

Investigation and Monitoring of Rheological Behavior of Mg(OH)₂ Nanoparticles at the Water / Oil Interface

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Abstract

Objectives of this study focused is understanding the mechanisms involved in the stabilization of water / oil interfaces by solid nanoparticles (NPs). Magnesium hydroxide of different sizes and in different electrolyte concentrations were studied and compared, at a model water / cyclohexane interface, in a drop tensiometer. Gradual interfacial adsorption of NPs, initially dispersed in water, were followed by tensiometry and the interfacial behavior of NPs layers were characterized by two-dimensional rheology. Owing to the direct relationship between emulsion stability and the interfacial properties of these layers, different nanoparticulate systems were compared, magnesium hydroxide (Mg(OH)₂) NPs, with different size. In addition, the concentration of electrolytes (NaCl) in the bulk phase was shown to induce a partial NPs aggregation (so-called NPs flocs), with an important incidence on the interfacial layer stability. Theoretical phase shift was calculated from Winter and Chambon models corresponding to a two-dimensional gel behavior at the gel-point. This interfacial gelation results in strengthening the interfacial layer, and is actually a considerable advantage in the stabilization of Pickering emulsions.

Keywords: Nanoparticle, adsorption, emulsion, Pickering, surface tension, interfacial rheology

1. Introduction

Understanding the dynamic behavior of nanoparticles at interfaces has become important in recent years due to their important applications in many fields, including industrial and biomedical. The hydrophilic-lipophilic balance of colloidal nanoparticles plays a key role in their affinity for fluid interfaces (Dickson et al., 2006; Guzmán et al., 2012; Maestro et al., 2011; Sy et al., 2024b, 2018a; Tong et al., 2014; Wang et al., 2025). This property is very important in understanding the mechanisms of nanoparticle stabilization of nanoemulsions and emulsions. This stabilization phenomenon is known as the Pickering effect (Sy et al., 2018a; Wang et al., 2024; Yang et al., 2025). Indeed, Pickering and Ramsden demonstrated at the beginning of the last century the feasibility of surfactant-free emulsions stabilized lonely by solid particles. The originality of Pickering emulsions and nanoemulsions is their high stability, which makes them thermodynamically and kinetically stable. Indeed, the adsorption of solid particles at the oil-water interface is strong and almost irreversible, giving rise to the formation of a dense, barrier-like film around the droplets, and thus making them highly resistant to coalescence (Aveyard et al., 2003; Binks and Whitby, 2005; Bizmark et al., 2014a). This is actually due to the fact that the interfacial adsorption of particles, or nanoparticles (NPs) at the interface is irreversible, due to the fact that, unlike surfactants, the adsorption energy of the particles can exceed the average energy of thermal fluctuations by several orders of magnitude $|\Delta\mathcal{E}| \gg k_B T$ (Binks, 2002; Binks and Murakami, 2006; Garbin et al., 2012).

Thus, depending on the nanoparticles used, different mechanisms for stabilizing interfaces have been developed.

In some cases, the presence of nanoparticles at the interface has no effect on the stabilization of the interface, as reported (Ravera et al., 2006) using carbon particles at the water/hexane interface and showed that the effect of the particles on interfacial tension was negligible and that rheological measurements provided a viscoelasticity modulus (E) close to 0 in a frequency range of 0.005 to 0.2 Hz. These results have been confirmed (Vatanparast et al., 2017) with silica nanoparticles, always at the water/hexane interface. On the other hand, other authors have shown that the stabilization of the Pickering emulsion is significantly increased when a reduction in interfacial tension and an increase in interfacial elasticity are observed (Río and Neumann, 1997; Schick and Hubbard, 2006).

Based on these considerations, the present study focuses on understanding the interfacial behavior of nanoparticles and their relationship with emulsion stability. The system studied here is a water/cyclohexane model coated with $Mg(OH)_2$ nanoparticles. In this study, the interface of the model was maintained and observed in a drop tensiometer, analyzed by axisymmetric teardrop shape analysis (ADSA), in order to determine the interfacial and rheological properties, to determine the parameters controlling the self-assembly of nanoparticles at the interface, the structure of the nanoparticle layer and the viscoelastic properties.

