Response of Zeta Potential to the Fouling during Microfiltration of Surfactants

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The response of zeta potential, ζ_{obs} , to membrane surface condition and surfactants in solution was investigated from the viewpoint of the interaction between surfactant and membrane surface. The ζ_{obs} of three polyvinylidene difluoride (PVDF) microfiltration membranes, which had non-ionic hydrophilic, hydrophobic, and positively charged pore surfaces, with nominal pore size of $0.22\ \mu\text{m}$ were measured over wide range of the surfactants concentration. N-Dodecyltrimethyl ammonium chloride (DTAC) and Sodium Dodecyl Sulfate (SDS) were used as cationic and anionic surfactants, respectively. At the lower surfactant concentration (the conductivity below 20mS/m) the behaviors of ζ_{obs} mainly depended on the combination of membrane and surfactant used and they can be explained by the interaction between surfactant and pore surface. At the higher surfactant concentration the behaviors of ζ_{obs} mainly depended on type of surfactant rather than on membrane used. In the case of SDS the severe flux decline was observed at a certain concentration in all the membranes and the absolute value of ζ_{obs} decreased and approached to zero reflecting the flux decline.

Key words : zeta potential / fouling / microfiltration / surfactants

1. Introduction

In the membrane filtration processes the fouling phenomena are considered as the major problems in many applications and are caused by various components existing in the feed stream. Countermeasures against the fouling have been studied in terms of the development of anti-fouling membrane materials^{1~4)}, pretreatments of feed solution for removing or altering the foulant^{5~7)}, and the optimizing of designs of membrane module, processes, and operating and cleaning conditions^{8~10)}.

The fouling will be caused by physico-chemical interactions between the membrane and foulant and the main interactions are recognized as hydrophobic and electrostatic interactions. The water layer adjacent to the hydrophobic surface has a higher value of free

energy than that of the bulk water and adsorption of foulants is favorable because it reduces the total free energy of the system. A water layer next to hydrophilic surface can have a lower value of free energy than the bulk water and it interferes the adsorption of foulants on the surface. The hydrophilic surface modification of membranes has been attempted for applying anti-fouling property to membrane^{1~4)}. Electrostatic interactions arise from the interaction between fixed charge and/or fixed dipoles of membrane surface and foulant in aqueous solution. The origin of these surface charges is considered as the adsorption of specific positive or negative ions and/or ionization of specific chemical group on their surface.

The charge property of porous membrane can be characterized by zeta potential and the trans-membrane streaming potential (SP) method. Helmholtz-Smoluchowski (HS) equation has been usually used for determination of the zeta potential assuming that the pore has a cylindrical capillary with laminar flow and the surface conductivity and the electro double layer (EDL) overlapping in the pore are negligible¹¹⁾,

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Table 1 Features of surfactants

	Chemical formula	Molecular weight (g mol ⁻¹)	Critical micelle concentration(CMC) (25°C) ²⁸⁾
DTAC	C ₁₂ H ₂₅ -N(CH ₃) ₃ Cl	263.9	19.3mM (5.09g/L)
SDS	C ₁₂ H ₂₅ -OSO ₃ Na	288.4	8.13mM (2.34g/L)

$$\zeta_{\text{obs}} = \frac{\mu\lambda}{\varepsilon_0\varepsilon_r} \text{SP} \quad (1)$$

where ε_0 is the permittivity of free space, ε_r is relative dielectric constant, λ is electric conductivity, and μ is viscosity. However, the thickness of EDL cannot be negligible compared with pore size range of MF membranes especially in lower ion concentration. HS equation can underestimate the zeta potential because of the overlapping in pore and the surface conductivity¹²⁾. Thus, the zeta potential estimated from HS equation is “apparent” or “observed” one. However, it is useful for practical application because of its simple formulation.

Surfactant, which contains both hydrophilic groups and hydrophobic groups, plays important roles in membrane and membrane processes. In developing of membrane material surfactants are used as an additive to membrane polymer and surface modification agent for the formation of anti-fouling surface^{1~4)}. In membrane filtration process surfactant has been recognized as foulant of reverse osmosis (RO) or nanofiltration (NF) membranes^{12~15)}, and it has been used as cleaning agents of fouled membranes, and separation agents in micellar-enhanced membrane processes^{16~19)} and oily waste water treatment process^{13, 20~25)}. The behaviors of surfactants during filtration are of interest for efficiencies of the membrane separation processes.

