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Streaming Potential Measurements of Polyethersulfone Ultrafiltration Membranes to Determine Salt Effects on Membrane Zeta Potential

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A systematic study on the zeta potential of polyethersulfone membranes determined by streaming potential measurements was made to examine various salt effects. Chloride salts; KCl, NaCl, $CaCl_2$ and $MgCl_2$ and potassium salts; KCl, KNO_3, $KClO_3$, K_2CO_3, K_2SO_4 and $K_2Cr_2O_7$ were used to investigate the effects of cations and anions on the zeta potential of membranes, respectively. The zeta potential was obtained in 0.001 M salt solutions at the range of pH=4.0–8.0. The effect of ionic strength on membrane zeta potential was also investigated in the solution of KCl and Na_2HPO_4 with 0.001 M-0.1 M salt concentrations. At high pH values, anion adsorption on membrane surface had a more potent effect on zeta potential, while at low pH values, cation adsorption to membrane surface also possessed more potent effect on zeta potential. In general, zeta potential decreased with increasing ionic strength due to the compression of electrical double layer. However, preferential adsorption of ions on the membrane surface is another important parameter affecting zeta potential beside the ionic strength. The influence of ionic strength on the membrane zeta potential can be observed by performing FTIR-ATR analysis.

Keywords: Streaming potential; PES membrane; Zeta potential; Salt effects; Ionic strength

1. INTRODUCTION

Membrane-based separation is of the most important separation and purification processes for biotechnology industry. The main advantages of membrane separation as compared with other unit operations are low energy consumption, no additive requirements, no phase change, easy scale up and integration into other separation or reaction processes [1-3]. Membrane processes have wide range industrial application areas such as pharmaceutical, chemical, paper, semiconductor, textile, medical devices, waste water and purifying water [4].

However, membrane fouling is recognized as the main problem in the applications of industrial membrane processes. The electrokinetic properties such as zeta potentials of the membrane and the particles have a significant effect on the nature and magnitude of membrane fouling caused by the membrane–particle interfacial interactions. Membrane fouling is influenced by the surface chemistry of the membranes and colloidal particles, as well as by the ionic environment [5–7].

Zeta potential is a measure of the magnitude of electrostatic interactions between charged surfaces. It forms at the interface of a solid and a surrounding liquid. The zeta potential represents the surface charge which occurs in the presence of an aqueous solution when functional groups dissociate on surface or ions adsorb onto surfaces from the solution [6, 8].

The development of a net charge at particle surface affects the distribution of ions in the surrounding interfacial region, resulting in an increased concentration of counter ions close to surface. The liquid layer surrounding the particle consists of an inner region called the Stern layer and an outer region called the diffuse layer. Electrical double layer consists of Stern layer and diffuse layer. The electrical double layer thickness or Debye screening length, κ^{-1}, is calculated by using Eq. (1) [9].

$$\kappa^{-1} = \left(\frac{\varepsilon_o \varepsilon_r k_B T}{2000 e^2 I N} \right)^{0.5} \qquad (1)$$

In Eq.(1), ε_o is the dielectric constant of free space ($8.854\text{x}10^{-12}$ $\text{C.V}^{-1}\text{.m}^{-1}$), ε_r is the dielectric constant of water (78.5), k_B is Boltzmann’s constant ($1.38\text{x}10^{-23}$ J.K^{-1}), T is the absolute temperature (K), e is the magnitude of the electron charge ($1.6022\text{x}10^{-19}$ C), N is Avagadro’s number ($6.02\text{x}10^{23}\text{mol}^{-1}$), and I is the ionic strength of the salt solution (M). The ionic strength is calculated by using Eq. (2) [9].

$$I = \left(\frac{\sum z^2{}_i C_i}{2} \right) \qquad (2)$$

In Eq. (2), C_i is the ion concentrations and z_i is the ion valency.

In the Stern layer, the ions are strongly bound to particle surface. However, the ions are less firmly attached to particle surface in the diffuse layer. Within the diffuse layer there is a notional boundary and any ions within this boundary will move with particle when it moves in the liquid; but any ions outside the boundary will stay where they are, this boundary is called the slipping plane. The potential that exists at this boundary is known as the zeta potential [9-12]. Since the electrical potential at the solid surface cannot be measured directly, zeta potential is often considered as an adequate substitute.

