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Review

Experimental approaches to study thermodiffusion – A review

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ABSTRACT

A detailed review of the experimental investigations of the thermodiffusion/thermophoresis process in liquid and gaseous mixtures is presented. Experiments in the laboratories on earth as well as studies in a microgravity environment in space have been described. The former include the non-optical apparatus such as the *classical Soret cell*, *thermodiffusion column*, *two-chamber thermodiffusion cell* and the *thermal field-flow fractionation*, as well as the optical techniques, viz., classical Soret cell with beam deflection, thermal diffusion forced Rayleigh scattering, thermal lens method and the *microfluidic fluorescence* method. These methods are discussed along with their advantages and disadvantages. Experiments performed in the microgravity environment are also discussed.

1. Introduction

The establishment of a concentration gradient in a mixture when a temperature gradient is applied to it is called *Thermodiffusion* or the *Ludwig–Soret effect* or simply the *Soret effect*. This phenomena was first observed by Ludwig [1] and later studied in detail by Soret in the late 1900s [2,3]. An analogous term for the transport of particles suspended in a fluid under the influence of a thermal gradient is *thermophoresis*. In general, at the onset of a concentration gradient, a counter measure in the form of the Fickian diffusion process is simultaneously initiated. This Fickian diffusion tries to re-establish the equilibrium. Thus, the mass flux, J_m, in a binary mixture at any time can be written as

$$J_m = -\rho D \nabla c - \rho c(1-c) D_T \nabla T, \tag{1}$$

where ρ is the density of the mixture, c is the concentration of the reference component, D is the Fickian diffusion coefficient and D_T is the thermodiffusion coefficient. These coefficients give a measure of the molecular diffusion and the thermodiffusion in the mixture. ∇c and ∇T represent the gradients of concentration and temperature, respectively. At steady state when there is no mass flux

$$\nabla c = -S_T c(1-c) \nabla T, \tag{2}$$

where the Soret coefficient, S_T, is

$$S_T = \frac{D_T}{D}. \tag{3}$$

A related quantity that is used in studying the thermodiffusion process is the thermal diffusion factor, α_T, that is related to the Soret coefficient as

$$\alpha_T = T S_T. \tag{4}$$

In the literature, the thermodiffusion process is represented quantitatively using one of D_T, S_T or α_T. Often, the experimental data is translated to S_T or α_T and additional information on D is necessary to obtain D_T from Equations (3) and (4).

As recently mentioned by Platten [4], thermodiffusion can play an important role in many natural activities, viz., in the underlying physics of the solar ponds [5], demographics of an ocean [6] and also convection in stars [7]. It is important to reservoir engineers who attribute the distribution of the components of hydrocarbons in an underground oil reservoir to thermodiffusion [8–11]. Thermodiffusion is the underlying principle in the operation of experimental apparatus such as the Thermal Field-Flow Fractionation (ThFFF) that are used for the separation and characterization of polymers [12] as well as colloids [13]. Thermophoresis has also been employed to determine biomolecular binding curves [14]. The *Soret effect* is also speculated to play a role in the freezing process of foods [15]. Thus, there has been an increased amount of attention given to this phenomena.

Since its discovery over a century ago, the *Soret effect* has been studied in various systems: Gases [16,17], electrolytes [18], liquid hydrocarbons [19,20], alcohols [21,22], ferrofluids [23,24], polymers [25–28], proteins [29], combustion [30], surfactant micelles

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Nomenclature

B	Coefficient of absorption [m^{-1}]
D_{ij}	Molecular diffusion coefficients [$m^2\ s^{-1}$]
D_T	Thermodiffusion coefficient [$m^2\ s^{-1}\ K^{-1}$]
G	Acceleration [$m\ s^{-2}$]
h	Height [m]
J_m	mass flux [$kg\ m^{-1}\ s^{-1}$]
K	Thermal conductivity [$W\ m^{-1}\ K^{-1}$]
L	Length of the cavity [m]
P	Power [mW]
S_T	Soret coefficient [K^{-1}]
t	Time [s]
T	Temperature [K]
W_0	Beam width [m]
i	Index on the species or molecular diffusion coefficient matrix
j	Index on direction or molecular diffusion coefficient matrix
0	Initial value
α	Thermal expansion coefficient [$^\circ C^{-1}$]
α_T	Thermal diffusion factor
β	Mass expansion coefficient
η	Refractive index
Φ	Separation ratio
μ	Viscosity [Pa s]
ρ	Density [$Kg\ m^{-3}$]
τ	Relaxation time [s]

[31], latex particles [32] etc. Despite this, there is only a limited understanding of the macroscopic principles governing the *Soret effect*. For instance, in liquid mixtures of non-polar fluids, thermodiffusion is influenced by the mass, moment of inertia and the size of the molecule/particle [33]. Further, there is also a dependence on the chemical interaction between the molecules in the mixture [33,34]. In case of polar liquid mixtures, thermodiffusion is dictated by the interactions between the molecules. In Lennard–Jones fluids, the size of the molecules and their mass determine the direction of separation [35].

