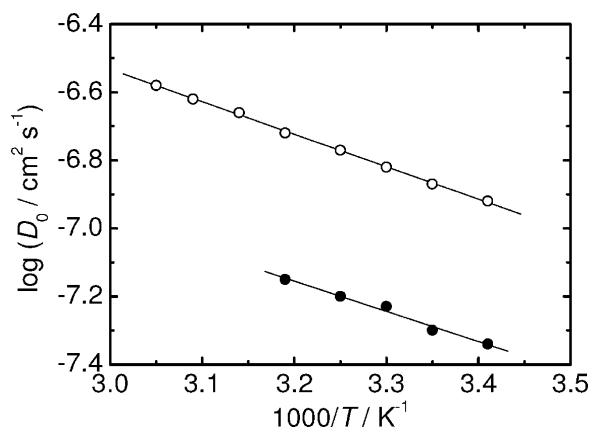

Figure 3. Plots of log D_0 as a function of the inverse of the temperature, $1/T$ for pullulan in water (○) and pullulan in DMSO (●) obtained by DLS experiment.

as $(\partial n/\partial c) = 0.131 \pm 0.004$ and $(\partial n/\partial c) = 0.059 \pm 0.010$ cm^3 g^{-1}, respectively. Here, the uncertainty denotes one standard deviation. Figure 1 shows a typical result of static LS for pullulan in water and in DMSO. The filled circles represent the extrapolated values to the zero concentrations and to the zero scattering angles. The parameters obtained by an ordinary analysis[41] were tabulated (Table S1, Supporting Information). Figure 2 shows typical results of a dynamic LS experiment for pullulan in water and in DMSO. The distribution functions $G(\tau)$ of the relaxation time τ is obtained by a CONTIN analysis.[42,43] The results indicate that the pullulan is monodisperse with a polydispersity index of $\mu_2/\bar{\Gamma}^2 \approx 0.3$, which was obtained by a third cummulant expansion to the decay rate. The inset of Figure 2 shows the average decay rate $\bar{\Gamma}$ as a function of the scattering vector q^2. The obtained parameters such as the translational diffusion coefficient D_0 at zero concentration and the hydrodynamic radius R_h are also tabulated (Table S1, Supporting Information).

In the investigated temperature range, the averaged expansion factor R_g/R_h of the polymer chain is $R_g/R_h = 1.81 \pm 0.02$ and 1.61 ± 0.05 for water and DMSO solutions, respectively. This result is typical for flexible coils in a good solvent with a broad molecular weight distribution. Our results are also in good agreement with previous reports.[44−46] The averaged second virial coefficient is $A_2 = 1.6 \times 10^{-4}$ cm^3 mol g^{-2} for pullulan in water and $A_2 = 4.1 \times 10^{-4}$ cm^3 mol g^{-2} for pullulan in DMSO. Therefore, both solvents can be regarded as good solvents. The chain dimensions and the other parameters are

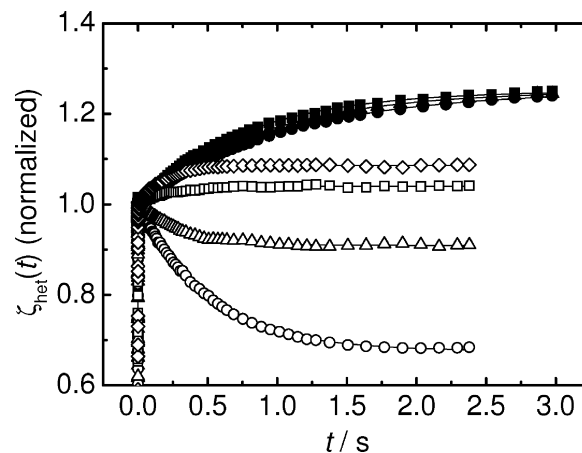**Figure 4.** Normalized heterodyne signals ζ_{het} of TDFRS experiment for 5.0 g/L pullulan in water (open symbols) and in DMSO (filled symbols) at different temperatures. The temperatures are 25.0 °C (○,●), 35.0 °C (△,▲]), 45.0 °C (□,■), and 50.0 °C (◇). The solid lines on the part of concentration signal refer to the fitting function according to eq 4.

almost constant in the experimental temperature range. The LS experiments revealed that the molecular parameters of pullulan in water and DMSO show no significant temperature dependence in comparison with the anomalous behavior of the Soret coefficient as mentioned below. The sample concentrations for LS and TDFRS experiments are in the same range, which allows us to compare these experimental results directly in respect to the concentration effect.