The knowledge of zeta potential can be invaluable in identifying the pH, kind of ion and ionic strength of solution that will give the successful membrane separation process for the industrial applications. The zeta potential also provides valuable information to explain the mechanism of interfacial interactions that occur at flat macroscopic surfaces such as polyethersulfone (PES) membrane.

The zeta potential can be determined by electrokinetic measurements such as streaming potential, electro–osmosis, sedimentation potential and electrophoresis. The induced electrokinetic effect depends on driving force and the nature of solid and liquid phases [13]. In electro–osmosis and electrophoresis methods, driving force is electrical force which leads to a mechanical motion, and in streaming current or streaming potential methods, driving force is an applied mechanical force which produces an electric current or electric potential [14]. The zeta potentials of membranes are generally determined with streaming potential measurements due to its versatility that allows handling planar surfaces [15-17], cylindrical capillaries and packed beds of granular or fibrous materials [11, 17, 18].

In the streaming potential process, the salt solution is forced by an external pressure to flow through a porous plug material, across a channel formed by two plates or down a capillary. The salt solution having a net charge flows in the channel and its flow gives rise to a streaming current, thereby generating a potential difference. This potential resists the mechanical transfer of charge, causing back conduction by ion diffusion and electro–osmotic flow. The transfer of charges due to these two processes is called the leak current. In equilibrium conditions, the streaming current cancels the leak current, and the measured potential difference is streaming potential [13].

Several researchers have used the membrane zeta potential as a key parameter to study the fouling characteristics of different membranes [6, 17, 18-20]. In most published studies on the zeta potential of polymeric membrane, the salt solutions of KCl or NaCl are used to simplify the data analysis [7, 11, 16, 21–24]. Data obtained with simple salt solutions are unable to provide enough information on the different extent of ion adsorption that may occur for the wide range of salts encountered in industrial applications of membrane separation [25, 26].

In this study, the influences of potassium salts (anions effect) and chloride salts (cation effect) and pH of the solution on the membrane zeta potential were comprehensively investigated; thus generating a set of crucial information for the effects of anion–cation encountered in industrial membrane applications as food, waste water treatment, pharmaceutical and cosmetic, biotechnology industries. The effects of ionic strength on membrane zeta potential were investigated in KCl and Na_2HPO_4 the salt solutions. The effect of ionic strength in Na_2HPO_4 solution was also analyzed by FTIR–ATR. PES membranes were used in the streaming potential experiments due to its unique properties such as mechanical strength, thermal and hydrolytic stability, formability and many industrial applications.

2. MATERIALS AND METHODS

2.1. Materials

In the streaming potential experiments, 30 kDa PES (Sartorius AG, 14659, Germany) membranes with a diameter of 47 mm were used. The effect of various cations on the zeta potential of PES membranes was examined with the chloride salts; KCl, NaCl, $CaCl_2$ and $MgCl_2$. The potassium salts; KCl, KNO_3, $KClO_3$, K_2CO_3, K_2SO_4 and $K_2Cr_2O_7$ were used to investigate the effect of anions on membrane zeta potential. Ionic strength effects were also examined with KCl and Na_2HPO_4 solutions. The salts used in the experiments were of analytical grade (obtained from Merck; Darmstadt, Germany). All salt solutions were prepared using deionized water (MilliQ system, Gradient model, Millipore, USA) with a resistivity of 18.2 MΩ cm^{-1}. The chemicals of KOH and HCl (Merck, Darmstadt, Germany) were used to adjust pH of salt solutions.

2.2. Determination of PES membranes zeta potential: Measurements of streaming potential

The measurements of PES membrane zeta potential were made using an Electrokinetic Analyzer (EKA SurPASS–type A, Anton Paar GmbH, Graz, Austria) equipped with a clamping cell (55 mm x 25 mm). The EKA system composed of an automatic pH titrator, an external pH and conductivity electrodes with a temperature sensor, a pressure sensors, a measuring (clamping) cell with Ag/AgCl electrodes on each end of the cell, and a VisioLab for SurPASS control and an evaluation software programme.

