Surfactant Drag Reduction and Heat Transfer Enhancement

DISSERTATION

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By

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Abstract

Some cationic surfactants with suitable counterions can self-assemble into threadlike micelles (TLMs) in aqueous solution. The presence of TLMs imparts to the aqueous system interesting characteristics such as non-Newtonian behaviors and drag reduction (DR) capability. Such characteristics of TLMs systems can be controlled by tuning a number of factors such as temperature, counterion type, surfactant and counterion concentrations, pH, etc.

In this work, a pH-responsive surfactant-counterion TLMs system was developed. It is composed of 4 mM amphiphilic surfactant oleyl bis(2-hydroxyethyl)methylammonium chloride (commercial name is Ethoquad O/12 PG, EO12) and 8 mM trans-o-coumaric acid (tOCA) as the counterion. The rheological response of this TLMs system to pH is unique in that it has viscoelasticity in both low and high pH levels. Cryogenic transmission electron microscopy (cryo-TEM) images confirmed the presence of TLMs at pH 3.5 and pH 9.8. This system also had DR capability at low and high pH. Real applications may require that viscoelasticity can be reversibly switched on and off many times. Even after 5 cycles of pH changes the reversible changes in shear viscosity (η) and also first normal stress difference (N₁) were still effective without significant decay. With its unique rheological behaviors, this TLMs system is potentially useful in either acidic or basic environment.
One promising application of surfactant DR solutions is in district heating or cooling systems (DHCS) to save pumping energy. However, surfactant DR solutions also have reduced heat transfer capability. Therefore, it is of practical importance to enhance the heat transfer capability of the drag reducing solution in heat exchangers while maintaining the DR capability in the rest of the DHCS.

Various mechanical devices have been employed to temporarily enhance the heat transfer capability of drag reducing surfactant solutions by disturbing the flow. However, in-flow mechanical devices result in additional pressure drop across the heat exchanger and so are not practical. In this work, a novel high-efficiency vortex (HEV) static mixer was designed and employed to locally enhance the heat transfer coefficient of a surfactant DR solution. Significant enhancement of heat transfer coefficients was observed with only modest pressure drop. The HEV static mixer had a performance number comparable to that of water. The enhanced heat transfer with moderate pressure drop by the HEV static mixer resulted from organized streamwise vortices naturally generated by the inclined tabs of the HEV static mixer.

To avoid the additional pressure loss by in-flow mechanical devices, this work also studied the use of external light irradiation to temporarily enhance the heat transfer capability. The ideal fluid should be drag reducing in its normal state. At the entrance of a heat exchanger, the fluid is irradiated by light, loses its drag reducing ability and has enhanced heat transfer capability in the heat exchanger. At the exit of the heat exchanger, the fluid is irradiated by a different light frequency which restores its DR capability. Thus
this method combines the benefits of reduced pumping energy costs and good heat transfer.

A light-responsive surfactant DR solution was developed. After UV irradiation, its DR capability was reduced and its heat transfer capability was enhanced. The TLMs were also broken resulting in reduced $\eta$ and $N_f$. But the effect of UV irradiation on this solution is not reversible. As a result, the DR capability can not be restored, which prevents this solution from being used in DHCS. However, studies of this light-responsive surfactant DR solution led to an improved DR solution that had reversible responses to light irradiations. This surfactant DR solution is a promising candidate for use in district heating and cooling systems, where its drag reduction and high heat transfer can be switched on and off repeatedly by external light irradiation.
Dedicated to my family
Acknowledgments

The completion of this dissertation is a mission impossible without support from many individuals. The greatest contribution comes from my adviser, Helen C. Kurtz Professor Emeritus, Dr. Jacques L. Zakin. I would like to sincerely thank him for his continuing guidance and encouragement. Whenever I need him for anything, he is always there ready to help. He has also spent so much time correcting errors, big or small, in my manuscripts. Even when he was hospitalized, he was still able to spend time correcting my drafts and presentation slides. His humor, kindness, enthusiasm, optimism, persistence and diligence have impressed me so much that I will take them with me as priceless treasure to wherever I will be in the rest of my life. To me, he is a great mentor noble researcher and a true friend forever.

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<th>Description</th>
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<tbody>
<tr>
<td>CMC</td>
<td>critical micellar concentration</td>
</tr>
<tr>
<td>cryo-TEM</td>
<td>cryogenic transmission electron microscopy</td>
</tr>
<tr>
<td>CTAB</td>
<td>cetyl trimethyl ammonium bromide</td>
</tr>
<tr>
<td>CTAC</td>
<td>cetyl trimethyl ammonium chloride</td>
</tr>
<tr>
<td>DHCS</td>
<td>district heating or cooling systems</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide-d6</td>
</tr>
<tr>
<td>DR</td>
<td>drag reduction, drag reducing</td>
</tr>
<tr>
<td>DRAs</td>
<td>DR agents</td>
</tr>
<tr>
<td>EHAC</td>
<td>erucyl bis(hydroxyethyl-methyl) ammonium chloride</td>
</tr>
<tr>
<td>EO12</td>
<td>Ethoquad O/12 PG</td>
</tr>
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<td>HCl</td>
<td>hydrochloric acid</td>
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<td>HEV</td>
<td>high-efficiency vortex</td>
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<td>heat transfer reduction</td>
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<td>NaOH</td>
<td>sodium chloride</td>
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<td>NaSal</td>
<td>sodium salicylate</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>PABA</td>
<td>4-phenylazo-benzoic acid</td>
</tr>
<tr>
<td>SIS</td>
<td>shear-induced structure</td>
</tr>
<tr>
<td>TLMs</td>
<td>threadlike micelles</td>
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<tr>
<td>tOCA</td>
<td><em>trans</em>-o-coumaric acid</td>
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### List of Symbols

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<tbody>
<tr>
<td>η</td>
<td>shear viscosity (Pa*s)</td>
</tr>
<tr>
<td>ξ</td>
<td>molar ratio of counterion to surfactant</td>
</tr>
<tr>
<td>%DR</td>
<td>percent drag reduction</td>
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<td>%HTR</td>
<td>percent heat transfer reduction</td>
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<td>radius (m)</td>
</tr>
<tr>
<td>Re</td>
<td>Reynolds number</td>
</tr>
<tr>
<td>V</td>
<td>mean flow velocity (m/s)</td>
</tr>
<tr>
<td>ω</td>
<td>angular velocity (1/s)</td>
</tr>
<tr>
<td>ΔP</td>
<td>pressure drop (Pa)</td>
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CHAPTER 1: Introduction

1.1 Drag reduction by additives

Drag reduction is a phenomenon in which, a small amount of additives in the fluid can significantly reduce the pressure loss of turbulent flows. This phenomenon can save energy consumption to transport fluid in pipes. In 1931, Forrest and Grierson [1] first observed reduced pressure loss of turbulent flow when they studied wood-pulp fiber suspensions in water. This reduction in pressure loss is termed turbulent drag reduction (DR), and it is beneficial in fluid transport because it translates into lower energy requirements for pumping the fluid. Since then, many additives including high-molecular-weight linear polymers and surfactants that form threadlike micelles (TLMs) have been studied as DR agents (DRAs) [2]. High polymers as DRAs were studied by Toms [3], while aluminum soaps as DRAs were studied by Mysels [4]. Polymers were more extensively studied in the early stage of DR research, probably because they were more effective [5]. Polymer DRAs have been utilized in the Trans-Alaska crude oil pipeline [6, 7] and in fire fighting [8], and have been studied for many other applications [9].
1.2 Surfactant drag reduction

In the presence of suitable counterions, some cationic surfactants can self-assemble to form threadlike micelles (TLMs) in aqueous solutions [10, 11]. These TLMs, resembling polymer molecules, entangle with each other and interfere with solvent movements, resulting in non-Newtonian behaviors, such as viscoelasticity [12, 13], flow birefringence [14, 15], and exhibit shear-induced structure [14, 16-19]. Such TLM solutions have been studied extensively for many applications such as oil field applications [20], home-care and personal-care products [21, 22], and drag reduction [5, 23, 24]. The percent DR by TLMs solutions can reach 80% or more [25-28].

Although polymers in pipeline transport found successful applications [7], they are mechanically degraded by high shear stress and permanently lose their DR effectiveness [29]. Therefore, to maintain their drag reduction effectiveness, polymeric DRAs have to be constantly replenished to the drag reducing solution. On the contrary, surfactant drag reducing solutions, retain their drag reduction ability even in recirculation systems without the constant addition of surfactant DRAs, because the surfactant threadlike micelles, which are essential to induce drag reduction [5, 30-32], can reassemble after being temporarily broken up by high shear stress [5, 33]. This reassembly is thermodynamically stable [34]. Thus this self-repairability makes surfactants promising DRAs in recirculation systems. Another advantage of surfactant solutions over high polymer solutions is that the drag reduction of surfactant solutions is potentially greater than that of high polymers according to the drag reduction asymptotes for high polymers [35] and surfactants [36].
1.3 District heating and cooling systems

Since surfactant TLMs solutions can maintain their drag reducing capability, they can be used in recirculation systems. A promising application of drag reducing fluids is in district heating/cooling systems (DHCS) [5, 37-39], in which hot or chilled water is recirculated. Surfactant DR solutions regain their DR effectiveness after mechanical degradation when passing through pumps while DR polymer solutions are permanently degraded by the shearing action of the pump. DHCS can provide heated or chilled water from a central station to buildings in a district for heating or for air conditioning. With centralized equipment, such systems can achieve efficiencies by eliminating furnaces, boilers and air conditioners in each building in a district. DHCS can utilize many kinds of energy sources from coal to geotherm, from natural gas to biomass. This flexibility makes DHCS more competitive in a time of increasingly expensive fuels [5, 40]. So, DHCS are widely used in Europe, Japan and Korea and are becoming of increased interest in the United States [40]. The energy consumption for pumping water usually takes up about 15% of the entire energy cost of DHCS [41]. This pumping energy consumption can be reduced by using a drag reducing water solution as a substitute for water.

1.4 Heat transfer reduction

However, drag reducing fluids have reduced heat transfer capability compared with water and the heat transfer reduction (HTR) is usually a little higher than DR [42-46]. Therefore, it is of practical importance to enhance the heat transfer capability of the drag
reducing solution in heat exchangers while maintaining the DR capability in the rest of the DHCS.

In surfactant drag reducing flows, suppressed velocity fluctuations in the radial direction [47, 48], reduced frequency of turbulent bursts [49-51], and also reduced radial turbulence [52, 53] have been observed, resulting in reduced heat transfer in the radial direction. These reduced turbulent characteristics are caused by the interaction between TLMs and the solvent. Long TLMs can probably damp turbulent eddies [54], and their alignment along the flow suppresses fluid movements in the direction normal to the flow [48, 52]. Therefore, the heat transfer can be enhanced either by intensifying the turbulence or by eliminating TLMs. A number of methods have been used in heat exchangers to enhance flow turbulence and to mechanically destroy TLMs. These methods include helical pipes [25], fluted-tube heat exchanger [55], wire meshes [56], static mixers at the heat exchanger entrance [33], and vortex generators [28, 57]. However, all of these methods involve in-flow mechanical devices, which directly interfere with the fluid flow, resulting in significant pressure losses.

1.5 Scope of this dissertation

In the following chapter, drag reduction literature is reviewed to help the reader understand the current research status on this subject. Chapter 3 covers details of the experimental methods and apparatus, which includes materials, sample preparations, nuclear magnetic resonance (1H NMR), rheology, zeta potential, cryo-TEM, light sources, recirculation system, drag reduction and heat transfer measurements. Chapter 4 describes a surfactant micelle solution with unique rheological responses to pH changes. Chapter 5
describes a mechanical device installed in the heat exchanger to enhance heat transfer with relatively low pressure drop. Chapter 6 proposes a novel method to temporarily enhance the heat transfer of drag reducing surfactant solution in a heat exchanger. Light-responsive surfactant micelles are employed in this method. A light-responsive surfactant TLMs solution is developed as a first step into this research direction. Chapter 7 describes a reversible light-responsive surfactant TLMs solution. This solution undergoes reversible changes upon different light irradiations. Such reversibility is a must to enhance heat transfer by external light irradiation.
CHAPTER 2: Literature Review

2.1 Drag reduction and TLMs

2.1.1 Drag reducing surfactant additives

Although polymers in pipeline transport found successful applications [7], they are mechanically degraded by high shear stress and permanently lose their DR effectiveness. On the contrary, surfactants are more viable in high shear stress applications because they can reassemble to reform their original microstructures in low shear stress regions and regain DR effectiveness [5]. This reassembly is thermodynamically stable [34]. Thus this self-repairability makes surfactants promising DRAs in recirculation systems, such as DHCS, in which DRAs experience high shear stress pump regions over and over again [5]. Maximum DR asymptotes have been established for polymer solutions [35] and micellar solutions [36]. The maximum DR achievable with threadlike micelles is greater than that with high polymers. A major advantage of threadlike micelles over high polymers is that they can reassemble after being broken up by high shear-stresses.

Three types of surfactants have been reported to be DR effective. They are ionic, nonionic and zwitterionic surfactants. The ionic surfactants have two sub-types: cationic and anionic. Cationic surfactants have positively charged amphiphilic structures. Cetyl trimethyl ammonium chloride (CTAC) and Cetyl trimethyl ammonium bromide (CTAB), for example, are two typical cationic surfactants that are DR effective with the addition of
appropriate counterions. An extensive study of cationic surfactants as DRAs was conducted by Chou [58]. The study covered the effects of temperature, chain length, head-group, mixed surfactants, structure of counterions, concentration, pipe diameter, etc. Anionic surfactants are also DR effective. Sodium oleate (0.2% by weight) with KCl (3.5%-10%) in water showed more than 80% DR in a smooth tube of 1 inch ID [59]. However, little research has been done on anionic surfactants as DRA’s because they react with Ca$^{2+}$ and Mg$^{2+}$ ions present in most water supplies and form precipitates, and thus lose DR effectiveness [5]. Nonionic surfactants are less sensitive to ions dissolved in water because they do not carry any charge. Nonionic surfactants with straight chain alkyl groups (C$_x$H$_{2y}$(OCH$_2$-CH$_2$)$_z$-OH, where x is 12 to 18, y is 2x+1 or 2x-1 and z is about 0.5x) are effective DRA’s [60]. Zwitterionic surfactants are a special kind of nonionic surfactant, because they carry both positive and negative charges on one surfactant molecule [61]. The zwitterionic surfactants are biodegradable and thus more environmentally friendly than many cationic surfactants [62, 63]. Mixed surfactants have also been studied for drag reduction. Lin et al. [64] studied the DR of mixtures of cationic surfactants with different alkyl lengths (C$_{22}$ and C$_{12}$). The mixture had a wider effective DR temperature range (4-120 °C) than the cationic C$_{22}$ surfactant alone with counterion.

2.1.2 Surfactant micelles

A typical surfactant molecule consists of a hydrophobic tail and a hydrophilic head. Surfactants form aggregates, namely micelles, when their concentration is higher than a critical micelle concentration (CMC). Figure 2.1 is the phase diagram for aqueous surfactant solution [65]. There is a special temperature called the Kraft Point, below
which the solubility of surfactants is very small, and most of the surfactants exist in an insoluble crystalline state. When the temperature is higher than Kraft Point, the surfactants are soluble. Above CMC, surfactant molecules form spherical aggregates as shown in Figure 2.1 [65]. When the concentration is above the CMCII line, spherical micelles change to TLMs or vesicles.

TLMs are much larger than the spherical ones. Both have diameters of about 5nm [66], due to the length of the alkyl chains. Hydrodynamic radii of micelles of some commercial cationic surfactants were determined by dynamic light scattering [67]. The hydrodynamic radii were in the range of 20-35nm.

2.1.3 Effects of counterions

Counterions promote the growth of TLMs in cationic surfactants, which is necessary for DR. The counterions can neutralize or disperse the electrostatic repulsion between the intra-micellar positive ionic headgroups [5]. Organic counterions with hydrophobic aromatic groups can penetrate into the hydrophobic part of the micelle. This increases the surfactant packing parameter and promotes the growth of TLMs [68]. Figure 2.2 is a schematic showing a section of the elongated threadlike micelle formed by an alkyltrimethylammonium chloride surfactant in the presence of sodium salicylate [69]. The phenol ring is located inside the hydrophobic core of the micelle, while the carboxylic group lies between the positively charged headgroups of the cationic surfactant. TLMs in solution can be directly observed by the technique of cryo-TEM [17, 26, 41, 64, 65, 70-73]. Figure 2.3 shows threadlike micelle images taken by cryo-TEM [63]. The threadlike micelle length can reach up to a few micrometers [68]. It is generally
believed that threadlike or TLMs are necessary for surfactant solutions to be drag reducing [5].

The ratio (\(\xi\)) of counterion to ionic surfactants also affects the formation of threadlike micelles and DR effectiveness. Lu et al. [71] studied the effect of molar ratio of counterion-to-surfactant on the viscoelasticity and DR effectiveness of cationic surfactant solutions. They found that viscoelasticity and drag reducing effectiveness increase with increasing \(\xi\). In one surfactant series, the threadlike micellar network became denser with increasing counterion/surfactant ratio, which was observed by cryo-TEM images.

