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Abstract

This thesis includes a theoretical and experimental analysis of electrophoresis of colloidal particles in non-Newtonian polymeric fluids with shear-rate dependent viscosities. A model is derived that predicts field dependent electrophoretic mobility in shear-thinning Carreau fluids. The latter effect is experimentally investigated for submicron particles in solutions of linear polyacrylamide using capillary electrophoresis. The mobilities of the particles studied in these solutions did not depend on field strength, yet the mobilities were consistently an order of magnitude greater than in water and glycerol solutions with similar bulk viscosities. The increase in particle mobility could be attributed to several mechanisms, however it is consistent with the depletion of polymer apparent viscosity of the fluid as it migrates by electrophoresis is the same as experienced by the particle in Brownian diffusion. A comparison of particle mobility in both glycerol and polyacrylamide solutions to diffusion coefficients of the particles measured by dynamic light scattering supports this conclusion.

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1 Introduction

Electrokinetics describes the hydrodynamics of charged interfaces in viscous electrolytes under the influence of an applied electric field. It is a 200-year-old field of study [1] with modern uses in DNA separations [2, 3], microfluidic pumping [4, 5], and other applications [6]. Often, electric fields are used to drive flows in and move species through complex, *i.e.* non-Newtonian, fluids. These fluids are known to exhibit properties such as shear-thinning, viscoelasticity, and/or normal stresses. Shear-thinning is the key property of drag reducing agents and viscoelasticity and normal stresses are responsible for many rheological effects such as rod-climbing, hole-pressure errors, and centripetal pumping [7]. Classical electrokinetic theory assumes the fluid of interest is Newtonian, thereby overlooking the potential impact of fluid rheology on electrokinetic flows. It has been theoretically shown that electrophoretic mobility of particles in shear-thinning fluids is greater than in Newtonian fluids [8, 9, 10]. There is also experimental evident that electroosmotic flow (EOF) of polymer solutions can depend on applied field strength, unlike in Newtonian fluids [11, 12].

It is predicted that the mobility of particles in shear-thinning fluids will also be a function of electric field strength. Furthermore, the non-Newtonian stresses in the bulk fluid will result in a mobility that is a function of particle size. A theoretical model is proposed to predict size and field dependent electrophoretic mobility of colloidal particles in shear-thinning fluids.

Guided by this model, an experimental scheme is undertaken to investigate both the electroosmotic mobility through silica capillaries and the electrophoretic mobility of small particles as a function of field strength and solution viscosity. For shear-thinning fluids, it is predicted that the mobility will increase with increasing field. The value of the mobility is also predicted to be greater than in a Newtonian fluid with equivalent zero-shear viscosity. The latter prediction is corroborated by comparing electrophoresis and electroosmosis in aqueous polymer solutions to solutions of glycerol and water over a similar viscosity range. Accounting for increasing viscosity and decreasing permittivity, the particle mobility in glycerol solutions should agree with predictions from classical electrokinetics.

The thesis is organized as follows. First, background on both classical (Newtonian) and non-Newtonian electrokinetics is reviewed. Second, the derivation and results for an analytical solution to electophoresis of a single particle in shear-thinning fluids is presented [59]. Finally, the electrophoretic mobility of polystyrene particles in glycerol solutions and polyacyrlamide solutions are experimentally investigated as a function of field strength and fluid viscosity.

2 Background and Theory

2.1 Newtonian (Classical) Electrokinetics

Consider a charged surface, immersed in an aqueous electrolyte solution. Counter-ions are electrostatically attracted to the surface while co-ions are repelled. This attraction is balanced by ion diffusion, establishing a diffuse layer of ions surrounding the particle [13]. For a binary electrolyte, the relation between the ion distribution and the surface potential is given by the Poisson-Boltzman equation,

$$\nabla^2 \left[\frac{e\psi}{k_B T} \right] = \left(\frac{2e^2 z^2 n_0}{\varepsilon_0 \varepsilon_r k_B T} \right) \sinh \left[\frac{e\psi}{k_B T} \right], \tag{2.1}$$

where n_0 is the bulk concentration of ions for a symmetric binary electrolyte, $\varepsilon_0 \varepsilon_r$ is electric permittivity of the fluid, z is the ion valence, k_B is the Boltzmann constant and T is fluid temperature. When ψ is less than the thermal voltage, $\frac{e}{k_B T} \approx 25 mV$ the Poisson-Boltzman equation can be linearized via the Debye-Hückel approximation to

$$\nabla^2 \Psi = \kappa^2 \Psi, \tag{2.2}$$

where

$$\kappa = \sqrt{\frac{2e^2 z^2 n_0}{\varepsilon_0 \varepsilon_r k_B T}}.$$
(2.3)

The length scale of this screening layer is known as the Debye length, $\lambda_D = 1/\kappa$. It is typically on the order of tens of nanometers and decreases as ion concentration increases. For example, a solution at 25°C with 10mM NaCl will have a Debye length of approximately 3nm.

When an electric field is applied, ions will move along the field lines, carrying fluid with

them. The excess counter-ions in the diffuse layer result in a net fluid flow. The diffuse layer screens the surface charge and the bulk fluid outside the diffuse layer is electro-neutral. Therefore, any motion of the bulk fluid is due solely to flow in the diffuse layer. The characteristic velocity, \mathbf{v}_t^s of the electroneutral bulk fluid due to the diffuse layer flow is a function of the fluid permittivity, ε , the potential drop across the diffuse layer, ζ , Newtonian fluid viscosity, η_0 , and the applied electric field tangential to the surface, \mathbf{E}_t , as given by the Helmholtz-Smoluchowski relation [14],

$$\mathbf{v}_s = -\frac{\varepsilon \zeta}{\eta_0} \mathbf{E}_t \tag{2.4}$$

If, instead of a flat plate, an insulating particle is freely suspended in an unbounded electrolyte solution and an electric field is applied, the local electroosmotic flow in the diffuse layer acts as a 'conveyor belt' of fluid along the surface. For $\kappa a \gg 1$ the freely suspended particle moves with

$$\mathbf{V}_0 = \frac{\varepsilon \zeta}{\eta_0} \mathbf{E}_\infty \tag{2.5}$$

which is the Helmholtz-Smoluchowski relation for electrophoresis.

Smoluchowski derived the expression for electrophoresis of a sphere in 1903 [14], and asserted that it was valid for any particle size or shape, assuming R/λ_D was large and $\frac{e\psi}{k_BT}$ was small and uniform. Years later, in 1970, Morrison demonstrated that under the same assumptions, the flow in electrophoresis is an irrotational potential flow and Smoluchowski's solution is attainable without assuming a particle size or shape *a priori* [15]. Reed and Morrison furthermore demonstrated theoretically that two particles with the same zeta potential in solution will migrate independently and with the same mobility. Acrivos, Jeffrey, and Saville applied Morrison's result to a suspension of identical spheres and predicted the suspension would migrate with the same velocity as a single isolated particle [16]. Zukoski and Saville measured the electrophoretic mobility of concentrated red blood cells (of the same surface charge) did not vary with changing concentration [17].

2.2 Non-Newtonian electrokinetic flow in shear-thinning fluids

Although electrophoresis through polymer solutions has been a common practice in analytical chemistry and separations since the early 1990s, theoretical examination of the influence of rheology on electrokinetic phenomena did not emerge in the literature until a decade later. A thorough history of the development of electrokinetics in non-Newtonian fluids up through 2013 is presented by Zhao and Yang [18]. For brevity, a few of the key studies are highlighted here.

2.2.1 Theoretical investigations of EOF in non-Newtonian fluids

Electroosmosis in non-Newtonian fluids has been studied extensively only in the past decade and half, with mostly theoretical contributions to the field, supplemented by a handful of experimental studies.

Das and Chakraborty analyzed EOF of power-law fluids in parallel plate microchannels with the small zeta potentials[19]. They were the first to derive an approximate solution for the velocity profile in this geometry. Zhao *et al.* took the analysis a step further to demonstrate how shear-thinning fluid rheology significantly affects both the EOF velocity profile and derived both an approximate and an exact solution for the velocity profile in slit microchannels (with low zeta potential, but non-neglible Debye length) [20, 21]. As the fluid deviates further from the Newtonian limit, the flow profile in the channel flattens. In addition, the Smoluchowski velocity in a power-law fluid is a non-linear function of Debye length and field strength. Berli and Olivares [22] predict flow rate and electric current as a function of simultaneous application of applied potential and pressure gradients of generalized Newtonian fluids (fluids with shear-dependent viscosity) through both slit and cylindrical microchannels and propose a generalized form of force-flux relations. Unlike previous studies, where the fluid in the diffuse layer is assumed to have a power-law viscosity, they adopt a depletion layer model. The flow in the Debye layer is assumed to be Newtonian due to repulsion of polymers from the channel wall, thereby decoupling electrokinetic and non-Newtonian effects. By this model, non-linear effects due to fluid shear-thinning are a result of the pressure driven flow in the capillary alone. Berli also found that pumping efficiency in power-law fluids was greatly increased compared to in Newtonian fluids in both rectangular and cylindrical microchannels [23]. Tang *et al.* used a lattice-Boltzman method to compute the velocity and electric potential profiles in EOF of power-law fluids between two parallel plates [24].

The limitations of the aforementioned studies is the assumption of small zeta potentials and the power-law constitutive equation. Although both conditions are the simplest to model, they are the least physically intuitive. Zhao and Yang [25] relax the Debye-Hückel approximation and develop an exact solution for EOF of power-law fluids over a flat plate, which can be assumed to be the slip velocity in the case of thin Debye layers. The EOF velocity scales nonlinearly with zeta potential, field strength, and Debye length. Vasu and De numerically evalute EOF of power-law fluids through microchannels without the Debye Hückel approximation and for arbitrary Debye length [26].

Another constitutive equation that models shear-thinning behavior is the Carreau relation [7]. Unlike the power-law fluid model, Carreau includes upper and lower bounds on the viscosity as a function of shear-rate. Zhao and Yang investigated EOF of Carreau fluids for the case of a thin Debye layer[27]. Sanchez *et al.* present a theoretical analysis of joule heating effects on EOF of Carreau fluids in slit microchannels [28]. Using lubrication theory and accounting for temperature dependence of viscosity and fluid conductivity, they predict joule heating induces a pressure gradient along the microchannel that alters the electroosmotic flow profile as a function of the rheological parameters of the fluid. Zimmerman, Rees, and Craven utilized finite element simulations to suggest using the EOF of a Carreau fluid in a T-junction to explore the rheometry of the solution as it samples several shear-rates through the flow of the device [29, 30].

