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Research Article

Moving Boundary Model to Estimate Diffusion Coefficient and Viscosity of Dextran Coated Magnetic Iron-Oxide Using Capillary Electrophoresis

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Abstract

Capillary electrophoresis serves as a suitable analytical method to characterize the properties of samples through the application of pressure and voltage within a capillary tube. We present a categorized interface boundary problem of liquids to estimate the diffusion coefficient (DC) and viscosity of dextran- coated magnetic iron oxide (Dextran-MIOS) confined in formic acid solution (FAS). We considered an interface, with a dimension greater than zero, between samples filled into the capillary tube followed by either FAS or water flow at constant pressure (10^4 pa). We fitted the time point corresponding to interface minimum frequency, maximum frequency, Inflection frequency, and also the apparent volume of liquid between the frequencies into viscosity and moving boundary diffusion models. We used the factorial design of experiments for the design/evaluation of sample constituents by considering the concentration of FA (C_{FA}) and volume fraction of Dextran-MIOS ($VF_{Dextran\text{-}MIOS}$) on DC and viscosity. We observed a symmetry behavior of C_{FA} and $VF_{Dextran\text{-}MIOS}$ in samples on the DC of Dextran-MIOS during FAS flow, while there is a loss in symmetry during water flow. We observed a symmetry behavior of only $VF_{Dextran\text{-}MIOS}$ in samples on the viscosity of Dextran-MIOS during FAS flow, while there is a change in symmetry during water flow.

Keywords: Dextran Coated Magnetic Iron-oxide; Diffusion Coefficient; Viscosity; Formic Acid Solution; and Fractional Factorial Design

Introduction

Applications such as the dilution process, solute transport and biological processes require the knowledge of DC, and viscosity of solute to gain insight into the sample's physical and chemical properties [1]. More also, electrostatic interactions between charged colloidal particles in solution play a pivotal role in determining phase properties of colloidal suspensions. A method shows that to estimate DC, the graph must have (a) either a maximum or else a minimum and (b) an inflection point [2]. With capillary electrophoresis (CE), the Taylor dispersion technique has been extensively used to determine the DC of solute and viscosity of samples. A recent study suggests and uses the modification of Taylor dispersion techniques for characterizing the properties of nanoparticles with CE [3]. Using the Taylor dispersion technique, they observed the collective diffusion of suspension containing positively charged iron oxide particles to depend on both particle volume fraction (VF) and electrolyte ionic strength [4]. Using analytical, numerical techniques, and within the linear response theory, methods have also determined DC Values as a function balance between particle fluxes [5-7].

The interface gradient of liquids had been used to determine the viscosity of liquids [8] and nanoscale [9] samples, The method used in the study to determine the viscosity and other studies requires a sharp interface between two fluids (Zero thickness) and involves the use of immiscible fluid. However, recent studies have considered a theoretical approach for non-zero width, such that there is partial miscibility of liquids by using a diffuse interface model [10]. Several methods have also determined the viscosity of samples with CE using the interface between liquids subjected to fluid flow by pressure without the use of an electric field. An approach to determine the viscosity of samples using CE involves filling the capillary tube with a sample and then pumping with another sample at constant pressure and temperature [11,12]. The methods use the Poiseuille equation and the migration time of the boundary between the two liquids from the injection port to the detector for calculating the viscosity of an unknown sample [11,12]. A study also noted that the migration time of the liquid interface from the inlet to the detector region is directly proportional to the dynamic viscosity of the fluid [12].

As much of the developmental time needed to investigate solute's physical and chemical properties is often spent preparing and testing formulations. Considering the multivariate variable for characterizing the properties of solute samples with CE. A quality by design approach supersedes one factor at a time experimental approach by the utilization of statistical design of experiment (DOE). In recent studies, by selecting specific parameters of an experimental procedure, the DOE shows to be efficient in the design and evaluation of the experimental process [14-16].

