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PAPER

Temperature dependence of thermal diffusion for aqueous solutions of monosaccharides, oligosaccharides, and polysaccharides

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We studied the thermal diffusion behavior for binary aqueous solutions of glucose, maltotriose, maltohexaose, pullulan, and dextran by means of thermal diffusion forced Rayleigh scattering (TDFRS). The investigated saccharides with molar masses between 0.180 and 440 kg mol^{-1} were studied in the temperature range between 15 and 55 °C. The thermal diffusion coefficient D_T and the Soret coefficient S_T of all solutions increase with increasing temperature. For maltohexaose and the polymers the thermal diffusion coefficient changes sign from negative to positive with increasing temperature, whereas glucose and maltotriose show only positive values in the entire investigated temperature range. While we were able to find a master curve to describe the temperature dependence of D_T, we were not able to find a similar expression for S_T. This comprehensive study allows for the first time the determination of the interaction parameters for the polymer and the solvent within the theoretical framework suggested by Würger [*Phys. Rev. Lett.*, 2009, **102**, 078302].

1 Introduction

The diffusion of fluid mixtures has been studied extensively by experiments, theories, and computer simulations.[1,2] For a binary system under isothermal conditions, the diffusion of the solute molecules can be driven by a composition gradient well-known as Fick's law. Brownian motion is the origin of the fluctuation of molecules which results in the diffusion of solute molecules. The diffusion coefficient of a polymer in solution is usually determined by dynamic light scattering[3] and is related to the friction of the solute by the Stokes–Einstein relationship as

$$D(T) = \frac{k_B T}{6\pi\eta r}, \tag{1}$$

where r is the radius of the solute and η is the solvent viscosity. In the case of polymers the hydrodynamic radius R_h is used instead of r.[4] This equation indicates that the temperature dependence of the diffusion coefficient $D(T)$ relates to the product of the temperature T and the temperature dependence of the viscosity $\eta(T)$. On the other hand the diffusion coefficient D of polymers is related to the number of monomers N by $D \propto N^{-\nu}$ where the exponent ν depends on the chain expansion due to segment–solvent interactions.

For mixtures subjected to a temperature gradient at a constant pressure, one observes a diffusion current of the solute as a nonisothermal effect.[5] This is known as thermal diffusion or the Ludwig–Soret effect which leads to the formation of a concentration gradient.[6–8] In the case of a binary mixture, the flux of the solute $\boldsymbol{J}$ is phenomenologically described by the sum of two driving forces ∇w and ∇T as[5]

$$\boldsymbol{J} = -\rho D \nabla w - \rho w(1 - w) D_T \nabla T. \tag{2}$$

Here, w and ρ denote the solute weight fraction and the density of the solution, respectively. D and D_T are the mutual diffusion coefficient and the thermal diffusion coefficient, respectively. In a steady state where the mass flow vanishes ($\boldsymbol{J} = 0$), the concentration gradient is given by

$$\nabla w = -S_T w(1 - w) \nabla T. \tag{3}$$

Here, S_T ($= D_T/D$) is the Soret coefficient. The sign of the Soret coefficient indicates the direction of the flux of the solute. The positive sign of S_T means that the solute migrates to the cold side.[9] In general for organic solutions of polymers, the polymers move to the cold side due to their heavier mass and larger size in comparison with the solvent molecules.[10–13]

Due to the difficulty of nonisothermal conditions, there are fewer experimental studies on the thermal diffusion coefficient D_T and the Soret coefficient S_T compared to measurements of the mutual diffusion coefficient D. Especially, for aqueous solutions of biopolymers the number of publications is small, although the contributions of the Ludwig–Soret effect to biological processes are of general interest. Recently, the Ludwig–Soret effect of DNAs, proteins, and polysaccharides has been studied systematically.[14–19] One of the characteristics of the biopolymers is a sign inversion of D_T and S_T as a function

