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Soret effect in a nonionic surfactant system

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Abstract We studied the thermal diffusion behavior of $\mathrm{C}_{10}\mathrm{E}_8$ (decyl octaethylene glycol ether) in water by means of thermal diffusion forced Rayleigh scattering (TDFRS). We determined the two diffusion coefficients D_T, D and the Soret coefficient S_T in a concentration range from $w = 5$ %wt to 25 %wt in a temperature range from $T = 20$ °C to 40 °C. The obtained Soret coefficients S_T were positive for all temperatures and concentrations. Additionally, we also performed dynamic light scattering experiments in the same temperature range in order to compare the measured diffusion constants and characterize the system. Special attention was paid to the tiny amount of inert dye which needs to be added for absorption and thermalization of the light energy. The influence of an organic dye and an organic

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coloured salt on the experimentally determined transport properties has been studied. The results show that all coefficients are independent of the choice of the dye for this particular surfactant system.

1 Introduction

Surfactants are widely used as emulsifying agents and detergents and have been investigated thoroughly [1,2]. Those systems often exhibit interesting physicochemical properties. Especially nonionic surfactants of the general type C_mE_n, where m indicates the number C-atoms in the hydrocarbon chain, and n represents the number of ethylene oxide units $(\text{-OCH}_2\text{CH}_2)_n$-OH, have been studied intensively [3–5]. Due to alteration of m and n, head-group interactions and micelles size can be changed systematically. The delicate balance of alkyl-chain/water repulsion and repulsion between adjacent headgroups within the micelle, together with surface curvature and limitations due to alkyl chain packing lead to specific characteristics of C_mE_n as structural changes of the micelles, phase separation, critical phenomenon, and so on [3,4]. Furthermore, the addition of electrolytes and nonelectrolytes have a large effect on the phase behavior of nonionic surfactants because of their effect on the water structure and their hydrophilicity.

So far many properties of the nonionic surfactant systems have been investigated but there is limited knowledge on the thermal diffusion behavior for nonionic micellar solutions. Thermal diffusion describes the thermal diffusion current in the presence of a temperature gradient. In an binary fluid mixture with non-uniform concentration and temperature, the mass flow J_m of one component contains both contributions stemming from the concentration and from the temperature gradient [6]:

$$J_\mathrm{m} = -\rho D \nabla w - \rho w \left(1 - w\right) D_\mathrm{T} \nabla T. \tag{1}$$

D denotes the collective diffusion coefficient, D_T the thermal diffusion coefficient, ρ the mass density, and w the concentration in weight fractions. In a stationary state where the diffusion flow J_m vanishes the Soret coefficient S_T is given by

$$S_\mathrm{T} \equiv \frac{D_\mathrm{T}}{D} = -\frac{1}{w\left(1 - w\right)} \frac{\nabla w}{\nabla T}. \tag{2}$$

In recent years, considerable experimental effort has been devoted to the thermal diffusion of complex molecular systems, such as micellar phases of soluted surfactants, colloidal suspensions, and polymer solutions [7–11]. The Soret coefficient has been measured as a function of various parameters, such as charge, temperature and concentration of the diffusing particles, and the salt content [7]. For aqueous systems it turned out that hydrogen bonds can change the thermal diffusion behavior significantly by reversing the sign [10]. All experiments show that specific interactions and surface effects have a strong impact on thermodiffusive behavior. Also, the formation of micelles is dominated by interfacial effects. Therefore, it is expected that the shape of the micelles has an influence on the thermal diffusion behavior.

In the past, mainly ionic surfactant systems have been investigated [12, 13]. Recently, strong interaction effects for the Soret coefficient of an ionic micellar system have been observed, where the salt concentration dependence of the Soret coefficient for the micellar system is reversed going from very dilute to higher surfactant concentrations [7]. There is, however, very little knowledge about the thermal diffusion behavior of nonionic surfactants except for some preliminary studies on C_8E_4 in a thermal diffusion cell in the group of Piazza [14]. Due to the fact that the surfactant has a lower density than water and moves to the cold side, the measurements were complicated by convection.

