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THERMAL AND PHASE CHANGE CHARACTERISTICS OF SELF-ASSEMBLED PAO NANOEMULSION FLUIDS

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ABSTRACT

The strategy of adding solid particles to fluids for improving thermal conductivity has been pursued for more than one century. Here, a novel concept of using liquid nanodroplets for enhancing thermal performance has been developed and demonstrated in polyalphaolefin (PAO) nanoemulsion fluids. The PAO nanoemulsion fluids are spontaneously generated by self-assembly, and are thermodynamically stable. Their thermophysical properties, including thermal conductivity and viscosity, and impact on convective heat transfer are investigated experimentally. The thermal conductivity enhancement in these fluids is found to be moderate, but increases rapidly with increasing temperature in the measured temperature range from 35 $^{\circ}$C to 75 $^{\circ}$C. A very remarkable increase in convective heat transfer coefficient occurs in the nanoemulsion fluids due to the explosive vaporization at the superheat limit (i.e., spinodal states). The fluid heat transfer could be augmented through the heat of vaporization (which intuitively raises the base fluid specific heat capacity) and the fluid mixing induced by the sound waves. The development of such phase-changeable nanoemulsion fluids would open a new direction for thermal fluids studies.

NOMENCLATURE

C	heat capacity	(J/m^3 K)
h	convective heat transfer coefficient	(W/m^2 K)
H	heat of vaporization	(J/m^3)
k	thermal conductivity	(W/m K)
P	pressure	(N/m^2)
q	heat flux	(W/m^2)
T	temperature	($^{\circ}$C)
V	volume	(m^3)
ϕ	volume fraction	
μ	fluid viscosity	(N s/m^2)
ν	velocity	(m/s)
ρ	mass density	(kg/m^3)

INTRODUCTION

Cooling is one of the most limiting technical challenges faced by a multitude of diverse industry and military groups.[1-20] The coolants, lubricants, oils, and other heat transfer fluids used in today's thermal systems typically have inherently poor heat transfer properties. Hence, there is an urgent need for innovative heat transfer fluids with improved thermal properties over those currently available. The idea of adding solid particles to improve thermal conductivity has been pursued for more than 100 years since Maxwell's theoretical work. Early studies were confined to large particles (millimeter- to micron). About a decade ago, nanofluids –heat transfer fluids containing suspensions of solid nanoparticles– have been proposed to improve thermal performance of the base fluids.[1-3] Materials commonly used for nanoparticles include oxides such as alumina, silica, and titania, metals such as copper and gold, and carbon nanotubes.

Recently, the authors have proposed a radically new design for thermal fluids, "nanoemulsion fluids" that completely eliminates solid particles, and instead, uses liquid nanostructures.[12,21,22] Nanoemulsion fluids are suspensions of liquid nanodroplets (e.g., spherical droplets) in conventional thermal fluids, which are part of a broad class of multiphase

colloidal dispersions. The present work focuses on an experimental study of convective heat transfer of self-assembled polyalphaolefin (PAO) based nanoemulsion fluids, such as methanol in PAO and ethanol in PAO fluids. The thermophysical properties, including thermal conductivity and viscosity, and their temperature dependence are also investigated.

RESULTS AND DISCUSSION

The methanol/PAO and ethanol/PAO nanoemulsion fluids are spontaneously generated by self-assembly. These nanodroplets (<100nm in size) are in fact reverse micelles swollen with methanol or ethanol, and stabilized by the surfactant molecules sodium bis(2-ethylhexyl) sullfosuccinate (Sigma Aldrich) that have hydrophilic heads facing inward and hydrophobic tails facing outward into the base fluid PAO (Chevron Phillips Chemical Company). [23] PAO has been widely used as heat transfer fluids and lubricants. It is able to remain oily in a wide temperature range due to the flexible alkyl branching groups on the C-C backbone chain. Methanol and ethanol are chosen as the dispersed phase mainly because of their lower atmospheric boiling point. [24,25]

