

The Effects of Salting-Out Salts on Diffusion of a Non-Ionic Micelle (Tyloxapol)

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Abstract. Micelles represent an important example of nanoparticles with the ability to host nonpolar molecules in water. Understanding the effect of salts on micelle diffusion is important for enhancing particle insertion into porous materials in the presence of salt brines with application in enhancing oil recovery and soil remediation. In this poster, the effect of two salting-out salts (sodium sulfate and magnesium sulfate) on the diffusion of a non-ionic micelle (tyloxapol) is examined. Micelle diffusion coefficients were experimentally determined in aqueous salt solutions using dynamic light scattering at 25 °C. Our experimental results show that the micelle diffusion coefficient is approximately constant until a critical salt concentration is reached. After this concentration, micelle diffusion was found to decrease significantly, and this behavior reflects a corresponding increase in micelle size. To explain our experimental results, we introduce a two-state equilibrium model showing that relatively large surfactant aggregates become thermodynamically more stable than micelles at high salt concentrations. The results of our model will be used to examine the effect of salt gradients on micelle diffusion.

Introduction

Micelles are nanoparticles formed by the self-assembly of surfactants in water. The core is hydrophobic, and the outer layer is hydrophilic. The surfactant investigated in this work is shown in Fig. 1. Its micelles are nonionic globular colloidal particles with interfacial properties governed by Polyethylene Glycol (PEG) functional groups.

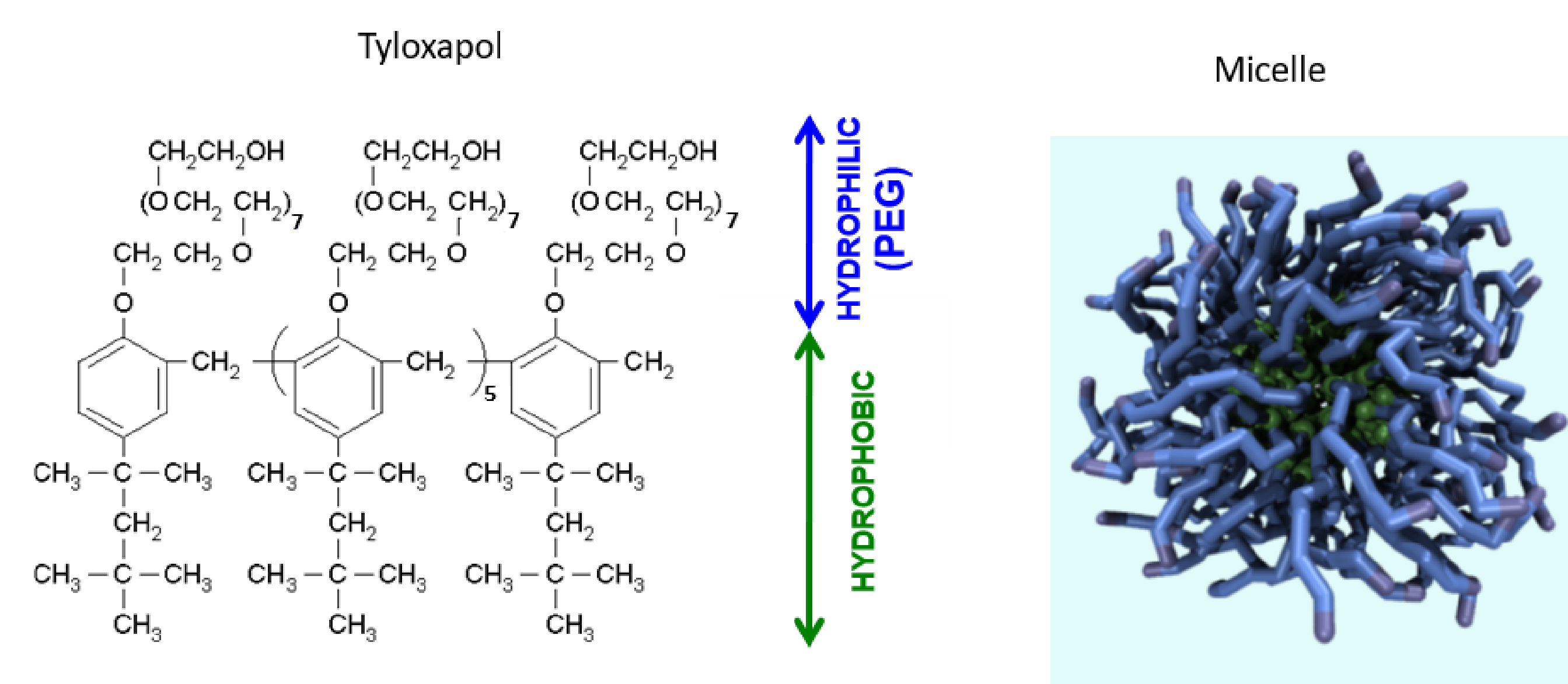


Figure 1. The chemical structure of the Tyloxapol surfactant and the micelle 3-dimensional structure in water.