An automatic pH titration was performed at room temperature over a pH range from 4.0 to 8.0. Streaming potential measurements were done using different salt solutions with a target ramp pressure of 0.5 bar. Before measurements membranes were thoroughly rinsed in MilliQ water and then they were equilibrated by soaking in appropriate salt solution. The pH values of the solutions were adjusted by the addition of 0.1 M KOH or 0.1 M HCl. For the flat samples, symmetrical and asymmetrical configurations can be used inside the clamping cell. In this study, we used the symmetrical configuration. In the symmetrical configuration, two identical membranes were mounted opposite of each other and separated by a spacer. A detailed flow diagram showing the preparation of the clamping cell for the streaming potential measurement was presented in Fig.1.

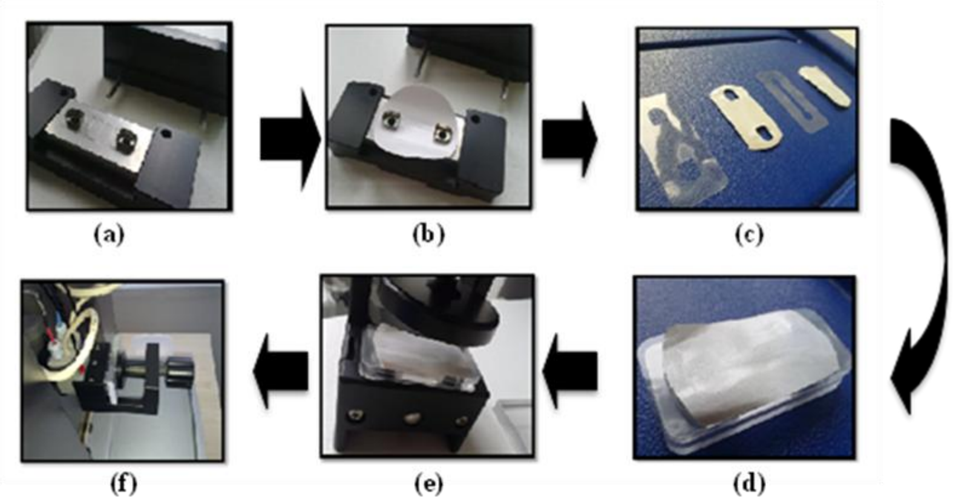

Figure 1. Schematic drawing of clamping cell preparation for the measurements of the streaming potential: Punching tool (a), punching holes of exact shape and position into membrane surface (b), preparation of membrane sandwich, from left to right; sealing foil, membrane, spacer and other membrane (c), placing of membrane sandwich on polymethyl methacrylate (PMMA) support plate (d), fixing membrane sandwich and PMMA with the pressure disk by tightening the knob of the clamping cell (e), mounting the clamping cell assembly on EKA (f).

After mounting the clamping cell assembly on EKA, the system was filled and then rinsed with 0.5 L of the degassed background salt solution. The salt solutions with concentration of 0.001 M were used in the experiments. For investigating the effect of the ionic strength on the zeta potential of the PES membranes, KCl solutions at 0.001 M, 0.01 M and 0.1 M concentrations, Na_2HPO_4 solutions at 0.01 and 0.1 M concentrations were prepared. In the streaming potential measurements, virgin PES membranes were used for each salt solution.

The EKA software programme (VisioLab for SurPASS version 2.10) calculated the zeta potential of PES membranes through the streaming potential data using the Helmholtz-Smoluchowksi equation (Eq. 3) [12, 13].

$$\zeta = \frac{dU}{dp}\frac{\eta}{\varepsilon\varepsilon_o}\frac{L}{A}\frac{1}{R} \qquad (3)$$

In Eq. (3), ζ is the apparent zeta potential of membrane, dU/dp is the slope of streaming potential versus pressure, η is the electrolyte viscosity, ε is the dielectric constant of electrolyte, ε_o is the vacuum permittivity, L is the length of the streaming channel, A is the cross–section of the streaming channel, R is resistance inside the measuring cell. All results in this study were reported in terms of apparent zeta potential data as calculated from Eq. (3). The values of apparent zeta potential were recorded as the average of three measurements.

