

Abstract

Non-ionic surfactants are important for a wide range of industrial applications including detergency, stabilization, and emulsification. These macromolecules play a critical role in oil-spill cleanup by stabilizing oil-in-water emulsions produced in the presence of nanoparticles, cosolvents, and other ionic or nonionic surfactants. This study investigates the effect of molecular architecture on micellization thermodynamics in aqueous solutions for a homologous series of Lutensol® nonionic surfactants. The two surfactant families studied are branched alkyl ethoxylate and branched alkyl alkoxyate surfactants. To our best knowledge, this is the first study that attempts to analyze single-branched surfactants. To conclude this study on molecular architecture, we additionally analyze the thermodynamic effects of 1) the ethylene oxide-based (EO) head group and 2) the propylene oxide (PO) segment which exists within the (EO) head group of the alkyl alkoxyate family. Conclusions from this study are useful in predicting interactions between oil and water in complex aqueous environments.

Introduction

Surfactants stabilize microemulsions by lowering surface tension and Gibbs' Free Energy.

The middle phase of an emulsion is surfactant-rich and acts as the interface between oil and water faces.

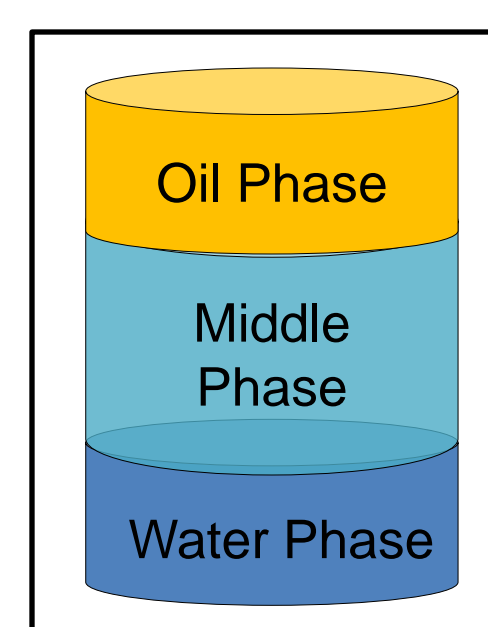


Figure 1. Emulsion of Oil and Water

Surfactants self-assemble in solution in order to minimize free energy. For traditional surfactants, this occurs through an increase in system entropy as hydrophobic moieties are removed from water and packed into hydrophobic domains, resulting in greater freedom for bulk water molecules.

Critical micelle concentration (cmc) data are useful for direct calculation of free energy and micellization enthalpy. Cmc can also indicate the most (or least) compatible molecular architecture and chemical composition in oil-water systems.

$$\Delta G = \Delta A\gamma - T\Delta S$$

$$\Delta G = RT \ln X_{cmc}$$

Lipophilic linkers contain a small hydrophilic head and a large hydrophobic tail. They equalize hydrophilic-lipophilic interactions in unbalanced systems by extending the reach of the surfactant into the oil phase and producing a greater degree of orientation in the oil phase

