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Electrokinetic behavior of membrane zeta potential during the filtration of colloidal suspensions

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Abstract

A study of the membrane zeta potential determined by the streaming potential was made to investigate the electrokinetic characterization as well as the monitoring for cake deposition on the surfaces of a filtration membrane. The membrane zeta potential related to the surface charge characteristics was determined for both flat-plate and hollow-fiber cases. In this study, we showed successfully that changes in membrane zeta potential could be used to investigate the behavior of cake deposition and fouling during the filtration of colloids. With the simultaneous monitoring for fully retentive membranes, it is found that both the permeate flux and the membrane zeta potential are decreased as the latex concentration increases. Since the development of cake layer is dependent on axial positions in the hollow-fiber membrane, the difference of zeta potential with respect to inlet and outlet positions has been observed.

Keywords: Electrokinetics; Streaming potential; Zeta potential; Colloid; Membrane filtration

1. 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,

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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]:

$$\frac{\Delta E}{\Delta P} = \frac{\zeta \varepsilon}{\eta \lambda} \quad (1)$$

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

In this study, the charge characteristics of the pore surface for flat-plate as well as hollow-fiber membranes were examined by measuring the streaming potential at different pH and ionic strength of electrolyte solution. The influence of concentration of latex colloids upon the filtration has been examined with simultaneously monitoring of the zeta potential of the membrane. 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.

2. Experimental

Each of the apparatus for flat-plate as well as hollow-fiber membranes was 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.

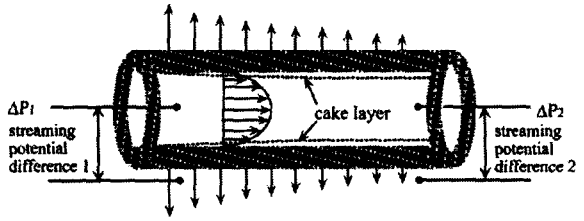

Fig. 1. Schematic of both local streaming potential differences and local pressure drops generated at inlet and outlet positions of a hollow-fiber membrane during colloid filtration.

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, poly-(acrylonitrile-co-vinyl chloride) XM50 flat type (Millipore, MA) and polysulfone PM2 and PM100 hollow fibers (Koch Membrane System Inc., MA) were used. their characteristics are given in Table 1. As model colloids, both a monodisperse polystyrene latex and a bovine serum albumin (BSA) protein were purchased from Sigma Chemical Co. (St. Louis, MO). Polystyrene latex with spherical shape has a mean diameter of 0.1 μm, while BSA is prolate ellipsoid 14 by 4 nm. The zeta potential of model colloids provided in Fig. 2 was determined using a Zeta-Plus (Brookhaven Instrument Co., NY).

Table 1
Characteristics of model membranes

	XM50	PM2	PM100
Hydrophilicity	Hydrophilic	Hydrophobic	Hydrophobic
Molecular weight cut-off, Dalton	5×10^4	2×10^3	1×10^5
Mean pore diameter, nm	5.5	2.2	11.0
Surface porosity, %	2.6	NA	5.2
Solute rejection, %:			
Polystyrene latex, 0.1 μm	98	98	95
BSA protein	95	98	35

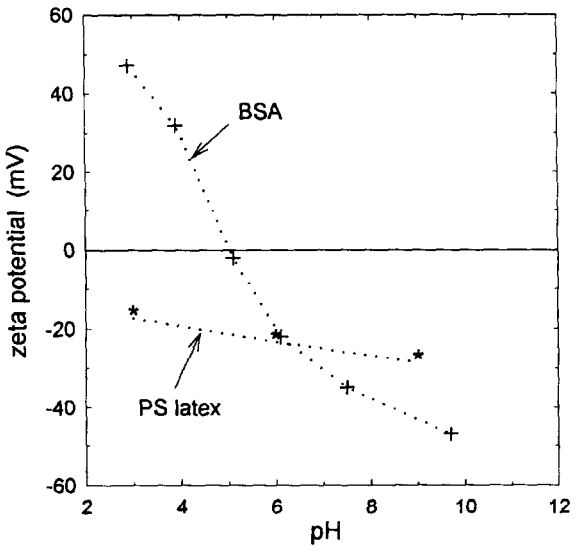

Fig. 2. The plots of zeta potential vs. pH for polystyrene latex and BSA protein with solution ionic strength of 1.0 mM KCl.