For dilute salts solutions, the zeta potential values are not reliable because the membrane surface conductance is not negligible [27]. In this study, the used clamping cell height is about 75 μm. At this distance between adjacent membrane sample surfaces, a strong contribution of interfacial conductance is not assumed, even at the used lowest ionic strength of 0.001 M [28].

2.3. FTIR–ATR analysis

The chemical changes due to phosphate ion adsorption on the surface of PES membranes after streaming potential measurement with Na_2HPO_4 solution were detected by a FTIR spectroscopy (Perkin Elmer Spectrum 100). The UATR (universal attenuated total internal reflection) accessory of the FTIR contained a ZnSe crystal. The spectra were taken at a resolution of 4 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1. Anion effects on apparent zeta potential of PES membranes

The zeta potential changes of PES membranes in KCl, KNO_3, $KClO_3$, K_2CO_3, K_2SO_4 and $K_2Cr_2O_7$ salt solutions as a function of pH are shown in Fig. 2. In the streaming potential experiments, the used salt solutions were prepared in 0.001 M concentration. PES membranes had negative zeta potential values under the studied conditions due to anion adsorption to hydrophobic PES surfaces. At the range of pH=4.0–8.0 values, PES membranes did not give any isoelectric point, that is the pH value at which the zeta potential of membrane is zero. With decreasing pH, the absolute zeta potentials of PES membranes slightly decreased at the range of pH approximately 5.5–8.0 for ClO_3^-, NO_3^-, CO_3^{2-}, $Cr_2O_7^{2-}$ and SO_4^{2-} anions.

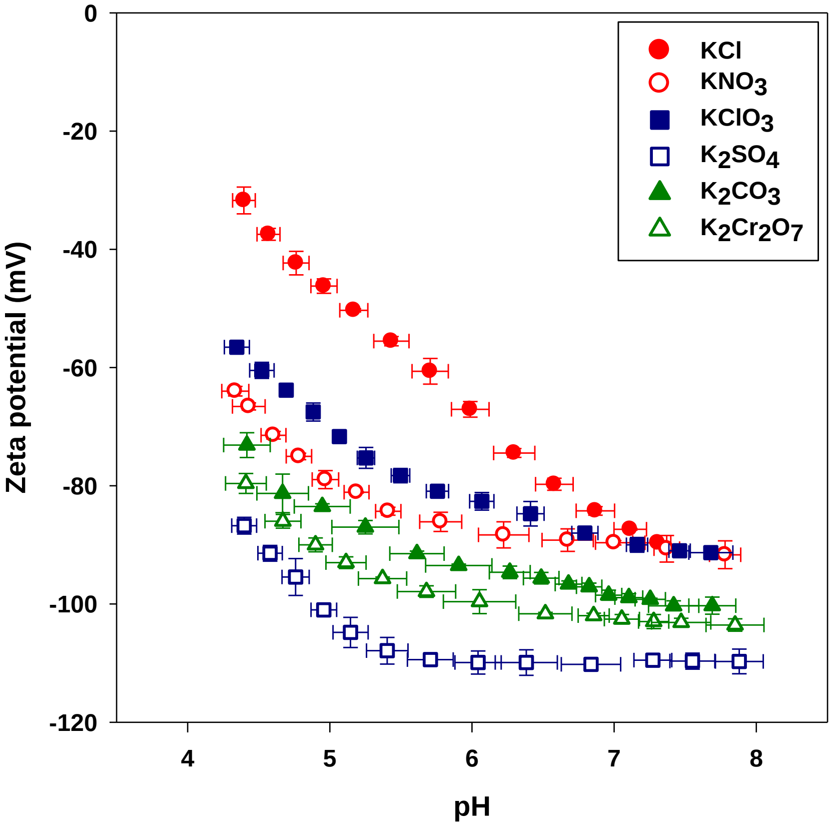

Figure 2. Anion effects on zeta potential of PES membranes as a function of pH in 0.001 M salt concentration

