

# Emulsion Polymerisation of Acrylamide in Supercritical Carbon Dioxide as Monitored by High-Pressure NMR

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Water in carbon dioxide microemulsions have been studied with the aim of producing stable emulsions for polymerisation of acrylamide monomer. The phase diagram for the monomer/surfactant/water/CO<sub>2</sub> mixture shows that an ammonium carboxylate perfluoropolyether (PFPECOONH<sub>4</sub><sup>+</sup>) surfactant solubilises water and acrylamide for water to surfactant ratios (W<sub>0</sub>) of 20. NMR diffusion measurements were used to estimate the micelle sizes and NMR spectroscopy to monitor the depletion of the acrylamide double bonds as the emulsion polymerisation proceeds.

## Introduction

Reactions involving supercritical carbon dioxide as the solvent have become increasingly important due to the ability to totally remove the solvent upon depressurization. Generally, CO<sub>2</sub> is a poor solubiliser for hydrophilic species, however it has been shown that these solutes can be dissolved by water-in-CO<sub>2</sub> inverse emulsions. These microemulsions can thus be utilized as environmentally benign media for reaction between many different species.

The stability of water-in-CO<sub>2</sub> microemulsions has been studied by many researchers[1-4]. Whilst many surfactants have been discussed, the most commonly used are perfluoropolyether salts, generally with an ammonium head-group. The stability of such surfactants and their emulsion forming behaviour has been related to the molecular weight of the species involved. It has been shown that PFPE with a molecular weight of about 2500 produces the highest W<sub>0</sub> values and can thus stabilize much larger aqueous cores than other molecular weight species[3]. Also, this surfactant forms stable micelles with a minimum amount of shear. This is a prerequisite for non-circulating, low-shear NMR experiments.

Polymerisation reactions in supercritical carbon dioxide have been extensively reported in the literature [6-8]. Whilst dispersion polymerizations have been shown to occur quite readily in supercritical carbon dioxide, inverse emulsion polymerizations are quite rare. This is due to the relatively high solubility of most monomers in supercritical CO<sub>2</sub> under modest conditions.

Acrylamide is a well known water-soluble monomer and has exhibited limited solubility in supercritical carbon dioxide. Conventional emulsion polymerisation of acrylamide has been extensively studied and provides some comparison for the inverse analogue in supercritical carbon dioxide. [9,10]

The aim of this research was to study the formation of acrylamide/water in supercritical carbon dioxide emulsions. Once emulsion behaviour was established, the emulsion polymerisation of the acrylamide monomer was investigated using high-pressure nuclear magnetic resonance.

## Materials and Methods

Ammonium carboxylate perfluoropolyether with a molecular weight of 2500 Daltons was obtained from Dupont under the tradename "Krytox® 157 FSL". The acid was neutralized to an ammonium salt by stirring in an excess of aqueous ammonia for 24 hours. The conversion process was monitored by depletion of the carboxylic acid peak ( $1775\text{ cm}^{-1}$ ) in the FTIR spectrum. The resultant surfactant was dried under vacuum at  $60\text{ }^{\circ}\text{C}$  for 2 days. Acrylamide monomer was purchased from Sigma Aldrich and recrystallised from benzene. The purity of the monomer was assessed using high resolution NMR with  $\text{D}_2\text{O}$  as the solvent. Azobisisobutyronitrile was recrystallised three times from methanol and stored at  $-4\text{ }^{\circ}\text{C}$ . Food grade  $\text{CO}_2$  was purchased from BOC gases and used as received.