Convection problems can be effectively avoided by the so called Thermal Diffusion Forced Rayleigh Scattering (TDFRS) method. In the experiment rather small temperature differences of several μK are sufficient to obtain a reliable measurement signal. A drawback of the method might be the fact that a tiny amount of dye is needed to convert the electric field energy by absorption into thermal energy. The chosen dye should show a strong optical absorption at the writing wavelength, but only a weak absorption at the readout wavelength of the otherwise transparent liquids. Ideally, the dye is inert, which means that the dye should not show any photobleaching and does not contribute to the diffraction signal. For organic mixtures it has been shown that the addition of an organic dye leads only to a very weak contribution, which does not influence the mean values but leads to slightly asymmetric error bars [15]. In the case of aqueous systems it is much harder to find an inert dye. Typically, the water soluble dyes change their properties and are dependent of pH, ionic strength and other parameters. For the investigation of the surfactant system we used two different dyes: basantol yellow [16], a tri-valent metal organic salt which is directly soluble in water, and alizarin, an organic dye which becomes soluble only in the presence of the surfactant. Both organic compounds probably change the balance of the hydrogen bond formation and it is expected that the phase behavior of the micelles is influenced. Especially for electrolytes there are numerous studies for surfactant systems [17–23]. Depending on the nature of the anion the two-phase boundary either shifts to lower or higher temperatures [23]. Due to the fact that the added dye is a tri-valent salt we expect a change of the phase behavior by addition of the dye. In order to study the influence of the dye we performed all measurements with both dyes.

In this paper we describe thermal diffusion measurements of the surfactant $C_{10}E_8$ in water in a concentration range from $w = 5 - 25$ %wt at 20,30 and 40 °C. Additionally, we also performed dynamic light scattering measurements to characterize the system.

2 Experiment and data analysis

2.1 Sample Preparation and contrast factors

$C_{10}E_8$ ($[CH_3(CH_2)_9\text{-}(OCH_2CH_2)_8OH]$, decyl octaethylene glycol ether; purity $\geq 98\%$; M.W. = 510.72) was purchased from Fluka BioChemika, Japan. The surfactant was used without further purification. The alizarin was purchased from Riedel-deHaën and basantol yellow we obtained from BASF.

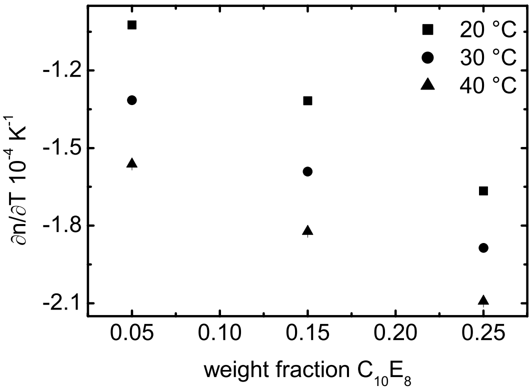

Fig. 1 $(\partial n/\partial T)_{w,p}$ of $C_{10}E_8$ in water as a function of the surfactant weight fraction at 20° (■), 30° (●) and 40° (▲). The samples contained the same small amount of basantol yellow [16] as used in the TDFRS experiment.

In order to prepare the samples for the TDFRS experiment a small amount of dye needs to be added to the samples. The dye has an absorption band at the wavelength of the writing beam, $\lambda_w = 488$ nm and is transparent at the read-out wavelength, $\lambda_r = 633$ nm. The absorption coefficient at λ_w was adjusted to a value $\alpha = 1.5 - 3$ cm^{-1}. This low absorption leads to a weight fraction of less than 10^{-5} basantol yellow. The weight fraction of the alizarin is of the same order of magnitude.

If we used basantol yellow as the dye, we first prepared an aqueous solution with the desired absorption using deionized water (Milli-Q). Then the surfactant was added and stirred at least for 4 hours at room temperature. In the case of the organic dye alizarin, we added the dye and the surfactant at the same time. The mixture was then also stirred at least for 4 hours at room temperature to mix all components thoroughly. After preparation the solutions were filtrated by a 0.45 μm filter (Spartan) directly in the sample cells. The sample cells for the TDFRS experiment were Quartz cells (Hellma) with a layer thickness of 0.2 mm. For the light scattering experiment we used cylindrical glass cells with an inner diameter of 8.5 mm. The optical path length of the cells for the $(\partial n/\partial T)_{w,p}$ experiment was 10 mm.

