

Unusual temperature gap in turbulent drag reduction of cationic surfactants with mixed counterions

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Abstract Unusual temperature gaps have previously been observed in the turbulent drag reduction effectiveness of Dobon and Habon cationic surfactant systems containing two anionic counterions of different binding strengths. Here, we report drag reduction data for a cationic surfactant with a mixture of dodecyl sulfate and tosylate counterions showing a temperature gap. Cryo-TEM images of nanostructures at different temperatures for this system support an explanation for this gap, based on the counterions' relative binding strengths.

Keywords Surfactant drag reduction · Temperature gap · Anionic counterion · Cryo-TEM · Counterion binding strengths

Introduction

Drag reduction (DR), the unusual reduction in pressure losses in turbulent conduit flow, has been observed in many aqueous surfactant formulations (Zakin et al. 2007; Zakin and Ge 2010; Kawaguchi et al. 2012). A reduction in pumping energy requirements of up to 90% has been reported for a number of

dilute surfactant systems. Surfactant DR is caused by the presence of long threadlike micelles formed by self-association of surfactant molecules. These nanostructures impart viscoelastic properties to their solutions. Breakup of the threadlike nanostructures when the surfactant solution is subjected to high shear is mitigated by their reformation by self-association when the solution enters a region of modest shear. Hence, these DR systems are suitable for use in recirculation systems such as district heating or district cooling systems, whereas high molecular weight polymer DR systems are not useful, as they are permanently degraded to ineffective low molecular weights when subjected to high shear pumps in recirculation systems.

Most surfactant drag-reducing solutions are effective over temperature ranges of several decades, the range depending on the nature of the surfactant and of the counterion, their concentration, and their molar ratios. An unusual temperature “gap” phenomenon was first reported by Kleuker et al. (1991) and then by Chou (1991) for the systems of cationic surfactants Dobon G (C₂₂ trimethylammonium 3-hydroxy-2-naphoate/sodium salicylate (NaSal)) and for Habon (C₁₆ trimethylammonium 3-hydroxy-2-naphoate/sodium salicylate (NaSal)), which showed DR temperature gaps at 60–80 °C, and at 50 °C, respectively. In these systems, drag reduction was observed at lower temperatures and then reduced at intermediate temperature range, regained at a still higher temperature range, before reaching an upper temperature limit for drag reduction. Chou attributed this “gap” phenomenon to the competition of two counterions, each of which was effective over different temperature ranges. Both surfactants without any NaSal were effective DRAs over wide temperature ranges. The “gap” phenomenon with these commercial cationic surfactants with NaSal was never reported again, and never published, probably because

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Habons were never commercialized as DRAs due to environmental concerns.

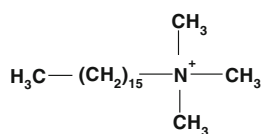
We have studied the DR behaviors of mixed cationic/anionic (catanionic) systems, cetyl-trimethyl ammonium tosylate (CTAT) mixed with sodium dodecyl sulfate (SDS) with excess sodium tosylate (NaTos) over a range of CTAT/SDS ratios, which have been reported separately. One formulation (85 wt.% CTAT, 15 wt.% SDS, and 0.07

wt.% NaTos) showed unusual DR behavior, namely a DR temperature gap, described below.

Experiments

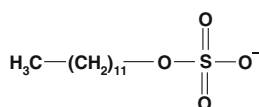
Surfactant solutions were prepared by overnight mixing of the three components:

Cetyl trimethyl ammonium p-toluene sulfonate



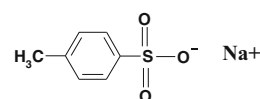
CTAT

(I) Sodium dodecyl sulfate



SDS

Sodium p-Toluenesulfonate



NaTosylate

DR was measured in a closed flow loop. The test section was a stainless tube, 1.22 m long, and an inner diameter of 6 mm. Flow rates were measured by a Rosemount 8100 magnetic flow meter; the pressure drop was measured by a Validyne pressure transducer. Details of the DR measurement techniques can be found in Zhang (2005). The friction factor, f , was calculated from the pressure drop, and compared with the friction factor of the solvent (water), f_s , at the same solvent Reynolds number. DR at different temperatures was calculated from the following equation over a solvent Reynolds number range of 3×10^3 to 3×10^5 .

$$\%DR = \frac{f_s - f}{f_s} \times 100 \quad (1)$$

A system is considered to be DR effective when the maximum %DR is greater than 50%.