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of temperature.[19] Typically, the sign of D_T and S_T is negative at lower temperatures, and the sign changes from negative to positive with increasing temperature. The negative sign means that the polymers migrate to the hot side of the fluid. Only for the water soluble poly(*N*-isopropylacrylamide) [PNIPAM] in alcohols a negative slope of $S_T(T)$ and $D_T(T)$ with temperature has been found. For these systems a sign inversion from positive to negative with increasing temperature is observed,[20,21] while the Soret coefficient of PNIPAM in water is always positive.[22] Piazza and co-authors suggested an empirical equation as follows[14,23,24]

$$S_T(T) = S_T^{\infty}\left[1 - \exp\left(\frac{T_{\mathrm{inv}} - T}{T_0}\right)\right] \tag{4}$$

to describe the temperature dependence of S_T. Here, S_T^{∞} represents a saturation value of S_T at high temperature, T_{inv} is the temperature where S_T changes the sign, and T_0 indicates the strength of temperature effects. This rather universal behavior holds for various systems, not only for colloidal suspensions but also for water soluble polymers.[19] Recently, Piazza and co-authors reported a scaled temperature dependence of S_T for colloidal systems as follows,[25]

$$\frac{S_T(\tilde{T})}{S_T^{\infty}} = 1 - \exp[A(1 - \tilde{T})]. \tag{5}$$

Here, $\tilde{T}$ is defined as $\tilde{T} = T/T_{\mathrm{inv}}$ and A is a dimensionless parameter as $A = T_{\mathrm{inv}}/T_0$. Although the physical meaning of the parameter A is still an open question, it is considered that the equation describes a universal behavior of the temperature dependence of S_T for colloidal systems. It is of great interest to study whether the same scaling behavior holds also for other systems. Thus, the first aim of this contribution is to study the temperature dependence of the Soret coefficient for binary systems composed of mono-, oligo-, and polysaccharides as solutes in water and to extend the recent studies by Blanco *et al.*[26,27]

Further we study the temperature dependence of the Soret coefficient S_T,[22,28–31] and the thermal diffusion coefficient D_T to compare it with other aqueous systems. Experimental data show an increasing D_T with increasing temperature for biopolymers and water-soluble synthetic polymers.[19] The slope of D_T *versus* temperature seems to be linear, although the slope and the sign inversion temperature depend on the systems.

Another purpose of the paper is to study the thermal diffusion as a function of the molecular weight at different temperatures. We cover a molecular weight range from the monomer with 0.180 kg mol^{-1} up to polymers with 440 kg mol^{-1}. Recently, Stadelmaier and Köhler reported a crossover behavior of the Ludwig–Soret effect for systems of polystyrene [PS] in various solvents as a function of molecular weight.[32] They revealed that D_T is scaled by the solvent viscosity η, and ηD_T does not depend on the molecular weight nor on the solvent quality in the molecular weight range of PS chains longer than the Kuhn segment length, whereas it depends on the solvent for shorter chains. This crossover behavior is predicted by the simulation work of Zhang and Müller-Plathe.[33] The simulation work was supported by an experimental study of very flexible glycols in ethanol, where D_T reaches already a constant value after 2 repeating units.[34]

Recently, Würger studied the molecular weight dependence of the thermal diffusion behavior theoretically.[35,36] He finds that the thermal diffusion coefficient depends on the radius of gyration R_G given by the scaling law $R = \ell \cdot N^{\nu} = \mu \cdot M^{\nu}$, with the degree of polymerization N and the scaling exponent ν, the radius of the single bead (monomer) a, the dynamic viscosity η, a numerical constant κ, the thermal expansion coefficient $\beta = -(1/c)\cdot \mathrm{d}c/\mathrm{d}T$ and the energies ε_p and ε_s of the bead forming the polymer and the solvent, respectively.

$$\frac{D_T}{D_T^{\max}} = 1 - \frac{\psi}{M^{\nu}} \tag{6}$$

with

$$\psi = \left[\frac{\varepsilon_s}{\varepsilon_p} + \frac{\varepsilon_s - \varepsilon_p}{\beta \varepsilon_p T}\right]\frac{6\pi a}{\kappa \mu} \tag{7}$$

He showed that the balance of the interactions between the segment and the solvent can give rise to a negative thermal diffusion coefficient in the low molecular weight regime, whereas for high molecular weights the thermal diffusion coefficient is independent of the molecular weight. When the interaction potential of the solvent ε_s is larger than that of the solute ε_p, a negative D_T is observed in the low molecular weight regime. This theory describes the experimental results of PS solutions well,[32,37] where it is shown that the long-range hydrodynamic interactions dominate the Brownian diffusion, while they are not important for thermal diffusion. This last point is in contradiction to the results for colloids, where hydrodynamic interactions are important for both diffusion processes.[38,39] It is interesting to investigate, whether Würger's results hold also for polar polymers such as the aqueous polymer solutions which have a negative thermal diffusion coefficient.

