1 Introduction

About 150 years ago *Carl Ludwig* and *Charles Soret* observed independently the process of thermal diffusion [1, 2] which is therefore also referred to as *Ludwig – Soret* effect. They found that if a temperature gradient is applied to a multicomponent mixture the components separate to a certain extend. Since then this effect was utilized in a wide range of applications. In 1939 for example *Clusius* and *Dickel* succeeded in separating gaseous chlorine into its isotopes using a thermal diffusion column [3, 4]. The same method was subsequently used for the enrichment of uranium in the *Manhattan Project* [5]. In the method of thermal field flow fractionation the thermal diffusion effect is utilized for the separation and analysis of polydisperse macromolecular and colloid systems [6, 7]. In recent years thermal diffusion has also become increasingly relevant for the characterisation of oil reservoirs, i.e. the elucidation of the distribution of crude oil components within the geothermal field [8, 9].

In the context of the phenomenological equations of irreversible thermodynamics (see e.g. [10]) the *Ludwig – Soret* effect is described as the diffusion, that results from the coupling of a heat flux and a mass flux (an introduction is given in section 2.1). Since the response to the temperature gradient is usually different for each component, a concentration gradient builds up which, as a *cross* effect, induces a mass diffusion in the opposite direction to the temperature gradient. In the steady state the ratio of this concentration gradient to the applied temperature gradient is thereby proportional to the ratio of the corresponding transport coefficients. Those are the thermal diffusion coefficient D_T and the mutual diffusion coefficient D. Accordingly, a quantitative measure for the strength and the direction (i.e. towards the cold or warm region) of the themal diffusion of a certain component in a multicomponent mixture is given by the ratio of both quantities, which is the definition of the *Soret* coeffient

$$S_{\mathrm{T}} \equiv \frac{D_{\mathrm{T}}}{D} \propto \frac{\nabla c}{\nabla T}\,. \qquad (1.1)$$

Although the process of thermal diffusion is studied and applied since more than 100 years, the underlying molecular mechanism is still far from being understood. While for binary mixtures of non-uniform gases the effect has already been described at the beginning of the last century within the kinetic gas theory, developed by *Enskog* and *Chapman* [11], for liquid systems no such general theoretical description exists. In some cases there is even a lack of qualitative predictions. Thus, it is of major interest to gain a deeper understanding of the underlying molecular mechanism of the thermal diffusion effect in liquids.

In this context, the thermal diffusion effect has in the last years been studied on a broad range of liquid systems. Many experiments have been performed on polar or non-polar mixtures of low molecular weight components (e.g. [12] [13] [14] [15-18]). Thereby, it was found, that in mixtures of polar liquids specific interactions between the molecules dominate the thermal diffusion behavior, while the mass and the size of the molecules are most important for *Lennard-Jones* fluids. Along with the improvement of experimental techniques in recent years [19] [20], investigations were extended to more complex systems, such as polymer solutions [19, 21-23], magnetic fluids [24], colloidal dispersions [25-27] or aqueous solutions containing surfactants [28-31] or bio-macromolecules [32]. Some general influences on the thermal diffusion behavior have thereby been established: The component with larger mass, larger diameter or larger moment of inertia usually moves towards the cold region. Thereby the exact dependence of S_{T} on the diameter of the diffusing spezies has controversely been discussed in recent time. While *Vigolo et al.* [33] and *Putnam* [34] found a linear size dependence of S_{T} for ionic microemulsions and spherical polystyrene nano-particles as well as lysozyme solutions, respectively, *Duhr* and *Braun* [35] found a quadratic size dependence for spherical polystyrene particles of µm-size. By studying the thermal diffusion behavior of polymer solutions it was found that the Soret coefficient S_{T} scales simply with the molecular weight of the polymers [36-38]; However at infinite dilution D_{T} has been found to become independent of the molecular weight [39].

The interactions-dominated contributions to the thermal diffusion behavior can roughly be devided in particle-solvent and interparticle contributions. Accordingly, in the highly dilute regime, interactions between the diffusing spezies and the solvent will influence the thermal diffusion behavior. Those interactions can for example be the breakdown of the hydrogen bond network of the solution [40] or the formation of an ionic double layer [30]. For systems of higher concentrations, on the other hand it was found that the interparticle interactions (or collective effects) dominate the thermal diffusion behavior [31]. As a general observation the results indicate, that the interfacial tension between the particles (i.e. either colloide, or aggregates) and solvent is of central importance (see [19, 41] for a review).

