



Aggregation and reactivity in aqueous solutions of cationic surfactants and aromatic anions across concentration scales



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ABSTRACT

The use of aqueous solutions as solvents in synthetic chemistry is one of the pathways towards more sustainable chemical processes. To increase solubility of reactants in aqueous solutions, surfactants can be used. In particular as a result of detailed kinetic studies involving probe reactions, our current understanding of the reaction environment offered by micelles is good to excellent. However, this understanding does not always translate well to reactions on a synthetic scale because concentrations are typically very different from concentrations used in probe reactions. These high concentrations may lead to changes in aggregate morphologies, in particular where aromatic anions are used in combination with cationic surfactants. An overview of aggregation processes and aggregate morphologies across concentration scales is presented together with a discussion of the resulting effects on reactivity in solutions containing cationic surfactants and (reactive) aromatic anions.

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1. Introduction

1.1. Water in organic synthesis

Water and aqueous solutions have been advocated as environmentally friendly, green, solvents for synthesis. Further advantages of water as a solvent include it being non-flammable and displaying favourable hydrogen-bonding properties. These hydrogen-bonding properties have been argued to underpin some of the remarkable rate accelerations observed in so-called “on-water” reactions [1] and such effects are thought to play a role in the recent finding of beneficial effects of water on the nucleophilic attack of butyllithium on imines and nitriles [2^{**}]. This remarkable finding illustrates the extent to which even the author of this article, despite a long-standing interest in aqueous chemistry, underestimated the possibilities of water in organic synthesis when he wrote that “butyllithium and water are simply not compatible.” [3].

1.2. Surfactant-supported synthesis

An argument that is frequently used against the use of water as a solvent involves the lack of solubility of many reactants typically used in organic synthesis. Even this disadvantage can be turned into an advantage, as we have recently shown in a synthetic procedure where a water-ethanol mixture was optimised to dissolve reactants but lead to crystallisation of the desired product [4]. Nevertheless, the usual

approach to deal with the solubility challenge is to use solubilising agents such as hydrotropes or surfactants. Hydrotropes are compounds incorporating both a hydrophobic and a hydrophilic moiety which are too small to lead to cooperative formation of assemblies but which nevertheless increase the solubility of hydrophobic materials in aqueous solutions [5–8]. For examples of surfactant-supported syntheses, the reader is referred to the review by Dwars et al. [9], to a review of the development of designer surfactants supporting a wide range of reactions by Lipshutz and Ghorai [10], and our previous reviews on reactivity in organised assemblies [11–14].

1.3. Micelle morphologies depend on surfactant shape

In aqueous solutions, surfactants form a variety of aggregates, from spherical micelles, rodlike micelles, wormlike micelles, to bilayers and vesicles. The aggregate morphology can be predicted with good accuracy using the packing parameter P , developed by Israelachvili and Ninham [15], which describes the shape of a surfactant molecule (Eq. (1)),

$$P = V/(a_0 \times l) \quad (1)$$

where V is the volume of the hydrocarbon chain(s) of the surfactant, a_0 is the effective headgroup surface area, and l is the length of the hydrocarbon chain in the all-trans conformation. For $P < 1/3$, the surfactant is cone-shaped and forms spherical micelles; for $1/3 < P < 1/2$ the surfactant has the shape of a truncated cone and forms wormlike micelles; for $1/2 < P < 1$ the surfactant has a cylindrical shape and forms flat

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bilayers or vesicles; for $P > 1$, the surfactant is an inverted truncated cone and forms inverted micelles.

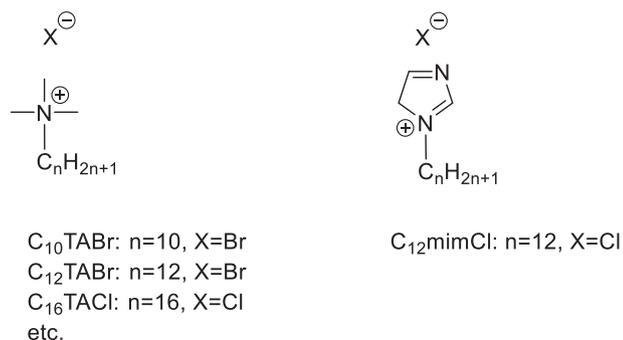
Structures of selected surfactants discussed in this review, which represent typical cationic surfactants, are shown in Scheme 1.

1.4. Micelles as reaction medium according to probe reactions

The many elegant examples of micelle-supported syntheses generate a series of conceptual challenges. The first challenge regards where reactants and products bind in micelles. The general view on this is that the most hydrophobic compounds enter the micellar core, leading to swelling of micelles, while more polar compounds tend to bind in the micellar Stern region. The second challenge involves what micelles look like in terms of reaction medium. This challenge has been addressed by several groups, typically using reactions involving very low concentrations ($\sim 10 \mu\text{M}$) of often neutral reactive chemical probes in combination with higher surfactant concentrations ($\sim 1\text{--}10 \text{ mM}$). For examples, see References [3,16–18,19,20–23]. The combined efforts of multiple groups have now resulted in a good understanding of typical micellar binding sites and what these sites look like in terms of reaction medium for a wide range of surfactant systems.