In this report the Ludwig–Soret effect of binary aqueous solutions of monosaccharides, oligosaccharides, and polysaccharides was studied by means of thermal diffusion forced Rayleigh scattering (TDFRS) as a function of temperature. The monosaccharide used in this study is D-glucose (Glc, M = 180.2 g mol^{-1}). Here, glucose is the basic constituent for all other samples. As oligosaccharides, maltotriose and maltohexaose are used. Maltotriose is composed of α-D-(1 → 4)-linked glucose [Glc(α 1–4)Glc(α 1–4)Glc, M = 504.4 g mol^{-1}]. Maltohexaose is also composed of α-D-(1 → 4)-linked glucose [Glc(α 1–4)Glc(α 1–4)Glc(α 1–4)Glc(α 1–4)Glc(α 1–4)Glc, M = 990.9 g mol^{-1}]. The polysaccharides are pullulan and dextran which have been well characterized in water.[40–42] Pullulan is composed of α-D-(1 → 6) linked maltotriose. Dextran is composed of α-D-(1 → 6)-linked glucose with some short α-D-(1 → 3)-linked glucose branching units. It is considered that the series of these saccharides is a good choice to study the Ludwig–Soret effect in regard to the molecular weight dependence from the monomer to high molecular weight polymers, because the regularity of the glycosidic bonds of solutes is changed in a systematic manner.

2 Experimental

Materials

Glucose, maltotriose, and maltohexaose were purchased from Wako Chemical and are used as received. Pullulan (Hayashibara Co.) was purified three times by a methanol precipitation from aqueous solution and dextran (Polymer Standard Service) was also purified.[43] The weight averaged molecular weights shown in this report for pullulan are 4.2 and 440 kg mol^{-1} and for dextran is 86.7 kg mol^{-1}.[18,19] Distilled and deionized water (milli-Q) was used as solvent. For TDFRS measurements a small amount of the dye, Basantol Gelb (BASF), was used to create the temperature gradient.[44] The concentration of the aqueous solutions of monosaccharides, oligosaccharides and pullulan(4k) was 10.0 gL^{-1}. The data of dextran and pullulan(440k) included from previous publications were measured at the concentration of 5.0 gL^{-1}.[18,19]

Methods

The Soret coefficient S_T, the thermal diffusion coefficient D_T, and the mutual diffusion coefficient D are obtained by the thermal diffusion forced Rayleigh scattering (TDFRS) method. The details of the TDFRS have been described elsewhere.[45,46] The TDFRS measurements were carried out in a temperature range from 15 to 55 °C. The temperature of the sample cell was controlled by circulating water from a thermostat bath with an uncertainty of 0.02 °C. The sample solutions were filtered directly into the optical quartz cell with a path length of 0.2 mm (Hellma) through a 0.22 μm membrane filter (Millipore).

The normalized heterodyne signal intensity of TDFRS experiments, $\zeta_{\text{het}}(t)$, to the thermal signal is related to the Soret coefficient S_T and mutual diffusion coefficient D as follows:

$$\zeta_{\text{het}}(t) = 1 + \left(\frac{\partial n}{\partial T}\right)_{p,w}^{-1}\left(\frac{\partial n}{\partial w}\right)_{p,T} S_T w(1-w)[1-\exp(-Dq^2 t)]. \tag{8}$$

Here, t is the time, n the index of refraction, q the scattering vector, $(\partial n/\partial T)_{p,w}$ and $(\partial n/\partial w)_{p,T}$ are the refractive index increments with temperature and weight fraction. $(\partial n/\partial T)_{p,w}$ and $(\partial n/\partial w)_{p,T}$ must be determined separately. A scanning Michelson interferometer operating at a wavelength of 632.8 nm is used.[47]

