

Rheology of Highly Concentrated Nanofluid with Surface-Modified Nanoparticles Synthesized in Supercritical Water

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論文内容要旨

Chapter 1. Introduction

A nanofluid (NF) is a dispersion of nanoparticles (NPs, 1–100 nm) in a liquid solvent or base fluid (BF).¹ Because of the existence of NPs in NFs, these fluids should exhibit unusual fluid properties, including magnetic properties, dielectric constants, thermal or electric conductance, and reflective indexes. Thus, NFs are expected to have various new applications in industries such as chemical processing, transportation, refrigeration, electronics, optics, medicine, energy, and environment.^{2–4} For such applications, the key issues for designing NFs are dispersing NPs (i.e., the phase behavior) and controlling the viscosity of the resulting NF. Although it has been recognized that these two factors should be closely related, few approaches are available to elucidate the underlying mechanism.⁵ Indeed, previously, synthesizing NPs with controlled sizes and solvent affinities (i.e., organic surface molecules) was not an easy task.

Supercritical hydrothermal synthesis is one method of synthesizing NPs with containing capping organic molecules on their surfaces. This research aimed to understand the relationship between the rheological and phase behaviors of NFs through a systematic study utilizing the same core particle (CeO₂) modified with surfactants with different chain lengths synthesized by the supercritical hydrothermal method using a variety of organic solvents.

Chapter 2. Background of Research

NPs tend to aggregate because of their high surface energy, which significantly affects the properties of the resulting NFs. The surface treatment of NPs with organic molecules can suppress this aggregation. Fatty acid surfactant-modified CeO₂ NPs can be obtained by *in situ* synthesis in supercritical water (SCW), and such NPs are dispersible in non-polar organic solvents up to certain volume fractions.⁶ The phase behavior of NPs in solvents (i.e., their dispersion/agglomeration at different concentrations) can be assessed by the naked eye because NFs are clear (i.e., the NPs are well dispersed) up to a certain volume fraction and subsequently become cloudy (i.e., at the cloud point) because of agglomeration. Ultraviolet-visible (UV-vis) spectroscopy can be also used to monitor dispersion/agglomeration (i.e., phase changes).

Rheological measurements of well-dispersed and agglomerated NFs have revealed a relationship between the rheological and phase behaviors of NFs. Well-dispersed NFs exhibit low viscosities, whereas agglomerated NFs have higher viscosities. The dependence of the shear rate on the viscosity is also important when attempting to relate the rheological and phase behaviors of NFs. Regarding well-dispersed NFs, very few research studies have addressed the effect of the surfactant chain length on the resulting viscosity. Furthermore, for agglomerated NFs, abundant research has investigated their

shear-dependent characteristics, such as shear thinning and thickening, but few studies have addressed the phase behavior or performed thermodynamic analyses.⁷

Thus, the first objective of this study is to elucidate the relationship between the phase behavior and the rheological behavior through a systematic study using NFs with the same core but surface molecules with different chain lengths synthesized by the supercritical hydrothermal method. The second objective is to clarify the effect of the chain length on the viscosity of well-dispersed NFs. Finally, the third aim is to correlate the shear thinning/thickening behavior and phase behavior considering the elucidated relationship between the phase and rheological behaviors.

Chapter 3. Phase Behavior of Surface-Modified Nanoparticles

CeO₂ NPs whose surfaces were modified with *n*-alkanoic acids with different chain lengths were synthesized by an *in situ* SCW method, and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy, and thermogravimetric analysis.⁶ Cube-shaped, nanometer-sized CeO₂ NPs were obtained. Table 1 summarizes the information about the surfactants, solvents, synthesized NPs, and prepared NFs involved in this study. NFs with wide concentration ranges were prepared by simply adding the required amount of NPs into each solvent. The NF concentrations are presented in vol%. The phase behavior of the NFs was assessed by observation with the naked eye. Fig. 1 demonstrates that the C₁₀-CeO₂-cyclohexane NFs were well dispersed (i.e., clear) up to 21.24 vol%, unclear at 23.44 vol% and agglomerated (i.e., cloudy) at 29.55 vol%. UV-vis spectroscopy was also performed to assess the phase behavior of the NFs. In most cases, both evaluations give similar results, although it was difficult to obtain UV-vis signals from highly concentrated NFs. Thus, naked eye observation was employed in this study.

