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Jin Wang[a]; Zheng Liu[a]; Jian Luo[a]; Qinghua He[a]; Fuxin Ding[a]; Naiju Yuan[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, TSINGHUA UNIVERSITY, BEIJING, PEOPLE'S REPUBLIC OF CHINA

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Determination of ζ-Potential by Measuring Electroosmotic Flux in an Alternating Electric Field and Its Applications in the Study of Membrane Fouling

JIN WANG, ZHENG LIU,* JIAN LUO, QINGHUA HE, FUXIN DING, and NAIJU YUAN

DEPARTMENT OF CHEMICAL ENGINEERING
TSINGHUA UNIVERSITY
BEIJING 100084, PEOPLE'S REPUBLIC OF CHINA

ABSTRACT

A new method for determining the ζ-potential of a membrane or other porous media is proposed in which an alternating electric field is applied in the measurement of the electroosmotic flux. Determination of the apparent ζ-potential of commercial microfiltration membranes was conducted under different alternating frequencies. An increase in the magnitude of ζ-potential is obtained as a result of increased alternating frequency. A dramatic change of the apparent ζ-potential was observed when the membrane was soaked for 24 hours in a solution containing bovine serum albumin (BSA). The magnitude of the ζ-potential approached zero at pH 4.9, which indicated the adsorption of BSA on the membrane surface. When the membrane sample was soaked for 24 hours in a BSA solution containing PEG 4000, a substantial increase in the magnitude of the ζ-potential compared to that in the BSA solution was obtained. In some cases the apparent ζ-potential obtained in the BSA-PEG 4000 solution was up to that obtained in the BSA-free solution. This demonstrated the shielding function of PEG 4000 as described elsewhere. The ζ-potential was shown to be a sensitive indicator of membrane fouling caused by protein adsorption.

Key Words. ζ-Potential; Membrane fouling; Protein adsorption

* To whom correspondence should be addressed. Telephone: 86-10-6278-5534. FAX: 86-10-6277-0304. E-mail: liuzheng@mail.tsinghua.edu.cn

INTRODUCTION

For membrane separation processes which are widely used in chemical and biochemical processes at present, concentration polarization and membrane fouling are the main problems that limit separation performance. To address these problems, different methods of membrane surface modification have been developed such as grafting of hydrophilic polymer on a membrane surface (2–4) and preadsorption of protein (4, 5). In our research on multichannel flow electrophoresis (MFE), we applied a hydrophilic polymer such as polyvinyl alcohol (PVA), polyethylene glycol 4000 (PEG 4000) (1) and polyvinylpyrrolidone k30 (PVP K30) into protein solution to shield the hydrophobic interaction between the protein and membrane. The protein transmembrane flux can be maintained at a high level in the presence of these polymers at their respective suitable concentration (6). Recent studies on the mechanism of membrane fouling mainly focused on the effects of membrane material, feed properties, and processing variables (7). Nyström et al. (8), Bowen and Cao (9), and Kim et al. (10) studied the effects of hydrophilicity and the charge property of a membrane on the membrane fouling, and they showed that fouling can be greatly reduced when the membrane and the protein in solution possess the same charge property. It can be concluded from their studies that the molecular interaction at the membrane surface plays the key role in the process of membrane fouling.

The membrane electrokinetic potential (ζ-potential) is an important parameter used to characterize the electrokinetic properties of a membrane in solution. Stevens et al. (5) reported that ζ-potential changes due to membrane surface contamination. In addition to methods based on streaming potential, measuring the flow rate of electroosmosis is another way to determine the ζ-potential of a membrane or other porous solid material (10, 11), by applying a dc electric field to measure the electroosmotic flow rate. In such a measurement the concentration polarization, i.e., the accumulation of solute in the vicinity of the membrane surface, occurs due to the differential migration of solute in solution and in the membrane. This leads to changes in the physiochemical properties including conductivity, the viscosity in the membrane surface region, and the electroosmotic flux. An increase in the conductivity may also affect the validity of the Smoluchowski equation, which is applicable for electrolyte strengths less than 10^{-3} M (12). Elimination of the concentration polarization is thus of essential importance for the determination of ζ-potential based on electroosmosis.