Park and Lee [31] adopted a more general constitutive equation to predict the effect of viscoelasticity on EOF in a square microchannel and solved for several combinations of rheological parameters using a finite volume method. In their model, increased stress due to fluid elasticity retarded the electroosmotic flow rate and reduced the sensitivity of EOF mobility to field strength. If an external pressure gradient is applied coincident with an applied electric field, appreciable secondary flows will develop in the microchannel due to fluid viscoelasticity.

Zhao and Yang recently investigated electroosmosis of power law fluids in a cylindrical microchannel [32]. Interestingly, they found that the EOF mobility is a function of channel geometry for finite Debye layer thickness. A solution is in terms of a non-linear differential equation that is solved numerically as a function of $Wi = \frac{k_B T \varepsilon E_0 \tau}{e\eta_0 \lambda_D}$, zeta potential, ζ , and power-law index, n. As long as Wi is not zero, EOF increases with zeta potential. As Wi increases, the model resembles the limiting case of EOF in a power-law fluid. For n < 1, EOF is greater than in a Newtonian fluid and increases with increasing Wi and/or decreasing n.

2.2.2 Experimental investigations of EOF in non-Newtonian fluids

Bello *et al.* [11] measured the electroosmotic mobility of methyl cellulose (MC) solutions in silica capillaries. They predicted that the EOF would be sufficiently supressed by the high viscosity fluid ($\eta_{MC} = 25cP$) in the Debye layer, however it was consistently observed that the mobility reduction was less than predicted by Smoluchowski relationship. They also observed that the EOF was a function of the voltage applied across the capillary. Particularly, that EOF in the MC solutions increased with increasing field strength. They attribute their observations to shear-thinning behavior of the solutions. For a power-law fluid, $\eta(\dot{\gamma}) = m\dot{\gamma}^{n-1}$, the electroosmotic mobility becomes

$$\mu_{eo,PL} = \left(\frac{\varepsilon_0 \varepsilon_r \zeta}{m}\right)^{1/n} \left(\frac{E}{\lambda_D}\right)^{1/n-1}.$$
(2.6)

Chang and Tsao measured drag reduction in the EOF of polyethylene glycol (PEG) solutions [33]. The mobilities in PEG were compared to ethylene glycol solutions of similar zero-shear viscosities. The ethylene glycol solutions behaved as predicted by Smoluchowski. However, in polymer solutions, they observed, like Bello, that the mobility was greater than predicted by Smoluchowski. For high molecular weight PEG the drag reduction is attributed to shearing of the polymers in the diffuse layer; for low molecular weight PEG it is attributed to the depletion of polymer from the surface.

Olivares, Vera-Candioti, and Berli [12] also measured electroosmosis of polymer solutions through capillaries. In their analysis they accounted for both polymer-wall interactions and the shear-thinning rheology of the fluid. For the case of strong polymer adsorption, the viscosity in the Debye layer is predicted to be much greater than in the bulk, due to the excess of polymer at the surface. Thus, the mobility will be less than predicted by Smoluchowski. Polymer adsorption may also alter the magnitude and even sign of the surface zeta potential. The opposite is predicted in the case of polymer depletion, where the polymer chains are entropically repelled from the wall. If the depletion layer is larger than the Debye length, the fluid near the wall is that of the solvent and the zeta potential theoretically is not altered by the presence of polymers in the bulk. In this limiting case, it would be predicted that EOF of the solution would equal that of the solvent. They studied carboxy-methyl cellulose (CMC) in sodium phosphate buffer and observed that the solutions exhibited mobilities between the two limits of adsorption and depletion predictions. Additionally, they observed an increase in mobility with increasing field strength, similar to Bello [11]. Addition of urea to the polymeric solution, however, shifted the mobility at all field strengths to those of the background electrolyte, suggesting a fully depleted layer near the wall and no non-Newtonian effects.

Bello *et al.* [11] and Olivares *et al.* [12] determined that electoosmosis (flow driven by an electric field) varied non-linearly with electric field in shear-thinning polymer solutions, unlike in Newtonian fluids. Similar non-linear effects are predicted for electrophoresis (particle motion driven by an electric field).

2.2.3 Theoretical investigations of particle electrophoresis in non-Newtonian fluids

In the past decade, Lee and Hsu and colleagues have published several theoretical investigations of electrophoresis of spherical particles in Carreau fluids for different external boundary conditions[34, 35, 9, 10, 36]. The resulting differential equations for the flow field are solved numerically with a pseudo-spectral method. Yeh and Hsu extended the analysis to a finite rod in a cylindrical channel [37]. These solutions are limited, however, by the application of an often aphysical external geometry as a boundary for the numerical simulations. Nevertheless, in their studies, the shear-thinning nature of the fluid is predicted to increase the particle mobility compared to in a Newtonian fluid with the same zero-shear viscosity. Additionally, the particle velocity scales non-linearly with zeta potential and applied field strength. This is consistent with the predictions for EOF mobility, where shear-thinning fluids increase mobility.

2.2.4 Experimental investigations of particle electrophoresis in non-Newtonian fluids

One of the the earliest papers on capillary electrophoresis is from Van Orman and McIntire [38]. Since then, capillary electrophoresis as grown into an often used analytical technique for particle separation [39, 40, 41, 42] and reviewed in depth [43, 44, 45].

Many experimental studies adapted the concept of gel electrophoresis to a capillary system. DNA, proteins, or other particles flow through polymer solutions [46, 47, 48]. Most of these studies interpret particle separations in these polymer solution filled capillaires with use the same terminology sieving-based electrophoresis in polymer gels. For instance, Ogston theory predicts the probability of particle penetration through a fiber "mesh" when the particle size is on the order of the mesh spacing [49, 50]. For large particles, the only mode of penetration into entangled solution is displacement of polymer chains, which causes local deformation of the network and additional drag on the particle. Chung, Kim, and Herr recently reviewed advances in polymer based sieving matricies for electrophoresis, including in entangled and semi-dilute polymer solutions [51].

Grossman *et al.* employed buffered polymer solutions as a sieving mechanism for DNA and other biological macromolecules [52, 53]. Separation of latex particles of different sizes was observed in semi-dilute polymer solutions where the particles' motion through and disruption of the entangled mesh of polymers affects their mobilities [54, 55].

Radko and Chambrach have one of the more extensive investigations of particle electrophoresis in polymer solutions. At the turn of the century, they published a review of CE experiments from the 1980s and 1990s [42]. An extended review of separation and characterization of micro- and nano-particles by capillary electrophoresis, including the effects of neutral background polymers on particle mobility and peak width was published in 2002 [43].

Radko et al. determined that the concentration of polyacrylamide with 3μ m polystyrene affects particle aggregation and therefore apparent particle mobility [56, 42]. The same group later observed electric field dependent retardation of polystyrene particles from 14 to 2170nm in the same linear polyacyrlamide. Up to 30nm, the relative mobility did not change with field, although it was function of particle size [47]. The small particles supposedly migrated through the entangled polymer solutions as they would through a porous media and the Ogston model was applied for these systems. However, the mobility of larger particles depended on both field strength and particle size. The relative mobility was related to the shear-rate of polymer network deformation. The large particles exert shear stress upon the polymer solutions, displacing chains and causing local deformations. In all cases, the relative mobility decreased with increasing polymer concentration, but not at the same rate as would be predicted using polymer solution zero-shear viscosity. Radko and Chrambach again measure CE of particles in semi-dilute polyacyrlamide of several different molecular weights and concentrations [57]. The relative mobility was unaffected by concentration in the low molecular weight fluids. In the highest molecular weight studied (18M), mobility of a given particle size decreased with increasing concentration. Both studies suggest that particle mobility in the polymer solution is a function of the local shear-field around the particle, that is, the local fluid rheology. Consideration of fluid rheology suggests an alternative terminology to characterize how microstructure deformation during electrophoresis and electroosmosis in a capillary impacts the particles' mobility.

3 A theoretical model for electrophoresis in shear-thinning fluids

3.1 Introduction

Morrison proved that Smoluchowski's result (2.5) does not depend on the particle size, provided the particles were dispersed in a simple, Newtonian electrolyte. If, as in electrophoresis, the primary interest is particle mobility as opposed to the entire flow profile, a solution for particle mobility can be found analytically rather than numerically. Leal described a technique for calculating the motion of rigid particles in a weakly non-Newtonian fluid using the Lorentz reciprocal theorem [58]. Not only does this method avoid calculating the complicated flow field around the particle, it provides a general formula to solve the unknown particle velocity in terms of known variables. Employing the Lorentz reciprocal theorem to obtain the electrophoretic velocity of a particle in a non-Newtonian fluid allows for the development of a comprehensive model without recourse to numerical simulations. The derivation and results presented below are published by Khair, Posluszny, and Walker [59].

3.2 Derivation of electrophoretic mobility in fluid with shear-dependent viscosity

A theoretical model for electrophoresis of particles of any shape in non-Newtonian fluids is given below. The fluid viscosity is presumed to depend on shear-rate [59] such that,

$$\eta = \eta_0 + \delta \eta_1(\dot{\gamma}), \tag{3.1}$$

where η_0 is a 'base' Newtonian viscosity, η_1 is a non-Newtonian (shear-rate dependent) 'correction,' and $\delta(<1)$ is a generic small parameter. Other assumptions, including those of uniform zeta potential at or less than the thermal voltage (≈ 25 mV), a thin diffuse layer with no surface currents, and fluid incompressibility are the same as for Smoluchowski and Morrison's derivations.



Figure 3.2.1: Reproduced from [59]. Electrophoresis of a uniformly charged particle under an electric field, \mathbf{E}_{∞} in a non-Newtonian fluid with stress, $\boldsymbol{\sigma}$. (a) Particle motion at recitilinear velocity, \mathbf{V} and angular velocity $\boldsymbol{\Omega}$, arising from electro-osmotic slip \mathbf{v}_t^s in the thin Debye layer (b). (c) Power-law and Carreau models for the non-Newtonian viscosity η_1 of Eq. (3.1).