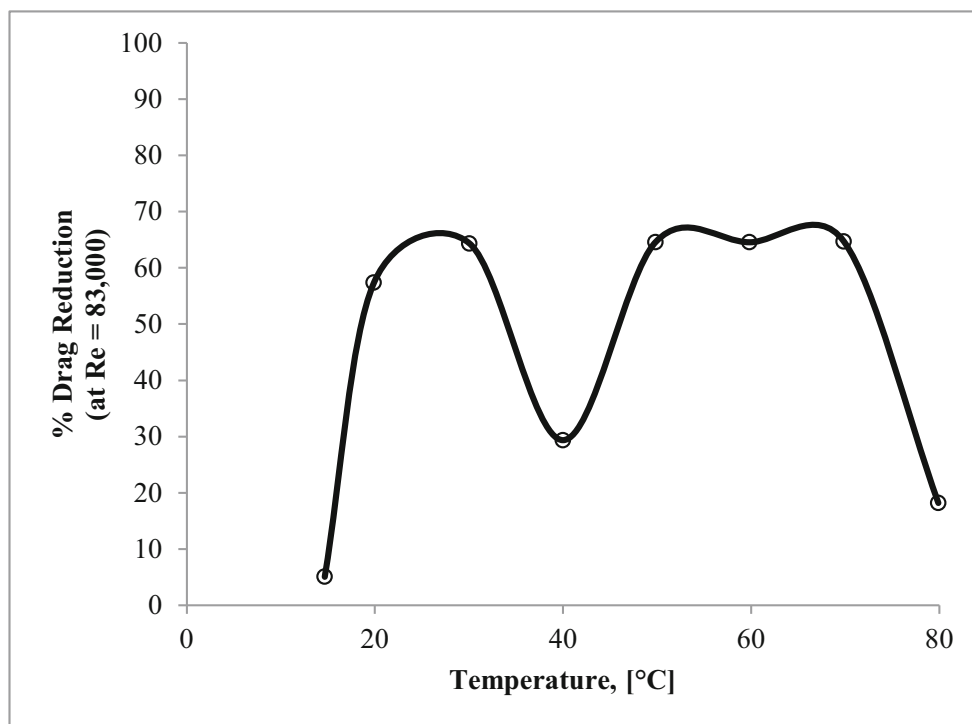
At each temperature, the %DR generally increases with Reynolds number, Re , until a maximum is reached. With further increase of Re , DR decreases because high wall shear stress causes micelle breakup to be more rapid than the rate of self-assembly. At each temperature, the wall shear stress at the maximum %DR is designated as the critical wall shear stress, τ_{wc} . Above this critical wall stress, τ_{wc} , DR decreases rapidly so τ_{wc} is a measure of the upper limit of effective DR. That is, high τ_{wc} indicates DR extends to high Re values. Decreases in the value of τ_{wc} at a fixed Reynolds number also reflect the effective DR temperature range.

All cryo-TEM images were taken at the George and Hannah Krumholz Laboratory for Advanced Microscopy of the Technion-Israel Institute of Technology. Cryo-TEM sample preparation was conducted in a temperature-controlled chamber with 100% humidity. A small drop of the studied solution was applied onto a perforated carbon film supported by an electron microscope copper grid. The drop was then blotted by a filter paper into a thin film, approximately 30 to 300 nm thick, and plunged into liquid ethane at its freezing point (~ 90 K). The process was rapid enough to vitrify the liquid, avoiding freezing artifacts. Images of the vitrified sample were recorded at a nominal objective lens underfocus of about 2 μm with a Philips CM120 transmission electron microscope operated at 120 kV, using an Oxford CT3500 cooling holder at about -180 °C (Talmon 2007).

Results

When the ratio of SDS to CTAT is higher than 5:95, the solutions phase separate, indicating the formation of large aggregates (Kawaguchi et al. 2012). The aggregates can be salted-in by adding 0.07 wt.% NaTos; they remain stable for months. The DR of CTAT/SDS:85/15 with 0.07% NaTos showed a surprising “temperature gap”, as shown by the sharp drop in DR (at $Re=83,000$) values above 30 °C, shown in Fig. 1.

