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Thermal Diffusion of Dextran in Aqueous Solutions in the Absence and the Presence of Urea

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The Ludwig−Soret effect was studied for aqueous solutions of dextran in the temperature range $15 < T < 55$ °C taking into account the effect of the addition of urea. In the absence of urea, the Soret coefficient S_T changes sign; it is positive for $T > 45.0$ °C but negative for $T < 45.0$ °C. The positive sign of S_T means that the dextran molecules migrate toward the cold side of the fluid; this behavior is typical for polymer solutions, whereas a negative sign indicates the macromolecules move toward the hot side. The addition of urea to the aqueous solution of dextran rises S_T and reduces the inversion temperature. For 2 M urea the change in the sign of S_T is observed at $T = 29.7$ °C and beyond that value S_T is always positive in the studied temperature range. To rationalize these observations, it is assumed that the addition of urea leads to an opening of hydrogen bonds similar to that induced by an increase in temperature.

I. Introduction

The Ludwig−Soret effect, also called thermal diffusion, concerns the mass flows of fluid mixtures, which are induced by a temperature gradient.[1−3] The Soret coefficient characterizes the magnitude of the effect. For steady-state conditions and binary mixtures, the Soret coefficient, S_T, is defined as

$$S_T = -\frac{1}{w_0(1 - w_0)}\frac{\nabla w}{\nabla T} \tag{1}$$

where T is the temperature, w is the mass fraction of component 1, w_0 means its equilibrium value, and ∇ indicates the gradient.[4,5] The Soret coefficient of component 1 in eq 1 has a positive sign when component 1 migrates to the cold side.[4] The Soret coefficient can also be expressed as

$$S_T = D_T/D \tag{2}$$

where D_T is the thermal diffusion coefficient and D is the ordinary translational diffusion coefficient.[6]

For polymer solutions and colloidal suspensions, where the solute molecules are much heavier than the solvent molecules,[7−10] positive S_T values have been observed; that is, the heavier components migrate to the cold side of the fluid.[7−11] These observations are analogous with the Chapman−Enskog theory, which describes the thermal diffusion in gas mixtures where hard sphere repulsions dominate the molecular interactions.[12−14] However, a few exceptions have been observed with aqueous polymer solutions. Giglio and Vendramini found negative S_T for solutions of poly(vinyl alcohol) in water.[15] Recently, we reported sign change behaviors of S_T for poly(ethylene oxide) (PEO) in ethanol/water mixture[5,16,17] and for poly(*N*-isopropylacrylamide) (PNiPAM) in ethanol.[18] For the protein solution, lysozyme in a buffer, an inversion has been reported by Iacopini and Piazza.[19] Although a deeper physical understanding of such phenomena with aqueous polymer solutions is still lacking, the thermal diffusion behavior can be attributed to single particle interaction and to collective contributions, if the system is dominated by short-range interactions.[20,21] It is therefore concluded that short-range interactions among solutes and solvents as well as the role of hydrogen bonding in the system should be studied in detail for a better understanding of changes in the sign of S_T. Indeed, the two-chamber lattice model for the system of PEO/ethanol/water developed by Leuttmer−Strathmann illuminated the significant role of hydrogen bonding for the description of such phenomena.[16,22]

It is well-known that highly polar molecules promote or break local structures of water; that is, the polar molecules dissolved in water have a large effect on the thermodynamic behavior of another solute. For example, urea is known as a structural destroyer of hydrogen bonding of water and denaturates proteins and DNA molecules.[23,24] It is therefore interesting to study the effect of such a polar molecule to clarify how the thermal diffusion properties of polymers are modified by their presence.

