

SHEAR RHEOLOGY OF SILICA NANOPARTICLE DISPERSIONS

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ABSTRACT:

The effects of particle concentration, particle size and temperature on the shear rheology of suspensions of silica nanoparticles are studied. Sterically or electrostatically stabilized silica nanoparticle dispersions with sizes ranging from 5–75 nm and particle volume fractions ranging from 0.22–25 % exhibited a constant viscosity within the shear rate range of 1–200 s⁻¹. There is a non-linear relationship between the concentration and the viscosity of these dispersions that depends on the radii and surface energy of these nanoparticles. We propose an effective maximum packing fraction model based on the concept of an effective particle radius, which takes into account the thickness of the electrical double layer and the surface coating material. The viscosities of all the dispersions collapse onto a universal curve as a function of the volume fraction normalized by the effective maximum packing fraction.

ZUSAMMENFASSUNG:

Der Einfluss der Konzentration und der Größe der Partikel sowie der Temperatur auf die scherrheologischen Eigenschaften von Suspensionen mit Silika-Nanopartikeln wurde untersucht. Sterisch und elektrostatisch stabilisierte Silika-Nanopartikel-Dispersionen mit einer Größe von 5–75 nm und einem Volumenanteil zwischen 0.22% und 25% wiesen eine konstante Scherviskosität im Schergeschwindigkeitsbereich von 1–200 s⁻¹ auf. Es besteht eine nichtlineare Beziehung zwischen der Konzentration und der Viskosität dieser Dispersionen, die von den Radien und der Oberflächenenergie der Partikel abhängt. Wir stellen ein Modell für die effektive maximale Packungsdichte auf, das auf dem Konzept des effektiven Partikelradius basiert. Dieses Modell berücksichtigt die elektrische Doppelschicht und die Beschichtung der Partikeloberfläche. Die Viskositäten sämtlicher Dispersionen lassen sich als Masterkurve als Funktion des Volumenanteils normiert mit der effektiven maximalen Packungsdichte darstellen.

RÉSUMÉ:

Les effets de la concentration en particules, de la taille des particules et de la température sur la rhéologie des suspensions de nanoparticules de silice ont été étudiés. Des dispersions de nanoparticules de silice stabilisées au moyen de forces électrostatiques ou stériques, avec des tailles variant de 5 à 75 nm et des fractions volumiques variant de 0.22 à 25%, présentent une viscosité constante pour des vitesses de cisaillement de l'ordre de 1 à 200 s⁻¹. Il existe une relation non linéaire entre la concentration de ces dispersions et la viscosité, qui dépend des rayons et de l'énergie de surface des nanoparticules. Nous proposons un modèle de fraction maximum effective de package, basé sur le concept d'un rayon effectif de particule, qui tient compte de l'épaisseur de la double couche électrique et du matériau recouvrant la surface. Les viscosités de toutes les dispersions tombent sur une courbe universelle en fonction de la fraction volumique normalisée par la fraction effective maximum de package.

KEY WORDS: silica nanoparticles; particle size; surface coating; effective maximum packing fraction; shear rheology

1 INTRODUCTION

The rheological behavior of colloidal dispersions has practical applications to many fields [1]. Recent advances in engineering of nanoparticles have expanded potential application of nanoparticle dispersions into the characterization and production of natural hydrocarbon forma-

tions [2]. Current subsurface technologies are insufficient to measure matrix and fracture properties between wells or to monitor changes in fluid saturation as reservoir pressure changes with respect to hydrocarbon production. An improved understanding of spatial distribution of fluids in the reservoir and their properties

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Figure 9 (left): The normalized effective maximum packing fraction with respect to maximum packing fraction, $\phi_{max}^{eff}/\phi_{max}$, as a function of dimensionless parameter l/a for modified surface and $A\kappa^{-1}/a$ for unmodified surface. The solid line is constructed using Equations 10 and 11.

