

Hydroxide-ion binding to nonionic interfaces in aqueous solution†

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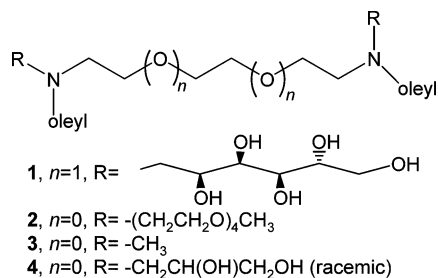
The mechanism of hydroxide ion binding to nonionic surfaces is explored by variation of the properties of the water-aggregate interface and by variation of the type of the aggregate.

In previous papers we reported the unconventional and amazingly rich pH-dependent phase behavior of carbohydrate-based gemini surfactants (CBGS, exemplified by **1** in Scheme 1).^{1–3} In the acidic pH region the protonation state of both nitrogen atoms determines the morphology of the aggregate in aqueous solution. At low pH and a significant protonation of both nitrogen atoms, spherical micelles are formed with the strong curvature of the aggregate resulting from substantial inter- and intramolecular head group repulsion and hydration. At higher pH the head group charge and hydration continually decrease leading to the subsequent formation of wormlike micelles and vesicles. These morphological changes can be rationalized on the basis of an increase of the packing parameter of the amphiphilic molecules.³ Most remarkably, the vesicles formed around pH 6.7 from partially protonated **1** (estimated intrinsic pK_{a1} ca. 8.1, pK_{a2} ca. 6.0) flocculated upon an increase of the pH to ca. 7.7, but at a still higher pH (ca. 8.7) an unexpected redispersal occurred of vesicles with the same size distribution as that before flocculation. Redispersal was accompanied by charge reversal as demonstrated by negative electrophoretic mobilities. We suggested that the negative ζ potential was due to hydroxide-ion binding to the deprotonated, nonionic vesicular surface. Specific binding of OH^- ions to hydrophobic surfaces in water is a known phenomenon,^{4,5} but it remains largely unexplained. Recent MD simulations⁶ provided

a possible mechanism for the counterintuitive binding process involving binding of OH^- ions within the first two preferentially oriented water layers away from the surface. The MD data confirm that the adsorption is specific for OH^- ions in accord with results obtained with vibrational sum frequency spectroscopy.^{7,8} However, in the case of CBGSs alternative mechanisms could involve deprotonation of one of the carbohydrate hydroxy groups or hydrogen bonding of the carbohydrate hydroxy substituents to OH^- ions.

There was a two-fold motivation for the present study: (1) to obtain compelling evidence for distinguishing between the three possible mechanisms of OH^- binding and (2) to further extend the scope of the interfaces capable of physisorption of OH^- ions. For these purposes we have examined the aggregation behavior of three novel compounds **2–4**, providing compelling evidence for OH^- binding to the interface.

We began by examining amphiphile **2** (liquid at room temperature) carrying methoxy-terminated tetra(ethylene oxide) groups instead of reduced carbohydrate units at both nitrogen atoms. This structural change prevents both OH^- -induced deprotonation and the hydrogen-bond donation effect. Nevertheless, similar morphological changes are observed as for **1**. At room temperature at low pH, **2** forms spherical micelles as evidenced by the wavelength of maximum fluorescence of the dye Nile Red bound to the aggregates and consistent with the low intensity of scattered light.⁹ As indicated by the decrease in the wavelength of maximum fluorescence of the dye Nile Red and the small increase in the amount of scattered light at pH 6.6 ± 0.2 wormlike micelles are formed followed by the formation of vesicles at pH 7.1 ± 0.2 , consistent with dynamic light scattering data (Fig. 1).¹⁰ Phase



Scheme 1 Structure of the gemini surfactants. R = oleyl (75% cis).

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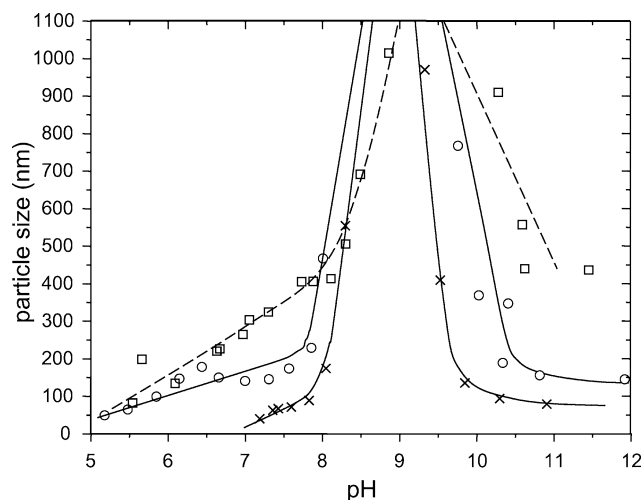