For the present study we applied an alternating electric field, as described in previous work on multichannel flow electrophoresis (13), in the measurement of electroosmotic flux. The concentrated layer can be periodically removed from the membrane surface. As a consequence, the distribution of ions

in the vicinity of the membrane surface will approach that obtained in the absence of the electric field. The apparent ζ-potential determined under an alternating electric field thus approaches the so-called "original ζ-potential," which is intrinsically defined by the double layer distribution of the ions.

An apparatus for measuring electroosmotic flux was created, and the ζ-potentials of two kinds of microfiltration membranes in different solution were determined. The experimental results showed that the magnitude of ζ-potential changes in response to both the alternating frequency and the membrane composition. Adsorption of bovine serum albumin (BSA) can be identified through a change in the magnitude of ζ-potential. The shielding function of PEG 4000 is demonstrated by the recovery of the magnitude of ζ-potential obtained in a BSA solution containing PEG 4000.

EXPERIMENTALS

Apparatus and Procedures

The experiment system is shown in Fig. 1. A membrane sample with a cross-sectional area of 0.905 cm^2 was set between the two reservoirs where two glass capillaries were mounted to measure the electroosmotic flow rate. The reservoir and the electrode cell were bridged by polyacrylamide gel columns. An alternating electric field was applied in a symmetric way during the experiments, i.e., equal running time for the two opposite directions. This was accomplished through the computer-controlled power supply. Prior to the

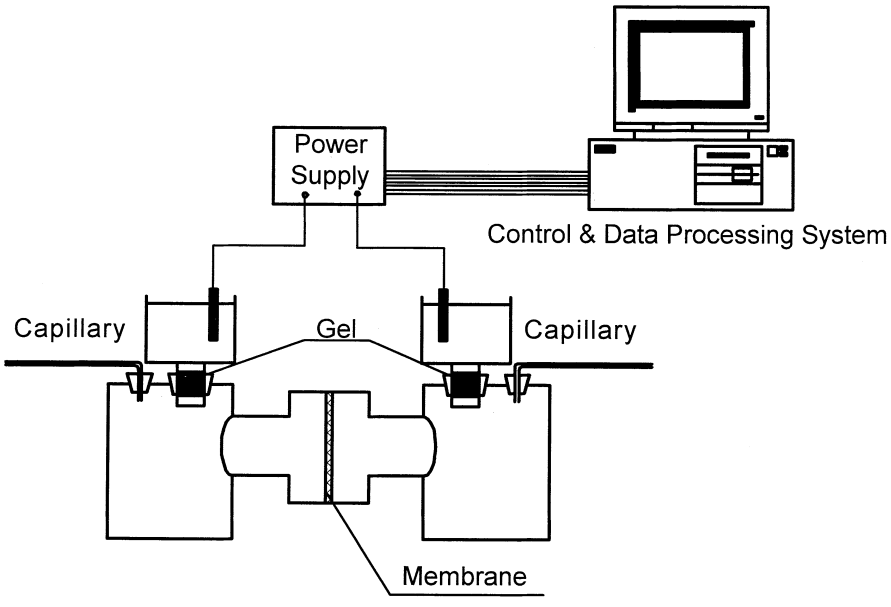

FIG. 1 Schematic view of the experimental system.

ζ-potential measurement, the membrane sample was soaked in the solution for 24 hours.

Materials

Two kinds of microfiltration membranes, HT Tuffryn and Supor, which had been used in our study of multichannel flow electrophoresis, were selected as the membrane samples for the present study. HT is described as a kind of hydrophilic polysulfone, and Supor is made of polyestersulfone according to a Gelman Sciences brochure. The pore sizes were 0.45 μm for HT and 0.8 μm for Supor.

Tris-HAc buffer was frequently used in our study of multichannel flow electrophoresis for the separation of BSA and HBB. Here, we chose 0.02 M Tris-HAc as the buffer system and BSA as the protein sample. The chemicals used in this study included BSA (Sigma, USA), Tris (Gibico, USA), PEG 4000 (Merck, Germany), and acetic acid (Beijing Chemical Company, People's Republic of China).