Here we report the experimental results of the holographic grating technique called thermal diffusion forced Rayleigh scattering (TDFRS) for determination of Soret coefficient. Dextran, a water soluble polysaccharide, used extensively in medical science,[25] flocculation,[26] pharmaceutical,[27] and agricultural[28] industries, was chosen for this study. It is mainly composed of α-D-(1 → 6)-linked glucose units and some short α-D-(1 → 3)-linked glucose branch units. To the best of our knowledge, this is the first study of the thermal diffusion phenomena for polysaccharide solution. In the present study, we found a thermally induced sign change of S_T of dextran in water without urea. With the addition of urea, the sign change behavior was obviously modified and which was discussed with

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taking into account the contributions of hydrogen bonding. Dextran has a big advantage to study the effect of the addition of urea in comparison with proteins and DNA molecules, because the dextran molecule is stable against the addition of a large amount of urea; that is, it does not show any precipitations or any chemical alterations.

II. Working Equation

The interpretation of TDFRS signals for the ternary system of polymer in the mixed solvent has already been reported in detail.[5] Briefly, the normalized heterodyne signal intensity ζ_{het} of the read out laser for binary mixtures is expressed as

$$\zeta_{\mathrm{het}} = 1 - \mathrm{e}^{-t/\tau_{\mathrm{th}}} - \frac{(\partial n/\partial w_1)_{P,T}}{(\partial n/\partial T)_{P,w_1}} w_{10}\,(1 - w_{10}) S_{\mathrm{T}} (1 - \mathrm{e}^{-q^2 D t}) \tag{3}$$

where τ_{th} is the time constant of the temperature grating, n is the index of refraction, P is the pressure, w_1 is the mass fraction of component 1, and w_{10} is its equilibrium value. For ternary mixtures

$$\zeta_{\mathrm{het}} = 1 - e^{-t/\tau_{\mathrm{th}}} - \frac{(\partial n/\partial w_1)_{P,T,w_2}}{(\partial n/\partial T)_{P,w_1,w_2}} w_{10}(1 - w_{10}) \times S_{1\mathrm{T}}(1 - \mathrm{e}^{-q^2 D_{11} t}) - \frac{(\partial n/\partial w_2)_{P,T,w_1}}{(\partial n/\partial T)_{P,w_1,w_2}} w_{20}(1 - w_{20}) \times S_{2\mathrm{T}}(1 - \mathrm{e}^{-q^2 D_{22} t}) \tag{4}$$

where w_k and w_{k0} are the mass fraction of component k and its equilibrium value, respectively, and D_{11} and D_{22} are diagonal elements of the matrix of diffusion coefficients. Equations 3 and 4 imply that a single diffusive process is expressed with the time constant $\tau = 1/(q^2 D)$ for binary mixtures, whereas two diffusive processes are expected with time constants $\tau_1 = 1/(q^2 D_{11})$ and $\tau_2 = 1/(q^2 D_{22})$ for the ternary system of a polymer in mixed solvent. Our experiments for dextran in urea/water showed a two-mode decay behavior (see section IV C) with time constants on the order of 10^{-3} s as the faster process associating with solvent diffusion and 10^{-1} s as the slower process corresponding to the polymer diffusion. These typical time constants of the diffusive processes were well separated on the time scale of the experiment. In analogy to binary mixtures, cf. eq 1, the Soret coefficients, $S_{k\mathrm{T}}$, for each process are defined as[5]

$$S_{k\mathrm{T}} \equiv -\frac{1}{\mathrm{w}_{k0}\,(1 - \mathrm{w}_{k0})} \frac{\nabla w_{\mathrm{k}}}{\nabla T} \tag{5}$$