With the thin diffuse layer, λ_D is smaller than the particle's local radius of curvature [15]. The problem is evaluated using matched asymptotic analysis: the electrokinetic flow in the diffuse layer is solved and used as a boundary condition for the bulk fluid problem [60]. In the diffuse layer, the particle is locally flat on the scale of λ_D , and the equation of motion reduces to a balance of electrical and viscous stresses,

$$\frac{d}{dy}\left(\eta(\dot{\gamma})\frac{d\mathbf{v_t}}{dy}\right) = \varepsilon\left(\frac{d^2\phi}{dy^2}\right)\mathbf{E}_t,\tag{3.2}$$

where y is the local Cartesian coordinate normal to the particle surface, \mathbf{v}_t and \mathbf{E}_t are the tangential velocity and electric fields respectively, and ϕ is the electric potential. The solution of \mathbf{v}_t as $y \to \infty$ is the tangential 'slip' velocity, and by our asymptotic analysis is also the velocity at the particle surface for the bulk fluid problem. This slip velocity is

$$\mathbf{v}_t^{\text{slip}} = \mathbf{v}_{0,t} - \delta \left\{ \mathbf{v}_{0,t} \int_0^\infty \eta_1(\dot{\gamma}) \frac{d\phi}{dy} \mathrm{d}y \right\},\tag{3.3}$$

where $\mathbf{v}_{0,t} = -\frac{\varepsilon \zeta}{\eta_0} \mathbf{E}_t$ is the O(1) contribution and the familiar Newtonian Helmholtz-Smulochowski slip velocity. The bulk fluid is electroneutral, so the momentum balance is simply the $\nabla \cdot \boldsymbol{\sigma}_H = 0$. The hydrodynamic stress tensor is expanded in δ ,

$$\boldsymbol{\sigma}_{H} = (-p_0 \mathbf{I} + 2\eta_0) + \delta(-p_1 \mathbf{I} + 2\eta_0 \mathbf{e}_1 + 2\eta_0 \eta_1 \mathbf{e}_0) + O(\delta^2), \qquad (3.4)$$

where \mathbf{e}_0 is the Newtonian rate-of-strain tensor and \mathbf{e}_1 is the non-Newtonian rate-of-strain tensor, p is pressure, \mathbf{I} is the isotropic identity tensor. The rate-of-strain is defined as $\mathbf{e}_k = \frac{1}{2}(\nabla \mathbf{v}_k + (\nabla \mathbf{v}_k)^T)$.

The O(1) solution for the bulk fluid velocity, \mathbf{v}_0 is the same as v_t^s in (2.5). As expected, the particle migrates with $\mathbf{V}_0 = \frac{\varepsilon \zeta}{\eta_0} \mathbf{E}_{\infty}$ and $\mathbf{\Omega}_0 = 0$, where \mathbf{V} and $\mathbf{\Omega}$ are the rectilinear and angular velocities of the particle, respectively. Unfortunately, even the simplest non-Newtonian fluid lends itself to a differential equation in fluid velocity without an analytical solution. However, since the particle migration is of primary interest, not the flow profile, the Lorentz reciprocal theorem is incorporated to solve directly for \mathbf{V}_1 , the non-Newtonian particle velocity. This only requires knowledge of the O(1), i.e. Newtonian, solution and an 'auxiliary' Stokes flow problem with the same geometry [61, 62]. The reciprocal theorem is

$$\int_{V} \mathbf{v}_{1} \cdot (\nabla \cdot \boldsymbol{\sigma}_{aux}) \mathrm{d}V = \int_{V} \mathbf{u}_{aux} \cdot (\nabla \cdot \boldsymbol{\sigma}_{1}) \mathrm{d}V, \qquad (3.5)$$

where σ_{aux} and \mathbf{u}_{aux} are the auxiliary Stokes flow stress and velocity tensors, while \mathbf{v}_1 and $\sigma_1 = -p_1 \mathbf{I} + 2\eta_0 \mathbf{e}_1 + 2\eta_1(\dot{\gamma}) \mathbf{e}_0$ are the $O(\delta)$ velocity and stress tensors from (3.4). Integration of (3.5) over the entire volume of fluid outside the diffuse layer and further manipulation yields

$$\mathbf{V}_1 \cdot \mathbf{F}_{aux} + \int_S \mathbf{v}_1^{slip} \cdot (\boldsymbol{\sigma}_{aux} \cdot \mathbf{n}) \mathrm{d}S + \boldsymbol{\Omega}_1 \cdot \mathbf{L}_{aux} = 2\eta_0 \int_V (\eta_1(\dot{\gamma})\mathbf{e_0} : \nabla \mathbf{u_{aux}}) \mathrm{d}V \qquad (3.6)$$

where S is the surface of the particle (outside the diffuse layer), V is the volume of fluid outside the particle, and \mathbf{F}_{aux} and \mathbf{L}_{aux} are the auxiliary Stokes flow force and torque on the particle, respectively. Equation (3.6) is applicable for any size, shape, or number of particles.

The simplest case is that of a single spherical particle with no rotation. The auxiliary flow chosen is that of a torque-free sphere translating under the imposed force \mathbf{F}_{aux} and $\mathbf{L}_{aux} = 0$. Appropriately scaled and non-dimensionalized, the $O(\delta)$ or non-Newtonian mobility is

$$\frac{M_1}{M_0} = \int_0^\infty \eta_1(\dot{\gamma}) e^{-y} \mathrm{d}y + \frac{3}{4\pi a} \int_V \eta_1(\dot{\gamma}) \mathbf{f}(\mathbf{r}) \cdot \mathbf{E} \mathrm{d}V$$
(3.7)

where

$$\mathbf{f}(\mathbf{r}) = \frac{1}{r^8} \mathbf{I} + \left(\frac{3}{r^6} - \frac{2}{r^8}\right) \frac{\mathbf{r}\mathbf{r}}{r^2}.$$
(3.8)

The first term on the right-hand side of (3.7) is the mobility contribution from the diffuse layer $M_{1,D}$ and the second term is the contribution from the bulk fluid $M_{1,B}$.

3.3 Results and Discussion

Power-law fluid Using a power-law constitutive equation, $\eta(\dot{\gamma}) = m\dot{\gamma}^{n-1}$, equation 3.7 becomes

$$V_{1} = -\frac{1}{n} \frac{m}{\eta_{0}} \left(\frac{V_{0}}{\lambda_{D}}\right)^{n-1} + \frac{3m}{2\eta_{0}} \left(\frac{3V_{0}}{2a}\right)^{n-1} \int_{0}^{\pi} \int_{1}^{\infty} \left(\frac{\sqrt{1+2\cos^{2}\theta}}{r^{4}}\right)^{n-1} f(r,\theta) dr d\theta, \quad (3.9)$$

where $f(r, \theta)$ is equation 3.8 evaluated in spherical coordinates with **E** as $E\delta_z$. The diffuse layer contribution scales as λ_D^{n-1} , as seen in previous electro-osmotic studies [11, 12]. A novel result is the explicit dependence on particle size, R, where the bulk contribution to the non-Newtonian velocity scales as R^{1-n} . The shear-thinning (thickening) behavior of a fluid where n < 1 (n > 1) enhances (retards) the motion of the particle by decreasing (increasing) the viscosity with increasing shear-rate. When the fluid is Newtonian (n = 1), the velocity reduces to the Smoluchowski equation (2.5). Figure 3.3.1 shows how this simple constitutive model results in a divergence when the power-law exponent is n = 0.25.



Figure 3.3.1: The additional contribution to the total velocity of the particle from outside the diffuse layer, $V_{1,B}$, has a discontinuity at n = 0.25 for (a) power-law fluids but not for (b) Carreau fluids. In the Carreau model, the velocity is positive when n < 1 (shear-thinning) and negative when n > 1 (shear-thickening).

Carreau Fluid The power law constitutive equation poorly describes the fluid behavior at extreme shear-rates, because it has no upper or lower bounds on viscosity. A more physically realistic constitutive relation is the Carreau model [7, 63, 64, 65],

$$\eta_1(\dot{\gamma}) = \eta_0 \left[\left(1 + (\tau \dot{\gamma})^2 \right)^{\frac{n-1}{2}} - 1 \right].$$
(3.10)

The two mobility contributions in a Carreau fluid are

$$\frac{M_{1,D}}{M_0} = 1 - \int_0^\infty \left(1 + \operatorname{De}_D^2 \exp(-2y)\right)^{\frac{n-1}{2}} e^{-y} \mathrm{d}y$$
(3.11a)

$$\frac{M_{1,B}}{M_0} = \int_V \left(1 + \mathrm{De}_B^2 g(\dot{\gamma}_0)\right)^{\frac{n-1}{2}} h(\dot{\gamma}_0) \mathrm{d}V$$
(3.11b)

where

$$g(\dot{\gamma}_0) = \left(\frac{3\sqrt{1+2\cos^2\theta}}{2r^4}\right)^{n-1} f(r,\theta), \quad h(\dot{\gamma}_0) = \left(\frac{3\sqrt{1+2\cos^2\theta}}{2r^4}\right)^2.$$

The velocity naturally depends on two Deborah numbers, $\text{De}_B = \frac{\tau V_0}{R}$ and $\text{De}_D = \frac{\tau V_0}{\lambda_D}$, which are the ratio of the relaxation timescale of the fluid, τ from equation (3.10) to the observation timescale (characteristic length scale divided by particle velocity). In Figure 3.3.2, each contribution to the Carreau mobility (equation 3.11) is plotted against De_D and De_B for several values of n. Both contributions are positive(negative) for n < 1(> 1), corresponding to an increase(decrease) in particle mobility in a shear-thinning(thickening) fluid.

At low De, the time-scale for non-Newtonian behavior of the fluid, τ , is small with respect to the observation time-scale, indicating that the fluid will have only minor qualitative differences from a Newtonian fluid and thus the particle is expected to move as it would in a Newtonian fluid [7]. As shown in Figure 3.3.2a, the diffuse layer contribution of a shear-thinning fluid approaches a constant velocity as τ approaches infinity, albeit an order of magnitude



Figure 3.3.2: The normalized diffuse layer (a) and bulk fluid (b) mobility contributions for a Carreau fluid plotted against the relevant Deborah numbers [59].

greater than the Newtonian case because the viscosity has been reduced to the lower Newtonian limit. In shear-thickening fluids, the constitutive model provides no infinite-shear-rate bound, so, \mathbf{V}_1 continually decreases with increasing fluid velocity (increasing τ). While the diffuse layer contribution is related to the changing viscosity of the fluid, the bulk fluid contribution to the particle velocity only comes from non-Newtonian stresses. Thus, Figure 3.3.2b shows no bulk contribution at high and low De, where the fluid exhibits Newtonian behavior.

The theoretical analysis presented above begs the question of whether the impact of rheology is experimentally relevant. The perturbation scheme adopted in the model, whereby $\delta \ll 1$, indicates that the non-Newtonian contributions to the instantaneous electrophoretic motion are modest in magnitude. However, over a period of time the instantaneous deviation from Newtonian behavior calculated herein may lead to an appreciable cumulative effect [58, 59]. Note that τ can be on the order of seconds; hence taking $\tau \sim 1$ s, $\lambda_D \sim 10$ nm, $R \sim$ 1μ m, and $V_0 \sim 10\mu$ m/s yields $\text{De}_D \sim O(10^3)$ and $\text{De}_B \sim O(10)$, suggesting that Deborah numbers leading to appreciable non-Newtonian mobility contributions, M_1 are experimentally attainable (Figure 3.3.2).