The absolute zeta potential of PES membrane varied almost linearly with solution pH over the range from 4.0 to 8.0 for Cl^- anion. Below pH=5.5, the dependence of zeta potential on pH appeared to follow an exponential behavior for the other anions. The absolute zeta potential decrease was in this order: $SO_4^{2-} > Cr_2O_7^{2-} > CO_3^{2-} > NO_3^- > ClO_3^- > Cl^-$, that is, the SO_4^{2-} anion is more effective than the $Cr_2O_7^{2-}$ anion for higher absolute zeta potential values under the studied pH range. As shown in Fig. 2, the absolute zeta potentials of PES membranes observed with the divalent anions were higher than that observed with monovalent anions. The salt concentrations of 0.001 M were used for all electrolyte solutions and the calculated ionic strengths from Eq. (2) for the monovalent and divalent anion solutions were 0.001 M and 0.0025 M, respectively. It is well known that an increase in ionic strength of salt solution decreases thickness of electrical double layer leading to a decrease in zeta potential. The electrical double layer thicknesses calculated from Eq. (1) were 9.54 nm and 6.03 nm for 0.001 M and 0.0025 M ionic strengths, respectively. The absolute zeta potentials of PES membranes were higher in divalent anions solutions (SO_4^{2-}, $Cr_2O_7^{2-}$, CO_3^{2-}) with higher ionic strength, in a marked contrast to conventional electrical double layer theories. It is conceivable that the increase in absolute zeta potential for divalent anion solutions is due to specific anion adsorption on the PES membrane. This behavior is very similar to that reported previously by Burns and Zydney [25] and Zhao et al.[26] for other membranes.

Anions adsorption to PES membrane surface caused the negative zeta potential. Especially, anions possessed a more potent effect on the PES membrane zeta potential at the range of pH=5.5-8.0. Below pH=5.5, it was observed that the adsorption of K^+ cation acting as counter–ion was enhanced; thus, a less negative zeta potential was acquired.

3.2. Cation effects on apparent zeta potential of PES membranes

To investigate the effect of various cations on the zeta potential of PES membrane the chloride salts; KCl, NaCl, $CaCl_2$ and $MgCl_2$ were used in the streaming potential experiments. In Fig. 3, there is plotted zeta potential changes of PES membrane in 0.001 M salt solutions as a function of pH. In KCl, NaCl, $CaCl_2$ and $MgCl_2$ salt solutions, PES membranes presented negative zeta potential values under the studied pH range. For K^+ and Na^+ cation solutions, the absolute zeta potential of PES membranes decreased when pH was decreased. With decreasing pH, the adsorption of the monovalent cations (K^+ and Na^+) increased; thus, a less negative surface charge was obtained. The absolute zeta potential of PES membranes was very similar in Ca^{2+} and Mg^{2+} solutions which are consistent with the absence of any significant specific interactions with membrane for these divalent cations. The values of zeta potential remained almost the same all over pH range for Ca^{2+} and Mg^{2+} cations.

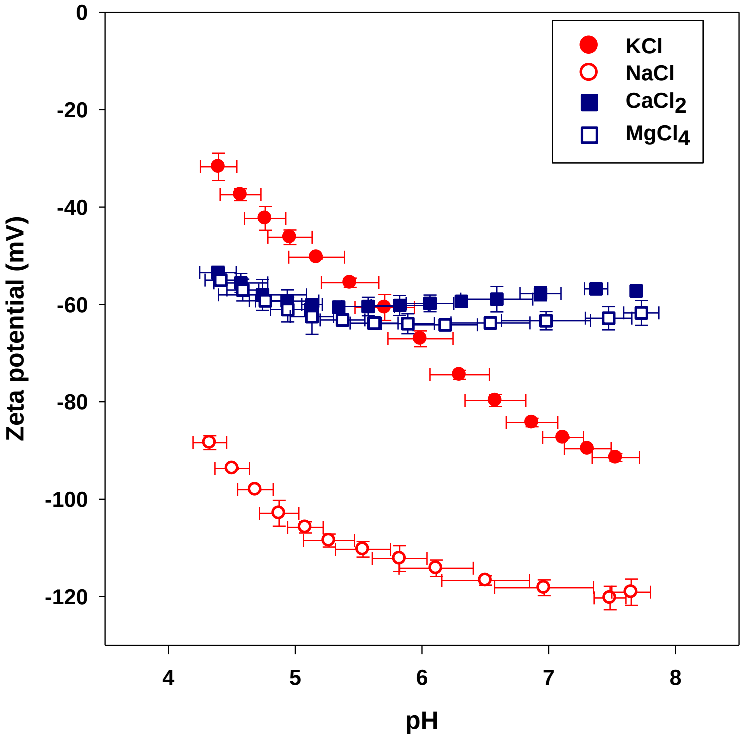

Figure 3. Cation effects on zeta potential of PES membranes as a function of pH in 0.001 M salt concentrations

