Ethoxylated Nonionic Surfactants in Hydrophobic Solvents: Separation Using Membrane Immobilized Poly-acrylic Acid

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Abstract

It is established in the literature that certain polyelectrolytes like poly-acrylic acid and ethoxylated nonionic surfactants form complex in aqueous solution due to hydrogen bonding between carboxyl group of PAA and ethylene oxide group of the surfactants. In the present study, pure ethoxylated surfactant solution in a hydrophobic solvent is permeated through a partially cross-linked PAA composite membrane to quantify the extent of separation of the surfactants in the heterogeneous system. In addition, the permeation properties of the PAA functionalized membrane were studied to establish certain characteristics of the membrane like porosity and thickness of PAA layer inside membrane pore as a function of pH. Role of ethylene oxide group variation in surfactant separation for the heterogeneous system was established by performing experiments with pure surfactants having same alkyl chain length but varying ethoxylate chain lengths. It was observed that the surfactants with higher number of ethylene oxide groups per molecule exhibit higher extent of separation from the hydrophobic solvents. The pH sensitivity of the PAA-surfactant complex is established by verifying its reversibility under varying pH conditions and it was used successfully for regeneration and reuse of the membrane.

Introduction

Interaction between poly-acrylic acid (PAA) and ethoxylated nonionic surfactants has been studied for the last few decades and is receiving increasing attention in recent studies due to its scientific and industrial importance.[1-6] It is established that certain polyelectrolytes like poly-acrylic acid and ethoxylated nonionic surfactants form complex in aqueous solution due to hydrogen bonding between carboxyl group of PAA and ethylene oxide group of the surfactants. In addition to hydrogen bonding, the interaction is enhanced due to hydrophobic attraction between alkyl chain of the surfactants and PAA.[7] The complex formation begins when the surfactant exceeds a particular concentration called critical aggregation concentration (denoted by CAC or T_1). At a particular higher concentration, polyelectrolyte is saturated with surfactant and formation of micelles takes place in the bulk. The PAA-surfactant complex is pH sensitive and the complexation is observed only in narrow pH range. Above pH 5 there is no complex formation and below pH 3 PAA forms a precipitate with the ethoxylated surfactants which redissolves in excess surfactant.[6] The composition of PAA-$C_{12}E_8$ complex (1.8 moles of EO per mole of carboxyl group) as determined by Anghel et.al.[1] suggests that not all the ethylene oxide units participate in the complex formation. The ethylene oxide units remain free or form loops or cross each other in the complex.

The main aim of this work was to study the surfactant-PAA interaction in a heterogeneous system involving the surfactants dissolved in a hydrophobic Siloxane solvent. The PAA was immobilized inside membrane pores and the solution of surfactant was permeated through the functionalized membrane. The extent of interaction was studied by evaluating the amount of the pure surfactant captured by the membrane during the permeation process. The effect of ethylene oxide chain length on PAA-surfactant interaction was quantified in such a system. The particular Siloxane solvent was selected for the study because of its role as a “green” replacement solvent for the toxic and volatile PCE type solvents for various surfactant based cleaning operations. In addition, the permeation properties of the PAA functionalized membranes were studied to establish certain characteristics of the membrane like porosity and thickness of PAA layer inside membrane pore as a function of pH.

Experimental Section

Materials : The hydrophobic siloxane solvent (D5; $C_{10}H_{30}O_5Si_5$) was obtained from Alfa Aesar. Pure surfactants used for fundamental studies are polyoxyethylene glycol n-dodecyl ether ($C_{12}E_n$) i.e. $C_{12}H_{25}(OCH_2CH_2)_nOH$, (n = 3, 5 and 8) and were obtained from Nikko Chemical Co. (Tokyo, Japan). Analysis by gas chromatography revealed single peak indicating high purity of the surfactants. Hydrophilized Durapore Polyvinylidene Fluoride (PVDF) microfiltration membranes with an average pore size of 650 nm was obtained from Millipore Corporation. Poly-acrylic acid was obtained from Polysciences Inc. as an aqueous solution with a concentration of 25 wt% and molecular weight of 50,000. HPLC grade isooctane and deionized ultrafiltered water was purchased from Fisher Scientific.

