Temperature dependence of the diffusion, thermodiffusion and Soret coefficient of a dilute polystyrene/toluene solution as measured by means of a transient holographic grating technique

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ABSTRACT

We have measured diffusion, thermodiffusion and Soret coefficients of a dilute solution of polystyrene in toluene by means of the transient holographic grating technique of thermal diffusion forced Rayleigh scattering over a temperature range from 10 to 50 °C. The results show a systematic deviation from optical beam deflection measurements over a narrower temperature interval of the order of ten percent but the identical temperature dependence. A comparison with previous measurements from our laboratory, new control measurements and literature data does not lead to a clear conclusion about the correct values. From the diffusion coefficient a temperature independent hydrodynamic radius is obtained. Both the Soret coefficient and the viscosity-scaled thermodiffusion coefficient ηD_T, for which a universal value has been reported in the case of asymmetric systems with large solute entities, decrease with temperature.

1. Introduction

The overwhelming body of experimental data for thermodiffusion and Soret coefficients has been measured at or around room temperature for binary liquid mixtures of small molecules. Temperature-dependent studies on non-ionic mixtures are notably scarce. They show a complicated picture with no simple and predictable behavior of the temperature dependence of the Soret coefficient S_T.

Measurements for binary mixtures of small molecules have revealed a tendency for a decreasing modulus of S_T with increasing temperature [1–4], but this rule is not strict. For low ethanol concentrations, the Soret coefficient of ethanol in water is positive, i.e., ethanol goes to the cold side. For high ethanol concentrations, it is the other way around: ethanol now goes to the hot side with a sign change concentration at $c \approx 0.29$. The modulus of S_T decreases with increasing temperature but the concentration of the sign change remains constant [2,3]. Such temperature-independent fixed points have also been found for non-aqueous mixtures. In Ref. [1] it has been shown that for many systems S_T can be factorized into a product of a temperature and a concentration dependent function with a temperature-independent fixed point. Depending on the actual mixture and its composition, S_T can increase or decrease with temperature. Zhang et al. have reported a positive Soret coefficient for toluene/n-hexane over the entire composition range, which decreases with temperature [5] but does not change its sign.

For polymer solutions there are even less temperature dependent data and the situation is less clear than for small molecules. Kita et al. e.g., investigated the temperature dependence of poly(*N*-isopropylacrylamide) (PNIPAM) in monohydric alcohols. In ethanol they found a sign change of the Soret coefficient at 34 °C from positive at low to negative at high temperatures [6]. For the same thermoresponsive polymer in water, they observed a pronounced maximum of S_T around the coil-globule transition at 30 °C, but no sign change [7]. Wang et al. report different signs of S_T of polyethylene oxide in water/ethanol mixtures, depending on the solvent composition, but generally only a weak temperature dependence [8]. The Soret coefficient of pullulan in DMSO and in water was measured by Kishikawa et al. who observed a sign change from negative to positive in water but not in DMSO [9]. Brimhall et al. have studied the temperature dependence of the thermal diffusion factor α and the thermodiffusion coefficient D_T of different polystyrene molar masses in ethyl benzene, which can be viewed as the effective repeat unit of the polymer. They found that α decreases with temperature whereas D_T increases [10]. Iacopini et al. report an increase of S_T with temperature for a number of different polymeric and colloidal solutes in aqueous solution. In these systems, S_T starts with negative values at low temperatures and then monotonously increases, thereby changing its sign, until it reaches a positive plateau at high temperatures. The temperature dependence in these systems shows universal behavior and can be well described by an
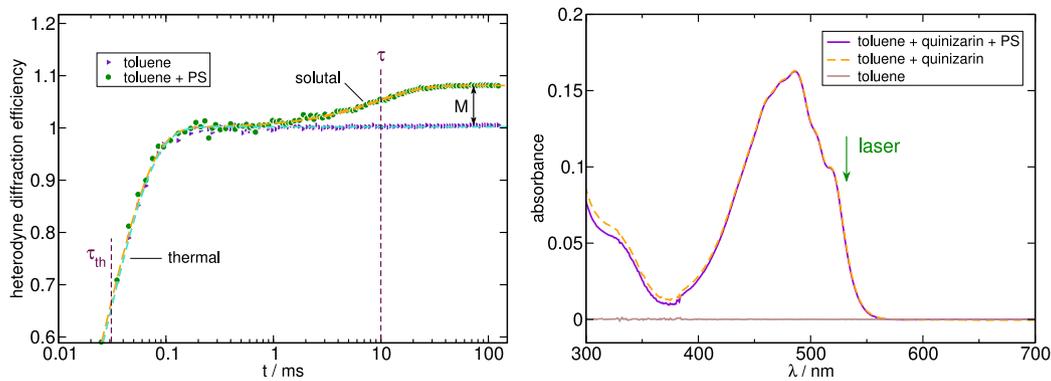