Fig. 1 Temperature gap for drag reduction (at $Re = 83,000$) for CTAT(85 wt.%)/SDS(15 wt.%)/NaTosylate(0.07 wt.%). Note high DR at 30 and 50 °C and low DR at 40 °C



However, DR observed below and above 40 °C may be caused by different surfactant nanostructures, as will be discussed later.

Figure 2a–c show the micellar nanostructures at 25, 40, and 50 °C of the CTAT/SDS:85/15 with 0.07 wt.% NaTos system, which shows a DR temperature gap at 40 °C. The solution is uniform but cloudy from 25 to 50 °C. The cloudiness of the sample indicates that larger aggregates in the system coexist with threadlike micelles. Dense, solid-like aggregates can be seen by digital light microscopy images in Fig. 3 ($T = 25$ °C). Due to their exceptionally large size, these aggregates were likely to be expelled from the grid during cryo-TEM sample preparation, and are not seen in Fig. 2a–c. Therefore, cryo-TEM is not able to demonstrate the complete variety of nanostructures in this system. However, the smaller aggregates that are not excluded from the cryo-specimen are well preserved, because those specimens are vitrified, not frozen, namely, the liquid in the cryo-specimens is super-cooled, a glass, and has not undergone a freezing change of phase which could lead to artifacts. Figure 2a–c clearly shows three of the aggregate types in this system. At 25 °C, threadlike micelles are clearly visible (Fig. 2a). As the temperature increased to 40 °C, perforated membrane liposomes were formed with very few threadlike micelles (Fig. 2b), corresponding to the decrease in the DR effectiveness of the system. These vesicles transformed to threadlike micelles at 50 °C, coexisting with lamellar-like aggregates as shown in Fig. 2c. The large number of threadlike micelles at 50 °C, compared to 40 °C,

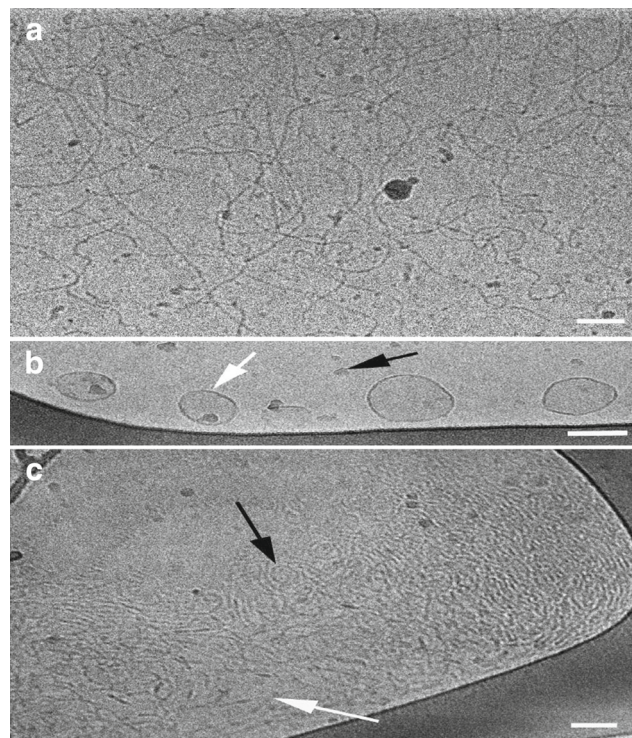


Fig. 2a–c Cryo-TEM images of a network of threadlike micelles in **a**) 10 mM CTAT/SDS:85/15 with 0.07 wt.% NaTos at 25 °C. The solution has high DR effectiveness at 25 °C, **b**) 10 mM CTAT/SDS:85/15 with 0.07 wt.% NaTos at the drag reduction gap temperature, 40 °C. Imperfect vesicles (white arrows) are observed. The solution has significant loss of DR at 40 °C, **c**) 10 mM CTAT/SDS:85/15 with 0.07 wt.% NaTos at 50 °C. White arrows point to lamellar-like aggregates, coexisting with threadlike micelle tangles (black arrow). The solution regains DR effectiveness at 50 °C. Bars are 50 nm