Membrane Preparation : Aqueous solution of poly-acrylic acid (25 wt%, MW=50,000) containing ethylene glycol (4.3 wt%) as cross linking agent was passed through the membrane under application of vacuum. The membrane used was a commercial low-pressure microfiltration PVDF membrane with nominal pore size rating of 650 nm. The membrane was then heated in oven at 110~120 ^{0}C for 3 hours to allow partial cross-linking reaction to occur. The ether linkage formed between the carboxyl and hydroxyl groups generates the cross linked PAA network. Dry membrane weight was measured before and after processing to determine quantity of PAA immobilized in the membrane matrix. In general the PAA loading for a 15 cm^2 membrane varied between 0.07 g to 0.1 g.

Membrane Experiments with Water and D5 Solvent : Sepa ST Membrane Cell from Osmonics was used to carry out the permeation and surfactant capture studies. The solutions of desired concentrations (200 mg/L for $C_{12}E_8$ and 50 mg/L for $C_{12}E_5$ and $C_{12}E_3$) of pure ethoxylated surfactants in water and D5 were prepared. To determine the PAA-surfactant interaction, 20 ml solution of the surfactant was permeated through the PAA functionalized membrane at 2.04 bar transmembrane pressure. In the case of surfactant capture from D5 solution, 0.1% water was added to the D5 solution. The membrane was wetted with water before the surfactant capture experiment was performed. The feed and permeate samples were analyzed by GC-FID for the surfactant concentration. All the experiments were conducted at 25 ^{0}C unless otherwise specified.

Analysis : The surfactant concentrations in the organic phase were measured with a Varian CP-3800 temperature programmable gas chromatograph equipped with a Chrompack capillary column of 15m length, 0.25mm internal diameter, and with Sil 8 CB as coating phase. The detector was FID mode. Chrysene-d12 was used as an internal standard during the analysis. The aqueous phase to be analyzed was partitioned with the pure organic phase and the partitioned organic phase was analyzed for surfactant concentration using GC-FID. The aqueous phase concentration was calculated using partition coefficients and mass balance. To be consistent, the pH of the aqueous solution of the surfactant was adjusted to 3 before carrying out partitioning with the organic phase.

Results and Discussion

Permeation Study for PAA Functionalized Membrane : Permeability of PAA functionalized membrane was determined by flux measurement at varying pressures and compared with bare membrane permeability. The significant reduction in flux is a clear indication that PAA has been successfully functionalized inside membrane pores (Figure 1).