III. Experimental Section

A. Sample. Dextran was donated from Polymer Standard Service GmbH (Mainz, Germany) and fractionated by Continuous Spinning Fractionation[29] using water as a good solvent and methanol as a poor solvent. One fraction was used in this study, and the weight- and the number-averaged molecular weight of dextran were determined as $M_{\mathrm{w}} = 86.7$ kg/mol and $M_{\mathrm{n}} = 44.9$ kg/mol by GPC. The polydispersity was $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.9$. Dextran standard samples were used for the calibration of GPC. Deionized water (milli-Q) was used as solvent. Urea was purchased from Acros Organics (New Jersey, U.S.A.). In this study, 1.0, 5.0, and 10.0 g/L dextran in water and solutions of 5.0 g/L dextran in urea/water mixtures with different urea compositions were prepared with a trace amount of the dye, Basantol Yellow 215 (BASF). The absorption spectra of the dye in the solution of dextran/urea/water agreed well with the solutions of dextran/water and urea/water which indicates no special contributions of the dye to the system. Detailed descriptions about the absorption spectra were presented in ref 5. The sample solutions were filtered directly into a quartz cell for TDFRS experiments through 0.22 μm membrane filter (Millipore).

Table 1. Refractive Index Increments with Respect to the Mass Fraction $(\partial n/\partial w_2)_{P,T,w_1}$ of Dextran in the Mixed Solvent of 0, 2, and, 5 M Urea in Water as Well as $(\partial n/\partial w_1)_{P,T}$ of Urea in Water

solution	$\partial n/\partial w$
dextran in water	0.134_0
dextran in 2 M urea/water	0.125_2
dextran in 5 M urea/water	0.108_9
urea in water[a]	0.158_3

[a] The value was obtained from ref 32.

B. Methods. The experimental setup for TDFRS has been described in detail elsewhere.[30] In brief, the interference grating is written by an argon ion laser operating at the wavelength of $\lambda = 488$ nm. The grating was read out by a He−Ne laser ($\lambda = 632.8$ nm). A rectangular quartz cell with a path length of 0.2 mm (Hellma) was used for sample solutions. 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. TDFRS measurements were carried out at the temperature range from 15 to 55 °C, where the temperature of the sample cell was controlled by circulating water from a thermostat with an uncertainty of 0.01 °C.

To determine the Soret coefficient, the refractive index increments with respect to mass fraction $(\partial n/\partial w)$ and to the temperature $(\partial n/\partial T)$ have to be determined separately. The quantities $(\partial n/\partial w_1)_{P,T,w_2}$, $(\partial n/\partial w_2)_{P,T,w_1}$, and $(\partial n/\partial T)_{P,w_1,w_2}$ were measured by means of a scanning Michelson interferometer operating at a wavelength of 632.8 nm.[10,31] The values of $(\partial n/\partial w)$ were measured at room temperature and $(\partial n/\partial T)$ were obtained from interference signals in the temperature range of ±0.5 K for the respective points.

The diffusion coefficient of dextran in homogeneous solutions was measured for comparison purposes by dynamic light scattering (DLS) using a Kr-ion laser as the light source ($\lambda = 647.1$ nm) and an ALV-5000E correlator to obtain correlation functions of scattered light. A cylindrical cell, having an inner diameter of 18 mm, was placed in a thermostated bath, the temperature of which was controlled to ±0.01 °C. The sample solution was filtered directly into the cylindrical cell through 0.22 μm membrane filter (Millipore). The sample solutions were kept at the measurement temperature for at least 1 h to ensure equilibrium before starting data acquisition.

IV. Results and Discussion

A. Contrast Factors. Refractive index increments with respect to the mass fraction $(\partial n/\partial w)$ for the systems of dextran in water with and without urea are shown in Table 1. $(\partial n/\partial w)$ of urea in water was obtained from CRC Handbook of Chemistry and Physics[32] and is also shown in Table 1. Typical results of temperature dependence of $(\partial n/\partial T)$ for the systems of 5.0 g/L dextran in water and 5.0 g/L dextran in urea/water are displayed in Figure 1. The values of $(\partial n/\partial T)$ for 1.0, 5.0, and 10.0 g/L dextran in water were identical within the experimental uncertainty in the measured temperature range.

