

INVESTIGATION OF TRADE HYDROCARBONATED SURFACTANTS BEHAVIOUR IN SC CO₂ FOR SURFACE DECONTAMINATION IN THE NUCLEAR INDUSTRY

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ABSTRACT

Hydrocarbonated surfactant behaviour have been investigated for set a decontamination process using surfactant and supercritical carbon dioxide (SC CO₂).

The cloud point behaviour of several tri-bloc polymer surfactants (Pluronics) and hydrocarbonated surfactant (Decyne-diol) in supercritical carbon dioxide has been investigated in the frame of nuclear decontamination. Thus, the influence of pressure and temperature on the solubility of these commercial hydrocarbonated surfactants in SC CO₂ has been studied. For each Pluronic surfactant, the P-T diagram exhibits a slope value which depends on the molecular weight (Mw). This parameter is linked to the hydrophilicity of the surfactant. So, the more hydrophilic is the surfactant, the lower the slope is. In addition, the water / SC CO₂ interfacial tension in the presence of Pluronics has been worked out. An interfacial saturation concentration (ISC) has been evidenced. In these conditions, the ISC measurement seems to be a promising tool to predict the “CO₂-philic” classification of surfactants in SC CO₂ (as surfactants lipophilic classification with CMC in oil media).

I. INTRODUCTION

Extraction of polar compounds in supercritical carbon dioxide (SC CO₂) requires additives to enhance polarity of the SC CO₂. In recent years, fluorinated compounds have been shown to exhibit a higher solubility in SC CO₂ compared to hydrocarbonated surfactants¹. However the use of fluorinated compounds might cause the generation of fluorhydric acid (HF). Waste management processes have to avoid the formation of hazardous gas like F₂. It is the reason why the interest for Non Fluorinated Surfactant (NFS) has recently grown up to substitute fluorinated surfactants^{2,3}.

Some of them used in this study are Pluronics and contain poly ethylene oxide (PEO) and poly propylene oxide (PPO). They are tri-block copolymers (PEO)_x-(PPO)_y-(PEO)_y (PE series) and (PPO)_x-(PEO)_y-(PPO)_x (RPE series). Since many years, they find industrial applications in several fields as detergency, dispersion stabilization, foaming, emulsification, lubrication, etc...⁴. In order to obtain an efficient surfactant in SC CO₂, it must be soluble in this medium. It is important to assess the conditions of pressure and temperature required to solubilize the surfactant. The pressure-temperature diagram characterizes the surfactant behavior in SC CO₂. The more CO₂-philic compound will be soluble in milder conditions of pressure and temperature. We compared Pluronic behaviour with Decyne diol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylate (1.75 EO/OH) (DD 1.75) and 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylate (15 EO/OH) (DD 15).

The solubility is not a sufficient criterion to assess the efficiency of a trade surfactant. The surfactant has to be able to decrease the interfacial tension between the polar phase and the apolar SC CO₂ fluid.

The main goal of this study is to improve the knowledge of the surface active properties of trade hydrocarbonated surfactants in a SC CO₂ medium. This work aims at investigating the effect of the surfactant on the water-CO₂ interfacial tension in order to assess the surfactant behaviour in SC CO₂. Before studying the interfacial activity of the trade surfactants, a first part of this work focuses on their solubility behaviour in SC CO₂. The assessment of the solubility behaviour is achieved by cloud point measurements. We will try to develop a model to explain the several phenomena that occur during the solvation of the surfactant in SC CO₂.

II. MATERIAL AND METHODS

(DD 1.75) and (DD 15), were purchased from Fluka (purity=99.8%). Pluronics were donated by BASF Corp.