For the Arquad S-50/NaSal (sodium salicylate) system, A higher \(\xi=2.5\) induced a higher DR effective upper temperature limit than \(\xi=1\) [68]. This effect was also observed in the Arquad 16-50 (5mM)/ 3,4-dimethylbenzoate (5mM) system and in the Arquad 16-50 (5mM)/ 3,4-dichlorobenzoate (5mM) system [17]. The higher \(\xi\) also apparently changed the viscoelastic Arquad S-50/NaSal (\(\xi=1\)) solution to become nonviscoelastic with increased branched threadlike micellar microstructure at \(\xi=2.5\) [17, 68, 74]. Similar results were observed by Usui et al. [75]. At very high molar ratios of counterion to surfactant. They suggested a special drag-reducing state, which gave a remarkable DR but showed very weak viscoelasticity.

2.2 Rheology of drag reducing surfactant solutions

It has been suggested that the viscoelasticity is related to DR and that elastic properties help to prevent the formation of turbulent eddies and thus the kinetic energy from dissipating [58, 59, 71, 76]. The rheology of drag reducing surfactant solutions has been
studied to examine the mechanism of DR ability of surfactant solutions. Viscoelasticity (like first normal stress difference and swirl recoil), shear-induced structure (SIS) and high extensional viscosity are observed in many DR surfactant solutions. Many researchers, (Savins [59], Chou [58], Bewersdorff [76] and Lu [77]) proposed that the viscoelasticity is related to DR. It was suggested that elastic properties of the solutions help to prevent the forming of turbulent eddies and thus the kinetic energy from dissipating. But exceptions have been reported [74].

Nash [78] used the swirl decay time (SDT) to characterize viscoelasticity. Smaller the SDT indicated greater viscoelasticity of the solution. Elson [79] found that shorter SDT correlated well with the critical wall shear stress for loss of drag reduction. The first normal stress difference ($N_1$) is, however, a more accurate way to characterize viscoelasticity.

At low shear rates, drag reducing surfactant solutions may have Newtonian or shear thinning behaviors, but in most cases the shear viscosity suddenly increases as shear rate increases to some critical value due to shear-induced structure (SIS) of the micelles [63]. SIS was also proposed to be responsible for DR effectiveness [30]. However, drag reducing surfactant solutions without viscoelasticity or SIS have been observed [74]. Qi and Zakin [80] suggested that high extensional/shear viscosity ratio instead of SIS or viscoelasticity may be a requirement for surfactant solutions to be drag reducing, but there are exceptions to this also [63].
2.3 Heat transfer reduction

While surfactant solutions are DR effective, their heat transfer ability is low compared with water. Aguilar et al. [45] examined the coupling issue between drag reduction and heat transfer reduction (HTR). They found the ratio between the heat transfer reduction and drag reduction was nearly constant from the onset of DR to the departure from the asymptotic regime. They concluded that heat transfer and drag are coupled. They [46] also used solutions with viscosity close to water to determine the maximum heat transfer reduction asymptote, and found the ratio of maximum heat transfer reduction asymptote to maximum drag reduction asymptote was 1.06, independent of Reynolds number. This reduced heat transfer ability is unfavorable in applying DR surfactant solutions to DHCS. So it is critical to recover the heat transfer ability temporarily in regions where high heat transfer ability is desired as in heat exchangers.

Although the nature of the drag reduction and heat transfer reduction in drag reducing surfactant solutions are complicated, the heat transfer reduction may be related to two characteristics of turbulent drag reduction flows. In drag reducing surfactant solutions, the viscous sublayer region is $0 < y^+ < 11.6$, whereas it is $0 < y^+ < 5$ in Newtonian fluids [81]. This thickened viscous sublayer of the drag-reducing flow has a greater thermal resistance between the wall and the bulk fluid, and therefore decreases the heat transfer ability of the solution [54]. Another observation is that the velocity fluctuations in the radial direction in turbulent flow are greatly suppressed [47, 82]. By using particle image velocimetry, Kawaguchi [49] also found the strong vorticity fluctuation near the
wall disappeared in a drag reducing surfactant solution. The suppressed radial velocity fluctuations reduce the mass and heat transfer ability of the fluid in the radial direction [54].

2.4 Disturbing devices

Since the thickened viscous sublayer and the suppressed radial velocity fluctuations of drag reducing surfactant solutions are two factors causing heat transfer reduction, methods that can either thin the viscous sublayer or intensify the radial velocity fluctuation can increase the heat transfer locally. Many disturbing methods have been proposed to enhance the heat transfer ability of surfactant solutions.

Compared with a straight pipe, helical pipes (Figure 2.4(a)) produce significantly higher friction factors and heat-transfer coefficients of surfactant solutions. Both heat transfer and turbulent drag increase with increasing curvature ratio [25]. A fluted inner tube heat exchanger (Figure 2.4(b)) enhanced heat transfer for a cationic surfactant solution at Reynolds number of 10,000-50,000, but the pressure drop penalty for heat transfer enhancement of the cationic surfactant solution flowing through the fluted tube was moderately high [55]. Wire coils (Figure 2.4 (c)) of different diameters also increase the heat transfer coefficients [83]. Grooved tubes (Figure 2.4(d)) were also studied to enhance heat transfer of surfactant solutions [84]. No HTR was observed in some velocity range in the grooved tube with ridge of narrow pitch. A row of low-profile vortex generators (Figure 2.4(e)) in the span-wise direction on the heating surface was tested by Zhou et al. [57] to enhance heat transfer in a drag-reducing fluid
(CTAC/NaSal). The average Nusselt number was increased by about 170% for Re=7,000, 12,000 and 16,200.
2.5 Pulsating flow

The enhancement of heat transfer by pulsating flow has long been studied in chemical engineering. The effect of pulsations on the overall heat transfer coefficient of a shell-and-tube heat exchanger was investigated [85]. Under pulsation flow, the heat transfer coefficient was increased by 31% compared with steady flow. Karamercan [86] also increased the heat transfer coefficient with pulsations. Effects of pulsation amplitudes and frequencies were studied. The enhancement was highest in the transition flow regime. Although pulsating flow can enhance heat transfer, there has been no report on pulsating flow used to enhance heat transfer of drag reducing surfactant solutions.

The enhancement of heat transfer by pulsating flow has been ascribed to three factors, cavitation [87], increased turbulence [87] and forced convection in the boundary layer [86]. Karamercan summarized the three factors. Bubbles may be formed in the fluid due to cavitation when pressure in the liquid drops below the local vapor pressure. This occurs most likely at the hottest point, which is in the boundary layer next to the tube wall, if the main loop fluid is heated. Therefore, the formation and collapse of these bubbles agitates the boundary layer and thus enhances heat transfer. Pulsation increases the axial flow periodically in the pulsation cycle, which, in turn, thins the boundary layer in the tube. Also the formation of eddies due to the periodic pressure variations introduces convection in the boundary layer.
2.6 Breaking TLMs

Since the threadlike structures of surfactant micelles are essential to drag reduction and thus to heat transfer reduction, using mechanical devices to destroy or degrade the threadlike surfactant structures is another option [80]. Metal grids installed in the flow tube of a CTAC solution increased the heat transfer ability [88]. Three types of wire mesh of different wire diameter and opening space were evaluated for their effect in promoting heat transfer and the corresponding pressure loss in a two-dimensional channel [56]. The heat transfer coefficient in the region downstream of the mesh was improved significantly. An overall evaluation was conducted relating effective heat transfer enhancement with the cost of pressure loss. An equivalent length of about 162 hydraulic diameters of pressure loss was required in order for heat transfer to be enhanced to approach values for water.

Static mixers (Figure 2.5(a)) and honeycombs (Figure 2.5(b)) were also studied to break up the microstructures of surfactant solution [33]. Static mixers and honeycombs were installed at the entrance. The effects of mixer length and the recovery time of TLMs were also investigated. A 15-element static mixer (type A) enhanced the heat transfer ability of both a cationic and a mixed zwitterionic/anionic DR solution with a modest pressure drop penalty, about four times the pressure drop of water with no disturbing devices. In contrast, the honeycomb did not enhance the heat transfer ability of either solution very much, although the pressure drop was low. To break the TLMs, ultrasonic energy was also studied to enhance heat transfer [89]. This method was effective on
solutions of Ethoquad T13-50/NaSal and of SPE98330/HCHO/Trilon A but was not economical in energy cost.

The recovery time for nanostructure of the cationic DR solution is short and it generally decreases with increasing temperature [33, 90]. Gasljevic et al. studied the recovery of the drag-reducing properties of a cationic surfactant solution and a nonionic surfactant solution after degradation by mechanical stresses [90]. The recovery time was dependent on the temperature and the concentrations of surfactant and counterion but was independent of the flow velocity. The recovery time was shorter at higher concentrations of surfactant and counterion and at higher temperature.

### 2.7 Photo-responsive counterions

Heat transfer enhancement by intensifying turbulence and by destroying threadlike micelles has been reported, but there have been no methods reported in the molecular scale. The viscosity and gelation of mixtures of hydrophobically modified poly(acrylic acid) (HM-PAA) and a cationic photo-responsive surfactant were studied [91]. The hydrophobic *trans* form, with a planar azobenzene group, had a maximum viscosity of $5.6 \times 10^4$ cP observed. Upon UV light irradiation, the *trans* form was converted to the *cis* form, which had a lower viscosity of $2.2 \times 10^3$ cP. The effects of azobenzene-modified cationic surfactant (4-butylazobenzene-4'-oxyethyltrimethylammonium bromide) (AZTMA) on a threadlike micellar solution of CTAB/NaSal was studied by Sakai et al. [92]. The network of TLMs in the *trans*-AZTMA solution resulted in a very high viscosity. This high viscosity was significantly decreased upon UV light irradiation. This photo-induced viscosity change was reversible between the *trans-* and *cis*-AZTMA
solutions. The authors explained that the bulky structure of *cis*-AZTMA is likely to disrupt the structure of TLMs.

The syntheses of such photo-responsive fluids are generally multi-step processes, which are both labor- and time-consuming. This demanding synthesis makes the availability of photorheological fluids limited to a few select research groups. And the scaling up of the synthesis makes it even less practical for commercial applications [93]. So there is a need to develop commercially available photorheological fluids. Two such systems have been reported.

The first one is a simple class of photorheological fluids developed by Ketner *et al.* [93] The fluids can be prepared from relatively inexpensive chemicals. The fluids consist of the cationic surfactant, CTAB, and the light-responsive organic derivative, *trans*-ortho-methoxycinnamic acid (OMCA). Aqueous mixtures of CTAB (60mM)/*trans*-OMCA (50mM) in basic solution self-assembled into long, TLMs. As a result, the fluid viscosity was about 10,000 times that of water. Upon irradiation by UV light (280 to 400nm), *trans*-OMCA underwent a photoisomerization from its *trans* to its *cis* form, which had much weaker binding ability to CTAB. This resulted in transforming the large TLMs into smaller micelles, which was confirmed by SANS. The smaller micelles in turn resulted in much lower viscosity, that is, close to that of water. So, the threadlike micelle structure and hence the viscosity were changed dramatically by the irradiation with UV light.

This process is irreversible, or the reverse may take a very long time. However, this transformation from *cis* to *trans* can be catalyzed by iodine [94, 95]. The mechanism for
cis/trans isomerism is assumed to be a three-step process involving attachment of an iodine atom, an internal rotation, and a detachment of the iodine atom [96].

A second photorheological fluid was developed with reversible viscosity change by Raghavan et al. [97]. The new surfactant/counterion system consisted of a cationic surfactant, erucyl bis(hydroxyethyl-methyl) ammonium chloride (EHAC), and an organic moiety, trans-4-phenylazo-benzoic acid (trans-PABA).

The initial 40 mM EHAC (40mM)/PABA (22mM) solution has a low viscosity. When irradiated with UV light (320-360nm), trans-PABA isomerizes to cis-PABA and the zero-shear viscosity increases 10,000-fold. When the fluid is irradiated with visible light (420-460nm), the isomerization is reversed and the fluid viscosity is restored to its initial value. So a reversible photorheological transition was developed using light sources of different wave lengths. The above system therefore is promising in controlling the heat transfer ability and DR ability of drag reducing surfactant solutions.
2.8 Figures

Figure 2.1 A simplified phase diagram for aqueous surfactant solutions.

Reference: [65]
Figure 2.2 Schematic of WLM structure of quaternary alkyltrimethylammonium chloride with NaSal counterion.

Reference: [69]
Figure 2.3 Cryo-TEM images of 5 mM EO12/7.5 mM NaSal in water and in 20% EG/W (inset) at 25 °C.

Reference: [63]
Figure 2.4. Disturbing devices reported.

Note: (a) helical pipes [25], (b) fluted inner tube [55], (c) wire coils [83], (d) grooved tube [84], (e) vortex generators [57].

Figure 2.5 Micelle breakers.

Note: (a) static mixers, (b) honeycomb [33].
CHAPTER 3: Experimental Methods

3.1 Materials

Ethoquad O/12 PG (EO12, donated by Akzo Nobel) was used as the surfactant in this dissertation. It is a mixture of alkyl bis(2-hydroxyethyl)methyl ammonium chlorides (75 wt%) and propylene glycol (25 wt%). Composition of the alkyl groups in EO12 are approximately 82% oleyl, 12% saturated C16, 4% saturated C14, and 1% saturated C12.

Sodium hydroxide (NaOH) and hydrochloric acid (HCl), diluted as needed, were used to adjust pH of all solutions in this dissertation. NaOH (purity > 98.6%) was purchased from Mallinckrodt Chemicals. HCl (concentration > 73.1%) was purchased from Fisher Scientific.

3.2 $^1$H NMR

$^1$H NMR spectra provide information that helps to identify the chemical and its configuration. Information of the binding of counterions with surfactants can also be extracted from $^1$H NMR spectra. Samples in this dissertation were prepared in deuterium oxide (D$_2$O). In some cases, dimethyl sulfoxide-d$_6$ (DMSO) was used to dissolve aggregated structures in the solution. Experiments were performed at ambient temperature with a Bruker DPX 400 MHz NMR spectrometer in the Department of Chemistry at The Ohio State University.
3.3 Rheology

Rheological experiments were carried out on an ARES rheometer (TA Instruments). The shear viscosity ($\eta$) and first normal stress difference ($N_1$) as functions of shear rate were measured on the rheometer. A Couette tool was used for the viscosity measurements at room temperature. The bob of the Couette tool has a 25 mm outer diameter and a 32 mm length and the cup has a 27 mm inner diameter. A cone-and-plate geometry with a 50 mm ID and a 0.02 rad cone angle was used to measure $N_1$ and also $\eta$ vs. shear-rate at different temperatures. The temperature was controlled by connecting a circulator (NESLAB RTE-111 with 50% ethylene glycol as coolant) to the plate. Figure 3.1 is a photo of the ARES with cone-and-plate tool installed and cooling circuit connected. The measured $N_1$ readings were corrected for inertial effects according to the following equation [98]:

$$N_{1\text{ corrected}} = N_{1\text{ measured}} + 0.15\rho\omega^2 R^2$$

where $\rho$ is the density of the solution, $\omega$ the angular velocity and $R$ the radius of the cone.

3.4 Zeta potential and dynamic light scattering

Zeta potential and dynamic light scattering were measured using a Malvern Instruments Zetasizer Nano-ZS with backscatter detection at 173°. Samples were loaded in disposable optical cuvettes with 1 cm path length and equilibrated at 25°C. The laser wavelength on the instrument was 532 nm. The correlator on the instrument probed times of 500 nanoseconds and greater. More details have been described previously [99].
3.5 Cryo-TEM

Cryo-TEM studies on selected samples were carried out at the Technion-IIT’s Laboratory for Advanced Microscopy. Cryo-TEM sample preparation was carried out in a controlled environment vitrification system at 100% relative humidity at desired temperatures. A small drop of the studied solution was applied on a perforated carbon film supported on a copper electron microscope grid, and then blotted by filter paper into thin films about 10-30 nm thick. The grid was then plunged quickly into liquid ethane near its freezing point (~ 90 K) to vitrify the liquid and avoid crystallization and was then transferred to the low temperature stage of the TEM [73].

3.6 Light sources and irradiation

A 100 W Black-Ray® long-wave UV lamp (broad band centered at 365nm, Figure 3.2) was used as a UV source to irradiate light-sensitive samples. A 15 W LED lamp (radiation peaked at 450nm, Figure 3.3) were used as a visible light source to irradiate light-responsive samples. Before irradiation, all foam on the surface was removed so that light was not blocked. Samples were continuously stirred with a magnetic stirrer during irradiation. The experimental setup for UV irradiation is illustrated in Figure 3.4.

3.7 Recirculating system

A schematic of the recirculation system for drag reduction and heat-transfer experiments is shown in Figure 3.5. Figure 3.6 is a front view of the recirculation system. The system consists of a reservoir tank, a pump, two heat exchangers, an electric heater, a chiller, two circulators, a magnetic flow meter (TOSHIBA LF404), a number of
T-type thermocouples, and a series of pressure transmitters (OMEGA PX2300 series). The shell side of the tube-in-tube heat exchanger has two circulators (NESLAB RTE-111 and VWR 1160) connected in series, while the shell side of the fluted tube-in-tube heat exchanger is connected to a chiller (Bay Voltex). All the tubes, pipes and heat exchangers are insulated with Nomaco K-Flex polyolefin to minimize heat exchange with the environment. The pumping system consists of a centrifugal pump (PROCON) with a motor controller (BALDOR Adjustable Speed Drive) to regulate the pump rotation in the range of 0 to 1969 rpm. The flow rate (0.04 to 0.35 L/s) is monitored by a flow meter.