Since micelles possess a hydrophobic inner core, they can encapsulate nonpolar molecules such as hydrocarbons. In Fig. 2, it is shown how micelles may be used to extract hydrocarbons from porous materials in an aqueous environment. In this figure it is also shown how salt gradients could be used to boost micelle insertion into the pores, enhancing hydrocarbon extraction.

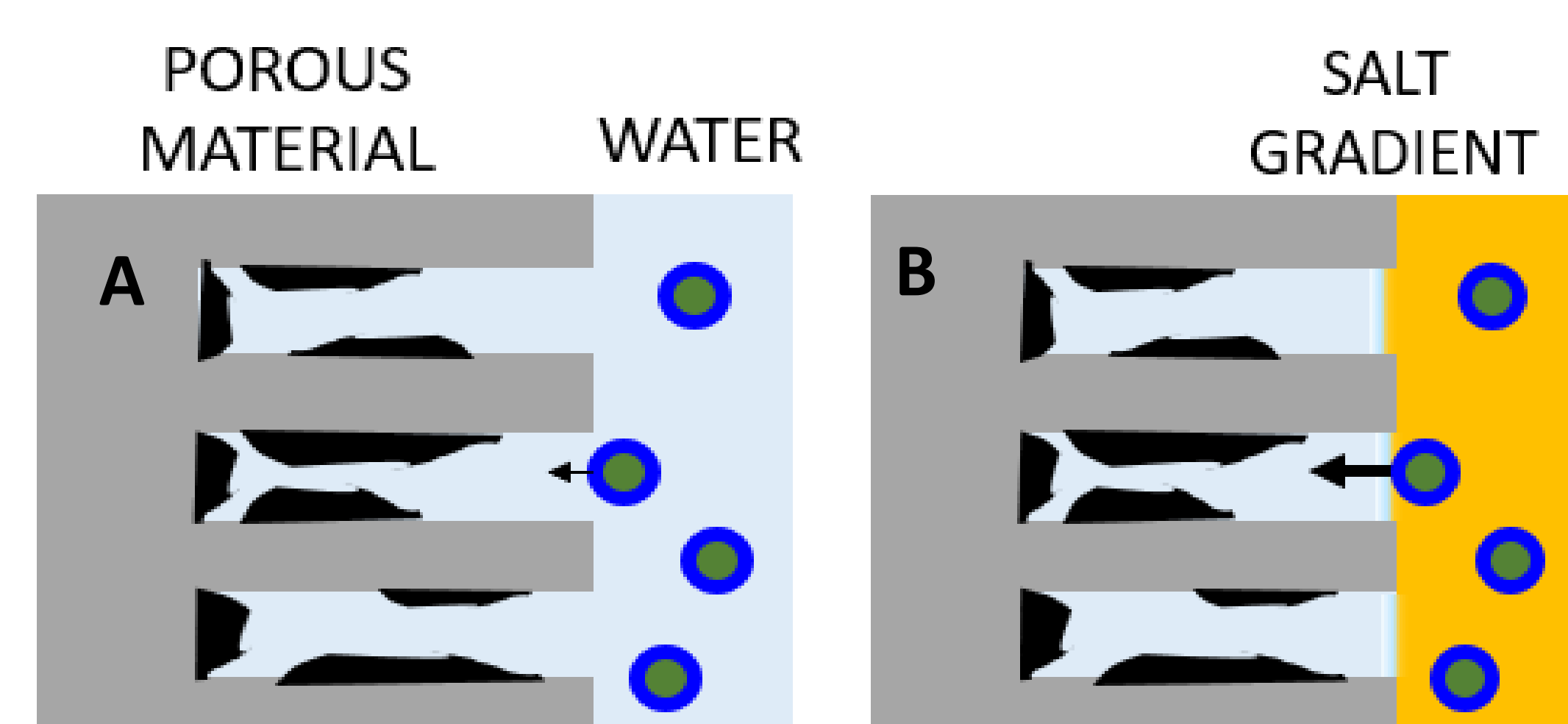


Figure 2. (A) Micelle diffusion into porous material is slow in water. (B) Micelle diffusion into the pores may be boosted in the presence of salt gradients. This favors the extraction of hydrocarbon molecules (shown as black domains inside the pores).