We plotted the translational diffusion coefficient D_0 obtained by DLS measurements as function of temperature. As shown in Figure 3, the logarithm of D_0 decreases linearly as function of the inverse temperature. The magnitude of the diffusion coefficient of pullulan in water is larger than that of pullulan in DMSO due to the difference in the solvent viscosity ($\eta_{water} = 0.89$ and $\eta_{DMSO} = 1.99$ mPa·s at 25 °C). The slope is the same for both solutions and the temperature dependence can be described by an Arrhenius type equation as

$$D_0 = D_{0,c} \exp\left(-\frac{E_D}{RT}\right) \tag{3}$$

where $D_{0,c}$ is a constant, R is the gas constant, and E_D is the activation energy for diffusion. The activation energy E_D was obtained by a least-squares-fit to eq 3 as $E_D = 18.1 \pm 0.4$ kJ mol^{-1} for pullulan in water and $E_D = 16.6 \pm 1.3$ kJ mol^{-1} for pullulan in DMSO. The uncertainty corresponds to one standard deviation. The activation energy shows no significant difference for both solutions. The observed temperature dependence in the dilute concentration range is in good agreement with previous study.[45]

Thermal Diffusion of Pullulan. The normalized heterodyne signals ζ_{het} of the TDFRS experiment of 5.0 g L^{-1} pullulan in water and in DMSO as a function of the temperature are shown in Figure 4. Open and filled symbols refer to solutions of pullulan in water and in DMSO, respectively, and different shapes of the symbols designate different temperatures. The rapid increase of the normalized heterodyne signal $\zeta_{het}(t)$ corresponds to the establishment of the temperature gradient in a 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 within a time scale of seconds. For
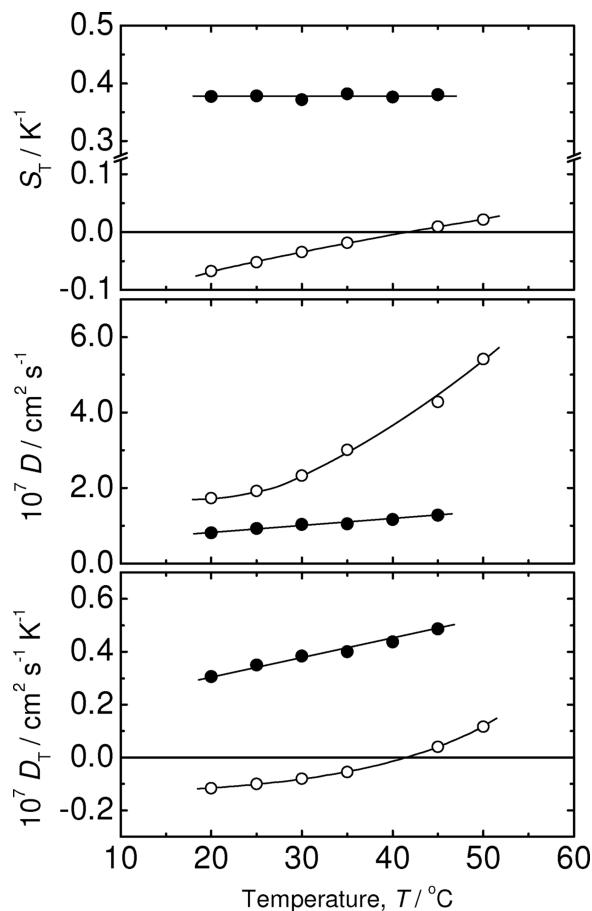
Figure 5. Temperature dependence of Soret coefficient S_T, translational diffusion coefficient D, and thermal diffusion coefficient D_T of 5.0 g/L pullulan in water (○) and in DMSO (●) obtained by TDFRS.

pullulan in water, the curvature of the signal changes its direction from downward to upward with increasing temperature. The turnaround of the signal corresponds to the sign change of the Soret and the thermal diffusion coefficient, whereas the signals $\zeta_{het}(t)$ of pullulan in DMSO show an increase and the curves for all temperatures overlap. This indicates that there is no significant temperature dependence for the formation of a concentration gradient.