An electric heater (TrueHeat 1500W) maintains the main loop temperature from room temperature up to ~ 50°C. The chiller in the annulus loop of the fluted tube-in-tube heat exchanger (with a coolant of 50% ethylene glycol and 50% water) cools and maintains the temperature of the main loop. The temperature of the shell side of the tube-in-tube heat exchanger is mediated by the circulators and can be varied from 0° to 90°C. The flow rate in the shell side is preset for each experiment to keep the heat transfer resistance on the shell side constant. Temperatures at all locations are measured by the thermocouples (T1 through T4 and T9 through T12).

The differential pressures of straight pipe sections are measured by the pressure transmitters (P1 through P10). Transmitters P1 through P9 measure consecutive sections of straight pipe. P1 measures the pressure difference across a section of 50 pipe diameters. P2 measures the differential pressure across a pipe section of 180 diameters, including the tube-in-tube heat exchanger. P3 through P9 each measures differential pressures across 80 diameter lengths downstream of the tube-in-tube heat exchanger.
The recirculation loop has a total length of about 25 m and can hold up to 16 L of liquid. The smooth stainless pipe has an inner diameter (ID) of 10.2 mm and an outer diameter (OD) of 12.7 mm. The reservoir tank has a volume of 14 L. The 0.914 m long tube-in-tube heat exchanger has the same tube diameter. The ID of the outer shell is 50 mm. All heat transfer measurements were taken on the tube-in-tube heat exchanger. All the thermocouples, pressure transmitters and flow meters are connected to the data acquisition system detailed by Ge [99].

### 3.8 Drag reduction and heat transfer

To obtain %DR, pressure drops were measured in a range of flow rates at fixed temperatures. The friction factor was calculated according to Equation 2:

$$f = \frac{\Delta PD}{2 \rho LV^2}$$

where $f$ is the friction factor, $\Delta P$ the pressure drop across the test section, $D$ the inner diameter of the pipe, $\rho$ the density of the solution, $L$ the length of the test section, and $V$ the mean flow velocity. Since $\rho$ was essentially identical for the solutions and the solvent (water), the extent of DR (relative to water) could be calculated according to Equation 3:

$$\% DR = \frac{f_{water} - f}{f_{water}} \times 100\%$$

where %DR is percent drag reduction, $f_{water}$ the friction factor of water. For direct comparison, $f_{water}$ and $f$ were taken at the same solvent Reynolds number ($Re$). $f_{water}$ was measured and the data fit the von Karman Equation for water flowing in smooth circular...
pipes (Equation 4) at $Re>10,000$. This equation was used for subsequent calculations of $f_{water}$:

$$\frac{1}{\sqrt{f_{water}}} = 4.0 \log \left( Re \cdot \sqrt{f_{water}} \right) - 0.4$$  \hspace{1cm} (4)$$

Heat loss per unit time in the annulus and heat gain per unit time in the inner tube were measured to ensure they were balanced. The difference was generally less than 5% and was mostly less than 3%. The average of these two quantities was used to calculate heat transfer coefficients. The inlet temperature ($T_3$) was controlled to ± 0.3 °C, and the log-mean temperature difference between the annulus and tube was controlled at 35 ± 0.3 °C. Thermocouple (T4) at the exit of the tube-in-tube heat exchanger was placed at the center of the flow to measure the mean temperature of the fluid. However, this measurement was complicated by a radial temperature gradient established in the fluid once it got heated by the inner wall of the heat exchanger. Therefore, a static mixer was placed just upstream of T4 so that the fluid was well-mixed before reaching that point. Good heat balances could then be obtained under approximately steady-state conditions. The modified Wilson-plot method was used to calculate the heat transfer coefficient and Nusselt number ($Nu$) of the solution [54]. Percent HTR (relative to water) was then calculated by Equation 5:

$$\%HTR = \frac{Nu_{water} - Nu}{Nu_{water}} \times 100\%$$  \hspace{1cm} (5)$$
where \( \%HTR \) is percent heat transfer reduction, \( Nu_{\text{water}} \) is the Nusselt number of water. \( Nu_{\text{water}} \) and \( Nu \) were taken at the same solvent \( Re \). The physical properties of water were used to calculate \( Re \) values.

### 3.9 Water baselines

To validate the drag reduction and heat transfer measurements, baselines of water were obtained and were compared with existing correlations. The \( f_{\text{water}} \) was measured and the data were in agreement with the von Karman Equation (Equation 6) for water flowing in smooth circular pipes at \( Re>10,000 \) (Figure 3.7). Therefore, this equation was used to calculate subsequent \( f_{\text{water}} \) and \( \%DR \).

\[
\frac{1}{\sqrt{f_{\text{water}}}} = 4.0 \log\left(Re \cdot \sqrt{f_{\text{water}}} \right) - 0.4
\]

(Equation 6)

Experimental results for \( Nu \) vs. \( Re \) for water at 10 °C for \( Re > 10,000 \) were also in good agreement with the Dittus-Boelter equation (Equation 7) for water heated in a smooth tube (Figure 3.8). Therefore, this equation was used to calculate subsequent \( Nu_{\text{water}} \) and \( \%HTR \).

\[
Nu = 0.023Re^{0.8}Pr^{0.4}
\]

(Equation 7)

where \( Pr \) is the Prandtl number, defined as the ratio of viscous diffusion rate to thermal diffusion rate.
3.10 Figures

Figure 3.1 ARES (TA Instruments) with cone-and-plate tool installed and cooling circuit connected.
Figure 3.2 100 W Black-Ray® long-wave UV lamp (broad band centered at 365nm).
Figure 3.3 15 W LED lamp, with radiation peak at 450nm (upper: power off, lower: power on)
Figure 3.4 Experimental setup for UV irradiation on a sample solution.
Figure 3.5 Schematic of apparatus for drag reduction and heat transfer experiments.
Figure 3.6 Front view of the recirculation system.
Figure 3.7 Experimental Fanning friction factor compared with von Karman Equation.
Figure 3.8 Experimental Nusselt number compared with Dittus-Boelter Equation.
CHAPTER 4: A Surfactant Micelle System with Unique Responses to pH

4.1 Introduction

Some studies have shown that the formation and growth of surfactant TLMs are dependent on solution pH. Kawasaki et al. [100] reported that reversible transformation from long fibrous micelles to vesicles of oleyldimethylamine oxide can be controlled by changing the solution pH, which affected the degree of protonation of the surfactant. Vesicles of some sugar-based Gemini surfactants were also found to transform to threadlike micelles when the pH was tuned from neutral to acidic [101, 102]. While these pH-dependent micellar phase behaviors are due to dissociation or protonation of the functional groups on the surfactants, organic counterions (or hydrotropes) that are sensitive to pH can also induce phase transitions of cationic surfactant micelles. Low pH values enables isomers of phthalates to bind with Kemamine Q-2803C [58] and cetyltrimethylammonium bromide (CTAB) [103] to form threadlike micelles, which were absent at high solution pH. Similar dependence of micelle behavior on solution pH was also observed in the mixture of N-erucamidopropyl-N,N-dimethylamine and maleic acid [104]. The CMC was also found to be affected by pH. For example, the CMC of dodecyldimethylamine oxide solution decreased with increasing solution pH [105].
The transition between micelles and reverse micelles of some diblock copolymers could be controlled by pH [106, 107] Bütün Chécot et al. [108] reported that the size of diblock copolymer micelles could be manipulated by pH reversibly. But the shape of the micelles formed by the diblock copolymer was globular not threadlike or cylindrical, so these copolymer solutions are not likely to be drag reducing.

Investigations [109-112] of pH effects on DR of high polymer solutions have been conducted in an attempt to study the relationship between the molecular conformation of polymers and the drag reduction effectiveness, since polymer conformation is dependent on solution pH. Frommer et al. [111] found that a more extended structure of the polymer could create greater drag reduction. Islam et al. [113] studied the pH effect on drag reduction on a poly(vinyl alcohol) hydrogel tube surface modified with poly(acrylic acid). The dissociated poly(acrylic acid) made the tube surface hairy and soft at a higher pH value, resulting in a slippery surface and thus a higher drag reduction.

TLMs are essential to surfactant drag reduction ability [5]; and the properties of surfactant micelles are also dependent on solution pH. Therefore, surfactant drag reduction can possibly be controlled by pH variation. However, few studies of the pH effects on drag reduction of surfactant solutions have been reported. Chou [58] investigated the pH effect on drag reduction ability of three solutions of cationic surfactant with three isomers of phthalate respectively. While the solution containing terephthalate counterion is not drag reducing at pH ranging from 4.0 to 11.0, drag reduction of both solutions containing phthalate and isophthalate, respectively, increases significantly with lower solution pH. This dependence is due to ionization of both
carboxyl groups on the isomers of phthalates at high pH level. Too many ionized carboxyl groups result in overlapping of the electron clouds, which destabilized the threadlike micellar structure.

Recently, more and more interest has been directed to stimuli-responsive TLMs to develop “smart viscoelastic fluids” [114], whose viscoelasticity can be controlled via external stimuli such as pH [103, 104, 115, 116], light [92, 93, 117-119], temperature [120-123], and redox reaction [124]. Among those, pH stimulus is of particular interest since it is a simple, fast and reversible method. Surprisingly, few studies on pH responsive TLMs have been reported. Reversible conversion between threadlike micelles and vesicles of oleyldimethylamine oxide can be induced by pH changes, but the slow conversion takes more than 24 h [115, 116]. Rapid conversion can be attained in surfactant-counterion systems [103, 104], but these systems have viscoelasticity only in one lower pH interval of the whole pH range.

In this work, a fast pH-responsive surfactant-counterion micelle system has been developed. At low pH, EO12 (4mM) and trans-OCA (8mM) self-assemble into TLMs, which are essential to viscoelasticity and drag reducing effectiveness. As pH increases into the medium range, the threadlike micelles aggregate into a separate phase. The resulting two phase system is water-like and is not drag reducing. However, as pH increases further to higher level, the threadlike micelles are dispersed in the solution again, and the solution regains its viscoelasticity and drag reducing ability. The micellar phase behaviors were suggested by rheological properties and demonstrated by cryo-TEM.
This pH-sensitive solution consists of amphiphilic surfactant EO12 and *trans*-o-coumaric acid (tOCA) as the counterion. There have been reported other pH sensitive surfactant micellar solutions, whose characteristics, such as micelle size and rheology behaviors, either are monotonic functions of pH or peak at only one pH value. This pH sensitive surfactant micellar solution is unique in that it has threadlike micelles, viscoelasticity and drag reduction capability at both low and high pH values. These unique responses to pH make this solution useful for switchable application in either acidic or basic environments.

4.2 Experimental

4.2.1 Materials

The surfactant used in this pH-responsive system was EO12, detailed in Section 3.1. It is composed of 4mM EO12 and 8mM tOCA as the counterion. tOCA with purity greater than 98.0% was purchased from TCI America. The threadlike micellar system was prepared by mixing EO12 and tOCA in distilled water followed by stirring for 5 min. pH of the solutions was adjusted by adding 0.5 M NaOH or 0.5 M HCl aqueous solutions. An Oakton pH 11 meter was used to determine the pH.

4.2.2 $^1$H NMR

Samples for $^1$H NMR were prepared in D$_2$O. The oily phase was carefully separated and was dissolved in DMSO before $^1$H NMR measurements. Experiments were performed at ambient temperature with a Bruker DPX 400 MHz NMR spectrometer in the Department of Chemistry at The Ohio State University.
4.2.3 Rheology

For normal rheological measurements, pH was adjusted and stabilized before experiments. The solution usually reached a stable pH value soon after HCl or NaOH was added. For reversibility experiments, 0.5 M NaOH or 0.5 M HCl were added alternately to 20 mL solution. Since it is difficult to reach exactly the same pH every time, only approximate pH values were obtained. But this does not compromise the reversibility of the rheological responses to pH changes in principle.

4.2.4 Drag reduction

Drag reduction experiments started from low pH. pH was increased by adding NaOH pellets to the recirculation system. The drag reduction was measured after a stable pH was reached by pumping the solution continuously. Details of the drag reduction experiment are described in Section 3.8.

4.2.5 Other analytical experiments

UV-Vis spectra were collected on a Hewlett-Packard 8452A Diode Array Spectrophotometer after sample solutions were diluted by 100 folds. Zeta potential and DLS measurements were carried out within 24 hours after sample solutions were prepared. Samples for cryo-TEM were prepared at different pH values at Ohio State and shipped to the Technion in Israel for cryo-TEM imaging.

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4.3 Results and discussion

4.3.1 Physical appearances

At different pH levels, 4mM EO12 + 8mM tOCA solution has different appearances as shown in Figure 4.1. The solution at pH 3.7 is colorless and transparent. The letter “A” of the word “STATE” can be clearly seen. At pH 6.7, the solution looks cloudy and no letters can be seen through the milky sample. The suspended micro-drops agglomerate and eventually form a separate phase. Interestingly, in D$_2$O, this separated phase is the upper phase while in H$_2$O, it is the lower phase. This suggests the oily phase density is between that of D2O (1.105 g/cm$^3$) and H2O (0.998 g/cm$^3$). At pH 9.7, the separate phase is re-dissolved and the solution is transparent again with a greenish tint. The letter “N” of the word “UNIVERSITY” can also be clearly seen.

4.3.2 Rheology

The 4mM EO12 + 8mM tOCA solution shows different flow behaviors at different pH levels. At pH 3.6, the solution is viscoelastic and recoils when the stirring ceases, while at pH 6.7, it behaves like a Newtonian fluid. But the solution regains viscoelastic behavior at pH 9.7. $\eta$ and $N_1$ of these three samples at 25°C are illustrated in Figure 4.2. At pH 3.6, $\eta$ first increases at low shear rates due to the well-known SIS of the TLMs [18, 26, 30, 125]. As the shear rate increases over 25 s$^{-1}$, the solution shows shear-thinning behavior. Its $N_1$ has a steep jump in the shear rate range of 25 to 63 s$^{-1}$ and increases slowly up to 356 Pa at 1000 s$^{-1}$, indicating the solution has elasticity at high shear rates. Although the solution at pH 6.7 also shows shear thinning behavior,
suggesting that there might be some particles like globular micelles, no evidence of SIS is observed and the $\eta$ is significantly lower over the shear rate range of 10 to 1000 s$^{-1}$. The absence of SIS and low $\eta$ indicate that there are barely any TLMs in the solution. In addition, its $N_l$ is essentially zero throughout the shear rate range, which also indicates that there are not enough TLMs present. For the solution at pH 9.7, a strong SIS is observed in the shear rate range of 40 to 100 s$^{-1}$. The SIS is followed by shear-thinning behavior, and $\eta$ is almost the same as that of pH 3.6. Its $N_l$ increases steadily with shear rate with a maximum of 465 Pa at 1000 s$^{-1}$, indicating the presence of TLMs.

**Figure 4.3** shows the responses of $\eta$ and $N_l$ to pH at the shear rate of 1000 s$^{-1}$. Both $\eta$ and $N_l$ have two peaks over the pH range of 2 to 12. As pH increases from 2.6 to 3.6, $\eta$ and $N_l$ increase significantly by over 2 and 8 times respectively and reach their local maxima in the acidic range. They drop quickly as pH increases further and become constant in the medium pH range. As pH increases from 8.7, they again increase significantly by more than 3 and 35 times respectively at pH 9.7 and reach their second local maxima in the basic range. As pH exceeds 9.7, both $\eta$ and $N_l$ fall significantly. The dual viscoelastic behavior over the pH spectrum is unique and makes this pH-responsive micellar solution viscoelastic in either acidic or basic systems, and thus potentially useful in systems that are both acidic and basic at different times or locations.

Real applications may require that viscoelasticity can be reversibly switched on and off many times. The rheological responses to pH were tested for 5 cycles of pH changes. **Figure 4.4** shows that the high $\eta$ at low pH is reduced at medium pH and is increased at high pH. **Figure 4.5** shows high $N_l$ at low pH is reduced at medium pH and is increased.
at high pH. Even after 5 cycles of pH changes the reversible changes in $\eta$ and $N$ are still effective with no significant decay.

4.3.3 Cryo-TEM

It is well known that TLMs can induce viscoelasticity as they entangle under shear. So the changes in viscoelasticity correspond to changes in TLMs. At low and high pH levels, EO12 and tOCA are expected to form TLMs, while at medium pH level, different micelle structures are expected. The morphology of possible micelles in their native forms in the solution can be directly observed by cryo-TEM. Figure 4.6 through Figure 4.9 are cryo-TEM images of nanostructures of the 4 mM EO12 + 8 mM tOCA solution at different pH levels. At pH 3.5, randomly curled TLMs permeate evenly throughout the solution. The micelles are long and inter-connecting with each other. In fact, no free ends of the TLMs can be found in the cryo-TEM image. These TLMs do not aggregate and thus make the solution a stable colloidal system. At pH 5.5, however, no TLMs are present. Instead, only very large aggregates like membrane sheets are observed. These large aggregates make the colloidal system cloudy and form a separate phase eventually. At pH 8.0, micelles show up again. The upper image shows a lamellar structure (onion-like structure). Numerous micelles are wrapped up by a number of layers. The lower image shows a similar structure with fewer outer layers but a much larger inner region with densely populated short micelles. One can hardly tell the shape of the micelles. They are probably threadlike micelles encompassed by the lamellar structure. The structures at pH 8.0 are definitely different from those at pH 5.5, and they form a dispersed phase in the solution and also make the solution cloudy. At pH 9.8, well developed TLMs are
observed. They are randomly curled and evenly distributed in the solution. The micelles are long and inter-connecting with each other with no free ends observed. The pH 9.8 solution’s η and $N_r$ are generally larger than the low pH peaks commensurate with the large threadlike micelles. Interestingly, closed loop micelle is also observed close to the center of the image. Since these TLMs are evenly distributed in the solution, they stabilize the solution, forming a transparent colloidal system.