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Results

An essential aspect of our research is understanding effect of salt on micelle aggregation state. This can be characterized by measuring the micelle diffusion coefficient as a function of salt concentration for two salts: Na₂SO₄ and MgSO₄. We used dynamic light scattering (DLS) to determine micelle diffusion coefficients (D) at 25 °C. In Fig. 3, our data were fitted to the linear equation $D=D_0(1+K\phi)$ to extract the infinite dilution micelle coefficient (D_0). The value of D_0 was then used to calculate the micelle hydrodynamic radius as a function of salt concentration and type.

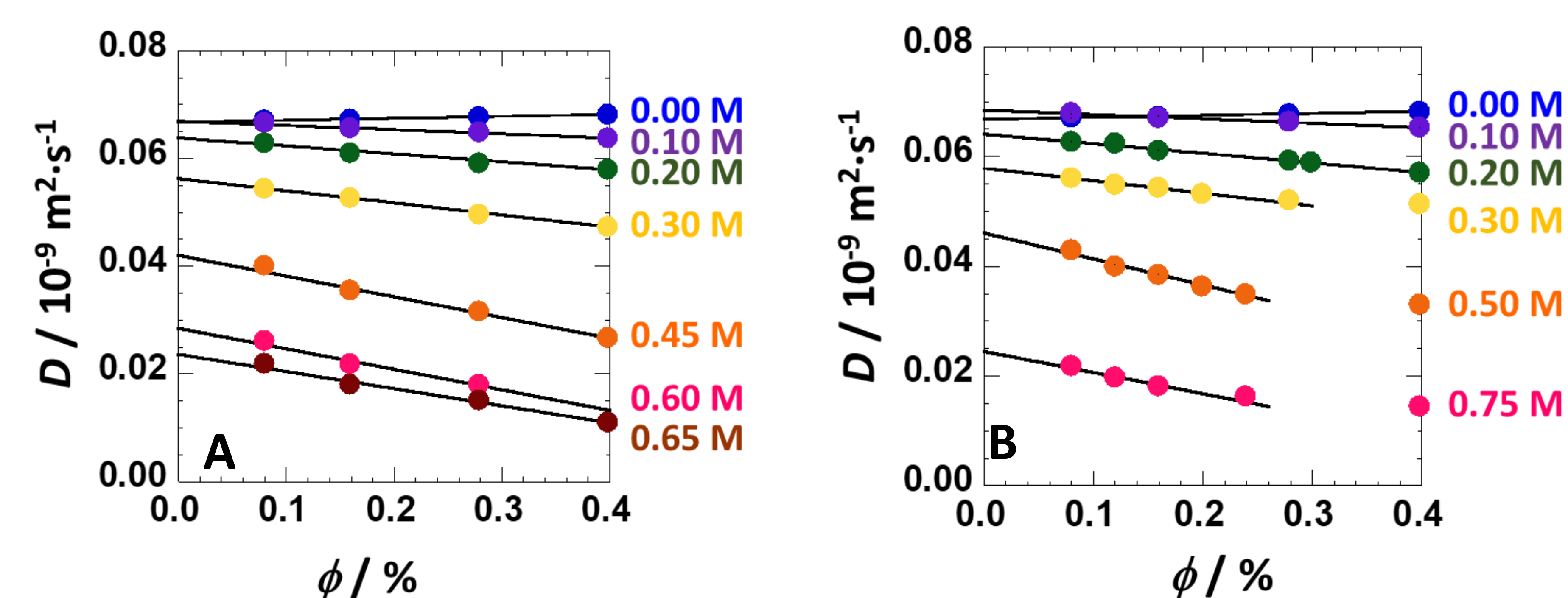


Figure 3. Diffusion coefficient (D) of tyloxapol micelles as a function of surfactant volume fraction (ϕ). In the presence of aqueous (A) Na₂SO₄ and (B) MgSO₄. Appended numbers are salt molar concentration.

The values of R_h in Fig. 4 were calculated from D_0 using the Stokes Einstein equation. The hydrodynamic radius remained approximately constant up to the osmolarity of ≈ 1 M for both salt cases and then significantly increased.

