미세기공의 중공사를 이용한 단백질 여과에서의 흐름 전위의 계면동전기 거동에 관한 실험 연구

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Experimental observations on electrokinetic behavior of flow-induced streaming potential during protein filtration with microporous hollow-fibers

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Introduction

Recent experimental results have indicated that the physicochemical conditions of the solution can have a significant influence on the membrane filtration of colloids or biomolecules [1]. Therefore, any attempt to investigate the membrane filtration of colloidal systems requires adequate knowledge of the long-range colloidal interactions both on transport and thermodynamic properties. The electric double layer formed at the boundary between a solid surface and an electrolyte solution determines the electrokinetic property of materials.

The zeta potential can be defined, which is used as the electrokinetic value associating a realistic magnitude of surface charge. In general, the streaming potential E generated by the electrokinetic flow effect within an electric double layer of charged channel is applied to determine the (apparent) membrane zeta potential ζ by using the Helmholtz-Smoluchowski (H-S) equation [2-4]:

$$\frac{\Delta E}{\Delta P} = \frac{\zeta \varepsilon}{\eta \lambda} \tag{1}$$

where ΔP is the pressure drop [Pa] across the pore channel, η the solution viscosity [Pa · s], λ the solution conductivity [$m^{-1} \cdot \Omega^{-1}$], and ε the dielectric constant of the electrolyte solution [$s \times m^{-1} \cdot \Omega^{-1}$].

In this study, the charge characteristics of the pore surface for hollow-fiber membranes were examined by measuring the streaming potential at different pH of electrolyte solution. The influence of BSA protein upon the filtration was examined with simultaneously monitoring of the zeta potential of the membrane with different pore sizes. We also measured the axial position-dependent zeta potential of the hollow-fiber so as to effectively identify the effect of cake layer upon the membrane fouling.

Experiments

The apparatus for hollow-fiber membrane were properly developed in our laboratory, with which both the *in-situ* streaming potential and the permeate flux could be measured simultaneously. Regarding a device for streaming potential of flat-plate membrane, details of the system and procedure have been described elsewhere [2-4].

For the streaming potential difference at inlet as well as outlet positions of a hollow-fiber depicted in Fig. 1, pairs of Ag/AgCl electrodes were installed very carefully both inside and

outside of each position. The Ag/AgCl electrodes were prepared by anodic deposition of chloride on silver with a DC power supply at 0.4 mA/cm^2 for 30 min. A wire-type electrode with 0.25 mm in diameter installed inside the membrane takes about 6 % of the internal cross-sectional area of the hollow-fiber to allow undisturbed flow condition. A spiral electrode is installed on the corresponding external positions of the hollow-fiber so that it can sense the minute streaming potential difference.

After the system was stabilized at a given ΔP, the difference between streaming potential was measured using a digital multimeter (HP34970A, Hewlett-Packard Co., CA) connected to the two electrodes. Transmembrane pressure was adjusted up to 0.3 % of the maximum flow rate by using a micrometer capillary valve (Gilmont Inst., IL). Solution conductivity was measured using a conductivity meter (Model 32, YSI, OH).

Asymmetric porous membranes, polysulfone PM2 and PM100 hollow-fibers (Koch Membrane System Inc., MA) were used. Their characteristics are given in Table 1. As model colloids, a bovine serum albumin (BSA) protein was purchased from Sigma Chemical Co. (St. Louis, MO). BSA is prolate ellipsoid 14 by 4 nm. The zeta potential of BSA colloid provided in Fig. 2 was determined using a Zeta-Plus (Brookhaven Instrument Co., NY). The zeta potential of BSA changes from positive to negative with the increase of pH. Compared to the latex, the variance range on the zeta potential of BSA is larger.

Results

1. Electrokinetic characterization

Streaming potential differences were measured at several discrete pressure drops, and this approach gives more accurate and reproducible data than using a continuous pressure type. We found that repeat measurements were highly reproducible, confirming the precision of the measurement. From the linear relationship between ΔE and ΔP, the variability of the zeta potential values yielded less than 8 %. Fig. 3 displays that the isoelectric points of PM100 membrane is formed around pH 9.4. The increasing behavior of the absolute value of zeta potential with increasing pH is similar to that previously reported for other membranes [5]. As shown in Fig. 3 for the zeta potential of the PM100 hollow-fiber membrane, the absolute value of the zeta potential at an outlet of a hollow-fiber is lower than that at an inlet. This behavior is mainly ascribed to the fact that the flow rate becomes decreasing as it goes to the outlet due to the radial permeation, and thus the pressure drop becomes changed. We recognized that the zeta potential difference was less than 5 % according to the flow directions of permeate. It should be pointed out that the membrane zeta potential determined from Eq. (1) is an apparent value. In order to obtain a more rigorous zeta potential, one would need to consider the correct H-S equation [6].

2. Monitoring the membrane fouling of a partially and fully retentive case

In order to account for the behavior of cake deposition of partially retentive membrane, an aqueous solution containing a 300 ppm of BSA was filtered using a PM100 hollow-fiber membrane. As already given in Figs. 2 and 3, the pores of a hollow-fiber membrane are positively charged at pH 6.0, while the surface of BSA is negatively charged.

