Effects of Pore Size and Conductivity of Electrolyte Solution on the Measurement of Streaming Potential and Zeta Potential of Microporous Membrane

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In order to clarify the effect of electric double layer overlapping in the pore of microporous membrane on the measurements of streaming potential (SP) and the apparent zeta potential, ζ_{obs} , of the pore surface, the mixed cellulose ester microporous membranes having different pore sizes ranging from 0.025 to 0.8 μm were used. The dependence of SP on KCl concentration was measured by the continuous measuring method of SP over the wide range of KCl concentration. Both the SP and the ζ_{obs} estimated from the measured SP had the maximum negative value at a certain value of KCl concentration, which depended on the pore size. The ζ_{obs} obtained from the different pore sizes did not coincide with each other even at the higher κr , which is the ratio of pore radius, r , to Debye length, κ^{-1} , where the electric double layer overlapping was assumed to be negligible. However, it was demonstrated that the relationship between SP and KCl concentration could be evaluated from the theoretical calculation by using the fitting parameters of surface charge density and pore size. The calculated pore size of membrane tested was the same order of nominal one.

Key words : microporous membrane / streaming potential / zeta potential / membrane characterization

1. Introduction

Microporous membrane like membrane filter is widely used in various fields of industry in order to trap the particles of larger size than the pore size of membrane, and to allow the smaller size particle to pass through it. However, the classification of particles by their size is difficult since the smaller substances can be trapped inside or outside the pores by various physical and chemical interactions during filtration. Hence, the understanding of sur-

face properties such as charge and hydrophilicity in addition to pore structure is gaining importance for the prediction of separation performance of microporous membrane.

The surface charge property of microporous membrane can be characterized by the streaming potential (SP)¹⁾. When the electrolyte solution is forced to pass through a microporous membrane at a trans-membrane pressure of P_{TM} , it generates an electrical potential difference of E_{TM} across the membrane. In this paper the streaming potential (SP) is defined as the potential difference per unit trans-membrane pressure, i.e. $\Delta E_{TM} / \Delta P_{TM}$ (see Fig. 2). From the measured SP the apparent zeta

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potential of pore surface, ζ_{obs} , can be calculated by the Helmholtz-Smoluckowski (HS) equation (Eq.(1)), assuming the following ideal conditions that the pore has a cylindrical capillary with laminar flow and that the surface conductivity and the electric double layer overlapping are negligible¹⁾.

$$\zeta_{\text{obs}} = \frac{\mu \lambda}{\varepsilon_0 \varepsilon_r} \frac{\Delta E_{TM}}{\Delta P_{TM}} = \frac{\mu \lambda}{\varepsilon_0 \varepsilon_r} \cdot SP \quad (1)$$

where μ is the viscosity of solution [Pa·s], λ is the conductivity of solution [S m⁻¹], ε_0 is the permittivity of free space [F m⁻¹], and ε_r is the relative dielectric constant of solution [-]. However, the microporous membranes commonly used do not satisfy these ideal conditions for the HS equation, since they have the non-uniform pore structure and the smaller pore size in comparison with the electrical double layer thickness. The degree of double layer overlapping can be evaluated by the dimensionless pore radius, κr , which is the ratio of pore radius r to Debye length κ^{-1} ^{2~7)}. The Debye length is about 30nm for 0.1mM KCl solution and 4nm for 10mM KCl solution⁸⁾, and therefore, the double layer overlapping cannot be negligible at a lower KCl concentration when using the membrane of smaller pore size below 1 μ m. At a lower electrolyte concentration HS equation leads to a substantial underestimation of ζ_{obs} against the true value of zeta potential^{9,10)}. Hence, the κr condition at which HS equation can be applicable has been reported^{2~7)}. However, the reported κr condition depended on the kinds of membrane or the experimental conditions of researchers, that is, $\kappa r > 1.5$ for polycarbonate (PC) membranes of pore size 0.03 – 0.4 μ m²⁾, $\kappa r > 10$ for PC membranes of 0.1 – 0.2 μ m³⁾, $\kappa r > 1$ for zirconium and titania UF membranes of M.W.C.O 10kDa and 150kDa⁴⁾, $15 < \kappa r < 45$ for alumina/titania membranes of pore size 0.22 – 0.45 μ m⁵⁾, and $\kappa r > 1$ for polyethersulfone UF membranes of M.W.C.O 20kDa

