Molar mass and temperature dependence of the thermodiffusion of polyethylene oxide in water/ethanol mixtures

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In this work we study the molar mass dependence of the thermodiffusion of polyethylene oxide at different temperatures in ethanol, water/ethanol mixture ($c_{\text{water}} = 0.7$) and water in a molar mass range up to $M_w = 180000$ g/mol. Due to the low solubility of polyethylene oxide oligomers in ethanol the measurements are limited up to $M_w = 2200$ g/mol. The specific water/ethanol concentration 0.7 has been chosen, because at this weight fraction the thermal diffusion coefficient, D_{T}, of water/ethanol vanishes so that the system can be treated as a pseudo binary mixture. The addition of ethanol will degrade the solvent quality, so that we expect a change of the interaction energies between polymer and solvent. The analysis of the experimental data within a theoretical model shows the need of a refined model, which takes specific interactions into account.

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I. INTRODUCTION

Thermodiffusion or thermophoresis is a phenomenon where a mass transport is induced by a temperature gradient in a multicomponent system. In the last five years the effect gained a lot of interest due to applications in biotechnology.[1] The response of molecules, polymers and colloids to a temperature gradient depends on many parameters such as charge, size and the hydrophilic and hydrophobic balance. The last plays an important role in the drug discovery process.[2]

For sufficiently small gradients, the mass flux induced by a temperature gradient ∇T is proportional to $-D_{\text{T}} \nabla T$, where D_{T} is the thermal diffusion coefficient. Thermodiffusion establishes a concentration gradient ∇c, which in turn give rise to a mass flux equal to $-D \nabla c$, where D is the mass diffusion coefficient. The two fluxes counter balance in the stationary state and the ratio of the established concentration and temperature difference $\Delta c/\Delta T$ is proportional to the Soret coefficient S_{T}, which is defined as $S_{\text{T}} = D_{\text{T}}/D$.

There have been numerous studies of both organic and aqueous mixtures, trying to explain the mechanism of thermodiffusion.[3–6] Many physical parameters such as molar mass, viscosity, thermal expansion and moment of inertia have been related to the thermal diffusion coefficient D_{T} using empirical correlations.[7–9] Apart from the low molar mass mixtures, polymer solutions and colloid suspensions have also been investigated.[10,11] While organic polymers have been studied over a wide concentration and molar mass range,[6,12] the investigation of water soluble polymers is less complete and concentrates on the molar mass and temperature dependence.[13–15]

Among water soluble polymers, polyethylene oxide (PEO) is of special interest due to its delicate balance of the opposing effects of water-PEO and water-water hydrogen bonding and the resulting complex phase behavior in water.[16,17] Beside a single measurement of poly(vinylalcohol)[18] it was the first polymer with a negative Soret coefficient in ethanol/water mixtures, which had been systematically investigated.[11,13] While PEO is well soluble in water the solubility in ethanol decreases with increasing molar mass.[19,20] Some previous studies of PEO show that the solvent quality has a significant influence on the sign change of S_{T}. Ethylene oxide oligomers tend to accumulate at the warm side in pure ethanol, which is a bad solvent for high molar mass PEO. If the water content increases, which means the solvent quality improves, the system becomes more thermophobic and ethylene oxide oligomers and also PEO diffuses to the cold region.[11,13,19]

This behavior could qualitatively be understood with a two-chamber lattice model for thermodiffusion in liquid mixtures and dilute polymer solutions.[21,22] The lattice model includes compressibility and directed hydrogen bonding between PEO and water molecules. Within this model the sign change of the Soret coefficient of PEO in the water/ethanol mixture and also the sign change within the binary solvent mixture have been found, in agreement with experimental data. Note that the sign change in the binary mixture could only be reproduced when the mixed water/ethanol interaction parameter had been adjusted to the tabulated density values of the solvent mixture,[22] while a calculation of the mixed interaction according to Berthelots geometric mean could not reproduce the sign change of the binary mixture. It turns

out that the cross interaction has to be stronger than the like-like interaction. This has also been observed in molecular dynamic studies.[23]
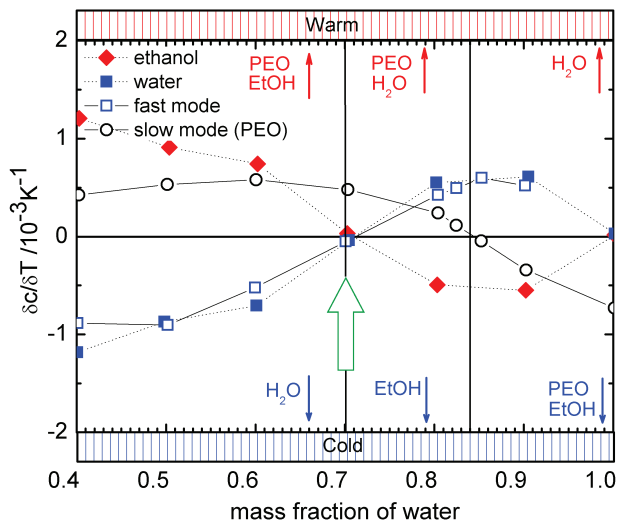