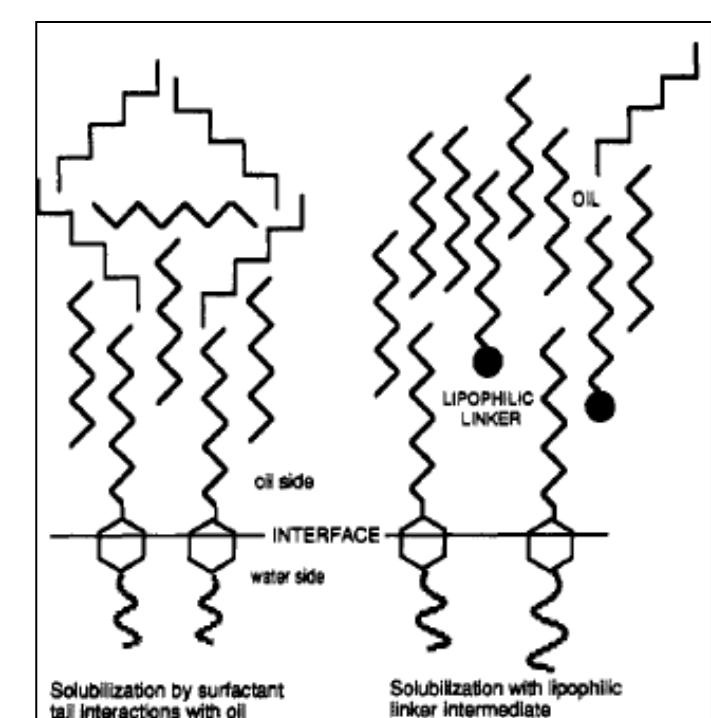


Figure 2. Lipophilic Linker Effect

Modifying the structure of the surfactant molecule to incorporate lipophilic linker ability eliminates the need for a cosurfactant.