The normalized heterodyne signal $\zeta_{het}(t)$ is related to the Soret coefficient S_T and the translational diffusion coefficient D as follows

$$\zeta_{het}(t) = 1 + \left(\frac{\partial n}{\partial T}\right)^{-1}\left(\frac{\partial n}{\partial w}\right)S_T w(1-w)[1-\exp(-q^2 Dt)]$$

(4)

Here, t is the time, n is the index of refraction, and q is the scattering vector.[47] Figure 5 shows the temperature dependences of the Soret coefficient S_T, translational diffusion coefficient D, and thermal diffusion coefficient D_T of 5.0 g/L pullulan in water and in DMSO. Here, S_T and D were obtained by a nonlinear least-squares fit of the concentration part of $\zeta_{het}(t)$ signal to eq 4 with the contrast factors, $(\partial n/\partial T)$ and $(\partial n/\partial w)$. The contrast factor $(\partial n/\partial T)$ of pullulan solutions were determined by a Michelson interferometer are presented as $(\partial n/\partial T)/K^{-1} = 9.5759 \times 10^{-3} - 8.2729 \times 10^{-5}T + 2.3863 \times 10^{-7}T^2 - 2.3491 \times 10^{-10}T^3$ for 5.0 g L^{-1} pullulan in water in the experimental temperature range of $20 < T_e/°C < 50$ and $(\partial n/\partial T)/K^{-1} = $

$-8.1970 \times 10^{-3} + 7.3633 \times 10^{-5}T - 2.3300 \times 10^{-7}T^2 + 2.4579 \times 10^{-10}T^3$ for 5.0 g L^{-1} pullulan in DMSO in the experimental temperature range of $20 < T_e/°C < 40$. The refractive index increments with respect to the mass fraction were obtained as $(\partial n/\partial w) = 0.131 \pm 0.004$ for pullulan in water and $(\partial n/\partial w) = 0.056 \pm 0.010$ for pullulan in DMSO. The thermal diffusion coefficient D_T was calculated using the relation $D_T = S_T D$.

As shown in Figure 5 we observe negative Soret coefficients at low temperatures for pullulan in water. The negative sign of S_T implies that the pullulan molecules move to the warm side. The Soret coefficient S_T increases with increasing temperature and the thermally induced sign change occurs at 41.7 °C. Contrary, the solution of pullulan in DMSO shows a positive sign of S_T for all temperatures and no significant temperature dependence. The translation diffusion coefficient D and the thermal diffusion coefficients D_T of pullulan increase with increasing temperature for aqueous and DMSO solutions. The diffusion coefficients D of 5.0 g/L pullulan at 25.0 °C obtained by TDFRS experiment is $D = (1.92 \pm 0.09) \times 10^7$ cm^2 s^{-1} for water solution and $D = (0.92 \pm 0.18) \times 10^7$ cm^2 s^{-1} for DMSO solution. These values agree within 12% with those obtained from DLS measurement as $D = 1.71 \times 10^7$ cm^2 s^{-1} for 5.0 g L^{-1} pullulan in water solution and $D = 0.81 \times 10^7$ cm^2 s^{-1} for 5.0 g L^{-1} pullulan in DMSO, respectively. Although both LS studies of pullulan in water and in DMSO do not show any significant temperature dependence of their thermodynamic properties, the temperature dependence of S_T and D_T of pullulan differs substantially in water and DMSO. A similar behavior has also observed for solutions of PNiPAM in ethanol, where the Soret coefficient also changes its sign, while the solvent quality is good for all investigated temperatures.[35] These results indicate that the behavior of thermally induced sign change of Soret coefficient has no direct correlation with the solubility properties determined by LS under homogeneous temperature conditions. This observations is in contrast with the results for PEO in ethanol/water mixtures. For this system, a negative Soret coefficient in mixtures with a low water content correlates with bad solvent conditions. While a positive Soret coefficient in pure water corresponds with good solvent conditions.[28]