Thermal conductivity and viscosity are macroscopically observable parameters that affect the thermal performance of the fluids, and their characteristics are investigated in the PAO based nanoemulsion fluids. The thermal conductivity of the pure PAO and PAO based nanoemulsion fluids (4 vol % and 8 vol %) was measured in the temperature range from 35 $^{\circ}$C to 75 $^{\circ}$C using a 3ω-wire method. Unlike the conventional hot-wire method, [26] the 3ω-wire method determines the fluid conductivity by detecting the frequency dependence of temperature oscillation in a metal wire. [11-13,22,27-30] One advantage of this 3ω-wire method is that the temperature oscillation can be kept small enough (below 1K, compared to about 5K for the hot-wire method) within the test liquid. Calibration experiments were performed for oil and water at atmospheric pressure. Literature values were reproduced with an error of <1%.

The relative thermal conductivity of the methanol/PAO and ethanol/PAO nanoemulsion fluids are plotted in Fig. 1. The relative thermal conductivity is defined as k_{nf}/k_o, where k_o and k_{nf} are thermal conductivities of the base fluid and nanoemulsion fluids, respectively. The PAO thermal conductivity is experimentally found to be 0.143 W/m K at room temperature, which compares well with the literature values. [25] As seen in Fig. 1, the relative thermal conductivity, or the thermal conductivity enhancement, increases rapidly with increasing temperature in the measured temperature range. However, the magnitude of the conductivity increase is rather moderate in both methanol/PAO and ethanol/PAO nanoemulsion fluids, eg, 18% increase at 75 $^{\circ}$C for 4 vol % ethanol/PAO fluids. These experimental results are within the range predicted by the traditional Effective Medium Theory. [4,31-33] However, the dependence of the relative thermal conductivity on the ethanol concentration is found to be pretty weak in both methanol/PAO and ethanol/PAO nanoemulsion fluids, and the

reason is still under investigation. It is noteworthy that methanol and ethanol have thermal conductivity only slightly higher than PAO, k_{PAO}=0.143 W/mK, $k_{methanol}$=0.199 W/mK and $k_{ethanol}$=0.158 W/mK at room temperature. [24,25]
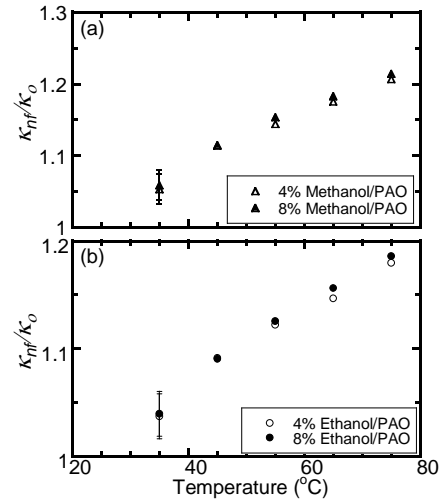

Figure 1 (a) Relative thermal conductivity of the methanol/PAO nanoemulsion fluids and (b) the ethanol/PAO nanoemulsion fluids vs. temperature.

The dynamic viscosity of the pure PAO, the methanol/PAO and ethanol/PAO nanoemulsion fluids was measured using a commercial viscometer (Brookfield DV-I Prime). Results for the viscosity are shown in Fig. 3. The viscosity of the pure PAO and the PAO nanoemulsion fluids has been measured at spindle rotational speed from 6 to 30 rpm and exhibits a shear-independent characteristic of Newtonian fluids. Unlike the relative thermal conductivity, the relative viscosity is found to decrease with increasing temperature in both methanol/PAO and ethanol/PAO nanoemulsion fluids, e.g., a decrease from 1.88 to 1.61 for 4 vol % ethanol/PAO nanoemulsion fluids when the temperature rises from 23 to 75 $^{\circ}$C. The similar trend of the relative viscosity has also been observed in many other nanofluid systems.