3.4 Conclusion

The model clearly predicts that non-Newtonian rheology causes the mobility to have an explicit dependence on particle size, unlike in a Newtonian fluid. When the Deborah numbers are rewritten in terms of mobility and field, $De_B = \frac{\tau \mu_0 E}{R}$ and $De_D = \frac{\tau \mu_0 E}{\lambda_D}$, the model also predicts a field strength dependence [59]. While the latter conclusion agrees with previous theoretical predictions, the former is a novel contribution elucidated by this computational approach, since the particle size is only relevant when accounting for non-Newtonian bulk stresses. Nevertheless, the dependence of mobility on particle size has experimentally observed in experiments by Radko and Chambrach [55].

The following sections of this thesis investigate how electrophoretic mobility is experimentally related to varying field strength and rheological parameters in polymer solutions. Mobility in these non-Newtonian fluids are compared to particle mobilities measured in viscous Newtonian fluids and to predictions from the model above.

4 Materials and Methods

4.1 Materials

Linear polyacrylamide (CAS 9003-05-8) was purchased from Sigma-Aldrich (92560-10G Lot-BCBG1068V). The molecular weight is reported to be (5-6)M M_w. Glycerol, 99%, (CAS 56-81-5) was purchased from Sigma-Aldrich (G9012-1L Lot050M0182V). Glycerol was mixed with deionized water and the appropriate amount of a 50mM KCl stock solution to reach a final concentration of glycerol with the total ion concentration of the solutions kept at 10mM KCl. Fluorescent sulfonated polystyrene latex particles (20nm FPSS) were purchased from Molecular Probes (FluoSpheres F8845). The charge on the particles arises from sulfate groups introduced during the polymerization [43]. Benzyl alcohol (CAS 100-51-6) from Acros Organics (LotA0239895) was used as a neutral marker for capillary electrophoresis experiments. The benzyl alcohol was diluted to 0.5wt% in 10mM KCl.

Two different methods were utylized to measure electrophoresis of the FPSS particles. First, light scattering techniques to measure particle diffusion and electrophoretic mobility are described. This is followed by a description of the three-plug capillary electrophoresis methodology including a discussion on the choice of particle size. Finally, viscosity of the solutions was measured in both a concentric cylinder Couette cell rheometer and Cannon-Ubbeholde dilution viscometers.

4.2 Light scattering techniques

4.2.1 Dynamic Light Scattering (DLS)

Dynamic light scattering (DLS) is a technique for measuring hydrodynamic size of colloidal particles. The diffusion of the particles due to Brownian motion is measured and converted to a hydrodynamic diameter using Stokes-Einstein equation,

$$D = \frac{k_B T}{6\pi\eta_0 a}.\tag{4.1}$$

A laser passes through the sample cell and intensity fluctuations of the incident light are measured. The rate at which the fluctuations change are more rapid for smaller particles than for larger particles. This rate of decay is measured by correlating the signal in intensity at time t to that at time $t + \delta t$, $t + 2\delta t$, and so forth. The time at which the correlation starts to decay indicates the mean size of the sample and the slope of that decay indicates the polydispersity of the sample [66]. The diffusion coefficient, D, is determined by a single exponential fit to the correlation function, $G(\tau)$,

$$G(\tau) = A \left[1 + B \exp\left(-2(Dq^2)\tau\right) \right], \qquad (4.2)$$

where A is the baseline of the correlation function and B is the intercept, and

$$q = \frac{4\pi n}{\lambda_0} \sin\left(\frac{\theta}{2}\right). \tag{4.3}$$

The magnitude of the scattering vector, \mathbf{q} , is a function of the refractive index of the dispersant, n, wavelength of the laser λ_0 , and the scattering angle, θ . The Malvern Zetasizer Nano NSP (Malvern Instruments, Worcestershire, U.K.) uses non-invasive backscatter (NIBS), where θ is 173°. The specific instrument is equipped with a He-Ne 633nm laser. The refractive index is specified by the user. For PAAm solutions, the refractive index was assumed to be that of water, 1.333. The refractive index of pure glycerol and 50% glycerol are 1.474 and 1.398 respectively. The refractive index of these and other glycerol solutions have been tabulated in literature [67].

Solutions for DLS measurements were created by adding 0.5mL of 2% 20nm FPSS to 3mL of PAAm or glycerol solution to a 4mL polystyrene cuvette. The solution was mixed by inverting the sample several times. After tapping the cuvette gently to release any trapped bubbles, the cuvette was placed in the Zetasizer and diffusion measured as described above. Diffusion of particles in the polyacrylamide solutions were measured several times over the course of three days in order to observe time-dependent effects. From DLS, we can determine how the particle diffusion changes with changing fluid viscosity. Using Stokes-Einstein, the diffusion coefficient of a particle of known size gives a rough estimate of the viscosity of the fluid sampled by the particles.

4.2.2 Phase Analysis Light Scattering (PALS)

Phase analysis light scattering (PALS) is a derivative of laser doppler velocimetery (LDV) and is used to measure electrophoretic mobility of colloidal particles. Similar to DLS, LDV measures how the intensity of scattered light from colloidal particles flucuates with time. Unlike diffusion, however, charged particles in an electric field have a directed motion, rather than random flucuations. As the particles move, the frequency of the scattered light is shifted due to the doppler effect [68, 69]. Rather than comparing the intensity of the scattered light to itself, as in DLS, the frequency of the scattered intensity, ω_s is compared to the frequency of the incident light (or a reference beam). Several cycles are required to garner enough data to determine the mobility, which can be difficult when the mobility is small or the field cannot be applied for a long time. If, instead, the time series of the phase, Φ_s is measured, a full Doppler cycle is not necessary to obtain the same information as with frequency comparison. The frequency is defined as

$$\omega_s = \frac{\mathrm{d}\Phi_s(t)}{\mathrm{d}t} = \mathbf{q} \cdot \left[\langle \mu_e \rangle \, \mathbf{E}(t) \pm \mathbf{v}_c \right], \tag{4.4}$$

where \mathbf{v}_c is the velocity of particles due to thermal flucuations. This contribution is virtually eliminated by averaging over many cycles [69]. The Malvern Zetasizer Nano ZSP uses the M3 measurement technique to account for EOF effects in the cell. First, the field is applied with a high frequency for a short time. Since the particles will respond faster than the liquid frequency, EOF is essentially suppressed However, information about the mobility distribution is lost in this measurement. The instrument takes a second measurement, at a lower frequency for longer time, to recover the mobility distribution information [70].

Electrophoresis uses DTS1060 sample cells. The cell used in this instrument is a folded polycarbonate capillary cell made from with gold-plated beryllium-copper electrodes with a 4mm path length [71]. Solutions were made by the same method used for DLS. A pipette was used to draw 1mL of sample and insert it into the zeta cell. After three consecutive runs, the solution in the cell is discarded and the cell rinsed with deionized water and methanol.

Although PALS is a fast and simple measurement of mobility and can measure lower mobilities, there are still limitations to the technique. First, the maximum field strength capable in the Zetasizer is 30 V/cm (150 V over 50mm folded capillary cell). To investigate

the effect of field strength on particle mobility, a wider range of field strengths are preferred.

Another concern is the reactivity of the electrodes in the PALS sample cell with the polymer. Experimentally, it was observed that under the applied field, the polyacyrlamide solutions caused significant corrosion of the electrodes, which affected the purity of the sample. Therefore, an alternative method of measuring particle electrophoretic mobility was implemented to supplement mobility determined from the PALS technique.

4.3 Capillary Electrophoresis

A Beckman Coulter (Indianapolis, IN) P/ACE MDQ commercial capillary electrophoresis (CE) instrument equipped with UV detector was also used to measure particle electrophoresis and electroosmosis in silica capillaries. In capillary electrophoresis, a small plug of sample is injected at one end of a capillary filled with an electrolyte. When a voltage is applied across the length of the column, the sample moves due to EOF at the capillary walls and electrophoresis due to the sample itself. With the commercial instrumentation, 1kV to 30kV can be applied over the 30cm capillary (33-1000 V/cm). Thus there is a much wider range of field strengths possible compared to the PALS technique. The PAAm solutions also do not react with the platinum electrodes in the commercial CE instrument.

Both 50μ m and 75μ m internal diameter fused silica capillaries were purchased from Polymicro Technologies (Phoenix, AZ). The capillaries are coated with polyimide to an outer diameter of 360 μ m. The coating is burned off 20cm from the injection end of the capillary as a window for the detector. The capillary is then threaded into a capillary cartridge that holds it in the CE instrument. Coolant fills the capillary cartridge, which reduces Joule heating in the capillary and maintains the capillary at a constant temperature (25°C in all experiments). The portion of the capillary surrounded by coolant is referred to as the thermostated region. An adapter at the detection window sets the detection length to 0.8 mm along the capillary. The UV light is filtered to $\lambda = 214$ nm, as this wavelength was experimentally observed to give the strongest signal with both the benzyl alcohol and polystyrene relative other UV filter options.

An important part of the CE procedure is preparing the capillary column. A fresh column was cut for each new fluid under investigation. The column is conditioned prior to each sequence by rinsing consecutively deionized water, 50% methanol, 0.1M HCl and finally 0.1M NaOH, each for 20 minutes at 20 psi. The final step with NaOH strips the surface of the column of hydrogen ions, leaving exposed Si-O⁻. With the column stripped, it is then rinsed with deionized water for 5 minutes to flush out the NaOH and then with the background electrolyte fluid (BGE) for up to 30min before experiments commence. This allows ample time for the freshly stripped column to adapt to the particular fluid.

The neutral marker is prepared by adding 20μ L of the 0.5% benzyl alcohol (BA) in 10mM KCl to 180μ L of the BGE solution. A pipette is used to mix the solution in the 200μ L sample vial. The sample of particles and neutral marker is made by adding 10μ L of the 0.5wt% BA and 20μ L of 2wt% solution of particles to 180muL of the BGE solution. Again, the solution is mixed by pipette in a sample vial. BGE vials are filled with 1.5mL of the BGE solution.