Fig. 1. Left: Heterodyne TDFRS diffraction efficiencies normalized to the thermal signal amplitude. The flat plateau of the pure solvent toluene and the additional slow solutal response with amplitude M of the polymer solution are clearly separated. Right: Absorption spectra of dye solutions in toluene with and without polymer. The arrow marks the wavelength of the writing laser (532 nm). PS($M_w = 4.88$ kg/mol)/Tol, $c = 0.01$, $\theta = 25$ °C.

empirical fit function with only a few adjustable parameters [11,12]. A similarly increasing Soret coefficient, including a sign change with increasing temperature, has also been observed for polyethylene oxide in a water/ethanol mixture [13].

In our study we have measured the Fickian diffusion coefficient D, the Soret coefficient S_T and the thermodiffusion coefficient $D_T = S_T D$ of the short polymer polystyrene (PS, $M_w = 4.88$ kg/mol) in the good solvent toluene (Tol). The measurements were performed to support an empirical parametrization of S_T in Ref. [14], which was originally only based on the measurement of the temperature dependence of a single high molar mass polymer with $M_w = 90$ kg/mol [15]. This result for S_T was already used in Ref. [14], but the data for all three transport coefficients have neither been published nor discussed so far.

2. Experimental

The measurements were performed by means of the transient holographic grating technique of thermal diffusion forced Rayleigh scattering (TDFRS). A writing beam of 532 nm wavelength (Coherent VERDI) with a power between 400 and 1000 mW was used for writing and a HeNe-laser (JDS Uniphase, 632.8 nm) for readout of the refractive index grating in a heterodyne detection scheme [16]. The grating period, which defines the diffusion length, was (10.07 ± 0.02) μm. The samples for the TDFRS measurements were slightly colored for optical absorption at the writing wavelength with the inert dye quinizarin. Additional optical beam deflection measurements were performed as described in Ref. [17]. Fig. 1 shows two normalized heterodyne diffraction efficiencies, one for the pure toluene and the other one with polymer. The slow solutal response is clearly timescale-separated from the fast thermal signal. Because of the short diffusion length, the time constants are very short: approximately $\tau_{th} = 31$ μs for the thermal and $\tau = 10$ ms for the solutal one.

The thermal contrast factor was measured interferometrically as described in Ref. [18] with the correction of Ref. [2]. For the low polymer concentrations in our experiments, it can be approximated by $(\partial n / \partial T)_{p,c} (T) = -5.618 \times 10^{-4}$ K$^{-1} - 6.6 \times 10^{-9}$ K$^{-2}(T - 273.15$ K$) - 4.2 \times 10^{-9}$ K$^{-3}(T - 273.15$ K$)^2$. The solutal contrast factor was determined from a concentration series as $(\partial n / \partial c)_{p,T} (T) = 8.66 \times 10^{-2} + 1.56 \times 10^{-4}$ K$^{-1}(T - 273.15$ K$)$. Polystyrene (PS) (PSS-ps4.5k, lot ps150410, $M_p = 4.84$ kg/mol, $M_w = 4.88$ kg/mol, $M_w/M_n = 1.04$) was obtained from PSS Polymer Standards Service GmbH. The solvent was toluene (Tol) (VWR AnalaR NORMAPUR, article 28676.297, purity > 99.5%).