and 200kDa⁷⁾. Further more, the following different dependence of measured ζ_{obs} on the salt concentration was observed; the negative value of ζ_{obs} increased with the increase in the salt concentration^{5, 11, 12)} and showed the maximum value^{2, 6, 9, 13)} or a constant value^{3, 4, 7, 14)} at a certain salt concentration range. That is, the dependence of ζ_{obs} on salt concentration and pore size has not been cleared over the wide range of salt concentration and pore size owing to their limited experimental conditions.

In this study, the effects of pore size and electrolyte concentration, which directly relate to the electric double layer overlapping, on the measured SP and ζ_{obs} were studied by using the newly developed method previously reported¹⁵⁾. The membranes of different pore size ranging from 0.025 μ m to 0.8 μ m, of the same chemical composition, were chosen for the investigation. KCl solutions was used as the electrolyte. The dependence of SP on KCl concentration was also analyzed by a theoretical model^{1, 8)}, which correlates SP with ionic strength, pore size and surface charge density, and was compared with the experimental results.

2. Theory of the streaming potential^{1, 8)}

In this model the membrane is treated as an array of parallel uniform cylindrical pores. The value of SP is given by the following equation,

$$SP = \frac{\Delta E_{TM}}{\Delta P_{TM}} = \frac{q_p}{\lambda_{\text{eff}} \kappa \mu} \frac{I_2(\kappa r_p)}{I_1(\kappa r_p)} \quad (2)$$

where q_p is the surface charge density of membrane pore [C m⁻²], λ_{eff} is the effective conductivity of electrolyte solution in the pores [S m⁻¹], μ is the viscosity of electrolyte solution [Pa s], and $I_1(\kappa r_p)$ and $I_2(\kappa r_p)$ are modified Bessel functions of the first kind of order 1 and 2, respectively. r_p is the pore radius [m]. κ^{-1} and λ_{eff} can be

shown as follows,

$$\kappa^{-1} = \left(\frac{\varepsilon_0 \varepsilon_r RT}{F^2 \sum_i z_i c_i} \right)^{1/2} \quad (3)$$

$$\lambda_{eff} = \lambda_{avg} + \frac{q_p^2}{\mu} \left(1 - \frac{I_o(\kappa r_p) I_2(\kappa r_p)}{I_1^2(\kappa r_p)} \right) \quad (4)$$

$$\lambda_{avg} = \lambda_o \left\{ 1 + \frac{q_p \kappa^{-1} F}{\varepsilon_0 \varepsilon_r RT} \left(\frac{2}{\kappa r_p} - \frac{1}{I_1(\kappa r_p)} \right) \frac{\sum_i z_i^3 u_i c_i}{\sum_i z_i^2 u_i c_i} \right\} \quad (5)$$

where R is the ideal gas constant [$\text{J mol}^{-1} \text{K}^{-1}$], T is the absolute temperature [K], F is the Faraday constant [C mol^{-1}], z_i is the valence of species i , c_i is the concentration of species i on the center line of pore [mol m^{-3}] and u_i is the mobility of species i [$\text{m}^2 \text{mol J}^{-1} \text{s}^{-1}$]. λ_o [S m^{-1}] and λ_{avg} [S m^{-1}] are the conductivity of the center line of pore and the average conductivity in the pore, respectively.

3. Materials and methods

3.1 Membrane and electrolyte

The membranes made of mixed cellulose ester (MCE), of which brand name were MF Millipore, having nominal pore sizes of 0.025, 0.05, 0.1, 0.22, 0.45 and $0.8 \mu\text{m}$ were used. The pore structure of these membranes are non-uniform and asymmetric. The pure water flux of each membrane and the maximum pore size estimated from the bubble point test are listed in Table 1. Potassium chloride (Wako special grade) was used as electrolyte, and KCl solution was prepared with ultrapure water

Fig. 1 Experimental apparatus for streaming potential measurement: 1: N_2 gas cylinder, 2: KCl solution reservoir, 3: Pressure controller, 4: Pressure holding tank, 5: Temperature control bath, 6: Membrane filter for particle removal, 7: Pressure transducer, 8: Electrodes, 9: Digital multi meter, 10: Measuring membrane holder, 11: Conductivity flow cell, 12: Filtrate reservoir, 13: Electric balance, 14: Personal computer.

supplied by Milli Q system. pH of the solution was 5.5 ± 0.1 . No adjustment of pH was done.