Fig. 2 shows that the latex surfaces are negatively charged where the magnitude of the negative zeta potential increases with increasing of pH. 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.

3. Results and discussion

3.1. 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%. Figs. 3a and 3b display that the isoelectric points of XM50 and PM100 membranes are formed around pH 3.0 and pH 9.4, in respect. The increasing behavior of the absolute value of zeta potential with increasing pH is similar to that previously reported for other membranes [5]. In Fig. 3a, our experimental results were compared with the previous results for polycarbonate track-etched membrane to conform the reliability of the experimental system employed in this study [6].

As shown in Fig. 3b 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 is 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 [7].

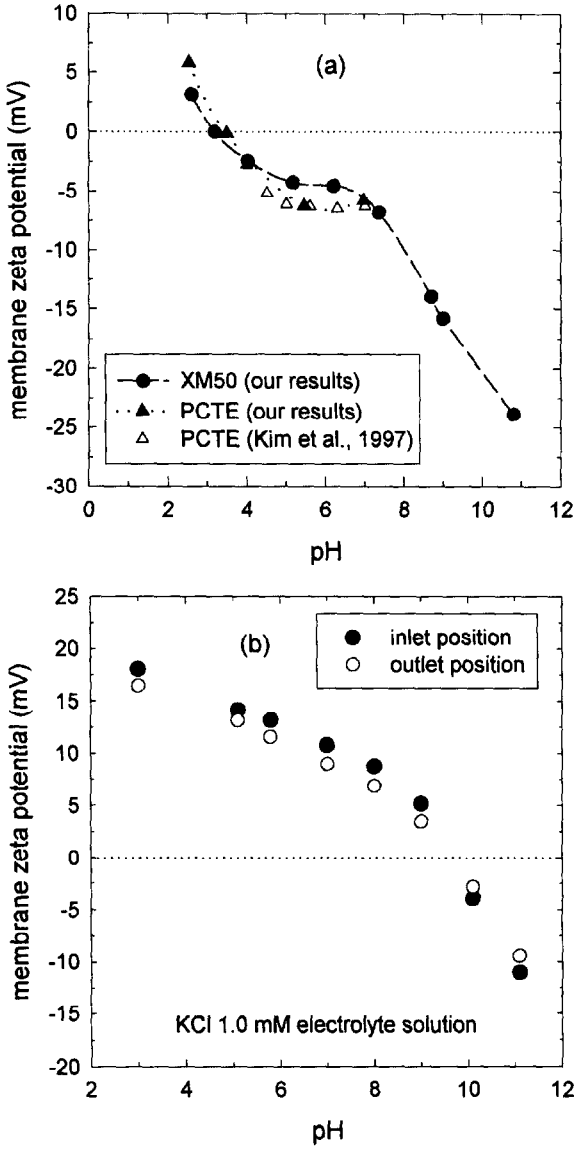

Fig. 3. The membrane zeta potential as a function of solution pH at 1.0 mM KCl concentration for flat-plate (a) and hollow fiber at inlet and outlet positions (b).

