Self-Assembly of CO_2 Nonionic Surfactants in Ionic Liquids

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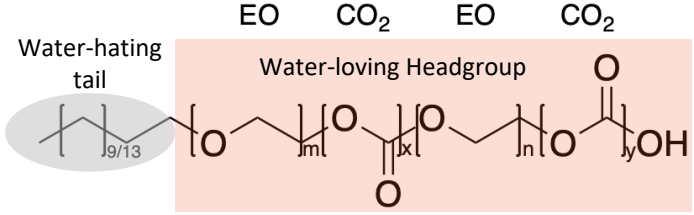
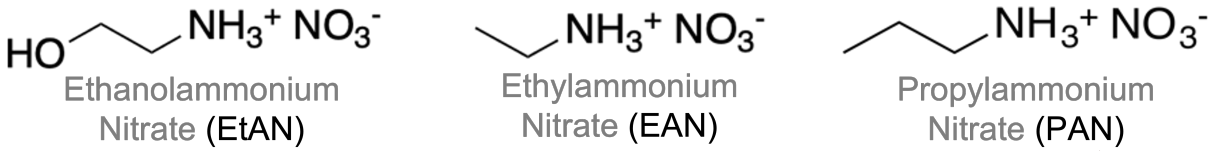
Greener Surfactant

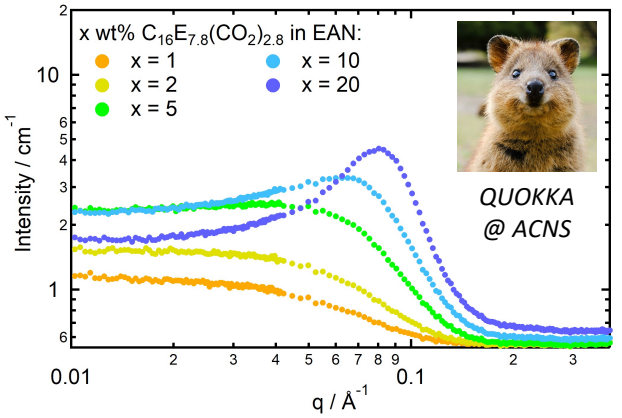


While being the headgroup of the workhorse nonionic surfactant, ethylene oxide (EO) is an unsustainable petrochemical product. This prompt us to seek for biorenewable substitutes and CO_2 immediately stands out as a resource. Recent studies of nonionic surfactants containing CO_2 groups have shown they are promising surface-active molecules. In addition to reducing consumption of fossil fuels, **the tendency to form liquid crystals in water of these surfactants are largely suppressed by incorporating CO_2 units**,[1] allowing them to be conveniently handled as liquids at very high concentrations.

Designer Solvent

Ionic liquids (ILs) are an emerging class of liquids purely composed of ions. Among many other favourable liquid properties, a display of diverse intermolecular interactions is common to many ILs. This enable them to be excellent mediums for self-assembly and they are known to support structures ranging from micelles to liquid crystals. As the solvent, **ILs offer a platform with tuneable amphiphilicity and solvation behaviours**,[2] making them promising solvent for the rational design of new functional soft matters.





Model-Free Analysis

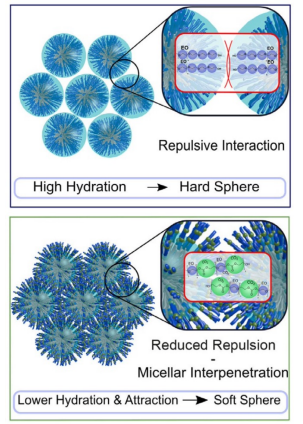
$$I(0) = \phi \cdot (\Delta SLD)^2 \cdot V \cdot S(0)$$

$$S(0)^{-1} = \frac{(1+2\phi_{hs})^2 - 4\phi_{hs}^3 + 4\phi_{hs}^4}{(1-\phi_{hs})^4}$$

$$\phi_{hs} = B_{Solv}\phi(1 - A_{Soft}\phi)$$

By assuming hard sphere interaction between micelles, we can estimate the solvation and softness.

CO_2 wt% in Headgroup	Water[1]		EAN	
	A_{Soft}	B_{Solv}	A_{Soft}	B_{Solv}
0	0.01	1.72	1.70	3.18
4	0.37	1.64	----	----
10	0.50	1.63	----	----
12-14	0.52	1.58	1.54	2.33
27	0.55	1.51	1.25	2.04



- Micelles are wetter and softer in EAN than water.
- Although the trend is reversed, micelles are significantly wetter and softer in EAN than in water even at the highest CO2 content, confirming liquid crystal phases are missing.
- *Solvent-Headgroup interaction can be engineered through solvent composition and CO_2:EO ratio!*

References:

[1] V. J. Spiering, A. Ciapetti, M. T. Lima, D. W. Hayward, L. Noirez, M. S. Appavou, R. Schomacker, and M. Gradzielski, ChemSusChem **13**, 601 (2020).

[2] R. Hayes, G. G. Warr, and R. Atkin, Chemical Reviews **115**, 6357 (2015).