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Formation of AgCl nanoparticle in reverse microemulsion using polymerizable surfactant and the resulting copolymer hybrid membranes

Li-guang Wu [a], Ting Wang [a,*], Zeng Jiang [b]

[a] College of Environmental Science and Engineering, Zhejiang Gongshang University, Hangzhou, 310012, China
[b] Department of Chemical Engineering, Zhejiang University, Hangzhou, 310027, China

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ABSTRACT

AgCl nanoparticles were synthesized in water—in—oil microemulsions using polymerizable 2-acrylamido-2-methyl propane sulfonic acid (AMPS) as the surfactant and a glycidyl methacrylate (GMA)/methyl methacrylate (MMA) mixture as the oil phase. AgCl/poly(GMA-co-MMA-co-AMPS) copolymer hybrid membranes were prepared by *in situ* microemulsion polymerization. The morphology of the AgCl particles and hybrid membranes was characterized by UV-visible spectrophotometry, transmission electron microscopy, and scanning electron microscopy. A size decrease was observed in the AgCl nanoparticles with increased surfactant and salt concentrations. The AgCl nanoparticles maintained an even dispersion in the hybrid membranes. The separation performance of the hybrid membranes was evaluated by pervaporation experiments of benzene/cyclohexane mixtures. The high solubility of the polymerizable surfactant in the MMA-GMA mixture led to better hybrid membrane performance compared with the hybrid membranes prepared by macromolecular surfactant. The swelling–sorption behavior of benzene and cyclohexane indicated that the equilibrium swelling–sorption amounts in all hybrid membranes were larger than in membranes without the nanoparticles. When the surfactant and salt concentrations were both 0.3 mol L^{-1}, the equilibrium swelling–sorption amounts in the hybrid membranes reached a maximum.

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1. Introduction

Given the widespread applications of membrane separation in pollution control and in the chemical industry, increasing attention has been paid to the synthesis of high separation performance membranes. Organic–inorganic hybrid membranes are membranes with significant separation performance for many organic mixtures [1–4]. The π complexation between silver ions and olefins or aromatic hydrocarbons has drawn much interest to hybrid membranes with AgCl nanoparticles [5,6]. Many preparative methods for hybrid membranes with AgCl nanoparticles have been reported [7–9]. Among these methods, *in situ* microemulsion polymerization is the most noteworthy. In a microemulsion preparation, nanoparticles are first synthesized in a microemulsion consisting of a polymerizable monomer, such as methyl methacrylate (MMA), as an oil phase. After the polymerization of the monomer, the hybrid membranes containing the AgCl nanoparticles are synthesized [10]. In recent research on *in situ* microemulsion polymerization, small-molecule surfactants (*e.g.*, dioctyl sodium sulfosuccinate or AOT) have usually been added as emulsifiers. However, these surfactants have poor compatibility with the polymer. Therefore, small-molecule surfactants cannot be combined uniformly with the polymer during polymerization. After polymerization, these small-molecule surfactants and the polymer may form two phases. Thus, the structure of the microemulsion with small-molecule surfactants is destroyed. Without the protection of the water pools, small particles aggregate into large particles, reaching several micrometers in size and appearing in the membrane after polymerization [10]. To solve this problem, an investigation of hybrid membranes prepared by *in situ* microemulsion polymerization using a triblock copolymer F127 as the surfactant was initially conducted. Given the favorable affinity between the surfactant and poly(MMA), small AgCl nanoparticles were formed in the microemulsion and were distributed evenly in the hybrid membrane after polymerization [11]. However, the weak solubility of F127 in the MMA solution limited the number of AgCl particles in the microemulsion, thereby inhibiting the separation performance of the hybrid membranes [11].

In this present study, polymerizable 2-acrylamido-2-methyl propane sulfonic acid (AMPS) was used as a surfactant to prepare the hybrid membrane. During monomer polymerization, AMPS was also polymerized and efficiently integrated into the membrane

* Corresponding author. Tel.: +86 571 88071024 7017; fax: +86 571 88865762.
E-mail address: zjwtwaiting@hotmail.com (T. Wang).

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structure, and the surfactant continuously inhibited the aggregation of AgCl nanoparticles. Based on these findings, preparative experiments were designed to explore the effect of different conditions on AgCl nanoparticle morphology and hybrid membrane performance.

2. Experimental

2.1. Materials

Glycidyl methacrylate (GMA) was obtained from Aladdin Shanghai Pure Crystalline Chemical Reagent (Shanghai, China) and purified by vacuum distillation. MMA was obtained from Shanghai Coral Chemical (Shanghai, China) and was also purified by vacuum distillation. Both the GMA and the MMA were used as the oil phase in the microemulsion. The AMPS surfactant was obtained from Tokyo Kasei (Japan). 2,2-Azobisisobutyronitrile (AIBN), which was used as an initiator, was purchased from Shanghai Chemical Reagent. Other reactants used in the preparations (silver nitrate [$AgNO_3$] and sodium chloride [NaCl]) and separation experiments (benzene and cyclohexane) were obtained from Shanghai Chemical Reagent. All reagents were of analytical grade.

2.2. Synthesis of AgCl nanoparticles

AMPS of different quantities (0.210, 0.630, or 1.005 g) and 10 mL each of GMA and MMA (with a 3:2 volume ratio) were combined in a three-necked flask under ultrasonic stirring at room temperature. Then, 30 μL of $AgNO_3$ (or NaCl) aqueous solution of different concentrations was added to the GMA/MMA mixture (10 mL) in the ultrasonic bath. After 10 min, a homogeneous GMA/MMA microemulsion of $AgNO_3$ or NaCl was generated. AgCl nanoparticles were generated by mixing the $AgNO_3$ and NaCl microemulsions in one flask to react for 30 min.