The temperature derivative of the refractive index $(\partial n/\partial T)_{w,p}$ was determined at $\lambda_r = 632.8$ nm, using a scanning Michelson interferometer [24]. Figure 1 shows $(\partial n/\partial T)_{w,p}$ of $C_{10}E_8$ in water as a function of the weight fraction. The refractive index increments $(\partial n/\partial w)_{p,T}$ were determined with an Abbe refractometer at three different temperatures T =20, 30 and 40°C to $(\partial n/\partial w)_{p,T}$=0.134, 0.132 and 0.130, respectively.

2.2 TDFRS and DLS

The TDFRS experiment operates as follows: A grating, created by the interference of two laser beams ($\lambda_w = 488$ nm), is written into a sample. A small amount of dye, dissolved in the sample, converts the intensity grating into a temperature grating (thermal grating), which in turn causes a concentration grating by the effect of thermal diffusion. Both gratings contribute to a combined refractive index grating, that is read out under Bragg condition by another laser of different wavelength ($\lambda_r = 632.8$ nm). Analyzing the time dependent diffraction efficiency the transport coefficients (mutual diffusion coefficient D, thermal diffusion coefficient D_T and Soret coefficient

S_{T}) can be obtained, requiring neither external calibration nor absolute intensity measurement. Other characteristic features of TDFRS experiments are the elimination of convection due to the low temperature modulation of several μK, and the short equilibration times of the order of milliseconds, as well as the simultaneous yielding of the transport coefficients in one single measurement. A more detailed description of the set-up can be found elsewhere [25, 26]

The dynamic light scattering (DLS) measurements were carried out in the angular range $20^\circ < \theta < 120^\circ$. A Kr-ions laser was used as the light source (wave length $\lambda = 647.1$ nm). An ALV-5000E correlator was used to measure the correlation function of scattered light. The cylindrical sample cell was placed in a temperature controlled bath with a temperature stability of $\delta T = \pm 0.1^\circ$C, the temperature of which was controlled with an uncertainty of 0.1 °C. The sample solutions were kept at measured temperature for at least 30 minutes to ensure equilibrium before starting data acquisition.

2.3 Data analysis

The normalized heterodyne diffraction intensity of the TDFRS experiment for a binary mixture is given by:

$$\zeta_{\mathrm{het}}(t) = 1 + \left(\frac{\partial n}{\partial T}\right)^{-1}_{w,p} \left(\frac{\partial n}{\partial w}\right)_{p,T} S_{\mathrm{T}} w(1-w) \left(1 - e^{-q^2 D t}\right) \tag{3}$$

The quantities $(\partial n/\partial T)_{w,p}$ and $(\partial n/\partial w)_{p,T}$ do not follow from the TDFRS experiment and have to be determined separately.

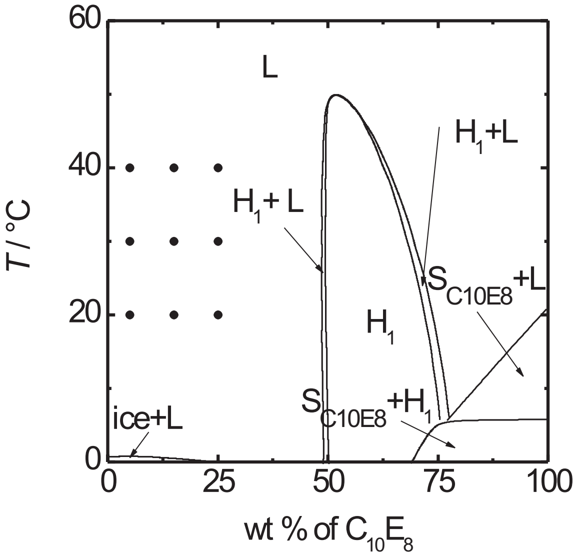

Fig. 2 Schematic phase diagram of $C_{10}E_8$ [27] in water. The different regions are abbreviated in the following way: micellar solution (L), hexagonal (H_1) and the solid of pure $C_{10}E_8$ (S_{C10E8}). The solid circles represent the concentrations and temperatures where TDFRS measurements have been performed.