FIG. 1: Overview of the concentration change, δc, per applied temperature difference, δT, in the binary water/ethanol mixture and the ternary of PEO/water/ethanol mixture. Closed and open symbols represent data for the binary and ternary systems, respectively. The block arrow marks the concentration at which the Soret coefficient of the binary mixture water/ethanol vanishes. The dotted lines are guides to the eye. Data are taken from Ref.13. In the ternary mixture the cross diffusion of water in ethanol/PEO and ethanol in water/PEO is neglected, and the observed fast process in the diffusion on signal of the Thermal Diffusion Forced Rayleigh Scattering is identified with the diffusion of water in water/ethanol. Further details can be found in the text.

Figure 1 summarizes the results of high molar mass PEO in the water/ethanol mixture and relates it to the binary mixture. The closed and open symbols represent the concentration change as a function of the water content for the binary and ternary systems, respectively. In the ternary mixture the fast and slow modes are separated signals from the Thermal Diffusion Forced Rayleigh Scattering (TDFRS) measurements.[13] The slow mode reflects the concentration change of PEO in water/ethanol mixture, while the fast mode reflects the concentration change of water within the solvent mixture. In this particular case with a high molar mass PEO ($M_w = 2.65 \times 10^5$ g/mol) the two process are on very different time scales, so that the movement of the solvent components and the polymer can be separated. The data determined from the fast mode of ternary mixture (open square) agrees with the results of the binary mixture (solid square). In the measured range, two concentrations are crucial. For systems with a water mass fraction below 0.7, both in the binary and the ternary mixtures, ethanol accumulates at the warm side. When the water concentration increases, ethanol changes its behavior and enriches at the cold side. PEO in ternary system shows a similar behavior. It accumulates at the

warm side when the water concentration is below 0.84 and vice versa. The sign change of PEO and ethanol indicates the change of interactions not only between PEO and the solvent, but also within the solvent. We should expect the change of water content i. e. solvent quality is reflected in the interaction parameters.

An already well-established behavior of polymers, both polar and non-polar, at infinite dilution is that the thermal diffusion coefficient D_T becomes independent of molar mass for long enough chains.[19,24,25] Different analytical approaches have been so far employed to explain this behavior.[26–28] Yang and Ripoll[28] make use of a scaling argument and consider the relevance of the hydrodynamic interactions[29] for both the thermophoretic force (proportional to the Soret coefficient) and the friction coefficient. The size dependence of the two quantities results into a precise cancellation, which leads then inevitably to a size-independent D_T. Zhang and Müller-Plathe[30] perform non-equilibrium molecular dynamics simulations with a bead-spring polymer model. Their results show that the chain length for which the plateau value is reached, depends on the flexibility of the chains. In the simulations, more flexible chains reach a constant D_T at shorter chain lengths compared to rigid chains. Describing the chain length in terms of the persistence length l_p, D_T becomes constant when the chain length is of around two to three times l_p. Recent experiments with short ethylene oxide oligomers in ethanol confirmed the simulation results[19] and found that D_T of the ethylene oxide oligomers in ethanol reached the plateau earlier than the D_T in water. This can be expected due to the formation of a hydration shell in water, which should lead to a higher rigidity of the aqueous system.

Several attempts have been made to describe the molar mass dependence with theoretical models. Rauch and Köhler proposed an empirical equation derived from the data of polystyrene in toluene[25]:

$$D_T = \frac{(M - M_e)D_T^\infty + M_e D_T^e}{M} \quad (1)$$

here M_e is the molar mass of the end group, D_T^e is the thermal diffusion coefficient of the end group, D_T^∞ is the thermal diffusion coefficient at infinite molar mass.

Duhr and Braun developed a model to describe the chain length (L) and charge (σ) dependence of thermodiffusion behavior of DNA. The Soret coefficient is expressed as proportional to the surface area (A) and Debye length (λ_{DH}).[31] Here the DNA molecules are treated as spheres, so using the scaling behavior of $D_T \propto L^{-0.75}$, they find $D_T \propto L^{-0.25}$. This model can only describe the charged systems, therefore we cannot apply it to PEO.

Eslamian and Saghir derived a model by considering the solvent as viscous flow surrounding the polymer. They assume that the net heat of transport of the solvent molecules equals the activation energy of viscous flow of the solvent in the pure state. Soret coefficient is expressed in terms of activation energies. This model

requires the input data of the heats of transport, which are to our best knowledge not known for our system.