AE & APE Surfactants

Branched Alkyl Ethoxylate Surfactants (AE) C_iEO_j

Lutensol® XP Surfactants:
XP-30, 50, 70, 80, 90

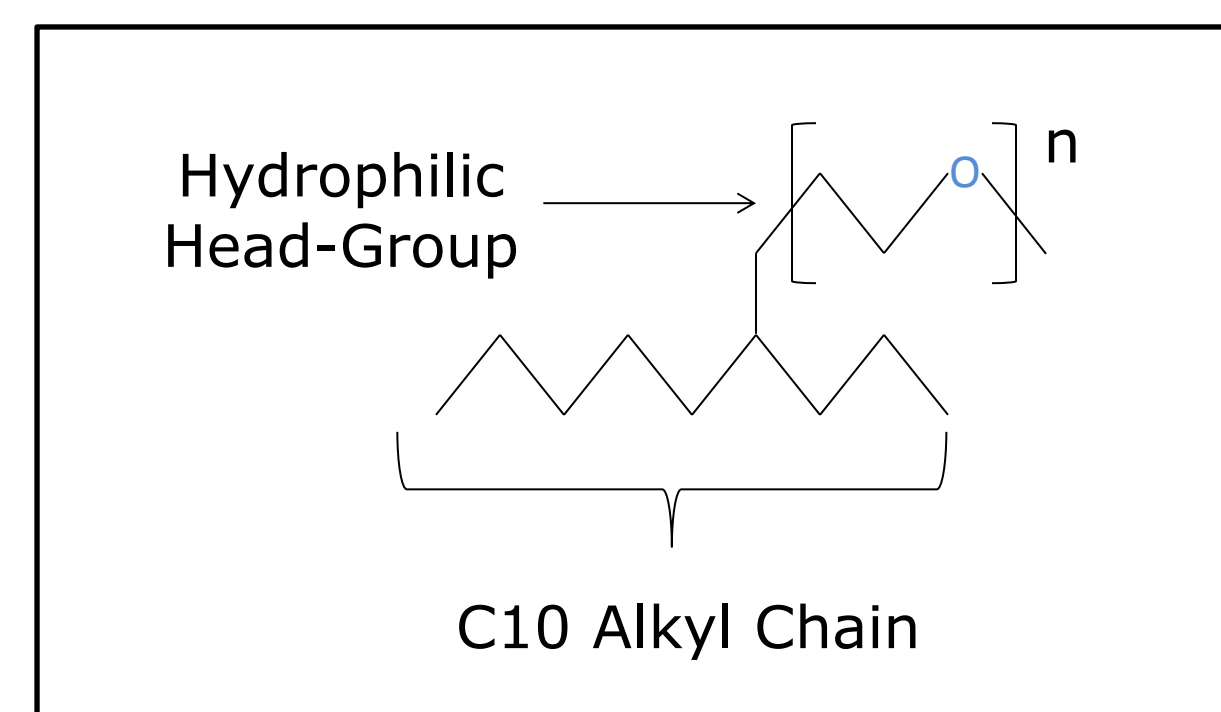


Figure 3. Structure of Lutensol® XP-Surfactant

Branched Alkyl Propoxy Ethoxylate Surfactants (APE) $C_iPO_nEO_j$

Lutensol® XL Surfactants:
XL-50, 70, 80, 90, 100, 140

XL contains a PO segment

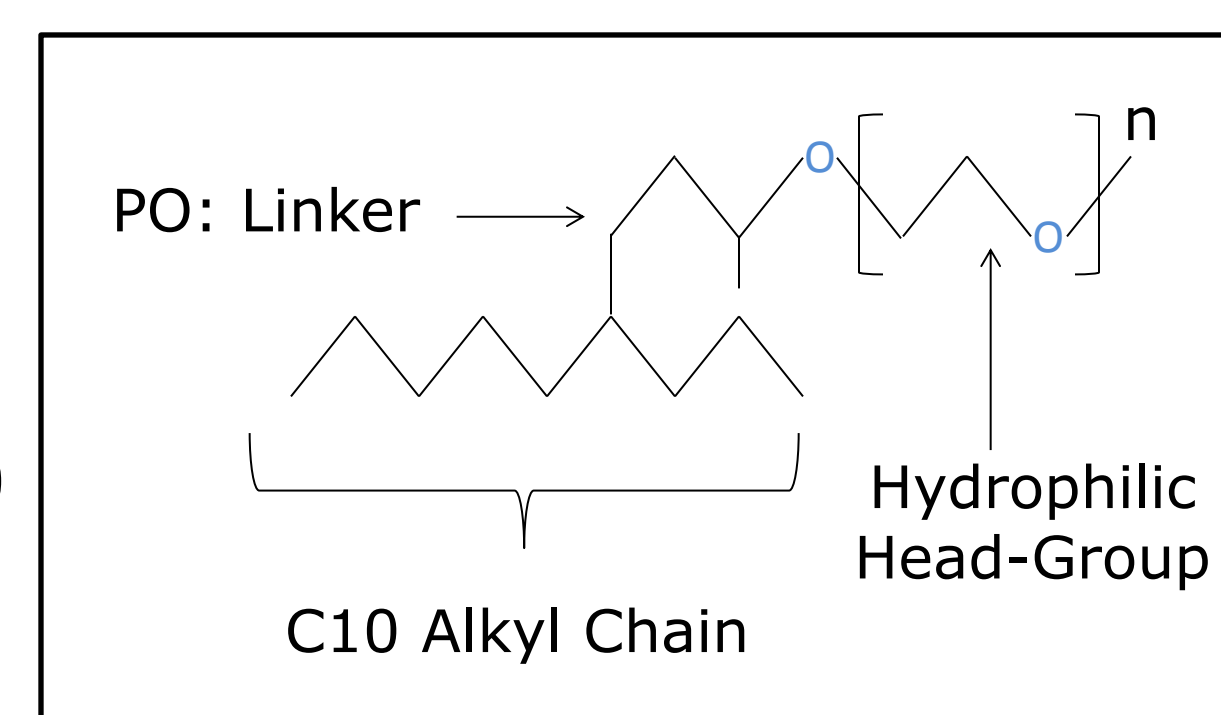


Figure 4. Structure of Lutensol® XL-Surfactant

Methods

Fluorescence spectroscopy is useful for evaluating the critical micelle concentration (cmc) and micropolarity of surfactant solutions.

