Beyond the Effective Solvent: How Fractionation and Solvent-Solvent Interactions Drive Micellization in Binary Solvents

Anne Floor den Ouden [1,2], Mark Vis [1,2], Remco Tuinier [1,2]

[1] Laboratory of Physical Chemistry, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, Netherlands
[2] Institute for Complex Molecular Systems, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, Netherlands

a.f.d.ouden@tue.nl

We have investigated the role of solvent fractionation on micellization in mixed solvents. Amphiphilic block copolymers can self-assemble into micelles in a selective solvent: one that preferentially solvates the solvophilic block(s). In many practical situations, the solvent consists of two (or more) different species. A common simplification in the theory of block copolymer self-assembly treats binary solvent mixtures as a single effective solvent characterized by averaged interaction parameters. We show that this approximation can break down: solvent fractionation, the unequal partitioning of solvent components between micelle cores, coronas, and interfaces, fundamentally alters micelle properties like aggregation number, and can drive morphology transitions that a single-solvent description fails to predict. We have systematically varied the core-solvent, corona-solvent and solvent-solvent Flory-Huggins interaction parameters to study the effect of solvent fractionation and solvent-solvent interactions using Scheutjens–Fleer self-consistent field lattice computations [1]. We compare the resulting structures with single-solvent reference systems at the same averaged interaction parameter and with an experimental system of poly(1,2-butadiene-b-ethylene oxide) (PB-PEO) micelles in water-tetrahydrofuran (THF) solvent mixtures [2]. Additionally, we examine morphology transitions induced by changes in binary solvent composition and selectivity. These results establish that binary solvents cannot be replaced by an effective single solvent without loss of predictive power, and they open a practical route to morphology control through tuning of solvent composition.

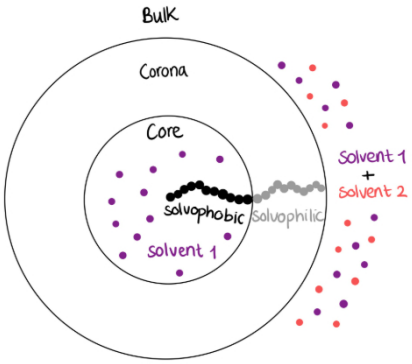

Illustration of solvent fractionation into the core of the micelle.

References:

[1] Fleer, G., Stuart, M. C., Scheutjens, J. M., Cosgrove, T., & Vincent, B. (1993). *Polymers at interfaces* . Springer Science & Business Media.
[2] Kelley, E. G., Smart, T. P., Jackson, A. J., Sullivan, M. O., & Epps, T. H. (2011). Structural changes in block copolymer micelles induced by cosolvent mixtures. *Soft Matter* , 7(15), 7094-7102.