2. Materials and Methods

2.1 Materials

HPLC-grade cyclohexane, polyethylene glycol 6000, potassium chloride, sodium hydroxide were purchased from Sigma-Aldrich (Saint Louis, USA). Magnesium nitrate hexahydrate $Mg(NO_3)_2 \cdot 6H_2O$ was purchased from MERCK (Darmstadt, Germany). Ultrapure water was obtained using the Milli-Q filtration system (Millipore, Saint-Quentin-en Yvelines, France).

2.2 Methods

2.2.1 Synthesis of Magnesium Hydroxide Nanoparticles

The synthesis of magnesium hydroxide nanoparticles was carried out by a precipitation reaction developed in our previous work (Sy et al., 2018b). Two samples of powder were retained: one dispersed directly in an ultrasonic bath alternating with a vortex for 10–15 min and another which had undergone an ultra-Turrax (IKA® T25 digital Ultra-Turrax) and sonicator (Sonic Materials vibra-cell 75043) treatment for 2 min of Ultra-Turrax at 24,000 rpm and 5 min of ultrasonication. $Mg(OH)_2$ nanoparticles with two different diameter (21 nm and 45 nm) were obtained.

2.2.2 Nanoparticles Characterization

Size distributions and polydispersity index (PDI) were measured by dynamic light scattering (DLS), along with ζ potentials, with a NanoZS® Malvern apparatus (Malvern, Orsay, France). The helium/neon laser, 4 mW, operated at 633 nm, with the scatter angle fixed at 173° and the temperature maintained at $25^\circ C$. DLS data were analyzed using a cumulant-based method. ζ potentials measurements were performed right after formulation, determining the electrophoretic mobility of the particles, according to the Henry's equation under the Smoluchowski approximation. All experiments were performed in triplicate.

2.2.3 Dynamic Interfacial Tension Measurements and Dilatational Rheology

The dynamic interfacial tension γ was measured with a drop tracker tensiometer (Teclis, Longessaigne, France), according to the ADSA method. A rising drop of cyclohexane is formed and maintained in a thermostatically controlled cell filled with an aqueous phase containing the solid nanoparticles at a concentration of 0.08 wt.%. The shape of the drop was recorded in real time with a video camera. Thus, its Laplacian form gave the values of the interfacial area and the surface tension. All experiments were carried out at $25^\circ C$ in triplicate. Dynamic interfacial tension data will be analyzed using the classical Ward and Tordai model (Ward and Tordai, 1946). Accordingly, Eq. (S1) and (S2) will be used to interpret the early and late stage of the nanoparticles interfacial adsorption, corresponding to $(t \rightarrow 0)$ and $(t \rightarrow \infty)$, respectively (Bizmark et al., 2014b; Eastoe and Dalton, 2000; Kutuzov et al., 2007a; Liggieri et al., 1996; Ward and Tordai, 1946).

The two-dimensional complex modulus E of the adsorption layers was obtained from the measurement of interfacial tension variations in response to a sinusoidal variation of the surface (Saulnier et al., 2001; Wüstneck et al., 1997). The amplitude chosen, and the frequency of the sinusoidal variations are applied to the piston of the syringe by computer-controlled servomotors. When the selected temperature is stabilized in the container, the drop is formed. The nanoparticles present in the aqueous phase gradually adsorb at the interface, making decrease the surface tension γ . Once equilibrium is reached, the rheology experiments are performed for different frequencies (0.0033 Hz, 0.005 Hz, 0.0066 Hz, 0.01 Hz, 0.016 Hz, 0.022 Hz, 0.033 Hz, 0.066 Hz, 0.1 Hz,

0125 Hz and 0166 Hz). The final dataset gives the viscoelastic module E and the loss angle ϕ . The behavior disclosed were found similar to those of macromolecules at interface, gathering a specific behavior of a gel-like structure at gel-point (Bouriat et al., 2004). The surface area was around 17.5 mm² and the amplitude of the deformation values did not exceed 10 % of the drop volume (Anton et al., 2012; Arla et al., 2011; Dicharry et al., 2006; Velázquez et al., 2017).

