



Determination of nanoparticle diffusion coefficients by Taylor dispersion analysis using a capillary electrophoresis instrument

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ABSTRACT

The collective diffusion coefficient D_C of diluted suspensions of positively charged iron oxide maghemite particles was experimentally investigated using a capillary electrophoresis instrument on the grounds of Taylor dispersion theory. Conditions for this approach to be applicable to nanoparticles of mean solid diameter below 10 nm were set in this work, enabling precisions on D_C determination of less than 2% relative standard deviation (RSD). Significantly different D_C values were thus measured for particle populations differing in solid number mean diameter by only 2 nm. The obtained values were compared to the z-average diffusion coefficient derived from dynamic light scattering (DLS) experiments and used for the calculation of the Stokes radius. The measured diffusion coefficients appeared to be dependent on particle volume fraction and electrolyte ionic strength. These observations were eventually discussed in terms of particle interactions.

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1. Introduction

The knowledge of diffusion coefficients is of great practical relevance because it is a key parameter in a large number of processes involving colloids, such as sedimentation, membrane filtration and a number of biochemical applications [1,2]. When considering a population of monodisperse particles, the diffusive motion of one particle is influenced by the presence of its neighbors. Indeed, one should distinguish between the self-diffusion coefficient D_S on the one hand, which describes the fluctuating trajectory of a tracer particle among others and is obtained by a time average of the position correlation function, and the collective diffusion coefficient D_C , also termed gradient or mutual diffusion coefficient, on the other hand, which describes the relaxation of a concentration gradient, and appears in Fick's law of diffusion. D_S and D_C coincide at infinite dilution (D_0) but differ for more concentrated suspensions where they both depend on interparticle interactions: hydrodynamic interactions mediated by the solvent and direct colloidal interactions [3,4].

From an experimental point of view, dynamic light scattering (DLS) has become the most popular technique to determine D_C values. The idea of using the dispersion of a solute plug in a laminar Poiseuille flow as an alternative technique to determine diffusion coefficients of solute molecules was presented long time ago in Taylor's classic paper [5]. This method is attractive as it offers a

possibility for a fast evaluation of diffusion coefficients and thus estimation of the effective dimensions of the particles in a given solution (the Stokes radius). This method was used to determine diffusion coefficients of analytes in gaseous [6] or liquid phase [7–9], either pure [7,8] or in binary mixtures [6,9]. Taylor dispersion analysis (TDA) was also applied for the size characterization of nanoparticles such as surfactant-protected platinum clusters [10] or thiolate-protected gold clusters [11]. More recently, capillary electrophoresis (CE) instrument was shown to be particularly well suited for performing TDA as it offers all the functions of injection, detection and data acquisition in a single automated apparatus [12–17]. Bello et al. [12] first demonstrated the very high reproducibility of the technique and reported relative differences between experimental and tabulated diffusion coefficient values of less than 2% for both small ions and proteins, in the absence of solute–wall interaction. For the case of polydisperse polymers, Cottet et al. [16] emphasized the influence of the detection mode (molar concentration vs. mass concentration-sensitive) on averaging diffusion coefficients and particle sizes. Moreover a separation step can be considered prior to TDA, allowing size characterization of the different compounds constituting a mixture [17]. Besides classical corrections for the width of the injection sample zone and the detector aperture [18], Sharma et al. [14] introduced the need to account for unsteady-state flow that occurs during injection and pumping of solute pulses or fronts through the capillary when using a CE instrument. Eventually, Belongia and Baygents [13] extended the technique to the measurement of diffusion coefficients of colloidal particles ranging in size from 0.19 to 0.83 μm (hydrophilic

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and hydrophobic polystyrene latex particles and hydrophobic poly-methyl methacrylate particles, as well as Tobacco mosaic virus). Diffusion coefficients obtained using the CE instrumentation were compared to those determined by DLS. Good agreement was found with relative deviations of less than 5% in the absence of capillary wall interaction or size effect motions. Moreover, guidelines on data reliability were established, indicating situations for which abovementioned error factors could be neglected.

In this context, this work aimed to assess the TDA method to determine the mean collective diffusion coefficients (and mean hydrodynamic radii) of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticle populations having a mean solid diameter much smaller than those previously studied, i.e. in the range of 6–10 nm. Methodological choices and corrections for experimental departures from ideality were discussed and obtained results were compared to those derived from DLS measurements. The influence on measured collective diffusion coefficients of particle volume fraction and of ionic strength of the medium suspension was highlighted and the results were discussed in terms of interactions between particles.

2. Theoretical background

It is well known that the velocity of a fluid flowing through a cylindrical tube under a steady-state laminar flow varies over the tube cross-section according to a parabolic function of the radius, reaching its maximum at the tube axis and approaching zero at the tube wall. Solute particles introduced into the flow move with the fluid along the tube axis with different velocities corresponding to their positions in the tube cross-section, but molecular diffusion redistributes them over both the cross-section and the tube axis. The coupling of the non-uniformity of the fluid velocity to molecular diffusion leads to a specific mechanism of dispersion called “Taylor dispersion” [12], resulting in the local concentration C of a solute being a function of axial position x , radial position r and time t , according to

$$\frac{\partial C}{\partial t} + 2u \left(1 - \frac{r^2}{R_C^2}\right) \frac{\partial C}{\partial x} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial C}{\partial r}\right) \quad (1)$$

where u is the mean fluid velocity (measured as the length of the capillary from inlet to detector L_D divided by the time required to reach the detector, t_R), R_C is the tube radius and D is the diffusion coefficient.

