Chemical Engineering Science 153 (2016) 165–173

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Colloid particle transport in a microcapillary: NMR study of particle and suspending fluid dynamics

Einar O. Fridjonsson [a,b,*], Joseph D. Seymour [a]

[a] Department of Chemical and Biological Engineering, Montana State University, Bozeman, MT, USA
[b] School of Mechanical and Chemical Engineering, The University of Western Australia, Crawley, WA 6009, Australia

HIGHLIGHTS

- NMR 'active' colloidal particles at 22 vol% flowed through a μ-capillary
- Simultaneous measurement of particle and suspending fluid phase dynamics
- Dynamics of suspending fluid contains particle structure information
- Shear induced migration within μ-capillaries
- Results provide experimental data for further investigation and model verification

ARTICLE INFO

Article history:
Received 3 April 2016
Received in revised form
20 June 2016
Accepted 3 July 2016
Available online 6 July 2016

Keywords:
Microcapillary
Colloids
NMR
Hydrodynamic dispersion
Particle dynamics

ABSTRACT

Precise manipulation of the hydrodynamic interaction between particles is particularly important for operation of microfluidic devices. Shear-induced migration gives rise to dynamical patterns within the flow that have been observed in a range of systems. In this work NMR 'active' colloidal particles ($a=1.25$ μm) at volume fraction of 22% in an aqueous phase are flowed through a μ-capillary ($R=126$ μm) and the transport dynamics of the particle and suspending fluid phases are studied using dynamic NMR techniques. Simultaneous interrogation of shear rheology of the suspending fluid and particle phases of colloidal suspensions is presented. The dynamic behavior of the suspending fluid is shown to carry within it information about the structure of the colloidal particle ensembles on the time scales investigated ($\Delta=25$ ms → 250 ms) providing rich experimental data for further investigation and model verification. The importance of determining the particle concentration profile within μ-capillaries is explicitly demonstrated as shear induced migration causes significant concentration gradients to occur at strong flow conditions (*i.e.* $Pe_p=270$).

1. Introduction

The transport dynamics of colloid particles (diameter ($2a$): 1 nm to 10 μm (Russel, 1981)) suspended in a liquid, is important in many industrial and environmental processes and has therefore received significant attention in the scientific literature (Brady and Vicic, 1995, Vermant and Solomon, 2005). Precise manipulation of the hydrodynamic interaction between particles is important for operation of microfluidic devices (Stone et al., 2004); shear induced migration of the suspended particles being particularly important (Reddig and Stark, 2013). Microfluidic applications of shear induced migration include generation and manipulation of emulsion droplets (Christopher and Anna, 2007), polystyrene microspheres (Sochol et al., 2011) and biological cells (Yun et al., 2013). Flow induced migration gives rise to dynamical patterns which have been observed in a range of systems. These include coiling of semi-flexible polymers (Chelakkot et al., 2012, Harasim et al., 2013), anomalous crystal phonon modes (Beatus et al., 2007), collective dynamics (Janssen et al., 2012), inertial migration (Di Carlo et al., 2009) and shear induced migration (Semwogerere et al., 2007, Snijkers et al., 2013).

An important example is the Segre–Silberberg effect caused by inertial forces acting on the particles in non-zero Reynolds number (Re) flow (Leal, 1980) where rigid spheres assemble on an annulus at approximately 0.6 of the internal radii of a circular tube during laminar flow (Segre and Silberberg, 1962). When non-zero Re bounded shear flow is introduced to sphere trajectories a rich class of solutions is observed (Subramanian and Koch, 2006), while at non-inertial conditions a threshold for irreversibility and chaos is

* Corresponding author at: The School of Mechanical and Chemical Engineering, The University of Western Australia, Crawley, WA 6009, Australia.

http://dx.doi.org/10.1016/j.ces.2016.07.005
0009-2509/

observed in many body particle suspensions where time reversible equations of motion should govern (Pine et al., 2005).

Forces which determine the particle dynamics are hydrodynamic, Brownian and interparticle (Brady, 1993). The hydrodynamic forces are due to the presence of fluid between particles which allows the propagation of particle interactions including those due to the application of a linear external shear field. Brownian forces are due to the stochastic motion of the suspending fluid molecules impacting the suspended particle. In colloidal suspensions, the particles in a suspending fluid are small enough that Brownian forces affect their dynamics (Brown 1828; Einstein 1906; Smoluchowski, 1906). Interparticle forces can be divided into those due to the excluded volume repulsion, electrostatic interaction, van der Waals forces (short-range and attractive), entropic forces and steric forces (either steric repulsion or attractive depletion) (Russel et al., 1989). If a colloidal suspension is unstable it can flocculate, *i.e.* form aggregates of colloidal particles due to the removal of the electrostatic barrier separating particles, due to addition of flocculants (charged polymer), depletants (non-adsorbed polymers) or colloid deformation (Russel et al., 1989). Mono-disperse hard-sphere colloidal suspensions are the simplest type of colloidal suspension, where the particles interact through hydrodynamic and Brownian forces, and can be fully characterized by the volume fraction (ϕ) and the particle Péclet number (Pe_p) (Brady and Vicic, 1995). They can also be used to form the building blocks for understanding more complex colloid suspensions (Brady, 1996, Yurkovetsky and Morris, 2008).