In general, an increase in solution temperature weakens the formation of hydrogen bonds, thus, the negative sign of S_T might be correlated with the strength of the water solvation layer surrounding polymers. This hypothesis is supported by the observations for pullulan in DMSO, which is a polar aprotic solvent not forming hydrogen bonds with the polymer. Here, the S_T is positive and we do not observe any significant temperature dependence of S_T. An analogous behavior of S_T was reported in the other polysaccharide solution, dextran.[31] Dextran is mainly composed of α-(1→6)-linked glucose with some short α-(1→3)-linked glucose branch units. It should be noted that pullulan and dextran are composed of the same smallest constituent, glucose, but they have different glycosidic bonds to their chains. Both of them are physiologically inactive biopolymers and water-soluble, and fundamental solution properties have been studied well.[45,46] In Figure 6, the S_T of different dextran solutions is plotted in comparison with the results of pullulan in water and in DMSO. Dextran in water (■) shows a sign change at 45 °C from negative to positive with increasing temperature. The results are comparable with the results of the pullulan in water (○). Only the slope is slightly steeper compared to the dextran system. The agreement of the temperature dependence of S_T could be originated from chemical contributions of glucose as their smallest constituent. For dextran
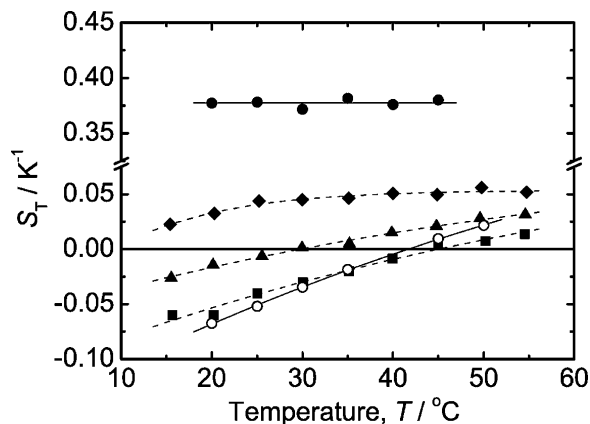
Figure 6. Soret coefficient S_T of pullulan in water (○) and pullulan in DMSO (●), dextran in water (■), dextran in 2 M urea/water (▲), and dextran in 5 M urea/water (◆). The results of dextran solutions are obtained by ref 31 and the molecular mass of the dextran is reported as $M_w = 86.7$ kg mol^{-1}. The concentration of polysaccharides is 5.0 g/L for all solutions. The curves are fitted functions according to eq 5.

solutions the addition of urea leads to an increase of S_T and the sign change temperature shifts to lower temperatures. It may be assumed that urea destroys the hydrogen bonding ability, thus the addition of urea shifts the Soret coefficient of pullulan toward more positive values. The effect has the same tendency as an increase of the solution temperature, which also destroys the solvation structure. In other words, the negative sign of S_T for polysaccharides is the result of formation of a solvation structure via hydrogen bonds.

The magnitude of the Soret coefficient of dextran does not depend on the concentration in the diluted concentration range.[31] Also, the temperature dependent sign change of the Soret coefficient of poly(*N*-isopropylacrylamide) in ethanol is independent of the concentration in range from 0.2−5.0 g/L.[35] We expect for pullulan solutions that there is no significant concentration dependence of the Soret coefficient because pullulan in water shows a very similar temperature dependence as the Soret coefficient of dextran in water. LS experiments for pullulan solution revealed that the size of pullulan and the second virial coefficient of the pullulan solutions do not show a temperature dependence in the experimentally investigated temperature range. The apparent difference of the temperature dependence of the obtained quantities between LS and TDFRS experiment indicates that the slope of the temperature dependence of the Soret coefficient is not related to simple physical quantities such as size, mass of molecules, and second virial coefficient. Although the second virial coefficient describes the polymer−solvent interactions, it is only a first order approximation and is apparently for these polar systems not capable to describe the thermal diffusion behavior, which is a more subtle second order cross effect. As in the case of the aqueous and the nonaqueous solutions of dextran with and without urea, the solvation by the surrounding water molecules will be essential. It is expected that pullulan has a layer of solvated water molecules, which are also in contact with the bulk water. Apparently the thermal diffusion properties probed in the TDFRS experiment are more sensitive to subtle changes in the water structures than the properties measured in the LS experiment. The changes in the water structure could be examined by means of the other experiments studying dynamics such as NMR, IR, dielectric relaxation spectroscopy, or the other methods, but so far there are no data available in the literature.