Here, our goal is to use CE and present a simplified method that enables the determination of DC and viscosity of dextran coated MIOS(Dextran-MIOS). The DC and viscosity of Dextran-MIOS in formic acid solution (FAS) were determined by filling the capillary with a sample and then pumping with either water or equivalent FAS in samples at constant pressure, temperature, and no applied field strength. A factorial DOE was used to design and test the DC and viscosity of Dextran-MIOS by considering $VF_{\text{Dextran-MIOS}}$ and C_{FA} in samples. A Molecular dynamics simulation was used to enhance the investigation of sample constituents by relating curves of free and potential energies to DC, and viscosity of samples.

Moving boundary model for estimating DC and viscosity

We hypothesized the measurement of the DC of two media by modifying the moving boundary diffusion equation reported by J. Crack [17] and fitting CE data into figure 1 and equation 1. We give the general equation representing the volume and DC of two media relating to an interface, Where V and D represent the volume and DC of a sample. The parameter $\sigma = k * A_L$, represents the interface boundary condition between sample filled and baseline flow.

$$V = 2\sigma(D * t/\pi)^{1/2}$$

Equation 1

$$D = \frac{\pi}{4\sigma^2} \times \frac{V^2}{t}[m^2/s]$$

Equation 2

Point ($-\infty \ldots t_{minimum}$), and Point $t_{minimum}$ represent the region of a capillary tube filled sample with constant intensity and minimum time through which the intensity starts to change.

Point ($t_{minimum} \ldots t_{maximum}$), and Point $tmaximum$ represent interface region between sample filled in capillary and maximum time point that change in intensity stops. Point ($t_{maximum} \ldots +\infty$) represent the region of solvent flow with constant intensity. At the interface region ($t_{minimum} \ldots t_{maximum}$), there exit an inflection point($t_{inflection}$).

We assume that diffusive transport is not restricted to scalar quantities, such as the concentrations, or the temperature of the liquid within the capillary tube. Vector quantities, such as the momentum density of the sample within the capillary tube, can be transported diffusively and then leading to momentum changes, and therefore to a force possibly viscous forces. This requirement is already apparent from the conservative of the momentum equation [3], we consider the momentum change as a function of capillary geometry that is attributed to the volume of liquid within the capillary tube to the detector window. By relating the lateral surface area of the cylindrical capillary tube, the volume (V) of diffusing substances for Dextran-MIOS in FAS within the minimum and inflection time point from the capillary inlet to the detector (volume flux across capillary).

$$V = \frac{V_t * t_{inflection}}{t_{minimum}} - V_t$$

Equation 3

Where $V_t = volume\ of\ cylinder$. The time duration of samples within the boundary of Dextran-MIOS in FAS is given as t (sec) which is obtained by the positive difference between point $t_{minimum}$ and $t_{inflection}$. Where k represent the momentum constant of the diffusing substance at the interphase and was obtained by calculating the integral of the curve f (t), f (t), $k = \int_{t_{minimum}}^{t_{inflection}} f(t)\,dt$.. The lateral surface area A_L for a cylinder is given by $A_L = 2 * \pi * r * l$, where r and l represent the inner radius of the capillary tube and capillary length from the inlet to the detector.

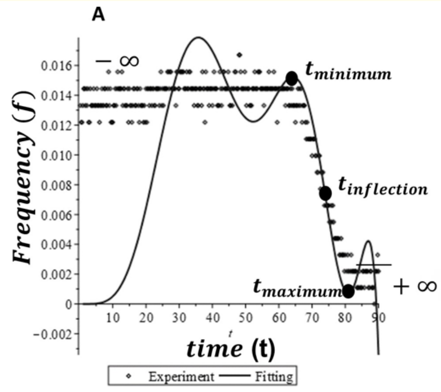

Figure 1: Interface Flow model for calculating DC and Viscosity of Dextran-MIOS in FAS samples.

