

NANOFILTRATION OF SURFACTANTS IN SUPERCRITICAL CO₂ : EXPERIMENTAL EVIDENCE OF ADSORPTION-BASED RETENTION PHENOMENA

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Abstract

This paper presents the preliminary results obtained addressing surfactant separation from CO₂. Dead end filtration experiments have been performed using a ceramic membrane (mixture of Al₂O₃/TiO₂/ZrO₂). Different systems having different compositions representative of nuclear applications have been studied: a simple scCO₂/surfactant system and a water in sc CO₂ microemulsion.

Introduction

Use of surfactants in supercritical carbon dioxide (sc CO₂) for nuclear decontamination or non decontamination purposes has raised much interest [1-4]. For cleaning or decontamination applications, surfactants can be used to enhance the efficiency of sc CO₂ for the removal of hydrophilic pollutants or radioelements. These organic molecules can impact negatively the benefit from using scCO₂ as they become a waste after use and need complementary operations to destroy or dispose them. For nuclear purposes it is highly interesting to recycle them as much as possible as the disposal or processing of mixed organic molecules and contamination containing radioelements is expensive.

The separation of surfactant from contamination is thus a key interest as it can enable the surfactant recycling in the CO₂. Moreover, the removed contamination generally composed of metallic ions or metal oxides is then almost free of any organics and can be processed in existing wastes processing facility. In addition, as the sc CO₂ viscosity is low, the pressure across the separation medium (membrane) can be also low thus avoiding high pressure drops generally required for efficient separation when using classical physical separators (cyclones).

Coupling of scCO₂ extraction with nanofiltration membrane has been already studied at CEA in the past [5-6]

Experiments

The experiments described in the following were conducted with various inorganic membranes defined in **Table 1**. These membranes were single or three channel membranes made of a mixture of Al₂O₃/TiO₂/ZrO₂. The membranes used were 155 mm long and have an external diameter of 10 mm.

Membrane kD	Material		Membrane geometry	
	MWCO / g/mol	Pore size / nm	Module type	Thickness / mm
1	1,000	0.6	single channel	2.0
1	1,000	0.6	three channel	1.0
5	5,000	2.0	single channel	2.0
5	5,000	2.0	three channel	1.0
50	50,000	20	three channel	1.0
300	300,000	100	three channel	1.0

Table 1. Properties of inorganic membranes

The benefit at using inorganic membranes is clearly that no interactions with scCO₂ are expected together with a high chemical resistance and a high resistance toward molecule irradiation. The experimental setup for the nanofiltration using inorganic membrane in Sc-CO₂ is presented in **Figure 1**. The high pressure reactor (11) having electromagnetic stirrer (10), is used to form the microemulsions or the dispersions. Also, the reaction taking place inside can be observed clearly through two sapphire windows to both sides of the reactor. The inorganic membrane is placed inside of the membrane housing (12). Effective surface areas of single channel and three channels are 25 cm² and 52 cm², respectively. This system can be operated at a maximum trans-membrane pressure of 1.0 MPa. Liquid CO₂ from CO₂ tank (1) goes through liquid pump (2) into the reservoir to preheat with the heat exchanger and prevent the flow fluctuation. The temperature is controlled at 40±1 °C by an oven (25) and the water circulation pump. The pressure of permeation and retention is minutely regulated by the actuator valves (16, 17). The total flow of permeation and retention is measured by gas meters (21, 22). All permeation experiments were done on fresh membranes with cleaning for each run.