Assay Methods

The conductivity of the solution was measured by a DDS-11A conductivity meter made by Shanghai Leici Instrument Corporation (Shanghai, People's Republic of China). The viscosity of the solution was measured by an Ubbelohde viscometer made by Beijing Glass Instrument Company (Beijing, People's Republic of China).

RESULTS AND DISCUSSION

ζ-Potential was calculated according to the Smoluchowski equation (12) by inserting the average value of the flow rate measured with two capillaries simultaneously,

$$\zeta \frac{J_v}{I} = \frac{\varepsilon_0 \varepsilon_r \zeta}{\eta \kappa} \tag{1}$$

where J_v and I stand for the flow rate and current density, respectively, η is the viscosity of the solution, and κ, the conductivity of the solution inside the pore, is assumed to be equal to that in the bulk solution. ε_0 is the dielectric constant of the vacuum, and ε_r is the relative dielectric constant of the electrolyte.

Effect of the Alternating Frequency of an Electric Field on the Measurement of ζ-Potential

The ζ-potentials of HT and Supor membranes in 0.02 MTris-HAc solution at different pHs are shown in Fig. 2. In all experiments described in this paper, an electroosmotic flux from anode to cathode was observed, indicating

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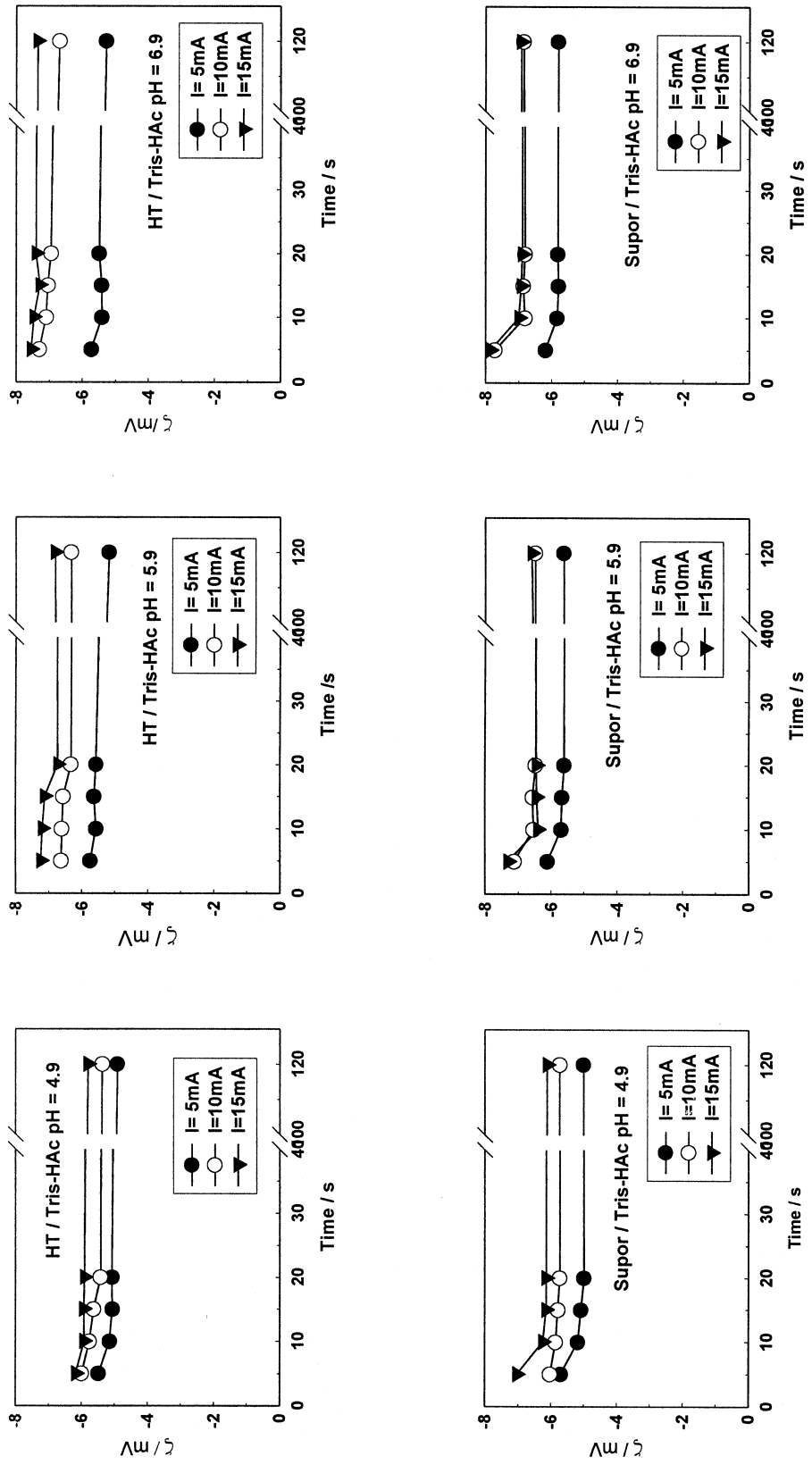