3. Results and discussion

Figs. 2–4 show the diffusion, thermodiffusion and Soret coefficients, respectively, as a function of temperature for a polymer mass fraction of $c = 0.01$. In addition to the TDFRS data, also OBD measurements over

a narrower temperature interval, previous own TDFRS measurements for room temperature and literature data are plotted. All results are for polystyrene of identical or similar molar mass in toluene. There is obviously a systematic deviation between the TDFRS and the OBD data for all three coefficients D, D_T and S_T, with the OBD data being smaller by approximately 10 to 20 percent. While this is not an excessive difference, it exceeds the uncertainty of a few percent typically encountered for binary mixtures [19]. The samples for the TDFRS and for the OBD experiment were prepared from the same batches of both the polymer and the solvent.

Unfortunately, we have not been able to find the reason for this discrepancy. Tests with binaries composed of the well-characterized Fontainebleau benchmark systems showed a perfect agreement between both techniques and also a potential contribution from the dye in the TDFRS experiments could be excluded by reference measurements with different dye concentrations and by a measurement with dye but without polymer, which yielded a perfectly flat baseline (Fig. 1). The absorption spectrum of the dye in toluene did not change after the addition of the polymer, which is shown in Fig. 1(right). In particular, there is no indication of any peak broadening or shift that could be indicative for a selective adsorption of the dye by the polymer. The two solutions for the spectra were prepared from a stock solution of quinizarin in toluene, which was split into two parts. To one part, 1% of polystyrene was added and to the other 1% of toluene in order to guarantee a constant dye concentration. A possible influence of convection has been excluded by variation of the laser power (TDFRS) and the temperature gradient (OBD), which both did not change the measured values for the transport coefficients. In Ref. [20] it was shown how correct D_T values can be extracted from the initial rise of the solutal TDFRS signal even in case of signal distortion by convection. Similar arguments also hold for OBD. Since all of our experiments could perfectly be described by the respective time-dependent TDFRS and OBD fit functions, which directly yield all three coefficients D, D_T and S_T, there was no need to resort to a separate consideration of the initial slopes.

The TDFRS results are perfectly reproduced by TDFRS control measurements with new samples (TDFRS 2) and they also agree with unpublished TDFRS data measured in our laboratory during a master thesis in 2020 (TDFRS 3) [21]. Older TDFRS measurements (TDFRS 4) [18], performed with almost the same instrument, which underwent only minor modifications since then, also show a good agreement with the new TDFRS data for the diffusion coefficient D. Both D_T and S_T are, however, in support of the OBD results. Furthermore, the OBD measurements of D_T are backed by thermal field flow fractionation (TFFF) data by Schimpf and Giddings [22]. Extensive OBD measurements on PS in Tol over a broad concentration and molar mass range, performed in the group of Sengers, show a broader scatter for the molar mass independent D_T [23]. The range covered by these data is indicated by a
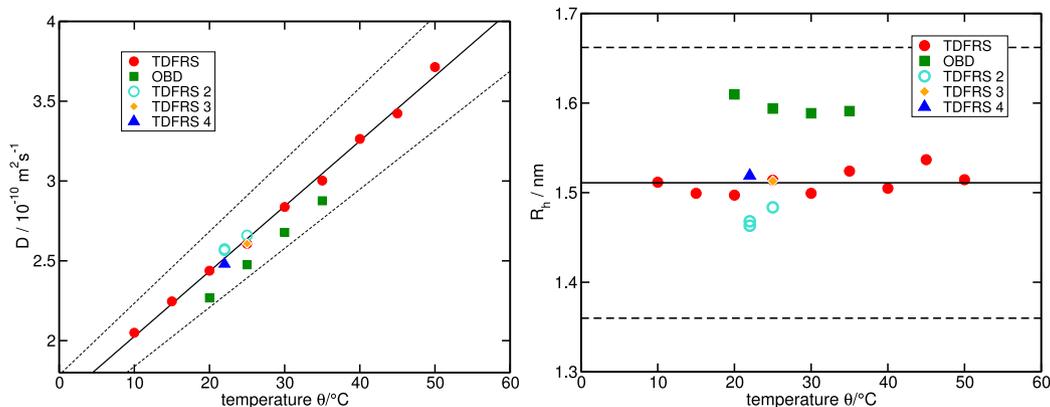
Fig. 2. Left: Diffusion coefficients as measured by TDFRS and OBD in comparison to previous (TDFRS 3) and new control (TDFRS 2) measurements and literature data from Ref. [18] (TDFRS 4) for similar molar masses and concentrations. The solid line is a linear fit to the new TDFRS data and the two dashed lines represent ±10% intervals. Right: Hydrodynamic radii R_h as calculated from the diffusion coefficients according to Eq. (1). The solid line is a linear fit to the new TDFRS data and the two dashed lines represent the ±10% intervals from the left figure. PS($M_w = 4.88$ kg/mol)/Tol, $c = 0.01$.