The cryo-TEM images indicate that the state of TLMs, dispersed or flocculated, is critical to the physical appearances and rheological properties of the solution. The question is what determines the state of the TLMs. Electrostatic forces are likely to play an important role in this process. A mechanism is proposed in Figure 4.10. The tOCA has dual pKa; 4.5 for the carboxylic group and 9.6 for the hydroxyl group. At pH lower than 4.5, the majority of tOCA molecules are not dissociated and carry zero charge. When these zero-charged tOCA molecules combine with EO12 molecules, which carry one positive charge, the resulting TLMs have a positive net charge, which prevents the agglomeration of neighboring TLMs due to the electrostatic repulsion. When pH increases to the medium level, the carboxylic group on the majority of the tOCA molecules is dissociated, resulting in one negative charge on the tOCA molecules. If tOCA combines with EO12 at 1:1 molar ratio, these negatively charged tOCA molecules, in turn, neutralize the positively charged EO12 molecules, resulting in the flocculation of TLMs. As pH further increases, the hydroxyl group begins to dissociate, making TLMs negatively charged and re-disperse in the solution.
4.3.4 Zeta potential

The magnitude of zeta potential can be used to evaluate the potential stability of the colloidal system. Since zeta potential is the potential at the slipping plane of a particle, it reflects the sign of the charge the particle carries. With large negative or positive zeta potential, particles tend to repel each other and stay dispersed stably in the system. But if the zeta potential has low values, the electrostatic repulsion is not strong enough to prevent the flocculation of the particles. Zeta potentials for the 4 mM EO12 + 8 mM tOCA solution at different pH levels were measured as shown in Figure 4.11. Zeta potential generally decreases as pH increases. The zeta potential has its greatest value of 33 mV at pH 3.6. At pH 8.7, it declined to zero. As pH increases further, the decrease in zeta potential is not significant. And it levels off at its lowest value of -4.5 mV at pH 10.5. The results show that the micelles carry positive charge at low pH and negative charge at high pH. It also helps to explain the stable dispersion of TLMs due to strong electrostatic repulsion at low pH and the flocculation of TLMs and the observed phase separation due to the weak electrostatic repulsion at the medium pH level. At pH=9.8, the zeta potential is -3.8 mV, which should not be able to prevent the TLMs from flocculating. One explanation is that the zeta potential can not be correctly obtained as the solution at high pH has a green color, which coincides with the color of the laser (532 nm) of the Zetasizer instrument. The stable dispersion of TLMs at high pH might also be maintained by other effects, for example, steric effects, in addition to the electrostatic repulsion. This low positive zeta potential phenomenon in a stable colloidal system was also observed by Ge [26].
4.3.5 $^1$H NMR

The proposed mechanism above has one assumption, which is that tOCA and EO12 combine at a 1:1 molar ratio when the TLMs flocculate and form a separate phase. This ratio can be extracted from $^1$H NMR spectra. The two separated phases of solution at pH 6.6 were analyzed by $^1$H NMR. **Figure 4.12** is the $^1$H NMR spectrum of the oily phase of 4mM EO12 + 8mM tOCA at pH 6.6. Peaks of both tOCA and EO12 appear in the spectrum. The peak group on the left end corresponds to the two hydrogen atoms on positions a and b of tOCA as noted on the figure. The peak area is set at 1.00. Peak “c” is one of the EO12 peaks. It corresponds to the two hydrogen atoms on the second carbon from the nitrogen atom on the long alkyl chain. The peak area is 1.02, which is very close to the peak area of tOCA’s hydrogen atoms at positions a and b, showing that the molar ratio of tOCA to EO12 is essentially 1:1. It should be noted that some other peaks of EO12 do not reflect the same ratio as EO12 has mixed alkyl groups detailed in Section 3.1.

**Figure 4.13** is the $^1$H NMR spectrum of the D$_2$O phase of 4mM EO12 + 8mM tOCA at pH 6.6. In the high ppm region, tOCA peaks are observed. On the other hand, no EO12 peaks were observed in the low ppm region. Only peaks for propylene glycol, which is the solvent of EO12, are observed. This NMR spectrum shows that there are no EO12 molecules dissolved in the D$_2$O phase, which means, all EO12 molecules go into the separated oily phase with tOCA. Since the starting concentration of tOCA is 8mM, twice the concentration of EO12, it is reasonable that excessive tOCA should remain in the D$_2$O phase as tOCA and EO12 at 1:1 molar ratio form the separate oily phase.
4.3.6 Drag reduction

The effects of pH on drag reduction capability of EO12 + tOCA were also studied at two concentrations (4 mM/8 mM and 2.7 mM / 5.4 mM) and at two temperatures (10 °C and 20 °C). Figure 4.14 shows the drag reduction of the solution of 4 mM EO12 + 8 mM tOCA at different pH at 10°C. At pH 3.1, the solution is not drag reducing. Instead, the solution has higher resistance to flow compared with water. As pH increases to 3.56, the solution shows increasing drag reduction capability and reaches a maximum value of 43% at Re of 13000. It loses DR capability sharply as Re exceeds 13000. As pH still increases, the solution shows much better drag reduction. In the pH range of 4.15 to 9.47, DR capability reaches high values at Re of 10000, and maintains 70% as Re increases to the maximum values the experiment can reach. When pH increases to 9.99, the solution suddenly loses its DR capability totally. As pH increases to higher values, the solution regains its DR capability. But the DR capability is not as strong as that in the pH range of 4.15 to 9.47. However, the DR capability can not maintain its high values at high Re, it starts to decrease at Re of 12000 and 16000 for pH 10.67 and 10.88 respectively. The DR capability decreases still further as pH increases to 11.91, at which the maximum %DR is only 38% at Re of 13000.

So the DR capability of the solution of 4 mM EO12 + 8 mM tOCA depends heavily on pH. It starts from negative, increases to maxima, disappears, restarts and decreases as pH increases from 3.10 to 11.91. This dependence is reflected in Figure 4.15, which shows the DR of the solution 4 mM EO12 + 8 mM tOCA against pH for different Re at 10°C. When the solution is drag reducing, its DR capability increases with Re.
Figure 4.16 shows the drag reduction of the solution of 4 mM EO12 + 8 mM tOCA at different pH at 20°C. Generally, the dependence of DR capability on pH is similar to that at 10 °C. At pH 2.73, the solution is not drag reducing, rather the solution has higher resistance to flow than water. As pH increases to 3.29, the solution shows increasing drag reduction capability and reaches a maximum value of 56% at Re of 22000. As pH increases further, the solution shows much better drag reduction. In the pH range of 4.64 to 8.55, DR capability reaches values of 70% or greater at Re of 10000 and above. When pH is increased to 10.67, the DR capability decreases at Re greater than 18000. With further pH increase to 10.83, the solution regains its good DR capability. The DR capability again decreases as pH further increases to 11.93. The maximum %DR is only 51% at Re of 27000.

The dependence of DR capability on pH at 20°C is shown in Figure 4.17. There is no sudden loss of DR capability in the entire pH range as seen in Figure 4.15 for 10°C. This is probably due to the higher solubility and flexibility of the separated oily phase for medium pH at higher temperature. The separated phase is dispersed in the system by the high shear stresses in the pump and higher temperature softens the dispersed oily particles to take fiber-like shapes, which might induce drag reduction. This mechanism might be similar to the reduced pressure loss of turbulent flow of wood pulp fiber suspensions that were observed by Forrest and Grierson [1]. This mechanism might also help to explain the good drag reduction at medium pH levels, where the solution eventually separate into two phases and loses viscoelasticity as shown in Figures 4.1 through 4.9.
DR experiments were also carried out for the solution at a lower concentration (2.7 mM EO12 + 5.4 mM tOCA). Figure 4.18 shows the drag reduction of the solution of 2.7 mM EO12 + 5.4 mM tOCA at different pH levels at 10°C. At pH 2.14, the solution is not drag reducing. Instead, the solution has greater resistance to flow than water. When pH increases to 3.36, the solution shows increasing drag reduction capability and reaches a maximum value of 62% at Re of 8500. It loses DR capability sharply as Re exceeds 8500. At pH 4.85, the solution loses its DR capability completely. As pH increases to the range of 5.61 to 6.77, the DR capability is improves. It reaches a maximum in the pH range of 7.97 to 9.68. DR capability reaches high values at Re of 10000, and maintains 70% as Re increases to the maximum values the experiment can reach. As pH further increases to 10.83 and to 11.47, the DR capability decreased gradually. %DR has a maximum value of 60% at Re of 12000 and 25% at Re of 11000 at pH 10.83 and 11.47 respectively.

The dependence of DR on pH is shown in Figure 4.19, which shows the DR of the 2.7 mM EO12 + 5.4 mM tOCA solution against pH for different Re at 10°C. Generally, the solution has two DR effective regions through the entire pH range. In the pH range of 3.94 to 4.85, the DR capability has a gap. In the pH range of 2.14 to 3.94, the solution shows higher DR capability at lower Re. The low drag reductions at high Re are because of less resistance to mechanical shear degradation. However, when the solution is drag reducing at pH above 5, its DR capability increases slowly with Re.

Figure 4.20 shows the drag reduction of the solution of 2.7 mM EO12 + 5.4 mM tOCA at different pH at 20°C. At pH 2.14 and 3.36, the solution is drag reducing only at low Re (below 9500). At Re greater than 9500, the solution has higher resistance to flow
than water. When pH increases to 3.94, the solution shows very strong drag reducing capability. The %DR is maintained at high values, 70%, throughout the Re range. As pH increases to 4.85, the DR capability suddenly decreases to the level of pH 2.14 and 3.36. It reaches a maximum value of 75% at Re of 6300 and rapidly loses DR capability as Re exceeds 6300. As pH increases to the range of 5.61 to 9.68, the DR capability is restored to a significant level. %DR reaches high levels at low Re and maintains it throughout Re range measured. When pH increases to 10.83, the solution gradually loses its DR capability at high Re. As pH increases to 11.52, its DR capability is not as significant as that in the pH range of 5.61 to 9.68. The maximum %DR is only 40% at Re of 22000.

The dependence of DR capability on pH is shown in Figure 4.21, which shows the DR of the solution 2.7 mM EO12 + 5.4 mM tOCA against pH for different Re at 20°C. Generally, the solution also has two DR effective regions through the entire pH range. At the pH 4.85, the solution is not DR. In the pH range of 3.36 to 4.85, the solution shows higher DR capability at lower Re. This is also true for the pH range of 5.6 to 9.68. For pH 10.83, %DR starts to decrease at high Re. For the low Re of 7500, the solution is drag reducing throughout the pH range.

For the solution of 4 mM EO12 + 8 mM tOCA, the DR capability has two effective regions through the entire pH range at 10 °C. However, there is no significant DR gap at 20°C. For the 2.7 mM EO12 + 5.4 mM tOCA solution, the DR capability has two effective pH regions at both 10 °C and 20 °C. The DR gap is on the low pH side for the solution of 2.7 mM EO12 + 5.4 mM tOCA, while it is at a high pH value for the solution of 4 mM EO12 + 8 mM tOCA at 10 °C.
4.4 Conclusions

The 4 mM EO12 + 8 mM tOCA solution is pH-responsive. The rheological responses of this system to pH are unique in that it has viscoelasticity at both low and high pH levels. The viscoelasticity changes are induced by the morphology changes of TLMs as observed in cryo-TEM images. The solution is viscoelastic when the TLMs are well dispersed, but it loses viscoelasticity and has phase separation when the TLMs flocculate at medium pH. The TLMs’ behavior is dependent on pH, because TLMs have different electric charges at different pH levels as suggested by zeta potentials. The difference in electric charges of TLMs stems from the dual pKa of the counterion tOCA, as tOCA carries different charges at different pH. When it combines with EO12 at 1:1 molar ratio, the net charge of the TLMs varies from -1 to 0 and to +1. When the net charge is non-zero, it generates repulsion between neighboring TLMs and prevents them from flocculating, giving a stable colloid with viscoelastic behavior. The 1:1 molar ratio of EO12 to tOCA in the separated oily phase was confirmed by $^1$H NMR spectra. The solution of two concentrations at two temperatures shows two drag reduction regions over the entire pH range. The discrepancy between DR capability and viscoelasticity might be caused by DR effects induced by deformed particles of the oily phase dispersed by high shear stress and turbulent movements of the fluid. This mechanism will stimulate interest in developing similar systems that have dual or multi peaks of viscoelasticity over the pH range for special applications.
4.5 Figures

Figure 4.1 Appearances of 4mM EO12 + 8mM tOCA solution in vials at pH=3.7 (left), 6.7 (middle) and 9.7 (right).
Figure 4.2 $\eta$ and $N_1$ of solutions at different pH against shear rate.

Note: Diamonds: pH=3.6, squares: pH=6.7, triangles: pH=9.7. Solid symbols: $\eta$, open symbols: $N_1$. 
Figure 4.3 \( \eta \) and \( N_1 \) of 4mM EO12 + 8mM tOCA at shear rate of 1000 s\(^{-1}\) against pH.

Note: solid squares: \( \eta \), open circles: \( N_1 \).
Note: pH values are indicated near each data point.
Figure 4.5 $N_1$ of 4mM EO12 + 8mM tOCA at shear rate 1000(1/s) against pH cycles.

Note: pH values are indicated near each data point.
Figure 4.6 Cryo-TEM image of 4mM EO12 + 8mM tOCA at pH 3.5.

Note: the thick black structure is supporting carbon fiber
Figure 4.7 Cryo-TEM images of 4mM EO12 + 8mM tOCA at pH 5.5

Note: the thick black structures are supporting carbon fiber
Figure 4.8 Cryo-TEM images of 4mM EO12 + 8mM tOCA at pH 8.0.
Figure 4.9  Cryo-TEM image of 4mM EO12 + 8mM tOCA at pH 9.8.
Figure 4.10  Proposed mechanism based on electric static.

Note: the size of the drawing reflects the relative concentration.
Figure 4.11  Zeta potential of 4mM EO12 + 8mM tOCA against pH at 25°C.
Figure 4.12. $^1$H NMR spectrum of the oily phase of 4mM EO12 + 8mM tOCA at pH 6.6.
Figure 4.13: $^1$H NMR spectrum of the D$_2$O phase of 4mM EO12 + 8mM tOCA at pH 6.6
Figure 4.14 Drag reduction of the solution 4 mM EO12 + 8 mM tOCA at different pH at 10°C.
Figure 4.15 Drag reduction of the solution 4 mM EO12 + 8 mM tOCA against pH for different Re at 10°C.
Figure 4.16 Drag reduction of the solution 4 mM EO12 + 8 mM tOCA at different pH at 20°C.
Figure 4.17 Drag reduction of the solution 4 mM EO12 + 8 mM tOCA against pH for different Re at 20°C.
Figure 4.18 Drag reduction of the solution 2.7 mM EO12 + 5.4 mM tOCA at different pH at 10 °C.
Figure 4.19 Drag reduction of the solution 2.7 mM EO12 + 5.4 mM tOCA against pH for different $Re$ at 10°C.
Figure 4.20  Drag reduction of the solution 2.7 mM EO12 + 5.4 mM tOCA at different pH at 20 °C.
Figure 4.21 Drag reduction of the solution 2.7 mM EO12 + 5.4 mM tOCA against pH for different $Re$ at 20°C.
CHAPTER 5: Enhancing Heat Transfer by an HEV Static Mixer

5.1 Introduction

Polymeric DR solutions lose drag reducing effectiveness in pumping because the relatively long polymer molecules are degraded in high shear stress regions of piping systems [29]. Surfactant drag reducing solutions, on the other hand, retain their drag reduction ability even in recirculation systems without the constant addition of surfactant DRAs, because the surfactant threadlike micelles, which are essential to induce drag reduction [5, 30-32], can reassemble after being temporarily broken up by high shear stress [5, 33]. Thus, surfactant DRAs are promising for use in recirculation systems such as DHCS [5, 37, 38].

However, drag reduction is accompanied by heat transfer reduction for both polymeric [42, 44, 126-128] and surfactant [33, 55, 89, 129, 130] DRAs. Heat transfer reduction is found to be always greater than drag reduction for a given Reynolds number [127, 131, 132]. Aguilar et al. [133] examined the coupling issue between DR and HTR for both polymer and surfactant DRAs. They found the ratio between the heat transfer reduction and drag reduction was nearly constant from the onset of DR to the departure from the asymptotic regime. They [46] also determined the ratio of the maximum heat
transfer reduction asymptote to the maximum drag reduction asymptote to be 1.06 for $Re>20,000$.

The mechanism of the reduced heat transfer has been investigated. Sellin et al. [81] found the viscous sublayer region in drag reducing surfactant solutions was significantly thicker than that in Newtonian fluids. This thicker viscous sublayer makes greater thermal resistance between the bulk drag reducing fluid and the wall of the heat exchanger, and therefore decreases the heat transfer ability of the solution [54]. At the same time, the velocity fluctuations in the radial direction in turbulent flow are also greatly suppressed [47, 48], resulting in reduced heat transfer in the radial direction [54].

A few other characteristics of Newtonian turbulent flow were observed to be different in drag reducing flow. With the aid of particle imaging velocimetry, the disappearance of strong vorticity fluctuation [49], and reduced strength and inhibited frequency of turbulent bursts were observed [50, 51]. Reduced wall-normal turbulence intensity was also observed by Laser Doppler velocimetry [52, 53]. In short, the reduced heat transfer is due to the thickened viscous sublayer and the inhibited turbulence, which are caused by TLMs in surfactant drag reducing solutions.

