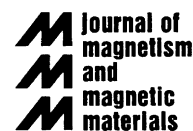




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Transport properties of an ionic magnetic colloid: experimental study of increasing the ionic strength

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Abstract

The phase separation of an ionic magnetic colloid in zero magnetic field by increasing the ionic strength is well known [Universite Paris VI, France, 1987; J. Colloid Interface Sci. 132 (1989) 1]. The present work deals with investigation of an ionic ferrofluid by increasing the ionic strength in the range of 0–0.14 mol/l, being safely below the threshold value at which the effect of phase separation occurs. By the optical grid setup [Fourth International conference PAMIR, France, 2000], the main transport properties of a ferrofluid, i.e. translational mass diffusion and thermal diffusion (Soret) coefficients, are measured. The obtained results show a strong dependence of mass diffusion coefficient and no dependence of the Soret coefficient upon increasing the ionic strength. It is possible to explain both these effects theoretically; nevertheless, there is the lack of an exact theoretical model due to its complexity.

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1. Introduction

Magnetic colloids (ferrofluids) are colloidal dispersions of magnetic particles of typical size about 10 nm in a liquid carrier. Two ways to eliminate the aggregation of particles are known: a steric hindrance provided by a surfactant coating of the particles (surfacted ferrofluids), or ensuring the electrostatic repulsion by charging the particles (ionic ferrofluids).

The main transport properties of magnetic colloids are translational mass diffusion coefficient D_M and thermal diffusion (Soret) coefficient S_T . They both determine in a binary mixture the particle volume fraction flux j quantitatively:

$$j = -D_M(\nabla\varphi + S_T\varphi(1 - \varphi)\nabla T), \quad (1)$$

where φ is the particle volume concentration and T is the temperature.

Transport coefficients D_M and S_T have been investigated recently by different experimental methods [1–3]. Development of exact theoretical models of the Soret effect in magnetic colloids demands more investigations

in this field. Due to this, the dependence of transport properties of an ionic ferrofluid on the ionic strength may be of great interest, being experimentally studied in the present work.

2. Ionic ferrofluid and the effect of phase separation

An ionic ferrofluid sample, used in these experiments, consists of positively charged hard $\gamma\text{-Fe}_2\text{O}_3$ particles in acid aqueous medium, the neutrality of which is reached by adding NO_3^- counterions. The magnetogrulometric analysis indicates the standard deviation $\sigma = 0.38$ with respect to a lognormal particle size distribution, and the average diameter of the hard particles $d_0 = 10.5$ nm. Measurements of density indicate the initial volume concentration of the hard particles $\varphi_0 = 6.3\%$.

The total ionic strength I of a solution is defined as

$$I = \sum_i c_i z_i^2, \quad (2)$$

where c_i is the concentration and z_i the valence of the i -sort of presented ions. The total ionic strength is low in a pure ionic ferrofluid sample (pH = 2 gives $I \approx 0.02$ mol/l),

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but it can be increased very many times by dissolving a salt, e.g. NaCl. However, the effect of phase separation in ionic ferrofluids by increasing the ionic strength (as well as the temperature or externally imposed magnetic field) is well known [4,5]. This effect appears in the form of separation into two liquid phases at reaching the threshold ionic strength of the counterions I_0 (since the particles are charged positively, “counterions” stay for all negative ions). The formation of settling spherical droplets (in the diameter of some micrometers) of concentrated phase occurs in the more diluted one. Experiments prove that I_0 for a given sample is rather independent of the initial volume concentration φ_0 , whereas it is strongly dependent on the particle size distribution [4,5]. An empirical formula to estimate the threshold ionic strength of the counterions is found in Ref. [5]:

$$I_0 = \frac{2.4 \times 10^4}{N_A d_H^3}, \quad (3)$$

where d_H is the hydrodynamic diameter of the particle, determined from the transient birefringence measurements (since d_H is related to the rotation of the anisotropic or even chained particles, usually it exceeds d_0 3–5 times). With the used ferrofluid sample $d_H \leq 50$ nm, proving the threshold ionic strength of the counterions to be not below 0.3 mol/l.