From the above it becomes clear that for a systematic investigation of the thermal diffusion behavior careful attention must be paid to the experimental design and in particular the choice of the model system [25]. Versatile model systems to study the thermal diffusion behavior of high molecular weight particles in a low molecular solvent are colloidal dispersions. Thereby the particles might be regarded as *big atoms* [42], that interact via *simple, well-defined forces* [25]. However, this approach also rises difficulties: The control of colloidal stability needs to be considered [26, 43]. In addition the chemical microstructure and particle morphology of colloidal particles, which have a major influence on the interfacial particle-solvent interaction is not always reproducible within two individually synthesized batches [44-46].

Promising model systems to study the thermal diffusion behavior systemtically are aqueous surfactant solutions and microemulsions [47-50]. In such systems the surfactant molecules self-assemble e.g. in form of micelles or microemulsion droplets, that can be regarded as the diffusing spezies, in the same way as the particles in colloidal systems. Compared to colloidal particles these thermodynamically stable surfactant systems do not require any additional stabilisation. Furthermore, self-asssembly occurs spontaneously and thus avoids the difficulties associated with the chemical synthesis of colloidal particles. Furthermore, by variation of the composition or temperature, the size and shape of the thermodynamically stable aggregates can systematically be varied, which offers the possibility to study the influence of those properties on the *Soret* coefficient.

The first studies on surfactant systems were mainly focussed on ionic [30, 31, 51, 52] and mixed ionic/non-ionic [53] micelles. These studies demonstrated that at low surfactant concentrations the *Soret* coefficient is strongly influenced by the *Debye – Hückel* length, while at higher surfactant concentrations electrostatic interparticle interactions are dominant. Non-ionic surfactants in contrast provide model systems that allow studying the influence of parameters such as size, shape and concentration of the diffusing spezies without considering any electrostatic interactions.

There are, however, up to now only very few publications [28, 29] that investigate the thermal diffusion of non-ionic surfactant aggregates. One reason for this lack might be the fact that many commonly used non-ionic surfactants have a lower density than water, which causes overlaying convection effects in several experimental methods, such as thermal diffusion cells that are cooled from below and heated from above [19, 29]. *Wiegand et al.* [54] performed first measurements of the thermal diffusion behavior of the non-ionic surfactant dodecyl hexaethylene glycolether ($C_{12}E_6$) in water using the classical thermal diffusion forced *Rayleigh* scattering (TDFRS) method, that avoids convection problems [29] (refer to section 3.2). Thereby, the motivation was to investigate the thermal diffusion behaviour of the aggregates at intermediate temperature (T = 25 – 30 °C) while changing their shape by the variation variation of the surfactant concentration.

However, for these measurements and further investigations on a wider range of non-ionic *n*-alkylpolyglycol ether surfactants (C_iE_j) in water [28] the raw data, being obtained from the TDFRS experiments, deviates significantly from the expected pattern: Instead of the expected one-mode signal a two-mode signal is generally found at lower surfactant concentrations and higher temperatures. *Ning et al.* [28] suspected, that this deviation is connected to the presence of ionic dye molecules in the sample, which need to be added in order to absorb the laser light that creates the temperature gradient. It remained an open question, if the dye affects also the structural and thermodynamic properties of the aqueous surfactant system. It is thus one topic of this work to investigate the influence of the ionic dye on the properties of water – C_iE_j systems.

As it was mentionend above, numerous works in the literature reveal a close connection between the *Soret* effect and the interfacial particle-solvent interaction [25, 30, 35, 53], which in turn is related to the interfacial tension between the particle and the solvent [25]. However, the experimental determination of the interfacial tension between the particle and the solvent is a sophisticated task. Contrarily, in microemulsion systems the interfacial tension is experimentally accessible and can systematically be varied with tuning parameters, such as composition and temperature [50, 55, 56]. Thus, microemulsions provide a unique model system in order to study the relation between the *Soret* coefficient and the particle/solvent interfacial tension. Furthermore, as it was mentionend before, the size of the aggregates in microemulsion systems can be systematically varied. Accordingly, those systems allow also investigating the controversely discussed relation between the *Soret* coefficient and the size of the diffusing spezies. Nevertheless, investigations of the thermal diffusion in microemulsions are yet rare [33]. In this context, the main topic of this work was the formulation and characterisation of non-ionic microemulsions as model systems that allow relating their structural and thermodynamic properties to the results of thermal diffusion studies, i.e. the *Soret* coefficient.