3.2 Apparatus and measurement method

The apparatus for the SP measurement is shown in Fig. 1. The E_{TM} was measured with the digital multimeter (ADVANTEST-R6441). The P_{TM} was measured by the pressure transducer (KYOWA PVL-5KB). The conductivity of filtrate (i.e. KCl solution) was measured by the conductivity meter with flow cell (TOA-CM40G). The above apparatus is designed so that the influence of ionic strength, i.e. conductivity of solution, on SP could be measured continuously and accurately by changing the value of P_{TM} and the concentration of electrolyte solution by the method as is explained below.

The membrane holder for SP measurement was made of polycarbonate. The Pt-black wire elec-

Fig. 2 The relationship between the trans-membrane pressure, P_{TM} , and the trans-membrane electrical potential, E_{TM} , for the membrane of pore size 0.22 at the variation of KCl concentration.

trodes of 0.2mm diameter were set at both sides of the membrane. The effective membrane area was 3.0cm². A prefilter of 0.22 μm pore size was used to previously remove the contaminant particles existing in the upstream flow toward the measuring holder. Feed solution was kept at 298K in the temperature control bath.

Ultrapure water and KCl solution were prepared in the pressure holding tank and the KCl solution reservoir, respectively. Applied pressure was controlled by repeating the following three steps; 1) pressurizing from 0 kPa to 50 kPa, 2) holding its pressure, and 3) depressurizing to 0 kPa. The pressurizing speed was adjusted to the optimum one as was shown in our previous paper by the computer control¹⁵⁾. During this cycle E_{TM} , P_{TM} , and conductivity of filtrate were recorded by a computer at the regular interval of 1 sec. The data obtained in the pressurizing step were employed for the estimation of SP. The KCl concentration of the test solution was increased continuously and slowly by pumping the KCl solution of high concentration in the electrolyte reservoir into the pressure holding tank with stirring.

Fig. 3 The relationship among the conductivity of KCl solution, the SP measured from the data shown in Fig. 2 and the calculated ζ_{obs} from Eq. (1). The dotted line shows the theoretical line calculated from Eqs. (2) ~ (5).

4. Results and discussion

4.1 Typical results obtained in the membrane of pore size 0.22 μm

The relationship between the trans-membrane pressure, P_{TM} , and the trans-membrane electrical potential, E_{TM} , for the membrane of pore size 0.22 μm at various KCl concentrations is shown in Fig.2. These results show the validity of the measurement from the linear plots of P_{TM} vs. E_{TM} for each KCl concentration. The SP ($= \Delta E_{TM} / \Delta P_{TM}$) at the different KCl solution was determined as the slope of linear regression line.

Fig. 3 shows the variation of SP and ζ_{obs} calculated from the measured SP against the conductivity of KCl solution. The SP was evaluated as negative value in all the conductivities tested, and showed a maximum negative value at a lower conductivity around $\lambda = 2 \times 10^{-4} \text{ S m}^{-1}$, and then decreased with the increase in conductivity and approached to zero. The dotted line in Fig. 3 shows the theoretical SP calculated from Eqs. (2) ~ (5).