FIG. 2 The magnitude of ζ-potential as a function of the alternating frequency, indicated by the running period of the alternating electric field in a protein-free solution. Top: HT membrane. Bottom: Supor membrane.

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that both HT membrane and Supor membrane were negatively charged in Tris-HAc solution in the given range of pH. A reproducible response of the magnitude of the ζ-potential to the alternating frequency is obtained for both HT and Supor—the magnitude of the ζ-potential approaches the maximum at the highest alternating frequency. The magnitude of the ζ-potential decreases with an increase in the running time. When the running time is over 20 seconds, the ζ-potential is almost independent of the alternating period.

As discussed in the Introduction, concentration polarization will lead to the accumulation of $Tris^+$ and Ac^- inside the membrane pore surface and result in a decrease in the magnitude of the ζ-potential. An increase in the alternating frequency effectively hindered the development of the concentration polarization, reduced the local conductivity and, consequently, led to an increase in the magnitude of the ζ-potential.

It is known that when the diameter of a membrane pore is much larger that the thickness of the electric double-layer, the ζ-potential should be independent of the electric field strength as indicated by the current density (12). However, the results shown in Fig. 2 and in the following illustrations, reveal that the current dependency of the ζ-potential measurement obtained at 5 mA is smaller in magnitude than those obtained at 10 and 15 mA. This is mainly due to the experimental error in measuring the electroosmotic flow rate by the glass capillary, which becomes more significant when the electroosmotic flow rate is low. Improving the accuracy and the precision of the determination of the electroosmotic flux was the focus of the following study.

Characterization of Membrane Fouling by the ζ-Potential

The ζ-potentials of HT and Supor membranes in 0.02 M Tris-HAc solution containing BSA is shown in Fig. 3. Compared with the results shown in Fig. 2, the magnitude of ζ-potential decreased dramatically for both HT and Supor, and the effect of alternating frequency on ζ-potential became more conspicuous. Several points are worthy of note. First, the ζ-potential does not reach a stable value even after a 20-second running period. This may reflect the development of concentration polarization at the membrane surface. Second, at pH 4.9 the ζ-potential of HT approachs zero, resembling the net charge of BSA. This indicates the occupation of BSA on the surface of membrane. In this case the ζ-potential is determined by the charge property of BSA, whose net charge is zero at pH 4.9. Finally, the magnitude of the ζ-potential obtained at pH 5.9 and 6.9 in BSA solution also shows a considerable reduction compared to that of the BSA-free solution shown in Fig. 2, especially at a low alternating frequency. In this case the concentrated BSA layer not only contributes to the changes in surface charge properties but also to the changes in the other local physicochemical properties including viscosity and conductivity, which may lead to an additional reduction in the magnitude.