vertical bar in Fig. 3(left) and is in good agreement of our OBD results. The values of D and S_T in the same publication are more difficult to compare, since both quantities depend on the polymer molar masses, which are different from ours.

Thus, we are left with this somewhat unsatisfactory situation that the deviations between the different experiments, which exceed the usual uncertainty of a few percent, remain unexplained. Nevertheless, the temperature dependence of the new TDFRS measurements, which cover a much broader temperature interval, is in agreement with the one of the OBD data and shall be discussed in the following.

The temperature dependence of the diffusion coefficient is plotted in Fig. 2(left). The deviation between OBD and TDFRS is somewhat below 10 percent and acceptable. The speeding up of diffusion with temperature is accounted for by the Stokes–Einstein equation

$$D = \frac{k_B T}{6\pi \eta_0 R_h} \tag{1}$$

with k_B being Boltzmann's constant, R_h the hydrodynamic radius of the polymer and η_0 the temperature dependent viscosity of the solvent toluene. For the latter, standard reference data are provided by Santos et al. [24] at a pressure of 0.1 MPa:

$$\ln \eta^* = -5.2203 + \frac{8.964}{T^*} - \frac{5.834}{(T^*)^2} + \frac{2.089}{(T^*)^3} \tag{2}$$

The reduced variables are $T^* = T/T_0$ and $\eta^* = \eta_0(T)/\eta_0(T_0)$ with $T_0 = 298.15$ K and $\eta_0(T_0) = 554.2$ µPa s. Fig. 2(right) shows the constant temperature-independent hydrodynamic radii as calculated according to Eq. (1) from the diffusion coefficients in Fig. 2 and the viscosities from Eq. (2). The dashed lines in Fig. 2(right) represent the ±10%-interval around the mean value.

In absence of a comprehensive theory for D_T and S_T, we will discuss these two coefficients only phenomenologically. Similar to the Fickian diffusion coefficient D, also the thermodiffusion coefficient D_T increases with temperature, albeit somewhat weaker. While it is known that the viscosity is an important factor for the thermodiffusion coefficient [22,25–27], it does not entirely reproduce the observed temperature dependence, as can be seen from the product ηD_T in Fig. 3(right), which decreases with increasing temperature.