In this study the response of ζ_{obs} to membrane surface condition and surfactants in solution were investigated from the viewpoint of the interaction between surfactant and membrane surface. The ζ_{obs} of three polyvinylidene difluoride (PVDF) MF membranes, which had non-ionic hydrophilic, hydrophobic, and positively charged pore surfaces, with nominal pore size of 0.22 μm were measured. N-Dodecyltrimethyl ammonium chloride (DTAC) and Sodium Dodecyl Sulfate (SDS) were used as cationic and anionic surfactants, respectively. A high throughput measurement of SP²⁶⁾ was conducted in order to measure ζ_{obs} over a

Fig. 1 Experimental apparatus ; ① N₂ cylinder, ② pressure regulator, ③ pressure transducer, ④ thermo bath, ⑤ feed tank, ⑥ pump, ⑦ feed mixing tank, ⑧ digital multi-meter, ⑨ Pt-black electrode, ⑩ membrane, ⑪ membrane holder, ⑫ conductivity cell, ⑬ beaker, ⑭ electric balance, ⑮ personal computer.

wide range of surfactant. At first ζ_{obs} of three PVDF membranes was studied using KCl solution and then the effects of the surfactants on the zeta potential were discussed.

2. Experimental

2.1 Membranes and chemicals

PVDF microfiltration (MF) membranes having three different surface chemistry, which were hydrophilic (GVWP Durapore, Millipore), hydrophobic (GVHP Durepore, Millipore), and positively charged hydrophilic (Charged Durepore, Millipore), with a nominal pore size of 0.22 μm were used. The only difference among these membranes was the surface chemistry. According to manufacturer's patent²⁷⁾ and catalog the hydrophilic membrane has no ionized group on the pore surface and the hydrophobic membrane is made of plain PVDF and the positively charged membrane has positive ionizable group on the pore surface.

Potassium chloride (KCl) (Wako Pure Chemical Industries) solution was used as a non-surface active

Fig. 2 The pulse pattern of applied pressure and the definition of streaming potential.

electrolyte solution. KCl solution was prepared with ultra pure water and filtered with a $0.5 \mu\text{m}$ membrane filter before use. N-Dodecyltrimethyl ammonium chloride (DTAC) (Wako Pure Chemical Industries) and Sodium Dodecyl Sulfate (SDS) (Wako Pure Chemical Industries) were used as cationic and anionic surfactants, respectively. The features of these surfactants were shown in Table 1.

2.2 Experimental apparatus

Fig. 1 shows the experimental apparatus. A dead-end membrane housing (25 mm diameter, effective filtration area 3.0 cm^2) with platinum black electrodes for streaming potential measurement was used. The permeate flux, J , filtration pressure, P_{TM} , electrical potential across membrane, E_{TM} , electric conductivity, λ , of filtrate were measured with a electric balance (Shimadzu, EB3300SW), pressure transducer (Kyowa, PVL-5KB), digital multi-meter (Advantest, R6441), electro conductivity meter (TOADKK, CM40G), respectively. The measured data were recorded by a personal computer. The temperature in the feed tank and the mixing tank was kept at 298K. During filtration the concentration of the feed component in the feed mixing tank can be increased continuously by adding feed component to the mixing tank.

Fig. 2 shows the pulse pattern of applied pressure for SP measurement during filtration and the definition of SP. All filtration experiments were conducted with this pulse pattern pressure.

The SP was defined as the slope of linear regression for E_{TM} versus P_{TM} plots, as $\Delta E_{\text{TM}} / \Delta P_{\text{TM}}$.

$$\text{Streaming Potential (SP)} = \frac{\Delta E_{\text{TM}}}{\Delta P_{\text{TM}}} \quad (2)$$

The E_{TM} versus P_{TM} plots showed good linearity, showing the validity of this measurement.

Fig. 3 Effects of KCl concentration on ζ_{obs} of hydrophilic, hydrophobic, and positively charged membranes.

2.3 Filtration procedure

Membrane was wetted by alcohol before use and set to the membrane holder. Flux and SP were measured with pure water. And then the filtration was conducted by the pulse pattern pressure. During the filtration the concentration of the feed component in the feed mixing tank was gradually increased by adding the feed component. SP and flux were measured during the filtration.

