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**ABSTRACT
BOOKLET**





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Thermodiffusion of magnetite nanoparticles in ferrofluid-doped micellar systems and in ferrofluids.

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ABSTRACT

Transport phenomena in complex fluids is one of the most interesting subjects of research nowadays in the field of Condensed and Soft Matter Physical-Chemistry. One of these transport properties is the thermodiffusion, also called Ludwig-Soret effect. In brief, let us consider a binary fluid mixture characterized by a volume fraction of one of its components (named φ). If this initially homogeneous mixture is subjected to a thermal gradient, a flux is observed for this component in the fluid, parallel to the temperature gradient. The Ludwig-Soret effect couples the temperature gradient to a concentration flow in the system. This effect is measured by the so called Soret coefficient (S_T) or the thermal diffusion coefficient (D_T) which is proportional to the ratio of the volume-fraction current density and of the temperature gradient. This topic of research is interesting not only from the fundamental point of view but also from its potential technological implications. Despite this effect has been discovered more than one century ago, a physical understanding of it is not fully achieved, probably because different processes may be present in the thermal gradient-induced mass flux.

In the case of a binary mixture, S_T can be written as:

$$S_T = \frac{D_T}{D} = -\frac{1}{\varphi} \frac{\nabla \varphi}{\nabla T}, \quad (1)$$

where T , D_T and D are the absolute temperature, the thermal diffusion coefficient (in $\text{m}^2\text{s}^{-1}\text{K}^{-1}$) and the mass diffusion coefficient (m^2s^{-1}), respectively.

However, we have adopted a different, but physically equivalent framework where, in the limit of $\varphi \ll 1$:

$$S_T(\varphi) = \varphi \frac{D_T}{D} = \varphi S_T, \quad (2)$$

S_T (φ is the *concentration-dependent Soret coefficient*). The $S_T(\varphi)$ definition is particularly useful in our experiment since in the technique we are using to investigate the Soret coefficient we measure, for a given φ , $-\nabla \varphi / \nabla T$. So, the linear dependence of $S_T(\varphi)$ on φ can be experimentally verified.

The Z-Scan (ZS) experimental technique is used to measure the concentration-dependent Soret coefficient of surfacted magnetic nanoparticles in water (pure ferrofluid FF) and in a micellar lyotropic mixture (lyotropic doped with ferrofluid FL).

In the time-resolved version of the ZS experiment, a mechanical chopper provides a square-wave light intensity profile, which exhibits a periodical succession of ON and OFF states of equal Δt duration. During an ON period, nonlinear effects appear, and temperature T has enough time to reach a steady state in the sample. Conversely, during an OFF period, no nonlinear effects take

place, and temperature increase has time enough to decay. During the time interval Δt the particular phenomenon under investigation reaches its saturation. The sample position z is fixed during a sequence of one ON state and one OFF state. The experiment consists of measuring the sample transmitted intensity $\Gamma(z, t)$ as a function of time during the ON period, at each (fixed) sample position z .

In both cases investigated (FF and FL systems), the magnetic particle contribution to the concentration-dependent Soret coefficient is shown to be proportional to its concentration. In the case of the ferrofluid-doped lyotropic system, it was possible to evaluate the micellar concentration-dependent Soret coefficient associated to the micelles under a temperature gradient.

The concentration-dependent Soret coefficient of the FF system (Table 1) shows a linear behavior with the volume fraction of magnetic material in the solution, with Soret coefficient $S_T = S_T^{FF}(\phi)/\phi = (4.4 \pm 0.1) \times 10^{-1} K^{-1}$. This result agrees with those previously published for cationic water-base surfacted ferrofluids, where magnetic grains tend to go away from the hottest region of the sample.

Table1: Label of the investigated ferrofluid samples, their volume fraction of magnetic material and the concentration-dependent Soret coefficient associated to the magnetic nanoparticles $S_T(\phi)$.

Samples	$10^3 \times \phi(\%)$	$S_T(\phi) (10^{-4} K^{-1})$	$S_T^\dagger(\phi) (10^{-4} K^{-1})$
FL1	1.36	2.70 ± 0.09	0.45 ± 0.09
FL2	1.85	2.9 ± 0.1	0.7 ± 0.1
FL3	2.69	3.1 ± 0.1	0.9 ± 0.1
FL4	3.34	3.4 ± 0.1	1.2 ± 0.1
FL5	4.34	3.8 ± 0.1	1.6 ± 0.1

The $S_T(\phi)$ as a function of ϕ of the FL system also presents a linear (Table 2) behavior but the linear coefficient of the best fitting function is different from zero: $S_T(\phi) = A + B_T^{FL} \times \phi$, with $A = (2.25 \pm 0.1) \times 10^{-1} K^{-1}$, and $B_T^{FL} = (3.39 \pm 0.08) K^{-1}$.

