

## SLOOKING AT MICELLISATION OF GRADIENT COPOLYMERS IN SUPERCRITICAL CARBON DIOXIDE

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Self-assembly properties of small molecules into large supramolecular assemblies have been a matter of interest for scientists for more than a century now. One might thus tend to believe that the spontaneous formation of, e.g., micelles of surfactant molecules in water, has given up all its secrets. Indeed, many possible morphologies of micelles have been discovered and characterised by soft matter scientists, in particular using small angle neutron scattering (SANS). The careful measurement of micellar properties by SANS has contributed greatly to our understanding of the multiple forces acting between the different parts of the molecules, like between the hydrophobic tails, or between the hydrophilic head groups, and their implications on micellar structure and interaction. The importance of industrial applications, like detergency, enhanced oil recovery, or mineral flotation, have also been and still are a powerful motor of this research area. Obviously, the behaviour of a surfactant system, like cleaning power, depends strongly on its capacity to take up hydrophobic, oily substances in aqueous solvents, a process naturally promoted using micelles as molecular transport vehicles.

solvating properties can be tuned by applying moderate pressures: CO<sub>2</sub> becomes supercritical (scCO<sub>2</sub>) close to room temperature (T > 31.1°C), at P > 73.8 bar. Unfortunately, molecules which are amphiphilic with respect to water do not automatically possess self-assembly properties in scCO<sub>2</sub>. One partner of this collaboration, the school of chemistry in Montpellier (ENSCM) has a long-standing record of synthesizing new types of molecules, with amphiphilic properties with respect to scCO<sub>2</sub>. The primary scope of such developments is the design of new systems having self-assembly properties in scCO<sub>2</sub>.



Fig. 2: Cloud point observation. Left: the polymer is soluble and light reflexes are transmitted through the sample. Right: the system is below the cloud point and thus opaque.

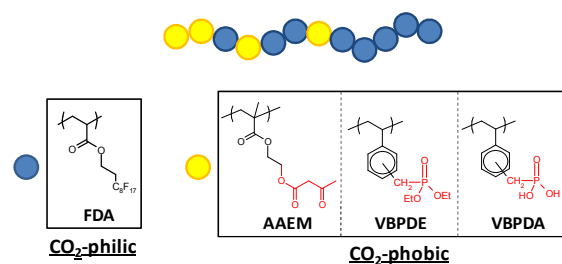


Fig.

1: Different gradient copolymers used in this study.

The natural driving force of surfactant self-assembly is amphiphilicity, i.e. it is due to the opposite behaviour of the head and tail groups with respect to water: the hydrophobic groups induce aggregation in order to minimize contact with water molecules. It is then a natural objective of surfactant studies to transpose this behaviour to other solvents, and in particular to CO<sub>2</sub>. Compared to organic solvents, CO<sub>2</sub> has many advantages: it is non toxic, cheap and environment-friendly. But most importantly, its

In this project, we have developed and tested a variety of polymeric surfactants, i.e. molecules where the CO<sub>2</sub>-philic and CO<sub>2</sub>-phobic groups are actually small polymer blocks. As compared to smaller surfactant molecules, this allows us to add additional functions to the molecule, a point to which we come back below. Three purpose-synthesized molecules are presented in Figure 1. In all cases, the CO<sub>2</sub>-philic part - poly(FDA) - is the same. These fluorinated molecules are known to be highly soluble in scCO<sub>2</sub>, a feature which can be easily tested by visual inspection of the solubility limit called the cloud-point as shown in Figure 2.

The CO<sub>2</sub>-phobic parts are represented in Figure 1 [1]. By themselves, they are virtually insoluble in

scCO<sub>2</sub>, whereas the polymeric surfactant molecules built with them and FDA are found to be extremely soluble. Polymeric CO<sub>2</sub>-surfactant molecules have become well-studied over the past two decades. A novelty with our system is that, instead of synthesizing block copolymers by a two-step process, we have prepared gradient copolymers in a one-step process. Such gradient copolymers have so far been rarely studied in CO<sub>2</sub>, and never by SANS.