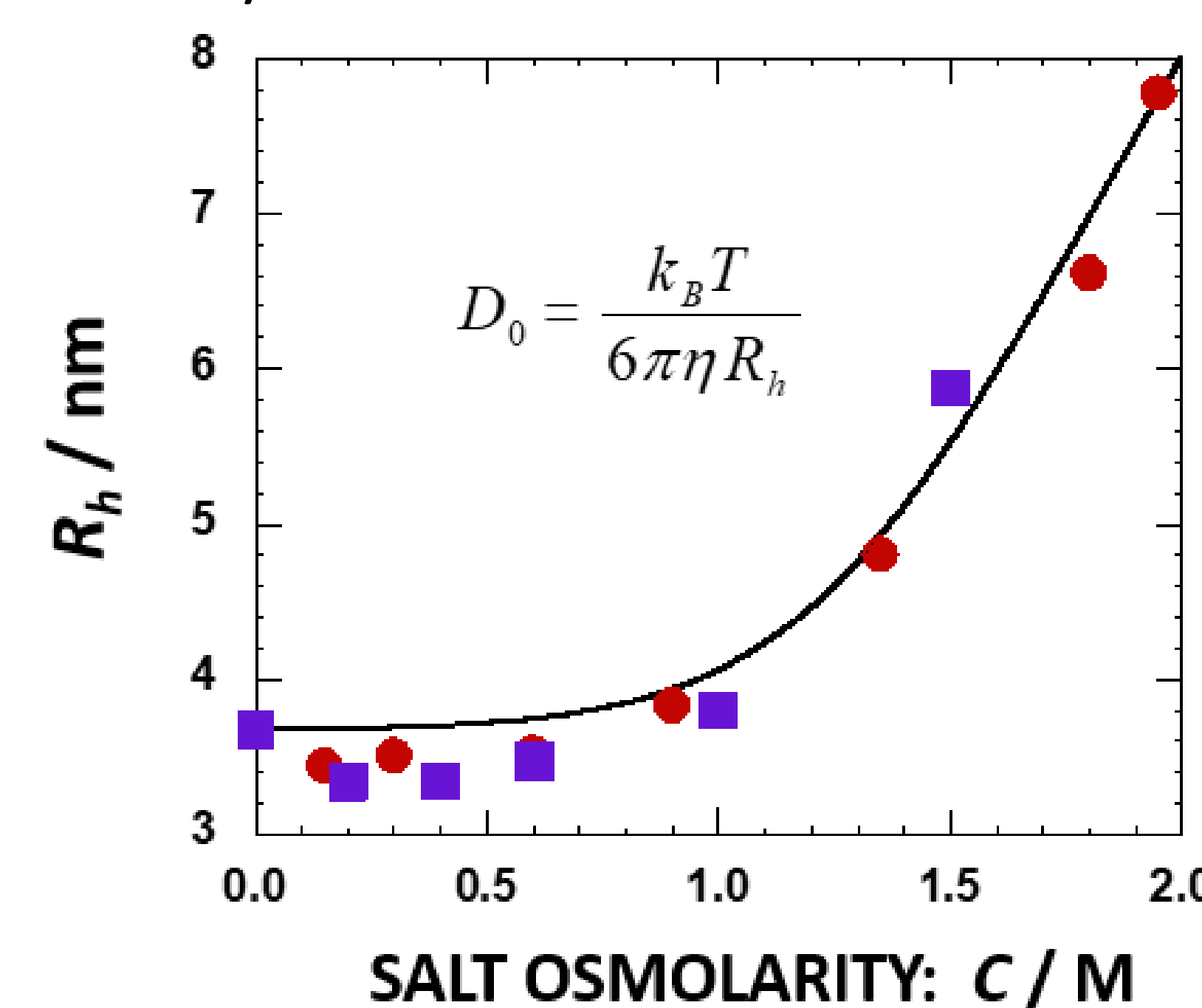
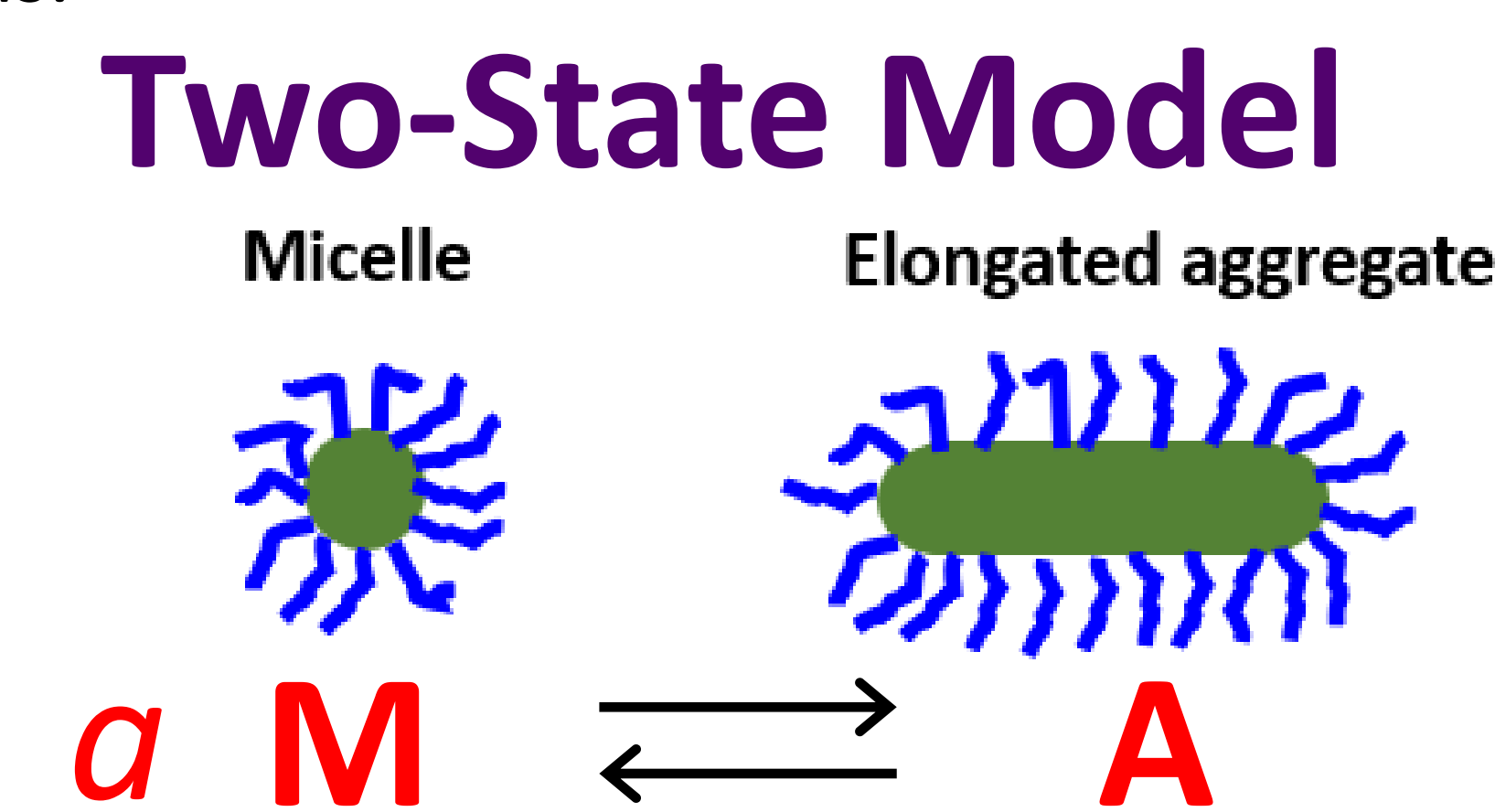