3. Results and Discussion

3.1 Solid Nanoparticles Characterization

The concentration of NaCl, that impacts on the nano-emulsion stability and properties, was set at 2 mM as an optimized value obtained from a previous report (Sy et al., 2018b). Addition of electrolyte in solution impacts on the NPs surface charge and gradually induces its screening. As a result, attractive component of the inter-nanoparticle interactions will increase inducing the slight flocculation of the Mg(OH)₂ nanoparticles. This is reported in Table 1, where sizes and ζ potentials were gradually compared from the NPs suspension with and without increase of NaCl concentration, for two different formulations (21 and 45 nm).

Table 1. Z-average, PDI and ζ potential of different solid nanoparticles used in the study.

	Z-average (nm)	PDI	ζ
Mg(OH) ₂ NPs	21 ± 5	0.15 ± 0.02	-10 ± 1
Mg(OH) ₂ NPs	50 ± 10	0.20 ± 0.01	-6 ± 1
45 nm Mg(OH) ₂ NPs (2 mM NaCl)	111 ± 8	0.39 ± 0.04	-4 ± 1
21 nm Mg(OH) ₂ NPs (2 mM NaCl)	170 ± 10	0.36 ± 0.04	-1.0 ± 0.6

These results shows an impressive increase of the size, about 150 nm and 65 nm, as well as a drop in absolute potentials, about 9 and 3 mV, for the 21 nm and 45 nm Mg(OH)₂ NPs, respectively. Such a behavior has been shown, in previous reports (Binks and Lumsdon, 1999; Briggs, 1921; Sy et al., 2018a), beneficial for the stability of Pickering emulsions, justifying our choice in the present study.

3.2 Analysis of Dynamic Surface Tension Curves

The surface tension response for the nanoparticle-free bare interface was first measured for impurities and the resulting voltage values ranged from 48 to 50 mN.m⁻¹. Thus, in the early stages of adsorption ($t \rightarrow 0$) (Equation S1), the interfacial tension decreases rapidly. Subsequently, the decrease in interfacial tension slows down and eventually reaches a dynamic equilibrium where the maximum coverage of the interface with the nanoparticles is achieved ($t \rightarrow \infty$). was obtained by intercepting a curve of the variation of the interfacial tension against $(1/t)\gamma_{t \rightarrow \infty}\gamma_{t \rightarrow \infty}^{1/2}$, as suggested by equation (S2). This equation has already been applied to describe the transient variation in surface and interfacial tension in the presence of nonionic amphiphilic molecules or macromolecules in the aqueous phase (Bağ and Podgórska, 2016; Desbrières et al., 2017; Göbel and Joppien, 1997; Goswami et al., 2015; Muñoz et al., 2000).

Table 2. Steady state surface tension (γ_{∞}) parameters obtained from analysis of at late-stage of NPs adsorption

	$(d\gamma/dt)^{-1/2}$ (N. m ⁻¹ . s ^{-1/2})	$\gamma_{t \rightarrow \infty}$ (mN.m ⁻¹)	R ²
21nm Mg(OH) ₂ NPs	132.4 ± 0.1	19.230 ± 0.001	0.978
45nm Mg(OH) ₂ NPs	74.5 ± 0,1	18.000 ± 0.001	0.989
21 nm Mg(OH) ₂ NPs (2 mM NaCl)	82.1 ± 0.3	21.170 ± 0,004	0.912
45 nm Mg(OH) ₂ NPs (2 mM NaCl)	225.0 ± 0.6	22.310 ± 0.007	0.828

We also noticed that this decrease occurred with the increase in the size of nanoparticles that did not contain NaCl. Similar results have been obtained by (Kutuzov et al., 2007b) by studying the effect of adsorption of

cadmium selenide nanoparticles on a water/oil interface. Thus, with Mg(OH)₂ 45 nm nanoparticles, the interfacial tension reaches an equilibrium value of 18.0 mN.m⁻¹, and 19.2 mN.m⁻¹ for Mg(OH)₂ 21 nm nanoparticles (Table 2). This phenomenon can be explained by the fact that a very high adsorption energy of the nanoparticles has been observed when their diameter increases. In addition, as the diameter of nanoparticles increases, they undergo less rearrangement at the interface because they are less mobile (Sy et al., 2024a).