B. Binary System of Dextran in Water. The temperature dependences of the Soret coefficient, S_{T}, of the diffusion coefficient, D, and of the thermal diffusion coefficient, D_{T}, are shown in Figures 2 and 3 for 1.0, 5.0, and 10.0 g/L dextran in water. These values were obtained by a least-squares fit of the experimental heterodyne signals ζ_{het} to eq 3. The error bars mean one standard deviation. At 45.0 °C, the sign of S_{T} and ζ_{het}

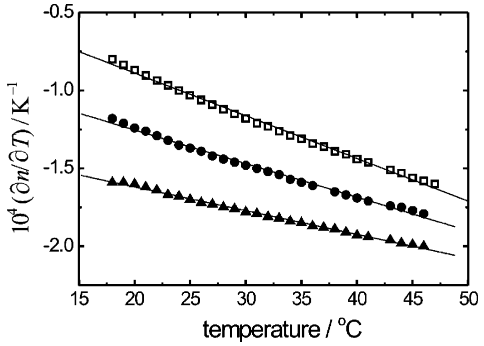

Figure 1. Refractive index increment with respect to the temperature $(\partial n/\partial T)_{P,w_1}$ for a solution of dextran (5.0 g/L) in the mixed solvent urea/water as a function temperature, where the urea concentrations in water are 0 (□), 2 (●), and 5 M (▲).

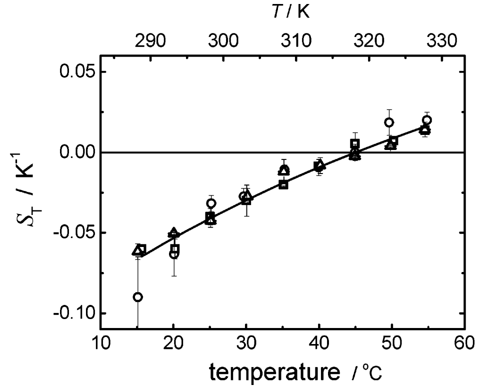

Figure 2. Soret coefficient, S_T, for aqueous dextran solutions of dextran of 1.0 (○), 5.0 (□), and 10.0 g/L (△), respectively, as a function of temperature. The solid line is fitted according to eq 6.

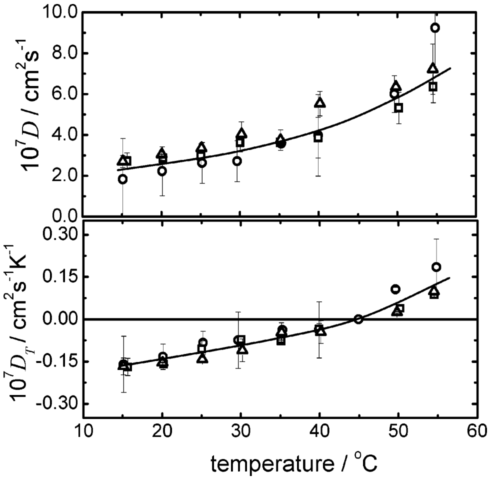

Figure 3. Diffusion coefficient, D, and thermal diffusion coefficient, D_T, for aqueous dextran solutions of dextran of 1.0 (○), 5.0 (□), and 10.0 g/L (△) as a function of temperature.

changes from negative to positive as T is raised. At $T > 45$ °C the dextran molecules migrate to the cold side of the fluid, as is typical for polymer solutions ($S_T > 0$), whereas at $T < 45$ °C they migrate to the warm side ($S_T < 0$). This seems to be the first observation of a change in sign for a polymer solution in pure water. The magnitude of S_T does not show any significant concentration dependence under the present experimental condition, consequently the above inversion temperature is identical for all concentrations measured. The diffusion coefficients of dextran in water at 25 °C obtained from TDFRS experiment are $D = 2.63 \times 10^{-7}$ cm^2/s for 1.0 g/L and $D = 2.98 \times 10^{-7}$ cm^2/s for 5.0 g/L; these data agreed well with those from DLS measurement, which are $D = 2.77 \times 10^{-7}$ cm^2/s for 1.0 g/L and $D = 3.16 \times 10^{-7}$ cm^2/s for 5.0 g/L. The diffusion coefficient was not obtained at $T = 45$ °C by TDFRS experiment where the signs of S_T and D_T change. Because the amplitude of heterodyne signal of TDFRS vanishes at this temperature, the diffusion coefficient cannot be evaluated [cf. eq 3].