Würger assumed that the solvent molecular structure and the Brownian motion of the solute differ with respect to the friction coefficient. He expressed the molar mass dependence of the thermal diffusion coefficient D_T for dilute solutions by

$$D_T = \frac{\beta \varepsilon_p}{6\pi\eta a} - \frac{\beta \varepsilon_s + (\varepsilon_s - \varepsilon_p)/T}{\eta \tilde{\ell} M^\nu} \qquad (2)$$

where a is the radius of the monomer, β is the thermal expansion coefficient, η is the dynamic viscosity, $\tilde{\ell}$ is a constant, ε_p and ε_s are the polymer-solvent and solvent-solvent interaction energies, respectively.[27,32] Furthermore it has been used that in diluted polymer solutions, the diffusion coefficient D depends strongly on the molar mass M and can be described by a scaling law as $D \propto M^{-\nu}$, where $\nu = 0.6$ is a scaling exponent.[33] This approach considers only van der Waals interactions and in the case of an attractive interaction ε_p and ε_s are positive numbers, describing the depth of the potential well. his model has been used by other authors to describe the data of several polymers in different organic solvents. They found that $\beta\varepsilon_p$ is characteristic for the polymer, but independent of the solvent, which means the interaction between polymer and solvent relates only to the thermal expansion coefficient of the solvent.[34]
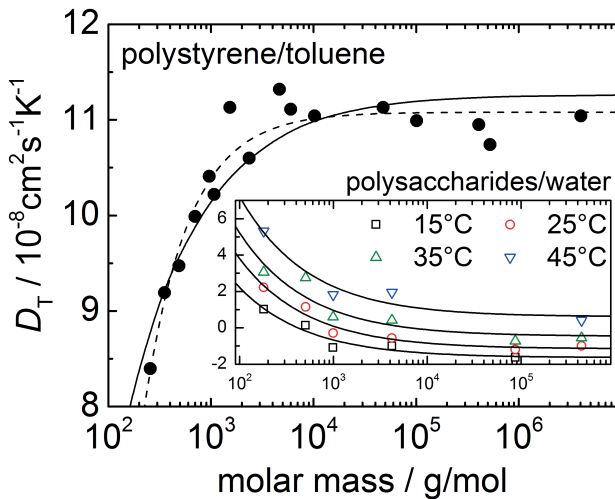

FIG. 2: Molar mass dependence of the thermal diffusion coefficient D_T of styrene oligomers and polystyrene in toluene. The dashed line and solid line present the fits of Eq. 1 and 2, respectively. The inset shows D_T of saccharide oligomers and polyaccharides in water and the lines correspond to a fit of the molar mass dependence according to Eq.2. The data have been taken from references 25 and 15.

Fig 2 shows D_T for styrene oligomers and polystyrene (PS) in toluene as function of the molar mass[25] and the fitted curve according to Eq. 1 (dashed line) and Eq. 2 (solid line). From the model of Würger the interaction energy between polymer and solvent $\varepsilon_p = 1.7 \cdot 10^{-19}$ J

($\approx 41kT$) can be determined. A determination of the ε_s for this organic system is presently not possible, because there are no temperature dependent measurements. The model from Rauch and Köhler reaches the plateau of D_T earlier than the model of Würger and describes the PS data better. But the phenomenological model gives only empirical parameters without physical meaning..

The inset of Fig 2 shows the molar mass dependence of D_T of saccharide oligomers and polysaccharides in water[15] described by Würger's model. It turns out that ε_p lies between $-2.4 \cdot 10^{-19}$J ($T = 15°$C) and $+0.16 \cdot 10^{-19}$J ($T = 45°$C). The obtained values are in the same order of magnitude as in the case of styrene oligomers and polystyrene in toluene, but the negative interaction energies at low temperatures would imply a repulsive potential, which seems to be unphysical and shows that one needs to be careful, if one applies this model to polar systems.

In order to determine the interaction parameters for PEO in water, ethanol and the water/ethanol mixture molar mass and temperature dependent measurements are required. Note that our experimental method works primarily for binary mixtures therefore we have to choose a specific water/ethanol mass fraction in order to be able to identify the diffusion stemming from the low molar mass ethylene oxide oligomers in the solvent mixture. One possible water/ethanol composition is $c_{water} = 0.7$, where the thermodiffuisve contribution from the binary water/ethanol mixture can be neglected. Additionally we studied also the system in pure water and pure ethanol. Note that PEO with a high molar mass is not soluble in pure ethanol so that the measurements are limited to $M_w \leq 2200$ g/mol. In order to determine both interaction energies, temperature dependent measurements had to be performed.