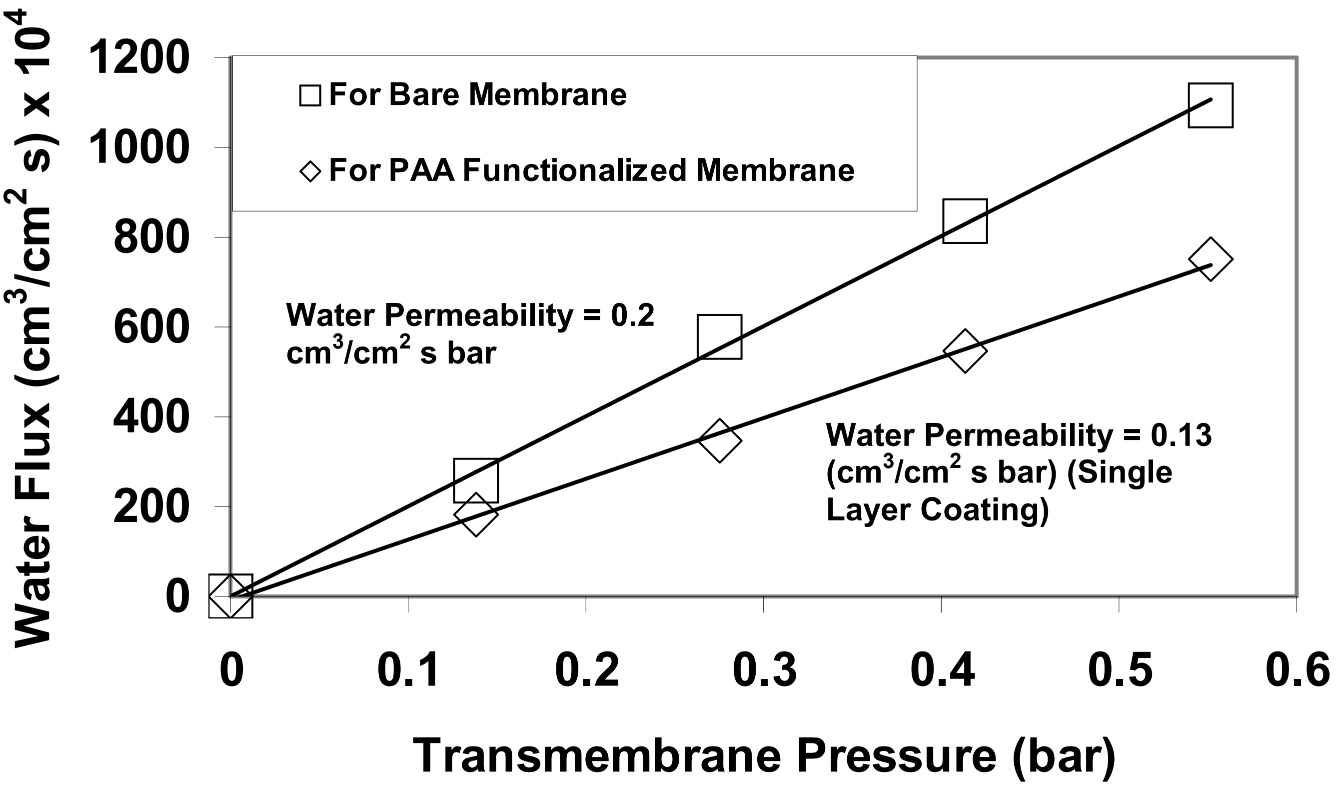

Figure 1. Effect of PAA functionalization (single layer coating) on water flux (pH = 5.8) through hydrophilized PVDF Membrane (650 nm).
For three layer coating (not shown in figure) water permeability = 1 x 10^{-4} cm^3/cm^2 s bar.

Under the assumption of uniform cylindrical membrane pores, the permeability (A_i) can be represented using Hagen-Poiseuille relation as follows:

$$A_i = \frac{J_i}{\Delta P} = \frac{\varepsilon_m r_p^2}{8\mu_i \tau L} \tag{1}$$

Where

J_i: Permeate flux, ε_m: Membrane Porosity, r_p: Pore Radius, μ: Viscosity,

L: Thickness of Membrane, τ: Tortuosity of the membrane pore and ΔP: Applied Transmembrane Pressure

For the bare membrane water permeability experiment, the values of the parameters are:

$\frac{J_w}{\Delta P} = 2\times10^{-8} m^3/m^2 s\ Pa$, $r_p = 3.25\times10^{-7} m$, $\mu = 1\times10^{-3} Pa\ s$, $L = 1.25\times10^{-4} m$ and $A_m = 1.5\times10^{-3} m^2$.

Substituting this data in Equation (1) yields $\varepsilon_m/\tau = 0.189$

The effect of PAA functionalization on pure water transport at varying pH levels is shown in Figure 2.