Table 1 Pore size and surface charge density calculated from the curve fitting

Nominal pore size d_n [μm]	Pure water flux [$\text{m}/(\text{s} \cdot \text{Pa})$]	Maximum pore size d_b [μm]	Pore size by curve fitting d_f [μm]	q_p by curve fitting $10^3[\text{C}/\text{m}^2]$
0.025	7.17×10^{-10}	—	0.021	3.0
0.05	2.14×10^{-9}	0.194	0.033	2.6
0.1	4.23×10^{-9}	0.225	0.044	2.2
0.22	6.67×10^{-8}	0.824	0.14	2.1
0.45	2.34×10^{-7}	1.41	0.22	1.5
0.8	6.17×10^{-7}	2.91	0.30	1.2

The theoretical line could be well fitted with the experimental plots of SP at the conductivity above $5 \times 10^{-4} \text{ S m}^{-1}$. The estimated fitting parameters of surface charge density, q_p , and pore radius, r_p , are listed in Table 1. In this calculation the values of q_p and r_p are assumed to be constant regardless of the value of λ . The relationship between the pore size of membrane and the fitting parameters will be discussed in § 4.2. The reason why the negative value of SP decreased at the higher solution conductivity would be explained by the increase in the solution conductivity, λ_{eff} , and the decrease in the Debye length, κ^{-1} , as is seen in Eq. (2).

The negative value of ζ_{obs} increased with the increase in conductivity and showed the maximum value of -30mV around the conductivity of $1 \times 10^{-2} \text{ S m}^{-1}$. The lower value of ζ_{obs} at the lower conductivity can be explained by the invalidity of the assumption for Eq. (1) and the less amount of anion adsorption on the pore surface. A.Szymaczuk et al.⁹⁾ has shown that Eq. (1) can lead to a substantial underestimation of the zeta potential at low electrolyte concentration because of the surface conductance caused by counter-ions in the region near the pore surface, which is negligible in the bulk solution at higher concentration. The equilibrium condition of anion adsorption on the microporous membrane would be described by

Langmuir's adsorption isotherm model or Freundlich's one¹⁶⁾. This fact means that the common polymer membrane has no ionization functional groups on the pore surface and has only a low net charge in a low conductivity aqueous solution like pure water. Therefore, the disagreement between the measured SP value and the calculated one at the lower conductivity, that is, the appearance of the maximum of negative value of SP, would be due to the lower value of q_p .

4.2 Effect of pore size on SP and ζ_{obs}

The effect of KCl concentration on SP is shown in Fig. 4 for the membranes with pore size ranging from 0.025 to $0.8 \mu\text{m}$. The measured SP were negative regardless of KCl concentration or pore size, and were divided into two groups according to the value of SP. The upper panel in Fig. 4 shows an enlargement of the lower panel.

In all the membrane pore sizes, the negative value of SP showed the maximum at a lower KCl concentration and decreased with the increase in the KCl concentration and approached to zero at the KCl concentration above $5 \times 10^{-5} \text{ M}$. Further, for a given KCl concentration the negative value of SP increased with the increase in pore size when the KCl concentration is lower than $1 \times 10^{-4} \text{ M}$.

Fig. 5 shows the effect of KCl concentration on ζ_{obs} estimated from the SP at various pore sizes of membranes shown in Fig. 4. In all the pore sizes, it was observed that the negative value of ζ_{obs} increased with an increase in KCl concentration from an initial lower value and showed the maximum, and then decreased again gradually. For a given KCl concentration below $2 \times 10^{-4} \text{ M}$, the nega-

Fig. 4 Effect of KCl concentration on the SP for membranes of pore size ranging from 0.025 to 0.8 μm . The upper panel shows an enlargement of the lower panel. The solid lines show the theoretical lines calculated from Eqs. (2) ~ (5).

Fig. 5 Effect of KCl concentration on the ζ_{obs} at the membranes having different pore size.

tive value of ζ_{obs} became larger as the pore size increased. The ζ_{obs} of membranes tested here didn't show any definite value for the change in the KCl concentration or pore size, even if the ionic strength condition and the chemical composition

Fig. 6 Effect of membrane pore size on the relationship between ζ_{obs} and κr .

of membranes are the same.

The ζ_{obs} was plotted as a function of the dimensionless pore radius, κr , in Fig. 6 in order to evaluate the effect of electric double layer overlapping on ζ_{obs} . The r was assumed to be equal to a half of the nominal pore size. The ζ_{obs} did not overlap on one line and distributed on a belt region against κr , although the similar curve of κr vs. SP was obtained in each pore size. This means that the ζ_{obs} obtained from different pore sizes did not coincide with each other.