II. EXPERIMENTAL DETAILS

A. Sample Preparation and Characterization

Ethylene glycol ($\geq 99.8\%$), diethylene glycol ($\geq 99\%$), triethylene glycol ($\geq 99\%$) were purchased from Sigma Aldrich. PEO with an average molar mass Mw of 240, 660, 2200, 5400, 180000 g/mol were purchased from Polymer Source and 33660, 79565 g/mol were obtained from Max-Planck-Institute for Polymer Research. The polydispersity index (PDI) for all purchased polymers are between 1.07 and 1.2. Solvents were prepared from Milli-Q water and absolute ethanol from Merck. All solutions were filtered through 0.2 μm inorganic membrane filters from Anotop into Hellma quartz cells with an optical path length of 0.2 mm. The filter does not change the concentration, which was validated by measuring the refractive index before and after filtering. For the polymers with low molar mass ($M_w < 6000$ g/mol) the polymer mass concentration was 2% well below the overlap concentration c^*, while c^* is around 0.7% for the $M_w =$

180000 g/mol.[35] Therefore we performed additional measurements for the polymers with $M_{\mathrm{w}} > 30000$ g/mol at lower concentrations and extrapolated the measured coefficients to infinite dilution.

B. Infrared Thermal Diffusion Forced Rayleigh Scattering (IR-TDFRS)

A detailed description of the recently modified IR-TDFRS can be found in the paper by Blanco et al..[36] This setup is optimized for aqueous systems and has been used to study the transport properties in different aqueous systems of non-ionic surfactants,[37] saccharide solutions,[38] nucleotides[39] and anisotropic bio-colloids.[36]

The normalized heterodyne scattered intensity $\zeta_{\mathrm{het}}^{th}(t)$, assuming an ideal excitation with a step function, is given by,

$$\zeta_{\mathrm{het}}^{th}(t) = 1 - \exp\left(-\frac{t}{\tau_{\mathrm{th}}}\right) - A\left(\tau - \tau_{\mathrm{th}}\right)^{-1}$$
$$\left\{\tau\left[1 - \exp\left(-\frac{t}{\tau}\right)\right] - \tau_{\mathrm{th}}\left[1 - \exp\left(-\frac{t}{\tau_{\mathrm{th}}}\right)\right]\right\}$$

with the steady state amplitude A equal to,

$$A = \left(\frac{\partial n}{\partial c}\right)_{p,T}\left(\frac{\partial n}{\partial T}\right)_{p,c}^{-1} S_{\mathrm{T}} c\left(1 - c\right) \qquad (3)$$

where c is the mass fraction of the ethylene oxide oligomers or polymers, τ_{th} the heat diffusion time, $(\partial n/\partial c)_{p,T}$ and $(\partial n/\partial T)_{p,c}$ are refractive index contrast factors with respect to mass concentration at constant pressure and temperature, and with respect to temperature at constant pressure and mass concentration, respectively. The refractive index contrast factors are measured independently from the TDFRS measurements. The details about measuring refractive index contrast factors are described in Ref. [39].

C. Choice of the water/ethanol composition

With our experimental method we determine the thermodiffusion properties from the diffraction efficiency of a refractive index grating. Therefore, the method is primarily for binary systems. Only in special case such as for high molar mass PEO the process stemming from the polymer and the solvent can be separated due to their different time scales.[13] This approach will not be possible in the case of the low molar mass compounds. Only for two specific water/ethanol concentrations, when the concentration signal stemming from the water/ethanol mixture is negligible an investigation of the ternary system is still feasible. At water mass fraction around $c_{\mathrm{water}} = 0.19$ the contrast factor $(\partial n/\partial c)_{p,T}$ vanishes, so that the amplitude A of the concentration signal (c.f. Eq. 3) vanishes.

Unfortunately, the zero of $(\partial n/\partial c)_{p,T}$ shifts to higher water fractions with increasing temperature,[40] so that for each temperature the water/ethanol composition needs to be adjusted. Another possibility is a water mass fraction of $c_{\mathrm{water}} = 0.7$,[3,9,13,40–42] where the Soret coefficient of the water/ethanol mixture vanishes for all temperatures (c.f. Fig. 1). Fig. 3 shows the typical signal of the measurements. The black squares and green triangles are the signals of the water/ethanol/PEO mixture with $c_{\mathrm{water}} = 0.7$ and water/ethanol mixture with $c_{\mathrm{water}} = 0.7$ mass fraction, respectively. The concentration plateau is fairly flat, which shows no contribution of the solvents. The red star symbols present the measurement of PEO in pure water.
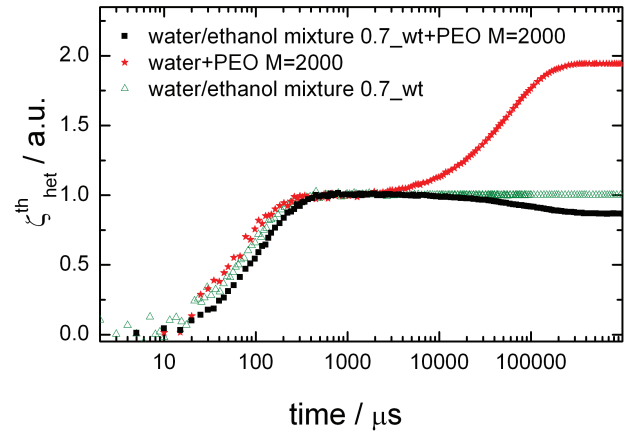