3 Results and Discussion

Figure 2 shows the phase diagram for decyl octaethylene glycol ether($C_{10}E_8$) in water [27], which shows in the displayed temperature range no two-phase region. In the literature it is reported that there is a critical temperature around 85 °C, but no critical concentration is given [5,28]. TDFRS experiments were carried out in the micellar solution phase which are indicated by solid circles in the phase diagram. In the investigated temperature and con-

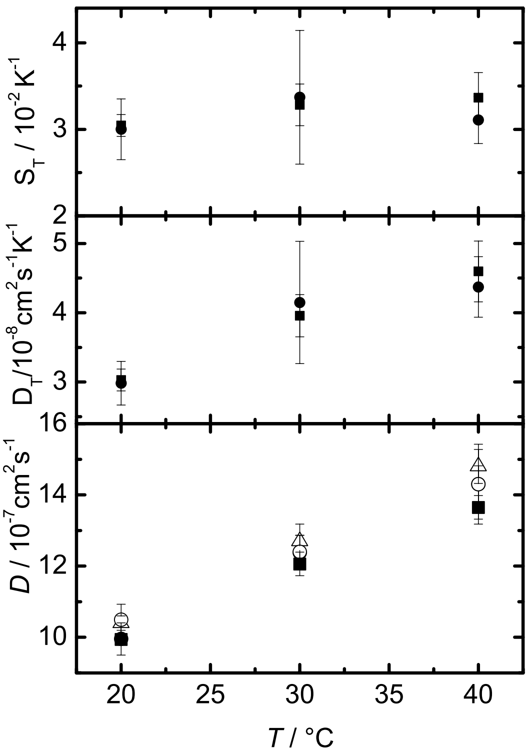

Fig. 3 Soret coefficient, thermal diffusion coefficient and diffusion coefficient of $C_{10}E_8$ ($w = 0.15$) in water at different temperatures containing basantol yellow (●) and alizarin (■). For comparison the diffusion coefficients were also determined by DLS measurement without dye (△) and with basantol yellow (○).

centration range $C_{10}E_8$ in water forms probably only spherical micelles, but it might be expected that at higher concentrations close to the hexagonal phase also cylindrical micelles are formed. 4. The experimental temperature and concentration range is far from the critical temperature so that the diffusion of the micelles is still not dominated by the critical slowing down.

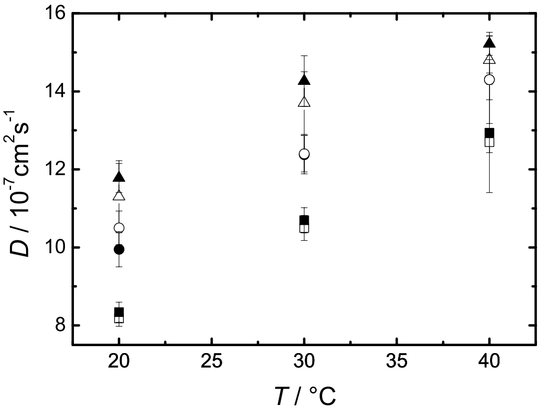

Fig. 4 Diffusion coefficient of $C_{10}E_8$ in water for different surfactant concentrations ($w = 0.05$ (■), $w = 0.15$ (●), $w = 0.25$ (▲)) in dependence of temperature. The open symbols refer to DLS experiment while the solid symbols refer to the TDFRS measurements. In both experiments the solutions contained basantol yellow.

One crucial aspect is the addition of the dye. It needs to be scrutinized that the dye does not change the phase behavior of the surfactant system. As already mentioned in Section 1, especially due to the addition of an electrolyte as in the case of basantol yellow, the phase behavior of the surfactant system can be changed significantly [23]. Another complication might come from the hydrophobic/hydrophilic hybrid nature of basantol yellow which might act as a cosurfactant. Therefore, we made also measurements with alizarin as organic dye and compared the results obtained for the diffusion coefficient by the TDFRS experiment with DLS measurements, which were also performed without dye. The results for a surfactant concentration of