Table 1: Surfactants, solvents, NPs, and NFs used in this study.

Surfactants	NPs	Solvents	NFs
Hexanoic acid (C ₆ -)	C ₆ -CeO ₂	Cyclohexane	C ₆ -CeO ₂ -cyclohexane
Octanoic acid (C ₈ -)	C ₈ -CeO ₂	Decalin	C ₈ -CeO ₂ -cyclohexane
Decanoic acid (C ₁₀ -)	C ₁₀ -CeO ₂	Dodecane	C ₁₀ -CeO ₂ -cyclohexane
Stearic acid (C ₁₈ -)	C ₁₈ -CeO ₂		C ₁₈ -CeO ₂ -cyclohexane
			C ₈ -CeO ₂ -decalin
			C ₁₀ -CeO ₂ -dodecane

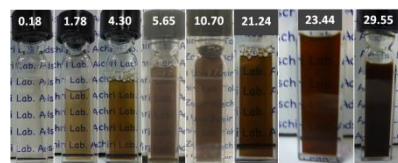


Fig. 1. Images of C₁₀-CeO₂-cyclohexane NFs.

Chapter 4. Relationship Between the Rheological and Phase Behaviors of Nanofluids

To investigate the relationship between the rheological and phase behaviors of NFs, rheological measurements were

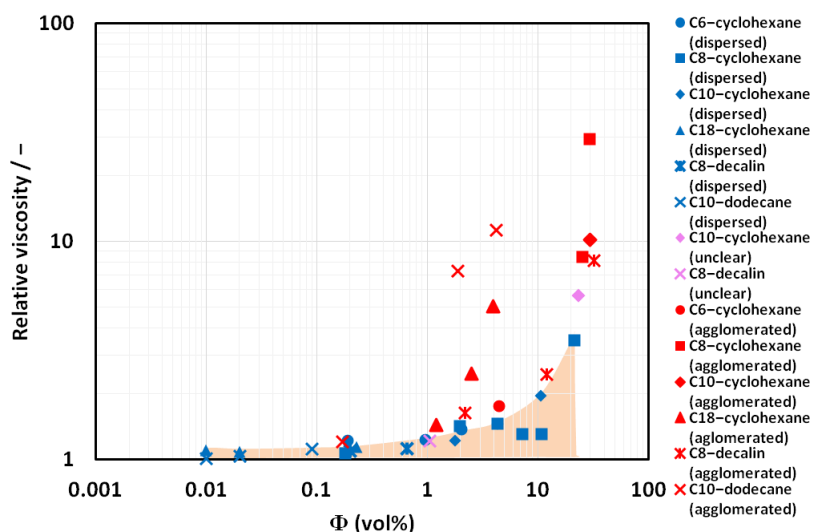


Fig. 2. Relative viscosities of NFs as a function of the volume fraction of NPs.

performed using various well-dispersed and agglomerated NF systems with a wide range of concentrations. The experimental results revealed clear links between the rheological and phase behaviors of NFs. When the NFs were well dispersed, their viscosities were lower. Conversely, when the NFs were agglomerated, their viscosities were higher. Rheological measurements also demonstrated that well-dispersed NFs exhibit low viscosities with Newtonian characteristics. To compare the viscosities of NFs of

different solvents (BFs), the relative viscosity (i.e., the viscosity of an NF divided by the viscosity of the BF) was calculated and plotted as a function of the volume fraction of NPs for all NFs, as shown in Fig. 2. The initial viscosity of each NF at the lowest shear was used to calculate the relative viscosities of the NFs. Clearly, well-dispersed NFs exhibited lower relative viscosities (blue symbols) and fall in the common zone indicated by the green area in Fig. 2. The relative viscosities of well-dispersed C_8 - CeO_2 -cyclohexane NFs at 7.21 and 10.78 vol% are very low and remain in the lower region of the common zone. Conversely, agglomerated NFs show relatively high viscosities (red symbols), and fall above that common zone.