3 Results and discussion

Fig. 1 shows the Soret coefficient S_T, the thermal diffusion coefficient D_T, and the mutual diffusion coefficient D, as a function of temperature, for 10.0 gL^{-1} aqueous solutions of glucose, maltotriose, maltohexaose, and pullulan(4k), and for 5.0 gL^{-1} aqueous solutions of dextran and pullulan(440k). Earlier studies[18,19] showed that the concentration effect on the thermal diffusion behavior is small in this concentration range, so that the experimental results for the different concentrations can be compared. The curves in the plot of S_T are obtained by a nonlinear least-square fit using eqn (4), and the lines in the plot of D_T and D are obtained by linear regression, which at first glance seem to describe the data sufficiently well. Later we will see that a non-linear equation to describe the temperature dependence of D_T similar to eqn (4) gives more consistent results. The obtained parameters T_{inv}, S_T^{∞}, and T_0 in eqn (4) are summarized in Table 1. All samples show an increase in S_T, D_T, and D with increasing temperature. S_T and D_T of glucose and maltotriose in water have a positive sign in the investigated temperature range, though it is expected that the sign change takes place at lower temperatures. For all other systems S_T and D_T change their sign from negative to positive with increasing temperature in the investigated temperature range. The sign change temperature increases with increasing molecular weight of saccharides. The magnitude and the slope of S_T for polymers are apparently larger than that of glucose and oligosaccharides. In contrast, the magnitude and the slope of D_T for polymers become smaller with increasing molecular weight. The diffusion coefficient D increases linearly on the semi-logarithmic plot with increasing temperature for all samples in the investigated temperature. The plots of D as a function of the inverse of absolute temperature (Arrhenius plot, data not shown) show linear lines for all samples with the activation energies between 17 kJ mol^{-1} and 31 kJ mol^{-1}.[19] Here, the activation energy shows no apparent correlation with the molecular weight because the activation energy might also depend on branching effects and other conformational changes between the monomer, oligomer and polymer. On the other hand, the temperature dependence of the thermal diffusion coefficient D_T clearly shows that the slope decreases with increasing molecular weight as shown in Fig. 1. The temperature and the molecular weight effect will be discussed in detail below.

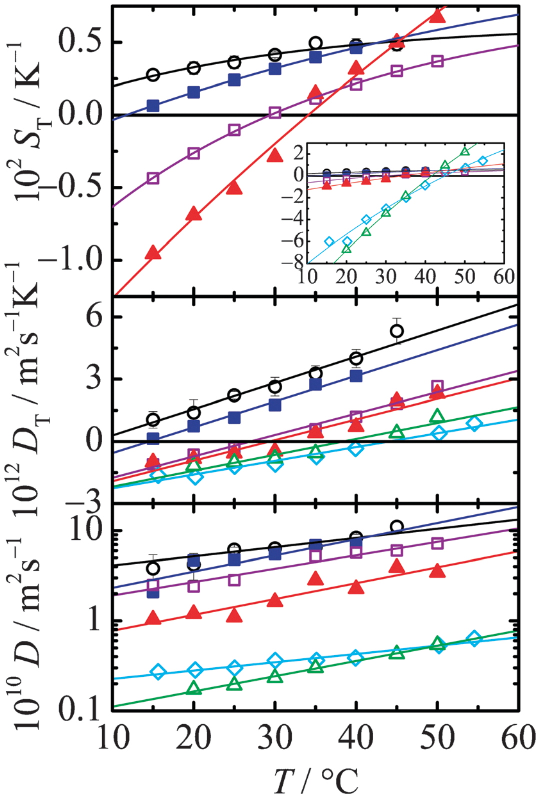

Fig. 1 Soret coefficient S_T, thermal diffusion coefficient D_T, and mutual diffusion coefficient D for aqueous solutions of glucose (○), maltotriose (■-blue), maltohexaose (□-purple), pullulan-4k (▲-red), dextran (◊-cyan),[18] and pullulan-440k (Δ-olive).[19] The curves in S_T are fitted using eqn (4), and in D_T and D the lines are obtained with linear regression. S_T of dextran and pullulan(440k) is only shown in the inset.

3.1 Temperature effect of Soret coefficient

The results of the temperature dependence of the Soret coefficient $S_T(T)$ were described well by eqn (4) for all samples

Table 1 The values of T_{inv}, S_T^∞, and T_0 obtained with eqn (4) and A obtained by eqn (5) for mono-, oligo-, and poly-saccharides in water. Also the values of D_{T0} and T_1 obtained with eqn (9), where T_{inv} is the value obtained from S_T with eqn (4) for mono-, oligo-, and poly-saccharides in water. Here, ± means one standard deviation