The pressure at which the polymer begins to precipitate is the cloud point pressure, so-named because this is the pressure at which the system reversibly appears cloudy due to the scattering of light by the aggregates. The principle and equipment were described elsewhere⁵. The mixture was stirred for 20 min and then the cell was heated to 338K. The w/w% concentration was determined by knowing the amount of sample, the initial cell volume, and the initial pressure and temperature of the solution. To ensure a good initial solvation of the polymer in CO₂, the pressure was increased to 34MPa by decreasing the cell volume. The solution was allowed to stir for 20 min at a given temperature before cloud-point assessment, performed by lowering the pressure from about 34MPa by slowly increasing cell volume until the surfactant begins to come out of the solution, *i.e.* cloud point being defined as the reversible onset of a fully opaque solution.

The drop tensiometer (Tracker, IT Concept, Longessaigne, France) allows the determination of the interfacial tension by analyzing the axial symmetric shape (Laplacian profile) of the pendant drop of CO₂-saturated water in pressurized CO₂. The apparatus consisted of a view cell under CO₂ atmosphere, a light source (Fischer Bioblock, USA), a CCD camera (TelicamElvitec, France) equipped with an optical focus (VS-LD 75, Elvitec, France), a computer, a high-pressure syringe pump (Nova Swiss, Switzerland) for the water droplet formation, and a motor (4842, Parr, USA). The CO₂ feed is insured by a high-pressure piston CO₂ pump (Lewa, USA) (Figure1).

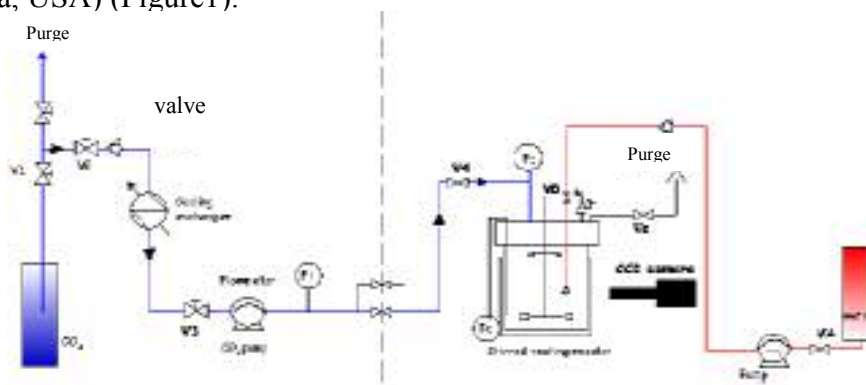


Figure 1 : Apparatus scheme for interfacial tension measurements

Pendant drops were formed at the end of a stainless steel tube, 1.58 mm outside diameter (Swagelok, USA), connected to a high-pressure syringe pump operated by hand. Therefore, it was not possible to maintain constant the area of the drop during the time of experience. Although, the volume variation did not affect strongly the interfacial tension evolution. The

experimental value was taken when interfacial tension becomes stable along time. A value average was in this time region. The interfacial tension was determined by digitizing and analyzing the profile of the droplet using a CCD camera coupled to a video image profile digitizer board connected to a computer.

The theoretical part was described elsewhere⁶.

Before investigating the effect of surfactant on the water/CO₂ interfacial tension (γ), the experimental set-up has been checked with a binary water/CO₂ system in the absence of surfactant. The interfacial tension γ was measured for different pressure (in the range of 4-16 MPa) at 313K temperature.

III. CLOUD POINT MEASUREMENT

Figure 2a shows the cloud point measurements for DD 1.75 and DD 15. Curves indicate that DD 1.75 dissolves in SC CO₂ in milder conditions of pressure and temperature than DD 15. Moreover, due to its smaller hydrophilic PEO chain length compared to DD 15 while the hydrophobic (CO₂-philic) part is kept constant, DD 1.75 is less hydrophilic. Therefore, DD 1.75 is more easily solubilized in SC CO₂. The structures of the studied Pluronics enable the screen the effect of the composition as well as the effect of the molecular weight (figure 2b) of the tri-block copolymers on their solubility behaviour in SC CO₂. It must be kept in mind that PEO is more hydrophilic than PPO. Conversely, PPO is more hydrophobic (*i.e.* more CO₂-philic) than PEO.