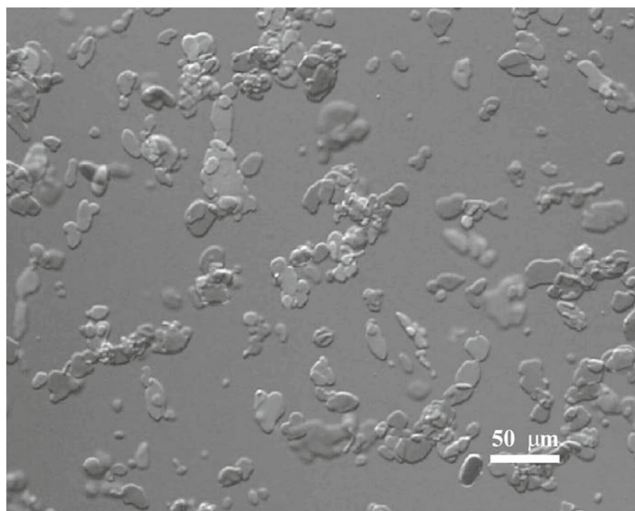


Fig. 3 Digital light microscopy (DLM) image (Nomarski optics) of large aggregates, possibly formed by CTA^+/DS^- , in 10 mM CTAT/SDS:85/15 with 0.07 wt.% NaTos at 25 °C

coincides with the recovery of DR effectiveness at this temperature.

Nanostructures

Salt-free CTAT/SDS mixtures precipitate at a weight fraction of SDS as low as 5%, reflecting their tendency to form very densely packed aggregates. At 25 °C, the uniform yet still cloudy solution of CTAT/SDS:85/15 with 0.07% NaTos contains the densely packed threadlike micelle networks shown in Fig. 2a. Salkar et al. (1998) suggested the coexistence of threadlike micelles, consisting of $\text{CTA}^+/\text{tosylate}$ ions and a CTA^+/DS^- complex with a solid-like structure. Addition of SDS breaks the balance of the two types of aggregates. Because DS^- is more strongly bound to the CTA^+ ions at higher temperatures, tosylate ions dissociate from CTAT and enter the water phase.

Habon was prepared by making a mixture of cetyltrimethylammonium bromide (CTAB) and 3-hydroxy-2-naphthoate (HNC) at 1:1 molar ratio, with the sodium and bromide ions removed by ion exchange. The HNC^- ions, with naphthoate rings, bind very strongly to the CTA^+ because of their high hydrophobicity. It has been suggested that HNC can be viewed as an anionic surfactant. Narayanan et al. (1997), Hassan et al. (1998), and Horbaschek et al. (1998) studied the system denoted as CTAHNC, which is essentially the same system as Habon, with non-associative electrolytes such as sodium bromide present. In the salt-free system they observed, by optical microscopy, densely packed vesicles at ambient temperature, which transformed to threadlike micelles at 46 °C. The transition domain has a width of about 20 °C (40 to 60 °C), where vesicles and threadlike micelles coexist (Merdes et al. 1997). Addition of NaBr to the CTAHNC

vesicles caused precipitation, which was attributed to the increased ionic strength that reduced the repulsive interactions between vesicles. That caused aggregation of vesicles into a condensed precipitate. The solution with salt remained turbid until temperature was increased to 60 °C.

The “gap” phenomenon

Chou (1991) suggested that the gap of the 2.85 mM Habon/9.375 mM NaSal system at 50 °C resulted from the competition of the two counterions (Sal^- and HNC^-) for sites on the micellar surface. The 5 mM CTA/12.5 mM Sal system has a DR effective temperature range from 15 to 70 °C, indicating that at temperatures above 50 °C that the Sal^- ions begin to disassociate from the micelles. The HNC^- ions have stronger associating ability and the 2.85 mM Habon (molar ratio of HNC^- to $\text{CTA}^+ = 1$) solution is DR effective from 40 to 100 °C. As noted above, the CTAHNC system showed a temperature-induced transition from vesicles to threadlike micelles at 46 °C (Horbaschek et al. 1998; Merdes et al. 1997), close to the temperature gap he observed at 50 °C. Thus, there are a series of phase transitions in the 2.85 mM Habon/9.375 mM NaSal system as temperature increases. At temperatures below 50 °C, where both counterions are effectively bound to CTA^+ ions, the $\text{CTA}^+/\text{Sal}^-$ threadlike micelles coexist with the $\text{CTA}^+/\text{HNC}^-$ vesicles, but only the former gives DR. At temperatures around 50 °C, the binding ability of the Sal^- ions starts to drop, while the HNC^- ions are still highly associated due to their stronger resistance to thermal motion. The change in the relative binding ability changes the balance between the two types of aggregates in solution. The proportion of threadlike $\text{CTA}^+/\text{Sal}^-$ micelles decreases, favoring the formation of CTAHNC vesicles; thus, the solution loses its DR properties. At temperatures above 50 °C, enough CTAHNC vesicles transform into threadlike micelles, so that the solution regains its DR effectiveness.