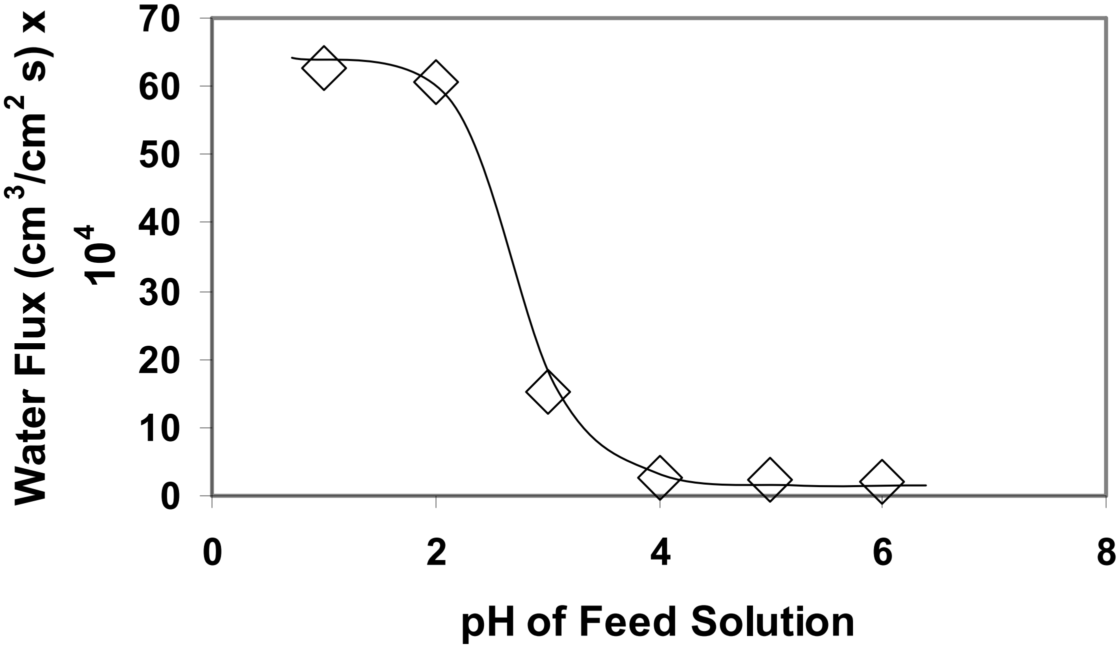

Figure 2. Permeate Water Flux as a function of pH for PAA functionalized PVDF membrane (650 nm, 3 layer PAA coating, Transmembrane pressure = 2.04 bar)

The pH sensitivity of the flux In the case of membranes functionalized with macromolecules such as polypeptides is reported in literature.[8-9] In the case of PAA functionalized membranes higher pH levels result in ionization of carboxyl groups to form negatively charged carboxyl ions. The electrostatic repulsion between the adjacent carboxyl ions results in extended random coil conformation of PAA chains, which poses increased resistance for water flow through the membrane pores. In the present case of partially crosslinked PAA composite membrane, the PAA chains may not be able to extend to the fullest extent due to cross-linking at various points throughout the chains. But from Figure 2 it is evident that the extension of PAA chains is sufficient to cause the flux drop at higher pH levels. It was estimated that the hydrodynamic pore radius decreased from 325 nm to 120 nm due to functionalization and it further decreased to 50 nm due to extension of PAA chains at higher pH.

Interaction of the Pure Nonionic Surfactants with Immobilized PAA inside Membrane Matrix : The surfactant concentration in the feed and permeate obtained by GC-FID was used to calculate amount of surfactant captured by the functionalized membrane during the permeation process. To eliminate the effect of varying PAA loading per membrane sheet that was used for surfactant capture experiment, the extent of surfactant capture was reported in terms of the moles of surfactant captured per mole of free carboxyl groups. It was assumed that ethylene glycol was completely utilized for crosslinking the PAA chains and all the remaining carboxyl groups were free for interaction with the surfactant. The surfactant capture studies were carried out for the pure ethoxylated nonionic surfactants ($C_{12}E_n$) with same alkyl chain length but varying number of ethylene oxide groups per molecule.

As discussed earlier the ethylene oxide group of the surfactant actively contributes for polyelectrolyte-surfactant interaction through hydrogen bonding. Higher ethylene oxide content per molecule should result in enhanced interactions with PAA and thus resulting in high separations. The amount of surfactant captured per mole of PAA indeed increases exponentially with increasing number of ethylene oxide groups per molecule (Figure 3).