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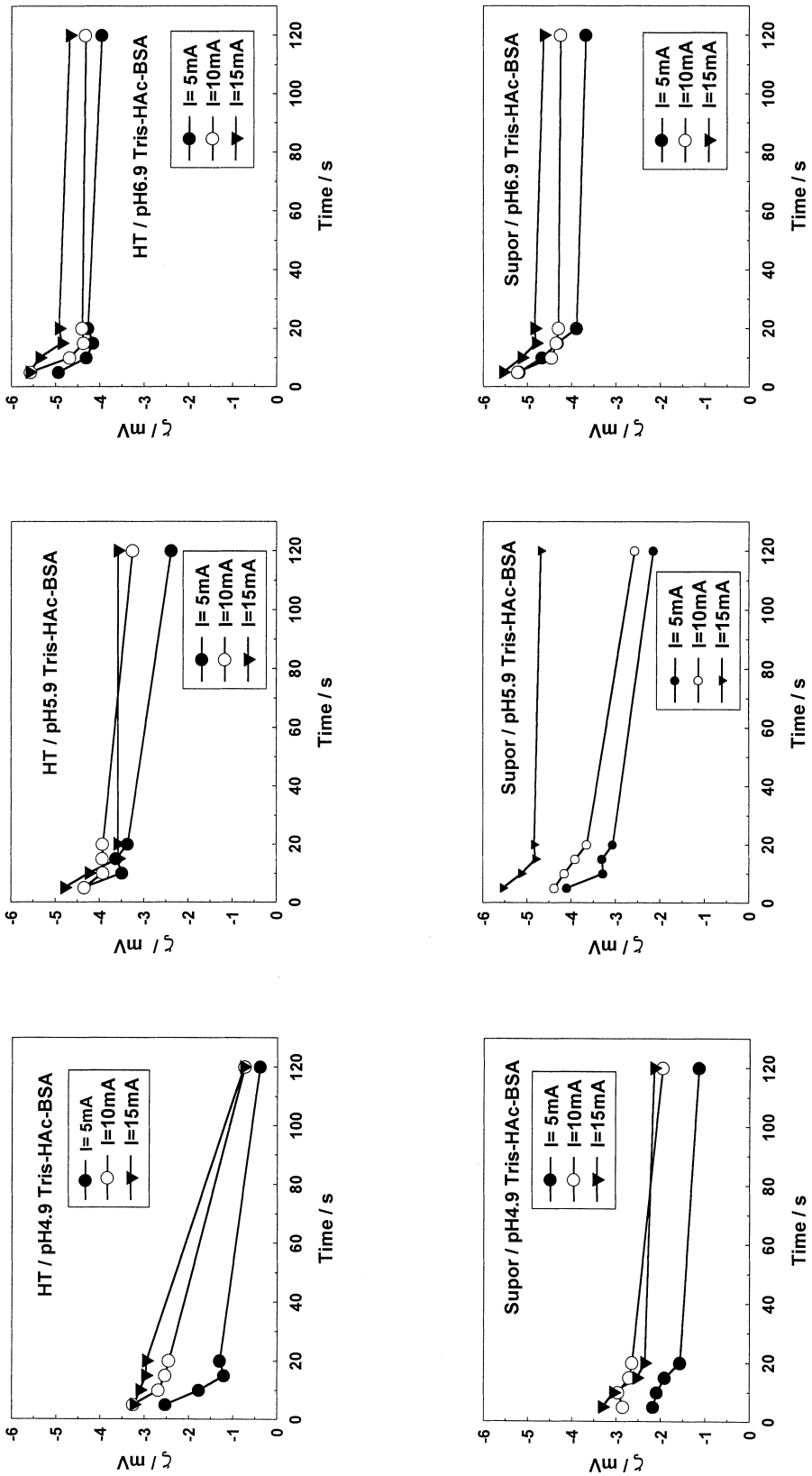

FIG. 3 The magnitude of ζ-potential as a function of the alternating frequency, indicated by the running period of the alternating electric field in a BSA solution. Top: HT membrane. Bottom: Supor membrane.