The reason that the observed gap temperature is higher than the lower temperature limit for drag reduction of the pure Habon (CTAHNC) without NaSal solution (40 °C) and the observed vesicle-threadlike micelle transition temperature (46 °C) is the presence of excess Sal^- ions. As the Sal^- ions lose their binding ability at around 50 °C, they behave more like a common electrolyte ion such as Br^- , whose main effect is increasing the ionic strength. The CTAHNC vesicles tend to aggregate into a condensed state as in the CTAHNC-NaBr system, as noted above (Merdes et al. 1997), which does not transform to threadlike micelles until 60 °C.

Chou (1991) also studied DR of the CTAC (cetyltrimethylammonium chloride)/NaHNC mixed systems at HNC^- to CTAC molar ratios of 0.67, 1, 1.5, and 2.5. Those mixtures are similar to Habon solution with additional NaCl and NaHNC. The lower temperature limits for DR were 40 °C for the ratio 0.67, 1, and 1.5 systems, and between 60

and 70 °C for the ratio 2.5 system. Increasing the molar ratio of HNC^- to CTA^+ led to poorer DR at low temperatures. Because of the excess NaSal in Chou's 2.85 mM Habon/9.375 mM NaSal solution, the concentration of CTA^+ ions available to HNC^- was much lower than the total CTA^+ ions present. Thus, the molar ratio of HNC^- to available CTA^+ to form $\text{CTA}^+/\text{HNC}^-$ vesicles was larger than the unity value in pure Habon (CTAHNC) systems, increasing the lower temperature limit for drag reduction, which led to the temperature gap of the Habon/NaSal system at 50 °C, at which the dominant aggregate morphology is that of vesicles.

We observed a similar phase transition in the CTAT/SDS:85/15 system with 0.07% NaTos, which has a DR temperature gap at 40 °C. The DS^- and tosylate ions compete for binding with CTA^+ ions, resulting in coexistence of CTA/tosylate threadlike micelles and a CTA^+/DS^- complex. At 25 °C threadlike micelles are present (Fig. 2a), and the solution is DR, but the micelles dissociate as tosylate ions lose their binding ability at 40 °C. However, this temperature is not sufficiently high for enough of the CTA^+/DS^- complex to transform to DR effective threadlike micelles. As seen in Fig. 2b, threadlike micelles are absent in the solution at 40 °C, while flake-like bilayers and vesicles make up the major nanostructures. Therefore, the solution loses much of its DR ability. With further increase in temperature, the CTA^+/DS^- aggregates transform into threadlike micelles. Figure 2c clearly shows such transition at 50 °C, at which the solution regains its DR effectiveness.

In summary, the proposed mechanism for the DR temperature “gap” involves one cationic surfactant CTA, two counterions I_1 and I_2 with binding abilities $I_1 < I_2$ (DS^- acts as a strongly binding counterion), and two critical temperatures, T_{c1} and T_{c2} . In the CTA^+ solution with only one of the counterions, threadlike micelles form in the CTA/I_1 system, while vesicles or a lamellar phase form in the CTA/I_2 system. In the

mixture of $\text{CTA}/I_1/I_2$, at a temperature $T < T_{c1}$, both I_1 and I_2 have high binding affinity to the CTA micelles, and CTA/I_1 threadlike micelles coexist with CTA/I_2 vesicles. The two aggregates are in dynamic equilibrium depending on the temperature, ratio of CTA/I_1 and CTA/I_2 , and possibly shear. At the temperature T_{c1} , the binding affinity of counterion I_1 starts to decrease, driving the equilibrium nanostructure toward vesicles. T_{c2} is the temperature for the transition of the dense complex CTA/I_2 into threadlike micelles. Systems containing a significant amount of the CTA/I_2 complex require a high T_{c2} for the transition into threadlike micelles. For the temperature gap to occur, T_{c1} must be lower than T_{c2} , so that there is a temperature range in which the thermal energy is large enough to breakup the CTA/I_1 threadlike micelles, yet low enough not to induce the transition of the CTA/I_2 vesicles to threadlike micelles.

