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Diffusion of charged nano-disks in aqueous media: Influence of competing inter-particle interactions and thermal effects

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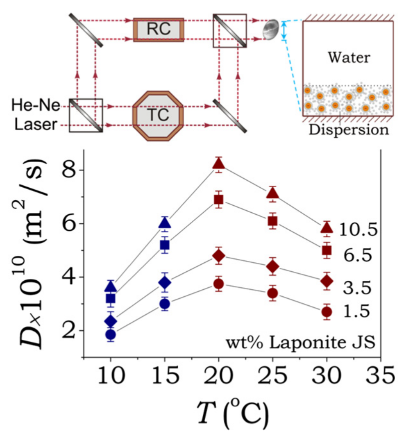
HIGHLIGHTS

- Measurement of binary diffusivity of a suspension in water by optical interferometry.
- Binary diffusivity of Laponite disks is found to be larger than the self-diffusivity of the corresponding hard disks.
- Binary diffusivity of Laponite clay shows non-monotonic temperature dependence.
- The work is the first study on binary diffusion coefficient of nanoclay suspension.
- The work has implications in processability and stability of colloidal dispersions.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work we investigate binary mass diffusion of negatively charged disk-shaped nanoparticles of Laponite JS in ultrapure water using Mach-Zehnder interferometry aided by a sensitivity analysis. We observe that binary mass diffusivity of aqueous suspension shows a consistent enhancement with concentration of Laponite at a given temperature. The dependence on temperature, however, is observed to be non-monotonic, wherein the binary mass diffusivity first increases with temperature up to 20 °C while decreasing at higher temperatures. We propose that the observed non-monotonic dependence of binary diffusivity on temperature is due to competing effects such as: thermal energy of Laponite particles, that of counterions, and the magnitude of charge on the Laponite particles. These factors affect the aggregation rate of Laponite particles leading to the behaviour observed in the experiments. Interestingly the binary diffusivity of Laponite obtained in the present work is significantly higher than the self-diffusion coefficient of a corresponding hard disk. We propose that enhanced binary diffusivity is due to repulsive interaction among the Laponite particles that augments mobility of the solute in ultrapure water.

1. Introduction

Colloidal suspensions of nanometric-sized particles have enormous academic as well as industrial importance. The physical properties of the colloidal suspensions are determined by the

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characteristics of a dispersed phase as well as that of a continuous phase. The consequent inter-particle interactions influence agglomeration of the particles, and therefore the stability of a suspension. Among various physical properties, it is particularly important to understand how thermo-physical properties such as momentum, thermal and mass diffusivities are influenced by altering the nature of a continuous as well as a dispersed phase as these properties directly affect the processability of a suspension. The diffusion processes are also of interest because of their appearance over several orders of length and timescales (Larson, 1998). Furthermore, since diffusivities are sensitive to the microstructural changes that occur within a colloidal suspension, the former can be used to infer about the latter. In the present work, we investigate binary diffusion behaviour of aqueous colloidal suspensions of electrically charged, disk-shaped particles of Laponite JS using the laser light interferometry. Laponite is primarily used as a rheological behaviour modifier in commercial products such as personal care, home care, pharmaceutical, agrochemical, and paints (BYK-Chemie-GmbH, 2016). We observe that the dependence of diffusivity on temperature and concentration renders greater insight into the inter-particle interactions and the agglomeration dynamics of the aqueous Laponite suspension. To the best of our knowledge this work is the first to estimate and analyse binary (mutual) diffusion coefficient of clay particles in general and Laponite particles in particular.

The determination of momentum diffusivity ($\nu = \eta/\rho$, where η is viscosity and ρ is density) as well as thermal diffusivity ($\alpha = k/(C_P\rho)$), where k is thermal conductivity and C_P is heat capacity) is known to be straightforward. For the former primarily a rheometer is used wherein application of gradient in velocity field leads to estimation of viscosity (Larson, 1998). On the other hand, for an estimation of thermal conductivity, various apparatus are available wherein a temperature gradient is induced in a material (Rohsenow et al., 1998). In both measurements velocity as well as temperature gradient is applied externally. Determination of binary mass diffusivity on the other hand is comparatively difficult, since concentration gradient is required to be created inside a material.

