일반강연 II-2

Micellar Enhanced Ultrafiltration Using PEO-PPO-PEO Block Copolymer

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PEO-PPO-PEO 블록공중합체를 사용한 마이셀 증진 한외여과법 (유해유기물의 가용화 및 분리특성)

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1. Introduction

Low molecular harmful organics such as 1-naphthol and phenol are widely used in industries, and pose serious environmental problems. Wastewater containing low molecular harmful organics may be ejected from various sources including metal-plating industries, circuit-board manufacturing process, photographic and photo-processing industries, refineries and metal-tailing leachate. The pollution of nation harbors, waterways and ground water resources with these organics has reached critical portions, and might also give hazardous influence on human health.

Micellar enhanced ultrafiltration(MEUF) is a recently developed process to remove dissolved organics and/or heavy metals present in small or trace quantities from aqueous solution. In this system, the fatal defect is leakage of surfactants especially at low concentration below CMC(critical micelle concentration), which becomes a secondary pollution. Our group proposed to use biosurfactant and polymeric micelle to solve problems mentioned above.

In this study we investigated a modified MEUF using PEO-PPO-PEO (polyethyleneoxide-polypropyleneoxide-polyethyleneoxide) block copolymers for the removal of organic solutes such as 1-naphthol and phenol from aqueous wastewater. We proposed PEO-PPO-PEO block copolymers as new surfactants for forming micelles in MEUF, and investigated the solubilization characteristics and efficiency for the removal of 1-naphthol and phenol. PEO-PPO-PEO block copolymers are environmentally mild and safe as biosurfactants.

2. Experimentals

2-1. Materials

Three kinds of plulonic P103(MW = 4,950, PPO/PEO ratio = 1.79), P85(MW = 4,600, PPO/PEO ratio = 0.77), F108(MW = 14,600, PPO/PEO ratio = 0.19) were purchased from Asahi Electrochemical Co. LTD. They were dialyzed for 1 week with distilled water, and a cellulose acetate membrane(MWCO 3,500) was used to remove small quantities of impurities. They were dried, and reweighed before use. Phenol and 1-naphthol were purchased from Wako Pure Chemicals, and used without further purification.

2-2. Apparatus

2-2-1. Dialysis

An equilibrium dialysis system(10 ml) was purchased from Sanplatech Co. LTD. Cellulose acetate membranes of various MWCO(molecular weight cut off) of 1,000, 3,500, 8,000, 10,000, 12,000, 30,000, and 50,000 were purchased from Spectrum Co. LTD., and used after being immersed into pure water in 500ml beaker for two days. Temperature was controlled with a shaker at 60 shakings/min.

Rejection coefficient(R) for dialysis is defined as follows:

$$R = 1 - Cper/Cret \quad (1)$$

where Cper and Cret refer to the analytical concentrations of solute in permeate and retentate samples, respectively.

2-2-2. Ultrafiltration

Polysulfone ultrafiltration membrane(MWCO = 10,000, area = 0.085 m2) was used. The observed rejection(Robs) is defined as Equation (2):

$$Robs=1 - Cper/Cfeed \quad (2)$$

where Cfeed is the concentration of solute in feed solution. Ultrafiltration for the total reflux system was examined .

2-3 Analysis

Dynamic light scattering method(Otsuka DLS 7,000, He-Ne laser) was used to investigate the size of micelle. CMC was analyzed with Whilhelmy type surface tensiometer(Shimadzu ST-1). Phenol(270nm) and 1-naphthol(293nm) were analyzed by UV/VIS spectrophotometer(Shimadzu 3210). The concentrations of PEO-PPO-PEO copolymer were analyzed by TOC(Total Organic Carbon Analyzer, Shimadzu TOC-500).

3. Results and Discussion

Surface tension for aqueous solutions containing the polymers was examined to find the effective concentration(CMC) of the polymers for separation. It can be found that P103 shows the lowest CMC among the

polymers used. CMC of P103 can be found to be 0.08wt.%. On the other hand, CMCs of P85 and F108 found are 4 and 1 wt. %, respectively, both of which are much higher that of P103. Surface tension data can be compared with those of Alexandria et. al. They are somewhat different from our data, but the tendency that P85 has the highest CMC and P103 the lowest CMC is the same between two experimental results. It is expected that P103 is the most effective for forming micelle solution and shows better rejection of solute among the polymers.