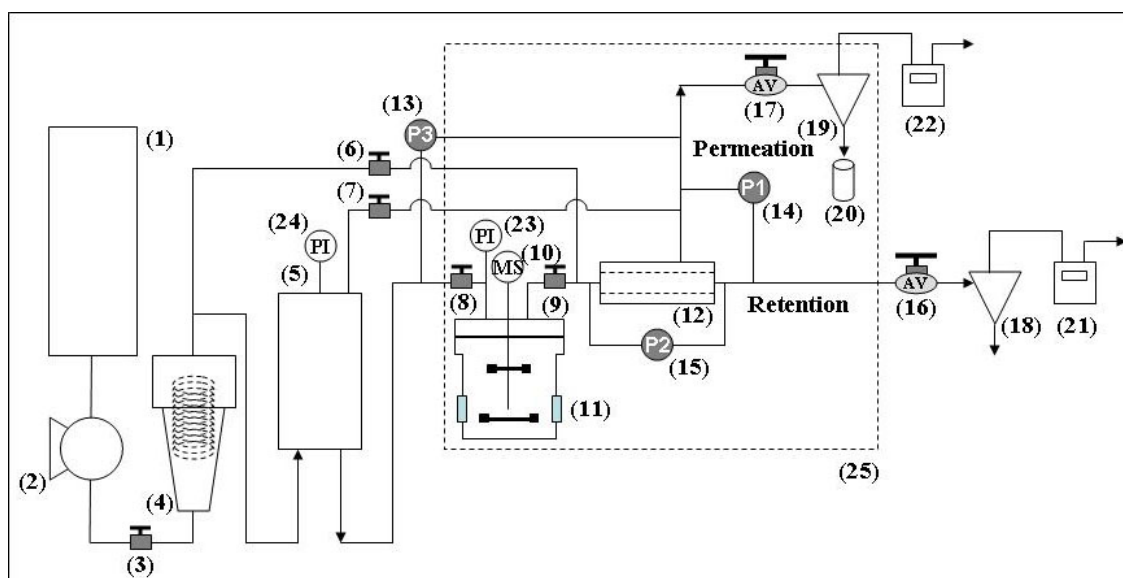


Figure 1. Experimental setup for nanofiltration using inorganic membrane in Sc-CO₂ process

Results and discussion

Effect of Flow Rate in Surfactant Permeation : **Figure 2** shows the kinetic behavior of the permeation effect as a function of flow rate. For this, a triblock copolymer from the Pluronic family PE6100 (M.W. = 1650 g/mol), which has a molecular weight larger than the MWCO (1 kD) of membrane, was prepared [7]. After mixing with PE6100 and CO₂ in the reactor for 20 min, 270 mL of CO₂ was fed at a constant flow rate. In a fixed quantity (270 mL) interval, the permeated surfactants

were collected in the separator and were measured by a microbalance. Throughout each experiment, 1,080 mL of CO₂ was flushed totally. As mentioned above, in general, PE6100 can not pass through the membrane. However, as seen from **Figure 2**, the surfactant was permeated as increasing the flow rate. At the low (2 mL/min) flow rate, the effect was not high due to the adsorption of the surfactant onto the membrane. However, some surfactant of about 15% was permeated through the membrane. The reason is because the polymer surfactants rarely have the exact molecular weight and there is always a distribution around an average value. Moreover, the surfactant can be folded and it is thus possible that it can enter the pores as it has already been observed in the case of surfactant nanofiltration in water [8]. In the case of PE 6100, this is a highly probable situation, since the surfactant molecule comprises two hydrophilic ends that absorb preferentially onto the membrane whereas only the hydrophobic block located in the middle of the molecule extends inside the supercritical CO₂. It can be also observed that the permeation rate, was steeply increased for flow rates over 2 mL/min. At 2 mL/min, a rather constant value of permeation amount is reached. This suggests that equilibrium occurs at the membrane surface between adsorption forces and permeation mechanical forces. Consequently, such a result implies that the flow rate is a very important parameter that governs the separation rate of surfactant material at the membrane surface.