Experimental Method

Sample preparation, and experimental design

A 2-factorial-3-level DOE was used to design and analyze the effect of sample constituents on DC and viscosity with STATISTICA™ Ver.12.0 software package (Stat Soft Inc., USA). Briefly, we added Dextran coated MIOS suspension to different concentrations of FAS. The entire system of each experiment contains an equivalent volume of 10 ml. To enable efficient adsorption of FA on the particle's surface. The Dextran-MIOS in FAS was then analyzed 12 hours after mixing. Table 1 represents the chosen samples' C_{FA} (0.5 mol/L, 1.0 mol/L, and 1.5 mol/L), and the $VF_{Dextran\text{-}MIOS}$ suspension (0.1, 0.2, and 0.25) in the sample.

Std. order	C_{FA} (mol/L)	$VF_{Dex\text{-}tran\text{-}MIOS}$	DC (10^{-10} m²/s)		Viscosity (10^{-4} Pa*s)	
	x	y	FAS flow	H_20 flow	FAS flow	H20 flow
1	0.5	0.1	6.388	3.140	6.701	6.176
2	0.5	0.2	4.661	2.400	6.342	6.704
3	0.5	0.25	4.081	2.630	6.583	6.704
5	1.0	0.2	4.162	0.937	6.542	6.823
6	1.0	0.25	7.756	0.458	7.032	7.200
7	1.5	0.1	4.421	0.356	7.117	6.730
8	1.5	0.2	1.802	0.302	6.686	6.401
9	1.5	0.25	3.012	0.389	7.070	7.054

Table 1: The content of FAS and Dextran-MIOS NPs, including the calculated DC viscosity of sample, temperature: 30 - 360C, pressure = 100mbar (n = 3).

Instrumental setup and determination of DC and viscosity

To estimate the DC and viscosity, UV-Visible-absorbance measurements were performed with fabricated CE systems (CE1000, Fanavaran Nano Meghyas Technologies, Tehran, Iran). A capillary tube with an internal diameter of 100 um, an external diameter of 357.5 um, and a total length of 72 cm (58 cm to the detector) was used. Samples were filtered with a PTFE filter. Successive flushes conditioned new capillaries (200 mbar, for 10 min) with 50% ethanol, 0.1 M NaOH and then with water.

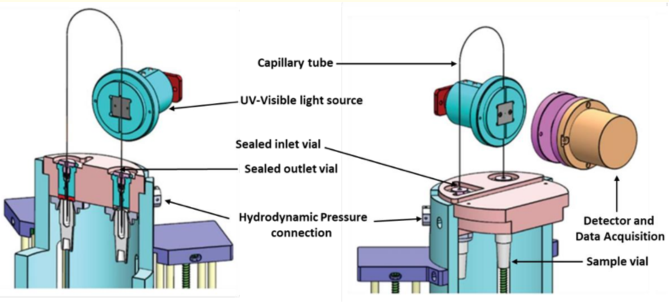

Figure 2: Instrumental Setup.

According to figure 2, we performed two experimental steps with CE to determine the DC and viscosity of each prepared sample in table 2:

- Filling the capillary tube with sample (Dextran-MIOS in FAS) followed by FAS flow at 100 mbar.
- Filling the capillary tube with sample (Dextran-MIOS in FAS) followed by water flow at 100 mbar.

We normalized the discrete data from each step $|f - \min(f)|$and then fitted it into a regression polynomial using the least square method as shown in equation 5. Where F represent the intensity of absorbance, t represents the time point of data, where $\beta_{n=0\ldots\infty}$ represents the regression coefficient of each degree of the polynomial.

$$f(t) = \sum_{n=1}^{n=\infty} \beta_n t^n$$

Equation 4

We determine the minimum and maximum time values numerically by differentiating $f(t)$ and set to zero ($f'(t) = 0$). We derived the inflection points numerically by differentiation twice and setting the value to zero $f''(t) = 0$. According to equation 5, we determine viscosity as a function of capillary length (l, to detector window), the total length L, of the capillary with an inner diameter D_i, flow pressure P and time the sample takes to flow through the capillary [12]. Where t_m represents the mean of minimum, maximum and inflection time points.