Our preliminary experiments for the aqueous solutions of monosaccharides, disaccharides, and trisaccharides show that they have a positive sign of S_T and do not show any sign change in the same experimental temperature range. These results indicate that the sign change behavior of S_T depends on molecular mass of polysaccharides. Similar observation is reported on various solutions of polystyrene and its monomer and oligomers by Köhler et al.,[48] where the magnitude of S_T of monomers tend to be small and sometimes show opposite sign of S_T in comparison with longer chains of polystyrene. As another aspect for the sign change behavior, the sign change temperatures of the aqueous solutions of pullulan and dextran are at 41.7 and 45.0 °C. Brenner suggested that the sign change behavior for low molecular mixtures is associated with the thermal expansion of water.[49] However, we do not find any correlation for aqueous polysaccharide solutions between the thermal expansion coefficient of the solvent and the sign change temperature as suggested by Brenner.

The curves describing the temperature dependence of S_T in Figure 6 were obtained by a least-squares fit to the empirical equation proposed by Iacopini and Piazza as[32]

$$S_T(T) = S_T^\infty \left[1 - \exp\left(\frac{T_{inv} - T}{T_0}\right) \right] \quad (5)$$

Here, S_T^∞ represents a saturation value of S_T at high temperatures, T_{inv} is the temperature where S_T changes the sign, and T_0 indicates the strength of temperature effects. The obtained parameters for the pullulan and the dextran solutions are tabulated in Table 1. Furthermore, the parameters of S_T^∞, T_{inv}, and T_0 obtained for several polymers, which show a sign change of S_T as a function of temperature, were collected from literatures and are also listed in Table 1. As shown in the list, a sign change of S_T with temperature has been found for some proteins, lysozyme, and β-lactoglobuline, as well as DNA and synthetic polymers of PEO and PNiPAM. The solvents, polymer concentrations, and the other experimental conditions are also listed. An overview of all systems is shown in Figure 7 where the figure is divided into two parts for clarity. The numbers in the figures and in parentheses in the subsequent paragraphs refer to the systems that are listed in Table 1.

There are three groups that can be divided by the slope of S_T against temperature. First group shows positive slope including pullulan/water (1), dextran/water (3), dextran/urea/water (4,5), lysozyme/salts/buffer solution (6,7), β-lactoglobuline/NaCl/buffer solution (8), DNA/buffer solution (9−11), and PEO/ethanol/water (12−14), as shown in Figure 7a. The second group with a negative slope of S_T consists of PNiPAM/methanol (16), PNiPAM/ethanol (17), PNiPAM/1-propanol (18), and PNiPAM/1-butanol (19) in Figure 7b. For PNiPAM in alcohols, the increase of hydrophobic strength such as in the series methanol, ethanol, propanol, and 1-butanol, leads to a decrease in the Soret coefficients with increasing temperature. The systems have a weak hydrogen bond capability and complicated hydrophilic and phobic balance of PNiPAM might be the origin of the negative slope. It indicates a different mechanisms for the sign change compared to the other aqueous mixtures. Rigorously speaking, some of them do not show a sign change in the experimentally investigated temperature range T_e, but the extrapolated values of sign change temperature could be obtained by a least-squares fit to eq 5. As a third group, pullulan/DMSO (2) and PNiPAM/water (15) are also plotted in Figure 7b, it is hard to predict a sign inversion temperature because of