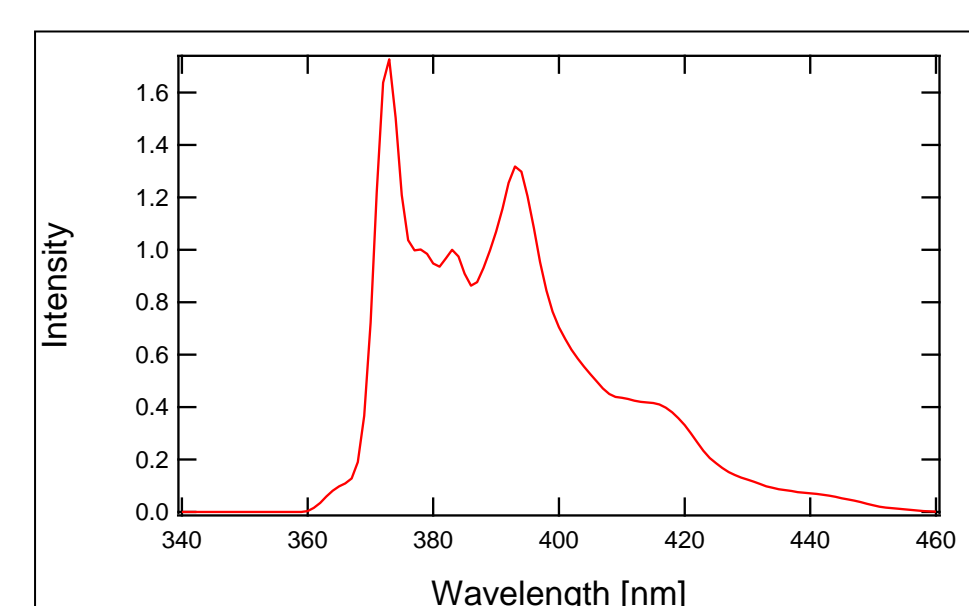


Figure 5. Fluorescence Output

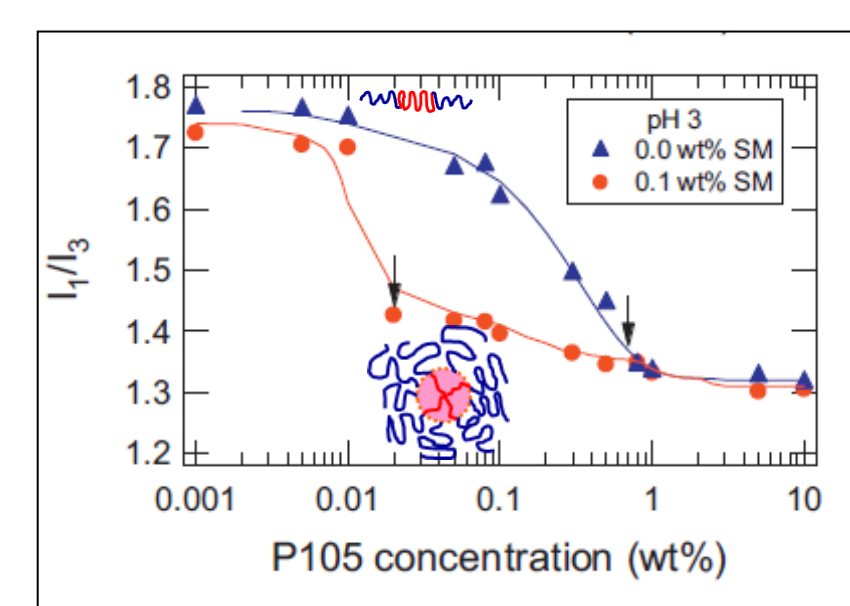


Figure 6. I1/I3 vs. Concentration Curve

Fluorescence experiments utilize pyrene as a "reporter", as it is soluble in hydrophobic media. Pyrene reports the polarity of its local environment. It emits five vibronic peaks when excited by light.

The ratio of the third peak to the first peak (I_1/I_3) reports the polarity in the pyrene local environment. Low values indicate hydrophobic environments, thus indicating micelle formation.