The curve describing the temperature dependence of the Soret coefficient in Figure 2 was obtained by a least-squares fit to the empirical equation proposed by Iacopini and Piazza[19] as

$$S_T(T) = S_T^{\infty}\left[1 - \exp\left[\frac{T_{\mathrm{inv}} - T}{T_0}\right]\right] \tag{6}$$

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 to the strength of temperature effects. The parameters obtained by means of eq 6 will be presented and discussed in the next section, which deals with the ternary system of dextran/urea/water.

A thermally induced change in the sign of S_T was reported for solutions of poly(N-isopropylacrylamide) (PNiPAM) in ethanol where S_T was identical for both the dilute and the semidilute solutions.[18] It should be mentioned that S_T changed-from positive to negative with increasing temperature; that is, the slope of S_T versus temperature is opposite to that observed in the present study. Furthermore, ethanol is good solvent for PNiPAM at all temperatures according to the second virial coefficients obtained by static light scattering. The other systems which show thermally induced changes in the sign of S_T are solutions of PEO in ethanol/water[5] and of lysozyme in a sodium acetate buffer with added sodium chloride.[19] For these systems, the slope is positive and thus agrees with the result obtained for the dextran solutions. The difference in the slope is probably related to the choice of solvent; that is, water as the major component of solvent has a positive slope, whereas the alcohol system yields a negative slope. It was suggested for low molecular mixtures that the simple energetic consideration for water systems qualitatively explains the sign change behavior,[33] whereas for alcoholic systems, the energetic argument needs to be complemented with taking into account an entropic contribution.[34]

The exothermal Θ-temperature for aqueous dextran solutions is 44.7 °C and the solubility decreases by heating.[35] The solubility of polymers in water is closely related to the formation of hydrogen bonds, which shows a strong temperature dependence. The strength of hydrogen bonding is weakened by heating, thus the solubility of dextran becomes poorer. Surprisingly, the Θ-temperature of dextran is in good agreement with the sign inversion temperature T_{inv}. At theta conditions, the mixture is in a pseudoideal condition; that is, the polymers are in the boundary between good and bad solvents where they behave as an unperturbed chain. The coincidence of the sign inversion temperature with the Θ-temperature has not been substantiated with other systems. To clarify this result, one needs to study various systems at theta condition, taking into account thermodynamic parameters of polymer solutions. In a recent report concerning aqueous solutions PNiPAM, having a LCST (lower critical solution temperature) with the second virial coefficient being zero at 30.6 °C did not show any sign change of S_T in the temperature range 20 °C $< T <$ 38 °C.[37] PEO solutions in pure water exhibit a LCST behavior at around 100 °C [ref 36] and show no sign change of S_T in the accessible temperature range (18 °C $< T <$ 38 °C).[5] These findings

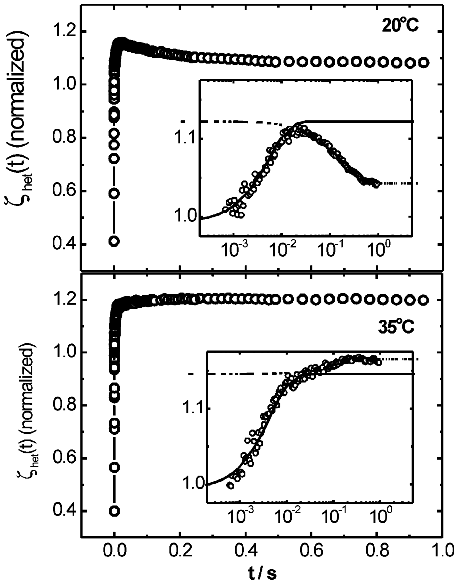

Figure 4. Typical normalized TDFRS signals of solutions of dextran (5.0 g/L) in the mixed solvent 2 M urea/water at 20.0 and 35.0 °C. The insets show semilogarithmic plots in which the curves were obtained by fitting to eq 4 with the fast mode (full line) and slow mode (dashed line).