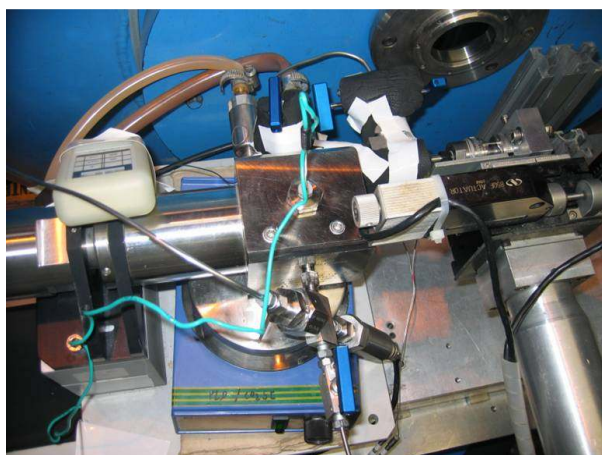


Fig. 3: Photo of the Niobium pressure cell in front of the beam-tube, and the variable volume view-cell with sapphire window on the left.

As stated above, it is crucial for applications to have micellisation in scCO<sub>2</sub>. The fundamental question we have to address is if such gradient molecules still present sufficiently strong self-assembly properties. The experimental challenge encountered in CO<sub>2</sub>-systems is that measurements have to be performed under high pressure. Therefore, we have used a pressure vessel in Niobium, which displays a neutrons transmission superior to 90% at 6 Å, allowing direct micellisation studies of our polymeric surfactant in scCO<sub>2</sub>. The experimental set-up is shown in Figure 3.

A large number of parameters had to be explored in order to obtain a comprehensive view of the aggregation properties of our gradient copolymers [2]. Besides thermodynamic parameters like pressure and temperature, we have studied self-assembly as a function of concentration, molecular weight and composition. In Figure 4, the effect of decreasing pressure is shown. The increase in intensity can be translated in a higher average aggregation number, from unimers to about three. Concomitantly, the typical size increases from about 25 to 33 Å. Summarizing this study which extended over several runs of neutron beam-time over the past years at LLB, we found that aggregation is enhanced for high concentration of polymer, low

temperatures and pressures, and for a copolymer having a high fraction of CO<sub>2</sub>-phobic units.

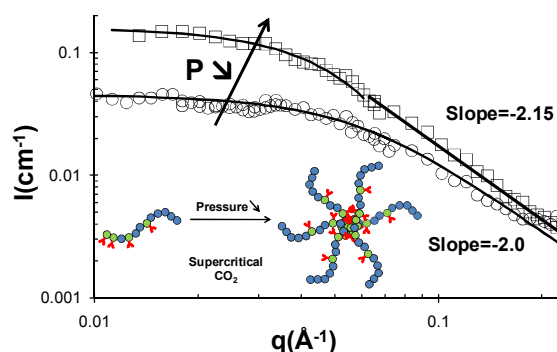


Fig. 4: Influence of pressure. SANS data for a gradient copolymer with AAEM units at C=4 %wt of polymer vs. CO<sub>2</sub>: T=40 °C, P=140 bar (□) and T=40 °C, P=210 bar (○), with the Debye fit indicating a random coil, respectively. The arrow indicates the evolution with decreasing pressure.

We have thus demonstrated that our gradient copolymer system is capable of micellisation in scCO<sub>2</sub>. From this rather academic question, an interesting connection to recent developments in green chemistry can be drawn by adding a particular function to our molecules. One of the problems of nuclear waste management is that washing contaminated industrial workers' cloths generates huge quantities of possibly radioactive water. By switching to scCO<sub>2</sub> as a solvent, one may capture radioactive ions in micelles, and then dispose of the clean CO<sub>2</sub> - thereby concentrating the ions in much smaller quantities of surfactant. This is the reason why we have added the particular functions (acetoacetoxy, phosphonate ester and phosphonic diacid represented in red in Figure 1) to the molecules depicted above. Having shown their micellisation in scCO<sub>2</sub>, it is hoped that our study will open the way to a new, 'greener' treatment of nuclear waste.

#### References:

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- [2] T. Ribaut, J. Oberdisse, B. Annighofer, I. Stoychev, B. Fournel, S. Sarrade, P. Lacroix-Desmazes, Soft Mater, 2009 (DOI: 10.1039/B912268K).

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