Chapter 5. Shear Thinning and Thickening in Nanofluids

Shear thinning: During the viscosity measurement, as the shear rate increased, the viscosity of the agglomerated NFs decreased gradually and approached a constant or low value. This phenomenon is called shear thinning.⁷ Fig. 3 shows the shear thinning in C_{10} - CeO_2 -dodecane NFs at different concentrations. Some other CeO_2 -based NFs also exhibited shear thinning characteristics. The relative viscosity after shear (i.e., decreased viscosity) is plotted in Fig. 4, which clearly shows that the relative viscosities of various agglomerated NFs approach the common zone established for the well-dispersed NFs. This result implies that under shear energy, the agglomerated NFs collapsed, resulting in a clear colloidal (well-dispersed) solution.

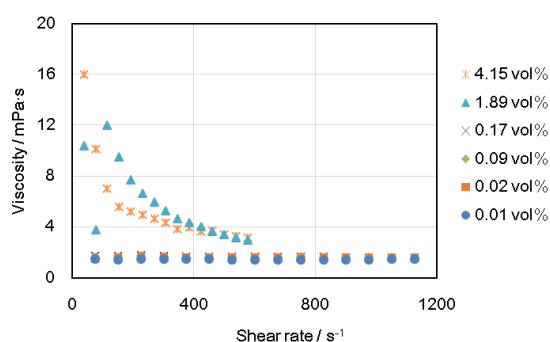


Fig. 3. Shear thinning in C_{10} - CeO_2 -dodecane NFs.

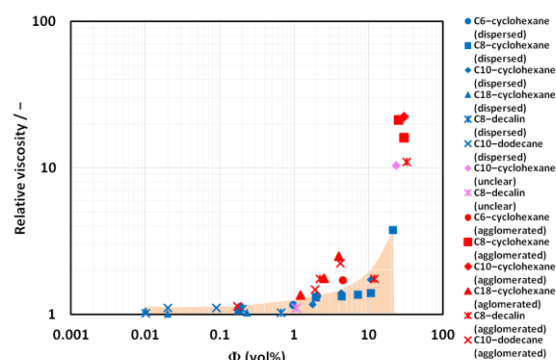


Fig. 4. Relative viscosity after shear thinning.

Shear thickening: Shear thickening was observed in 25.19 and 29.72 vol% C_8 - CeO_2 -cyclohexane, 23.44 and 29.55 vol% C_{10} - CeO_2 -cyclohexane, and 32.09 vol% C_8 - CeO_2 -decalin NFs. The shear thickening in 32.09 vol% C_8 - CeO_2 -decalin NFs is shown in Fig. 5. To explain the shear thickening phenomenon, potential energy diagram was considered. Two wells exist in the potential energy diagram with a potential energy barrier. Initially, agglomerated NFs with low potential energy remained in the shallow well. When the shear energy supplied to NFs was sufficient relative to the potential barrier, the NPs transitioned from shallow well to deeper well, and trapped in the deeper potential well with the minimum distance between particles. Larger and sometimes ordered cluster formation in deep wells decreases the dispersibility and increases the viscosity of NF.

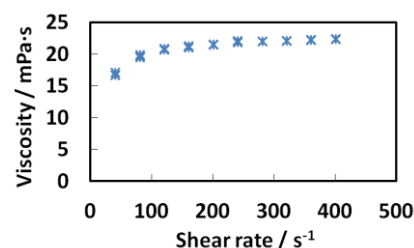


Fig. 5. Shear thickening in C_8 - CeO_2 -decalin NFs.