The order of cation for higher absolute zeta potential changed with pH unlike the order of anions. At the range of pH=6.0–8.0, the absolute zeta potential decrease was in this order: $Na^+ > K^+ > Mg^{2+} \approx Ca^{2+}$. In this pH range, PES membrane zeta potentials were consistent with electrical double layer theory, that is, the absolute zeta potentials of PES membranes observed with the lower ionic strength (0.001 M for KCl and NaCl) were higher than that observed with the higher ionic strength (0.0025 M for M $CaCl_2$, and $MgCl_2$).

A similar result has been obtained by Zeng et al., in the study of the charge of polysulphone hollow–fiber ultrafiltration membranes in different conditions of ionic strengths [18]. This decrease in zeta potential with an increase in ionic strength could be explained by the compression of electrical double layer. This observation has been reported in many literatures [6, 8 ,25 ,26] . The absolute zeta potentials decreases were in this order: $Na^+ > Mg^{2+} \approx Ca^{2+} > K^+ >$ at the range of pH=4.0–6.0. It was observed that, the adsorption of cations on PES membrane surface became more important to obtain less negative zeta potential at low pH range for monovalent cations.

3.3. Ionic strength effects on zeta potential of PES membranes

Fig. 4 shows the pH dependence of the zeta potential of the PES membrane in KCl solution at the three ionic strength of 0.001 M, 0.01 M and 0.1 M. For 1:1 salt solutions, the values of ionic strength are equal to its salt concentrations. As shown in Fig. 4, with the decrease of the pH from 8.0 to 4.0, the absolute membrane zeta potential decreased in 0.001 M KCl solution. At low pH values, PES membranes presented positive zeta potentials which decreased when ionic strength was raised from 0.01 M to 0.1 M KCl. The PES membranes, having positive zeta potentials, passed through an isoelectric point at approximately pH=5.53 for 0.01 KCl and pH=5.75 for 0.1 M KCl. With increasing ionic strength from 0.01 to 0.1 M, the isoelectric point of PES membranes did not change significantly; so that it can be assumed that neither K^+ nor Cl^- ions specifically adsorbed on the membrane surface. Since KCl is an indifferent electrolyte, the isoelectric point of PES membrane was not affected by the increase ionic strength from 0.01 M and 0.1 M. A similar result was also reported by Szymczyk et al. The authors informed that there was absence of a specific adsorption of Cl^- and K^+ ions on the alumina–titania membrane surface [29].

At pH values above the isoelectric point of PES membrane, the zeta potentials of PES membranes became negative for 0.01 M and 0.1 M ionic strengths. The values of zeta potentials of PES membrane became significantly smaller as the ionic strength increased due to decreasing of the electrical double layer thickness. The thicknesses of electrical double layer calculated from Eq. (1) were 9.54 nm, 3.02 nm and 0.95 nm in 0.001 M, 0.01 M and 0.1 M ionic strengths, respectively. A high ionic strength makes the salt solution more conductive. Moreover, at higher ionic strength, few counter-ions in the diffuse layer result in a smaller zeta potential. At low ionic strengths, the membrane zeta potential are less screened, which leads to the presence of more counter–ions in the diffuse layer and then to a higher zeta potential value [26, 30].