If T_{c2} is lower than T_{c1} , the temperature ranges in which CTA/I_1 and CTA/I_2 threadlike micelles exist overlap, and no “temperature gap” is observed. This may be the situation in the CTAT/SDS:90/10 system, which did not have a “temperature gap” for DR. In addition, the 90/10 system had higher DR (see Fig. 4) effectiveness than the 85/15 system, especially from 30 to 60 °C, which may be attributed to more complete transition to threadlike micelles in this temperature range.

Conclusions

A drag reduction “temperature gap” is reported for a surfactant/two counterion system, in which one of the counterions is an anionic surfactant. Cryo-TEM nanostructure images demonstrate why drag reduction is lost and regained as temperature increases. This temperature gap and two previous examples are explained in terms of the relative binding strengths of the two counterions.

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References

- Chou L-C (1991) “Drag Reducing Cationic Surfactant Solutions for District Heating and Cooling Systems” Ph.D. Dissertation, The Ohio State University, Columbus, OH
- Hassan PA, Candau SJ, Kern F, Manohar C (1998) *Langmuir* 14:6025–6029
- Horbascsek K, Hoffmann H, Thunig CJ (1998) *Colloid Interface Sci* 206: 439–456
- Kawaguchi Y, Li F-C, Yu B and Wei J-J (2012) “Turbulent drag reduction by surfactant additives”, John Wiley & Sons, Singapore Pte. Ltd

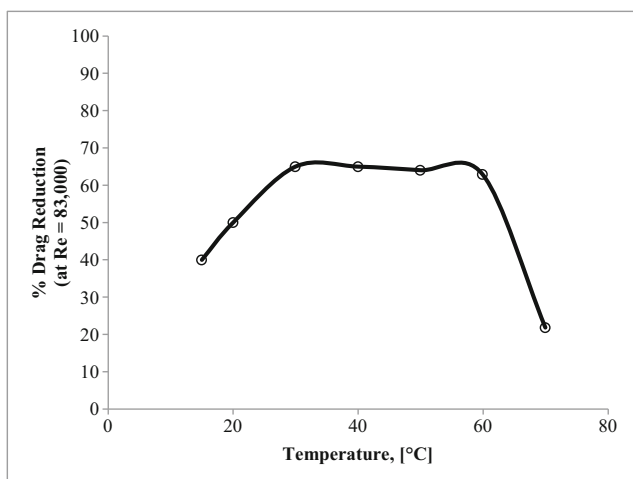


Fig. 4 Temperature dependence of drag reduction (at $Re = 83,000$) for CTAT(90 wt.)/SDS(10 wt.)/NaTosylate(0.07 wt.%). Note lack of temperature gap at 40 °C as shown in Fig. 1

- Kleuker H-H, Althaus W, Steiff A, Weinspach PM (1991) Proc. Int. Symp. on Fluids for District Heating, Bohm B (ed) Technical University of Denmark, Copenhagen, Denmark, 123–137
- Merdes E, Narayanan J, Oda R, Kern F, Candau SJ (1997) *J Phys Chem B* 101:2256–2258
- Narayanan J, Manohar C, Kern F, Lequeux F, Candau SJ (1997) *Langmuir* 13:5235–5243
- Salkar RA, Mukesh DS, Samant D, Manohar C (1998) *Langmuir* 14: 3778–3782
- Talmon Y (2007) Chapter 5, Cryogenic-Temperature Transmission Electron Microscopy (Cryo-TEM), in *Giant Micelles: Properties and Applications*, Surfactant Science Series, R Zana and EW Kaler (Eds) Vol. 140, CRC Press, Taylor and Francis, New York, pp 163–178
- Zakin JL and Ge W (2010) “Polymers and Surfactant Drag Reduction in Turbulent Flows” in *Polymers Physics: From Suspensions to Nanocomposites and Beyond*. L. Utracki and A.M. Jamieson (eds) John Wiley, Hoboken, NJ
- Zakin JL, Ge W, Zhang Y (2007) Chapter 16, Drag Reduction by Surfactant, in *Giant Micelles, Properties and Applications*, Surfactant Science Series, R. Zana and E.W. Kaler (Eds) Vol. 140, CRC Press, Taylor and Francis, New York, pg 473–492
- Zhang Y (2005) “Correlations Among Surfactant Drag Reduction, Additive Chemical Structures, Rheological Properties and Microstructures in Water and Water/Co-Solvent Systems” PhD Dissertation, The Ohio State University, Columbus, OH