As a unique feature of self assembled systems a certain concentration exists at which the monomerically dissolved surfatant molecules start to self-aggregate to micellar structures. This concentration is referred to as critical micelle concentration (cmc). It was recently proposed [57] that the *Soret* coefficient as function of the surfactant concentration in binary aqueous surfactant solutions might exhibit an abrupt change at the cmc. In order to clarify this point, as a third topic in this work we want to perform systematic studies on aqueous solutions of surfactants of the type *n*-alkyl glucoside (C_iG_j), that exhibit a fairly high cmc in order to correlate the commonly determined cmc with the trend of the *Soret* coefficient at the respective concentration.

1.1 Motivation and Objectives

This work was performed within the scope of a joint project that was initiated in order to combine the expertise of *T. Sottmann* and *R. Strey* (University of *Cologne)* in the field of surfactant systems and microemulsions with the expertise of *S. Wiegand* (*FZ Jülich*) in the field on thermal diffusion. The major task of this collaboration is the study of the thermal diffusion behavior of the surfactant systems and microemulsions by means of the thermal diffusion forced *Rayleigh* scattering (TDFRS) method. The basis of these studies is a careful characterization of the thermodynamic and structural properties of the self-assembled nanostructured fluids under study. Three particular systems were used in order to elucidate certain aspects of the thermal diffusion behavior:

(i) At first, the pseudo-binary surfactant system water – $C_{12}E_6$ – Basantol® Yellow 215 should be studied in detail in order to investigate the influence of the ionic dye which has to be added to the systems under study in the classical TDFRS experiment. As has been described above, this dye is considered to be responsible for an unexpected two-mode signal in these experiments [28].

Particulary the microstructure of the surfactant system should be studied by means of small angle neutron scattering (SANS) as a function of both, the surfactant concentration and the temperature. In addition, the influence of the dye should be compared with that of the ionic surfactant sodium dodecyl sulphate (SDS).

(ii) The formulation and characterisation of water-rich non-ionic microemulsions is the second objective of this work. The complex phase-behavior and microstructure of microemulsions of the type water – *n*-alkane – non-ionic surfactant (C_iE_j) has been extensively studied by *Kahlweit* and *Strey* and various other groups at the end of the 1980s (see e.g. [47, 50] for a review). On the basis of this knowledge droplet microemulsions with adjustable size should be formulated at constant temperature. In order to obtain the droplet size and other structural parameters, the microstructure of these systems should be studied with SANS as well. Using these systems, the size dependence of the *Soret* coefficient on the microemulsion droplet size should subsequently be investigated isothermally. Another objective is to study the relation between the interfacial tension between the solvent and the diffusing microemulsion droplets [53] and their thermal diffusion behavior. Therefore the interfacial tension between the coexisting aqueous microemulsion and the oil excess phase should be measured using the *spinning drop* method. The results should then be related to the measurements of the *Soret* coefficient, which are performed by the group in *Jülich*.

(iii) The last but not least objective of this work is focused on the detection of the critical micelle concentration (cmc) in aqueous non-ionic *n*-alkyl glucoside (C_iG_j) surfactants systems by means of thermal diffusion forced *Rayleigh* scattering measurements. Thus, systematic surface tension measurements should be performed in order to extract the cmc and the effective surfactant head group area, under variation of the temperature, the alkyl chain length and the number of surfactant head groups. Again the results should then be related to the measurements of the *Soret* coefficient, which are performed by the group in *Jülich*.

This thesis is organized as follows: In the next section the fundamentals of the thermal diffusion effect, non-ionic binary surfactant systems and microemulsions are briefly reviewed. Furthermore a brief introduction into neutron scattering is given, that includes the presentation of the scattering models that were applied in this work. Afterwards, the important experimental tool dynamic light scattering and the TDFRS experiment are briefly introduced. Thereby it should be noted that the TDFRS experiments were not performed as part of this work. However, since the results of these experiments are partly discussed, the method is also presented. The presentation of the results and their discussion are presented seperately for the three aspects that were adressed in this work: (i) First the results of the investigations on the influence of Basantol® Yellow 215 on the binary surfactant system $H_2O - C_{12}E_6$ are presented. (ii) At second follows the investigation of the *Soret* effect at the critical micelle concentration of aqueous solutions of *n*-alkyl glucoside (C_iG_j) surfactants. (iii) In the third part the investigations of non-ionic microemulsions of the type $H_2O - C_{12}E_5 - n$-alkane as model system for thermal diffusion studies are presented. Each of those parts contains a short motivation, which also recalls the objectives for the respective part. This structure should allow to understand each part in its own context. In the end of this thesis a summary is given that resumes the main results of this work and briefly adresses some ideas for further investigations.