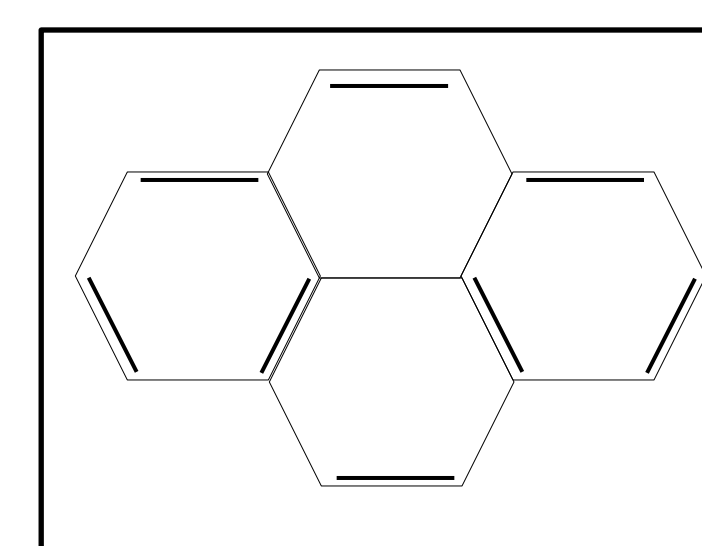


Figure 7. Pyrene

References

- Acosta, E.J., Harwell, J.H., Sabatini, D.A. (2004) *Journal of Colloid and Interface Science*, 274: 652-664.
 Bethod, A., Tomer, S., Dorsey, J. (2001). *Talanta*, 55: 69-83.
 Graciaa, A., Lachaise, J., Cucuphat, C., Bourrel, M., Salager, J.L. (1993) *Langmuir*, 9: 669-672.
 Sarkar, B., Venugopal, V., Tsianou, M., Alexandridis, P. (2013) *Colloids and Surfaces A*, 422: 155-164.
 Sarkar, B., Alexandridis, P. (2010) *Journal of Physical Chemistry B*, 114: 4485-4494.
 Uchiyama, H., Acosta, E., Tran, S., Sabatini, D.A., Harwell, J.H. (2000) *Industrial & Engineering Chemistry Research*, 39: 2704-2708.