	Soret coefficient				Thermal diffusion coefficient	
Solute	T_{inv}/°C	S_T^∞/K^{-1}	T_0/K	A	10^{12} D_{T0}/m^{2}s^{-1}K^{-1}	T_1/K
Glucose	−0.4 ± 7.7	0.006 ± 0.002	27.7 ± 22.2	9.9 ± 0.3	−2.51 ± 0.64	−41.4 ± 7.1
Maltotriose	11.7 ± 0.3	0.014 ± 0.002	67.8 ± 12.5	4.2 ± 0.1	−2.85 ± 1.55	−37.1 ± 14.7
Maltohexaose	29.4 ± 0.2	0.008 ± 0.001	33.1 ± 2.5	9.2 ± 0.1	−2.73 ± 0.35	−30.2 ± 3.0
Pullulan(4k)	34.1 ± 0.8	0.058 ± 0.069	123 ± 145	2.5 ± 0.1	−1.55 ± 0.44	−16.4 ± 3.4
Dextran	45.0 ± 1.1	0.127 ± 0.108	71.4 ± 52.3	4.5 ± 0.1	−3.50 ± 0.78	−43.2 ± 11.9
Pullulan(440k)	41.6 ± 0.2	0.234 ± 0.065	84.9 ± 21.9	3.7 ± 0.1	−1.47 ± 0.02	−14.3 ± 0.3

as shown in Fig. 1. The saturation value of S_T^∞ and the sign inversion temperature T_{inv} tend to have larger magnitudes for solute molecules with a larger molecular weight. Recently, Vigolo *et al.* reported the temperature dependence of $S_T(T)$ for the systems of SDS micelles in NaCl and NaOH aqueous solutions.[25] They revealed that the scaled Soret coefficient $S_T(\tilde{T})/S_T^\infty$ lies nicely on a single master curve when the $S_T(\tilde{T})/S_T^\infty$ is plotted against the normalized temperature $\tilde{T}$ ($= T/T_{inv}$). The master curve is described by the function of eqn (5). We follow the same route of investigating the temperature dependence of $S_T(\tilde{T})/S_T^\infty$ for the binary systems of saccharides in water.

Fig. 2 shows $S_T(\tilde{T})/S_T^\infty$ as a function of $\tilde{T}$ for all saccharide solutions. The bold curve is obtained by a nonlinear least-square fit with eqn (5) using all data points and the parameter $A(= T_{inv}/T_0)$ in eqn (5) was obtained as $A = 5.5 \pm 0.4$. Here, ± denotes one standard deviation. The thinner curves are obtained for each sample. The obtained parameter A is summarized in Table 1. The result indicates that there is no clear master curve for all saccharide solutions. In the case of the SDS micelle systems, the dimensionless parameter A was reported as $A \simeq 16$ where the Soret coefficients of SDS micelles are scaled well in the presence and absence of salt. For a suspension of *fd*-virus $A = 15$ and 6.6 had been found, depending on the concentration.[48] In this study for aqueous solutions of saccharides with a broad molecular weight range we do not find a master curve to describe the temperature dependence of the normalized Soret coefficients. One of the reasons is that scaling concepts for the diffusion coefficient hold only for the polymer range and fail in the oligomer and monomer range. Additionally the temperature variation of molecular interactions between solute and solvents needs to be taken into account.

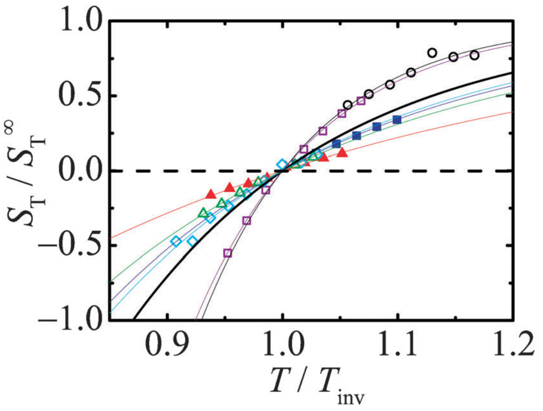

Fig. 2 The normalized Soret coefficient $S_T(\tilde{T})/S_T^\infty$ as a function of T/T_{inv}. The solid curve is obtained by a fitting using eqn (5) for all data points. Symbols have the same meaning as in Fig. 1.