Figure 4. Hydrodynamic radius (R_h) of tyloxapol micelles as a function of Na₂SO₄ (■) and MgSO₄ (●) osmolarity. Stokes Einstein Equation is shown as an insert where k_B is the Boltzmann constant, T is temperature, and η is the viscosity of the aqueous salt fluid.

Discussion

We developed a 2-state model explaining the observed behavior of R_h . According to our model, aggregates large compared to micelles become thermodynamically more stable at high salt concentrations.



Equilibrium Condition

Where α is fraction of aggregates, K is salting-out constant, a is aggregate-micelle stoichiometry ratio, C is salt osmolarity and C^* is salt critical osmolarity.

$$\alpha = a(1-\alpha)^a e^{(a-1)K(C-C^*)}$$

Aggregate Micelle Mobility Ratio (r) Equation

$$r = \frac{\ln(a + \sqrt{a^2 - 1})}{\sqrt{a^2 - 1}}$$

Equation of $R_h(C)$

$$\frac{R_h(C)}{R_h(0)} = \frac{(1-\alpha) + a\alpha}{(1-\alpha) + a\alpha r}$$

The experimental behavior of R_h is described by $a = 20$, $C^* = 2.8$ M, and $K = 0.23$ M⁻¹.

Conclusion

- The micelle size was found to be approximately constant up to salt osmolarity of 1 M. Then significantly increases for both MgSO₄ and Na₂SO₄.
- A two-state model was employed to describe the experimental behavior showing the model of large aggregates at high salt concentration.
- We are currently examining the effects of salt dependent surfactant assembly on micelle migration due to salt gradients.