Table 1. Values of S_T^∞, T_{inv}, and T_0 Obtained from Eq 5 for Various Synthetic Polymer and Biopolymer Solutions[a]

solute	solvent	concentration (g L^{-1})	S_T^∞ (K^{-1})	T_{inv} (K)	T_0 (K)	numbers refer to the curve in Figure 7	ref.
pullulan	water	5.0	0.23	314.8	84.9	1	this work
	DMSO	5.0				2	this work
dextran	water	5.0	0.13	318.2	71.4	3	31
	2 M urea/water	5.0	0.10	302.9	63.5	4	31
	5 M urea/water	5.0	0.05	282.5	11.1	5	31
lysozyme	400 mM NaCl/water (pH = 4.65)	7	0.0143	296.0	21	6	32
	100 mM NaCl/water (pH = 7.1)	10	0.0125	296.0	18	7	33
β-lactoglobuline	50 mM NaCl/water (pH = 7.0)	13	0.0385	294.3	38	8	38
plasmid DNA (6.7 kbp)	7.5 mM phosphate buffer (pH = 7.0)	0.6	0.3068	290.4	16	9	38
λ-DNA (50 bp)	1 mM Tris buffer (pH = 7.6)	<0.03	0.2333	274.4	101	10	34
λ-DNA (10 kbp)	1 mM Tris buffer (pH = 7.6)	<0.03	0.7345	278.1	10	11	34
PEO	water	5	0.1623	286.2	2	12	29
	EtOH/water (0.1/0.9 in weight)	5	0.1166	275.8	20	13	29
	EtOH/water (0.2/0.8 in weight)	5	0.1813	310.4	76	14	29
PNiPAM	water	1.0				15	36
	MeOH	10.0	0.1642	333.6	−26	16	37
	EtOH	10.0	−0.0882	307.0	34	17	37
	1-PrOH	10.0	−0.1096	285.8	40	18	37
	1-BuOH	10.0	−0.7646	284.9	345	19	37

[a] The fitting parameters S_T^∞, T_{inv}, and T_0 are obtained by a scanning and digitizing figure of photocopied articles, thus, the values might have a slight deviation from the original data of respective authors.
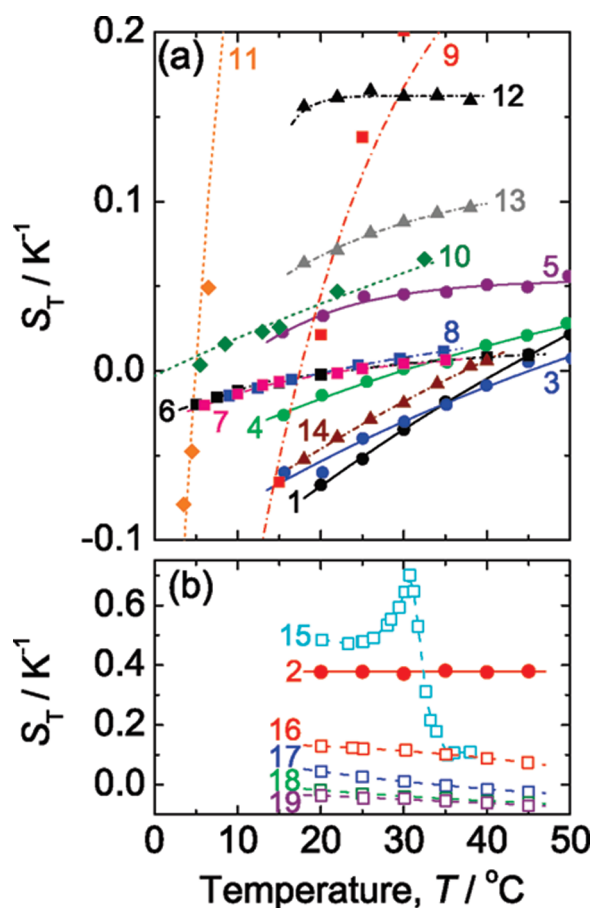

Figure 7. Soret coefficient S_T for various solutions as a function of temperature. Curves are drawn using eq 5 with fitting parameters, S_T^∞, T_{inv}, and T_0, listed in Table 1. The numbers refer to the systems that are also listed in Table 1.

the very weak temperature dependence in the case of pullulan/ DMSO and the nonmonotonic behavior of PNiPAM/water.