The effects of the polymers of P85, P103 and F108 on the rejection of 1-naphthol were investigated by dialysis as a function of polymer concentration . P103 shows the highest rejection coefficient up to 0.99. P103 may have the highest hydrophobicity among the polymers used because its PPO/PEO ratio(=1.79) is much higher than those of P85 and F108. And, 1-naphthol is a hydrophobic compound whose solubility in water is 700 PPM at 25°C according to the literature. In the case of phenol, solubility in water is 8.2% at 15 °C . From these results it can be said that 1-naphthol tends to be easily soluble into P103 polymeric micelles. P103 can be selected as an excellent enhancer among the plulonics used.

Mean diameter was analyzed by dynamic light scattering method. The hydrodynamic mean diameter of micelles increases with the addition of 1-naphthol within the solute concentration of 8mM. This indicates that the more the solute of 1-naphthol is solubilized into the polymeric micelle, the more the polymeric micelle enlarges. It is not clear whether the solute exist in the palisade region or sandwich region. However, it is a clear evidence of solubilization of solute into polymeric micelle.

MWCO of the membrane used varies from 1,000 to 50,000. P103 commences to permeate from MWCO of about 10,000, and the rejection of the polymer decreases rapidly with increasing MWCO above 10,000. It can be concluded that the optimum MWCO for the rejection of P103 is about 10,000 considering permeate flux.

It can be confirmed again that the optimum MWCO of the membrane for P-103 polymer is about 10,000, because the rejection coefficients for both 1-naphthol and phenol are nearly unchanged and maintained as the initial level up to MWCO of 10,000, but they decreases rapidly with the increase of MWCO above 10,000..

To find out a proper method for the regeneration and recycling of the polymeric surfactant(P103) used, the effect of temperature on the solubilization and rejection of solute in dialysis was investigated.

The rejection coefficients were found to vary significantly with the

temperature in the range of 15-45°C. The rejection coefficients for the temperatures of 25, 35 and 45°C are nearly the same and relatively high. However, the rejection coefficients for the temperature of 15°C show much lower values compared with those for the temperatures higher than 25°C. These results means that the solubilization of 1-naphthol and phenol into P103 polymer micelles decreases significantly at the temperature of 15°C so that the rejection coefficients become greatly lower than those for higher temperature by about 30 %, which may be due to the disruption or destabilization of the polymeric micelle.

CMCs and their surface tensions were measured as a function of temperature. CMC increases abruptly as the temperature decreases from 25 to 15°C. This is because the solubility of the polymer may decrease and the activity of the polymer as surfactant diminishes. The decrease of activity of the polymer induces the destabilization of micelles and desolubilization of solutes from the micelles. It is concluded that the optimum temperatures for the solubilization of solute into P103 polymeric micelles and for the desolubilization of solute from P103 polymeric micelles are 35-45 and 15°C, respectively, for the removal of solute by using P103 as an enhancer in MEUF.

To verify the results described above, MEUF experiments were performed at 25°C and feed pressure of 1.0 kgf/cm^2 using a PS membrane of MWCO 10,000 and P103 as an enhancer for the removal of 1-naphthol. The rejection coefficients measured as a function of P103 concentration are illustrated in Fig. 1. It can be concluded that the addition of P103 to 1-naphthol solution enhances the rejection very effectively in MEUF and P103 concentration should be maintained at more than 1.0 wt. % to obtain high rejection as expected above in dialysis. It can be confirmed that the results of MEUF coincide exactly with the results of dialysis.

4. Conclusion

PEO-PPO-PEO block copolymers were proposed to use as new surfactants for forming micelles in MEUF, and their solubilization characteristics and efficiency for the removal of 1-naphthol and phenol were investigated.

P103 is the most effective for forming micelle solution and shows better rejection of solute among the polymers of PEO-PPO-PEO block copolymers. The addition of P103 is very effective to enhances the rejection of solute in MEUF and P103 concentration should be maintained at more than 1.0 wt. % to obtain high rejection.