Table2: Label of the investigated ferro-lyotropic samples, their volume fraction of magnetic material and the concentration-dependent Soret coefficient associated to the magnetic nanoparticles $S_T(\phi)$

Samples	$\phi(\%)$	$S_T(\phi) (10^{-4} K^{-1})$
FF1	0.1	4.4 ± 0.8
FF2	0.2	8.8 ± 0.9
FF3	0.3	13 ± 1
FF4	0.4	18 ± 1
FF5	0.5	22 ± 1

The FL system is basically composed by amphiphilic direct micelles in water and surfacted magnetic particles. The thermal gradient imposed by the Gaussian beam may generate not only a concentration gradient of magnetic particles but also a concentration gradient of micelles. We propose to interpret the value of the linear coefficient A as related to the micellar concentration-dependent Soret coefficient of the undoped micellar system (i.e., FL in the limit of $\varphi \rightarrow 0$). In this framework, the concentration-dependent Soret coefficient associated specifically to the magnetic particles could be, in a first-order approach, as :

$$S_T^{FL}(\varphi) = S_T^m(\varphi_m) \left[\frac{\partial n}{\partial \varphi_m} / \frac{\partial n}{\partial \varphi} \right] + S_T^\dagger(\varphi) \quad (3)$$

Bourdon measured the mass diffusion coefficient of surfacted water-based ferrofluids, finding $D^{FF} \sim 2 \times 10^{-11} \text{ m}^2\text{s}^{-1}$, practically independent on φ . The mass diffusion coefficient of the magnetic nanoparticles in the ferrolyotropic mixture (D^{FL}) may be evaluated with the experimental values of the mean viscosity ($\eta_m \sim 46 \text{ cP}$) of the lyotropic mixture, and we found $D^{FL} \sim 10^{-12} \text{ m}^2\text{s}^{-1}$. Let us call D_T^{FL} and D_T^{FF} the thermal diffusion coefficients in the micellar and ferrofluid-doped systems, respectively. So, in both cases, D_T can be written as

$$D_T^{FL} = \frac{D^{FL} S_T^\dagger(\varphi)}{\varphi} = D^{FL} B_T^{FL}, \quad (4)$$

and

$$D_T^{FF} = \frac{D^{FF} S_T^{FF}(\varphi)}{\varphi} = D^{FF} B_T^{FF}, \quad (5)$$

and finally

$$\frac{D_T^{FL}}{D_T^{FF}} = \frac{D^{FL} S_T^\dagger(\varphi)}{D^{FF} S_T^{FF}(\varphi)} = 0.4. \quad (6)$$

The values of D_T allows us to evaluate an effective Soret mobility (μ_s) of the magnetic particles and an effective Soret viscosity (η_s) of the particular medium (water or micellar solution) where the magnetic nanoparticles of radius a (e.g., 5 nm) are suspended. The mobility is associated to the Soret-driven mechanism, which imposes the nanoparticle flow. The viscosity, on the other hand, is associated to the resistance of the medium to this nanoparticle flow. Using an analogy to the Einstein's relation $D(\text{m}^2\text{s}^{-1}) = \square k_B T$, where k_B is the Boltzmann constant, we have:

$$D_T = \mu_s k_B, \quad (7)$$

and

$$D_T = \frac{k_B}{6\pi\eta_s a}. \quad (8)$$

We find: $\mu_{FF} \sim 6 \times 10^{11} \text{ s kg}^{-1}$ and $\eta_{FF} \sim 2 \times 10^{-5} \text{ Pa.s}$; $\mu_{FL} \sim 2 \times 10^{11} \text{ s kg}^{-1}$ and $\eta_{FL} \sim 5 \times 10^{-5} \text{ Pa.s}$ for the pure ferrofluid and the micellar medium, respectively. These results show that the

mobility of the magnetic nanoparticles in the pure ferrofluid is about three times bigger than that in the ferrolyotropic. This fact is consistent with the values of the effective Soret viscosities calculated. Due to the larger particle's mobility in the pure ferrofluid when compared to the ferrolyotropic system, the pure ferrofluid needs a minimum laser beam Z-Scan time interval (the ON period) about three times smaller than that in the ferrolyotropic system to constitute the matter lens.

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