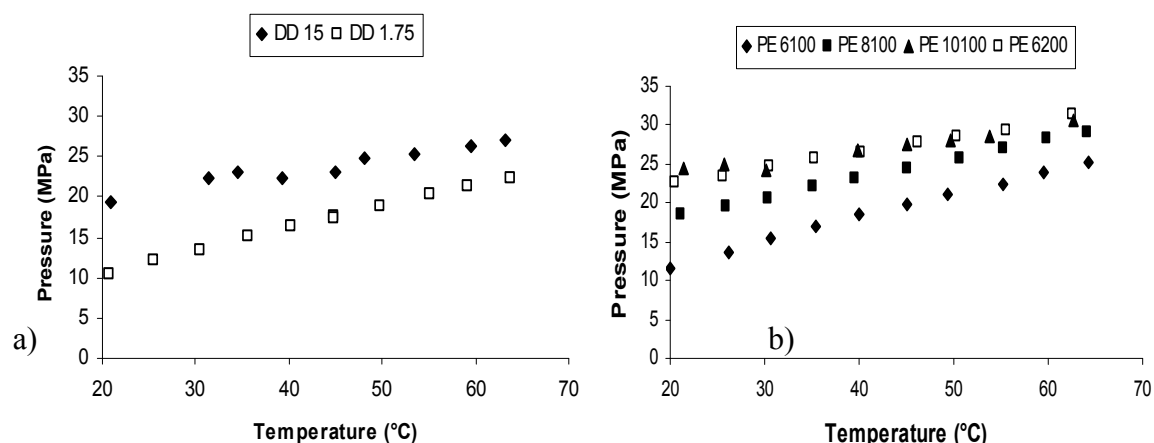


Figure 2 : Cloud point curves of a) DD 1.75 (at 0.13wt%) and DD 15 (at 0.14wt%); b) Pluronics PE 6100 (at 0.08wt% versus CO₂), PE 8100 (at 0.08wt% versus CO₂) and PE 10100 (at 0.1wt% versus CO₂)

In a case of a constant PEO/PPO weight ratio (10wt%-constant of HCB, ratio between hydrophilic and CO₂ philic interactions), figure 2b shows the increase in the cloud point with the molecular weight of the Pluronics at fixed temperature. This trend agrees with the theory which predicts a dependance of the solubility of polymers on molecular weight⁷.

In a case of a constant PEO chain length figure 2b shows that at fixed temperature, the cloud point pressure increases with the increase in the PEO chain length. From the linear regression of cloud point curves, the slope a has been calculated (in MPa.K⁻¹).

Table 1 present the values of the slopes for the four Pluronics.

Copolymer	PE 6100	PE 6200	PE 8100	PE 10100
Slope	0.2809	0.2020	0.2397	0.1627

Table 1 : Values of slopes from the linear regression of cloud point curves of PE 6100 (0.08 wt% versus CO₂), PE 6200 (0.1 wt% versus CO₂), PE 8100 (0.08 wt% versus CO₂) and PE 10100 (0.1 wt% versus CO₂) in CO₂

The slope describes the temperature dependence of the solubility behaviour of Pluronics in CO₂. We can see that the slope value is not constant for a constant PEO/PPO ratio. The HCB theory is not accurate for the understanding of the behaviour of surfactant in SC CO₂.

Furthermore, the slope is approximately proportional to the total molecular weight of the Pluronics, leading to the empirical equation 1:

$$\text{Slope } a = k.Mw \quad (1)$$

Where k is the slope of the linear fit $a = f(Mw)$. k is expressed in MPa.mol.g⁻¹.°K⁻¹.