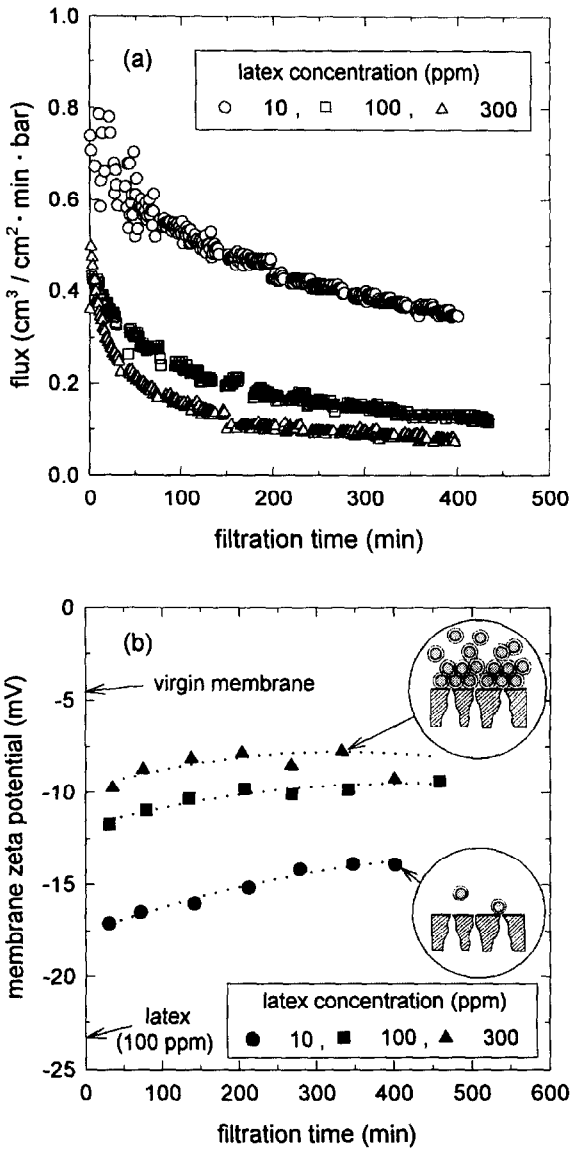

Fig. 4. Changes in the permeate flux (a) and membrane zeta potential (b) during the filtration as a function of latex concentration. Experiments were performed with an XM50 flat-plate membrane at 0.5 atm of transmembrane pressure, pH 6.0 and KCl 1.0 mM.

3.2. Monitoring the membrane fouling of a fully retentive case

As given in Table 1, a fully retentive behavior appears for the cases of the latex filtration with MX50 as well as the BSA filtration with PM2. Figs. 4a and 4b reveal the influence of particle concentration during the progress of latex filtration using XM50, in which a full rejection appears. As the latex concentration increases, both the permeate flux and the membrane zeta

potential are decreased. The growth of the cake layer has been indeed developed with increasing the latex concentration, and then a weakened electrokinetic flow owing to a lower permeate flux leads to a decrease of the membrane zeta potential. The values of the membrane zeta potential likely range between those of the virgin membrane and the latex particle.

3.3. *Monitoring the membrane fouling of a partially 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.

Fig. 5 shows the result of filtration progress, which reveals that the absolute value of the zeta

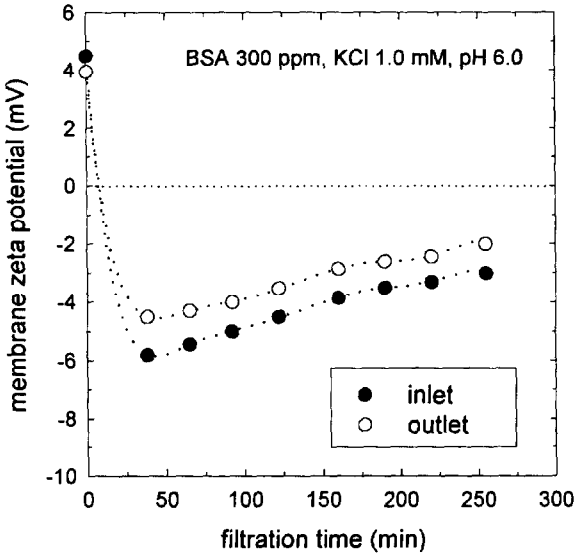

Fig. 5. Changes in axial position-dependent membrane zeta potential during the filtration of suspension with BSA 300 ppm. Experiments were performed with a PM100 hollow-fiber membrane at 0.2 atm of trans-membrane pressure.

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.

4. Conclusions

the charge characteristics of the pore surface for flat-plate as well as hollow-fiber membranes were investigated by applying the Helmholtz–Smoluchowski principle. We observed the development of a cake layer with full retention and the particle adsorption with partial retention during the time progress of filtration where the axial position-dependent zeta potential of the hollow fiber was significantly considered.

Acknowledgements

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