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Electrokinetic characterization of poly(vinyl butyral) hollow fiber membranes by streaming potential and electroviscous effect

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ABSTRACT

Streaming potentials and electroviscous effects were measured for two poly(vinyl butyral) (PVB) hollow fiber membrane modules with molecular weight cut off at 40 and 200 kDa (M40 and M200) in KCl and $CaCl_2$ electrolyte solutions. The results show that the PVB membrane has a weak negative charge due to the specific adsorption of ions, and the streaming potential of the membrane depends strongly on the salt concentration, type and valence of ions. The iso-electric points (IEP) of membranes M40 and M200 are both around 3.0 in KCl electrolyte solution and 3.5 in $CaCl_2$ electrolyte solution. The electroviscous effect increases with the increase of electrolyte concentration at low electrolyte concentration, it reaches a maximum at a certain concentration and then decreases with the increase of electrolyte concentration. The electroviscous effect is little greater for M40 than for the M200, and the electroviscous effect of KCl solution is greater than that of $CaCl_2$ solution under the same concentration. The zeta potentials for M200 have been calculated by streaming potential and the electroviscous effect. The values of zeta potentials calculated from streaming potential are less negative than those from electroviscosity measurements.

1. Introduction

It has been increasingly recognized that electrokinetic phenomena can significantly affect the performance of membrane process [1], and which has been used to supplement the traditional membrane characteristics. Moreover, electrokinetic phenomena are of importance as they are often used for determining the membrane zeta potential. The most widely used technique is measuring the streaming potential across the membrane pores to determine electrical surface properties of membranes [2]. When a hydrostatic pressure is applied over a porous membrane with charged pore walls, the liquid in the pores will move, dragging the ions present in the pore with it, and there will be an excess of counter-ions inside the pore because of the presence of the double-layer. The transport of these ions by the flow causes a potential drop across the membrane, the potential drop causes a conduction current of co-ions in the direction of the liquid flow and of counter-ions in the opposite direction. The ions moving along the electric field will drag solvent molecules with them, thus changing the flow field of the liquid, resulting in the increase of apparent viscosity, the electroviscous effect. This effect is negligible at high salt concentrations but can cause viscosity increase over 25% at intermediate and low concentrations. The electroviscous effect method is based on measuring the water flux through the membrane at different salt concentrations. The variations in water flux with salt concentration can be related to zeta potential or surface charge density through the electrokinetic flow theory [3]. It has been shown that values of zeta potential obtained by the electroviscous method compare well with those obtained from streaming potential data [4].

The streaming potential coefficient is one of the important electrokinetic phenomena, it can be defined as the ratio of the measured electrical potential drop to the hydraulic pressure difference across a micro-porous membrane in zero current conditions. The streaming potential measurement has become a common experimental technique for electrokinetic characterization of a porous membrane because streaming potential is easily measured and is particularly sensitive to the change of salt concentration when a salt solution passes through a charged membrane by a hydraulic pressure difference [5–8].

The streaming potential shows strong dependence on the pore radius of the membrane when the pore radius is comparable to the Debye length determined by salt concentration [9]. Because the surface conductivity of the pores is high, the electrical double layer (EDL) is overlapping and the profiles of the ion concentration and electrical potential are superposing [9]. Zeta potential is a parameter indicative of the interactions between membranes and salt solutions as far as it is a very easily measurable magnitude and sensitive to changes in concentration [10], which is the potential at the shear plane between the compact layer

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attached to the pore wall and the mobile diffusion layer on the surface of the membrane pores. The traditional way of determining the zeta potential for ultrafiltration and microfiltration membranes is to measure the streaming potential, and then zeta potential could be estimated by the Helmholtz–Smoluchowski equation. However, zeta potentials may be calculated based on the electroviscous effect of the membrane [11].

The iso-electric point (IEP) of the membrane is the pH value at which the streaming potential is equal to zero regardless of the ionic strength [12]. Usually, the IEP of a neutral polymeric membrane is low as anions are more readily adsorbed than cations in a non acid solution, which also makes the membrane surface negatively charged [11]. For the charged membranes, besides the sieving effect, the surface charge also plays an important role in the performance of the membranes [12–14]; it can favor the antifouling of the membrane and benefit the separation of charged electrolyte due to the electrostatic interaction.

The charging of a porous membrane surface in a solution usually comes about in two ways: one is the ionization or dissociation of the groups on the surface of the membrane pores, and the other is the adsorption of ions from solution onto the surface of the membrane pores. These lead to the formation of EDL that restores the electroneutrality in the solution. A microporous membrane can be regarded as a charged porous membrane to understand its separation performance better. It cannot be taken simply as a sieve that leads to the rejection of the solutes such as ions, molecules, clusters, aggregates, and even particles in solution [15]. The separation driving force of a charged membrane is hydraulic pressure difference. Therefore, charged membranes can reject inorganic salts of much smaller size than the membrane pore radius at a lower pressure. Reddy et al. [16] verified that a charged ultrafiltration membrane made of sulfonated polyethersulfone can reject inorganic salts like NaCl, Na_2SO_4, etc. due to the electrostatic repulsion even though it has pores much larger than the salts, and can separate amino acid or protein mixtures according to their iso-electric points. Huisman et al. [17] studied the effect of ion concentration on the salt retention for KCl solution of polysulphone ultrafiltration membranes, the salt retention vanished at very high salt concentrations, increased for decreasing salt concentrations.

