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Journal of Membrane Science 278 (2006) 251–260

journal of MEMBRANE SCIENCE

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# Adsorption of bovine serum albumin on polyether sulfone ultrafiltration membranes: Determination of interfacial interaction energy and effective diffusion coefficient

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Received 25 May 2005; received in revised form 1 November 2005; accepted 4 November 2005
Available online 19 December 2005

**Abstract**

A systematic study on the effects of ionic environments on the adsorption and diffusion characteristics of bovine serum albumin (BSA) inside/on 100 kDa polyether sulfone (PES) membranes was carried out. Static adsorption of BSA was investigated at the solution pH values of 3.78, 4.78, and 6.80; for the ionic-strengths of 0.01 and 0.1 M. Isotherms for BSA adsorption on PES membranes were correlated by the Freundlich equation. The maximum adsorption occurred at the pH value below the isoelectric point of the protein. With increasing ionic strength, the adsorbed protein on the membrane decreased. van der Waals and electrostatic interactions energies between the membrane and the protein were calculated by using the DVLO theory. Diffusion coefficients of BSA inside PES membranes were calculated by employing experimental data evaluated in a diffusion cell along with the data of adsorption isotherms into a developed model based on mass-balance. To detect the structural changes occurred, membrane surfaces were analysed by FT-IR–ATR measurements and SEM images. The results of the adsorption and diffusion experiments showed that adsorption and diffusive characteristics of BSA in 100 kDa PES membranes are agreed well with the theoretical calculations.

*Keywords:* Adsorption; Interfacial forces; Effective diffusion coefficient; Zeta potential; Bovine serum albumin

## 1. Introduction

Membrane processes are of great interest in separation of macromolecules such as proteins due to their several advantages mainly low energy consumption, no additive requirements and no phase change. However, many aspects of the fundamental mechanisms of membrane processes, such as membrane fouling, a phenomenon induced by interactions of molecules with membranes, are not fully explained and their applications on an industrial scale have lagged behind their expected growth [1]. Therefore, membrane separation is a technique that is still in need of further investigations. In the present study, we carried out a systematic research to express the protein adsorption, which occurs between bovine serum albumin (BSA) and 100 kDa polyether sulfone (PES) membranes in different ionic environments, through interfacial interaction energies between the membrane and the protein; also through diffusion coefficients of the protein inside membrane pores. However, it must be noted that all of the data obtained in this work have concerned the early stage of ultrafiltration runs; in other words, the membrane fouling in long term run with hydrodynamics conditions was not included.

Serum albumins are the most abundant of the proteins in blood plasma, accounting for about 60% of the total protein corresponding to a concentration of 42 g dm$^{-3}$ and provide about 80% of the osmotic pressure of blood. As a consequence, albumins have been used as model proteins in several biophysical, biochemical and physicochemical studies for many years [2]. A large number of these studies have been devoted to the interaction of proteins with polymeric membranes in order to understand the adsorption/fouling mechanism through protein–membrane interactions. In such studies, many parameters constituting ionic environments such as pH, type and concentrations of ionic species, and protein concentration have been taken into account [3–6]. Matthiasson [7] studied the adsorption kinetics of BSA on different kinds of membranes as well as the

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doi:10.1016/j.memsci.2005.11.008

amount adsorbed and hydraulic resistance of the adsorbed layer; reported that the adsorption increased with decreasing pH of the solution. Aimar et al. [8], reported that the amount of adsorbed BSA on polyacrylonitrile membranes increased with decreasing pH, with increasing bulk concentration, and contact time. Recently, Xu et al. [9] investigated the adsorption of BSA on polyethylene membrane as a function of the pH of the solution in addition to several parameters such as concentration, time and agitation speed; observed the maximum adsorption at the isoelectric point of the protein since the molecular size of a disordered protein was at its lowest value.

The quantification of interactions between macromolecules and membranes is usually a major concern in the studies on membrane fouling. Several attempts have been made to calculate the interfacial interaction energies between the protein and the membrane using the well-established fundamental theories, such as Derjaguin–Landau–Verwey–Overbeek (DLVO) and electrostatic double layer (EDL) theories [10–12]. Recently, as a new approach, the ability to quantify the diffusive properties of the protein is utilized as a useful tool for determining the best strategy in the control of membrane fouling [12–14]. Although adsorption – one of the key factors inducing fouling – has often been explained through complicated interactions among the membrane, protein and solution components, an in-depth insight is required related to the interfacial forces and diffusive properties of protein in membranes in order to make clear the origin of adsorption.