$$\eta = \frac{\Delta P * D^2}{32 * l * L} \times t_m$$

Equation 5

Results

We analyzed factorial DOE with the software package tools (STATISTICA™ Ver.12.0 (Stat Soft Inc., USA)) by choosing the C_{FA} and $VF_{Dextran\text{-}MIOS}$ in the sample as independent variables (Table 2). At a centered and scaled polynomial, table 2 shows the effect estimates and p-value of C_{FA} and Dextran coated MIOS in samples on calculated DC and viscosity. Using the software analysis tools by considering linear (x and y) and quadratic (x^2 and y^2) terms of C_{FA} and $VF_{Dextran\text{-}MIOS}$ in confined samples. When there is an increment in C_{FA} and $VF_{Dextran\text{-}MIOS}$ in the sample, the negative or positive values of effect estimate correspond to reduction or increment in DC, and viscosity, while the rank of the absolute value of the effect estimate corresponds to the order the parameter contributes to DC and viscosity. Equation 6 and the regression coefficient as shown in table 2 were used to predict and to derive a response surface plot for the values of DC, and viscosity of Dextran-MIOS in FAS.

$$z_v = \alpha_0 + \alpha_1 x + \alpha_2(x^2) + \alpha_3(y) + \alpha_4(y^2)$$

Equation 6

Procedures	Effect Estimate	p-value	Regression Coefficient	Effect Estimate	p-value	Regression Coefficient
	Sample filled-FAS Flow			**Sample filled- Water Flow**		
Diffusion Coefficient	R^2=0.8171; Adj: 0.5732. MS Residual = 1.652289			R^2=0.97313; Adj: 0.93731. MS Residual = 2.519481		
α_0	4.990	0.002	9.766	1.311	0.001	6.855
α_1	-1.965	0.141	18.598	-2.374	0.00	-8.236
α_2	2.570	0.091	-10.281	-0.733	0.066	2.931
α_3	-1.312	0.340	-137.984	-0.345	0.314	-6.563
α_4	-1.845	0.131	369.228	-0.061	0.800	12.183
Viscosity	R^2=0.97212; Adj: 0.93458. MS Residua l= 0.0052381			R^2=0.73192; Adj: 0.37447. MS Residual = 0.67087		
α_0	6.792	0.000	8.125	6.703	0.000	6.069
α_1	0.416	0.006	1.350	0.200	0.413	2.566
α_2	0.117	0.158	-0.467	0.296	0.279	-1.183
α_3	-0.053	0.500	-27.604	0.434	0.178	-11.001
α_4	-0.389	0.005	77.861	-0.199	0.376	39.704

Table 2: Effect estimate, p-Value of effects, and regression coefficient of C_{FA} and $VF_{Dextran\text{-}MIOS}$ on the DC, and viscosity.

Temperature: 30-360C, Pressure=100mbar (n = 3).

a) MS Residual: Mean Square, Reg Coeff: Regression Coefficients.

Discussions

As a function of increasing C_{FA} or $VF_{Dextran\text{-}MIOS}$ in the samples, the DC of samples during FAS flow either decreases up to a minimum and then increases or increases up to a maximum and then decreases (Figure 3a and effect estimate from table 2). As a function of increasing C_{FA} and $VF_{Dextran\text{-}MIOS}$ in samples, the DC of samples during water flow reduces (See figure 3B and effect estimate from table 2).