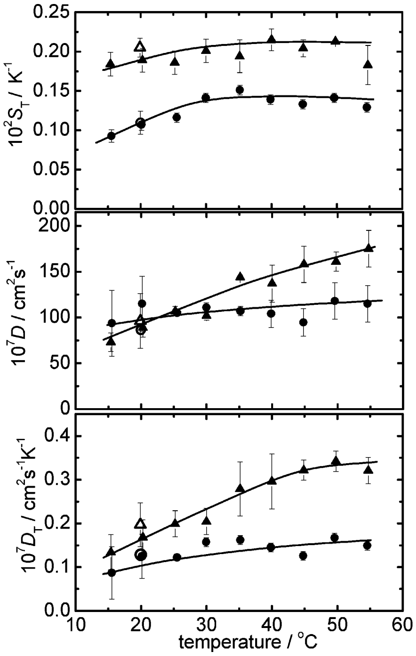

Figure 5. Soret coefficient, S_T, diffusion coefficient, D, and thermal diffusion coefficient, D_T, of urea as a function of temperature. Closed symbols correspond to the results obtained from the fast mode for the ternary systems, dextran in 2 M urea/water (●) and dextran in 5 M urea/water (▲). The open symbols correspond to the results for the binary systems of 2 M urea in water (○) and 5 M urea in water (△).

demonstrate that the coincidence of the inversion temperature of the present system with its theta temperature is not general. Further considerations in regard to the contribution of hydrogen bonding will be presented in the next section dealing with the effect of urea as a hydrogen bonding breaker.

C. Ternary System of Dextran in a Urea/Water Mixture. Figure 4 presents typical normalized TDFRS signal of 5.0 g/L dextran in the solvent of 2 M urea/water as a function of time after the intensity grating has been switched on at time $t = 0$. The insets show the same data on a semilogarithmic time scale. The linear plots include data from the rapid increase of $\zeta_{\rm het}(t)$ as the temperature modulation is established on the time scale $\tau_{\rm th}$, which is less than 1 ms. For later times, two mode behavior was observed on typical time scales of $\tau_1 \sim 10^{-3}$ s and $\tau_2 \sim 10^{-1}$ s. This can be seen clearly in the semilogarithmic plots of $\zeta_{\rm het}(t)$, where the signals of the establishment of the temperature modulation has been omitted for clarity. The solid and dashed lines in the insets were obtained by a least-squares fit to eq 4 and represent the fast and the slow mode, respectively.

Figure 5 shows the Soret coefficient, S_T, the diffusion coefficient, D, and the thermal diffusion coefficient, D_T, obtained from the fast mode for the ternary system (filled symbols). Open symbols correspond to the values obtained from a 2 M and a 5 M urea in water; these data agreed well with the values obtained from the fast mode of ternary system. This finding suggests that the fast mode observed in the ternary system is associated with the diffusive mode of the solvent, i.e., the urea/water mixture. The diffusion coefficient of urea obtained from TDFRS experiment is in a good agreement with the reported value $D = 1.38 \times 10^{-5}$ cm^2 s^{-1} at 25 °C.[38] In the previous report for the ternary system of PEO in the mixed solvent ethanol/water, we also observed a similar two mode behavior with TDFRS experiments.[5] The respective modes were interpreted as the development of the concentration gradient for ethanol/water (fast mode) and the formation of the concentration gradient of PEO in the mixed solvent (slow mode). In analogy to PEO/ethanol/water, the fast mode observed in this study is associated with the concentration gradient of urea/water, whereas the slow mode corresponds to the signal of the concentration gradient of dextran in the mixed solvent. The positive value of the Soret coefficient means that the urea molecules migrate to the cold side of the fluid. In the measured temperature range, the values of S_T, D, and D_T for 5 M urea solution tend to be larger than those of 2 M urea. However, we do not discuss the concentration and temperature dependences of resultant values obtained from the fast mode because of large uncertainty due to experimental difficulties for this aqueous solution and lack of experimental data for comparison. In Figure 4, the signal intensity of the slow mode (dashed line) decreases with time at 20 °C, whereas at 35 °C, it increases. This observation implies a change in the sign of the Soret coefficient, where the slow mode corresponds to the establishment of concentration gradient of dextran molecules in the mixed solvent as mentioned above.