3. Results and discussion

The ζ_{obs} will depend on the surface charge, pore size, and conductivity in pore. At first ζ_{obs} was measured with KCl solution and the effect of the conductivity on ζ_{obs} was discussed. And then ζ_{obs} was measured with SDS and DTAC solutions and ζ_{obs} was discussed from the view point of the charge condition of pore surface. During the measurements the rejection of surfactants, which was determined by conductivity, was not observed. The adsorption of surfactant on membrane can be characterized by ζ_{obs} ^{29~31}. It is considered that the change in ζ_{obs} is due to the adsorption of surfactants in this study, although there was no direct evidence of the adsorption because the change in concentration of surfactants by the adsorption was too small to detect during the adsorption process.

3.1 Effect of KCl concentration on ζ_{obs}

Fig. 3 shows the effect of KCl concentration on ζ_{obs}

Fig. 4 Effects of concentration of surfactants on ζ_{obs} in the three membranes. (A) hydrophilic membrane, (B) hydrophobic membrane, (C) positively charged membrane with SDS, DTAC and KCl solutions.

in the three PVDF membranes. In the hydrophilic membrane the curve of ζ_{obs} showed negative charge and the concave down shape. The absolute value of ζ_{obs} at the conductivity below 5 mS/m would be lowered due to the overlapping of EDL in the pore. As this hydrophilic pore surface has no ionizable groups the origin of the negative charge would be adsorption of anion, i.e. chloride ion, on the pore surface. The hydrophobic membrane, of which surface chemical composition is plain PVDF carrying no ionizable groups, showed very little negative charge. These results show that the hydrophobic surface has little affinity to chloride ion compared with the hydrophilic surface. The positively charged membrane showed positive charge deriving from the surface ionizable group. It was seemed that in the hydrophobic and the positively charged membranes the adsorption of ions

Fig. 5 Effect of DTAC concentration on ζ_{obs} and flux of the hydrophilic, hydrophobic and positively charged PVDF membranes.

had little impact on the origin of the charge.

It is expected that the absolute value of ζ_{obs} will decrease in the higher ionic strength due to compression of EDL¹¹⁾. The absolute value of ζ_{obs} of the positively charged and hydrophilic membranes decreased in the conductivity above 20 mS/m although the experimental data in much higher conductivity could not be measured because the E_{TM} was too small to measure by the experimental apparatus.

3.2 Effect of surfactant on ζ_{obs} in the lower surfactant concentration (conductivity below 20 mS/m)

It is expected that the surface charge density of pore surface will be drastically altered by the adsorption of surfactants. The charge condition of pore surface will be altered to positive by dodecyltrimethyl ammonium (DTA) ion and to negative by dodecyl sulfate (DS) ion. The ζ_{obs} of the three PVDF membranes were measured using DTAC solution and SDS solution. In this section the effect of surfactants on ζ_{obs} at the conductivity below 20 mS/m was discussed. Fig. 4 shows the

Fig. 6 Effect of SDS concentration on ζ_{obs} and flux of the hydrophilic, hydrophobic and positively charged PVDF membranes.

effects of the SDS, DTAC and KCl concentration on ζ_{obs} in the three membranes. Although in this concentration range the absolute value of ζ_{obs} should be affected by the overlapping of EDL, the sign of ζ_{obs} will reflect the sign of surface charge.

In the hydrophilic membrane ((A) in Fig. 4) ζ_{obs} showed negative value in all the solution at the conductivity below 10 mS/m. The origin of these negative charges would be adsorption of anions, which are chloride ion in DTAC and KCl solutions and dodecyl sulfate (DS) ion in SDS solution. In the case of DTAC solution ζ_{obs} showed a minimum at about 2 mS/m and became positive at the conductivity above 15 mS/m. This increase in ζ_{obs} would reflect the increase in DTA adsorption. The condition of the minimum was not clear from these observations although it is expected that the minimum would reflect the competitive adsorption of anions and DTA. In the case of SDS solution ζ_{obs} showed almost same behavior as that in KCl solution in the conductivity below 5 mS/m and increased after showing a minimum at around 6 mS/m.

This increase will be discussed later combined with flux decline.