4.3 Comparison the measured SP with the calculated one

The solid lines shown in Fig. 4 were the theoretical curves calculated from Eqs. (2) ~ (5) with the assumption of constant surface charge ($q_p = \text{const.}$). When KCl concentration is above $1 \times 10^{-4} \text{M}$, the calculated curves could be well fitted to the measured data of SP. However, the maximum negative value of SP observed in the lower concentration could not be simulated. Although the reason for the discrepancy between the measured SP and the calculated one in the lower KCl concentration is not clear, some following possible explanations are given, that is, the assumption of the constant surface charge density in the calculation

may be invalid as was mentioned before, and the Debye-Hückel approximation for the Boltzmann distribution⁸⁾, which describes the radial concentration profile of ions in the pore, in the derivation of the theory may not be valid.

The surface charge density, q_p , and pore diameter, d_f , estimated from the curve fitting are listed in Table 1 together with the pure water flux and the pore size evaluated from the bubble point test, d_b [m]. The d_f increased with the increase in the nominal pore size d_n , although the d_f was always evaluated smaller than d_n . From the fact that the pore size calculated from Eqs (2) ~ (5) is the same order of nominal pore size of membrane tested, our method is said to be applicable to roughly estimate the pore size of microporous membrane. As for the q_p , the estimated values of q_p were the same order of the value reported by Kontturi et al¹⁷⁾. However, the q_p decreased with the increase in pore size, which means that the adsorption of anion apparently occurred strongly as the pore size decreased, although the ζ_{obs} was evaluated lower as the pore size decreased. The reason for the dependence of q_p on pore size is not also made clear in this stage. The meaning of these fitting parameters will be discussed in detail in combination with the adsorption isotherm of ions and the limitation of the assumption used in the theory in our future work.

Conclusion

The effects of pore size and the KCl concentration (i.e. solution conductivity) on the measurement of SP and ζ_{obs} were studied using the membranes which have six different pore sizes ranging from $0.025\ \mu\text{m}$ to $0.8\ \mu\text{m}$ and the same chemical composition. Both of SP and ζ_{obs} gave the maximum negative value at a certain value of KCl concentration. The negative value of SP and ζ_{obs}

increased with the increase in pore size at the same KCl concentration. The ζ_{obs} obtained from the membranes of different pore sizes didn't coincide with each other even at the higher κr condition where the electric double layer overlapping was assumed to be neglected. The dependence of SP on the higher KCl concentration could be simulated by a theoretical model, and the surface charge density and the pore size could be evaluated as the fitting parameters by the analysis. The calculated pore size of membrane tested was the same order of nominal one.

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Nomenclature

c_i :	Concentration of species i on the center line of pore	[mol m ⁻³]	T :	Absolute temperature	[K]
d_b :	Pore size estimated from bubble point	[m]	u_i :	Mobility of species i	[m ² mol J ⁻¹ s ⁻¹]
d_f :	Pore size estimated from curve fitting	[m]	z_i :	Valence of species i	[-]
d_n :	Nominal pore size	[m]	ϵ_0 :	Permittivity of free space	[F m ⁻¹]
E_{TM} :	Electric potential difference across membrane	[V]	ϵ_r :	Relative dielectric constant of solution	[-]
F :	Faraday constant	[C mol ⁻¹]	ζ_{obs} :	Apparent zeta potential	[V]
P_{TM} :	Pressure difference across membrane	[Pa]	κ^{-1} :	Debye length	[m]
q_p :	Surface charge density	[C m ⁻²]	λ :	Conductivity of solution	[S m ⁻¹]
r :	Pore radius	[m]	λ_{avg} :	Average conductivity of solution in pore	[S m ⁻¹]
r_p :	Pore radius used in Eqs. (2) ~ (5)	[m]	λ_{eff} :	Effective conductivity of solution in pore	[S m ⁻¹]
R :	Ideal gas constant	[J mol ⁻¹ K ⁻¹]	λ_0 :	conductivity of solution on the center line of pore	[S m ⁻¹]
SP :	Streaming potential defined by Eq (1)	[V Pa ⁻¹]	μ :	Viscosity of solution	[Pa s]