FIG. 3: Heterodyne signal of TDFRS of different solvents. Black square symbols present the signal of PEO 2200 g/mol in a water/ethanol mixture ($c_{\mathrm{water}} = 0.7$). Stars show the measurement of PEO 2200 g/mol in pure water and triangles are the signal of the binary water/ethanol mixture ($c_{\mathrm{water}} = 0.7$), which shows no concentration plateau. All experiments have been performed at a temperature of T=25°C.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Results

Fig. 4 shows the Soret coefficient S_{T}, the diffusion coefficient D and the thermal diffusion coefficient D_{T} at $c \to 0$ as function of the molar mass in ethanol, water/ethanol mixture ($c_{\mathrm{water}} = 0.7$) and pure water, from left to right. All the samples are measured in the temperature range between 15°C and 45°C with a temperature step of 10°C.

In ethanol S_{T} stays rather constant for molar mass below 660 g/mol. Then S_{T} drops dramatically at 2200 g/mol and changes from positive to negative for all investigated temperatures. No clear trend with temperature can be observed. The Soret coefficient S_{T} in water/ethanol mixtures decreases monotonically. The val-

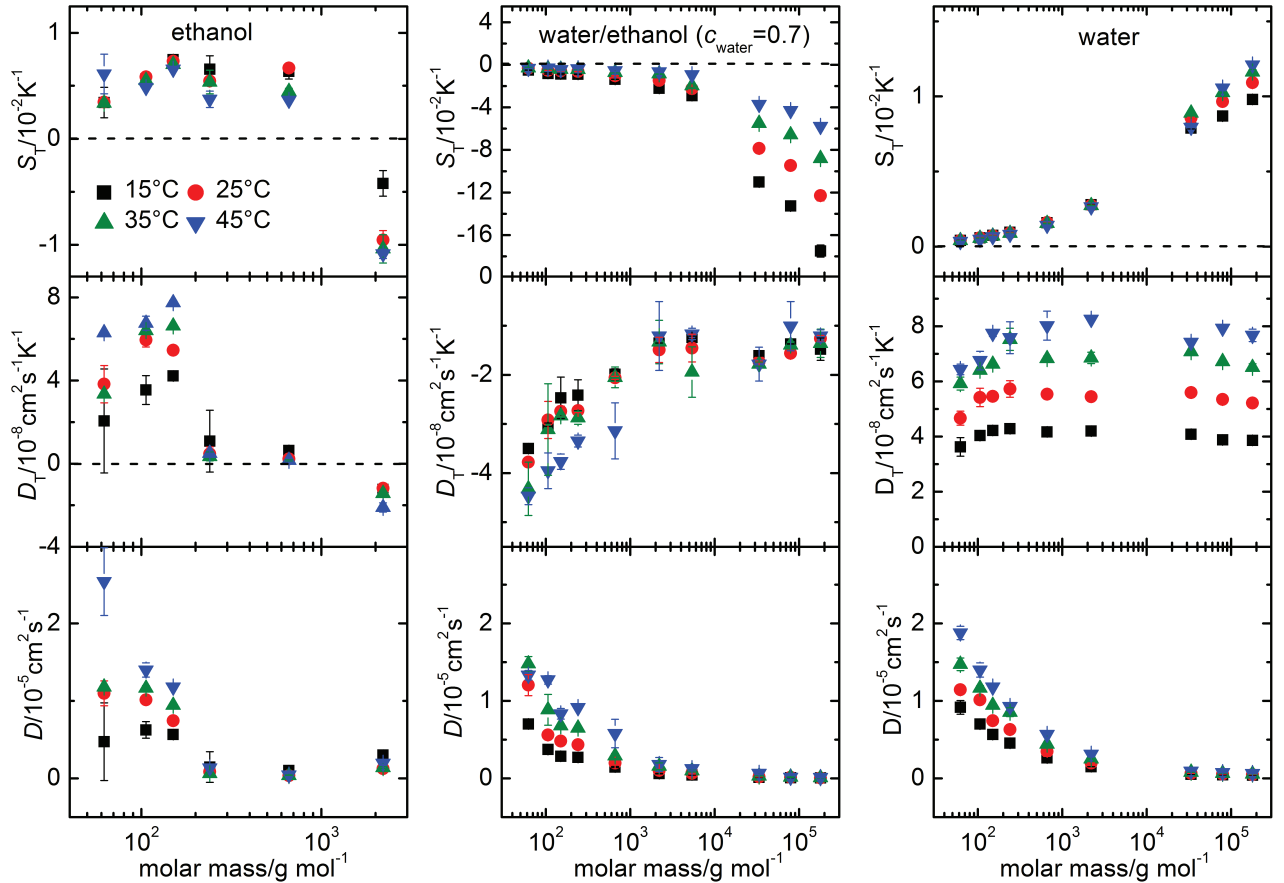FIG. 4: S_T, D and D_T of ethylene oxide oligomers and polymers as a function of molar mass in the dilute limit $c \to 0$ in ethanol, water/ethanol mixture ($c_{water} = 0.7$) and water from left to right. All samples are measured at four temperatures in the range between 15°C and 45°C presented by square, circle, up triangle and down triangle symbols, respectively.