The temperature dependence of the Soret coefficient is proportional to $1/T^2$ for the binary mixture theoretically.[20−22] For aqueous solution, it is suggested that sign change of S_T is related to the thermal expansion of water.[38,49] Systematic experiments for low molecular mixtures show that the Soret coefficient is proportional to the temperature.[50,51] The recent investigation of associated mixtures showed that for many systems the Soret coefficient isotherms intersect.[52] For some systems, such as ethanol/water and DMSO/water, the intersection point is identical with the concentration where the Soret coefficient changes its sign and the hydrogen bond network breaks.[53] At concentrations above this intersection concentration, the Soret coefficient increases and, below S_T, decreases with increasing temperature. Depending on the concentration, low molecular weight mixtures show either an increase or a decrease, as observed for aqueous polymer solutions displayed in Figure 7.

If one focuses on biopolymers such as polysaccharide (1, 3−5), protein (6−8), and DNA (9−11), all three types of polymers have a positive slope of S_T and show a sign change. The behavior is well described with the eq 5 proposed by Iacopini and Piazza.[32] It should be mentioned that the saturation values S_T^∞ and the slope of S_T of the polysaccharides are apparently large in comparison with the other systems showing positive slopes such as proteins (6−8) and PEO (12−14), as can be seen in Figure 7a, except for DNA (9−10). The magnitude of the Soret coefficients of proteins are very small $S_T^\infty < 0.03$ K^{-1}. The studied aqueous solutions of pullulan and dextran are binary systems, while the other systems are ternary or multicomponent systems contain salts and buffer components or alcohol. It indicates that the charges or the additional ingredients to the solution may lead to a modification or disturbance of the local structure of water and which may induce a decrease of the magnitude of S_T as well as a change of the slope of S_T against temperature. In fact, pullulan in DMSO (2) and dextran in urea/water (4,5) show a weaker temperature dependence of the Soret coefficient than the binary aqueous solutions of pullulan (1) and dextran (3). Probably the positive slope of the temperature dependence of the Soret coefficient is associated with the interactions between segments and water, that is, the solvation is necessary to have a positive slope of S_T, which eventually leads to a negative sign at low temperatures. The 10 kbp λ-DNA (11) and 6.7 kbp plasmid DNA (9) solutions show a strong temperature dependence of the Soret coefficient. In these systems the effect of charges on DNA has to be accounted for.[32,34] This feature is of great interest for utilizing
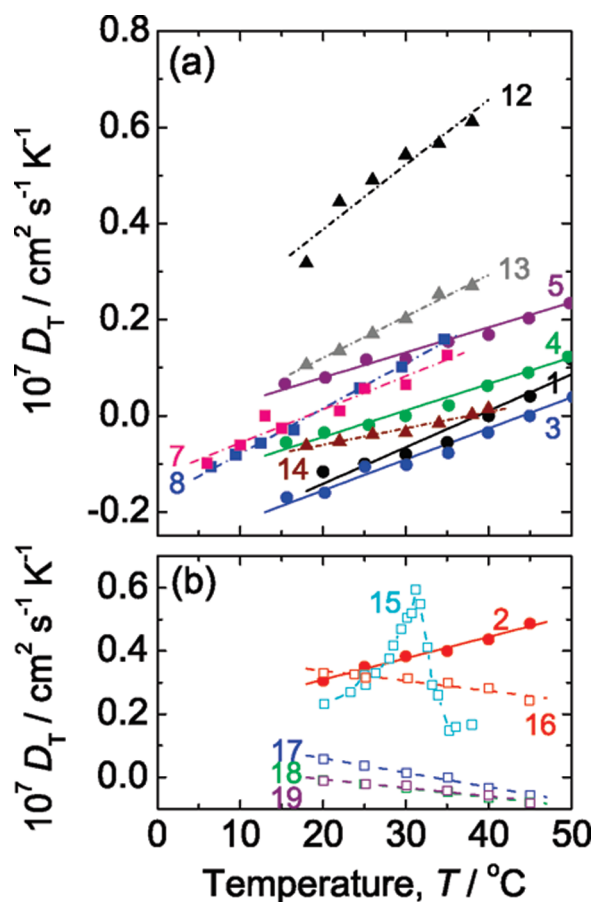
Figure 8. Thermal diffusion coefficient D_T for various solutions as function of temperature. The lines are obtained by fitting of a linear regression, except for PNiPAM in water. The numbers are the same meaning with Figure 7 and listed in Table 1.