2.3. Preparation and characterization of the hybrid membrane

AIBN was added to the GMA/MMA microemulsions (30 mL) with AgCl nanoparticles to initiate polymerization at 60 °C to 65 °C for 2 h. The reaction solution obtained was coated on a polysulfone film (molecular weight cut-off=20,000). The AgCl/poly(GMA-co-MMA-co-AMPS) hybrid membranes on the polysulfone film were obtained by continuing the reaction for 12 h at 60 °C to 65 °C. The thickness of the top nanocomposite layer was measured at ~25 μm by scanning electron microscopy (SEM).

2.4. Pervaporation (PV) experiments of benzene/cyclohexane mixtures

The membrane was positioned in a stainless-steel permeation cell. The membrane area in contact with the feed was 19.6 cm^2, the cell temperature was thermostatically controlled, and the vacuum at the downstream end was maintained at about 160 Pa by a vacuum pump. The experiments for the benzene/cyclohexane mixture were conducted in a continuous steady state and operated at a constant temperature of 30 °C. The PV vapor was condensed by liquid nitrogen (N_2). After 2 h of cycling in a PV apparatus, the composition of the permeation was analyzed with a gas chromatograph equipped with a thermal conductivity detector (GC-950, Shanghai Haixin Chromatography Instruments, China).

The separation performance of a membrane is characterized by two parameters: flux and selectivity. Flux is the rate of feed component permeation through a unit area of the membrane at unit time. Two commonly used flux units in PV processes are kg m^- h^{-1} and g cm^{-2} s^{-1}. The permeation flux (J) and the separation factor (α) of all components were calculated using the following equations:

$$J = \frac{\Delta m}{S \bullet \Delta t}, \tag{1}$$

$$\alpha(A/B) = \frac{Y_A / Y_B}{X_A / X_B} \tag{2}$$

where Δm is the permeated weight during operation time Δt, S is the membrane area (19.6 cm^2), α is selectivity (separation factor), and X and Y are the molar concentrations of the components in the feed and permeate, respectively. The A and B subscripts denote the two components to be separated.

2.5. Swelling measurement of the hybrid membrane

The degree of swelling (DS) of the membrane at a given interval (10 min within the first hour, then every half-hour) is defined as

$$\mathrm{DS}\ (g/g) = \frac{m_1\text{-}m_0}{m_0} \times 100 \tag{3}$$

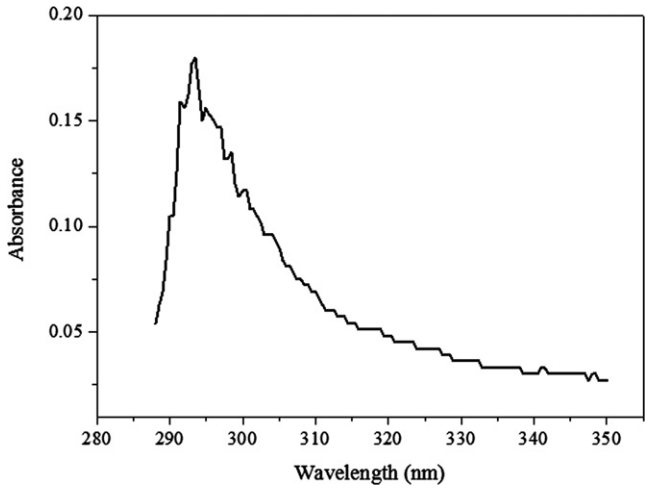

Fig. 1. Absorption spectrum of AgCl nanoparticles prepared in the AOT microemulsion. (0.1 mol L^{-1} AOT, $C_{AgNO3}=C_{NaCl}=0.3$ mol L^{-1}, $\omega=10$).

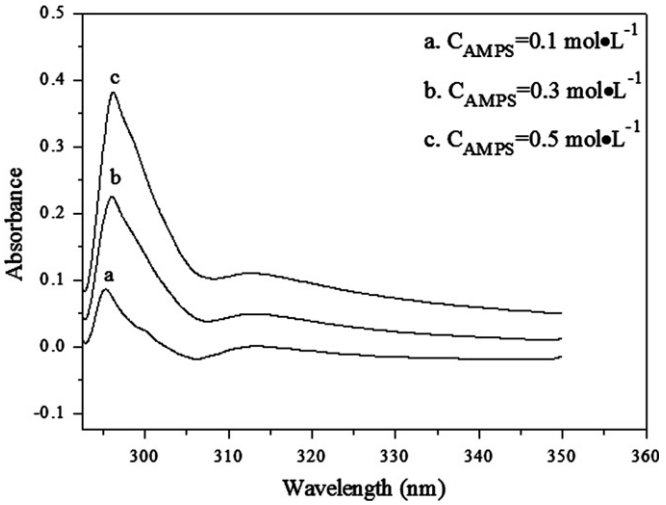

Fig. 2. UV–vis absorption spectra of AgCl nanoparticles at different C_{AMPS}. $\omega=11.1$ (ω is H_2O to surfactant mole ratio in the microemulsion), $C_{NaCl}=C_{AgNO3}=0.3$ mol L^{-1}).

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