3.3 Dilatational Interfacial Rheology

The complex viscoelastic modulus is one of the most important rheological parameters that allows the quantification of the relationship between surface interfacial layer modification and associated dilatation stress (Ravera et al., 2010; Velázquez et al., 2017). In general dilatation rheology are related with studies of the coalescence of droplets and the stability of liquid films and emulsions (Liggieri et al., 1996; Velázquez et al., 2017). The impact of the size of solid nanoparticles without NaCl on dilatational rheology was studied according to frequency sweep tests, reported in Figure 1. The results shows the viscoelastic modulus and loss angle as a function of frequency for Mg(OH)₂ 45 and 21 nm NPs (Figure 1).

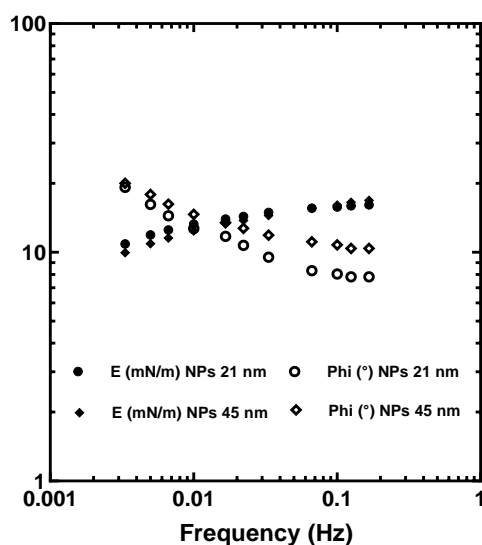


Figure 1. Viscoelastic modulus (E, closed symbols) and loss angle (Phi, open symbols) for Mg(OH)₂ 45 and 21 nm NPs as a function of frequency

The first observation is that the interfaces are almost elastic. We see an elastic modulus that increases with frequency as the phase shift decreases. Indeed, at low frequency of expansion, the slow variation in the shape of the interface gives the nanoparticles enough time to reduce the interface tension gradient resulting from the modification of the interfacial area. As the frequency of expansion increases, the solid nanoparticles will not have time to decrease the interfacial tension gradient. As a result, the expansion module increases as the expansion frequency increases. This remark remains valid for all sizes of nanoparticles (Fig. 3). Similar results were obtained by Lai et al. (Lai et al., 2016) by studying interfacial dynamic properties and dilatational interfacial rheology of bisquaternary ammonium dibromides solutions at air-water interface. Their results suggest that the diffusion-controlled relaxation process is dominant in a frequency range below 0.5 Hz. However, it should be noted that for our study, this phenomenon has only been observed for frequencies below 0.1 Hz. This elastic behavior of the interfaces has been confirmed by the very low values of the slope of $\log|E| - \log(\omega)$ for Mg(OH)₂ NPs without NaCl (Figure 2a). According to Tong et al. (Tong et al., 2014), the lower the slope is, the more elastic the film appears. In addition, for nanoparticles of Mg(OH)₂ of 21 and 45 nm, from 0.1 Hz, the elastic moduli are within the same orders of magnitude. Suggesting that it reached an elastic modulus limit at high frequency (Desbrières et al., 2017). In studying the dilatational rheology of oil / water interfaces covered by amphiphilic polysaccharides derived from dextran, the Lucassen-van den Tempel model was used to explain (Lucassen and Giles, 1975; Lucassen and Van Den Tempel, 1972; Lucassen-Reynders and Lucassen, 1994) to

explain this phenomenon by the existence of an elastic modulus limit E_0 at which relaxation phenomena had no effect (therefore, the value of the elastic modulus was a constant). The stabilization of E at higher frequencies for the 21 nm NPs could follow a similar behavior, involving here also an inhibition of relaxation phenomena.

Since NaCl created nanoparticle flocculation as aggregates, it was interesting to study the rheological behavior of the interfaces after adsorption of the aggregates. Figure 2 shows the variations of elastic modulus and phase shift as a function of frequency. Here, we compare the rheological response of two nanoparticle suspensions at the same concentration of 0.8 g.L^{-1} . The NaCl concentration of the nanoparticle suspension was set at 2 mM, as chosen up to now. The results are reported in Figure 2.