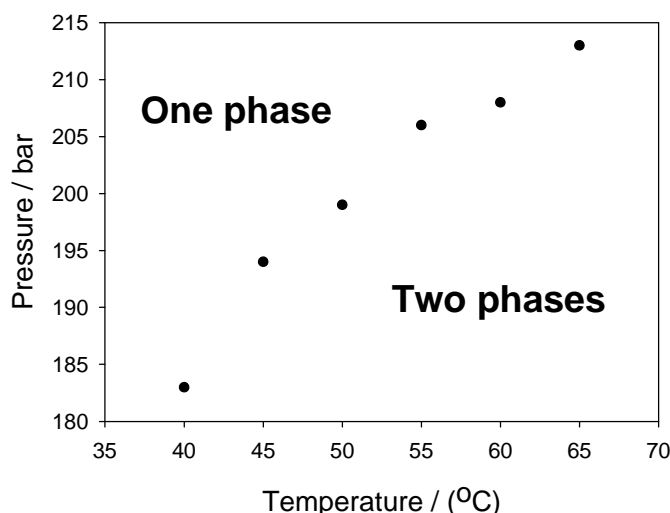
Microemulsions were initially formed in a high-pressure view cell equipped with sapphire windows. The view cell was purchased from Thar Technologies and had a maximum operating pressure of 650 bar at  $45\text{ }^{\circ}\text{C}$ . Our experiments were predominantly conducted at 300 bar pressure. Phase equilibria were measured by adding all components to the cell and pressurizing to 300 bar. Temperature equilibrium was achieved using a water bath. Upon micelation, the  $\text{CO}_2$  was slowly vented from the system and the onset of the cloud point was recorded.

High-pressure NMR was measured using a custom built NMR cell which fits neatly into a 10 mm birdcage resonator. The cell was machined from polyether ether ketone and could be consistently operated at 300 bar and  $40\text{-}60\text{ }^{\circ}\text{C}$  without failure. The rigid polymer cell has an extremely short  $^1\text{H}$   $T_2$  relaxation time. In order to minimize residual signal from the polymer cell, all spectra were recorded using a Hahn-echo pulse sequence with an echo time of 1 ms or greater. In this way, the broad signal from the PEEK cell was removed from all  $^1\text{H}$  NMR spectra.

Polymerisations were conducted in the high-pressure view cell by loading all components into the cell, followed by heating in the water bath and pressurisation. A magnetic stirrer bar was operated by a stirrer plate beneath the bath. Typically, a 2:3 ratio of acrylamide to water was added to the cell with the desired water to surfactant ratio. All experiments used 0.015 wt % of surfactant. Upon depressurisation, the molecular weight of the polymer was determined using solution viscometry.

## Results

The phase behaviour of PFPE surfactants has been reported in the literature [1]. Generally, single phases can be observed below 500 bar for  $W_o$  values up to 35. The cloud points were measured for the acrylamide/water/ $\text{CO}_2$  system and are shown in Figure 1. Here, an emulsion was formed in the absence of stirring, presumably from shear arising from the injection of the  $\text{CO}_2$ .



**Figure 1** : Phase diagram for acrylamide/water/ $\text{CO}_2$  emulsion.  $W_o = 20$  and the acrylamide to water ratio of 2:3.

Below the line of points the surfactant and water mixture separated from the  $\text{CO}_2$  and two phases were observed. Above the curve, a single transparent phase was observed indicating microemulsion formation. The phase curve that we observed for a water and acrylamide microemulsion is similar to that reported by Nagashima et al. [1] for a water in  $\text{CO}_2$  system. We have shown that addition of the acrylamide to the aqueous phase has minimal effect on the thermodynamic stability of the micelle.

The size of the micelles formed in a water/ $\text{CO}_2$  emulsion is of particular interest since the kinetics of polymerisation in mini or microemulsions vary considerably. Lee et al. [11] have used SANS to measure the sum of core radius and the surfactant tail length of emulsions formed using PFPE based surfactants. The radius was reported as being 2 nm and the tail length about 1.3 nm. These very small micelle sizes are reflected in the transparency of the single phase mixture observed using the view cell.