In a standard CE measurement, a sample is injected with a neutral marker at one end of the capillary (which is already filled with BGE solution). A voltage, V, is applied across the capillary. The neutral marker will migrate due to electroosmosis in the capillary. The elution time of the marker, $t_{\rm m}$ is used to determine the electroosmotic velocity, U_{eo} , in the capillary,

$$U_{eo} = \frac{L_D}{t_{\rm m}}.\tag{4.5}$$

The electroosmotic mobility is calculated by dividing the velocity by the field strength applied, $E = V/L_T$, where L_T is the total length of the capillary (30cm). The sample will be carried by the electroosmotic flow and move by electrophoresis. Assuming the electroosmotic velocity in the capillary is greater than the electrophoretic velocity of the sample, the electrophoretic velocity is determined by the elution time of the sample, t_s where

$$U_{obs} = \frac{L_D}{t_{\rm s}}, \text{ and}$$
(4.6)

$$U_{ep} = U_{eo} - U_{obs}.$$
(4.7)

The standard or '1-plug' method is limited when U_{eo} and U_{ep} are small or close in magnitude to each other, since t_m and t_s are inversely proportional to velocity. The Smoluchowski equation with the high bulk viscosities in the glycerol and PAAm solutions predict particle and EOF mobilities an order of magnitude smaller than in water. For instance, if the EOF mobility is 0.34μ m-cm/V-s (as predicted when $\eta_0 = 10\eta_w$) the neutral marker will take 58 minutes to elute at 5kV. A difference of 0.1μ m-cm/V-s between the EP and EOF mobilities at the same voltage results in sample elution times of nearly 200 minutes. Problems associated with applying electric fields for long times include Joule heating and dielectric breakdown in the fluid [72]. To avoid those issues, an alternative method is described below to measure electrophoresis in a CE column.

4.3.1 Three Plug Method

Williams and Vigh [72] suggested a three-plug method to measure small mobilities in capillary electrophoresis. In this method, mobilities are measured by the difference in elution time between multiple peaks rather than the absolute elution time of a single peak. With the threeplug method a single experiment takes 10-20 minutes, even for small or similar mobilities. Errors in mobility associated with unthermostated regions of the capillary (near beginning and end of capillary) and variable EOF within and between different capillaries are minimized.

A sequence begins with an initial conditioning step and 30 min flush with the background electrolyte solution, followed by 10 to 20 consecutive runs in the same fluid. In each run, EOF and electrophoresis can be measured simultaneously. First, a plug of sample and neutral marker (N_1, S) is injected hydrodynamically into the column. The injection pressure used varies with the fluid viscosity, but the injection time was kept at 5 seconds for each injection and each fluid. This first plug is pushed further into the column at pressure ΔP for time t_p . A second plug of neutral marker alone (N_2) is then injected and again pressure ΔP is applied for the same t_p . At this juncture, the two plugs are in the thermostated region of the capillary and the separation distance between them is known. A voltage, V, is applied for some time, t_v , across the capillary. If a positive (normal) voltage is applied, both neutral markers will move with the EOF towards the detector and away from the injection port. If a negative (reverse) voltage is applied, both neutral markers move away from the detector and back towards the injection port. The sample is affected by both the EOF in the column and its own electrophoretic mobility. The direction the sample moves will depend on which mobility is greater. Finally, a third plug of the neutral marker (N_3) is injected and pressure ΔP is applied until all three plugs pass the detector. Intensity data is collected at a rate of 32Hz and plotted with time as an electropherogram in P/ACE MDQ 32Karat Software 3.0 (Beckman Coulter, Indianpolis, IN). Figure 4.3.1 is a sample electropherogram, where each sample or marker plug is identified by a peak as labeled. Separation between peaks is used to calculate mobilities. The location, height, and width of peaks are determined using **mspeaks.m**, a function in the Bioinformatics Toolbox of Matlab R2014a [73]. The algorithm converts raw data to a list of peaks by smoothing the signal using undecimated wavelet transform with Daubechies filter [74]. The speed at which the peaks move past the detector is the mobilization velocity, v_m [72],

$$v_m = \frac{L_D}{t_{N_3}},\tag{4.8}$$

where L_D is the length from the injection port to the detector (20cm) and t_{N_3} is the time of elution for the third peak (Figure 4.3.1). The difference in peak spacing multiplied by the mobilization velocity is the distance between the sample and marker plugs in the capillary. The electroosmotic velocity is that distance divided by t_v ,

$$U_{eo} = \frac{\left[(t_{N_3} - t_{N_2}) - (t_{N_2} - t_{N_1})\right]v_m}{t_v},\tag{4.9}$$

where t_v is adjusted by the ramp-up time of the voltage (0.17min). The electrophoretic velocity is calculated from the separation distance between t_{N_1} and t_S .

$$U_{ep} = \frac{[t_{N_1} - t_S]v_m}{t_v}.$$
(4.10)

As in the one-plug method, mobility is calculated by dividing the velocity by the field strength applied, $E = V/L_T$.

Figure 4.3.1 overlays two electropherograms when no voltage is applied (black line) and



Figure 4.3.1: Three plug method sample electropherogram. Black line is with no voltage applied. Gray line is with 6kV applied for 1min. This particular solution is 0.4g/dL PAAm.

when 6kV is applied for 1 minute (gray line). For the case with no field, the distance between the peaks is constant, that is

$$t_{N_3} - t_{N_2} \approx t_{N_2} - t_{N_1} \approx t_p - t_d,$$

where t_d is a delay time determined experimentally. When a field is applied, the spacing between peak t_{N_1} and t_{N_2} is the same as before, as both move away from the detector (they elute later than in the no-field case). In the particular example shown, the EOF is greater than electrophoresis of the particles, causing the particles to move in the same direction as the neutral marker. EOF and EP can be measured separately as well using this method. If the first plug is only a neutral marker (no sample), the EOF is calculate with equation 4.9. This can be a check to verify the particles in the first peak do no interfere with the EOF measurement. On the other hand, if the first plug has only particles (no neutral marker), the electrophoresis of the particles is determined by

$$U_{ep} = \frac{[(t_{N_2} - t_S) - (t_p - t_d)]v_m}{t_v}.$$
(4.11)

Thus, the three plug method is used to measure electrophoretic mobility of polystyrene particles in glycerol and PAAm solutions.

4.3.2 Particle size constraints

Because of the use of pressure to push the particles through the column in the three plug method, the suitable particle sizes are limited. The Peclet number, Pe, is the ratio of the convection of the sample to the Brownian diffusion of the sample. In pressure-driven flow with velocity, U, particle diffusion (given by the diffusion coefficient, D) outweighs convection through the capillary of radius R and length L_T when

$$Pe = \frac{RU}{D} \ll \frac{L_T}{R}.$$
(4.12)

In this Taylor-Aris dispersion limit, particles experience both axial and radial diffusion [75] and the fluid bolus at time, t, will appear on the electrophoregram as a symmetric, Gaussian peak with width,

$$w_t = \frac{4\sqrt{\ln 2}\sqrt{D_{\text{eff}}t}}{U} \tag{4.13}$$

where the effective diffusion coefficient is

$$D_{\rm eff} = D \left[1 + \left(\frac{Pe}{\sqrt{48}} \right)^2 \right]. \tag{4.14}$$

The necessary particle size, a, to meet this requirement can be estimated by substituting the Hagen-Poiseuille equation,

$$U = \frac{R^2 \Delta P}{8\eta L_T}.$$
(4.15)

for U and the Stokes-Einstein equation 4.1 for D in equation 4.12. The maximum particle size is

$$a \ll \frac{4L_T^2 k_B T}{3\pi R^3 \Delta P}.\tag{4.16}$$

In a 50 μ m diameter column with $L_T = 30$ cm, T = 25°C, and $\Delta P = 1$ psi, the maximum particle size is 60 nm. The particle size could be increased if the radius of the capillary is reduced, however it becomes more practically difficult to inject highly viscous fluids into small capillaries. High pressures are also necessary to push the plugs through smaller capillaries in a reasonable amount of time (elution times typically between 5 and 20 minutes). As the pressure in the column is increased, as it will be in fluids with increased viscosity, the limiting particle size decreases. Particles were purchased in anticipation of future studies with florescent detection rather than UV detection. Sulfonated polystyrene latex particles modified with fluorescein were commercially available in 20nm and 200nm diameters. Thus, the smaller particles were chosen for this study.

4.4 Rheology of solutions

A complex fluid has intrinsic microstructure, which gives rise to non-Newtonian bulk rheological effects. The challenge of isolating rheological effects on electrophoresis requires development of a system in which (1) the electric field does not affect the microstructure, (2) the microstructure in turn does not affect the electrokinetics of the particles, and (3) the fluid rheology can be well characterized and fit to model constitutive relation(s).

The first condition is satisfied by stipulating that the microstructure remain non-ionic. Dilute and semi-dilute solutions of linear polymer such as nonionic polyacrylamide (PAAm) are known to follow the Carreau constitutive relation as in Figure 4.4.1, [7, 76]. Linear polyacrylamide is also the most widely used polymer for CE separations [51]. The PAAm solutions were compared to aqueous glycerol solutions with similar zero-shear viscosities (1-50 cP). The glycerol increases the fluid viscosity without imposing any non-Newtonian behavior to the fluid.

Viscosity of the solutions were measured in Cannon-Ubbeholde dilution viscometers and with a single-walled concentric cylinder (Couette cell or 'cup and bob') geometry in a TA DHR Rheometer. The bob is 28 mm diameter and 42 mm in length and the cup diameter is 30 mm.

4.4.1 PAAm solution rheology

Several concentrations of a 5-6M M_w linear polyacyrlamide (PAAm) in 10mM KCl were measured, ranging from 0.1g/dL to 1g/dL. Each solution was made from a stock solution of 1g/dL PAAm dissolved in deionized water. Solutions were adjusted to 10mM KCl by diluting with appropriate volume of a 50mM KCl stock solution. Figure 4.4.1 shows the viscosity versus shear-rate curves measured using the concentric cylinder geometry and flow sweep method. A minimum 5 minute equilibration time was used in the Peltier cup to maintain the temperature of the fluid at 25°C. The curves were fit to Carreau parameters using TRIOS software [77] and the parameters are summarized in Table 4.4.1. Additionally, viscosities of the more dilute polymer solutions (c ≤ 0.5 g/dL) were measured with Cannon Ubbeholde dilution viscosmeters (E47-100 and E732-50) in a temperature bath kept at 25°C. The viscosities measured by this technique are also reported in Table 4.4.1.