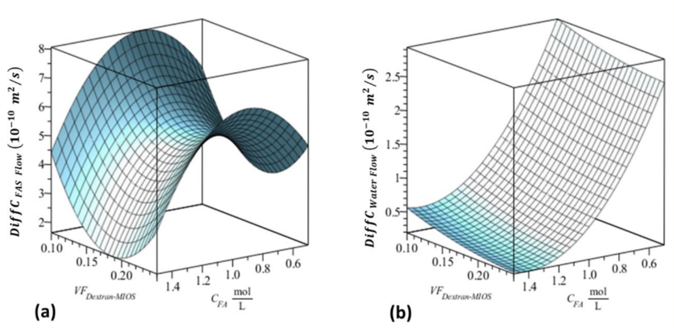

Figure 3: Response surface plot showing the effect of $VF_{Dextran-MIOS}$ and C_{FA} on (a). DC–the capillary tube filled with a sample followed by FAS flow (b) DC–the capillary tube filled with a sample followed by Water flow.

As a function of increasing C_{FA} in samples, the viscosity of samples during FAS flow reduces and then increases when increasing the $VF_{Dextran-MIOS}$ in samples. We obtained maximum viscosity values at a high C_{FA} (See figure 4a and effect estimate from table 2). As a function of increasing $VF_{Dextran-MIOS}$ in samples, the viscosity of samples during water flow increase and then reduce at increasing C_{FA}. At low $VF_{Dextran-MIOS}$ in samples, we observed minimum viscosity value (See figure 4b and effect estimate from table 2).

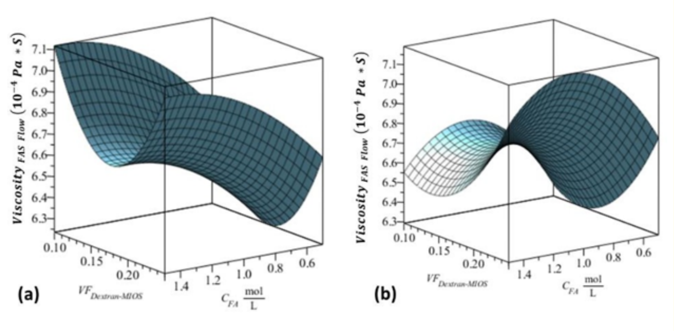

Figure 4: Response surface plot showing the effect of $VF_{Dextran-MIOS}$ and C_{FA} on (a). Viscosity–the capillary tube filled with a sample followed by FAS flow. (b) Viscosity–the capillary tube filled with a sample followed by water flow.

Reviewing the literatures, the DC for systems (such as in suspension and polymer solution) as a function of increasing concentration either increases up to a maximum point and then decreases or decreases up to a minimum and then increases [18-21]. As a result, they have attributed those effects to the mole fraction of the component in the sample. More also, the tracer DC of Fe in magnetite as a function of oxygen partial pressure at constant temperature decreases up to a minimum and then increases [22]. There are few and contradicting investigations on the viscosity of nanostructures. We might attribute this to the common observation that the addition of macroscale substances in systems directly leads to increased viscosity. A recent study also noted that the experimental coefficient of viscosity sensitivity at low-temperature increases and subsequently decreases, and also directly proportional to the potential energy curve for helium dimer [23]. Near the maximum solid concentration of a solid solute as a function of VF, a study noted that the viscosity of particle suspension increases exponentially with increasing concentration [24].

In estimating the properties of nanostructured materials, Van Der Waals and electrostatic interactions play a pivotal role in the diffusion process [25]. Diffusion processes occur in a fluid whenever they are transported in a manner resembling a random walk. As a result, particles will diffuse in momentum in the sense that a group of identical particles, all starting with the same initial momentum, will gain a spread in momentum values after some time. Considering the spreading of a sample within the capillary tube when subjected to constant flow pressure, we expect the random kick of MIOS in FAS during FAS flow to differ from that of water flow.

Conclusion

When pressure applies to a solute sample within a capillary tube of a CE device, several parameters such as temperature, pressure rate, solute density and sample constituents influence the DC and viscosity of solute samples. We have hypothesized a method to calculate the DC and viscosity of samples as a function of sample constituents through the computation of the time dependent bending within a capillary tube. Trends observed in our results show that the DC and viscosity estimation depends on samples' local environment during the application of pressure.

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Conflict of Interest

The authors have declared no conflict of interest.

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