Results

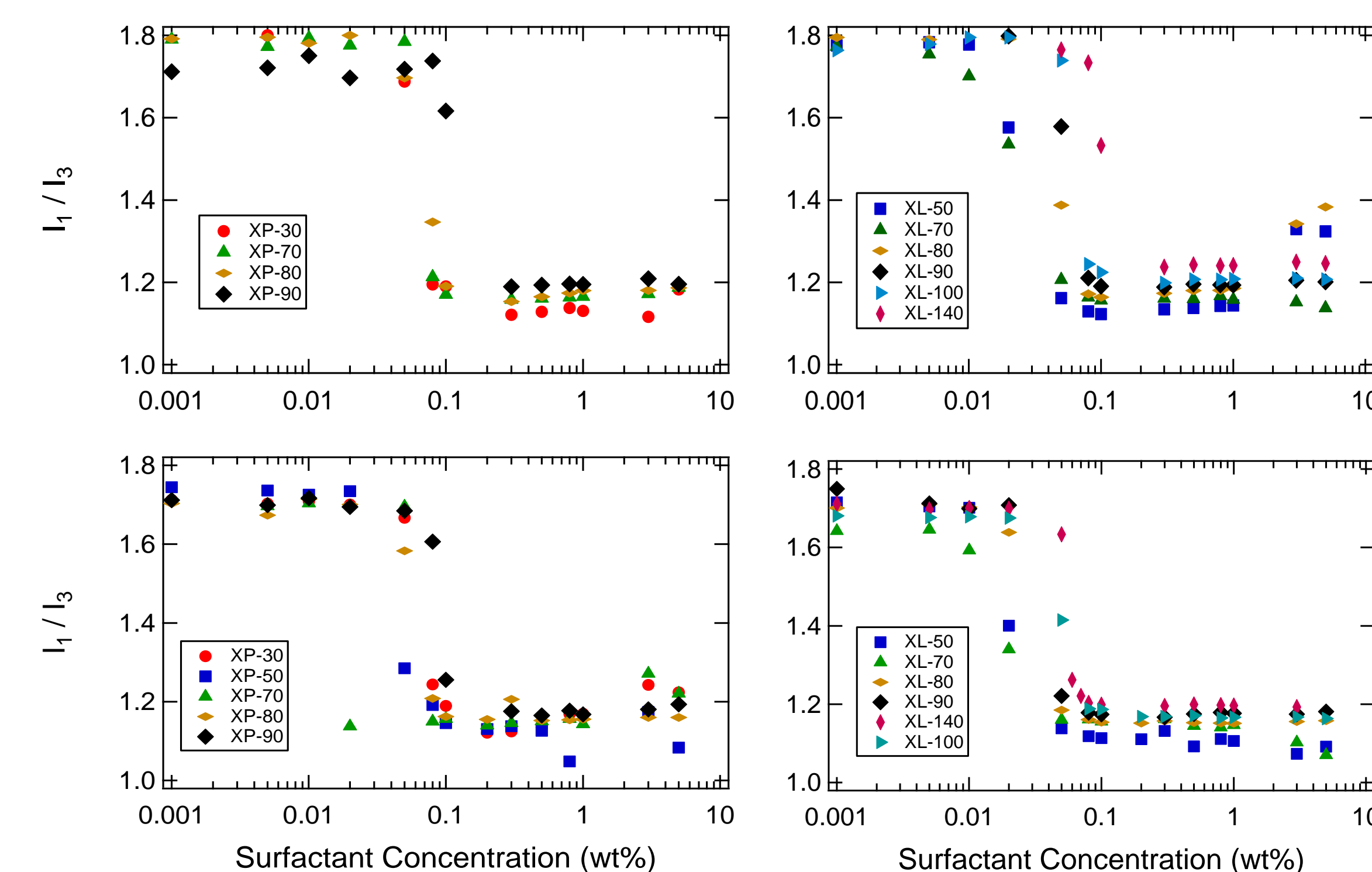


Figure 8. Summary of Fluorescence Results – Limited impact of temperature on cmc. Top L (22°C, XP®); Top R (22°C, XL®); Bottom L (50°C, XP®); Bottom R (50°C, XL®)

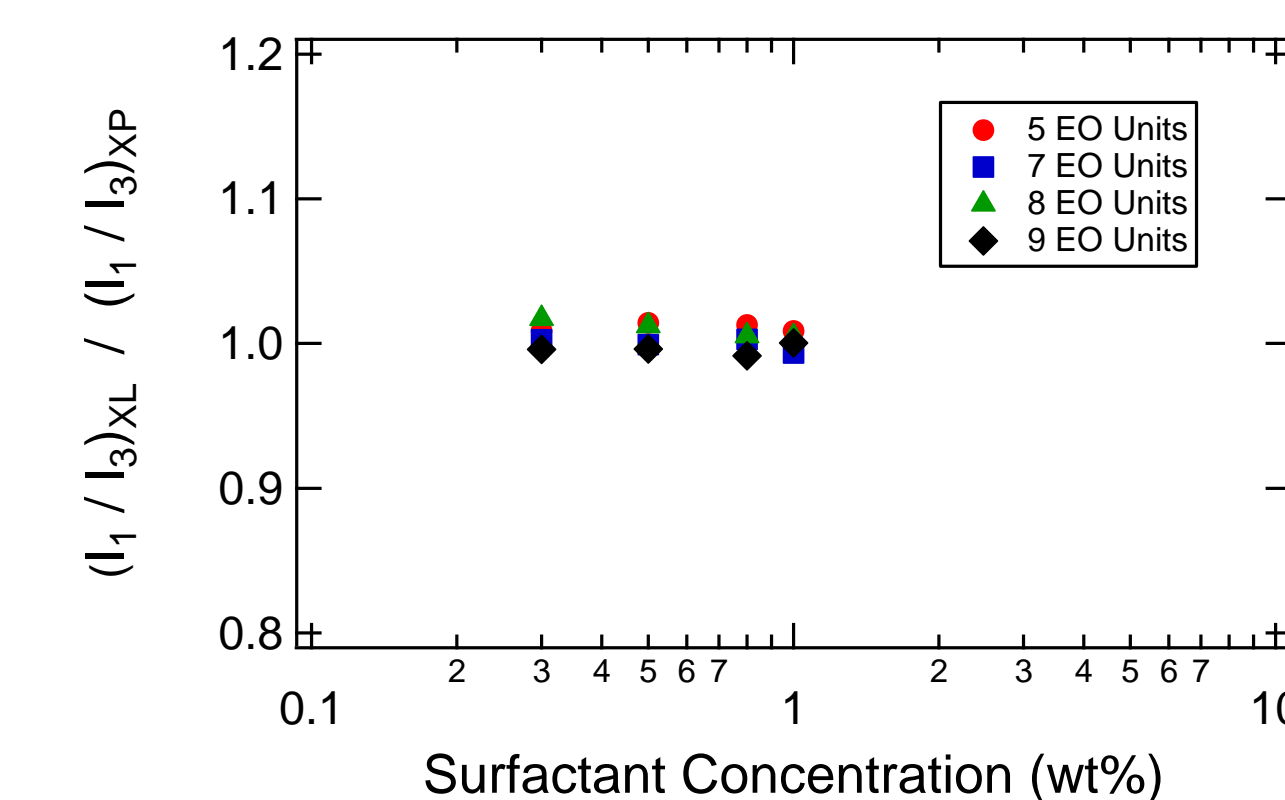


Figure 9. XL® vs. XP® I1/I3 Ratios

Below a 1 wt% concentration, the polarity of the micelle local environment is approximately equivalent in both XL® and XP® surfactants. Cmc for this family of surfactants is typically reached within a concentration of 0.1-1 wt%.