The rheological properties of polymer solutions are sensitive to concentration and can



Figure 4.4.1: Viscosity versus shear-rate of 5-6Mw PAAm for several concentrations of polyacrylamide as measured by single-walled Couette cell in TA-DHR rheometer

be divided into three concentration regimes: dilute, semidilute and entangled [78, 79]. In the dilute regime, polymer coils are fully separate from each-other, *i.e.* no coil-coil interactions. Therefore, the bulk viscosity of the fluid increases linearly with increasing concentration and shear-thinning effects are slight. At the overlap concentration, c^* , the polymer coils begin to "see" each other in solution and interact. This is the semi-dilute regime. Shear-thinning behavior begins to develop in this regime and the viscosity increases more rapidly with concentration. Figure 4.4.2 plots the viscosity (zero-shear viscosity from Carreau parameter fit for higher fluid viscosities and Ubbeholde viscometer for lower viscosity fluids, when applicable) against concentration. As shown in the figure, the viscosity of the PAAm in 10mM

C (g/dL)	$\eta_U (cP)$	$\eta_0 \ (cP)$	τ (s)	n
0.8(2)	-	40.0 ± 5.0	0.06	0.73
0.8(2)	-	40.0 ± 5.0	0.06	0.73
0.6(1)	-	15.7 ± 1.2	0.03	0.80
0.6(2)	-	20.3 ± 3.1	0.05	0.80
0.5	7.53 ± 0.3	9.3 ± 0.9	0.015	0.87
0.4	5.00 ± 0.2	7.30 ± 0.85	0.015	0.87
0.3	3.72 ± 0.1	3.51 ± 0.45	0.025	0.96
0.2	2.52 ± 0.1	2.39 ± 0.35	0	1
0.1	1.41 ± 0.1	1.66 ± 0.20	0	1

Table 4.4.1: Rheological parameters of several polyacrylamide concentrations: η_U is the viscosity determined by Ubbeholde viscometer, η_0 , τ , and n are Carreau parameters fitted to data from Couette cell rheometry (Figure 4.4.1). The 0.8g/dL solution and one of the 0.6g/dL solutions were made from a different stock solution of 1g/dL PAAm than the other solutions as indicated.



Figure 4.4.2: log(viscosity) versus log(concentration) of 5-6M Mw PAAm at 25°C. Closed circles are measured viscosity from Cannon-Ubbeholde viscometer, open circles are zero-shear viscosity from Carreau fit of curves in Figure 4.4.1.

KCl increases non-linearly with concentration, indicative of crossing from dilute to semi-dilute concentration regimes near 0.3g/dL. Radko and Chambrach also report c* near 0.3g/dL in the same molecular weight of linear polyacyrlamide in Tris-borate buffer [55].

4.4.2 Glycerol solution viscosity

The same Couette cell geometry was used to measure shear-stress versus shear-rate in the glycerol solutions. In Figure 4.4.3, the shear-stress is plotted against the shear-rate. The slope for each concentration determines the bulk viscosity of the fluid, as shown in the figure.



Figure 4.4.3: Shear stress versus shear-rate in Couette cell geometry in TA DHR rheometery for several concentrations of glycerol. Slope for each concentration determines the fluid bulk viscosity.

5 Results and Discussion

Electrophoresis of the 20nm particles was measured with two techniques in a concentration series of glycerol and a concentration series of polyacrylamide. The goal of the experiments is to probe effects of fluid viscosity and electric field strength on the particle mobility in non-Newtonian fluids compared to Newtonian.

5.1 Capillary electrophoresis in glycerol solutions

To consider the impact of rheology on the mobility of particles in polymer solutions, the mobilities are compared to those in glycerol solutions spanning a similar range of bulk viscosities. Both electroosmosis and electrophoresis experiments were conducted in the glycerol solutions using both PALS and CE techniques. As in the glycerol solutions, mobility measurements in polyacrylamide solutions were conducted using both light scattering and capillary electrophoresis.

5.1.1 Electroosmosis of glycerol solutions in silica columns

When measuring the electrophoresis of particles, particularly through a column or channel, one must account for electroosmosis due to charges at the surface of the column or channel. Electroosmosis experiments in the glycerol solutions were done separately from electrophoresis experiments, using just benzyl alcohol as a neutral marker. Concentrations of 0%, 10% and 20% utilized the standard 1-plug method (the marker is injected and a field is applied without any pressure driven flow). Concentrations of 30% and above utilized a 3-plug method, due to the increased viscosity (reduced mobility).

The electroosmotic mobility in several glycerol solutions through silica columns is com-

pared to the mobility of 100nm silica particles. The electrophoretic mobilities of silica particles were measured in the Malvern Zetasizer Nano, using PALS and compared to the EOF mobilities in Figure 5.1.1. In general, the mobility of the silica particles was greater than the EOF through the silica capillary.



Figure 5.1.1: A comparison of electrophoretic mobility of 100nm silica particles in glycerol solutions and electroosmotic mobility of glycerol solutions in 75μ m silica capillaries.

In Figure 5.1.2, the results from Figure 5.1.1 are replotted in with the mobility normalized by the mobility in solution with no glycerol. Rather than plotting against concentration of glycerol, the mobility is plotted against the ratio of solution permittivity and fluid viscosity as given in Table 5.1.1, normalized by the viscosity and permittivity of 0% glycerol. The viscosity used is from the stress versus shear-rate curves in Figure 4.4.3 and the permittivities for glycerol come from literature [67]. The line represents $\frac{\mu}{\mu_w} = \frac{\varepsilon_r \eta_w}{\varepsilon_w \eta_0}$ and is the mobility

C $(\%v/v)$	$\varepsilon_r \ (cP)$	$\eta_0~({ m cP})$
70	55.6	19.4 ± 0.2
60	60.0	10.9 ± 0.2
50	64.0	8.57 ± 0.5
30	70.0	2.44 ± 0.3
20	72.9	1.66 ± 0.3
10	75.7	1.32 ± 0.3
0	78.5	0.88 ± 0.02

predicted by Helmholtz-Smoluchowski, assuming the surface has a constant zeta potential.

Table 5.1.1: Viscosity and permittivity of glycerol solutions. The dielectric constant, ε_r , comes from literature [67], η_0 is determined from the slope of shear-stress versus shear-rate in Couette cell rheometry

The line in the figure indicates the expected mobility for a given viscosity and permittivity based on the Smoluchowski relationship. The assumption in the predicted line is that zeta potential of the surface remains the same as in the 0% case and independent of the presence of organic solvent. As this figure shows, Smoluchowski slightly overpredicts the mobility in the glycerol solutions. This could be explained by a reduction in zeta potential due to the presence of the organic solvent. Also, with the exception of the 20% glycerol solution, the particle mobility is closer to the predicted line than the EOF mobility, which suggests that the nature of the fluid has slightly more influence on the zeta potential of the silica capillary than the silica particles. Schwer and Kenndler observed a decrease in electro-osmotic velocity at 20 kV (208.3 V/cm) with increasing concentration of several protic solvents (methanol, ethanol, 2-propanol) [80] at basic pH in aqueous solutions. Silica acquires a charge through association and dissociation of hydrogen. The addition of organic solvents supposedly disrupts this process, thereby altering the zeta potential. The decrease in mobility (U/E) is steeper at lower concentrations than at higher concentrations of solvent [80]. Glycerol, another polar protic solvent, may have the same effect on the zeta potential of silica. Kosmulski measured the surface charge of silica particles in aqueous solutions of organic solvents by pontiometric



Figure 5.1.2: A comparison of electrophoretic mobility of 100nm silica particles in glycerol solutions and electroosmotic mobility of glycerol solutions in 75μ m silica capillaries. The mobility is scaled with the mobility of each measured in 0% glycerol and plotted against the ratio of the permittivity of the solution [67] and the fluid viscosity (as measured in Couette cell rheometer).

titration[81]. The charge is less negative with increasing concentration of organic solvent in mono alcohols such as those studied by Schwer and Kenndler. However, they suggest that polyalcohols (such as glycerol) are an exception [82], since titrations of silica in glycerol-water mixtures determined the surface charge to be independent of solvent composition, up to 20%.

These two studies and the data presented in Figure 5.1.2 suggest that for glycerol in silica columns, if there is a reduction in zeta potential due to the presence of the organic solvent, it is minimal. Additionally, the Smoluchowski equation will overpredict the mobility of silica in the glycerol solutions, and moreso for the microchannel than the particles.

5.1.2 Electrophoresis of polystyrene latex particles in glycerol

After considering EOF in Newtonian fluids, focus is shifted to electrophoresis in the fluids. Particle electrophoresis of 20nm sulfonated polystyrene latex was measured in several concentrations of glycerol using PALS at 150V. In Figure 5.3.2, the electrophoretic mobility, scaled by the mobility of particles in 10mM KCl, is plotted against the ratio of viscosity and permittivity, as was done with the electroosmosis experiments. The mobilities fall on the predicted line for Helmholtz-Smoluchowski, within error of each point and the prediction line. The agreement with Smoluchowski is significantly improved for the polystyrene latex compared to silica. This suggests that unlike in silica, the presence of glycerol does not significantly affect the zeta potential of the polystyrene particles.

Although the PALS measurements agree with Smoluchowski, they only sample one field strength. Capillary electrophoresis is used to measure the mobility of the particles at several different applied voltages. Since the mobility is anticipated to be independent of field in these Newtonian fluids, one representative concentration, the 50%v solution, is studied. This concentration in particular is used because its viscosity is similar to that of a 0.4 g/dL solution of polyacrylamide. The method used was a three-plug method, with particles injected first, a BA slug injected second, a voltage applied for some time, t_v , and finally a third BA slug injected. All three slugs are pushed through the column at a pressure of 2 psi. Figure 5.1.4 is a sample electropherogram for 50 percent glycerol with the three-plug method. Two different runs, one with no voltage applied overlaid with another with 5kV applied for 3min. The first, broad peak is the particles, while the second and third peaks are the neutral benzyl alcohol marker.