This reduced heat transfer ability is unfavorable in applying DR surfactant solutions to DHCS. So it is necessary to enhance the heat transfer ability locally in heat exchangers of DHCS without incurring a major energy penalty. Many devices have been studied to temporarily enhance the heat transfer ability of surfactant drag reducing solutions either by destroying the threadlike micelles or by disturbing the flow to enhance turbulence. To break threadlike micelle structures of surfactant solutions, ultrasonic energy [89] was
used, and heat transfer was enhanced slightly, but this method was not economical in energy cost, while other methods such as wire meshes [56], static mixers [33], and impinging jets [134] were aimed to temporarily break the threadlike micelles, but actually also disturbed the flow. Their relative contributions to enhanced heat transfer are not clear. To disturb the flow, still other methods employed contracted channel [135], grooved tubes [84], wire coils [83], helical pipes [25], and vortex generators[57]. Fluted tubes [55] were effective with relatively low pressure loss.

However, the secondary flow and vortices generated by these methods are randomly directed, which means there exists mixing in the flow direction as well as in the direction normal to the flow. Since heat transfer in heat exchangers is essentially in the normal direction, mixing in the flow direction does not help enhance heat transfer. Therefore, the brute and unorganized disturbance by the above devices cost unnecessary energy loss by inducing unnecessary mixing in the flow direction. A special static mixer [136], commonly called a high-efficiency vortex (HEV) static mixer, has been designed to generate organized streamwise vortices, which promote mixing in the direction normal to the flow. This static mixer consists of arrays of tabs inclining from the conduit wall in the flow direction at a certain angle, so that streamwise and counter-rotating vortices interconnecting with neighboring ones can be naturally generated at the tab tips. These special vortices are designed to enhance the mixing process and heat transfer between the conduit wall and the bulk fluid. The turbulent flow structure modified by HEV static mixer has been studied. Both intensified and inhomogeneous or anisotropic turbulent structures were observed [137]. Counter-rotating vortices behind the tabs were shown
both by experiments and simulations [138-140]. The HEV static mixer proved to enhance heat transfer and mixing in chemical reactions in integrated chemical reactor-heat exchangers [138, 141, 142].

Due to the organized streamwise vortices, which enhance radial convective transfer, HEV static mixers cost significantly lower pressure drop or energy loss than other conventional mixers to achieve equivalent performance in various applications [143]. Fasano [144] reported that a HEV static mixer required only one twelfth to one third of the pressure drop of other conventional mixers to achieve the equivalent blending performance and thermal mixing efficiency. In some emulsification processes, an HEV static mixer was 1000 times more energy efficient than other mixers [137, 145] It was also energetically efficient in enhancing heat transfer between two immiscible liquid phases in turbulent flow [146].

Surprisingly, HEV has not received attention in enhancing heat transfer in drag reducing flows despite its energetically economical applications in mixing and heat transfer. The effect of a HEV static mixer on the heat transfer of a drag reducing surfactant solution, namely 3 mM EO12+ 7.5 mM NaSal, was studied experimentally and compared with a common inline static mixer. The rheological properties and drag reduction ability of the surfactant solution were also measured.

5.2 Experimental

5.2.1 Materials

The surfactant used in this solution was EO12, described in Section 3.1. NaSal (purity > 99.8%) was purchased from Fisher Scientific. Surfactant/counterion solutions
were prepared for drag reduction and heat transfer experiments by stirring in a container for 8 hours at room temperature by a high shear disperser (Janke & Hunkel IKA Ultra-Turrax SD-45), followed by overnight storage at rest. Smaller solutions were prepared using magnetic stirrers in a beaker before rheological measurements.

5.2.2 HEV static mixer

The inner diameter of the tube-in-tube heat exchanger is 10.2mm. Since the commercially available HEV static mixers from Chemineer Inc are 2 inches or larger, a small HEV static mixer was fabricated. Tabs were first shaped by cutting the wall of a stainless steel tube with a 10mm outer diameter and 9mm inner diameter (purchased from McMaster-Carr), and then were pushed inwards and they formed a 30° angle with the tube wall. As shown in Figure 5.1(a), the isosceles trapezoidal tabs are 5 mm high and 5 mm and 3 mm in the wall base and the end base respectively. A group of three tabs are evenly distributed around the circle of one cross section of the tube. (Figure 5.1(b) is the cross section view of a tab group). Thirty two (32) such groups are evenly spaced at 28mm intervals along the tube. The distance between the wall base of the first tab group and the downstream end of the HEV tube is 868mm, illustrated in Figure 5.2(a). Figure 5.2(b) is the overall view of the 1009mm long HEV static mixer tube, which was inserted inside the tube-in-tube heat exchanger.

For the calculation of $Nu$ for the HEV static mixer, the sum of heat transfer resistances of the heat exchanger wall and the HEV tube was used. Since the HEV tube was tightly fitted against the inner wall of the heat exchanger, the total wall thickness was
assumed to be 3.5mm and the effect of holes that tabs left behind in the HEV tube and the wall-wall interface were ignored.

5.2.3 Helix static mixer

The plastic Helix static mixer, purchased from Cole-Parmer, had 10 helix elements, each element twisted in the opposite helical direction to the neighboring elements. Each element is 10mm long and has an outer diameter of 10mm (Figure 5.2(c)). This Helix static mixer was mounted inside the entrance of the tube-in-tube heat exchanger.

5.2.4 Drag reduction and heat transfer

Drag reduction and heat transfer experiments were carried out on the recirculation system described in Section 3.7. Methods for drag reduction and heat transfer measurements are detailed in Section 3.8.

5.3 Results and discussion

5.3.1 Viscoelasticity and drag reduction of EO12/NaSal (3mM/7.5mM)

Drag reducing surfactant solutions are usually shear thinning and show viscoelastic behaviors [5] such as the first normal stress difference ($N_I$). Figure 5.3 shows the shear viscosity of EO12/NaSal (3mM/7.5mM). This solution showed shear thinning behavior in the shear rate range of $50 \text{ s}^{-1}$ to $1000 \text{ s}^{-1}$ for 10 and 20 °C. The viscosity at 20°C was slightly lower than that at 10 °C, but it was significantly lower at 30 °C, where a shear induced structured in viscosity was observed near $100 \text{ s}^{-1}$. The $N_I$ of EO12/NaSal (3mm/7.5mM) is shown in Figure 5.4. $N_I$ values at 10 and 20 °C increased above $100 \text{ s}^{-1}$ with higher values at 10 °C. At 30 °C $N_I$ was essentially zero (data not shown here) in the
range of shear rates that was measured (0.1 to 1,000 s$^{-1}$), a surprising result in view of Qi et al.’s observation [147] that $N_1$ increased at shear rates near those at which shear induced structure was observed. Figure 5.5 shows the good drag reduction of EO12/NaSal (3mM/7.5mM) from 10°C to 60°C. Drag reduction increased rapidly at solvent Reynolds number of 20,000 for all temperatures and leveled off near 80%. Thus, this solution has a wide range of effective drag reducing temperatures.

5.3.2 Heat transfer reduction of EO12/NaSal (3mM/7.5mM)

Figures 5.6 and 5.7 show the Nusselt number and %HTR of the EO12/NaSal (3mM/7.5mM) solution with no mixer, Helix static mixer and HEV static mixer and Figure 5.6 also shows water with and without HEV static mixer. In the tube-in-tube heat exchanger without any mixer, the solution had very low Nusselt numbers, ranging from 12.3 to 27.9 in the Reynolds number range of 2300 to 22000. Therefore, the heat transfer reduction for this solution was high, starting from 55% at $Re=2300$ and increasing to 83% at $Re=22000$. Compared with %DR at 10°C, %HTR is slightly greater, confirming that the reduction in heat transfer is more significant than that of drag. Figure 5.8 shows the ratio of %HTR to %DR of EO12/NaSal (3mM/7.5mM) at 10°C. Because heat transfer and drag reduction experiments were not carried out simultaneously, the %HTR and %DR were not at the same Reynolds number, so %DR was obtained by interpolation to calculate the ratio. This ratio decreased from 3.0 at $Re=6,300$ and approached 1.1 as the Reynolds number increased to 22,000. This result is in agreement with the result reported by Aguilar et al. [46]
The Helix static mixer slightly increased the rate of heat transfer of the solution (Figure 5.6). The maximum Nusselt number it reached was 39 at $Re=17,000$, which was approximately 1.6 times that without any mixer. The $\%HTR$ was still high near 70% for $Re>12,600$. This Helix static mixer had opposite helical elements. As the fluid passed by, it was first divided and followed the twist of the first element in one direction. When it came to the second element, the fluid was divided again and was forced to follow the twist in the opposite direction. The constant dividing and alternately changing of twisting direction generated disturbances and extra shear stress in the flow. The disturbances should enhance the momentum and mass transfer in the radial direction and thus enhance heat transfer. And, if the shear stress was high enough, the threadlike micelles would be broken, and the solution should become water like and have higher heat transfer ability. While the heat transfer in the Helix mixer region was enhanced, the enhancement over the whole heat exchanger was not significant. Heat transfer reduction was apparently restored shortly downstream of this mixer. A Helix mixer as long as the tube-in-tube heat exchanger could be used to enhance the overall heat transfer throughout the heat exchanger but this would result in extremely high pressure drop across the long Helix static mixer. The pressure drop penalty of this Helix static mixer will be discussed in the following section.

The HEV static mixer with water enhanced the Nusselt numbers, compared with water without the HEV static mixer, especially at the $Re>15,000$ (Figure 5.6). The HEV static mixer with drag reducing solution had Nusselt numbers close to those of water at $Re<10,000$. At $Re=20,000$, it again approached the Nusselt number of water (Figure 5.6).
The Nusselt number with HEV static mixer with drag reducing solution ranged from three to five times that of solution without mixer. This significant enhancement of heat transfer was due to the HEV static mixer’s disturbance to the drag reducing flow. As discussed in the introduction section, tabs in the HEV static mixer cause intensified turbulence and streamwise counter-rotating vortices behind the tabs near the wall [137-140]. The streamwise counter-rotating vortices bring the heated fluid near the wall to the axis of the flow, and at the same time, the wall region is replenished with cold fluid from the center of the bulk flow to receive heat from the wall. Thus, the radial mixing and heat transfer were significantly enhanced. In this HEV static mixer, there were three tabs in each group at one cross section. The three tabs generate three pairs of vortices, that is three streams of fluid flowing from the bulk to the wall and three streams flowing from the wall to the bulk. As the fluid flows downstream, the streamwise vortices also move and become weaker. But when this portion of fluid hits the next group of tabs, new vortices are generated, enhancing radial mixing and heat transfer. This mechanism also explains the higher Nusselt number of water with HEV static mixer.

The high Nusselt number in the low Reynolds number range was unexpected. This might have resulted from the inaccuracy of temperature measurement because of the inhomogeneous temperature distribution of the viscoelastic solution flowing very slowly. The steep increase in the high Reynolds number range might be due in part to the breakup of threadlike micelles at high shear stress, as a high shear zone was observed at the top of HEV tab tips [137].
5.3.3 Pressure drop penalty

Pressure drops across the heat exchanger with mixer mounted and an additional section downstream were measured by P2 (refer to Figure 3.5 recirculating schematic). The total length of this section was 180ID (1836 mm). Figure 5.9 shows that the pressure drop for the 10-element Helix static mixer was three times that of HEV static mixer, although this Helix mixer was only 100mm long. If a Helix static mixer as long as the heat exchanger (914 mm) was used, the pressure drop would be extremely high. So the HEV static mixer was not energetically effective. In contrast, the HEV static mixer had a smaller pressure drop, while it enhanced the heat transfer much more. The pressure drop was also slightly lower than that of water with HEV static mixer. Without any mixer, both water and the solution had very low pressure drop. Figure 5.9 also shows that the maximum Reynolds number that water achieved at the maximum pump rate was 22,700 and 20,100 for no mixer and HEV static mixer, respectively. Although the pressure drop at P2 for solution with HEV static mixer was higher than that of water without mixer, the solution could be pumped at a maximum flow rate of 0.26 L/s ($Re=25,000$) compared with 0.24 L/s ($Re=22,700$) for water. To facilitate the comparison between the solution with HEV static mixer with water without mixer, a performance number, $p$, was defined as:

$$ p = \frac{Nu}{2 \sum_{i=3}^{8} \Delta P_i + \Delta P_2} $$

(8)
where $\Delta P_2$ is the pressure drop of the heat exchanger. $\sum_{i=3}^{8} \Delta P_i$ is the total pressure drop of the 400ID (4080 mm) section downstream of P2.

This pressure drop was doubled to include the pressure drop of the 400ID section upstream of the heat exchanger. Since the total length of the recirculation loop is more than 20 m, this estimation is conservative. **Figure 5.10** shows that as the Reynolds number increased, $p$ for water without mixer decreased to $1.39 \times 10^{-3}$ Pa$^{-1}$, while $p$ for solution with HEV is roughly constant at about $1.39 \times 10^{-3}$ Pa$^{-1}$. This means that for a tube-in-tube heat exchanger with 400ID sections upstream and downstream, the performance of the HEV static mixer was comparable to water without mixer for $Re>20,000$. If the distance between neighboring tube-in-tube heat exchangers is larger than 800ID, solution with HEV would have less energy consumption than water without HEV static mixer to achieve the same Nusselt number for $Re>20,000$ at 10°C. Thus, in longer flow systems, the HEV static mixer with solution will have a larger $p$ than water without mixers. In short, The HEV static mixer enhanced the heat transfer of the drag reducing surfactant solution with a relatively small energy penalty. The tabs of the HEV static mixer generate streamwise vortices, which enhance heat transfer in the radial direction. Few vortices in other directions, which would not be effective in enhancing heat transfer, are generated in the HEV static mixer and therefore, energy is not wasted in generating ineffective vortices, and is mainly used to generate streamwise vortices effective in enhancing heat transfer.
5.4 Conclusions

The surfactant solution, showed viscoelastic behavior at 10 and 20 °C and had excellent drag reducing ability, up to 80%, from 10°C to 60°C. The heat transfer ability of this solution was, however, reduced significantly. The ratio of %HTR to %DR decreased with Reynolds numbers and approached 1.1.

The HEV static mixer mounted in the tube-in-tube heat exchanger enhanced the heat transfer of EO12/NaSal (3mM/7.5mM) significantly throughout the range of Reynolds numbers tested. At high Reynolds number, the Nusselt number was close to that of water without any mixer. The heat transfer enhancement was due to the streamwise vortices generated by the HEV static mixer. The relatively low pressure drop was because the vortices were mainly streamwise. No pressure loss vortices in other directions, which could not enhance the radial heat transfer, were generated.

A Helix static mixer was also used to enhance the Nusselt number of EO12/NaSal (3mM/7.5mM) by destroying the threadlike micelles structures. This mixer may enhance the heat transfer in the mixer region, but did not enhance the overall heat transfer significantly. The extremely high pressure drop was due to the brutal disturbance to the flow and generation of vortices that did not improve heat transfer in the radial direction.

A performance number was used to evaluate the heat transfer ability at the price of pressure loss. Under assumed conditions the HEV static mixer performance number nearly matched that of water without mixer. If the neighboring tube-in-tube heat exchangers were spaced further apart than the assumed distance (800ID), the drag
reducing solution with HEV static mixer should have less energy consumption than water without mixer to achieve the same Nusselt number for $Re > 20,000$ at 10°C.

By adjusting the design parameters, such as the tab angle, the tab group distance and the tab size, even better performance number might be achieved.
5.5 Figures

Figure 5.1 Schematic of HEV static mixer. (a) tab dimensions, (b) cross section view of a group of three tabs.
Figure 5.2 (a) HEV static mixer tab locations, (b) partial view (left) and overview (right) of the HEV static mixer tube, (c) An original 12-element Helix static mixer.
Figure 5.3 shear viscosity of EO12/NaSal (3mM/7.5mM) at 10°C, 20°C and 30°C.
Figure 5.4 $N_1$ of EO12/NaSal (3mM/7.5mM) at 10°C and 20°C.
Figure 5.5. Drag reduction of EO12/NaSal (3mM/7.5mM) at 10°C, 20°C, 30°C, 40°C, 50°C and 60°C
Figure 5.6 Nusselt number of EO12/NaSal (3mM/7.5mM) at 10°C.
Figure 5.7 \%HTR of EO12/NaSal (3mM/7.5mM) at 10°C.
Figure 5.8 Ratio of %HTR to % DR of EO12/NaSal (3mM/7.5mM) at 10°C.
Figure 5.9 Pressure drops at P2 for heat exchanger section with mixers.
Figure 5.10 Performance number of solution with HEV static mixer and water without mixer.
CHAPTER 6: Enhancing Heat Transfer of a Photo-Responsive Micelle System

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6.1 Introduction

TLMs solutions are being considered for use in recirculating systems such as for district heating and cooling (DHC), where their DR properties help to save pumping energy [5]. However, the utility of these solutions in DHCS is limited because the same solutions also have reduced heat-transfer ability compared to pure water [42-46, 127, 128].

It is generally believed that threadlike micelles must be present for surfactant solutions to be drag reducing [5, 30-32]. Qi [54] proposed two mechanisms to explain how threadlike micelles can reduce drag. First, the long micellar chains may help to damp small turbulent eddies and reduce the dissipation of turbulent energy. Second, the alignment of threadlike micelles along the flow may cause anisotropic resistance to
turbulent vortices, resulting in suppressed flow fluctuations in the direction normal to the flow. The latter has been confirmed by Gyr and Buhler [48] and Tamano et al. [52].