ues are negative, indicating that PEO accumulates for all temperatures and molar masses at the warm side. The magnitude of S_T also increases with increasing temperature. In pure water S_T increases as a function of the molar mass, on the contrary to the other two systems. The values are all positive indicating that the ethylene oxide oligomers and polymers are thermophobic. Compared to the water/ethanol mixture the temperature dependence of S_T is less pronounced.

The diffusion coefficient D decreases with increasing molar mass for all solvents and increases with temperature. According to the Stokes-Einstein equation, diffusion coefficient is inversely proportional to the viscosity of the solvent and the temperature. As the viscosity of the water/ethanol mixture ($c_{water} = 0.7$) is higher than pure water,[43] the diffusion coefficients D increases slightly with increasing water content in our concentration range.

In pure ethanol the thermal diffusion coefficient D_T of ethylene oxide oligomers with low molar masses increases slightly and decreases for higher molar mass. Also the rise of D_T with increasing temperature is more pronounced for low molar masses. For the investigated mass fraction of 2% a sign change from positive to negative

occurs for molar mass of 2200 g/mol. In an earlier work by Klein and Wiegand[19] the sign change of D_T was already observed for the shorter dimer diethylene glycol with $M_w = 200$ g/mol at a higher mass fraction of 20%, which corresponds roughly to the same molar monomer concentration around 4 mM for a mass fraction of 2% of the ethylene oxide oligomer with $M_w = 2200$ g/mol. This observation confirms the picture that the interactions between ethanol, which is a bad solvent, and the individual monomer beads determine D_T. The sign change occurs at a certain molar concentration of the monomer beads. For water/ethanol mixture, D_T increases with increasing molar mass first rapidly and then reaches a plateau around the molar mass of 2200 g/mol. In the previous study of PS/toluene system, a similar molar mass dependence with a plateau around 2000 g/mol has also been observed, although it was in organic solvent and D_T was positive.[25] In another study of polysaccharides in aqueous system, D_T decreases as function of molar mass, but still reaches the plateau in the same range of molar mass.[15] In our study we found also that for low molar mass D_T decrease with increasing temperature, but for higher molar masses the data agree within the error bars. In pure water D_T shows a similar molar mass

dependence as found for aqueous and organic polymer solutions.[15,25] Our measurements show also a rise of D_T with increasing temperature.
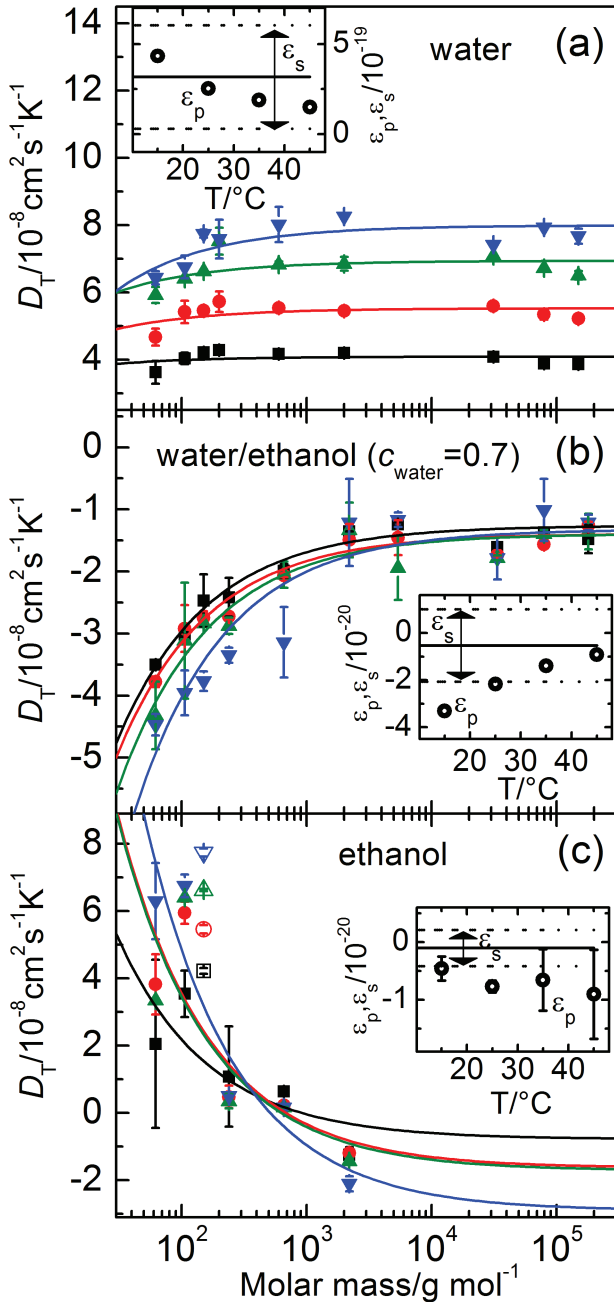