Detailed experimental, analytical and simulation studies have been conducted to investigate the behavior of hard sphere colloidal suspensions over the full range of volume fraction (ϕ) from dilute to close packed and for Pe_p numbers encompassing the rheological behavior from weak flow conditions ($Pe_p \sim 1$) to strong flow conditions ($Pe_p >> 1$) (Bergenholtz et al., 2002, Foss and Brady, 2000). In this paper, we focus on the dynamics in the shear flow dominated regime ($Pe_p >> 1$) for a $\phi = 0.22$ hard sphere suspension (Wassenius et al., 2003), where Pe_p and ϕ are defined as:

$$Pe_p = \frac{6\pi\eta_0\langle\dot{\gamma}\rangle a^3}{k_B T} \tag{1}$$

$$\phi = \frac{4\pi a^3 n}{3} \tag{2}$$

Here η_0 is the viscosity of the suspending fluid, $\langle\dot{\gamma}\rangle$ is the averaged shear rate, a is the mean radius of the colloidal spheres, k_B is the Boltzmann constant, T is the absolute temperature and n is the number density. The averaged shear rate is defined as $\langle\dot{\gamma}\rangle = \frac{4}{3}\frac{v_m}{R}$, where v_m is the maximum velocity in the μ-capillary and R is the radius of the μ-capillary. Additional dimensionless numbers used to characterise the flow are the tube Péclet number (Pe_t), particle *Reynolds* number (Re_p) and the tube *Reynolds* number (Re_t):

$$Pe_t = \frac{2R\langle v\rangle}{D_w} \tag{3a}$$

$$Re_p = \frac{a^2\langle\dot{\gamma}\rangle\rho}{\eta_0} \tag{3b}$$

$$Re_t = \frac{2R\langle v\rangle\rho}{\eta_0} \tag{3c}$$

In which $\langle v\rangle$ is the average velocity in the capillary, D_w is the diffusion coefficient of the suspending fluid and ρ is the density of the suspending fluid in the capillary.

In this study pulsed gradient spin echo (PGSE) nuclear magnetic resonance (NMR) techniques are used to independently measure the transport properties of the suspending fluid phase and particle phase by using oil filled hard sphere core shell particles. These NMR "active" particles have previously been studied with NMR to measure the diffusion characteristics of the internal oil (Wassenius et al., 2003) and velocimetry (Wassenius and Callaghan, 2004, 2005). They have been used to demonstrate irreversibility of particle motion at dilute concentrations (Brown et al., 2007), shear induced migration in capillaries (Brown et al., 2009) and hydrodynamic dispersion in microcapillaries (Fridjonsson et al., 2014b). They have also been used to study deposition in porous media (Fridjonsson et al., 2014a), flow partitioning in bifurcations (Fridjonsson et al., 2011), effects of oscillatory flow (Evertz et al., 2012) and transport dynamics in open cell polymer foams (Brosten et al., 2010).

The stochastic motion of colloidal suspension particles can be characterized by the Stokes–Einstein–Sutherland diffusivity,

$$D_{SES} = \frac{k_B T}{6\pi\eta_0 a} \tag{4}$$

Ideal hard-sphere colloids have short-range repulsive interparticle interactions and no long-range electrostatic interactions (Antl et al., 1986). To achieve hard-sphere colloidal interactions in experiments it is almost always required that the surface of the colloidal spheres be manipulated (Antl et al., 1986) and that some charge be present on the surface (Wassenius et al., 2003). For the colloidal particles used in this work the particles are charge stabilized by adding polyvinyl alcohol (PVA) to the suspending fluid which absorbs on the particle surface and generates short range repulsive forces. Further information on colloidal dynamics has been reviewed elsewhere (Russel et al., 1989, Stickel and Powell, 2005, Vermant and Solomon, 2005).

2. Materials and methods

NMR experiments were conducted using a Bruker 250 MHz superconducting magnet, a Mirco5 probe base and magnetic field gradient coil with $\mathbf{g}_{max} = 1.7$ T/m in three orthogonal (x, y, z) gradient directions. The flow setup is placed inside a 5 mm radio-frequency (rf) coil at a distance $> 2000R$ from the beginning of the microcapillary section of the flow setup so that all experiments are conducted on the steady state regime of colloidal migration due to shear induced migration (Semwogerere et al., 2007). To study the fluid dynamics of the colloidal suspension inside the capillary, spectrally resolved PGSE NMR techniques are used (Callaghan 1991, 2011; Price, 2009). These allow for the simultaneous independent investigation of the dynamics of both the colloid and suspending fluid phases of the suspensions (Brown et al., 2007). The dynamics are measured at $Q = 0.25$ and 0.50 mL/h. In the current work a microcapillary with internal radius (R) of 126 μm is used. The flow conditions (see Table 1) are characterized as strong flow ($Pe >> 1$) with inertial forces small when compared with viscous forces ($Re < 1$).

NMR can be used to measure the molecular motion of particular chemical species within a sample non-destructively by

Table 1
Dimensionless numbers (Pe_p, Pe_t, Re_p, Re_t) characterizing the flow conditions studied in the μ-capillary.

Q (mL/h)	Pe_p	Pe_t	Re_p ($\times 10^5$)	Re_t
0.25	270	160	4.6	0.35
0.50	540	321	9.3	0.70