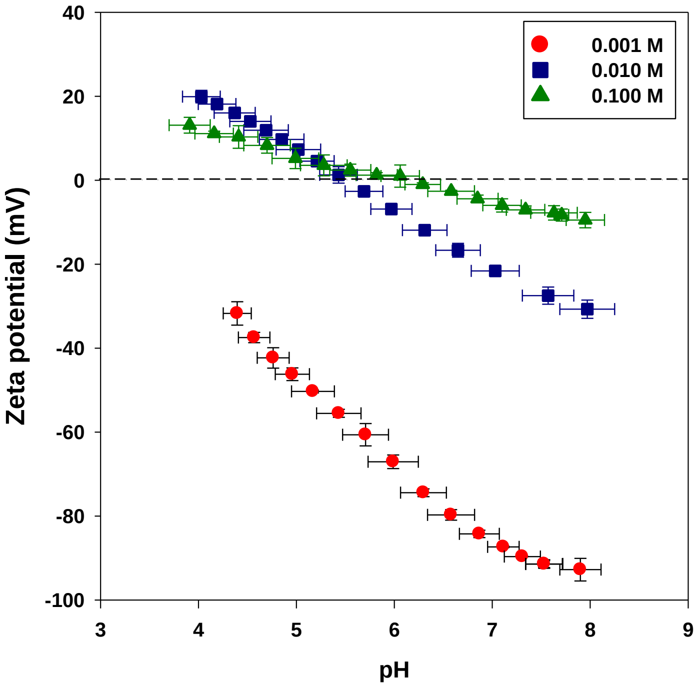

Figure 4. The zeta potentials of PES membranes as a function of pH in 0.001 M, 0.01 M and 0.1 M KCl solution

3.4. FTIR–ATR investigation of the effects of ionic strength on PES membrane zeta potential

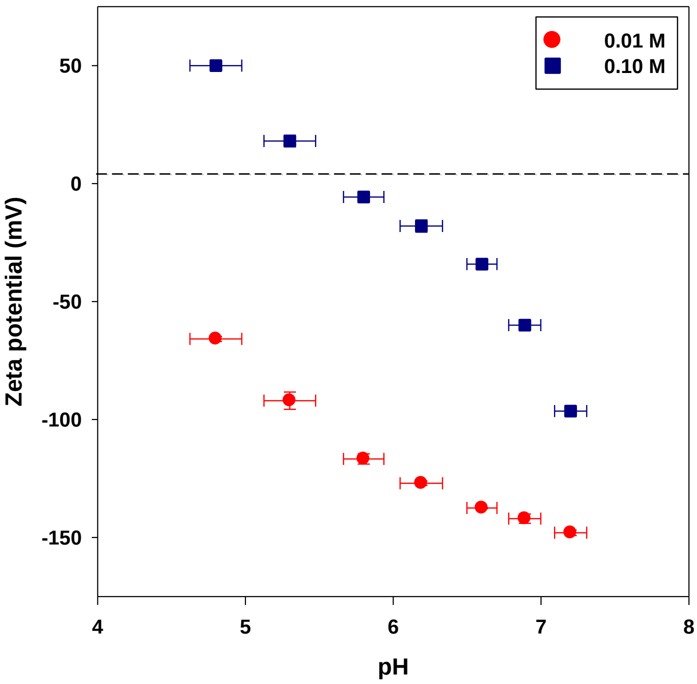

Figure 5. The zeta potentials of PES membranes as a function of pH in 0.01 M and 0.1 M Na_2HPO_4 solution

Fig. 5 shows the effect of ionic strength of Na_2HPO_4 solution on the zeta potential obtained at different pH. The absolute zeta potential of PES membrane in Na_2HPO_4 decreased when ionic strength was increased from 0.01 M to 0.1 M. A decrease in absolute zeta potential can be attributed to the compression of the electrical double layer. The reduction in double layer thickness arises from short distance screening of the surface charge as reported by Chiu and James [30]. PES membrane had an isoelectric point at pH=5.68 in 0.1 M Na_2HPO_4 solution.PES membrane surface was analyzed using the FTIR–ATR spectroscopy to detect the structural chemical changes originated by the phosphate ion adsorption as a function of ionic strength during the measurements of streaming potential. The FTIR–ATR spectra of PES membranes at 0.01 and 0.1 M Na_2HPO_4 are shown in Fig. 6. In order to make a comparison, the original spectrum of PES membrane was added to Fig. 6. One characteristic peak was inspected as the evidence of the adsorption of phosphate anion on the membrane surface, which is observed at 945.62 cm^{-1} [31]. The variation in the intensity of the phosphate peak with the ionic strength was in agreement with the electrical double layer theory, that is, the lowest intensity of the phosphate peak was observed at 0.1 M Na_2HPO_4 where the absolute zeta potential values were also the lowest due to compression of electrical double layer. It was also concluded that the increase in ionic strength decreased intensity of the phosphate peak due to the decrease in the extent of specific phosphate adsorption. The highest intensity of phosphate peak was observed at 0.01 M Na_2HPO_4 (Fig. 6).