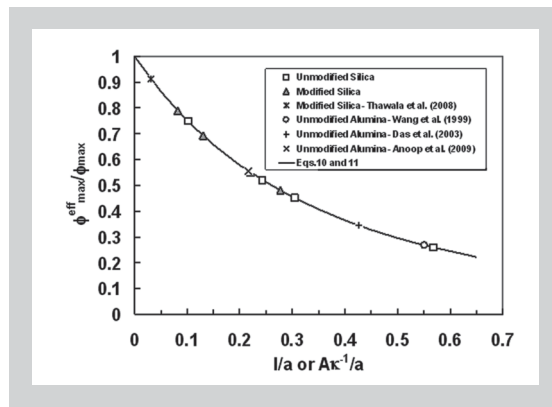
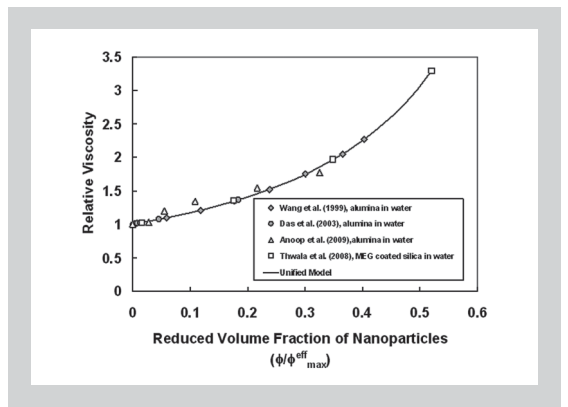


Figure 10: Viscosity ratio as a function of volume fraction of alumina nanoparticles in dispersed in water [13, 14, 40] and MEG coated silica nanoparticle dispersions [30]. The effective maximum volume fractions are determined by Equations 9 – 11. All the data collapse onto a single curve that is well represented by our unified model.



for surface modified and $A\kappa^{-1}/a$ for unmodified silica particles. The nonlinear dependence of $\phi_{max}^{eff}/\phi_{max}$ on dimensionless length described by Eqs. 10 and 11 is shown in Figure 9. The relationship between $\phi_{max}^{eff}/\phi_{max}$ and $A\kappa^{-1}/a$ or l/a indicates a significant deviation of ϕ_{max}^{eff} from ϕ_{max} (0.63) especially at small particle sizes (Figure 9).

We used our viscosity model (Equations 9–10/11) to predict the measured viscosity of alumina and silica dispersions at different volume fractions and sizes from [13, 14, 30, 40]. The particle sizes reported in these references were used to determine the corresponding model parameters (A or l) based on Figure 8. These model parameters were then used to calculate the viscosity (Equations 9 – 10/11). We assumed a double layer thickness of 5 nm since the information on the electrical double layer thickness was not given in these studies. All the calculated viscosities and their measured values from the references were plotted versus particle volume fraction in Figure 10. The relative viscosities of these dispersions collapse onto a single curve (Figure 10) as represented by the unified model (Equations 9 – 11).

4 CONCLUSIONS

In this study we have shown that silica nanoparticle dispersions exhibit a Newtonian behavior for shear rates ranging from 1 – 200 s^{-1} and particle concentrations ranging from 0.22 – 25 % by volume. The relative viscosity is a non-linear function of particle volume fraction and independent of temperature. The particle size and the surface type are also found to significantly influence the viscosity. The dispersion viscosity increases as particle size decreases. The unmodified, electrostatically stabilized silica nanoparticles exhibit greater viscosity than sulfonate coated, sterically stabilized silica nanoparticles at a given particle size and volume fraction.

A significant deviation from the predictions of hard sphere viscosity model occurs with our experimental results. Therefore, the electrostatic or steric interactions between silica nanoparticles should be taken into account. We propose a unified model to predict accurately the viscosity

of silica nanoparticle dispersions at a given solid volume fraction by introducing the concept of effective maximum packing fraction. The model parameters (A or l) could be determined experimentally or numerically based on, for instance molecular dynamics simulation. These parameters depend on nanoparticle size and surface properties. All the experimental data are successfully scaled by normalizing the volume fraction by the effective maximum packing fraction. A correlation is obtained between the effective maximum packing fraction and particle radius.

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