Figure 6 shows the temperature dependence of the Soret coefficient obtained from the slow mode by a least-squares fit to eq 4 for a solution of 5.0 g/L dextran in the mixed solvent. In the same way, the diffusion coefficient and the thermal diffusion coefficient of dextran were obtained as shown in Figure 7. The results for the binary solution of 5.0 g/L dextran in water (without urea) are also shown in Figures 6 and 7. A change in the sign of S_T was observed at 0 and 2 M urea/water solvents. The corresponding temperatures are 45.0 °C for 0 M urea and 29.7 °C with the addition of 2 M urea. No inversion was found in the case of 5 M urea within the measured temperature range. The diffusion coefficient D of dextran increases with increasing temperature, while the urea concentration dependence of D was not observed. As mentioned previously, the diffusion coefficient D of dextran obtained by TDFRS experiment is in good agreement with the results of DLS. The temperature dependence of thermal diffusion coefficient D_T showed similar tendency with the Soret coefficient; that is, with increasing urea concentration, the value of D_T increases and the inversion temperature $T_{\rm inv}$ shifts to lower values; for 5 M urea, D_T does not have $T_{\rm inv}$.

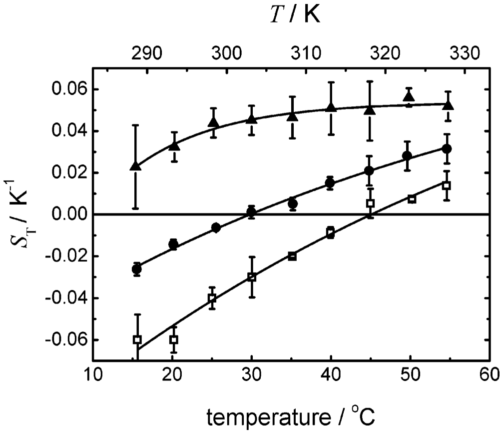

Figure 6. Soret coefficient, S_T, for solutions of dextran (5.0 g/L) as a function of temperature. Closed symbols correspond to the values obtained from the slow mode for the ternary systems of dextran in 2 M urea/water (●) and of dextran in 5 M urea/water (▲). Open symbols represent the results for the binary system of dextran in water (□). The solid lines are fitted according to eq 6.

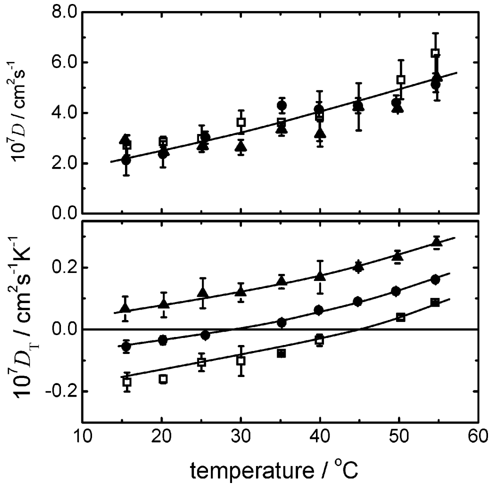

Figure 7. Diffusion coefficient, D, and thermal diffusion coefficient, D_T, for solutions of dextran (5.0 g/L) as a functions of temperature. Closed symbols correspond to the values obtained from the slow mode for the ternary systems of dextran in 2 M urea/water (●) and of dextran in 5 M urea/water (▲). Open symbols represent the results for the binary system of dextran in water (□).