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The Shielding Function of PEG 4000

Using hydrophilic polymer to shield the strong hydrophobic adsorption of protein was first illustrated by Galev and Mattiasson (14). The effectiveness of this method was also demonstrated in our work in multichannel flow electrophoresis (5). It was thus of interest to us to characterize the shielding function in terms of ζ-potential.

The values of the ζ-potential of HT and Supor obtained in 0.02 M Tris-HAc buffer containing PEG 4000 and BSA at different pH values are shown in Fig. 4. For ease of comparison, the ζ-potential obtained in protein-free solution, protein solution, and protein-PEG solution are all plotted in Fig. 5. All these results were obtained for a 20-second running period of the alternating electric field.

It is interesting to note that that the presence of PEG 4000 in solution leads to a significant increase in the absolute value of the ζ-potential for both HT and Supor. For the HT membrane at pH 5.9 and 6.9, only a minor difference in the ζ-potential can be seen between BSA-free solution and the solution containing BSA and PEG 4000. This indicates that adsorption of BSA on the membrane pore surface is prevented by the presence of PEG 4000, as also shown in our previous work on multichannel flow electrophoresis (1). However, at pH 4.9 the magnitude of the ζ-potential of both membranes could not reach that in the BSA-free solution.

It has been reported that protein adsorption on a membrane is strongly related to the charge properties of both the protein and the membrane (15–17). In the experiments described here, BSA is neutral at pH 4.9 and negatively charged at pH 5.9 and 6.9. Therefore, an increase in BSA adsorption on HT and Supor, both of which possess a negative ζ-potential, should only be expected when the pH changes from 6.9 to 4.9, where a decrease in the magnitude of the ζ-potential was achieved. This is demonstrated by the results shown in Fig. 5.

Hydrophobic interaction may also contribute to BSA adsorption. HT and Supor membranes are both polysulfone-based and consist of hydrophobic pore networks. The hydrophobic interaction between HT and Suppor with BSA may lead to exposure of the hydrophobic region of BSA and bind it to the membrane surface. In the presence of PEG 4000, PEG molecules may preferentially bind to the membrane surface though hydrophobic interaction and expose the —OH group outward to produce a hydrophilic environment. Unfolding of BSA may thus be hindered, and the electrorepulsive force between the membrane surface and BSA will prevent BSA adsorption. The shielding function may thus be a joint effort of both ion and ionionic interactions.