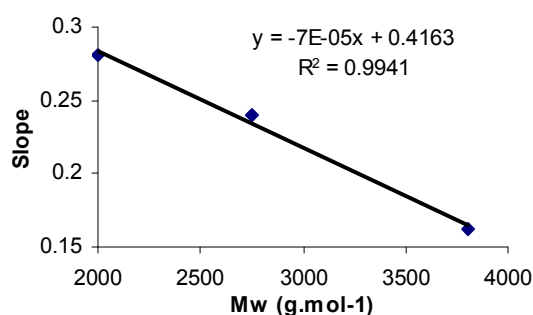


Figure 3 : Influence of the molecular weight on the slope value

As this parameter is linked to the hydrophilicity of the system, slope is correlated to the SC CO₂ / surfactant system. The value of the slope gives information about the temperature dependence of the system. Lower the slope is, more temperature dependent the system is. Advantageously, the fact that cloud point density decreases with the temperature illustrates the beneficial effect of temperature on the solubilization of Pluronics in CO₂. Since in first approximation⁸, the solvent power of CO₂ is expected to decrease with its density, enhanced solubility of Pluronics at higher temperature is probably caused by the weakening of polymer-polymer interactions.

IV.EFFECT OF THE SURFACTANTS ON THE WATER / CO₂ INTERFACIAL TENSION

Several surfactants have been investigated in SC CO₂ to assess their surface active properties in this media. Each surfactant is placed in the CO₂ phase and the amount of it corresponds to 0.1% wt versus CO₂ at 25 MPa and 40°C (figure 4).

All surfactants lower more the interfacial tension than pure CO₂. These trade surfactants are active in SC CO₂ despite their low solubility in this medium. At pressure above the critical pressure, the SC CO₂ is able to solubilise some molecules of surfactants which can diffuse to the water/CO₂ interface. Consequently, γ decreases below its value in the pure binary system water/CO₂ in the absence of surfactant. According to figure 3, all surfactants are similar in terms of performance.

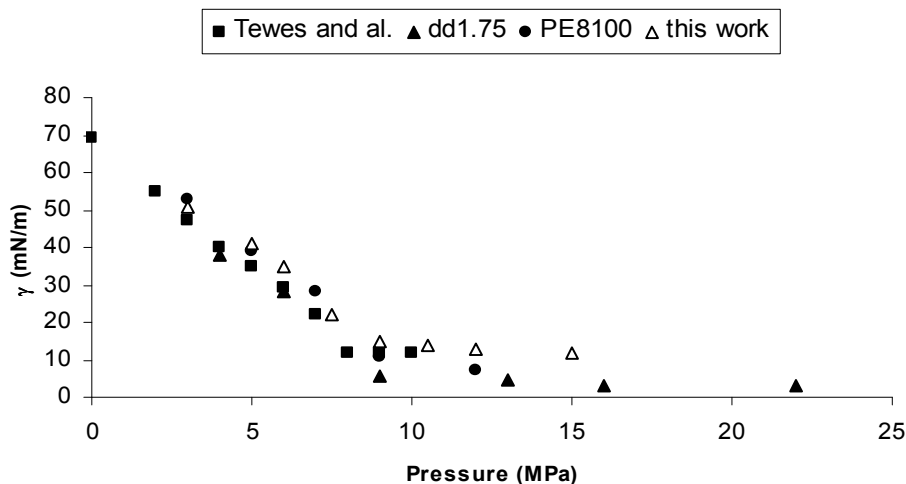


Figure 4 : Evolution of the water/CO₂ interfacial tension versus pressure of CO₂ at 313K without surfactant , and with DD 1.75 (0.1wt%), PE 8100 (0.1wt%).