Chapter 6. Summary and Conclusion

Various phase behavior assessments suggest that octanoic acid- and decanoic acid-modified CeO_2 NPs are stably dispersible in cyclohexane up to ~21 vol%. The rheology results indicate that well-dispersed NFs exhibit low viscosity with Newtonian characteristics and that shear thinning occurs only in agglomerated NFs. The relative viscosities of well-dispersed NFs fall in a common zone, irrespective of the solvent and surface-modified NPs used. Conversely, the relative viscosities of agglomerated NFs remain above the common zone. The experimental results indicated that shear thinning occurs in agglomerated NFs because of the decomposition of agglomerates, which implies improved dispersibility. Conversely, shear

thickening in highly concentrated NFs indicates larger cluster formation with decreased dispersibility. Shear thickening behaviors can be explained by considering the potential curves of NFs. Overall, the results suggest that the rheological behavior depends strongly on the phase behavior of NFs.

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論文審査結果の要旨

ナノ流体（高濃度ナノコロイド分散液）は、ナノ粒子の有する無機材料物性と流動性を同時に発現することから、有機無機ハイブリッド材料、プリントエレクトロニクス等、幅広い産業分野での利用が期待され、その開発が望まれている。しかし、ナノ粒子そのものの合成・ハンドリングの難しさから、ナノ流体の科学・技術は必ずしも十分には発達していないのが現状である。

本研究は、超臨界水熱法を用いた有機修飾基の長さを変えた有機修飾ナノ粒子を合成し、ナノ粒子の分散挙動および粘性挙動について系統的な実験を通して議論することで、ナノ流体の設計・制御の可能性を論じた。

本論文はその成果を纏めたもので、全6章から成る。

第1章は序論であり、本研究の背景及び目的を述べている。

第2章では、これまで報告されているナノ流体の粘性挙動に関する研究において、有機修飾基の長さを系統的に変えた研究が少なく、そのためナノ粒子と溶媒との親和性、それによる分散特性や粘性挙動との関係を必ずしも十分に議論されていないことを指摘するとともに、そこに本研究の位置づけを見出している。

第3章では、鎖長の異なるカルボン酸修飾 CeO_2 ナノ粒子を超臨界法により合成し、シクロヘキサン、デカリン、ドデカン中におけるナノ粒子の分散挙動について、ナノ粒子と溶媒との親和性の影響を明らかにしている。

第4章では、種々のカルボン酸修飾 CeO_2 ナノ粒子を用いたナノ流体の粘性測定を行い、粘性挙動に与える有機鎖長の影響を評価し、3章の分散挙動との比較を通して、これらに明確な相関があることを見出した。分散状態が良好な場合のみを抽出すると、溶媒に対する相対粘度は、修飾剤の長さ、溶媒の種類によらず、ナノ粒子の体積分率のみの関数でおおよそ整理できることがわかった。一方、分散状態が不安定となり凝集が進むと、いずれの場合も、この粘性・体積分率相関からずれ、ナノ流体の粘度は増大した。

第5章では、分散状態が悪く凝集が進んだ系について、せん断を加えた時に粘性が低下（シアニング）および増大（シアシックニング）する現象に焦点をあてている。せん断エネルギーを増大させるほど、ナノ流体の粘性は、4章において良好な分散系で得られた粘性・体積分率相関関数に漸近することを示すことで、せん断場においては良好な分散性が得られていることを示唆している。このような凝集系における粘性と分散性に与えるせん断エネルギーの効果について、シックニングも含め、粒子溶媒間の親和性の影響を粒子間ポテンシャルにまで帰着させた議論も行なっている。

第6章は総括である。

以上、要するに本論文は、ナノ流体中のナノ粒子の分散状態によってその粘性挙動が体系づけられることを定量的に示し、ナノ粒子の分散制御によりナノ流体の粘性挙動を設計できることを示したものであり、ナノ流体の設計と応用に関わる化学工学の発展に寄与するものとする。

よって、本論文は博士(工学)の学位論文として合格と認める。