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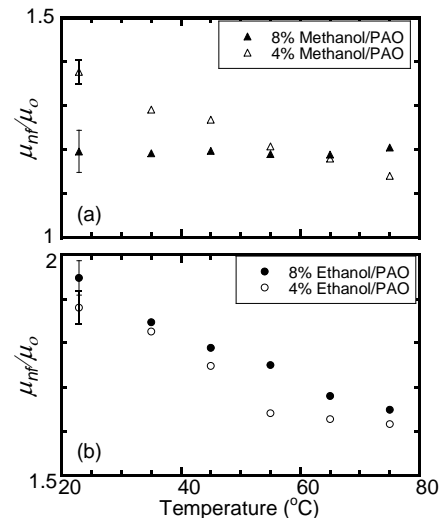
Figure 2 (a) Relative viscosity of the methanol/PAO nanoemulsion fluids and (b) the ethanol/PAO nanoemulsion fluids vs. temperature.

The convective heat transfer experiments were conducted using a test rig shown in Figure 3. In this experiment, a platinum wire 25μm in diameter and 3cm long is subjected to a cross flow of the fluids. This platinum wire serves as both the heater and the thermometer. It is heated electrically by use of a dc power supply, and so the dissipated heat can be calculated directly from its voltage and resistance. The wire temperature can also be determined from its electrical resistance. A thermocouple is used to measure the bulk temperature of the fluids, which is kept at 30 °C. The flow rate is maintained at 3cm/s for the fluids, monitored by a flow meter (King instrument company).
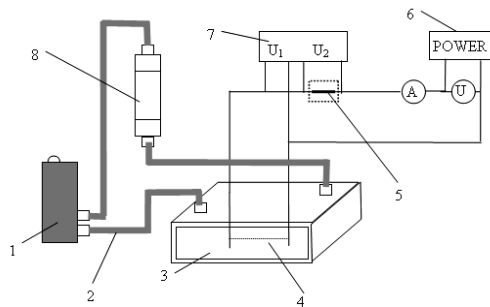
Figure 3 Test rig for convective heat transfer experiment. (1) Pump (2) Tube (3) Heating Vessel (4) Platinum Wire (5) Standard Reference Resistance (6) Power Supply (7) Digit Multimeter (8) Acrylic Flow Meter.
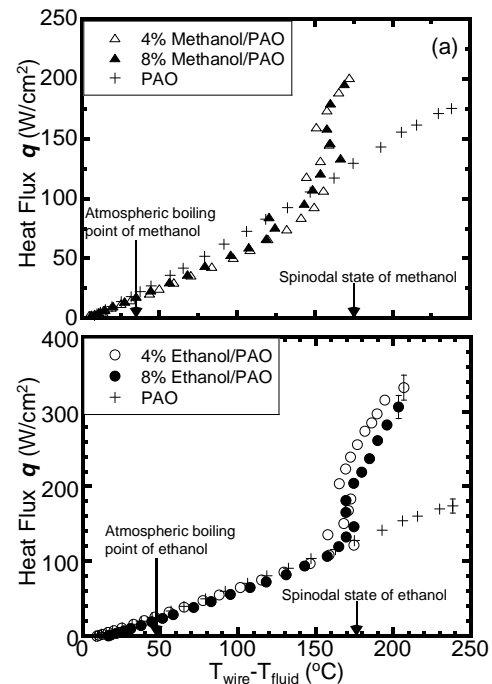
The convective heat transfer curves are plotted in Fig. 4 for the pure PAO and nanoemulsion fluids. The curve for the PAO is classified in the single-phase convection regime as the measured temperature range is far below its atmospheric boiling point.[34] When $\Delta T < 160$ °C (i.e., $T_{wire} < 190$ °C), the heat transfer coefficient values of all fluids including the pure PAO appear to be the same. This indicates that these methanol or ethanol nanodroplets have little effect on the fluid heat transfer efficiency without undergoing phase transition. When the heater temperature is further increased, however, an abrupt increase in convective heat transfer coefficient–by a factor of up to 2.2–is observed in the ethanol/PAO nanoemulsion fluids, compared to that of the pure PAO case. For example, the dissipated heat flux q is found to be 125 W/cm² and 275 W/cm² at T_{wire}-T_{fluid}=180 °C for the pure PAO and the 4 vol % ethanol/PAO nanoemulsion fluid, respectively.