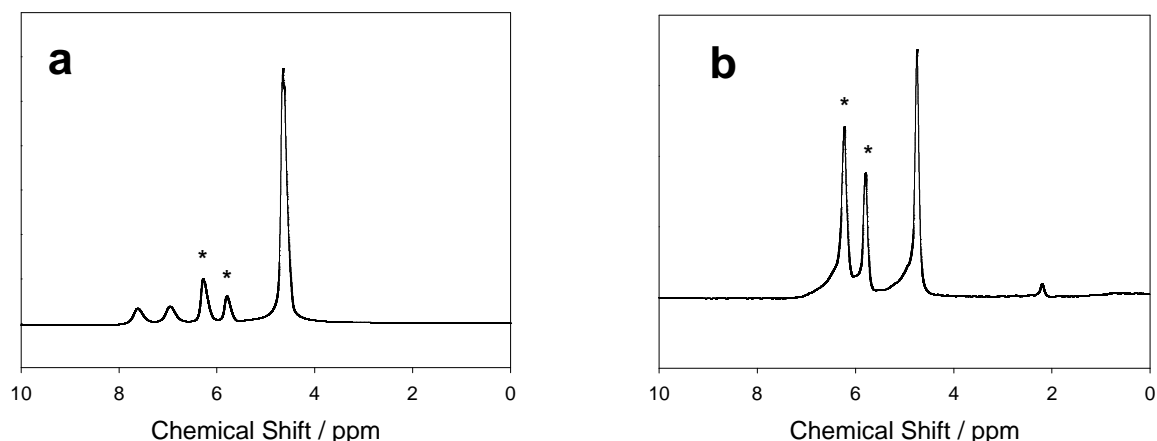
We have used high-pressure NMR spectroscopy and self-diffusion values for water in the micelle to estimate the core sizes using a method proposed by Nagashima et al. [1] Generally in a water/ $\text{CO}_2$  mixture, at least two types of water exist. These include bulk water and water within a

micelle core. For water in the core, the diffusion coefficient is much smaller than bulk water since it is constrained by the core boundary. An estimate of the hydrodynamic radius of the droplet can be made by using the corrected Stokes-Einstein equation for tracer diffusion.

$$D_D = k_B T (1 - \alpha \phi) / 6 \lambda \eta R_H \quad (1)$$

We measured the diffusion coefficient for water in the micelle at 300 bar and 40 °C and obtained a value of  $7.3 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ . This is much slower than the value obtained for pure bulk water in CO<sub>2</sub> in the absence of surfactant at this pressure and temperature ( $3.6 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ ). The other parameters in the Stokes-Einstein equation above have been calculated by Nagashima et al. for a similar system and for the purposes of our work can be applied to determine an approximate core size. In our case, the radius of the core is 2.3 nm which agrees very well with the neutron scattering data [1]. We are currently performing similar experiments for the water and acrylamide system.

High-pressure NMR was performed on the acrylamide/water/CO<sub>2</sub> system in which the acrylamide water mixture was stabilized into micelles by PFPE surfactant. Proton exchange is significant between the amide protons of acrylamide and water which leads to broadening of peaks in the low resolution NMR spectrum. In order to overcome the complication of the spectra, we performed our NMR experiments using deuterated water. Through view cell observations we found that substituting normal water with heavy water did not affect the micelle formation. Figure 2 shows the high resolution <sup>1</sup>H NMR spectra of acrylamide in water (a) and deuterated water (b). The acrylamide double bond peaks are labeled with an asterisk. By monitoring the depletion of these peaks the rate of decay of double bonds during the emulsion polymerisation of acrylamide could be followed.



**Figure 2 :** Acrylamide in water at 300 bar and 40 °C (a). The two broad peaks at low field are due to proton exchange between acrylamide and water. The peak at ~ 4.8 ppm is the water peak. The broad peaks due to exchange are absent in (b) where D<sub>2</sub>O was used instead of H<sub>2</sub>O at 300 bar and 40 °C. The peak at ~5 ppm is due to HDO.

The molecular weight of the resultant polymer was measured using solution viscometry in a Ubbelohde viscometer. In all cases, the polymer had a high molecular weight, typically around 5 million Daltons.

## Conclusion

We have demonstrated the use of high-pressure NMR spectroscopy to follow micelle formation in supercritical carbon dioxide. Using self-diffusion of the water within the micelle, we have shown that microemulsion formation is achieved. Similarly, the addition of the water soluble monomer acrylamide has little effect on the stability of the emulsion. We also show that acrylamide is produced via an emulsion route when stabilized by the PFPE surfactant and has a high molecular weight.

## References

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