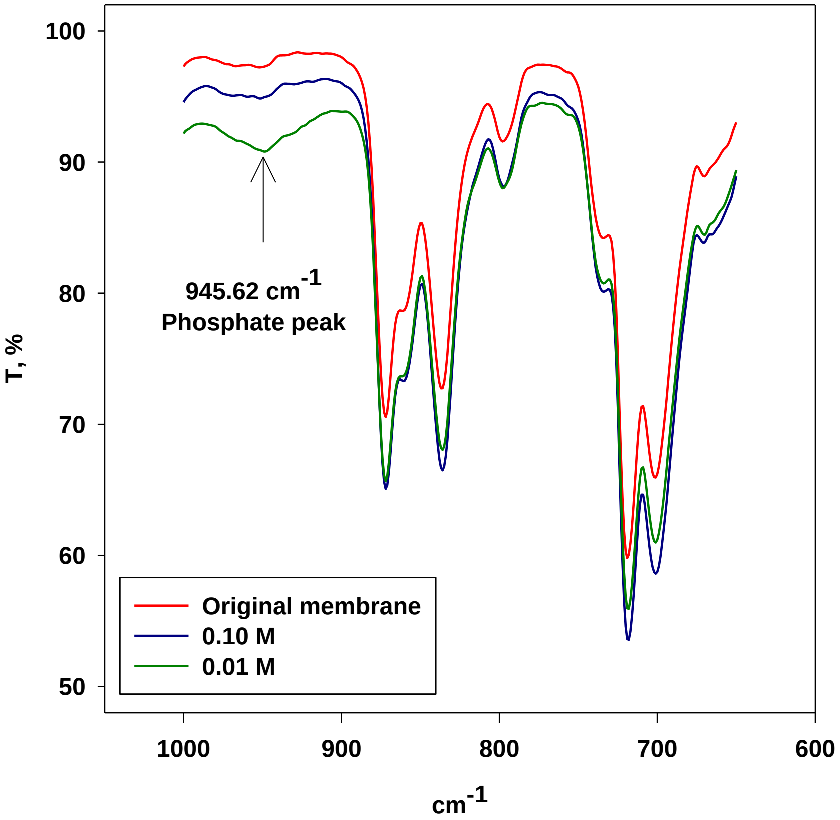

Figure 6. FTIR-ATR spectra of original PES membranes in MilliQ water and PES membranes in 0.01 M and 0.1 M Na_2HPO_4

4. CONCLUSION

In this study, the zeta potential of PES membrane was determined at different values of pH and various salt solutions by the streaming potential measurement using EKA system. Anion and cation effects on the zeta potential of PES membrane were investigated for monovalent and divalent ions. The effect of ionic strength on the zeta potential of PES membrane was also examined in KCl and Na_2HPO_4 solutions.

For the PES membrane, it seems to be reasonable to assume that anion adsorption to membrane surface has a more potent effect on zeta potential at the range of pH=6.0–8.0. It is well known that anions can approach more closely to hydrophobic surfaces (such as PES membrane), thus leading to more negative zeta potential. Cation adsorption to membrane surface also possessed more potent effect on zeta potential at pH below 6.0. Especially, adsorption of cations to the membrane surface may reduce the negative zeta potential of the membrane in the low pH region. According to electrical double layer theory, an increase in ionic strength decrease thickness of double layer leading to a decrease in zeta potential. However, preferential adsorption of ions on the membrane surface is another important parameter affecting zeta potential. The adsorption of ions on membrane surface can be observed by performing FTIR–ATR analysis.

To our literature knowledge, a direct relationship between the zeta potential of colloids and membrane fouling has been determined. The obtained results will provide valuable references for the research on membrane fouling and related applications. The availability of detailed data on zeta potential of membrane at different ionic environment will lead to better process control especially for the industrial membranes applications.

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