Assuming diffusion along the axis of the tube to be negligible, analytical solutions of Eq. (1) for front and pulse concentration profiles are given by Eqs. (2) and (3), respectively [14]:

$$\frac{\bar{C}}{\bar{C}_0} = \frac{1}{2} \pm \frac{1}{2} \operatorname{erf} \left[\frac{(t - t_R)}{\sigma \sqrt{2}} \right] \quad (2)$$

$$\bar{C} = \frac{M}{2\pi^{3/2} R_C^2 \sqrt{kt}} \exp \left[-\frac{(t - t_R)^2}{2\sigma^2} \right] \quad (3)$$

where \bar{C} is the mean solute concentration across the cross-section of the tube monitored as a function of time at a fixed position along the tube axis, k is the dispersion coefficient, M is the mass of solute particles in the pulse, \bar{C}_0 is the concentration of the front, t_R is the mean residence time (the time it takes to the solute moving with the mean velocity of the fluid u to reach the detector located at a distance L_D from the inlet of the tube), and σ^2 is the temporal variance of the elution profile related to the dispersion coefficient by [14].

$$\sigma^2 = 2 \frac{kt_R}{u^2} \quad (4)$$

Extending Taylor's theory, Aris [19] gave the following analytical expression for the dispersion coefficient:

$$k = D + \frac{R_C^2 u^2}{48D} \quad (5)$$

Thus the diffusion coefficient can be directly determined from t_R and σ^2 by solving Eq. (5) for D , t_R and σ^2 being obtained either by fitting experimental profiles [13,14] to Eqs. (2) and (3) or, in the case of a solute pulse, by calculating the first and second moments of the elution peak [12,15], respectively.

Conditions for Eq. (5) to be valid can be expressed in terms of two dimensionless parameters [14]: (i) the dimensionless residence time, $\tau = Dt_R/R_C^2$, which is the ratio of the mean solute residence time to the time required for a solute to diffuse a distance equal to the radius of the capillary; and (ii) Peclet number, $Pe = uR_C/D$, which describes the relative rates of mass transfer along the axis of the capillary due to convection and diffusion.

Thus Eq. (5) is valid when [20] (i) τ is greater than the time necessary for a radial concentration non-uniformity to reduce its amplitude by a factor of e ($L_D/U \gg 2R_C^2/3.8^2D$, i.e. $\tau \gg 0.14$) and could be reduced to its second term when (ii) axial diffusion is negligible compared to convection ($R_C^2 u^2/48D \gg D$, i.e. $Pe \gg \sqrt{48} \sim 6.9$). When these so called Taylor's conditions are satisfied, then the diffusion coefficient of the solute can be determined using Eq. (6):

$$D = \frac{R_C^2}{24\sigma^2} t_R \quad (6)$$

In this work, a 10:1 ratio was considered for Taylor's conditions to be fully satisfied, i.e. $\tau > 1.4$ and $Pe > 69$.

3. Materials and methods

3.1. Chemicals and reagents

Iron (II) chloride tetrahydrate, iron (III) chloride solution (27% (w/w) in aqueous solution), iron (III) nitrate, hydrochloric acid, ammonia, nitric acid, sodium chloride, acetone, diethyl ether and standard 1M and 0.1M HCl solution Normadose were purchased from VWR (Strasbourg, France). Didodecyltrimethylammonium bromide (DDAB) and ethylene glycol were provided by Aldrich (Saint-Quentin Fallavier, France). *N,N*-dimethylformamide was from Fluka (Saint-Quentin Fallavier, France). Water used throughout was produced by a Direct-Q 3 system (Millipore, Molsheim, France).

3.2. Ferrofluid synthesis

A cationic ferrofluid consisting of maghemite particles ($\gamma\text{-Fe}_2\text{O}_3$) dispersed in an aqueous solution of nitric acid ($\text{pH} \leq 2$) was first synthesized according to the procedure described by Massart [21]. The resulting suspension is polydisperse and size distribution ($P(D)$, D being the particle solid diameter) is usually assumed to be well described by a log-normal law [22].

$$P(D) = \frac{1}{\sqrt{2\pi}\sigma_0 D} \exp \left[-\frac{1}{2\sigma_0^2} \left(\ln \frac{D}{D_0} \right)^2 \right] \quad (7)$$

$\ln D_0$ being the mean value of $\ln D$ and σ_0 the standard deviation. A size sorting procedure [22] allowed isolation of three particle sub-populations with different size characteristics and reduced polydispersity (Table 1). After magnetic settling, particles were successively washed under stirring with deionized water, acetone and diethyl ether and then resuspended in HNO_3 . Magnetic measurements were performed using a home-made vibrating

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