It has been found in a number of works, that the product ηD_T plays a prominent role in thermodiffusion of asymmetric systems with large entities dissolved in small solvent molecules, such as polymers with Kuhn segments exceeding, say, 1 kg/mol [17,25–28]. In these systems the product of the thermodiffusion coefficient (or the thermophoretic mobility) and the viscosity assumes a universal value of $\eta D_T \sim 6 \times 10^{-15}$ Pa m^2 K^{-1}. This universal value could not only be observed for heavy solutes in many different solvents but also in the opposite limit

of vanishing mass of the solvent molecules for fixed solute molar masses. The latter could be achieved by the homologous series of the n-alkanes [28]. This universality means, that in all these systems the different thermophoretic migration velocities are solely caused by the different solvent viscosities. Also solutions of PS in Tol belong to this class of systems [26]. So far, all relevant experiments had been carried out close to room temperature and nothing was known about the temperature dependence of the universal value of ηD_T.

Fig. 3(right) represents the first such measurement. As was to be expected from the deviation of the TDFRS data for D_T in Fig. 3(left), the TDFRS data are larger than the universal value reported in the literature, whereas the OBD data show a very good agreement for the reference temperature of $\theta = 25$ °C. Both data sets show a clear tendency: the product of ηD_T decreases with temperature. Although this has now been measured only for a single system, it is most likely a general behavior of the universal value.

Since the temperature dependence of D_T is weaker than the one of D, the Soret coefficient $S_T = D_T/D$ decreases with increasing temperature, as plotted in Fig. 4. Because of the constant hydrodynamic radius, the temperature dependence of S_T essentially resembles the temperature dependence of ηD_T in Fig. 3(right), except for the factor T in the nominator of Eq. (1), which is only contained in S_T. Thus, solutions of PS in Tol belong to the class of systems with a positive Soret coefficient of the polymer and, correspondingly, a negative one of the solvent. This behavior is in agreement with the pseudo-isotope effect, which favors thermophobic migration of the heavier and thermophilic migration of the lighter component [29–35]. Similar to many mixtures of small organic molecules, the modulus of S_T decreases with increasing temperature [1–4].