To further the understanding of the factors governing thermodiffusion, experimental as well as theoretical research is being pursued by several researchers. A detailed review of the various theoretical models that have been employed to study thermodiffusion has been recently presented in Refs. [36,37]. On the experimental front, several techniques to investigate thermodiffusion have evolved. These include the classical Soret cell [38], thermogravitational column [39], the two-chamber thermodiffusion cell [17,40], thermal field-flow fractionation [41], the microfluidic fluorescence method [42–44], laser-beam deflection technique [21], thermal diffusion forced Rayleigh scattering [35,45,46], as well as the thermal lens technique [47]. The last four approaches involve optics.

While all the above experimental approaches have been used in various laboratories on earth, investigations of the *Soret effect* have also been made in a microgravity environment [48,49]. These are conducted on space platforms like the International Space Station (ISS) or free flying satellites (EURECA and FOTON missions). For these experiments, a two-chamber thermodiffusion cell is generally used and the entire procedure is automated (controlled from a control center on the ground). Nevertheless, some pre-flight preparation as well as post-flight analysis of the mixtures are done on the earth.

In this experimental review, these different experimental techniques are collectively presented. Specifically, the basic principles behind each approach are outlined and an attempt is made to identify the advantages and disadvantages of each method.

2. Experimental techniques

2.1. Classical Soret cell

A typical schematic of the classical Soret cell is shown in Fig. 1. Butler and Turner have presented the construction and calibration of one such Soret cell [38]. In this apparatus the experimental fluid is contained in a thin region of thickness δ between two plates. To avoid free convection, a thermal gradient is applied by heating the top plate ($T_1 > T_2$). In the experimental apparatus, the gap between the plates is maintained by brace. Into this brace, holes are drilled in order to draw samples from the chamber. This is generally accomplished via needles that draw a very small amount of sample from the chamber at locations close to the constant temperature boundaries. These extracted samples are analyzed for their density or the refractive index in order to obtain the concentration difference, Δc, at locations close to the two plates. This concentration difference is related to the Soret coefficient, S_T, as

$$\Delta c = -S_T c_0 (1 - c_0) \Delta T. \tag{5}$$

In a slight variation of sampling technique, by using cells equipped with several holes [50] one can collect samples at regular intervals. In this case, the concentration difference as a function of time can be given by

$$\frac{\Delta c(t)}{\Delta T} = -S_T c_0 (1 - c_0) \left(1 - 8/\pi^2 \sum_{\text{odd } n} \frac{e^{-n^2 t/\tau}}{n^2} \right). \tag{6}$$

In the above equation, the relaxation time, τ, is related to the Fickian diffusion coefficient, D, as

$$\tau = \delta^2 / \left(\pi^2 D \right). \tag{7}$$

Thus, knowing S_T at steady state from Equation (5) and using Equation (6) we can obtain D. D_T is then calculated via Equation (3).

The classical Soret cell has been used to study gaseous mixtures [51], binary liquid mixtures containing aromatic hydrocarbons [52–54] as well as binary organic liquid mixtures [55].

2.1.1. Advantages and disadvantages

The basic principles of the apparatus are fairly straightforward and the construction of the equipment is simple. Typical sample size that has to be drawn from the cell to be analyzed for their concentration is approximately 0.2×10^{-3} cm^3. This is a drawback of this approach since in drawing the samples, the inevitable mechanical disturbance to the system can introduce convection in the mixture that can destroy the Soret separation. One way to tackle this would be to use thin walled plates in the cell that will

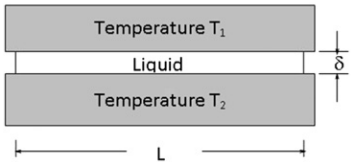

Fig. 1. A schematic of a Classical Soret Cell.