1.5. Scaling up organic reactions in micellar solutions

For reactions to be synthetically useful, higher concentrations of reactants are required which lead to higher concentrations of products as well. These higher concentrations may affect the micellar reaction medium, with implications for the validity of the reaction medium models derived using low concentrations of reactive probes. In addition, such reaction systems involve significant changes in composition during the reaction. The extent to which this forms a current challenge became clear to us in some of our recent work in which we attempted to exploit our understanding of the reaction environment offered by cationic micelles in the rational optimisation of a palladium-catalysed cross-coupling reaction in aqueous surfactant solution. While studying the kinetics of reactions involving arylboronic acids in micellar solutions of C_{16}TABr , we observed that observed rate constants for these reactions were not constant for different arylboronic acid concentrations despite the reactions following good first-order decay curves. In fact, increasing concentrations of phenylboronic acid resulted in decreases in the observed rate constants. This decrease in observed rate constants suggests that a process involving multiple molecules of phenylboronic acid coming together was causing the observed kinetic effects. We initially suspected that boroxines might form in the micellar solutions but did not find any evidence for this hypothesis. We then noted that the structure of the conjugate base of phenylboronic acid, phenylboronate, is reminiscent of hydrotropes. In addition to the structural similarity, we observed signs of viscoelasticity in some of our solutions containing



Scheme 1. Selected examples of cationic surfactants.

C_{16}TABr and phenylboronic acid [24], suggesting the possible formation of wormlike micelles.

We thus became interested in the effects of interactions between aromatic anions and cationic surfactants on aggregate morphology across concentration scales and their potential effects on reaction kinetics, all of course in aqueous solutions.

The concentration ranges of surfactants and aromatic anions involved in these solutions are key factors. For convenience, these concentration ranges are defined here relative to the critical micelle concentration (cmc) of the surfactant in water in the absence of additives. The concentration ranges of interest can thus be represented as in Fig. 1.

Fig. 1 shows the four quadrants defined by the relative concentrations of surfactant and aromatic anions. Fig. 1 also indicates where the concentration of the surfactant equals the concentration of the aromatic anion. Assuming full binding of the aromatic anion, combinations of concentrations on this line lead to singly charged surfactants and singly charged aromatic anions lead to the formation of “self-assembled zwitterionic surfactants”. We note, however, that many systems that have been studied also include chloride or bromide counteranions, and therefore this line only gives a general indication of the region where electrostatic charges cancel each other out.

This Review aims to cover what happens across these concentration regimes. We will first review these regimes in terms of non-reactive systems, followed by a discussion of kinetic effects across the concentration ranges.

2. Aggregate formation across the concentration scales

Before discussing time-dependent reacting systems, we first explore the types of structures formed in the four different quadrants by looking at examples of representative systems.

2.1. Quadrant A – anionic dyes dissolved in micelles

In quadrant A, an excess of surfactant dissolves a far smaller amount of aromatic anions. This concentration range is typically studied using UV–visible spectroscopy. Quadrant A is often represented by the final data points of studies of interactions between aromatic anions and cationic surfactants in quadrant C in which surfactant concentrations are increased while dye concentrations are kept constant. It is commonly assumed that in this range, surfactant aggregate morphologies are not significantly affected by the aromatic anions.

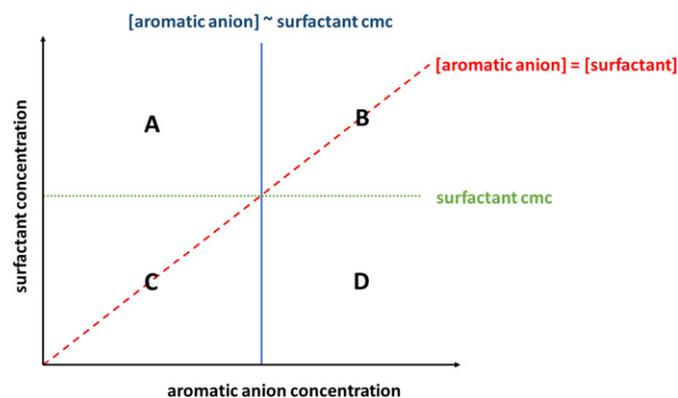


Fig. 1. The relative concentration ranges of surfactants and hydrotropes of interest can be divided into four quadrants. The red dashed line indicates equal concentrations of surfactant and hydrotrope.

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