4. Summary and conclusions

We have measured the temperature dependence of diffusion and thermodiffusion of a relatively short polystyrene with $M_w = 4.88$ kg/mol dissolved at low concentrations in toluene. The majority of the new experiments have been performed by the holographic grating technique of TDFRS, covering a temperature interval from 10 to 50 °C. Some additional measurements have been performed over a narrower temperature interval from 20 to 35 °C by means of optical beam deflection. The temperature dependencies of all three coefficients D, D_T and S_T are practically identical for both techniques, but there is a systematic shift of unknown origin. Repeated control measurements could not clarify the source of the observed discrepancies. Although literature data also do not provide a clear picture, they seem to be more in favor of the OBD results. We have found that the temperature dependence
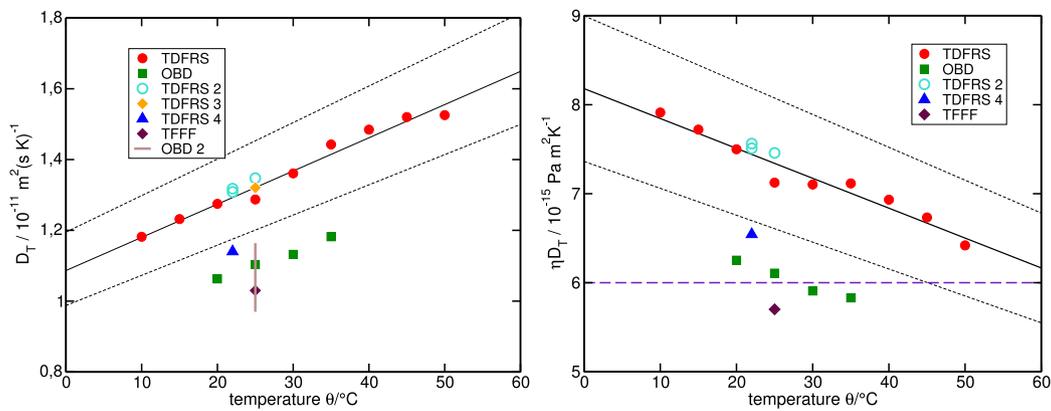
Fig. 3. Left: Thermodiffusion coefficients as measured by TDFRS and OBD in comparison to previous (TDFRS 3) and new control (TDFRS 2) measurements and literature data from Ref. [18] (TDFRS 4) for similar molar masses and concentrations. Also shown are TFFF data from Ref. [22]. The vertical bar (OBD 2) represents the range of data from Ref. [23] for various molar masses. The solid line is a linear fit to the new TDFRS data and the two dashed lines represent $\pm 10\%$ intervals. Right: Product ηD_T as calculated from the thermodiffusion coefficients and the viscosities according to Eq. (2). The solid line is a linear fit to the new TDFRS data and the two dashed lines represent $\pm 10\%$ intervals. PS($M_w = 4.88 \, \text{kg/mol}$)/Tol, $c = 0.01$.
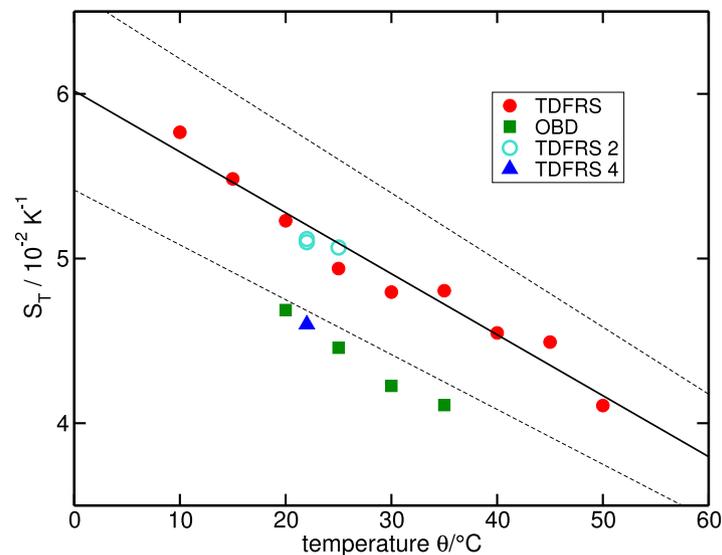
Fig. 4. Soret coefficients as measured by TDFRS and OBD in comparison to new control measurements (TDFRS 2) and literature data from Ref. [18] (TDFRS 4) for similar molar masses and concentrations. The solid line is a linear fit to the new TDFRS data and the two dashed lines represent $\pm 10\%$ intervals. PS($M_w = 4.88 \, \text{kg/mol}$)/Tol, $c = 0.01$.

of the diffusion coefficient is fully accounted for by the temperature dependence of T/η, corresponding to a constant hydrodynamic radius of the polymer. The situation is more complex for the thermodiffusion and the Soret coefficient. While D_T is, similar to D, also sped up by an increasing temperature, its temperature dependence is weaker. When the viscosity effect is factored out, the product ηD_T decreases with increasing temperature. The quantity ηD_T is of particular importance, since it assumes a universal value for many asymmetric systems with large solute and small solvent entities. So far, this universality has only been investigated at room temperature and our experiments show for the first time the decrease of this value with temperature. The Soret coefficient, where the viscosity effect is also factored out, shows a similar decrease. It should be kept in mind, however, that the Soret coefficient does not show the same universality as ηD_T when different systems are compared. What could not be resolved is the discrepancy between OBD and TDFRS measurements. Of course, this is a very unsatisfactory situation that needs to be investigated in more detail. Since a very good agreement between both methods has been observed for other systems, e.g., the Fontainebleau benchmark mixtures, and because of the effort already spent, we do not expect a quick and simple answer for this problem.

CRediT authorship contribution statement

J. Kantelhardt: Writing – original draft, Investigation, Formal analysis. **D. Sommermann:** Investigation, Formal analysis. **W. Köhler:** Writing – original draft, Supervision, Project administration, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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