this property to develop a new PCR method[54] and for studying DNA denaturation in the presence of urea.[55]

Figure 8 shows the thermal diffusion coefficient D_T for several aqueous solutions of polymers mentioned above. The numbers in the figure refer to the systems listed in Table 1. For some solutions, that is, lysozyme (6), plasmid DNA (9), and λ-DNA (10,11), no D_T values are available. In general, D_T shows a linear temperature dependence, although some systems such as PEO show slight systematic deviations. A clear exception for a linear temperature behavior is PNiPAM in water (15) due to its coil−globule transition. The thermal diffusion coefficient of PNiPAM is enhanced approaching to the Θ-temperature. The protein and polysaccharide solutions show a positive slope of D_T with temperature, while D_T of PNiPAM in various alcohols (16−19) has a negative slope. This indicates the existence of a different mechanism for the temperature dependence of the thermal diffusion process for this system, which is as mentioned above due to its hydrophilic and phobic nature. For dextran in urea/water (3−5), the slope of D_T decreases with increasing urea content. The same tendency is observed for PEO in ethanol/water (12−14) where the slope decreases with increasing ethanol content. These results indicate that the water structure is modified or disturbed by the addition of urea and/or ethanol, which leads to a weaker temperature dependence of D_T. Other studies as the denaturation of proteins showed that the addition of urea has a similar effect as an increase of the temperature.[54] Therefore, it is reasonable to assume that the weaker temperature dependence is a consequence of the fact that already part of the hydrogen bonds have been destroyed by the addition of urea,

so that the temperature has a smaller effect on the system. Although there are too few systematic measurements for protein and DNA solutions at this stage, it is expected that the thermal diffusion behavior is also influenced by charge effects in addition to properties such as mass and size of molecules. So far there are not enough thermal diffusion data for biological polymers, thus, further experimental and theoretical studies on biopolymer solutions are necessary to understand the mechanisms of temperature dependence of the thermal diffusion behavior.

Recently, Stadelmaier and Köhler reported the effect of hydrodynamic interactions with respect to the molecular weight dependence, where the sign change of the Soret and the thermal diffusion coefficient is revealed to correlate with the persistence length of the polymer chain.[48] This result is comparable with the simulation study by Zhang and Müller-Plathe.[56] These studies are important to understand the mechanisms of the sign change nature. Similar studies are desired for biopolymer solutions.

Conclusion

The Ludwig-Soret effect of pullulan in water and in DMSO is studied in a temperature range of $20 < T_e/°C < 50$ in water $20 < T_e/°C < 40$ in DMSO. The thermally induced sign change of the Soret coefficient was found at a temperature of 41.7 °C for aqueous solutions of pullulan. For temperatures above 41.7 °C pullulan molecules migrate toward the cold side ($S_T > 0$), whereas below 41.7 °C pullulan molecules migrate toward the hot side ($S_T < 0$). Contrary, for pullulan in DMSO, where DMSO is a polar aprotic solvent, the sign of S_T is always positive and shows no significant temperature dependence. These results imply that the thermal diffusion of polysaccharide is associated with the strength of the hydrogen bond capability of polysaccharide solutions. Biopolymers involving polysaccharide, protein, and DNA show a positive slope of the Soret coefficient and the thermal diffusion coefficient against temperature. The observed sign change behavior of S_T is well expressed by an empirical function proposed by Iacopini and Piazza. Binary solutions of polysaccharide in water have a strong temperature dependence and large saturation values of the Soret coefficient in comparison with protein solutions. This behavior might arose from the solvation characteristics of the systems or the influence of charges present in the protein solutions. Probably the positive slope of the temperature dependence of the Soret coefficient is associated with the interactions between segments and water, that is, the solvation is necessary to have a positive slope of S_T, which eventually leads to a negative sign at low temperatures.

Supporting Information Available. Obtained parameters of pullulan in water and in DMSO measured by static and dynamic light scattering are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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