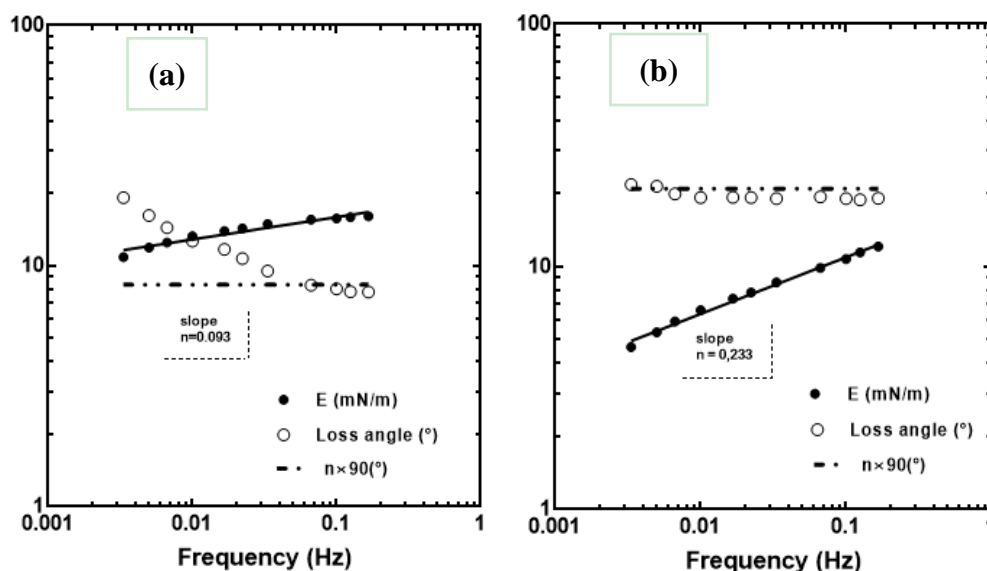


Figure. 2. Loss angle ($^\circ$) and Viscoelastic modulus of cyclohexane/water interface as a function of frequency: (a) 21 nm $\text{Mg}(\text{OH})_2$ NPs, (b) 21 nm $\text{Mg}(\text{OH})_2$ NPs in 2 mM NaCl

In Figure 2 (a), we see an elastic modulus increases according to a power law with the increase of the frequency and a phase shift decrease. This has already been discussed above, namely that the adsorption of NaCl-free nanoparticles at the interfaces gives them quasi-elastic properties. The measured phase shift calculated from Eq. 1 and 2 is far from the calculated theoretical value for all frequencies investigated. This remark remains valid for all nanoparticles without NaCl and 45 nm $\text{Mg}(\text{OH})_2$ NPs in 2 mM NaCl (Figure. 2a).

In Figure 2 (b), we found that the elastic modulus increases according to a power law with the increase of the frequency while the phase shift remains constant. This suggests that the system exhibits gelation point behavior. Indeed, the theoretical phase calculated from Eq. (1) and (2) corresponding to that of a 2D gel, shows a very good correlation with the phase shift values obtained from the experiment. This confirms that the aggregates adsorbed at the interfaces have given them a gel-like appearance. Winter and Chambon (Chambon and Winter, 1987; Winter and Chambon, 1986) have shown that the rheological characteristics of this state are easily deduced from rheological experiments (3D in their case). They found that for oscillation experiments, the elastic modulus and the phase shift (in degrees) must necessarily obey to Eq. 1 and 2:

$$E = S \cdot \omega^n \quad (\text{Eq. 1})$$

$$\phi = n \times 90^\circ \quad (\text{Eq. 2})$$

S is the strength of the gel. The value of n was obtained with the linearization of Eq. (1) and $0 < n < 1$ is a relaxation exponent. According to (Winter and Mours, 1997), the smaller the value of this exponent n , the larger the fractal dimension of the interfacial aggregates and approaches the topological dimension 2. On the other hand, the larger is the value of n , the smaller the fractal dimension of the gel aggregates and weaker is the gel. Literature reports in for the interfacial behavior of asphaltenes (Bouriat et al., 2004) adsorbed into an oil / water interfaces, a gel-point behavior giving rise to a value of $n = 0.277$. In some cases, the presence of this gel has even been correlated with the stability of water / oil emulsions (Dicharry et al., 2006). In our work, n was equal