Although the causes of reduced heat-transfer are complex, they may be related to two characteristics of DR solutions. First, the viscous sublayer in a viscoelastic fluid can be considerably thicker than in a Newtonian fluid [81]. This thickened viscous sublayer provides greater thermal resistance between the wall of a heat exchanger and the bulk flow of a DR fluid, and thus decreases heat transfer from the fluid to the wall [54]. In addition, threadlike micelles greatly suppress the velocity fluctuations in the radial direction in turbulent flow [47, 48], which reduces heat transfer in the radial direction [54]. Also in the region near the wall, reduced wall-normal turbulence intensity [52, 53], disappearance of strong vorticity fluctuation [49], and reduced strength and frequency of turbulent bursts [50] have been observed in drag reducing surfactant solutions. In short, the properties that allow threadlike micelles to reduce turbulent drag also cause them to negatively impact heat transfer.

Various in-flow devices have been studied to temporarily enhance the heat-transfer properties of a DR fluid, either by destroying threadlike micelles or disturbing the flow. These include fluted-tube heat exchangers [55], wire meshes [56], static mixers [33], metal grids [88], helical pipes [25], low-profile vortex generators [57], and impinging jets [134]. However, each of these devices creates additional resistance to the flow, causing a significant penalty in terms of energy-loss. One alternative to such in-flow devices is the use of ultrasonic energy to enhance heat transfer externally [89], however, this method was also not economical in energy cost.
Since organic counterions promote the growth of threadlike micelles in cationic surfactant systems [5, 10, 11], TLMs can be controlled by manipulating the structure of the counterions. Certain counterions with hydrophobic aromatic groups can bind strongly to cationic micelles with their aromatic rings buried into the hydrophobic core of the micelles [148]. Such binding of counterions neutralizes the charge on the surfactant headgroups and thereby decreases the effective area per headgroup, which in turn promotes the growth of cylindrical micelles at the expense of spherical ones [68]. For optimal binding to micelles, the counterion should be able to orient both its hydrophilic and hydrophobic parts in their favored environments [26, 68, 70, 149, 150]. If the molecular configuration of the counterion is altered by an external stimulus (e.g., light), adsorbed counterions could desorb, and *vice versa*. This aspect is used in the design of light-responsive micelles.

This study describes a new approach for enhancing the heat-transfer properties of drag-reducing micellar solutions. This approach involves the use of light-responsive threadlike micelles. Threadlike micelles can be made responsive to light by incorporating photo-sensitive groups in the structure of the counterions [151-153] or the surfactants [92, 114, 154, 155]. However, these custom-made surfactants are expensive and difficult to synthesize – hence, they are not viable candidates for DR systems. Recently, a range of light-responsive micellar fluids using only inexpensive commercially available components have been developed by Raghavan and co-workers [93, 117]. These fluids showed significant changes in their rheological properties upon exposure to UV light – they were hence termed photorheological (PR) fluids. Of particular interest here is the
system described by Ketner et al. [93], which was a mixture of the cationic surfactant, CTAB and the photosensitive counterion *trans*-OMCA. Mixtures of CTAB and OMCA were viscoelastic and long cylindrical microstructures were indicated by small-angle neutron scattering. When exposed to UV light, *trans*-OMCA was photoisomerized to its *cis* form and, in turn, the micelles became much shorter. These changes occurred because the binding affinity of *trans*-OMCA to CTAB micelles was much stronger than that of *cis*-OMCA.

In this study, drag-reducing fluids have been developed by combining OMCA with the cationic surfactant, EO12. EO12/OMCA solutions contain threadlike micelles and are thus effective at DR and their heat-transfer properties are poor. When the solutions are exposed to UV light (converting OMCA from *trans* to *cis*), the micelles get shortened, as shown here by cryo-TEM. In turn, the DR properties are reduced, but the heat transfer is substantially improved. Thus, our study suggests the possibility of switching a fluid between states conducive to effective drag-reduction and effective heat-transfer. It should be noted that success has not been achieved in reversing the isomerization to restore *trans*-OMCA and regain effective drag reduction. The goal is to switch off and on repeatedly between the two above states. Nevertheless, this counterion is selected due to its low-cost and availability to initiate our study on photo-switchable systems. Studies with photoreversible counterions will be explored in the future. Eventually, it is anticipated that switchable fluids exhibiting a combination of good drag reduction and heat transfer properties will prove attractive for use in recirculating DHCS. A proposed scheme for application of switchable fluids is shown in Figure 6.1.
6.2 Experimental

6.2.1 Materials and sample preparation.

The surfactant used in this solution was EO12, described in Section 3.1. OMCA in its native \textit{trans} form (purity > 99\%) as well as \textit{cis}-OMCA (purity > 98\%) were purchased from TCI America. Surfactant/counterion (4mM/5mM and also 4mM/8mM) solutions for drag reduction and heat transfer experiments were prepared by continuously stirring the solution in a bucket for 8 hours at room temperature with a high shear disperser (Janke & Hunkel IKA Ultra-Turrax SD-45). Sodium hydroxide was used to maintain the pH of the solutions between 8 and 10. The solutions were then left to rest overnight at room temperature. Solutions in smaller quantities were stirred with magnetic stirrers overnight before rheological and other analytical measurements. To minimize exposure to any light, all the solutions were well covered during preparation and storage.

6.2.2 UV-Vis spectroscopy

For UV-Vis spectroscopy, 10 mL of a given solution was placed in a Petri dish and irradiated for specific durations. Before taking UV-Vis spectra, samples were diluted by 100 folds to 0.04 mM EO12 to 0.05 mM OMCA. UV-Vis spectra were collected on a Hewlett-Packard 8452A Diode Array Spectrophotometer.

6.2.3 UV irradiation.

UV irradiation of samples was conducted with a 100 W Black-Ray\textsuperscript{®} long-wave UV lamp, which emits UV centered on the wavelength of 365 nm. For drag reduction and heat transfer experiments, 12 L of solution was divided into 24 portions of 500 mL. Each
portion was held in a beaker and was irradiated by UV under stirring for 30 min. Foams were removed before and during the irradiation.

6.2.4 Cryo-TEM

Samples for cryo-TEM imaging were prepared at Ohio State Campus and were shipped to Technion-Israel Institute of Technology, where further treatments and the imaging were performed. Samples were carefully sealed in vials wrapped with aluminum foil to minimize exposure to light. Details of the cryo-TEM imaging are described in Section 3.5.

6.2.5 Drag reduction and heat transfer

Drag reduction and heat transfer experiments were carried out on the recirculation system described in Section 3.7. Methods for drag reduction and heat transfer measurements are detailed in Section 3.8.

6.3 Results and discussion

6.3.1 UV-Vis spectra

To verify the photoisomerization of trans-OMCA to cis-OMCA by UV irradiation, UV-Vis spectra (Figure 6.2) were determined for a solution of 0.04mM EO12 + 0.05mM trans-OMCA, after different durations of UV irradiation and also for 0.05mM cis-OMCA without surfactant. For wavelengths higher than 220nm, cis-OMCA had two peaks at 256nm and 294nm, and trans-OMCA had two peaks at 270nm and 310nm. The two absorbance peaks of trans-OMCA were significantly higher than those of cis-OMCA. But after the sample was irradiated by UV for 1 min, the two peaks of trans-OMCA
shifted towards lower wavelength and were lower in magnitude. As the UV irradiation time increased, the two absorbance peaks shifted gradually to those of cis-OMCA and their magnitudes also decreased to the levels of those peaks of cis-OMCA after 5 min of irradiation. The presence of EO12 in the sample had no effect on the spectra of trans-OMCA or cis-OMCA (data not shown). The shift of absorbance peaks indicated that trans-OMCA isomerized to cis-OMCA by UV irradiation. The spectra obtained are nearly identical to those reported previously by Ketner et al. [93]. For further studies, sample compositions based on our previous experience with EO12-based drag-reducing fluids was selected. Specifically, a low concentration (4 mM) of EO12 was selected – this is to ensure that the sample viscosity remains quite low (i.e., comparable to water), which is an important consideration for DR systems. An equimolar or higher amount of OMCA was then added to the EO12 sample to induce growth of threadlike micelles.

6.3.2 Rheology

The effects of UV irradiation on the rheology of EO12/trans-OMCA samples were investigated with respect to the first-normal stress difference $N_1$ and the shear viscosity. From earlier work, it is known that for many DR solutions, a large value of $N_1$ at high shear-rates correlates with effective drag reduction. Figure 6.3 shows $N_1$ data at 25 °C for 4 mM EO12 solutions containing 5 mM and 8 mM, respectively, of trans-OMCA.

In the case of the 8 mM trans-OMCA sample, $N_1$ increased to ~ 220 Pa at 1000 s$^{-1}$. There was little loss of $N_1$ after UV irradiation of 100 and 200 s, but after 300 s of UV irradiation, the $N_1$ was reduced to much lower values, only ~ 10 Pa at 1000 s$^{-1}$. The other sample, which had a lower trans-OMCA concentration of 5 mM, showed lower $N_1$
(\sim 20 \text{ Pa}) \text{ even at } 1000 \text{ s}^{-1}. After 300 \text{ s of UV irradiation, the } N_t \text{ of this sample was reduced to essentially zero.}

Data on \( N_t \) were also obtained on the above samples at 10 \degree \text{C (Figure 6.4), which is in the range of the fluid temperatures (\sim 5 to 15 \degree \text{C}) used in district cooling systems. For the 8 mM } \text{trans-OMCA solution, Figure 6.4 shows that the } N_t \text{ values were high before UV irradiation. In fact, the sample was so viscoelastic that the high rotational rate of the plate destroyed the shape of the sample resulting in erratic data at shear rates greater than about 315 \text{ s}^{-1}. At shear rates above 40 \text{ s}^{-1} \text{ reduction of } N_t \text{ by 300 s of UV irradiation was observed. For the 5 mM } \text{trans-OMCA solution, Figure 6.4 shows that the } N_t \text{ values at high shear-rates were quite high before UV (\sim 300 Pa at 1000 \text{ s}^{-1}). UV irradiation for 300 s reduced } N_t \text{ to nearly zero in the shear rate range of 133 \text{ s}^{-1} to 421 \text{ s}^{-1}. However, it did rise to } \sim 240 \text{ Pa at 1000 \text{ s}^{-1}.}

The viscosity of the above solutions at 25 \degree \text{C was measured. For the 8 mM } \text{trans-OMCA sample, the viscosity in Figure 6.5 shows modest shear-thickening behavior up to a peak at } \sim 80 \text{ s}^{-1} \text{ followed by shear-thinning. Such a response, often termed shear-induced structuring (SIS), is typical of threadlike micellar solutions at these low surfactant concentrations. Similar results have been reported by other researchers [14, 17-19, 156, 157]. Also, UV irradiation reduces the viscosity across the range of shear-rates. For the 5 mM } \text{trans-OMCA sample, the viscosity was too low to be measured accurately by the Couette tool on our rheometer after 100 seconds of irradiation.}

Together, the above data show that UV irradiation of EO12/ \text{trans-OMCA samples for 300 s causes a drop in both their viscosity (Figure 6.5) as well as their viscoelasticity}
These results are consistent with the findings of Ketner et al. [93], which were acquired with a different cationic surfactant (CTAB) and at higher concentrations of both the surfactant and the trans-OMCA. The reductions in rheological properties are expected to be reflected in the nanostructure before and after UV, i.e., the threadlike micelles are expected to be shortened by UV.

6.3.3 Cryo-TEM

To obtain direct evidence for UV-induced nanostructural changes, cryo-TEM was used. Cryo-TEM images before and after 300 s of UV irradiation are shown in Figures 6.6 and 6.7 for the 4 mM EO12 + 8 mM trans-OMCA sample and in Figures 6.8 and 6.9 for the 4 mM EO12 + 5 mM trans-OMCA sample. Before UV, both samples (Figures 6.6 and 6.8) reveal numerous long threadlike micelles. The cryo-TEM image of the 8 mM trans-OMCA sample after UV (Figure 6.7) shows a reduction in the density of threadlike micelles, but there is no discernible difference in micellar lengths. In comparison, the 5 mM trans-OMCA sample after UV (Figure 6.9) showed only a few small threadlike micelles – i.e., the sizes of the micelles were considerably smaller than those present before UV, and are similar to those present in a 4 mM EO12 + 5 mM cis-OMCA sample (Figure 6.10). Thus, the expected reduction in micellar sizes due to UV irradiation is clearly seen in the case of the 5 mM trans-OMCA sample, while such a reduction is not readily apparent in the case of the 8 mM trans-OMCA sample with its higher trans-OMCA content.
6.3.4 Drag reduction and heat transfer

Drag reduction data for the 4 mM EO12 + 8 mM trans-OMCA sample at temperatures between 5 °C and 50 °C are shown in Figure 6.11. In such experiments, a percent drag reduction (%<em>DR</em>) of 50% or higher is a standard cut-off to demarcate effective drag reducers [58]. Based on this cut-off, the above solution is drag-reducing between 5 °C and 40 °C, but not at higher temperatures. At 5 °C, %<em>DR</em> reaches about 60% at a <em>Re</em> of 40,000 (higher <em>Re</em> values could not be attained at this temperature because of the high viscosity of the solution). From 15 °C to 30 °C, %<em>DR</em> levels off at about 70% at high <em>Re</em>. Finally, at 40 °C, the %<em>DR</em> peaks just above 50% at a <em>Re</em> of 55,000 and decreases as the <em>Re</em> is increased further. The loss of DR at high temperatures is because the length of threadlike micelles drops with temperature [58]. In sum, the data show that this EO12/ trans-OMCA solution is drag-reducing at low temperatures and thus might be a candidate for use in district cooling systems.

Figure 6.12 shows the drag reduction and heat-transfer properties of the above 4mM EO12 + 8 mM trans-OMCA solution at 10 °C before and after UV irradiation. Before UV, the %<em>DR</em> reaches about 75% at the highest <em>Re</em> (about 37,000). After UV irradiation, %<em>DR</em> peaks at about 68% at a <em>Re</em> of 23,000 and then decreases to 41% at a <em>Re</em> of 32,000. Based on the maximum %<em>DR</em> at a <em>Re</em> of 23,000, the critical value of the wall shear stress is 8.9 Pa for the irradiated sample compared with &gt;14.9 Pa, which is the highest value measured for the fresh solution. Essentially, the irradiated micelles are sensitive to shear degradation and thus less effective in drag reduction compared to the initial sample. Next, percent heat transfer reduction (%<em>HTR</em>) is considered. Before UV, the %<em>HTR</em> increased to
nearly 80% at high $Re$, indicating very poor heat transfer. After UV irradiation, the $\%HTR$ was about the same at $Re$ below 18,000, but decreased sharply at higher $Re$. Thus, UV irradiation improves the heat transfer properties of this solution at high $Re$, but not at low $Re$, which tracks roughly (in the opposite direction) the diminished drag reduction behavior. Aguilar et al. [46] noted that $\%HTR$ was always greater than $\%DR$, as also observed here.

Similar data for the 4 mM EO12 + 5 mM trans-OMCA sample at temperatures between 1 °C and 45 °C are shown in Figure 6.13. The solution is drag reducing ($\%DR > 50\%$) from 1 °C to 30 °C. The $\%DR$ reaches around 70% at intermediate values of $Re$ and then decreases with further increase in $Re$. The $\%DR$ at high $Re$ values are somewhat lower for this sample than for the 8 mM trans-OMCA sample (Figures 6.11 and 6.13), indicating that the micelles in this fluid are not as effective drag-reducers, but this system is still a good candidate for district cooling.

Figure 6.14 shows $\%DR$ and $\%HTR$ at 10 °C vs. Reynolds number for this solution before and after UV irradiation. Before UV, the $\%DR$ increases to 67% at a $Re$ of 24,000 and then decreases to 42% at a $Re$ of 31,500. After UV irradiation, the highest $\%DR$ is only 43% at a $Re$ of ~10,000, which is below the 50% threshold for drag reduction – i.e., this solution cannot be considered an effective drag-reducer. Turning now to the $\%HTR$, before UV, the $\%HTR$ increases to nearly 79% at a $Re$ of 16,000 and then decreases to 61% at a $Re$ of 26,000. However, after UV irradiation, the heat transfer was improved significantly, that is, the $\%HTR$ values are much lower for the irradiated sample and, in fact, the $\%HTR$ drops to nearly zero at $Re > 22,000$. That is, at high $Re$, the irradiated
sample shows enhanced heat transfer similar to that of water reflecting the diminished sizes of the micelle threads.

The effects on $Nu$ which are the ratio of convective to conductive heat transfer normal to the boundary, of this 4 mM EO12 + 5 mM trans-OMCA sample compared to those of water are shown in **Figure 6.15**. The $Nu$ values of the solution before UV increase with $Re$, but are well below those of water. After UV irradiation for 30 min, the solution shows significantly higher $Nu$ values, which approach those of water at $Re \sim 25,000$. Again, these results indicate the enhanced heat-transfer properties of the irradiated sample.

With these encouraging results for enhancing heat transfer, it is desirable to find conditions to reverse the isomerization of the photosensitive OMCA counterion back from cis to trans. As shown by **Figure 6.1**, the desired drag reducing solution should be irradiated to change its structure from trans to cis or cis to trans at the entrance to the heat exchanger (thus converting long micelles to short ones) and thereafter irradiation to isomerize it back to the original drag reducing solution at the exit from the heat exchanger (restoring the long micelles and thereby the DR properties).