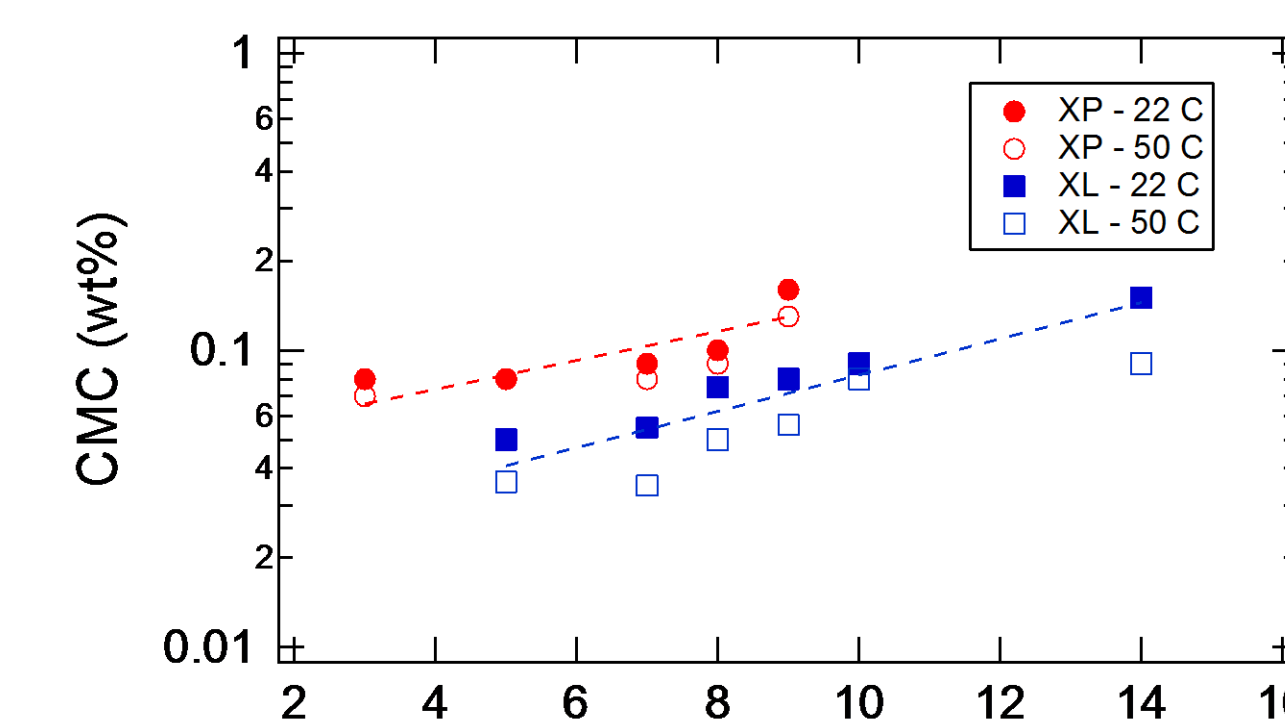


Figure 10. CMC vs. EO chain length

Like their linear cousins, branched AE and APE surfactants exhibit higher cmcs with higher HLB (larger hydrophilic headgroup)

There is greater sensitivity to temperature in the XL-series due to presence of PO