Poly(vinyl butyral) (PVB) hollow fiber membrane may have a wide application prospect because its hydroxyl groups can provide high hydrophilicity. It is important to obtain some direct knowledge of the membrane surface in actual applications and its dependence on the concentration and type of salts by using the streaming potential measurement. However, no work has been done with the aim of investigating the electrokinetic behavior of PVB hollow fiber membrane. Hence, the investigation on the electrokinetic properties of PVB hollow fiber membranes is necessary and important for their wide application.

The electrokinetic properties of two PVB hollow fiber membrane modules (M40 and M200) were investigated by the streaming potential and electroviscous effect. The PVB hollow fiber membranes used in this research were prepared via the TIPS method [18]. To investigate the influence of the type of electrolyte and its concentration, KCl and $CaCl_2$ electrolytes were used for the streaming potential and electroviscous effect, with the concentration ranging from 5.0×10^{-4} mol/L to 0.3 mol/L. The zeta potential for PVB hollow fiber membrane was calculated from streaming potential and electroviscous effect. The iso-electric points of the membranes in KCl and $CaCl_2$ electrolytes were also measured respectively.

2. Theory

When a difference of the electrical potential (ΔE) and pressure (ΔP) is applied across a membrane pore, a volume flux (J_v) and an electrical current (j) can be generated according to the following equations [12]:

$$J_V = L_{11}\Delta P + L_{12}\Delta E \tag{1}$$

$$j = L_{21}\Delta P + L_{22}\Delta E \tag{2}$$

where L_{11}, L_{12}, L_{21}, and L_{22} are coupling coefficients, these equations, from the linear theory of thermodynamics of irreversible processes, are applied to systems that are not very far from their equilibrium point. These equations are valid for any solute and solvent. J_v, ΔP and ΔE can be measured easily by experiments. When the electrical current (j) is zero, the streaming potential coefficient (v) is obtained for Eq. (2). When the electric current is set to zero

$$v = (\Delta E/\Delta P)_{j=0} = L_{21}/L_{22} \tag{3}$$

Using the streaming potential coefficient, apparent zeta potential can be calculated by the Helmoltz–Schmolukovski equation.

$$v = \frac{\varepsilon_0\varepsilon_r\varsigma}{\mu K} \tag{4}$$

where ζ is the zeta potential, V; $\varepsilon_0\varepsilon_r$ is the permittivity of the solution in the pore, C/(V m); μ is the viscosity, Pa s; and K is the conductivity of the electrolyte solution, S/m. Moreover, Eq. (4) is restricted to the limit of $r_p/k^{-1} > 10$ (r_p is pore radius, $k^{-1} = \sqrt{\varepsilon RT/(2F^2c)}$, is Debye length, F is Faraday constant, c is the concentration in solution mol/m^3, R is the molar gas constant, T is the absolute temperature).

The electroviscous effect is defined as the increase in apparent viscosity over the bulk value μ_a/μ_0 [19], which equals the decrease in flux compared to the value in absence of a streaming potential [3]. The zeta potential of membranes can be calculated by the electroviscous effect [4]. Levine et al. [20] showed that for a 1–1 electrolyte solution, the apparent viscosity in a cylindrical pore is related to the zeta potential of the pore surface as

$$\frac{\mu_a}{\mu_0} = \left(1 - \frac{8\beta(e\zeta/kT)^2(1-G)F}{(r_p/k^{-1})^2}\right)^{-1} \tag{5}$$

where μ_a is the apparent viscosity, μ_0 is the bulk viscosity of the electrolyte solution, ζ is the zeta potential of the capillary surface, k is the Boltzmann constant, G is a correction function for the overlapping double layers and F a correction function for high zeta potentials; G and F can be calculated according to r_p/k^{-1} and ζ [20]. For large values of r_p/k^{-1}, $G\approx0$ and $F\approx1$. Also, $F=1-G$ as $\zeta=0$, β is a dimensionless parameter describing the properties of the electrolyte.

$$\beta = \frac{\varepsilon_r^2\varepsilon_0^2k^2T^2}{16\pi^2\mu\lambda e^2(k^{-1})^2} \tag{6}$$

The apparent viscosity is easily obtained from water flux measurements at constant transmembrane pressure, the Debye length is calculated from the salt concentration, the conductivity can be measured, and the pore radius can either be measured. Thus all variables in Eq. (5) are known, except for ζ, as G and F depend on ζ for a certain electrolyte solution. The zeta potential can then be calculated from Eq. (5) by an iterative method.

3. Experimental

3.1. Membranes and chemicals

Two PVB hollow fiber membrane modules with molecular weight cut off (MWCO) at 40 and 200 kDa were used, and the other parameters of modules are given in Table 1. Before all experiments, the membranes were rinsed with distilled water to