$w = 0.15$ are displayed in Fig. 3. The Soret coefficients show a very weak temperature dependence, while the thermal diffusion and diffusion coefficient increase with temperature. The obtained results are independent of the chosen dye. The diffusion coefficients agree with the diffusion coefficients which were obtained from DLS experiment with and without dye. These results indicate that the added dyes do not have any significant influence on the diffusion of micelles, which implies the size and the structure of micelles are not modified by the addition of dyes in the experimental condition. This is also confirmed in Fig. 4, which shows the diffusion coefficients for $C_{10}E_8$ for different concentrations ($w = 0.05, 0.15, 0.25$) in dependence of temperature measured by DLS and TDFRS. The solutions for the DLS measurements contained the same amount basantol yellow as the TDFRS sample. The diffusion constants increase with temperature and the values obtained with the different methods agree within the error bars. The error bars refer to one standard deviation. Nevertheless, the diffusion coefficients determined by DLS seem to be systematically lower than the values obtained by TDFRS. This is probably caused by the different weighting of the two methods. The TDFRS signal is weighted by the mass, M, of the micelle, while the DLS correlation function is weighted by the square of the mass, M^2, of the micelle.

The Soret coefficient of $C_{10}E_8$ is S_T=0.032 ± 0.005 which is obtained from averaging over all data points shown in Fig. 3. The positive sign of S_T corresponds to that the concentration gradient is established with the

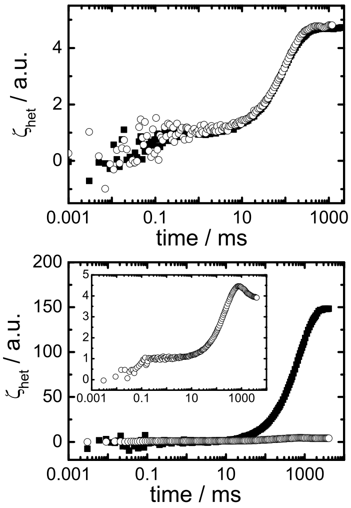

Fig. 5 Normalized heterodyne signal ζ_{het} measured for $C_{10}E_8$ ($w = 0.15, T =$ 20 °C; top figure) and $C_{12}E_6$ ($w = 0.05, T = 30$ °C; bottom figure) in water. The solutions contained either basantol yellow (○) or alizarin (■) as dye. In the lower figure the inset shows the enlarged diffraction signal ζ_{het} for the aqueous $C_{12}E_6$ with basantol yellow.

migration of micelles towards the cold side of the fluid. Here we use the sign notation for S_{T} as follows: In a binary mixture of A and B, S_{T} of A is positive if A moves to the cold side. Therefore, the sign does not depend on the density of two components. In the case of the SDS (sodium dodecyl sulfate) micelles, the sign of S_{T} is also positive [7]. The value of S_{T} of $C_{10}E_8$ has the same order of magnitude with SDS micelles, although we can not directly compare the magnitudes because of a huge contribution of electrostatic forces on thermal diffusion behavior for SDS systems. So far, there are no data for the Soret coefficient of nonionic micelle systems for comparison. It is desired, for example, to study other nonionic surfactants in the same family as C_mE_n. Indeed, ongoing research shows interesting features in regard to the choice of dye and to the dependencies of temperature and surfactant concentration. For instance, $C_{12}E_6$ in the micellar phase show a dramatic changes in their thermal diffusion behavior. The use of dye, alizarin, induces ca. 30-folds intensity of TDFRS signal in comparison with the dye basantol yellow (Fig. 5). Furthermore, $C_{12}E_6$ solution with basantol yellow showed a two-mode behavior. At the present stage, we do not discuss this point. But it needs to be pointed out that $C_{10}E_8$ is a well characterized system which forms only spherical micelles while other surfactants often show a transition to more elongated micelles. It suggests that a modification of interactions at the interface leads to a structural change of micelles which may have a relation with the thermal diffusion behavior to a great extent. To clarify these system dependence behaviors we will report the experimental results for several nonionic surfactant systems in the future.

4 Conclusions

The presently investigated surfactant $C_{10}E_8$ in water which shows the same behavior on thermal diffusion independently of the nature of the added dye by means of TDFRS and DLS experiments. On going research shows that this is not a general feature. Another nonionic surfactant $C_{12}E_6$ shows a drastic change in thermal diffusion behavior with the choice of the dye. To clarify under which circumstances the behavior remains stable or is changed will be object of future research.

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