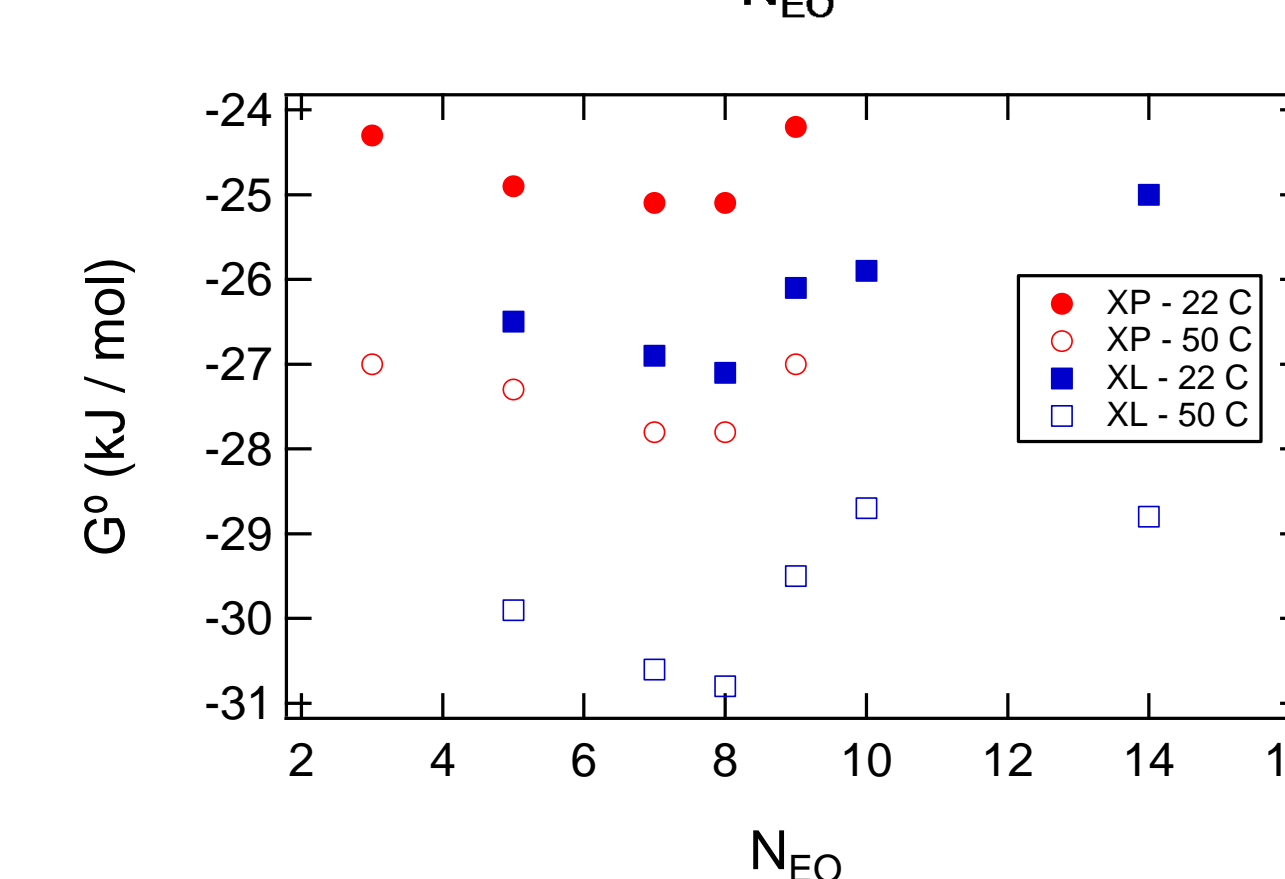


Figure 11. Free energy vs EO chain length

Free energy of micellization reaches a minimum for both XL® and XP® type surfactants when the hydrophilic head contains 7 or 8 EO groups.

Increasing temperature lowers the free energy of micellization. More negative values of free energy are the result of lower cmcs.

Surfactant	cmc (mol / L) at 22°C	ΔG_{mic} (kJ / mol) at 22°C	$\Delta G_{(PO)}$ (kJ / mol) at 22°C
XL - 90 $C_{10}(PO)_1(EO)_9$	1.07×10^{-3}	-26.6	2.38
XL - 80 $C_{10}(PO)_1(EO)_8$	0.81×10^{-3}	-27.3	1.48
XL - 90 $C_{10}(PO)_1(EO)_9$	1.42×10^{-3}	-26.0	2.63
XL - 100 $C_{10}(PO)_1(EO)_{10}$	1.43×10^{-3}	-25.9	2.43
XL - 140 $C_{10}(PO)_1(EO)_{14}$	2.05×10^{-3}	-25.0	2.44

Figure 12. Presence of PO segment in XL family creates a graded hydrophilic character throughout the molecule. Positive free energy values indicate hydrophilicity