In the literature on suspensions of nanoparticles, termed as nanofluids, there exist contradictory reports on the behaviour of thermal conductivity with respect to concentration of particles (and hence thermal diffusivity), wherein some groups claim anomalous enhancement in thermal conductivity with an increase in particle loading as well as particle aspect ratio (Michaelides, 2013; Yu et al., 2009). On the other hand, other groups do not observe any enhancement in thermal conductivity beyond what is predicted by the existing theories at low particle concentration (Buongiorno et al., 2009). On similar lines, various groups do observe an augmenting influence of nanoparticles on mass diffusivity (Fang et al., 2009; Kim et al., 2014; Krishnamurthy et al., 2006; Michaelides, 2013; Olle et al., 2006). Fang et al.(2009) determined mass diffusivity of a drop of Rhodamine B in water as well as 25 nm Cu-water nanofluids (0.1–0.5 vol%) by using the Taylor dispersion method. The authors found an increase in mass diffusion of the dye in nanofluids as compared to water at various temperatures. Also, the mass diffusion coefficient increased with increasing concentration and temperature. Krishnamurthy et al. (2006) reported enhanced mass diffusion through a liquid due to the addition of 20 nm Al_2O_3 nanoparticles. These experiments were carried out with mass diffusion of aqueous fluorescein dye, first in water and then in nanofluids of various concentrations of nanoparticles (0.1–1 vol%). Interestingly, both groups proposed Brownian motion-assisted micro-convection to be the mechanism for an enhancement of mass transport. However, there are a few reports that do not observe any anomalous enhancement in diffusivity For example, diffusion behaviour of fluorescent dye in aqueous nanofluids having different kinds of nanoparticles was studied by various groups (Ozturk et al., 2010; Turanov et al., 2009; Subbarao et al., 2011). In these studies molecular, self and tracer diffusion coefficients were measured respectively by using a microfluidic approach (Ozturk et al., 2010), fluorescence correlation spectroscopy (Subba-Rao et al., 2011) and transient hotwire and pulsed field gradient nuclear magnetic resonance method (Turanov and Tolmachev, 2009). Interestingly these authors did not observe any improvement in the mass diffusion coefficient due to increased concentration of nanoparticles in the base fluid. However, the enhancement or otherwise of mass diffusivity due to the presence of nanoparticles is not a subject of the present work and the discussion on the subject is kept limited.

In addition to binary diffusion, which is a non-equilibrium process as it drives the system towards equilibrium, self-diffusion as well as the tracer diffusion processes have also been reported in the literature (Dhont, 1996; Kaloun et al., 2005; Kleshchanok et al., 2012; Petit et al., 2009; Reis et al., 2005; Saha et al., 2015; van der Kooij et al., 2000). Self and tracer diffusion are similar since both occur under thermodynamic equilibrium conditions in the absence of a concentration gradient. Self-diffusion is the migration of a substance's own constituents (atoms, molecules or particles) due to thermal motion. In tracer diffusion, the migration of uniformly distributed tracer particles in the bulk of the solution results from the Brownian motion.

In the literature, various optical as well as non-optical techniques have been used to measure the binary mass diffusivity. Optical techniques include stereo microscope (Krishnamurthy et al., 2006), infrared microscopy (Gharagozloo and Goodson, 2011), spectroscopy (Gapinski et al., 2005; Marze et al., 2012; Subba-Rao et al., 2011), static and dynamic light scattering (Bartsch, 1998; Marze et al., 2012; Heitjans and Kärger, 2005; Strachan et al., 2006; Swan and Brady, 2011), Taylor dispersion (Fang et al., 2009), shadowgraphy (Kim et al., 2014) and interferometry (Zhang and Annunziata, 2008) while non-optical techniques comprise nuclear magnetic resonance (Marze et al., 2012; Heitjans and Kärger, 2005; Turanov and Tolmachev, 2009) stirred beaker technique (Olle et al., 2006) and the membrane cell (Velianti et al., 2014). An overview of the literature on transport phenomena in suspensions reveals that single beam optical techniques have often been used for investigation. Interest has been on finding a particle-level mechanisms and studying diffusion of colloids in the suspension under various thermophysical conditions. Theoretical estimates of the binary diffusion coefficients have been obtained from the measured physical properties of the suspension. Mass diffusion in a binary system containing a nanofluid using a high resolution optical technique, however, has not been reported.

In the present work, we measure binary diffusivity of Laponite JS (sodium magnesium fluorosilicate) solution in water. Laponite is a synthetic clay mineral where the oxygen atoms connect the tetrahedral layers of silicon atoms to the centrally located octahedral layer containing magnesium and lithium atoms, interlinked by oxygen anions and hydroxyl groups. It is commercially available in the form of white powder where Laponite crystals are found in stacks. A single Laponite crystal is a disk shaped nanometric-sized particle with 30 nm diameter and 1 nm thickness (Bhandari et al., 2013). It has divalent magnesium ions or monovalent lithium ions at the central octahedral layer which results in uniform distribution of negative charges on both surfaces of the disk (Shahin and Joshi, 2012). This deficit in positive charges is filled by sodium cations present at the interlayer space in the stack. Sodium cations are exchangeable and diffuse in water driven into the interlayers of stacked particles due to osmosis while forming an aqueous suspension of disk-shaped particles with negatively charged faces. Owing to the broken crystal, edges of Laponite particles possess positive