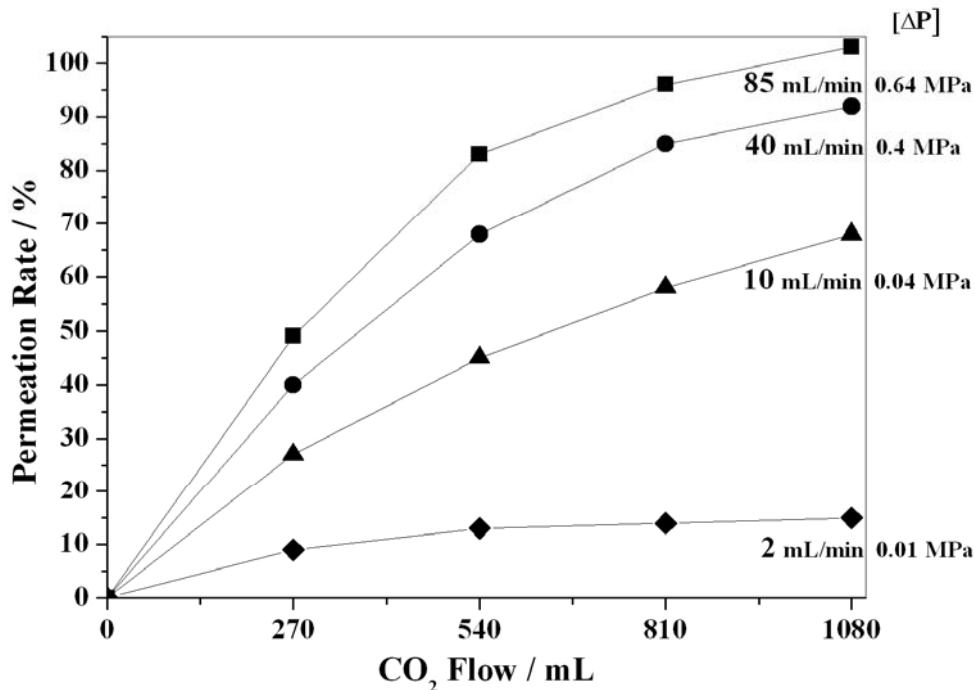


Figure 2. Effect of flow rate in membrane separation with 1kD (1 Ch.) membrane at 40 °C and 25 MPa.

Effect of Trans-membrane Pressure for Micro emulsion Permeation : Water-in-CO₂ microemulsions were permeated using 1 kD membrane. As mentioned above, microemulsions having contaminants should be recovered to reuse the surfactants as well as the CO₂. The water core of surfactant micelles with dissolved solute (contaminants) is expected to be separated from microemulsions using nanofiltration by means of the sieving mechanism. Free surfactants flowing through the membrane can then be recycled. Nonyl Phenol -4-polyexthoxylated (M.W. = 396 g/mol) was used to form the microemulsions. The flux variations of pure CO₂, CO₂/NP-4, and microemulsions (W = 20, 30) are presented in **Figure 3**.

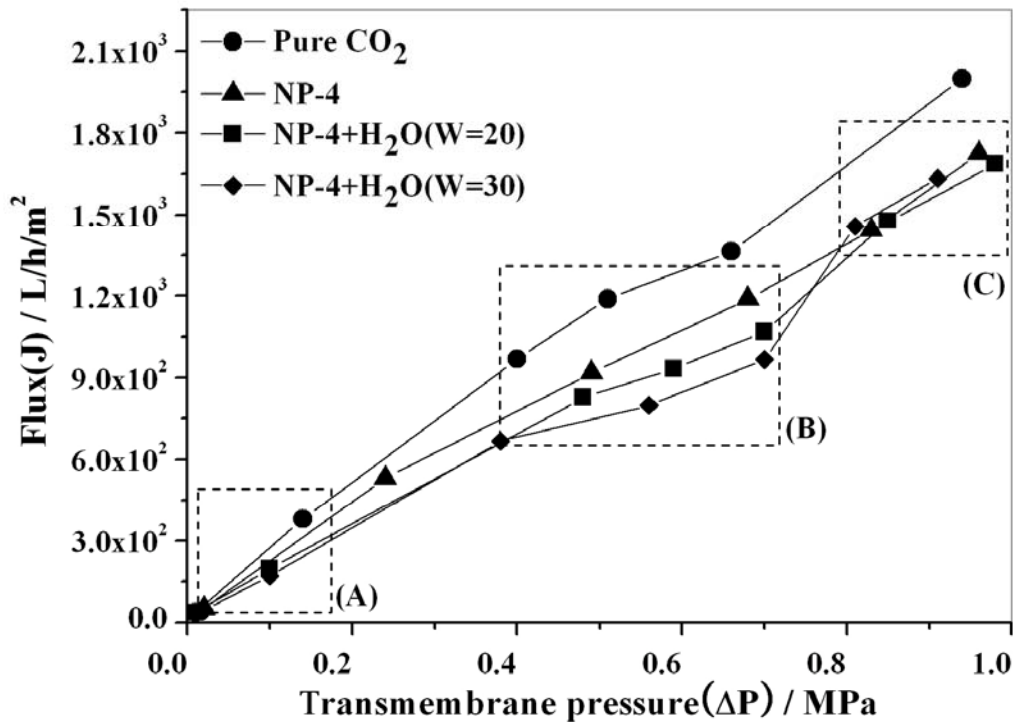


Figure 3. Microemulsion permeation as increasing the trans-membrane pressure with 1kD (3Ch.) membrane at 40 °C and 25 MPa.