### 6.4 Conclusions

UV irradiation of EO12/trans-OMCA results in isomerization of much of the trans to cis configuration, as confirmed by UV-Vis spectra. In turn, this causes a reduction in micelle size, as shown by cryo-TEM images. This results in significant reduction in viscosity and viscoelasticity of the solution. The drag reducing character of the solution is thereby lowered but its heat-transfer properties are substantially enhanced. The study
shows that the use of photosensitive micelles is a promising approach to developing effective drag reducing systems for use in district cooling and district heating systems.
6.5 Figures

Figure 6.1 The use of light-responsive fluids to ensure both efficient drag reduction in pipe flow as well as efficient heat transfer in the heat exchanger.
Figure 6.2 UV-Vis spectra for 0.04mM EO12 + 0.05mM trans-OMCA after different durations of UV irradiation and also for 0.05mM cis-OMCA.
Figure 6.3 UV effect on $N_1$ for EO12/trans-OMCA solutions of different concentrations at 25 °C
Figure 6.4 UV effect on $N_1$ for EO12/\textit{trans}-OMCA solutions of different concentrations at 10 °C.

Note: The erratic data for 4 mM EO12 + 8mM \textit{trans}-OMCA at shear rate greater than 316 s$^{-1}$ were due to the imperfect shape of the sample between the cone and the plate at high rotational speed.
Figure 6.5 UV effect on shear viscosity of 4 mM EO12 + 8 mM trans-OMCA at 25 °C
Figure 6.6 Cryo-TEM image of a 4 mM EO12 + 8 mM trans-OMCA sample before UV irradiation.
Figure 6.7 Cryo-TEM image of a 4 mM EO12 + 8 mM trans-OMCA sample after UV irradiation.
Figure 6.8  Cryo-TEM image of a 4 mM EO12 + 5 mM trans-OMCA sample before and after UV irradiation.
Figure 6.9  Cryo-TEM image of a 4 mM EO12 + 5 mM trans-OMCA sample after UV irradiation.

Note: the thick black structure is supporting carbon fiber
Figure 6.10 Cryo-TEM image for 4 mM EO12 + 5 mM cis-OMCA solution.

Note: the thick black structure is supporting carbon fiber
Figure 6.11 Drag reduction vs Reynolds number for aqueous solution of 4 mM EO12 + 8 mM trans-OMCA at different temperatures.
Figure 6.12 Drag reduction and heat transfer reduction vs Reynolds number for aqueous solution of 4 mM EO12 + 8 mM trans-OMCA at 10 °C before and after UV irradiation.
Figure 6.13 Drag reduction vs Reynolds number for aqueous solution of 4 mM EO12 + 5 mM *trans*-OMCA at different temperatures.
Figure 6.14  Drag reduction and heat transfer reduction vs Reynolds number for aqueous solution of 4 mM EO12 + 5 mM trans-OMCA at 10 °C before and after UV irradiation.
Figure 6.15 Nusselt number vs Reynolds number of 4 mM EO12 + 5 mM *trans*-OMCA solution before and after UV irradiation.
CHAPTER 7: Enhancing Heat Transfer of a Reversible

Photo-Responsive Micelle System

7.1 Introduction

A promising application of drag reducing fluids is in DHCS [5, 37-39]. However, drag reducing fluids have reduced heat transfer capability compared with water and the percent HTR is usually a little higher than the percent DR [42-46]. Therefore, it is of practical importance to enhance the heat transfer capability of the drag reducing solution in heat exchangers while maintaining the DR capability in the rest of the DHCS.

The heat transfer can be enhanced either by intensifying the turbulence or by eliminating TLMs. A number of methods have been used in heat exchangers to enhance flow turbulence and to mechanically destroy TLMs. These methods include helical pipes [25], fluted-tube heat exchanger [55], wire meshes [56], static mixers at the heat exchanger entrance [33], and vortex generators [28, 57]. However, all of these methods involve in-flow mechanical devices, which directly interfere with the fluid flow, resulting in significant pressure losses.

To avoid high pressure loss generated by in-flow devices, external stimuli have been studied to intensify turbulence in the heat exchanger. Qi et al. [89] used ultrasonic energy to externally enhance heat transfer, but this method was only partially effective and
required a large energy cost. Recently, light irradiation was proposed for use as an external stimulus to enhance heat transfer [119]. At the entrance of the heat exchanger, drag reducing fluid is irradiated by a light source to alter the molecular configuration of the counterion causing the solution to lose its TLM and its viscoelasticity. The resulting fluid is not drag reducing and has water-like behavior and enhanced heat transfer capability. At the exit of the heat exchanger, a different light source is used to restore the original molecular configuration and the TLMs and thus its DR capability. This concept is based on the fact that counterions must have proper geometry so that their hydrophilic and hydrophobic parts can fit in the surfactant environment to form TLMs [26, 68, 70, 149, 150].

Many photo-responsive TLMs have been developed using photo-sensitive counterions [93, 117, 151-153], In a previous study [119], *trans*-ortho-methoxycinnamic acid (*trans*-OMCA) was used as the light-responsive counterion due to its low-cost and availability. While UV irradiation did cause the solution to lose its viscoelasticity and enhanced the heat transfer, the fluid lost DR permanently due to the irreversible isomerization of *trans*-OMCA to *cis*-OMCA. It is desirable to find a counterion that can reversibly photo-isomerize and combine with surfactants to form TLMs in one configuration but lose this ability in the other configuration. Azobenzene derivatives have been widely used as key components of reversibly photo-responsive systems [158-164]. But these systems all consist of polymers, which degrade irreversibly when subject to high shear stresses induced by pumps in DHCS. Photo-responsive surfactant micelle systems without polymer have been developed by adding an azobenzene derivative,
AZTMA, to aqueous surfactant solutions [92, 165]. The reversible photo-isomerization of AZTMA enables the surfactant micelle systems to have reversible rheological changes with UV and visible light irradiations. However, AZTMA is neither commercially available nor easy to synthesize. In addition, one AZTMA containing system [165] has sodium dodecylbenzenesulfonate, which is sensitive to Ca$^{2+}$ and Mg$^{2+}$ generally present in tap water. In addition, Therefore, AZTMA containing systems are not suitable for DHCS application. Raghavan et al. [97, 166] reported a reversibly photo-responsive surfactant micelle system with trans-PABA as the counterion. The surfactant in this system was cationic and trans-PABA is relatively easy to synthesize.

A reversible photo-responsive aqueous surfactant micelle system containing 5 mM EO12 and 2 mM PABA was prepared. The fresh solution, containing trans-PABA, had TLMs and is viscoelastic. It is also drag reducing with reduced heat transfer capability compared to water. After this solution is irradiated by UV (wavelength centered at 365nm), trans-PABA isomerizes to cis-PABA, which is not able to form TLMs with EO12. The resulting solution has shortened micelles and is not viscoelastic. It loses its DR capability and has enhanced heat transfer capability in a range of Reynolds numbers. Irradiation by visible light can convert cis-PABA back to trans-PABA which restores the TLMs and the solution recovers most of its DR and HTR capabilities. Thus, this reversibly photo-responsive surfactant micelle system with switchable DR and HTR capabilities is ideal for use in recirculating DHCS to save pumping energy and maintain good heat transfer in heat exchangers. A proposed scheme for application of this photo-switchable fluid is shown in Figure 7.1.
7.2 Experimental

7.2.1 Materials and sample preparation

The surfactant used in this solution was EO12, described in Section 3.1. Propylene glycol in EO12 was removed by vacuum distillation. trans-PABA (purity > 99%) was synthesized from p-aminobenzoic acid (99%, Alfa Aesar) and nitrosobenzene(97%, Sigma-Aldrich) [167] and purified by recrystallization.

EO12/trans-PABA solutions in small quantities were prepared by mixing the two compounds in water using magnetic stirrers. Samples were stirred overnight before rheological and other analytical measurements. Large quantities of solutions for drag reduction and heat transfer experiments were prepared by stirring the solution in a bucket for 8 hours at room temperature with a high shear disperser (Janke & Hunkel IKA Ultra-Turrax SD-45). Solution pH was maintained between 8 and 10 using sodium hydroxide. All the solutions were well covered during preparation and storage to minimize exposure to light.

7.2.2 $^1$H NMR

Solutions were prepared and irradiated in D$_2$O instead of H$_2$O. NMR samples were prepared by diluting the solution with equal volume of DMSO. Experiments were performed within 2 hr after irradiation at ambient temperature. See Section 3.2.
7.2.3 Rheological measurements

To minimize isomerization, samples were stored in vials wrapped with aluminum foil and tested right after irradiations. The rheological experiments were performed in a dark environment. Details of the rheometer are described in Section 3.3.

7.2.4 Cryo-TEM.

Samples for cryo-TEM imaging were prepared at Ohio State Campus and were shipped to Technion-Israel Institute of Technology, where further treatments and the imaging were preformed. Samples were carefully sealed in vials wrapped with aluminum foils to minimize exposure to light. In addition, samples were kept at low temperature by dry ice during the shipping. The low temperature slows isomerization of cis-PABA to trans-PABA. Details of the cryo-TEM imaging are described in Section 3.5.

7.2.5 UV-Vis spectroscopy

For UV-Vis spectroscopy, 10 mL of a given solution was placed in a Petri dish and irradiated for specific durations. Before taking UV-Vis spectra, samples were diluted by 100 fold to 0.05 mM EO12 to 0.02 mM PABA. UV-Vis spectra were collected at room temperature on a Genesys 6 UV-Visible Spectrophotometer (Thermo Electron Corporation).

7.2.6 Drag reduction and heat transfer reduction

For DR and heat transfer experiments, 6 L of solution was divided into 12 batches of 500 mL. Each batch was held in a crystallizing dish and was irradiated with stirring for 3 hr. To minimize isomerization after irradiation, each batch was placed in a -20 °C freezer.
as soon as irradiation was completed. DR and heat transfer experiments were performed the day after irradiation. Experiments started from low temperature to high temperature and were carried out as quickly as possible.

7.3 Results and discussion

Reversible photo-isomerization of PABA in the presence of EO12 was investigated using UV-Vis spectra and $^1$H NMR. The resulting micellar shape and rheological properties were also examined by cryo-TEM and rheometer. Finally, the effects of this reversibility on DR and HTR in a large scale recirculation system were also studied.

7.3.1 Physical appearances

Figure 7.2 shows photos of the solution of 5 mM EO12 + 2 mM PABA before and after light irradiations. The fresh solution is yellow and it turns to a brownish yellow after UV irradiation. After a visible light irradiation, the solution turns to the same color as the fresh solution. A second UV irradiation again gives a brown color to the solution. The fresh solution and the solution after UV and visible light irradiations show viscoelastic behaviors observed directly. The solutions (#1 and #3) after UV irradiation, however, show water-like behaviors as observed by swirl tests. These physical appearances of color and rheological behaviors demonstrate the solution’s reversibility nature triggered by light irradiations.

7.3.2 UV-Vis spectra

To verify the reversible photo-isomerization between trans-PABA and cis-PABA by light irradiations, UV-Vis spectra (Figure 7.3) were obtained for the solution of 0.05mM
EO12 + 0.02mM \textit{trans}-PABA after UV and visible light irradiations. In the wavelength range of 220nm to 500nm, all of the four spectra had three absorbance peaks, denoted as Peak 1, 2 and 3 from left to right. For the fresh solution, containing \textit{trans}-PABA, the three peaks were at 231nm, 321nm and 427nm respectively. Among them, Peak 2 was a major one and Peak 3 was broad and small. After UV irradiation, Peaks 1 and 2 shifted to 251nm and 298nm respectively while Peak 3 stayed at 427nm. It should be noted that Peak 2 was significantly lower and Peak 3 grew slightly higher. The changes in spectra corresponded to the isomerization of \textit{trans}-PABA to \textit{cis}-PABA \cite{168, 169}. The UV irradiated solution was then irradiated by visible light. The resulting spectra were essentially the same as those of the fresh spectra, indicating the \textit{cis}-PABA reverted back to \textit{trans}-PABA. A second UV irradiation following the visible light irradiation again converted the \textit{trans}-PABA spectra to \textit{cis}-PABA spectra. These spectra confirmed that the photo-isomerization between \textit{trans}-PABA and \textit{cis}-PABA is repeatedly reversible in the presence of EO12.

7.3.3 Rheology

DR fluids usually show viscoelastic behaviors. Thus changing viscoelasticity can control the DR and HTR abilities of these fluids. UV and visible light irradiations triggered isomerization of PABA, which in turn reversibly changed the viscoelasticity of the EO12/PABA solution. \textbf{Figure 7.4} shows $N_\tau$ at 25 °C for 5 mM EO12 + 2 mM PABA after UV and light irradiations. The fresh sample had an increasing $N_\tau$ against shear rate, which is a typical elastic behavior. $N_\tau$ increased from zero up to ~ 240 Pa at 1000 s$^{-1}$. After UV irradiation, the solution showed water-like behavior and its $N_\tau$ decreased to
essentially zero in the shear rate range of 1 s\(^{-1}\) to 1000 s\(^{-1}\). This decrease in \(N_I\) confirmed that UV irradiation switched off the viscoelasticity of the solution. After a further irradiation with visible light, \(N_I\) again increased with shear rate almost coinciding with that of the fresh solution, indicating that \(N_I\) was restored by visible light irradiation. A second UV irradiation following the visible light irradiation again reduced \(N_I\) to essentially zero in the shear rate range of 1 s\(^{-1}\) to 1000 s\(^{-1}\).

**Figure 7.5** shows \(\eta\) at 25 °C. The fresh solution had shear thinning behavior in the low shear rate range, and it showed a modest shear-thickening in the shear rate range of 30 s\(^{-1}\) to 50 s\(^{-1}\). This shear-induced structure (SIS) of TLMs is a typical characteristic of threadlike micellar solutions [14, 17-19, 156, 157]. UV irradiation reduced the shear viscosity across the entire shear rate range. In the shear rate range of 30 s\(^{-1}\) to 50 s\(^{-1}\), negative values were measured. This was because the torque decreased to extremely low values that are beyond the limit of this rheometer’s torque sensor. After visible light irradiation, the shear viscosity was restored to that of the fresh solution. A second UV irradiation reduced the shear viscosity again. Thus the viscoelasticity of the solution could be reversibly tuned by light irradiations.

7.3.4 Cryo-TEM

The dependence of viscoelasticity on light irradiation indicated that the TLMs of the solution were broken by UV irradiation and restored by visible light irradiation. To confirm the changes in TLMs, cryo-TEM images were taken for fresh samples and samples after UV and visible light irradiations. **Figure 7.6** shows TLMs of the fresh 5 mM EO12 + 2 mM *trans*-PABA. Many of the TLMs are aligned and lay across the entire
image. Interestingly, the TLMs are straight, which may be a result of the blotting procedure before vitrification. After UV irradiation, only shortened micelles with much lower density were observed in Figure 7.7. This indicated that TLMs were not only broken but also mostly disassembled into free molecules in the solution. Figure 7.8 shows that long and straight TLMs reassembled after visible light irradiation. Thus the effects of reversible photo-isomerization of PABA were also reflected in the micellar structure. The presence and absence of TLMs directly resulted in the viscoelastic and non-viscoelastic behaviors of the solution.

7.3.5 $^1$H NMR

The photo-isomerization between trans-PABA and cis-PABA was also confirmed by $^1$H NMR analysis. Figure 7.9 shows the $^1$H NMR spectra for 5 mM EO12 + 2 mM trans-PABA before and after irradiations. The fresh sample had high peaks of EO12 but very low peaks of trans-PABA, indicating most of the trans-PABA molecules were not in detectable free form, as they intercalated with EO12 forming TLMs. After UV irradiation, significant cis-PABA peaks were observed, while the trans-PABA peaks were negligible. This means that trans-PABA molecules, both in free form and assembled in TLMs, were converted to cis-PABA by UV irradiation. The higher peaks of cis-PABA also indicate that cis-PABA was less capable of binding with EO12 to form TLMs compared with trans-PABA, resulting in more free cis-PABA molecules in the solution. Visible light irradiation on the UV-treated sample reduced the height of cis-PABA peaks to extremely low levels. This confirms that visible light irradiation converted most cis-PABA to trans-PABA that intercalated with EO12 to form TLMs.
The negligible peaks of trans-PABA indicate that all the trans-PABA that came from cis-PABA strongly intercalated with EO12 forming TLMs. Although no trans-PABA peaks were observed, they are likely to show up if the visible light irradiation is sufficiently long to convert all the cis-PABA to trans-PABA. \(^1\)H NMR spectra not only confirmed the reversible photo-isomerization between trans-PABA and cis-PABA, but also showed that cis-PABA does not bind with EO12 to form large aggregates, i.e., TLMs.