Figure 5 shows the result of filtration progress, which reveals that the absolute value of the zeta potential is higher at the inlet than that at the outlet, and this is consistent with Fig. 3b. The zeta potential changed from positive to negative about 20 min after the start of the

filtration, and this indicates that the properties of the charged membrane must have been changed during the filtration process possibly due to the adsorption or deposition of BSA particles, which were negatively charged at pH 6.0, onto the surface of the membrane. The absolute value of zeta potential decreases as the filtration proceeds and even a faster decreasing rate at the outlet; this appears to be due to the weakened electrokinetic flow resulting from the narrowed membrane pores due to the continued adsorption or deposition of BSA particles.

Conclusion

The charge characteristics of the pore surface for hollow-fiber membrane were investigated by applying the Helmholtz-Smoluchowski principle. We observed the development of cake layer with a full retention during the time progress of filtration, where the axial position-dependent zeta potential of the hollow-fiber was considered significantly.

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Table 1. Characteristics of model membranes

	PM 2	PM100
Hydrophilicity	Hydrophobic	Hydrophobic
Molecular weight cut-off, Dalton	2×10^3	1×10^5
Mean pore diameter, nm	2.2	11.0
Surface porosity, %	NA	5.2
BSA protein rejection, %	98	35

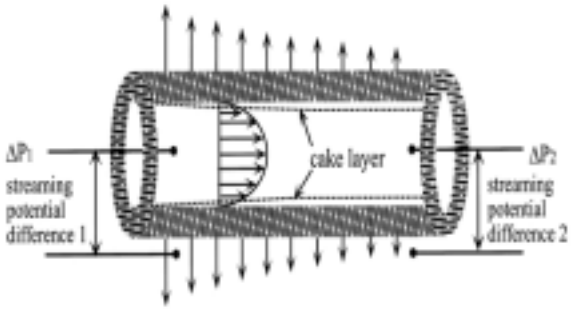

Fig. 1. Schematic of both local streaming potential differences and local pressure drops generated at inlet and outlet positions of a hollow-fiber membrane during colloid filtration.

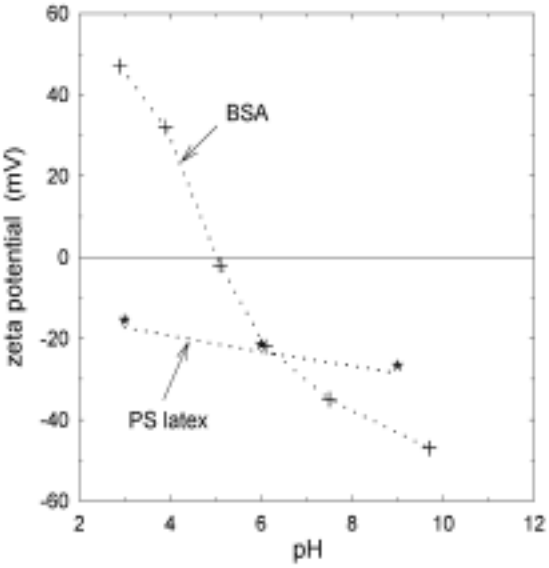

Fig. 2. The plots of zeta potential vs. pH for polystyrene latex and BSA protein with solution ionic strength of 1.0mM KCl.

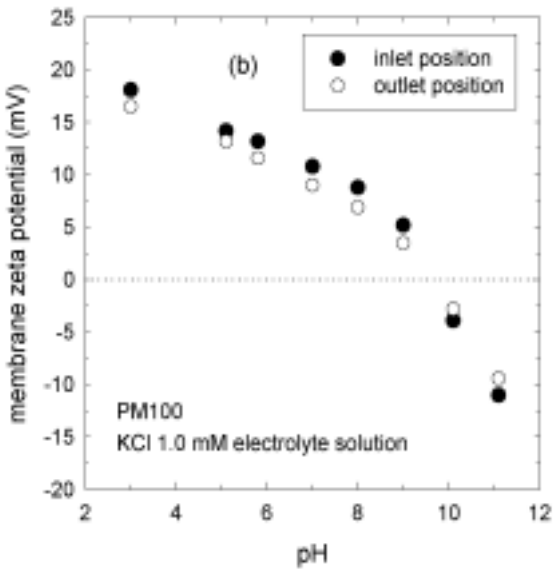

Fig. 3. The membrane zeta potential as a function of solution pH at 1.0mM KCl concentration for hollow fiber at inlet and outlet positions.

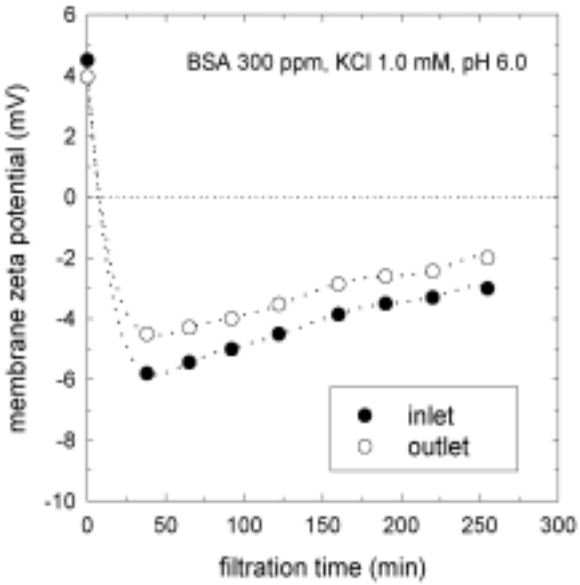

Fig. 4. Changes in axial position-dependent membrane zeta potential during the filtration of suspension with BSA 300 ppm. Experiments were performed with a PM100 hollow-fiber membrane at 0.2 atm of transmembrane pressure.