FIG. 5: Molar mass dependence of the thermal diffusion coefficient D_T with $c \to 0$ at 15, 25, 35, and 45 °C in (a) pure water, (b) the ethanol/water ($c_{\text{water}} = 0.7$) mixture and in (c) pure ethanol. The symbols for different temperatures are used as in Fig. 4. The open symbols have been excluded from the data analysis. Lines are fits according to Eq. 4. The inset shows the determined interaction parameters ε_p as function of temperature and the range of ε_s. For further details see text.

B. Discussion

In the following we will analyze the molar mass dependence of D_T at $c \to 0$. We rewrite Eq.2 in the following form

$$D_T = A(T) - \frac{B(T)}{M^\nu} \tag{4}$$

with

$$A(T) = \frac{\beta \varepsilon_p(T)}{6\pi\eta a} \tag{5}$$

$$B(T) = \frac{\beta \varepsilon_s(T) + (\varepsilon_s(T) - \varepsilon_p(T))/T}{\eta \tilde{\ell}} \tag{6}$$

and determine the temperature dependent quantities $A(T)$ and $B(T)$, which will give us the interaction parameters once the properties such as thermal expansion coefficient β, viscosity η and the radius a of the monomers are known. Describing the shape of the monomer of PEO by a sphere with radius a can only be a rough estimate. Using the van der Waals volumes of the chemical subunits[44] or the rubber volume of PEO[45] results in $a = 0.25$nm and $a = 0.21$nm, respectively. This 20% uncertainty in the radius will also lead to a similar relative error of the interaction parameter $\varepsilon_p(T)$

Fig. 5 shows the thermodiffusion data of ethylene oxide oligomers and polyethylene oxide in pure water, in the water/ethanol ($c_{\text{water}} = 0.7$) mixture and in pure ethanol. Note that the data in pure ethanol due to the low contrast have partially large error bars of more than 50%, so that we excluded the measurements of the trimer from the data analysis. There are two reasons that the signal amplitude A (c.f. Eq. 3) for the measurements in ethanol are so low: first the scattering of the low mass monomers and oligomers is weak and additionally the contrast factor $(\partial n/\partial c)_{p,T}$ is 30-60% lower in comparison with the solvent mixture and pure water.

The inset shows the interaction parameter ε_p, which has been determined directly from $A(T)$ using the literature data for the thermal expansion coefficient[46] and the viscosity.[47] For the two solvents containing ethanol ε_p is negative and in the order of 10^{-20} J, which is close to the interaction parameters used in the lattice model by Luettmer-Strathmann.[22] In the case of the aqueous system ε_p is up to one order of magnitude larger and shows a stronger temperature dependence.

The parameter $\varepsilon_s(T)$ and $\tilde{\ell}$ can be determined from the temperature dependence of $B(T)$. It turns out that this procedure gives only reasonable results for the aqueous system, while for the other systems the uncertainties in the parameters are very high and $\varepsilon_s(T)$ is orders of magnitude too large. In a second approach we used Eq. 6 at different temperatures and solved the linear equation system in order to determine $\varepsilon_s(T)$ and $\tilde{\ell}$. We found that $\varepsilon_s(T)$ spreads also over a wide range and we were not able to identify a temperature trend of $\varepsilon_s(T)$. Therefore we plotted in the insets of figure 5 only the average value of