Fitting curves in Figure 6 for the Soret coefficient were obtained by a least-squares fit to eq 6. The urea concentration dependence of the sign change temperatures T_{inv} were 45.0 °C (0 M), 29.7 °C (2 M), and 9.3 °C (5 M), although the temperature of 9.3 °C could not be achieved in the experiments. The asymptotic value of the Soret coefficient S_T^∞ of dextran decreases from 0.13 via 0.10 to 0.05 K^{-1}, and the parameter T_0 declines from 71.4 via 63.5 to 11.1 K as the urea content is raised from 0 M via 2 M to 5 M. For lysozyme solutions it is reported that the values of S_T^∞ and T_0 decrease with increasing the ionic strength of the solution.[19] The decreasing behaviors of S_T^∞ and T_0 with increase of ionic strength for lysoyzme solutions have a similar trend to those with increase of the concentration of urea for dextran solution. It indicates existence of an analogue mechanism of sign change behavior. However, in the lysozyme solution, electrostatic forces have a dominant role for the solution properties which could be different from the effect of urea for dextran molecules. As mentioned in the previous section for the binary system dextran/water, the strength of hydrogen bonding is weakened by heating which yields positive values of the Soret coefficient. In this study for the ternary system dextran/urea/water, the negative values of the Soret coefficient tends to become positive upon the addition of urea; this effect is analogous to that resulting from an increase in temperature. This observation implies that urea molecules destroy local structures of water; that is, the addition of urea has a similar contribution with heating for the sign change behavior of dextran solution.

From the fact that solutions of PNiPAM in water did not show any sign change of S_T upon heating, even when passing through the Θ-temperature where liberations of solvated water take place according to the consequence of the coil−globule transition of it, we conclude that there are no systematic trends for sign change behavior among these systems. The results suggest that chemical nature of polymers and the structure of water have complicated contributions for the sign change behavior and which is a sort of system dependence phenomena. The sign inversion behavior of S_T is diminished by the addition of urea. Although the role of urea for destroying the local water structure is still controversial,[23,24,39,40] it indicates that the thermal diffusion behavior considerably depends on the modification of local structures of water; that is, a modification of short-range interactions has a dominant role for the sign inversion of Soret coefficient of aqueous solutions of dextran.

Recently, inversions in S_T were studied by means of MD methods for aqueous solutions, where the sign change of alcohol/water mixtures was attributed to the strength of the molecular interactions.[41] By a thermodynamic consideration Ki and Wu predicted the sign change for the systems of ionic solutions.[42] At the present stage, it is not clear whether these approaches established for associating solutions can be adopted for aqueous polymer systems. Semenov and Schimpf developed a theoretical model of thermal diffusion considering molecular interactions that depend on the temperature-induced pressure gradient.[43] According to these authors, the Soret coefficient for polymer solutions should change sign, if the Hamaker constant between the solvent and the solute satisfies a certain condition. It is of interest to apply their theory for aqueous polymer solutions, whether the sign change behavior can be evaluated. To examine it, however, one needs to acquire physical parameters of the aqueous solution of dextran for the calculation.

V. Conclusion

The thermally induced sign change of the Soret coefficient for dextran solutions in water was found at the temperature 45.0 °C. The temperature above 45.0 °C dextran molecules migrate toward the cold side of the fluid ($S_T > 0$), whereas below 45.0 °C dextran molecules migrate toward the hot side ($S_T < 0$). When urea is added to the solution, the sign inversion temperature of Soret coefficient shifted to lower temperatures and the value becomes more positive. These observations imply that the strength of hydrogen bonding is weakened with the addition of urea similar to that induced by an increase in temperature.

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