3.2 Temperature influence on thermal diffusion coefficient

The thermal diffusion coefficient D_T increases linearly with increasing temperature for all samples (*cf.* Fig. 1) and the sign inversion temperature of D_T must be identical with the sign inversion temperature T_{inv} of S_T because of the definition $S_T = D_T/D$. However, it is found that the sign inversion temperatures determined using S_T with eqn (4) do not agree with the sign inversion temperature using a linear regression to describe the temperature dependence of D_T. The deviations become larger with increasing molecular weight of the samples. This result indicates that the temperature dependence of $D_T(T)$ is nonlinear. One possible attempt would be to combine the theoretical description of the diffusion coefficient by Eyring and combine it with the empirical approach by Piazza, but this would lead to a sum of two exponentials and four adjustable parameters, which cannot be determined reliably. Therefore, we express $D_T(T)$ by the following equation,

$$D_T(T) = D_{T0}\left[1 - \exp\left(\frac{\Delta T}{T_1}\right)\right]. \tag{9}$$

Here, D_{T0} represents the minimum D_T value, T_1 is an indicator of the strength of the temperature effect and $\Delta T = T_{inv} - T$ is the distance of the sign inversion temperature T_{inv} also determined from the temperature dependence of the Soret coefficient. This equation for $D_T(T)$ has the same form as eqn (4). Fig. 3 shows the $D_T(T)$ as a function of temperature with the fitted curves which are obtained by a nonlinear least-square fit using eqn (9). Here, we fixed T_{inv} to the value obtained for the Soret coefficient and treated D_{T0} and T_1 as adjustable parameters. The obtained values are summarized in Table 1.

The temperature dependence of D_T is described well by the fitting curve. To study the temperature effect on D_T in more detail, we plotted $D_T(T)$ as a function of ΔT ($= T_{inv} - T$) as shown in Fig. 4. It is found that all D_T values fall on a single master curve. The solid curve in Fig. 4 is obtained by a nonlinear least-square fit to all data points using eqn (9). The parameters D_{T0} and T_1 are obtained as $D_{T0} = (-4.78 \pm 0.91) \times 10^{-12}$ m^2 s^{-1} K^{-1} and $T_1 = 59.8 \pm 9.2$ K, respectively. In contrast to the Soret coefficient the mass or the size effect cancels out, so that we find a single master curve for D_T for all investigated saccharides when it is plotted

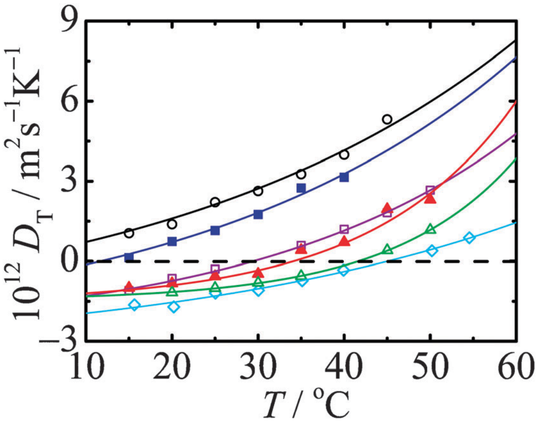

Fig. 3 Thermal diffusion coefficient D_T as a function of temperature T. Here, the curves are obtained by a fitting using eqn (9). Symbols have the same meaning as in Fig. 1.

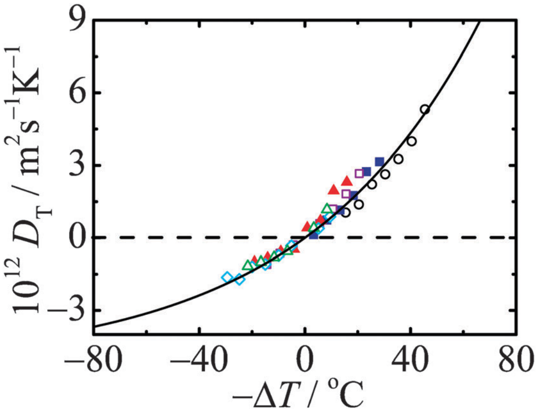

Fig. 4 Thermal diffusion coefficient D_T as a function of temperature difference ΔT for all saccharide solutions. Symbols have the same meaning as in Fig. 1. The curve is obtained by a nonlinear least-square fit according to eqn (9).

against ΔT. The result indicates that the curvature of D_T against temperature is not affected by the mass and the size of solute molecules, although the temperature dependence of S_T is apparently associated with the size and the mass of the solutes.

3.3 Molecular weight dependence

The molecular weight dependence of the Soret coefficients S_T at the selected temperatures 15, 25, 35, and 45 °C are shown in Fig. 5. The sign inversion of S_T from positive to negative shifts towards lower temperatures with increasing molecular weight. The magnitude of the negative S_T value becomes larger with increasing molecular weight, which is mainly due to the consequence of $S_T = D_T/D$ where D has the form $D \propto N^{-\nu}$. The lines in Fig. 5 are guides to the eye, because there is no theoretical expression available which describes the molecular weight dependence of the Soret coefficient S_T.