The causes of the observed abrupt increase in heat transfer coefficient can be examined by first evaluating the Hilpert correlation that works for laminar flow over a cylinder,[34]

$$h = A v^{0.33} \rho^{0.33} C^{1/3} k^{2/3} \mu^{0.0033},$$

where A is a constant, v is the fluid velocity, ρ is the fluid mass density, C is the fluid heat capacity, k is the fluid thermal conductivity, and μ is the fluid dynamic viscosity. The mass density ρ of the tested nanoemulsion fluids remains nearly

constant with the value of pure PAO, and therefore has little effect on the increase of heat transfer coefficient in the Hilpert correlation. The measured conductivity and viscosity increase is rather moderate in the PAO nanoemulsion fluids. Their net effects on heat transfer induced by the increased thermal conductivity and viscosity would be negligible in the PAO nanoemulsion fluids, which is consistent with the fact that when $T_{wire} < 200$ °C, the heat transfer coefficient of the ethanol/PAO nanoemulsion fluids is almost same as that of the pure PAO.

Figure 4 (a) Convective heat transfer curves for the methanol/PAO and (b) ethanol/PAO nanoemulsion fluids. Note that T_{fluid}=30 °C, the atmospheric boiling point is 65 °C for methanol and 78 °C for ethanol .

Therefore, the abrupt increase in heat transfer coefficient– by a factor of up to 2.2–would be mainly accredited to the vaporization of those ethanol nanodroplets dispersed in the base fluid PAO. A direct impact of the nanodroplet vaporization is that the heat of vaporization could significantly enhance the effective heat capacity of the fluid. The effective heat capacity can be evaluated using the formula: $C_{eff} = C_0 + \phi \cdot H_{droplet} / \Delta T$, where ϕ is the volume fraction of the phase-changeable nanodroplets, $H_{droplet}$ is the heat of vaporization of the nanodroplets per unit volume, and ΔT is the temperature difference between the heat transfer surface and the bulk fluid. In this experiment, if assuming ΔT=10 °C, the effective volumetric specific heat can be increased by up to 162% for the 4 vol % nanoemulsion fluid containing when the ethanol nanodroplets undergo liquid-vapor phase transition. This would provide as much as 38% enhancement of heat transfer coefficient according to the Hilpert correlation.

In addition, the nanodroplet vaporization can enhance heat transfer through inducing drastic fluid motion within the

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thermal boundary layer around the heat transfer surface. The methanol/PAO or ethanol/PAO interface constitutes a hypothetically ideal smooth surface, free of any solid motes or trapped gases, so the heterogeneous nucleation and ordinary boiling are suppressed. In this case, the methanol and ethanol nanodroplets can be heated to a temperature about 120 ^{o}C above their normal atmospheric boiling point. Such a temperature is very close to thermodynamic limit of superheat or spinodal state, and is only about 10% below its critical point. The spinodal states, defined by states for which $\partial P/\partial V\big|_{T,n}=0$,[35] represent the deepest possible penetration of a liquid in the domain of metastable states. When those methanol and ethanol nanodroplets vaporize after reaching their limit of superheat, the energy released could create a sound-shock wave, so-called vapor explosion.[36] This sound wave would lead to strong fluid mixing within the thermal boundary layer, therefore enhancing the fluid heat transfer.

It is also observed in Fig. 4 that the heat flux appears to only slightly vary in the cases of 4 vol % and 8 vol % PAO nanoemulsion fluids. No satisfactory explanation is currently available, and further study is needed.

CONCLUSION

In summary, the thermal and phase change characteristics of the methanol/APO and ethanol/PAO nanoemulsion fluids have been investigated experimentally. These fluids are spontaneously generated by self-assembly, are thermodynamically stable and can be mass produced. A remarkable increase in convective heat transfer coefficient–by a factor of up to 2.2–is observed experimentally in the 4 vol % ethanol/PAO nanoemulsion fluids. Such an increase in heat transfer coefficient is not caused by the increased thermal conductivity and viscosity of the fluids. The ethanol nanodroplets vaporize explosively after reaching their limit of superheat, thereupon enhancing the fluid heat transfer through the heat of vaporization (which intuitively raises the base fluid specific heat capacity) and the fluid mixing induced by the sound waves. The PAO nanoemulsion fluids are self-recoverable after the vaporization/condensation of the dispersed ethanol nanodroplets.

ACKNOWLEDGMENTS

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