Fig. 1 Maxima in the size distributions obtained by dynamic light scattering of solutions containing aggregates formed from **2** (x), **3** (□) and **4** (○) as a function of pH. Lines are only drawn to guide the eye.

separation (defined here as the formation of aggregates larger than 1 μm) is observed at $\text{pH } 8.4 \pm 0.2$, followed by redispersal of lamellar aggregates at $\text{pH } 9.2 \pm 0.2$ (Fig. 2A, showing vesicular aggregates upon charge reversal).

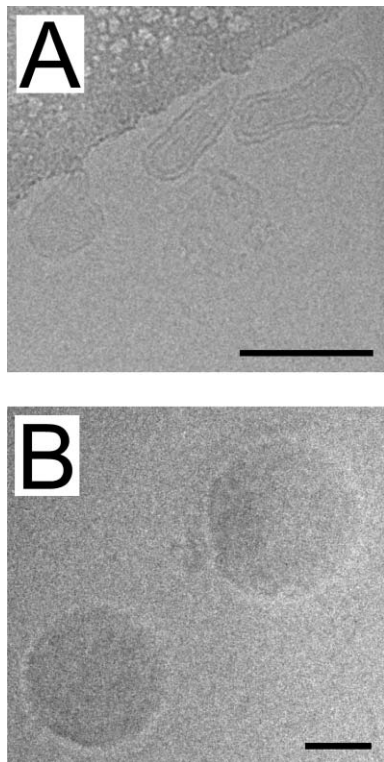


Fig. 2 Cryo-electron microscopy picture of **2** vitrified at 25 °C at pH 11.2 (A) and **3** at pH 6.8 (B). Bars represent 100 nm.

We next turned our attention to compound **3**, with two methyl substituents instead of the (reduced) carbohydrate units on the nitrogen atoms and which also forms spherical micelles at low pH. Light scattering increases dramatically at $\text{pH } 5.3 \pm 0.3$ due to formation of particles with diameters >50 nm (Fig. 1). Most notably, cryo-electron microscopy at pH 6.8 shows the presence of homogeneous particles, *i.e.* oil droplets, rather than vesicles (Fig. 2B). These droplets exhibit remarkable stability, as they are stable overnight. Apparently, **3** now behaves as an oil rather than an amphiphile, with the oil entering the core of the initially formed micelles to reduce contact with water when the surface charge decreases significantly. Finally, the steady reduction of the positive surface charge leads to growth of the droplets. Dynamic light scattering data indicate a continuing increase in droplet size until they phase separate. Rather surprisingly, the droplet size starts to decrease again at $\text{pH } >9.8 \pm 0.5$. The smaller particles that are formed repel each other, and these effects become more important with a further increase of the pH, consistent with increasing OH^- binding to the surface of the droplets. The pH values for phase separation and redispersal are somewhat less reproducible than for **2** as expected for OH^- -stabilized suspended oil droplets since their size and stability depend in a complex manner on

several parameters including the amount of dissolved air and aging.^{11,12}

Finally, compound **4**, also a liquid, and carrying 2,3-dihydroxypropyl substituents, exhibits behavior in between that of **2** and **3**. At pH 6.9 both small oil droplets and lamellar structures are observed. Phase separation occurs at $\text{pH } 8.4 \pm 0.1$, whereas exclusively oil droplets are formed at pH 9.6 as evidenced by cryo-electron microscopy (ESI†). The particle diameters decrease upon a further increase of the pH, as anticipated for increased OH^- binding to the interfaces (Fig. 1).

In conclusion, the present study shows that despite crucial structural differences, **1–4** in their unprotonated states all form molecular assemblies that possess the ability to adsorb hydroxide ions in water. Binding of strongly hydrophilic and hydrated hydroxide ions is a counterintuitive process. The hydration layers adjacent to the interfaces should provide the driving force for the physisorption process, with the permanent dipole moment of the OH^- ion interacting with the electrical potential gradient in the hydration shells.⁶ We find that the interfaces may both be lamellar (vesicular) or homogeneous (oil droplet). We conclude that not only rather hydrophobic (*i.e.* alkane-like such as **3**) interfaces, but also more hydrophilic interfaces such as those provided by **1**, **2** and **4** possess hydration layers that allow efficient binding of hydroxide ions.¹³ These results allow the design of novel amphiphilic systems carrying a pH-dependent charge provided by physisorption of hydroxide ions from the aqueous medium.

Acknowledgements

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