In order to get a better insight in the surface active properties of the surfactants, measurements of interfacial tension were performed at fixed temperature (313K) and pressure (25MPa) (*i.e.* above the cloud point of the surfactants) and at low concentration (below the concentration used for cloud point determination) to ensure a total solubility of the surfactants. The plots of γ versus Ln molar fraction of surfactant (PE6100 on figure 5a) and PE 8100 an figure 5b) permit to exhibit a break in the slope that correspond to the apparition of the interfacial saturation concentration (ISC) in the case of PE 8100

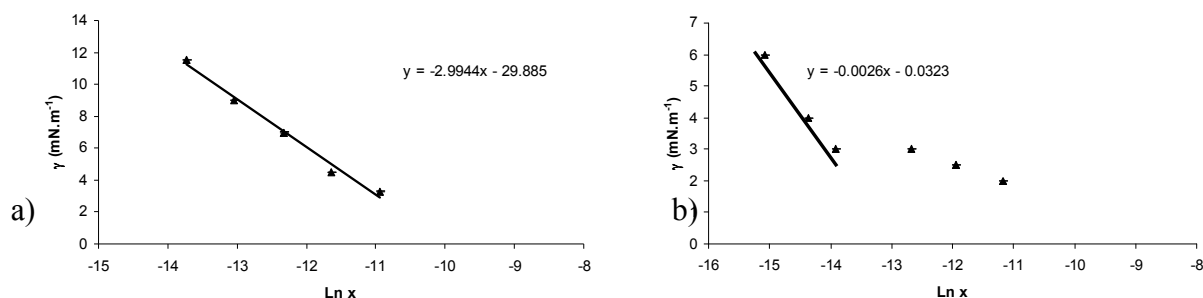


Figure 5 : Evolution of γ versus Ln of molar fraction of a) PE 6100 and b) PE 8100 in SC CO₂ at 25 MPa and 313K

	PE 6100	PE 8100	PE 10100
ICS (wt% versus CO ₂)	Expected >0.1%	0.004%	Expected <0.002%

Table 2 : Values of the interfacial saturation concentration (ISC) for PE 6100, PE 8100 and PE 10100 at 40°C and 25MPa (water/CO₂ interface)

According to cloud point curves, PE 6100 is more “CO₂-philic” compared to PE8100 and PE 10100 (PE 6100 is soluble in milder conditions of pressure and temperature). In classical lipophilic media, the higher lipophilic the surfactant is, the higher the critical micelle concentration (CMC) is⁴. We can expect the same behaviour in SC CO₂. PE 10100 is in accordance with this hypothesis. The slope of γ versus Ln[surfactant] according Gibbs equation appears too low to be before the ISC. According to the cloud point results, the Pluronic series at 10wt% EO follows the increasing CO₂-philic character in the order PE 10110 < PE 8100 < PE 6100. So, the ISC of PE10100 is probably at even lower concentration than the range studied herein.

V. CONCLUSION

The solvation of trade hydrocarbonated surfactants in CO₂ was studied in this work by cloud point measurements. Several parameters (molecular weight, surfactant concentration, EO % ratio) were screened and their effect on the position and slope of the cloud point curves was investigated. An increase in molecular weight, EO content or surfactant concentration shifts the cloud point upward (*i.e.* harsher conditions of pressure and temperature are required to solubilize the surfactant). In the same time, the slope of the cloud point curve decreases, indicating an enhanced beneficial influence of temperature on the solvation of the surfactants in CO₂. The slope gives information about hydrophilic character of the system and about its temperature dependence. This study highlights the limitation of the HCB model. The surfactant behaviour will be able to investigate using Statistical Associating fluid Theory (SAFT) and Lattice Fluid Hydrogen Bonding model (LFHB)⁹. The study of the interfacial tension proves the surface active properties of trade hydrocarbonated surfactant at the water/CO₂ interface. Trade hydrocarbonated surfactant like Pluronics are able to decrease significantly the interfacial tension between water and CO₂, down to 4 mN.m⁻¹ instead of 12 mN.m⁻¹ in the absence of surfactant. Using the γ versus Ln x plot and the Gibbs equation, it is possible to classify the surfactants in terms of CO₂-philic properties from their ISC. One of the several prospects is to create a predictive tool for the behaviour of surfactant in SC CO₂. One goal is to predict the CO₂-philic classification from the surface active properties of surfactants in more classical media (such as at the hexane-water interface).

VI. REFERENCES

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