3. Experimental section

Experiments on measuring the translational mass diffusion coefficient D_M and the Soret coefficient S_T as functions of the ionic strength have been performed by the grid setup [3]. The salt is added to the magnetic colloid by dissolving various doses of a 0.5 mol/l NaCl solution. The best dose is chosen to reach the ionic strength of the counterions of about 0.15 mol/l, which is safely below the threshold value $I_0 \approx 0.3$ mol/l, estimated by Eq. (3). Two salt dosing series have been carried out (see Figs. 1 and 2). With each particular dose of the salt 4–6 measurements of D_M and of S_T were performed.

4. Results and discussion

The main results of performed experimental work are collected in Figs. 1 and 2.

In the first degree of approximation, the obtained dependence in Fig. 1 is linear. Concerning Einstein–Stokes formula:

$$D_M = \frac{k_B T}{6\pi\eta_0 R_H} \quad (4)$$

and knowing that viscosity of the solvent η_0 changes quite negligibly by adding the salt, remarkable decrease

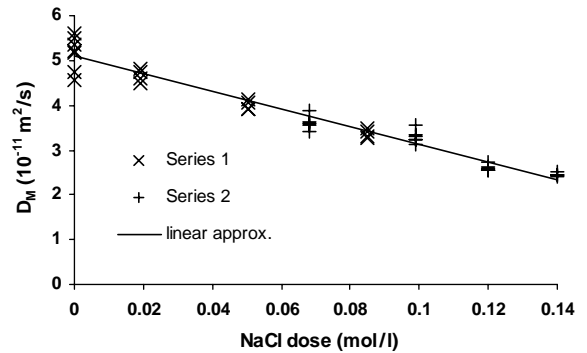


Fig. 1. Measured translational mass diffusion coefficient D_M by adding NaCl.

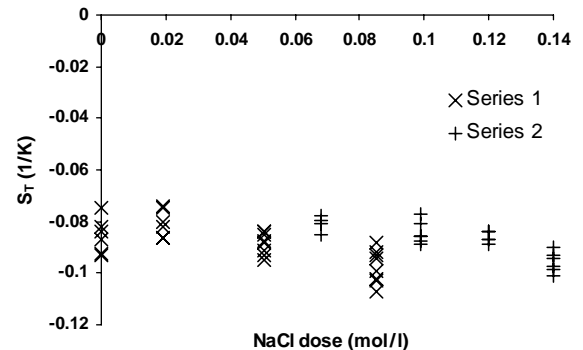


Fig. 2. Measured Soret coefficient S_T by adding NaCl.

of D_M (two times by adding ca. 0.13 mol/l NaCl) can be explained only by increasing the translational hydrodynamic radius R_H of the colloidal particles. The latter seems to be the initial stage of the phase separation: the formation of spherical droplets begins by aggregation of larger particles. As no settling is observed, one can conclude that the examined colloid does not lose the stability.

From Fig. 2 it is seen that in a rough evaluation the value of S_T is independent of the added NaCl dose. At the first glance, a notable dependence was expected here: the existing theoretical model of the Soret effect in ionic ferrofluids accounts for the double layer thickness D , and $D \propto 1/\sqrt{I}$ [6]. Nevertheless, the situation is more complicated because the theory predicts S_T to be proportional to R_H [6]:

$$S_T = -\frac{3\varphi R_H}{4TL_B} u, \quad (5)$$

where L_B is the Bjerrum length, and $u = u(2D/d_0, \zeta)$ is the dimensionless velocity of the particle, ζ being a constant surface potential of the particle. (Note that the difference between calculated value of S_T by Eq. (5) and the experimentally measured one does not exceed 30%.)

Regarding Eq. (5), in the first degree of estimation, by increasing the ionic strength the dependence $S_T = S_T(R_H)$ may compensate the decrease of S_T caused by reducing the double layer thickness D . Since the accuracy of experimentally obtaining the value of S_T is limited, more precise estimations cannot be discussed here.

5. Conclusions

The performed experiments indicate a strong dependence of mass diffusion coefficient and no dependence of the Soret coefficient upon increasing the ionic strength. A correct theoretical explanation of these results leads to solving a mathematical problem of three interactions: electrostatic (acting through the ionic strength), dipolar magnetic (as the particles are magnetic dipoles), and van der Waals interaction. Excepting the dipolar magnetic interaction, which cannot be neglected in case of employing ferrofluids, this problem may be solved by means of the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [7,8]. Unfortunately, there is no model which takes into account all the three mentioned interactions. Experiments, carried out in this work, allow to conclude about aggregation of larger particles that can be regarded as the initial stage of the phase separation.

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