7.3.6 Drag reduction and heat transfer reduction

DR data for the 5 mM EO12 + 2 mM trans-PABA solution at temperatures from 5 °C and 75 °C are shown in Figure 7.10. At low Re, the solution had negative %DR, which means the friction factor was higher than that of water due to the solution’s high shear viscosity at low shear rate. The solution had better DR ability at higher temperature. At 5°C, no DR was observed for the entire Reynolds number (Re) range. At 15 °C, %DR had a low peak, (19%), at a Re of 5000. As temperature increased, the solution showed DR over a wider range of Re. The DR ranges were 6500 to 14800, 7500 to 25000, 11000 to 36700 and 7000 to 60000 for 25°C, 35°C, 45°C and 55°C. The %DR peak value also grew from 45% at 25°C to 78% at 55°C. The Re, where %DR drops rapidly was denoted as the critical Re. At this critical Re, the shear stress reached a critical level that destroys TLMs, resulting in more water-like turbulent behavior and rapid drop in %DR. When temperature increased to 65°C and 75°C, %DR reached 78% and 80% respectively at the highest Re achievable. It is likely that the solution has even higher levels of DR at higher temperature.
Figures 7.11 through 7.13 show the DR and heat-transfer properties before and after light irradiations at 25 °C, 35 °C and 45 °C. The %DR was always lower than %HTR in the DR-effective range of $Re$. They increased together and decreased at the critical $Re$, as reported by others [42-46]. The results showed that UV irradiation turned off %DR and %HTR in a certain range of $Re$. UV irradiation shortened or weakened the TLMs responsible for drag reduction by reducing the concentration of $trans$-PABA, whose presence is essential to form TLMs. In the experiment, %DR and %HTR were only partially reduced because the irradiation did not completely convert $trans$-PABA to $cis$-PABA. To destroy TLMs severely, as observed in the cryo-TEM image (Figure 7.7), a higher powered UV lamp with wavelength narrowed near 321 nm should be used to irradiate the solution.

Here, the range of $Re$ in which %DR and %HTR were reduced is referred to as the responsive range of $Re$. Figure 7.13 shows that this responsive range of $Re$ had the widest span at 45 °C. So the effect of light irradiation is more pronounced at higher temperatures, offering a wider responsive range of $Re$ to manipulate. Due to the limit of the apparatus, no heat transfer experiments were performed above 45 °C, but a wider span is expected at temperatures above 45 °C as the solution was highly drag reducing at 75 °C. While the critical $Re$ of the UV-treated solution did not change much as the temperature increased from 25 °C to 45 °C, the critical $Re$ of fresh solution and restored solution increased significantly from ~ 13000 to ~ 30000. This significant increase might be due to the increased flexibility of the TLMs and higher reassembling rate of TLMs at higher temperatures. But for the UV-treated solution, these two factors have less effect on
broken micelle pieces present in less quantity. Visible light irradiation restored \%DR and \%HTR to almost the original level. The critical Re at each temperature was also restored to approximately the same value of fresh solution. The small differences were probably caused by incomplete isomerization of cis-PABA to trans-PABA. Longer and more intense irradiation should cause full recovery of the critical Re.

In short, DR together with HTR of EO12/trans-PABA solution were suppressed by UV irradiation and were restored by visible light irradiation. Thus, this drag reducing solution could be used in district heating and cooling systems to reduce pumping energy requirements and maintain effective heat transfer in the heat exchangers.

7.4 Conclusions

In district heating and cooling systems, it is desirable to use a smart fluid whose flow properties, such as DR and heat transfer capability, can be controlled by external stimuli. The 5 mM EO12 + 2 mM trans-PABA solution was developed to meet this need. This solution had drag reducing capability and reduced heat transfer capability. UV irradiation turned off its DR and simultaneously enhanced its heat transfer capability in a certain range of Re. The UV irradiation can be applied at the entrance of a heat exchanger so that the heat exchanger will have better performance. Visible light irradiation on the UV irradiated solution restored its drag reducing capability and reduced its heat transfer capability at the same time. This visible light irradiation can be applied at the exit of the heat exchanger so that DR and HTR are restored. The reversible changes stem from the reversible photo-isomerization between trans-PABA and cis-PABA, which was confirmed by UV-Vis spectra and \(^1\)H NMR spectra. \(^1\)H NMR spectra also suggested that
trans-PABA assembles with EO12 to form aggregates, but cis-PABA is not able to assemble with EO12, due to its unfavorable molecular geometry. Long TLMs were observed in cryo-TEM images for both the fresh solution and the restored solution. Significantly shortened micelles were found in small quantities after UV irradiation. The changes in the micelles were also reflected in reversible changes in rheological properties like shear viscosity and $N_1$. Thus, this study highlights the potential of switching on the EHT mode of a photo-responsive fluid at the inlet of a heat exchanger and switching on the DR mode at the outlet in a recirculating system. This study also demonstrates a potential application for other stimuli-responsive smart fluids.
7.5 Figures

Figure 7.1 The use of reversible photo-responsive fluids to temporarily enhance heat transfer in a heat exchanger.
Figure 7.2 Photo of the 5 mM EO12 + 2 mM PABA solution before and after light irradiations.

Note: Sample #0: fresh; Sample #1, after UV irradiation; Sample #2: after UV irradiation followed by visible light irradiation; Sample #3: Sample #2 after UV irradiation.

tACA on the label is actually trans-PABA.
Figure 7.3  UV-Vis spectra of 0.05mM EO12 + 0.02mM *trans*-PABA for fresh (black), after UV irradiation (green), after visible light irradiation (blue) and a second UV irradiation (red).
Figure 7.4  Effects of UV and visible light irradiations on $N_1$ of 5mM EO12 + 2mM PABA solution at 25 °C.

Legends: □, fresh; ◇, UV; Δ, UV followed by visible light; ○, UV and visible light followed by UV.
Figure 7.5 Effects of UV and visible light irradiations on $\eta$ of 5mM EO12 + 2mM PABA solution at 25 °C.

Legends: □, fresh; ◊, UV; Δ, UV followed by visible light; ○, UV and visible light followed by UV.

Note: The data for solutions after UV irradiation in the shear rate range of 10 to 50 s$^{-1}$ were negative due to the limited accuracy of the torque sensor.
Figure 7.6 Cryo-TEM image of fresh solution of 5 mM EO12 + 2 mM trans-PABA

Note: the dark black structure is the carbon support.
Figure 7.7. Cryo-TEM image of the solution of 5 mM EO12 + 2 mM trans-PABA after UV irradiation.
Figure 7.8. Cryo-TEM image of fresh solution of 5 mM EO12 + 2 mM trans-PABA after UV irradiation followed by visible light irradiation.
Figure 7.9 $^1$H NMR for 5 mM EO12 + 2 mM trans-PABA: (a) fresh; (b) after UV irradiation and (c) after UV and visible light irradiations. Inset: zoomed-in PABA peak region.
Figure 7.10 DR vs Reynolds number for aqueous solution of 5 mM EO12 + 2 mM trans-PABA at different temperatures

Legends: □, %HTR of fresh solution; ◇, %HTR of solution after UV irradiation; △, %HTR of solution after UV irradiation and visible light irradiation ; ■ %DR of fresh solution; ♦,%DR of solution after UV irradiation; ▲, %DR of solution after UV irradiation and visible light irradiation.
Figure 7.11  DR and HTR vs Reynolds number for aqueous solution of 5 mM EO12 + 2 mM trans-PABA after irradiations at 25 °C.

Legends: □, %HTR of fresh solution; ◊, %HTR of solution after UV irradiation; △, %HTR of solution after UV irradiation and visible light irradiation ; ■ %DR of fresh solution; ♦, %DR of solution after UV irradiation; ▲, %DR of solution after UV irradiation and visible light irradiation.
Figure 7.12  DR and HTR vs Reynolds number for aqueous solution of 5 mM EO12 + 2 mM \textit{trans}-PABA after irradiations at 35 °C.

Legends: □, \%\textit{HTR} of fresh solution; ◇, \%\textit{HTR} of solution after UV irradiation; Δ, \%\textit{HTR} of solution after UV irradiation and visible light irradiation; ■ \%\textit{DR} of fresh solution; ♦, \%\textit{DR} of solution after UV irradiation; ▲, \%\textit{DR} of solution after UV irradiation and visible light irradiation.
Figure 7.13  DR and HTR vs Reynolds number for aqueous solution of 5 mM EO12 + 2 mM trans-PABA after irradiations at 45 °C.

Legends: □, %HTR of fresh solution; ◊, %HTR of solution after UV irradiation; Δ, %HTR of solution after UV irradiation and visible light irradiation ; ■ %DR of fresh solution; ♦,%DR of solution after UV irradiation; ▲, %DR of solution after UV irradiation and visible light irradiation.
CHAPTER 8: Conclusions and Recommendations for Future Work

8.1 Conclusions

Surfactant TLMs impart to the aqueous system interesting characteristics such as non-Newtonian behaviors and DR capability. Such characteristics have led to extensive studies extensively of these solutions for many applications such as oil field applications, home-care and personal-care products, and drag reduction. By tuning a number of factors such as temperature, counterion type, surfactant and counterion concentrations, pH, etc, the behaviors of TLMs solutions can be controlled.

This work first developed a pH-responsive surfactant-counterion TLM system, namely EO12 and tOCA. The rheological response of this TLMs system to pH is unique in that it has viscoelasticity at both low and high pH levels. With these unique rheological behaviors, this TLM system is potentially useful in either acidic or basic environment. The viscoelasticity can be reversibly switched on and off many times. Even after 5 cycles of pH changes reversible changes in shear viscosity and first normal stress difference showed no significant decay. This reversibility makes the system more attractive in real applications. Cryo-TEM images confirmed the presence of TLMs at pH 3.5 and pH 9.8. TLMs were found to flocculate at medium pH levels, however. This system also had DR
capability at low and high pH. The reversible rheological responses to pH stems from the dual pKa of the counterion tOCA, as it carries different charges at different pH. When it combines with EO12, the net charge of TLMs varies. When the net charge is non-zero, it generates repulsion between neighboring TLMs and prevents them from flocculating. Thus the TLM suspension is a stable colloid with viscoelastic behaviors. The binding ratio of EO12 to tOCA in the separated oily phase was obtained from 1H NMR spectra.

Surfactant DR solutions can save pumping energy costs, if they are used as working fluid in district heating or cooling systems. However, surfactant DR solutions also have reduced heat transfer capability. Therefore, it is of practical importance to enhance the heat transfer capability of the drag reducing solution in heat exchangers while maintaining the DR capability in the rest of the DHCS. A high-efficiency vortex (HEV) static mixer was designed and employed to locally enhance the heat transfer coefficient of a surfactant DR solution with relatively low pressure loss. Significant enhancement of heat transfer coefficients was observed with only modest pressure drop. The HEV static mixer had a performance number comparable to that of water. The enhanced heat transfer with moderate pressure drop by the HEV static mixer resulted from organized streamwise vortices naturally generated by the inclined tabs of the HEV static mixer. The streamwise vortices enhance heat transfer in the radial direction. Few vortices in other directions, which would not be effective in enhancing heat transfer, are generated in the HEV static mixer and therefore, energy is not wasted in generating ineffective vortices.

The HEV static mixer still has pressure loss because it directly interferes with the flow. To avoid the additional pressure loss by in-flow mechanical devices, this work also
studied the use of external light irradiation to temporarily enhance the heat transfer capability of cationic/counterion surfactant systems. The ideal fluid should be drag reducing in its normal state. At the entrance of a heat exchanger, the fluid should have enhanced heat transfer capability by light irradiation, changing the configuration of the counterion. At the exit of the heat exchanger, the fluid should restore its DR capability by a different frequency of light irradiation. Thus this method combines the benefits of reduced pumping energy costs and good heat transfer.

A light-responsive surfactant DR solution was developed to realize this concept. The solution has a cationic surfactant with a light-responsive counterion, OMCA. After UV irradiation, the counterion had a different configuration. As a result, the solution’s DR capability was reduced and its heat transfer capability was enhanced, because its TLMs were broken. This also resulted in reduced η and $N_i$. The problem with this light-responsive solution is that the effect of UV irradiation on this solution is not reversible. As a result, the DR capability can not be restored, which prevent this solution from being used in DHCS. Nevertheless, studies of this light-responsive surfactant DR solution provided invaluable information that finally led to the discovery of an improved light-responsive DR solution.

The improved light-responsive DR solution had reversible responses to light irradiations. This surfactant DR solution, 5mM EO12 + 2 mM PABA, was drag reducing in its normal state. After UV irradiation, the counterion changed to cis configuration and solution lost DR capability and viscoelasticity, as the counterion took a configuration that did not favor formation of TLMs. As a result, heat transfer was also enhanced. After
visible light irradiation, the counterion configuration was reverted and the solution regained its viscoelasticity and became drag reducing again. This reversibility makes the solution a promising candidate for use in district heating and cooling systems, where its drag reduction and high heat transfer can be switched on and off repeatedly by external light irradiation.

**8.2 Recommendations for future work**

8.2.1 Improve the recirculation system

The recirculation system has been improved a number of times during this work. But there is still room for further improvements. Currently, the drag reduction and heat transfer measurements can not be conducted simultaneously because a static mixer is placed upstream of the thermocouple to accurately measure the temperature of solution leaving the heat exchanger, interfering with the exit temperature reading. Since there is no pressure transducer upstream of the heat exchanger, a pressure transducer is needed to measure the pressure loss across a section of tube before the fluid enters the heat exchanger. This will enable the researcher to measure both drag reduction and heat transfer simultaneously and will save the researcher significant amount of time.

For the heat transfer experiments, the chiller is sometimes too powerful and the highest temperature setting is 10°C. This cools the solution too fast in some cases. So it is necessary to establish a method that can set the temperature higher than 10 °C and/or control the flow rate of the coolant. At the same time, the heating capability of the two circulators is not large enough. More heating power is needed to increase the temperature difference between the drag reducing fluid and the coolant in the jacket. The higher
temperature difference would reduce the significance of errors from the thermocouples. In addition, more accurate temperature control is needed for the heating units.

Another necessary improvement is to discharge the solution from the recirculation system more easily. Currently, the discharge outlet is not positioned at the lowest point. So compressed air is used to blow the remaining solution out of the circulation system. It requires taking apart one connection in the recirculation system and mounting the air duct to the system. This can be simplified by installing a discharge outlet at the lowest point of the whole system. Other future improvements on the recirculation system include better thermocouples and reducing the volume of solution necessary for measurements.

8.2.2 Further studies on pH-responsive systems

In this work, a pH-responsive system with unique rheological responses to pH has been developed. The possible mechanism proposed is based on the electrostatic charges of the TLMs. However, further studies are still needed to explain in detail why the stable colloid system has low zeta potential at high pH. Generally, the zeta potential should be around 30 mV in order to stabilize the colloidal system. It is also possible that other effects such as steric effects might become important at high pH.

The pH-responsive system has bimodal viscoelasticity over the pH range. It would also be interesting to develop a pH-responsive system with even three or more peaks of viscoelasticity over the pH range. Since the bimodal viscoelasticity stems from the dual pKa of the counterion, using suitable surfactants and counterions with more pKa’s may form such an interesting pH-responsive system.
The discrepancy between DR and viscoelasticity also deserves further studies. More effort is needed to study the drag reduction capability of the two-phase systems, in which the TLMs form a separate oily phase. Under continuous pumping, the separated oily phase might be sheared to form fibrous structures and stay dispersed in the water. Visualization experiments may help to examine this hypothesis.

The viscoelasticity at both low and high pH levels enables this system to be potentially applicable in either acidic or basic environments. But such applications need to be identified.

8.2.3 Future studies on light-responsive systems.

It is desirable to use reversible light-responsive TLMs solutions in DHCS. However, more studies are needed to improve the performance of the reversible light-responsive system developed in this work. It takes long hours of irradiation to complete the isomerization of the counterions. To reduce the amount of energy and time of the irradiation, better light sources are needed. For example, light sources with higher power and narrow bandwidth at the precise wavelength. It is also desirable to screen for other counterions that have rapid responses to light irradiation.

There is another interesting phenomenon observed during the studies on the reversible light-responsive system. The EO12 + PABA system has viscoelastic behaviors when PABA has trans- configuration and has water-like behaviors when PABA has cis-configuration. However, for the EHAC (erucyl bis(2-hydroxyethyl) methyl ammonium chloride) + PABA system, the cis-PABA induces viscoelasticity while the trans-PABA does not. The only difference between EHAC and EO12 is the carbon chain length. 85%
of long carbon chain in EO12 is oleyl, while the long carbon chain of EHAC is erucyl. More studies are needed to understand why the 4-carbon difference in the chain affects the binding ability of PABA.

The 5 mM EO12 + 2 mM PABA system has good drag reduction at relatively high temperature but has poor drag reduction at low temperature. So this system is only suitable for district heating systems. To find a system that works for district cooling systems, more research is needed to develop a reversible photo-responsive system that is drag reducing at low temperatures.

In addition, since large amounts of solution are used in DHCS, it is essential to select surfactant drag reducers that are more environmentally friendly or biodegradable than the cationic surfactants studied here.

8.2.4 New stimuli-responsive drag reducing fluids

External light irradiation is one stimulus that can enhance the heat transfer without directly contacting the solution. There are other stimuli, for example, magnetic fields, that may also be employed to enhance the heat transfer temporarily in heat exchangers. Future study can explore the formulation of magnetic drag reducing TLM solutions. Incorporating magnetic nano-particles into the TLM solutions can possibly make the solutions responsive to external magnetic fields. Since magnetic fluids are mostly non-aqueous, efforts can be directed to the formulation of thread-like reverse micelles in non-aqueous systems based on existing non-aqueous magnetic fluids. At the same time, the non-aqueous system with thread-like reverse micelles and well suspended magnetic particles should still be drag reducing.
8.2.5 New applications of stimuli-responsive micelle solutions

In this work, three stimuli-responsive micelles solutions have been developed. While they still have limitations in their application in district heating and cooling systems, they might be employed in other applications. The principles in formulating those stimuli-responsive solutions may also be useful for future development of other stimuli-responsive micelle systems.
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