to 0.233, showing that macro-aggregates formed from the attractive inter-particles interactions of NPs have adsorbed at the interface and reorganize themselves in the form of fractal aggregates exhibiting a gel-point behavior with a fractal dimension of 0.233. Dynamic surface tension and dilatational rheology study are important parameters in understanding the stabilization mechanisms of Pickering emulsions. These parameters directly govern the behavior and the nature of the interfaces following the adsorption of solid nanoparticles. Some authors (Okubo, 1995; Wang et al., 2021) have previously demonstrated that interfacial tension lowering by solid particles is not the main mechanism for stabilizing Pickering emulsions. Therefore, the knowledge of the nature and behavior of the interfaces following the adsorption of solid nanoparticles is important information in understanding the stability of Pickering emulsions. Thus, the dilatational rheology experiments have shown that the adsorption of solid nanoparticles gives the interfaces elastic properties. This constitutes a considerable advantage in the resistance of the films preventing the occurrence of a coalescence event. In addition, an optimal concentration of NaCl could allow the solid nanoparticles to aggregate into flocs. The adsorption of these flocs to the interfaces could give the latter aspects of 2D gel. This aspect of gel is very important in the stabilization of the interfaces. Indeed, the flocs of nanoparticles have less mobility at the interface. This makes the droplets of emulsions covered with a rigid shell preventing the occurrence of a coalescing event. This lack of mobility of the flocs at the interfaces and consequently the absence of coalescence after formulation explains the fact that in our previous study, Pickering nano-emulsions formulated with the flocs of $\text{Mg}(\text{OH})_2$ nanoparticles made it possible to have droplets with a much thinner size and a smaller size distribution compared to Pickering nano-emulsions formulated with $\text{Mg}(\text{OH})_2$ nanoparticles without NaCl (Sy et al., 2018b).

4. Conclusion

This study focused on understanding the mechanisms of stabilization of interfaces by solid nanoparticles. Magnesium hydroxide of different sizes and under different electrolyte concentration were studied and compared. NPs were dispersed in water, their adsorption, surface properties and interfacial rheology were investigated on a water / oil model interface of a rising cyclohexane drop set up in a Tracker (drop tensiometer). Dynamic surface tension measurements revealed a sharp decrease of interfacial tension with $\text{Mg}(\text{OH})_2$ NPs without NaCl. For the flocs of nanoparticles aggregated that forms obtained with the presence of NaCl 2mM, a slow decrease of interfacial tension was observed unlike individual nanoparticles. Dilatational interfacial rheology study showed an elastic modulus that increases with frequency as the phase shift decreases for $\text{Mg}(\text{OH})_2$ NPs without NaCl. Which gives the interfaces elastic properties. The theoretical phase shift calculated from Eq. (1) and (2) corresponding to that of a 2D gel, shows a best correlation with the phase shift values obtained from the experiment for only 21 nm $\text{Mg}(\text{OH})_2$ NPs in 2 mM NaCl. This confirms that the aggregates adsorbed at the interfaces have given them a gel-like appearance. This gelation of the interface is a considerable advantage in the stabilization of Pickering emulsions. It reduces the probability of coalescence between two droplets of a Pickering emulsion and give them better stability.

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Authors' contributions

PM-S and M-D designed the study; PM-S, AR-D, and SM-D performed all experiments; LAD-D, AR-D, G-M, PM-S, and M-D analyzed the data; PM-S and N-A wrote the article with contributions from all authors; A-F, B-N, T-V, G-M, and M-D provided corrections and suggestions to the manuscript.

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Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Informed consent

Obtained.

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Data sharing statement

No additional data are available.

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Supplementary Informations

$$\gamma(t)_{t \rightarrow 0} = \gamma_0 - 2RTc \left(\frac{Dt}{\pi}\right)^{1/2} \text{ or } \left(\frac{d\gamma}{dt^{1/2}}\right)_{t \rightarrow 0} = -2RTc \left(\frac{D}{\pi}\right)^{1/2} \quad \text{Eq. S1}$$

$$\gamma(t)_{t \rightarrow \infty} = \gamma_\infty + \frac{RT\Gamma^2}{2c} \left(\frac{\pi}{Dt}\right)^{1/2} \text{ or } \left(\frac{d\gamma}{dt^{-1/2}}\right)_{t \rightarrow \infty} = \frac{RT\Gamma^2}{2c} \left(\frac{\pi}{D}\right)^{1/2} \quad \text{Eq. S2}$$

where R is the gas constant, T is the temperature, c is the molar bulk concentration, Γ is the molar surface concentration at steady state, and D is the nanoparticles diffusion coefficient.