The viscosity of the 50% solution was measured with a Cannon-Ubbeholde viscometer



Figure 5.1.3: Normalied electrophoretic mobility of 20nm FPSS in glycerol and PAAm solutions as measured by PALS versus the normalized zero-shear viscosity of solution and electrical permittivity. Line is theoretical electrophoretic mobility based on the mobility in 0% PAAm and effective viscosity with Smoluchowski relation.

and verified from the CE experiment itself. In pressure-driven flow, the average velocity of a Newtonian fluid is given by the Hagen-Poiseuille equation,

$$\langle v_{m_N} \rangle = \frac{R^2 \Delta P}{8\eta_{HP} L_T}.$$
(5.1)

Equation 5.1 predicts the speed at which the fluid will move through the column at a given pressure, and therefore when peak N_3 will elute in the three-plug method. In a given experiment, an effective viscosity, η_{HP} can be calculated from the actual value of t_{N_3} . The parameters used for the calculations are shown in table 5.1.2. Both the particle and benzyl alcohol peaks



Figure 5.1.4: Electropherogram in 50 percent glycerol with 0kV and with 5kV for 3min. The first, broad peak is the particles. The second and third peaks are the neutral benzyl alcohol markers. Only the first two peaks experienced the field. All three plugs were pushed through the column at 2psi.

had a symmetric Gaussian distribution, as evidenced in Figure 5.1.4. Therefore, Taylor-Aris dispersion is used to predict the peak widths. Table 5.1.3 compares the actual and predicted average peak widths for both the benzyl alcohol ($D_{BA} = 8 \times 10^{-8} \text{ cm}^2/\text{s}$) and polystyrene particles ($D_{PS} = 13.8 \times 10^{-8} \text{ cm}^2/\text{s}$). From Taylor-Aris dispersion equations, the width of peak N_3 predicted at 2psi is 0.32min. The actual peak width is 0.32 ± 0.06 min, or 0.92 ± 0.16 cm (4.6 percent) of the column. The Hagen-Poiseuille and Taylor dispersion analyses confirm the viscosity of the solution is what is measured by the Ubbeholde viscometer.

Figure 5.1.5 shows the mobility of the particles in 50% glycerol plotted against the applied electric field strength with 95% confidence intervals on the slope shown. The slope is linear with small confidence intervals, suggesting the electrophoretic mobility is constant with field strength, as expected in a Newtonian fluid.

Parameter	Value	
η_U	6.94 ± 0.02	cР
D_{BA}	80	$\mu { m m}^2/{ m s}$
$\mathbf{D}_{PS,water}$	13.8	$\mu { m m}^2/{ m s}$
ε_r [67]	64	
σ_c	0.280 ± 0.007	$\mathrm{mS/cm}$
L_D	20.8 ± 0.2	cm
L_T	31.0 ± 0.2	cm
Т	25	$^{o}\mathrm{C}$
ΔP	$1.98 \ pm \ 0.02$	psi

Table 5.1.2: Capillary electrophoresis parameters for 50% glycerol

	Predicted	Actual	
t_{N_3}	6.82	6.95 ± 0.53	\min
w_{BA}	0.32	0.32 ± 0.06	\min
w_{PS}	2.24	2.58 ± 0.13	\min

Table 5.1.3: Predicted and actual values for elution time and peak widths at 2psi in 50% glycerol through a 50 μ m i.d. capillary with $L_D = 20$ and $L_T = 30$.



Figure 5.1.5: Electropherotic velocity versus field strength of 20nm FPSS in 50% glycerol solutions. Slope with 95% confidence intervals also shown.

Table 5.1.4 compares the mobility measured with capillary electrophoresis with that measured by the PALS and predicted by Helmholtz Smoluchowski. The three values agree within their respective 95% confidence intervals. This agreement in mobility between two measurement techniques and the value predicted from theory reiterates the validity of both PALS and CE in measuring EP mobility of particles in viscous Newtonian solutions. The expected linear relationship between U_{ep} and E is confirmed in 50% glycerol.

5.2 Phase analysis light scattering on polystyrene particles in PAAm solutions

Polystyrene particle mobility was subsequently measured in several concentrations of polyacrylamide. The polyacrylamide reacts with the coating on the electrodes in the disposable zeta cells used for PALS with the Malvern Zetasizer and only a few PALS measurements could be made before the electrodes started to corrode. Nevertheless, measurements of mobility with time using PALS were conducted by taking only three measurements at a time and rinsing the disposable zeta-cell with deionized water and methanol between each measurement. Figure 5.2.1 shows the electrophoretic mobility over time of a the 20nm polystyrene latex particles in several PAAm concentrations. The mobility reaches steady-state on the order of 3 hrs. Time zero is the time the particles and polymer solutions were mixed.

The steady-state mobility is plotted alongside the glycerol results in Figure 5.1.3, scaled by the mobility of the particles in simple electrolyte. The normalized mobility is plotted against the ratio, ε/η_0 , also scaled by the permittivity and zero-shear viscosity in simple electrolyte solution (ε_w/η_w) . The line in the figure is the prediction in mobility by Helmholtz-Smoluchowski, for the mobility of a particle with constant zeta potential. For polyacrylamide, the permittivity is assumed to be that of water and the viscosity used is the viscosity measured in the Cannon-Ubbeholde viscometer. While particle electrophoretic mobility in the Newtonian (glycerol)

μ_{pred}	0.355 ± 0.050	$\mu \mathrm{m} ext{-}\mathrm{cm}/\mathrm{V} ext{-}\mathrm{s}$
μ_{ZS}	0.342 ± 0.068	$\mu { m m-cm/V-s}$
μ_{CE}	0.375 ± 0.020	μm -cm/V-s

Table 5.1.4: Mobiliy in 50% glycerol as measured in two instruments and predicted by Helmholtz-Smoluchowski.



Figure 5.2.1: The decrease in electophoretic mobility of 20nm FPSS in three concentrations of PAAm with time as measured by PALS in the Malvern Zetasizer Nano.

solutions were generally consistent with Helmoholtz-Smoluchowski, the mobility in polymer solutions was not. Mobility greater than that predicted in the Newtonian fluids is consistent with observations by Radko [46, 47] and predictions by Hsu and Lee for particles in Carreau fluids [8, 9].

Because of limitations in measuring mobility in polyacrylamide solutions using PALS, experiments with capillary electrophoresis were performed in the same solutions, using the three plug method. Electrophoretic mobility and electroosmotic mobility were calculated simultaneously in a given run. In each run, velocities are calculated according equations 4.9 and 4.10. Several consecutive runs in the same column and fluid with varying field and t_v make up one sequence. Mobility was calculated 'locally', by dividing the velocity measured in each individual run by the applied field, and 'generally', by the slope of velocity versus field in a given sequence.

5.3 Capillary electrophoresis in PAAm solutions

5.3.1 EOF in PAAm solutions

Dependence of electroosmosis on electric field was investigated for several concentrations of polyacrylamide. Bello [11] and Olivares [12] experimentally observed higher than expected EOF in polymer solutions. Unlike in previous papers, the EOF lacked a significant relation with field strength within a given sequence of experiments. The slope of the electroosmotic velocity with electric field was used to determine the mobility for the given sequence (*i.e.* a given fluid and capillary combination). As Figure 5.3.4 shows, this slope is equal to the mobility calculated for each run, within the error of the run.

The EOF mobility is compared to the effective viscosity, η_{HP} calculated based on the elution time of the last peak in the three plug method,

$$\eta_{HP} = \frac{R^2 \Delta P}{8L_D L_T} t_{N_3}.$$
(5.2)

In a power-law fluid [83], the Hagen-Poiseuille equation is modified to account for the shearthinning behavior,

$$\langle v_{m_{PL}} \rangle = \left(\frac{(1/n) + 1}{(1/n) + 3}\right) \frac{R^2 \Delta P}{4\eta_{HP} L_T}.$$
(5.3)

In 0.8g/dL PAAm, n = 0.73 and by equation 5.3, $\langle v_{m_{PL}} \rangle = 1.08 \langle v_{m_N} \rangle$. Experimental error between runs in 0.8g/dL is ~10%, thus equation 5.2 is suitable for estimating an effective



Figure 5.3.1: Electroosmotic mobility of 20nm FPSS in several PAAm solutions versus the effective viscosity of solution determined from Hagen-Poiseuille. Line is theoretical mobility based on EOF mobility in 0% PAAm and effective viscosity with Smoluchowski relation.

viscosity in the CE experiments, even in the shear-thinning fluids.

Figure 5.3.1 plots the EOF mobility measured in the PAAm solutions against this effective viscosity. The line shown in the figure is the predicted EOF mobility based on effective viscosity and the Smoluchowski relation, assuming the zeta potential in PAAm solutions is equal to the zeta potential in solutions with no PAAm.

However, the EOF is not consistent between multiple sequences with the same fluid and the column initial conditioning procedure. In several runs, the EOF is much higher than pre-

Conc (g/dL)	$\eta_{HP} \ (cP)$	EOF (μ m-cm/V-s)	EP (μ m-cm/V-s)
0.8	38.04 ± 2.2	0.79 ± 0.16	1.49 ± 0.038
0.8	35.25 ± 0.84	0.28 ± 0.07	1.79 ± 0.048
0.6	18.20 ± 0.11	2.42 ± 0.23	1.78 ± 0.079
0.6	20.54 ± 0.16	1.59 ± 0.15	1.99 ± 0.031
0.4	8.42 ± 0.05	2.36 ± 0.46	2.32 ± 0.035
0.4	7.17 ± 0.05	3.41 ± 0.37	2.61 ± 0.042
0.2	3.79 ± 0.06	0.760 ± 0.13	2.76 ± 0.13
0.2	4.03 ± 0.09	1.11 ± 0.76	2.91 ± 0.35

Table 5.3.1: Effective viscosities and both EOF and electrophoretic mobility of PAAm solutions, a comparison of two repetitions in the same fluid.

dicted, while other runs have mobilities equal to or less than predicted by Smoluchowski. Table 5.3.1 highlights several of these inconsistencies in multiple runs of the same fluid concentration. These results suggest that the column is 'dirtied' by the presence of the polymer.

5.3.2 Electrophoresis of polystyrene particles in PAAm solutions

With the three-plug method, EOF is accounted for in each run, rendering the electrophoresis measurements independent of electroosmosis. Despite the inconsistencies in electroosmosis in the PAAm solutions, the electrophoretic mobility of the polystyrene particles are consistent within a given fluid (Table 5.3.1).

In Figure 5.3.2, the electrophoretic mobility of the 20nm particles is plotted against the effective viscosity from equation 5.2. Unlike in the electroosmosis, the experimental results for electrophores have less scatter in mobility within and between runs (Table 5.3.1). In Figure 5.3.3, the electrophoretic mobility and the effective viscosity (equation 5.2) are scaled with the respective values measured in simple electrolyte solution. The mobility generally decreases with increasing viscosity, although it is not a linear decline nor is it as steep a drop in mobility as predicted by Helmholtz-Smoluchowski. Two possible mechanisms are proposed to explain the discrepancy between mobility measured and predicted by Smoluchowski. The



Figure 5.3.2: Electrophoretic mobility measured by capillary electrophoresis of 20nm FPSS in PAAm solutions versus the effective viscosity of the solution determined from Hagen-Poiseuille. Line is theoretical electrophoretic mobility based on the mobility in 0% PAAm and effective viscosity with Smoluchowski relation.

first is that shear-thinning of the polymer solutions reduced the 'microviscosity' experienced by the particles as they eluted through the solution. The 'local' mobility, calculated for each individual experimental run is compared to the 'general' mobility, the mobility determined by the slope of the velocity versus field strength in a given sequence. The second mechanism is polymer depletion. Polymer coils are entropically repelled from the particle surface, leading to a layer of solvent around the particle, depleted of polymer and subsequently having a lower local viscosity than the in the bulk of the fluid.