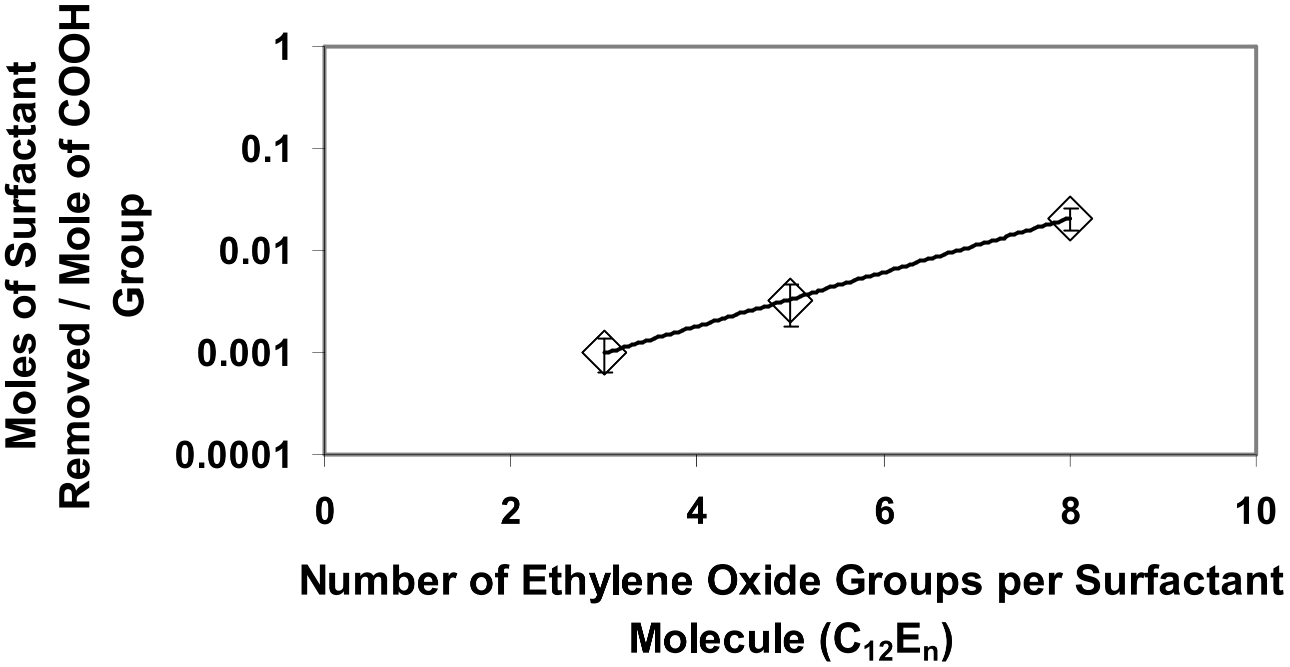

Figure 3. Pure surfactant ($C_{12}E_n$) capture by PAA functionalized PVDF membrane (650 nm, 3 layer PAA coating, Transmembrane pressure = 2.04 bar) from their solution in D5 (0.1% water was added to the surfactant solutions before permeating through the functionalized membrane)

Membrane Regeneration : Since the interaction between the ethylene oxide group of surfactant and carboxyl groups of PAA is result of hydrogen bonding between the two groups, it is pH sensitive. The complex formation occurs only in low pH (pH 2-5) range. This fact was verified by permeating slightly alkaline water (pH = 8) through the membrane.[10] The surfactant was collected as its aqueous solution on the permeate side. The aqueous phase analysis by partitioning and GC-FID showed that 70% of the captured surfactant in the membrane was collected in its aqueous permeate. The regenerated membrane was used again for the surfactant capture experiment and it picked up the surfactant. This established the reversibility of the surfactant-PAA complex. The successful regeneration and reuse of membranes can be exploited to develop a novel process for separation of the nonionic surfactants from organic solvents. Also the preferential separation of the surfactant molecules with higher number of ethylene oxide groups may be applied for purification of a surfactant mixture.

Conclusions

The partially crosslinked PAA composite PVDF membranes were successfully studied for interaction between PAA and the surfactant dissolved in a hydrophobic, siloxane solvent. It was established that amount of surfactant captured per mole of PAA increases exponentially with increasing number of ethylene oxide units per surfactant molecule. The pH sensitivity of the PAA-surfactant complex was verified by regeneration of the membrane using slightly alkaline water. The successful regeneration and reuse of the membrane can be exploited to develop a process for separation of nonionic surfactants from hydrophobic solvents and also for purification of surfactant mixture.

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