At low trans-membrane pressure, $\Delta P=0.1$ MPa (A), no considerable difference was observed. However, as seen in range of the trans-membrane pressure from 0.4 to 0.7 MPa (B), a flux decline in the case NP4 filtration is observed. This phenomenon increases in the case of micro emulsions and with the water load. When the surfactant is alone, the hydrophilic polyethoxylated part adsorbs onto the membrane and pore surfaces thus increasing the total resistance of the membrane. Addressing the micro emulsion case, micelles reach and adsorb onto the membrane, the surfactants then spread along the pore walls. The spreading will carry the water into the pores and simultaneously the pressure gradient pushes the solution into the filter pores with the flux to the pore walls. In the (B) case the process is dominated by the set up of an equilibrium between adsorption and hydrodynamic forces. Over 0.7 MPa of trans-membrane pressure (C), the value of flux increases suddenly and no difference with pure NP-4 is observed because of the intense trans-membrane pressure and flow rate. Hydrodynamic forces overcome adsorption forces in that case. Ultimately, the water core permeated through the membrane directly without any adsorption.

Experimental observations are qualitatively similar than in the case of the permeation of a single surfactant, suggesting a rather complex mechanism involving adsorption behaviour balanced by hydrodynamic forces at the membrane surface.

More work is needed to understand these phenomena in details. These preliminary results suggest also that a much lower cut off should be used for membranes to avoid surfactant penetration in pores. However, inorganic membranes having cut-off far under 1 kD is still a high challenging issue.

Conclusions

The behavior of a surfactant from the Pluronics family (Copolymer of ethylene oxide and propylene oxide) in sc CO₂ has been investigated. It was observed that the surfactant retention on the membrane was highly dependent from the hydrodynamics in the membrane pores.

In the case of water in sc CO₂ micro emulsions similar observations have been made with a higher degree of complexity because of the added water-membrane interaction.

Hypothesis to explain the permeation phenomena at the pore scale have been made taking into account for the hydrophilic nature of the membrane and the adsorption of the surfactant at the membrane/CO₂ interface.

One of the limitations encountered is probably the pore size of inorganic membranes which is still high. However the use of organic membranes is not acceptable for nuclear purposes since interactions with scCO₂ are expected that can impact negatively the membrane life duration and, also, irradiation damages from radioactive contaminants are unwanted.

We are now working on the elaboration of new membrane types using scCO₂ as a reactive medium to form an inorganic layer from organo metallic precursors.

References

- [1] Neil G. Smart, Thomas E. Carleson, Sadik Elshani, Shaofen Wang, and Chien M. Wai, Extraction of Toxic Heavy Metals Using Supercritical Fluid Carbon Dioxide Containing Organophosphorus Reagents, *Ind. Eng. Chem. Res.* 1997, 36, 1819
- [2] Moonsung Koh, Kwangheon Park, Doohyun Yang, Hakwon Kim, Hongdoo Kim, The Synergistic Effect of Organophosphorus and Dithiocarbamate Ligands on Metal Extraction in Supercritical CO₂, *Bull. Korean Chem. Soc.*, 2005, 26, 423
- [3] A.A. Murzin, V.A. Babain, A.Yu. Shadin, I.V. Smirnov, A.A. Lumpov, N.I. Gorshkov, A.E. Miroslavov, and M.Z. Muradymov, Supercritical Fluid Extraction of Actinide Complexes: II. SFE of Actinide β -Diketonates. *Radiochemistry*, 2002, 44, 467
- [4] Yoshihiro Meguro, Shuichi Iso, Zenko Yoshida, Osamu Tomika, Youichi Enokida, Ichiro Yamamoto, Decontamination of Uranium Oxides from Solid Wastes by Supercritical CO₂ Fluid Leaching Method using HNO₃-TBP Complex as a Reactant, *Journal of Supercritical Fluids*, 2004, 31, 141
- [5] S. Sarrade, G.M. Rios, M. Carles, Nanofiltration Membrane behavior in a Supercritical Medium, *Journal of Membrane Science*, 1996, 114, 81
- [6] S.J. Sarrade, G.M. Rios, M. Carles, Supercritical CO₂ Extraction Coupled with Nanofiltration Separation Applications to Natural Products, *Separation and Purification Technology*, 1998, 14, 19
- [7] J. Galy, K. Sawada, B. Fournel, P. Lacroix-Desmazes, S. Lagerge And M. Persin, Decontamination of solid substrates using supercritical carbon dioxide-application with trade hydrocarbonated surfactants", *Journal of Supercritical Fluids*, 2007, 42, 69 (2007)
- [8] G. Cornelis et al. Nanofiltration of nonionic surfactants : Effect of the molecular weight cut-off and contact angle of flux behavior *Ind. Eng. Chem. Res.*, 2005, 44, 7652-7658