In contrast we can use eqn (6) to describe the molecular weight dependence of the thermal diffusion coefficients D_T at the selected temperatures 15, 25, 35, and 45 °C as a function of molecular weight as shown in Fig. 6. The resulting ψ-parameters as a function of temperature are shown in the inset of Fig. 6. Besides some numerical constants ψ (*cf.* eqn (7)) depend on the thermal expansion coefficient β, the energies ε_p, ε_s of the polymer bead and the solvent, respectively. The dashed line is a fit with an adjustable thermal expansion coefficient β, while the solid line represents a fit, where β has been fixed to the experimentally observed thermal expansion coefficient of water.[49] It needs to be pointed out that the energy ratio of $\varepsilon_s/\varepsilon_p$ changes only slightly from 0.96 to 0.97 depending on an adjustable or fixed β, respectively. In the case of the organic mixtures the ratio of $\varepsilon_s/\varepsilon_p$ is larger than 1, resulting in an increasing thermal diffusion coefficient. It would be desirable to have also temperature and molecular weight dependent studies for organic polymers to regard the ratio of the interaction energies in this case. It is expected that the temperature is less pronounced compared to the polar systems.

So far there have been only a few molecular weight dependent studies for aqueous systems.[27,34,50] The studies of aqueous saccharide solutions are limited to the oligomer range and have not been analyzed in detail. On the other hand, for non-polar polymers in organic solvents the molecular weight dependence

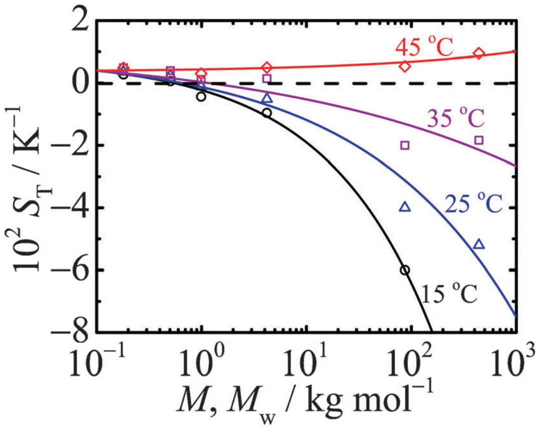

Fig. 5 Molecular weight dependence of Soret coefficient S_T obtained at 15, 25, 35, and 45 °C. Curves are drawn to guide the eye.

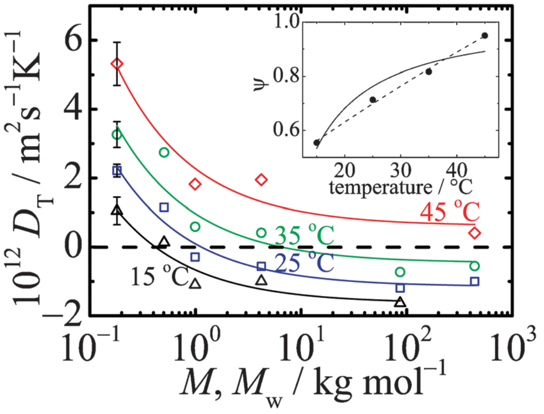

Fig. 6 Molecular weight dependence of thermal diffusion coefficient D_T at 15, 25, 35, and 45 °C. Lines are fits according to eqn (6). The inset shows the determined ψ-parameter as function of temperature. The dashed line is a fit with an adjustable thermal expansion coefficient β, while the solid line describes a fit with the experimentally determined β-values for water.

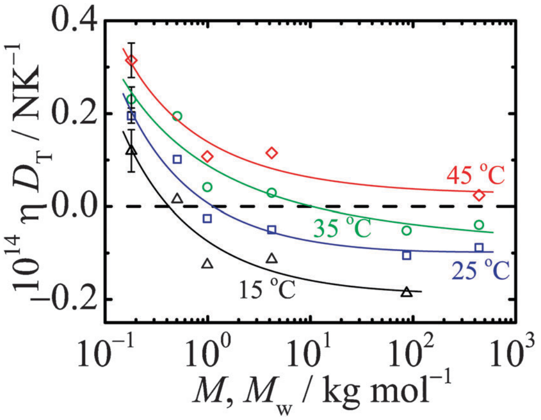

Fig. 7 Molecular weight dependence of thermal diffusion coefficient normalized by the inverse of viscosity ηD_T at 15, 25, 35, and 45 °C. Curves are fitted results according to eqn (6).