Factors such as pH and solution electrolyte concentration have a considerable impact on the strengths and types of electrostatic charges; and thus can lead to different protein and surface interactions under different conditions. Burns and Zydney [3] investigated the effect of solution pH on the transport of globular proteins with different surface-charge characteristics through PES membranes; and obtained the maximum protein-sieving coefficient near the protein isoelectric point (IEP). The authors postulated that the non-linear dependence of the sieving coefficient on pH was due to the non-linear dependence of BSA charge on solution pH. Moreover, attractive electrostatic interactions occurred when the protein and membrane had large opposite charges, causing a second maximum in transmission at a pH the isoelectric-points of the protein and membrane. Möckel et al. [4], studied the influence of membrane hydrophilicity, pH, and ionic strength on the static adsorption of *cys*-BSA, protein ultrafiltration performance, and cleanability. The authors found that BSA adsorption showed a maximum at its IEP and the increase in ionic strength led to stronger static adsorption and greater flux reduction for pH values on either side of the IEP. It was asserted that, hydrophilicity played an important role on the static adsorption besides the electrostatic aspects; ultrafiltration flux reduction decreased and cleanability increased with increasing level of functionality. Menon and Zydney [5] investigated the effect of specific ionic composition on the rate of BSA transport through PES membranes over a range of solution pH and salt concentrations; emphasized significant impact of electrostatic interactions on protein transmission. The effects of specific ions on BSA sieving were attributed to differences in net protein charge arising from differences in ion-binding affinity to protein surface and to differences in electrostatic shielding associated with differences in ion valence. Huisman et al. [6], studied protein–protein and protein–membrane interactions to explain the membrane fouling during the ultrafiltration of BSA solution over PES membranes. The experiments were carried out at pH values within a wide range using membranes of different cut-off values. The authors reported that protein–membrane interactions affected the fouling behaviour in the initial stages of the filtration; however, in the later stages of the process, protein–protein interactions dictated the overall performance as the less retentive membranes resulted the weaker interactions. The extent of coverage of membrane with protein was analyzed by the measurement of the streaming potential and by using AFM; the structure of the fouling layer was found to depend strongly on pH. Recently, we reported a part of our research results on protein–membrane–ionic environment interactions on the basis of chemical and electrochemical features of PES and cellulose triacetate ultrafiltration membranes and the BSA in solution [12]. Although the literature has a consensus that the ionic environment strongly affects the extent of adsorption, the results reported on the effects of pH and ionic strength on protein deposition are not fully converged. We obtained the highest degree of adsorption on 10 kDa PES membranes at pH 3.78 whereas the minimum adsorption was seen at the isoelectric point (pH 4.78) of BSA. With increasing ionic strength, the adsorbed protein on the membrane decreased. The electrostatic interactions and van der Waals energies between the membranes and the protein were calculated using the DVLO theory.

In the literature, there are some studies investigated the effects of ionic environments on the effective diffusion coefficients of the charged molecules in ultrafiltration membranes; however, the number devoted to proteins is few. Hu et al. [13] developed a Nernst–Planck diffusion model including intraparticle and film diffusions to study the diffusion of charged proteins in porous particles. The authors allowed hindered diffusion of proteins in the porous media for the model and they first introduced new concept of coupled mass transfer through a stagnant film. Varzakas et al. [14] used a diffusion cell and a polysulphone membrane for the estimation of the effective diffusion coefficient of endoglucanase and lysozyme enzymes. Diffusion coefficient was calculated from the slope obtained by fitting the amount of protein transferred through the membrane against time using the appropriate mathematical equation for the steady state. The authors examined the dependence of diffusion coefficient on enzyme concentrations and on pH; reported that lysozyme appeared to have a diffusion coefficient independent of concentration at its isoelectric point. Gutenwik et al. [15] studied the effects of pH and ionic strength on the effective diffusion coefficients of lysozyme and BSA in agarose gel in a diffusion cell. They used a parameter optimization technique to estimate the diffusion coefficients directly from experimental data. The authors showed the importance and influence of experimental conditions on diffusive properties in the gel; reported that the diffusion cell was an accurate and easy-to-use method for measurements of protein diffusion coefficients, although the required duration of the experiments was long for proteins. Xu and Fu [16] proposed a new method for simultaneous determination