As seen in Figure 5.3.4, there is no significant field strength effect on mobility in low concentrations of polymer. This is expected, since below c^* , the polymer solution is essential



Figure 5.3.3: Normalized electrophoretic mobility of 20nm FPSS in PAAm solutions versus the effective viscosity of solution determined from Hagen-Poiseuille scaled by the viscosity of 10mM KCl. Line is theoretical electrophoretic mobility based on the mobility in 0% PAAm and effective viscosity with Smoluchowski relation.

Newtonian (Figure 4.4.1). At higher concentrations, however, it was predicted, that the particle mobility would depend on field strength. This hypothesis is based on Deborah numbers calculated for 0.8g/dL, where $\tau = 0.06$ s and n = 0.73 (Table 4.4.1). For electric fields ranging from 67 V/cm (2kV) to 833 V/cm (25kV), and predicted mobility of 1.5μ mcm/V-s, De_B ranges from 300 to 3750 and De_D ranges from 2000 to 25000. Referring back to Figure 3.3.2, the diffuse layer Deborah number is at the upper end of the plot and over the entire range, $M_{1,D}/M_0$ is 0.75 to 0.8. Yet, Figure ?? shows that in it high concentrations of PAAm, both EOF and EP were constant with changing field strength, just as in lower concentrations.



Figure 5.3.4: Electrophoretic mobility of 20nm FPSS in (a) 0.1g/dL PAAm and (b) 0.6g/dL PAAm versus applied field strength. Closed circles are electro-osmotic mobility, open circles are electrophoretic mobility. Lines are the 'general' mobilities calculated from the slope of velocity with field strength.

This is demonstrated by comparing the 'local' mobilities with the 'general' mobility in each sequence. The limiting factor to observing any field effects is likely the particle size. Radko measured particle electrophoresis in buffered PAAm solutions the one-plug method and observed field dependent mobilities above but not below particles of 30nm [47]. They circumvented the long elution time issue by supressing the electroosmosis of the column physiochemically. Unfortunately, the use of the three plug method, while allowing for simultaneous measurement of electroosmosis and electrophoresis and providing a means to measure small mobilities, limited the size of particles available to use because of the parabolic flow profile in pressure-driven flow.

5.4 Microviscosity in glycerol and PAAm solutions

If shear-thinning is not responsible for higher mobility values, a second possible mechanism is the formation of a depletion layer around the particle and a 'microviscosity' near the particles less than that of the bulk fluid. If the length scale of this depletion layer is greater than that of the diffuse layer, the fluid in the diffuse layer is assumed to equal that of the solvent. This is the assumption made by Berli [22] in their analytical solution for EOF in power-law fluids. This is also observed by Olivares [12] in their EOF experiments with CMC and urea. However, when the diffuse layer is greater than the depletion layer and some polymer chains are in the diffuse layer, the viscosity is somewhere between the solvent viscosity and bulk zero-shear viscosity as observed by Olivares in CMC solutions without urea [12]. This agrees with the phenomena observed in the electrophoresis experiments described above, where the local microviscosity is

$$\eta_{micro,ep} = \frac{\varepsilon \zeta}{\mu_{ep}}.$$
(5.4)

As particles diffuse through a solution by Brownian motion, they also sample not the bulk viscosity but a local microviscosity,



$$\eta_{micro,D} = \frac{kT}{6\pi Da}.$$
(5.5)

Figure 5.4.1: Diffusion coefficient of 20nm FPSS normalized by diffusion coefficient measured in water versus the normalized zero-shear viscosity. The line is the predicted diffusion coefficient from Stokes-Einstein, equation 4.1. Filled circles: glycerol solutions, open circles: PAAm solutions.

Diffusion coefficients of the 20nm particles were measured in glycerol solutions mentioned above and in several concentrations of polyacrylamide. Figure 5.4.1 shows the diffusion coefficient scaled by the diffusion coefficient of the particles measured in 10mM KCl plotted against the ratio of solution viscosity to the viscosity of 10mM KCl. The viscosity used is the Carreau zero-shear viscosity measured by concentric cylinder. The diffusion of the particles can be predicted by Stokes-Einstein (equation 4.1) [75]. For a given particle size, a, the diffusion should decrease proportionally to viscosity, η_0 . This prediction is given as the line in Figure 5.4.1. The diffusion coefficient of the particles in glycerol solutions is consistent with predicted ratio.

The particles in polyacrylamide, on the other hand, have diffusion coefficients higher than predicted. This suggests that the particles are sampling a microviscosity greater than the bulk viscosity measured by rheology. However, the particles are also not sampling purely solvent, since D is lower than D_w and decreases with increasing concentration.



Figure 5.4.2: Diffusion of 20nm FPSS in PAAm solutions over time. Filled circles: 0.1g/dL PAAm, open circles: 0.2g/dL PAAm, filled triangles: 0.4g/dL PAAm, open triangles: 0.5g/dL PAAm, filled squares: 0.6g/dL PAAm.

Polymer-particle systems typically exhibit either adsorption of polymer onto the particle surface or depletion of polymer chains from the fluid surrounding the particle [84]. Polymers have a high affinity to adsorb to surfaces, which will affect the particle size and shape as well at its zeta potential [85]. The surfaces are charged but the microstructure is nonionic, thus electrostatic repulsion is not an option to reduce adsorption.



Figure 5.4.3: Electrophoretic mobility as measured by PALS of 20nm FPSS versus the diffusion coefficient in PAAm and glycerol. Filled circles: glycerol solutions, open circles: PAAm solutions. The line is the prediction $\eta_{micro,D} = \eta_{micro,ep}$.

Nonetheless, diffusion coefficients higher than predicted by Stokes-Einstein suggest that there is no adsorption, since polymer adsorption would increase the particle size, thus decreasing the diffusion coefficient. Polymer adsorption is also a time-dependent process. As Figure 5.4.2 shows, there is a lack of significant change in D with time, even after several days of measurements. This also suggests that adsorption of PAAm onto the particles is not a primary concern in the system studied. The exception is the 0.6g/dL solution, where the diffusion coefficient drops by 50% in the first couple hours. The final (lower) value of D was taken as the final diffusion coefficient for 0.6g/dl PAAm.

A means to compare the two calculations of η_{micro} is to plot the mobility ratio, μ_{ep}/μ_w against the diffusion coefficient ratio, D/D_w . Figure 5.4.3 shows that both the polyacrylamide solutions and glycerol solutions collapse onto the predicted line when the normalized mobility of 20nm FPSS is plotted against the normalized diffusion coefficient. This line predicts when $\mu_{ep}/\mu_w = D/D_w$, which is equivalent to $\eta_{micro,ep} = \eta_{micro,D}$. Since the data for both glycerol and PAAm solutions generally fall on this line, the local 'micro' viscosity of the solution around the particles can be measured by DLS and is the fluid viscosity actually sampled by the particles as they migrate by electrophoresis in polyacrylamide solutions.

5.5 Conclusions

Using capillary electrophoresis, the particle mobility is found to be independent of electric field in both viscous Newtonian and non-Newtonian fluids. This is as expected for Newtonian glycerol and low concentration polyacrylamide solutions, but contrary to predictions in higher concentration polyacrylamide, where shear-thinning is apparant. Although the glycerol solutions agreed with predictions for mobility according to Smoluchowski relationship, the mobility of the 20nm particles was greater than expected based on zero-shear bulk viscosities. This result is attributed to depletion layer of fluid around the particles as supported by diffusion measurements by DLS.

6 Summary and Conclusions

First, a model was developed that predicted novel size and field dependent electrophoretic mobility in shear-thinning Carreau fluids in the limit $\kappa a \gg 1$. In this model, the mobility of the particles is increased due to shear-thinning nature of the fluid. Unlike in a Newtonian fluid, the model for mobility in a shear-thinning fluid reveals that electrophoretic particle motion is a function of electric field strength and particle size.

The predicted field dependence was experimentally investigated using capillary electrophoresis (CE) and phase analysis light scattering (PALS) for 20nm polystyrene latex particles in polyacrylamide solutions. Electroosmosis was simultanously measured in the solutions using a three-plug method with capillary electrophoresis. The particle mobilities in several solutions of polyacrylamide were compared to those in glycerol solutions with similar bulk viscosities. The Newtonian glycerol solutions followed the Smoluchowski relationship for mobility, as expected. In the polymer solutions, particle mobility was consistently larger than predicted by Smoluchowski. Shear-thinning was hypothesized to be the cause of the large mobilities. As particles migrate through the polymer solution, they cause the surrounding fluid to deform, which for shear-thinning fluids means the local viscosity is reduced. Since the rate of shear is proportional to the particle velocity, it was predicted that mobility would increase with increasing applied field. However, in the particular systems studied, a field dependent mobility was not observed. The experimental limitation was particle size. Nevertheless, this is consistent with other CE studies of latex particles smaller than 30nm [55].

Despite the lack of field dependence, the electrophoretic mobility is still consistently larger than predicted by Smoluchowski, but less than the mobility in pure solvent. From this observation, it is suggested that a depletion layer is formed around the particle with a concentration of polymers much less than the bulk concentration. The viscosity in the vicinity of the particles is an effective 'microviscosity' that is less than the bulk or 'macroviscosity' of the fluid. A colloidal particle undergoing Brownian motion will also sample this 'microviscosity.' Since both electrophoretic mobility and particle diffusion are inversely proportional to viscosity, the two measurements are compared. The slope of mobility versus diffusion coefficient is approximately one, which supports the hypothesis of a depletion of polymer molecules around the particle contributing to higher than predicted mobilities.

Although the modeled shear-thinning effects were not observed in this particular particlefluid system, the influence of rheological behavior of fluids remains an important consideration in electrokinetic studies. Further investigation with larger particles may reveal shear-thinning effects, namely mobility that is a function of both field strength and particle size. For the three-plug method, the capillary radius must be reduced for the larger particles, which can be problematic in high viscosity fluids. Other aspect of non-Newtonian rheology that were not considered in this study are fluid viscoelasticity and normal stress coefficients. Another area for future work is the extension of the model to non-spherical particles and subsequent measurement of the mobility of those particles in capillary electrophoresis.

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