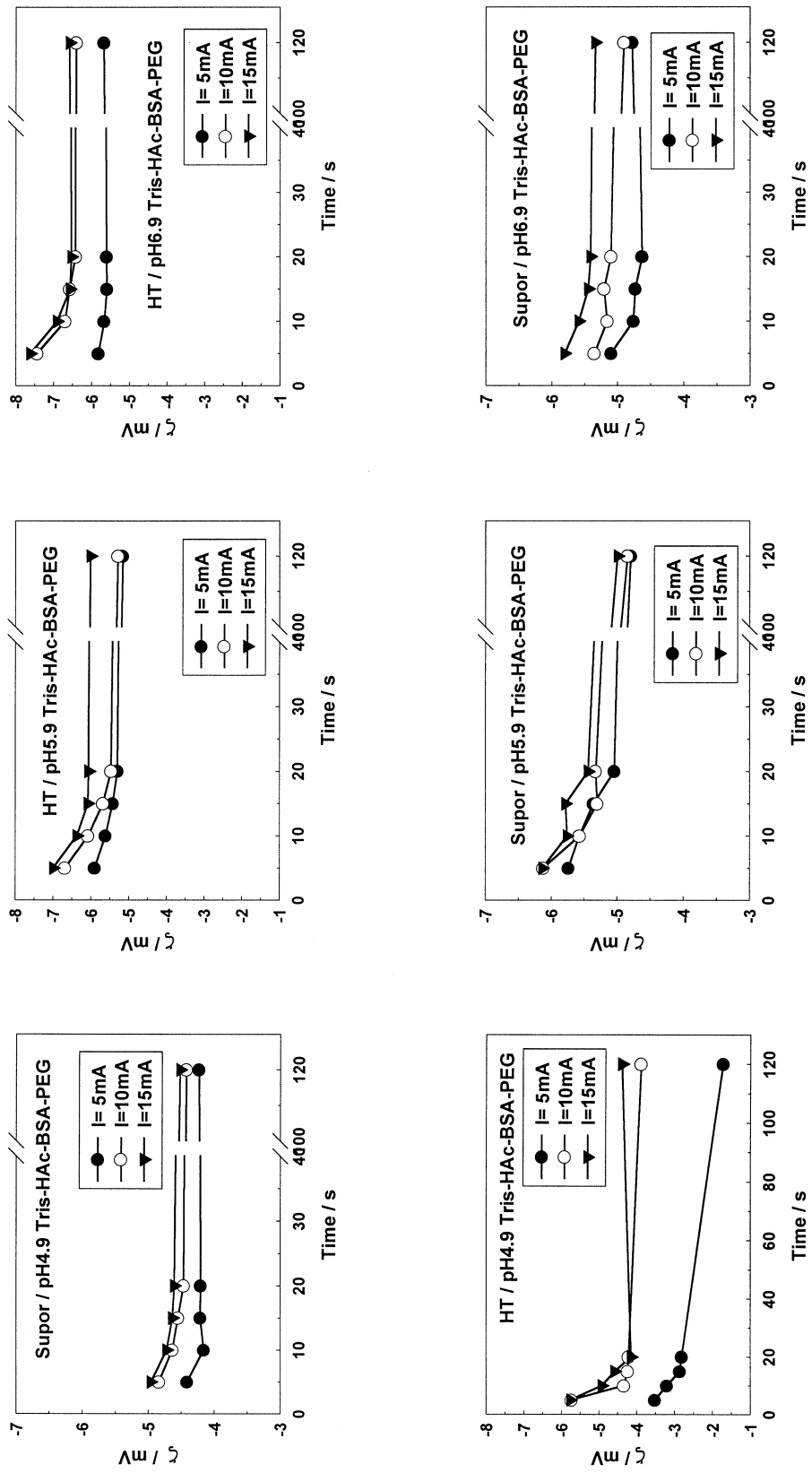

FIG. 4 The magnitude of ζ-potential as a function of the alternating frequency, indicated by the running period of the alternating electrid field in a BSA solution containing PEG4000. Top: HT membrane. Bottom: Supor membrane.