of the thermal diffusion coefficient has been studied in a number of publications.[12,33,37,51] For PS in various solvents the thermal diffusion coefficient is independent of the molecular weight in the high mass regime, where the sign of the thermal diffusion coefficient is positive.[32,37] The thermal diffusion coefficient scales with the inverse of the viscosity and the value of ηD_T is constant in the high molecular mass regime and even independent of the solvent. On the other hand, it decreases approaching the oligomer and monomer range, and sometimes even shows negative values in some solvents. The molecular weight dependence of the PS solutions is inverted compared to this study for saccharides in water, where the sign of the thermal diffusion coefficient of saccharides is negative in the high mass regime and becomes more positive with decreasing molecular mass as shown in Fig. 7. Here, the water viscosity is used to calculate ηD_T and the figure shows that ηD_T depends apparently on temperature, which has not been investigated for organic polymers. It might be interesting to notice that ηD_T has a dimension as force per temperature. The negative sign of D_T at high molecular weight can be explained qualitatively by the expression of Würger with a ratio of $\varepsilon_s/\varepsilon_p$ smaller than one. But here further temperature and concentration dependent studies are necessary to gain a better understanding of the thermal diffusion behavior of aqueous solutions.

In aqueous solutions, especially at low temperatures, interactions *via* hydrogen bonds dominate the thermal diffusion behavior. At higher temperatures the strength of hydrogen bonds in the system is weakened, so that entropic contributions become more important which often leads to an ordinal behavior of the thermal diffusion, *i.e.*, positive sign of S_T and D_T. As has been shown the impact of hydrogen bonds on the thermal diffusion behavior can not only be weakened by increasing the temperature, but also by adding a component like urea, which weakens the hydrogen bonds of the water soluble polymer.[19] As shown in Fig. 6 and 7 the thermal diffusion behavior changes sign with increasing molecular weight, which could be reproduced by the theoretical approach of Würger by modifying the ratio of interaction energies of the segments and the solvents. In general negative Soret coefficients are found under poor solvent conditions.[34,52,53] Here, the solubility of the solute molecules plays an important role. While for instance glycol has a positive Soret coefficient in ethanol, negative S_T-values are observed for diglycol and triglycol in ethanol and higher glycol oligomers are not soluble at all. The solution of pullulan in DMSO, where DMSO is polar and an aprotic solvent, shows only positive values of D_T and S_T.[19] So that we assume at least two key roles; the effects of hydrogen bonds network and of a low solubility, which can lead to negative Soret and thermal diffusion coefficient at lower temperatures and high molar masses in aqueous saccharide solutions.

4 Conclusions

For the binary systems of mono-, oligo-, and poly-saccharides in water, the temperature dependences of the Soret coefficient S_T and the thermal diffusion coefficient D_T have been studied. The sign inversion behavior of the Soret coefficient $S_T(T)$ lies not on a master curve proposed by Piazza and coauthors as $S_T(\tilde{T})/S_T^{\infty}$ *vs.* $\tilde{T} = T/T_{\mathrm{inv}}$. In contrast, the temperature dependence of the thermal diffusion coefficient $D_T(T)$ falls on a single curve on the plot of $D_T(T)$ *vs.* $\Delta T = T_{\mathrm{inv}} - T$. Moreover, it is found that the temperature dependence of $D_T(T)$ is nonlinear in the investigated temperature range. The plots of molecular weight dependence show that the D_T tends to saturate at a negative value for high molecular weight polymers, whereas it increases with lowering the molecular weight and changes the sign from negative to positive. The molecular weight dependence is upside down compared to the observed behavior for PS solutions, but it agrees with findings for aqueous solutions of water.[34] The molecular weight dependence of D_T can be described by a theoretical model by Würger, whereas the ratio of the interaction energies $\varepsilon_s/\varepsilon_p$ is smaller than one, while in the same model leads to a ratio larger than one for PS systems. This discrepancy between PS systems and aqueous saccharide solutions may be attributed to the effect of the interactions through hydrogen bonds, where the hydrogen bonds network in the system play a significant role in the thermal diffusion. To understand the molecular mechanism of this behavior, the temperature dependence of the segment–solvent interactions on their thermodynamic quantities needs to be taken into account.

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