In the hydrophobic membrane ((B) in Fig. 4) ζ_{obs} clearly showed the same sign of ions of surfactants in this concentration range, which are positive in DTAC solution and negative in SDS solution. These results suggest that the surfactants will adsorb on the hydrophobic surface by hydrophobic interaction and provide the charges. In the case of SDS solution ζ_{obs} showed a minimum and this behavior will be discussed later.

In the positively charged membrane ((C) in Fig. 4) ζ_{obs} showed positive value in the cases of DTAC and KCl solutions and negative value in the case of SDS solutions in this concentration range. In the cases of DTAC and KCl solutions the origin of the positive charges would be the surface ionizable group or adsorption of DTA ion. In the case of SDS solution the origin of the negative charge would be DS ion. This result suggests that the DS will adsorb on the positive charged surface by electrostatic attractive interaction and provide negative charge on the surface. In the case of SDS solution ζ_{obs} showed a minimum and this behavior will be discussed later.

From these observations in the concentration range below 20 mS/m the behaviors of ζ_{obs} depended on the combination of surfactant and membrane.

3.3 Effect of surfactant on ζ_{obs} in the higher surfactant concentration

Fig. 5 shows the effects of the DTAC concentration on ζ_{obs} and flux in the three membranes in the conductivity range from 0.5 mS/m to 200 mS/m. The severe flux decline was not observed although the flux varied at around the CMC of DTAC. ζ_{obs} increased with the increase in DTAC concentration at conductivity above 10 mS/m. This result suggests that the amount of adsorbed DTA ion would increase with the increase in DTAC concentration regardless of membrane used. The ζ_{obs} of the hydrophobic membrane was higher than those of the hydrophilic and positively charged membranes over the range of concentration studied. This result means that the hydrophobic interaction would enhance the amount of adsorbed surfactant. The ζ_{obs} at around the conductivity of 200 mS/m showed almost same value in the all three membranes.

Fig. 6 shows the effects of surfactant concentration on ζ_{obs} and flux in the filtration of SDS solution with

the three membranes in the conductivity range from 0.5 mS/m to 15 mS/m. In the conductivity below 7 mS/m the flux decline was not observed. At the conductivity of about 7mS/m the flux suddenly decreased in all the membranes. The reason of this flux decline, i.e. fouling, is not clear. It was not possible to measure ζ_{obs} in much higher SDS concentration because of this flux decline.

The ζ_{obs} showed negative over the concentration range in all the membranes, suggesting the adsorption of chloride ion and DS ion on the pore surface. In the conductance below 7 mS/m the thickness of the adsorption layer would be much smaller than pore size of these membranes because the flux decline was not observed in this concentration range. In all the membranes the ζ_{obs} decreased in the lower conductivity and increased and approached to zero after showing a minimum. The SDS concentration at the minimal zeta potential was almost same as the start point of the severe flux decline. The decrease in the absolute value of ζ_{obs} due to fouling was observed in other filtration systems^{32~35)} and this phenomenon has not been fully interpreted. A possible examination is that the location reflecting ζ_{obs} would shift from the membrane to the fouling part because the location of dominant pressure drop would shift from membrane to the fouling part and the ζ_{obs} of the fouling part would be small value.

From these observations in the higher surfactant concentration the behavior of ζ_{obs} depended mainly on type of surfactant rather than the type of membrane used.

4. Conclusion

The ζ_{obs} of the three PVDF membranes, which have non-ionic hydrophilic, hydrophobic and positively charged pore surfaces, with nominal pore size 0.22 μm was observed using KCl, DTAC and SDS solutions over wide range of the surfactants concentration. At the lower surfactant concentration (the conductivity below 20 mS/m) the behaviors of ζ_{obs} depended on the combination of membrane and surfactant used. At the higher surfactant concentration the behaviors of ζ_{obs} mainly depended on type of surfactant rather than on membrane used. In the case of SDS the severe flux decline was observed at a certain concentration in all the membranes and the absolute value of ζ_{obs} decreased and approached to zero reflecting the flux decline.

Nomenclature Symbols

E_{TM}	electrical potential across membrane	(V)
J	permeate flux	(m/s)
J_0	permeate flux of pure water	(m/s)
P_{TM}	filtration pressure	(Pa)
ε_0	permittivity of free space	(F/m)
ε_r	relative dielectric constant	(–)
λ	electric conductivity	(S/m)
μ	viscosity	(Pa s)
ζ_{obs}	zeta potential obtained from streaming potential measurement	(V)

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