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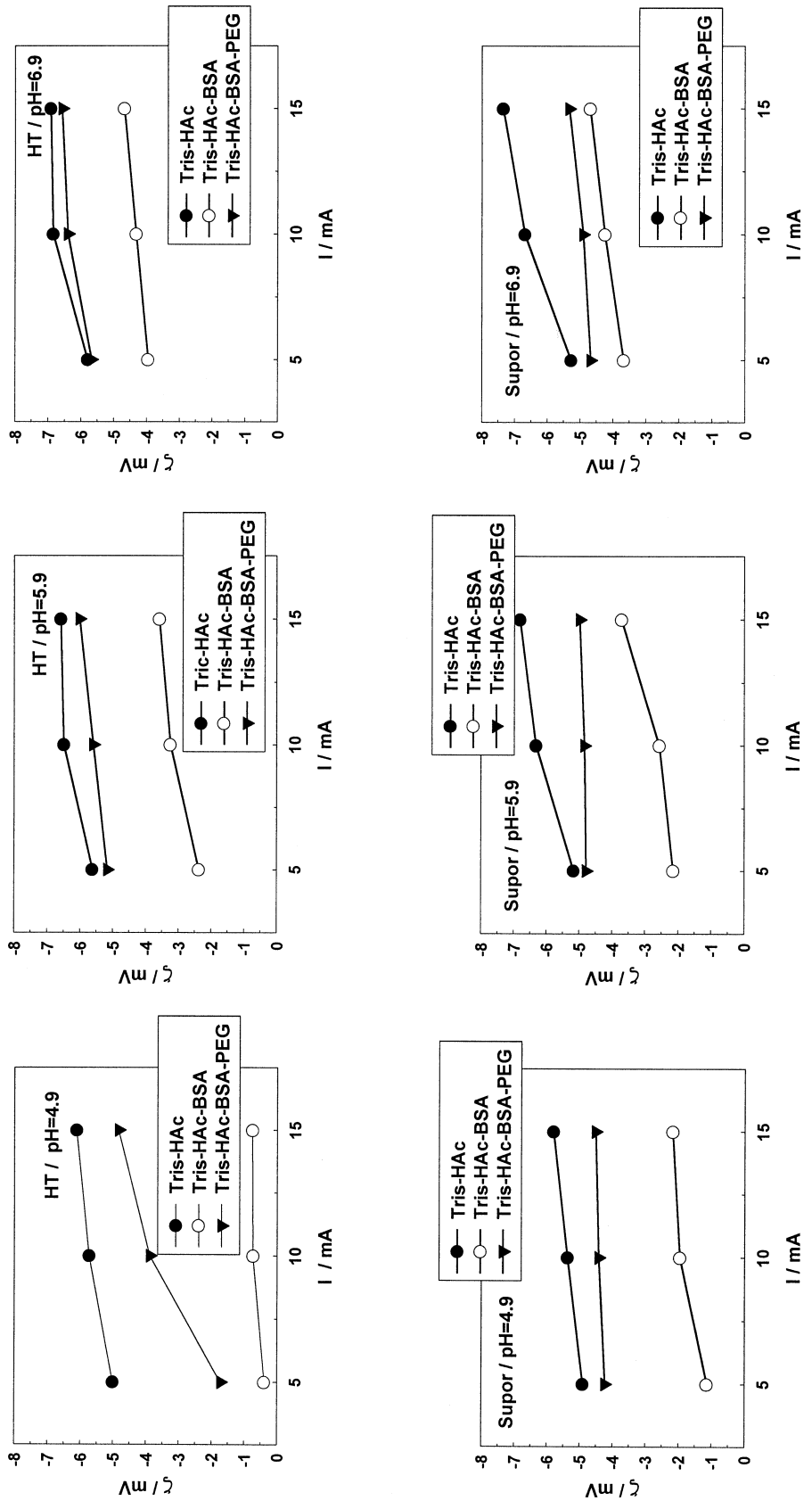

FIG. 5 Comparison of the magnitude of ζ-potential obtained in different solutions. Top: HT membrane. Bottom: Supor membrane.

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CONCLUSION

A new method for determining the ζ-potential of a membrane, based on the measurement of electroosomosis, is developed in present study. The method could also be applied to other porous solid media. Applying an alternating electric field in the measurement is effective in reducing concentration polarization and improving accuracy. The adsorption of BSA on a membrane can be illustrated by the change of the ζ-potential, as also described by Gölander and Kiss (18) and Stevens et al. (5). The shielding function of PEG 4000 is demonstrated by the recovery of the magnitude of the ζ-potential obtained when PEG 4000 is added to a BSA solution.

The results shown in Figs. 2, 3, and 4 also reveal the developing process of concentration polarization. For small electrolytes, such as $Tris^+$ and Ac^-, the concentration polarization can be fully developed within 20 seconds, as shown by Fig. 2. For large molecules, such as BSA, the development of concentration polarization is a relatively slow process which does not reach steady state after a running period of 120 seconds. It should be noted here that although the membrane sample was soaked in BSA solution for 24 hours prior to measurement, additional adsorption of BSA may occur in the presence of an electric field, as we observed in our recent experiment (19). When BSA adsorption is shielded by PEG 4000, the development of concentration polarization is similar to the case shown in Fig. 2. It is thus concluded that ζ-potential can serve as an indicator of the membrane fouling process.

For further investigation, a method to determine the amount of adsorbed protein should be developed to establish the relationship between membrane fouling and the change of the ζ-potential. An in-depth study from the perspective of molecular interaction should establish a better understanding of membrane fouling in filtration and in preparative electrophoresis using a membrane-partitioned multicompartment electrolyzer.

ACKNOWLEDGEMENT

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