$\varepsilon_s(T)$ as solid line. The double arrow marks one standard deviation indicated by the dotted line.
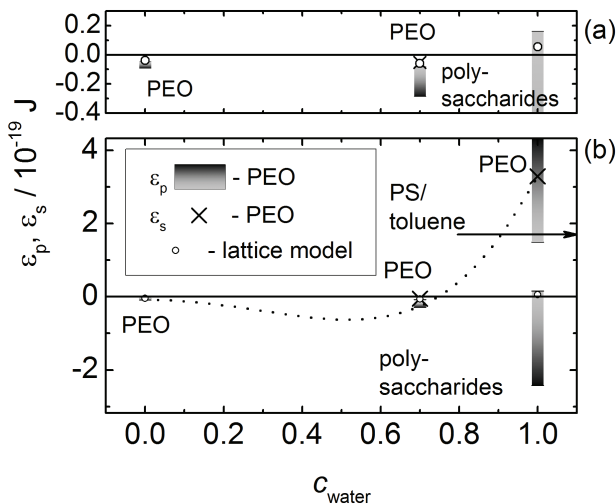

FIG. 6: Interaction parameters according to Eq. 4 for PEO and polysaccharides as function of the water/ethanol content. The filled areas show the variation of $\varepsilon_p(T)$ as function of temperature, whereas the blue part denotes the values at the lower temperatures. The cross marks the average value of $\varepsilon_s(T)$. The dotted line is a guide for the eye. Part (a) enlarges the area around $\varepsilon_s(T) = \varepsilon_p(T) = 0$ from part (b).

Figures 6(a) and (b) show an overview of the determined interaction parameters according to Eq. 4 as function of the water/ethanol mass fraction. Part (a) enlarges the area around $\varepsilon_p = \varepsilon_s = 0$. The temperature dependence found for $\varepsilon_p(T)$ is indicated by the gradient filled areas, whereas the dark and light grey parts refer to cold and warm temperatures, respectively. For comparison we show also the values for the two systems mentioned in the introduction. In this plot it becomes obvious that the change of $\varepsilon_p(T)$ is more pronounced in pure water than in the solutions containing ethanol. The cross marks are the average values of $\varepsilon_s(T)$, which are always in the same order of magnitude as $\varepsilon_p(T)$. In contrast to the observations found for aqueous mixtures,[23] where the cross interaction, in this case $\varepsilon_p(T)$, was always stronger than the like-like interaction, $\varepsilon_s(T)$, we cannot identify a clear trend, although the determined interaction energies are in the same range as the interaction parameters used in the lattice model by Luettmer-Strathmann.[22] The most striking point is the sign change with solvent composition. While the interaction parameters are positive for pure water, they become negative for the solutions containing ethanol. The observed trend looks very similar to the change of the Soret coefficient as function of the solvent composition as it has been measured before.[13] Another general trend, although hard to see for pure ethanol, is that the absolute value of $\varepsilon_p(T)$ becomes smaller with increasing temperature. This holds also for polysaccharides in pure water, although here $\varepsilon_p(T)$ is in

contrast to the PEO system negative, which cannot be understood, because water should be a good solvent for the polysaccharides, so that we would expect attractive interactions as in the case of the PS/toluene system.

For the organic polymer solution of polystyrene in toluene we find $\varepsilon_p(T) = 0.17 \cdot 10^{-19}$J at 22 °C, which is indicated by an arrow in figure 6(b). This finding agrees with the ε-values found for the system PEO/water.

IV. CONCLUSION

In this paper we presented the molar mass dependence of thermodiffusion of polyethylene oxide in ethanol, water/ethanol mixture ($c_{\text{water}} = 0.7$) and water in a temperature range between 15°C and 45°C. We found that in pure ethanol, S_T, D and D_T all decrease as function of molar mass, with a sign change from positive to negative in S_T and D_T at a molar mass around 2200 g/mol. In water/ethanol mixture ($c_{\text{water}} = 0.7$) S_T and D decrease and D_T increases monotonically with increasing molar mass. S_T and D_T are negative for all the molar masses, indicating that ethylene oxide oligomers and polymers are thermophilic in water/ethanol mixture. In pure water system S_T increases and D decreases as function of molar mass. D_T increases and then reaches a plateau.

For all compositions studied in this work the molar mass dependence can be described with a theoretical model derived by Würger.[32] The determined interaction energies ε_s and ε_p are positive under good solvent conditions (water) and negative otherwise. It needs to be pointed out that the theoretical model has been derived for organic polymer solutions with short range Van-der-Waals interactions and not for polymers in solvents with specific interactions, so that the model will not be capable to describe the investigated mixtures in detail. Nevertheless the determined interaction parameters lie in a reasonable range and compare well with other literature results.[22] The deficiency of the model becomes evident if we look at the analysis of polysaccharides in water. Although water is a good solvent for polysaccharides negative interaction energies are found indicating bad solvent conditions. Here a refined model needs to be developed which takes specific interactions such as hydrogen bonds into account.

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