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Buffer effects on the zeta potential of ultrafiltration membranes

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Abstract

Membrane charge can have a large effect on the performance of many ultrafiltration processes. Previous studies of membrane charge have generally been performed using solutions of simple monovalent salts; however, the effective surface charge can be strongly influenced by the binding or adsorption to the membrane surface of specific buffer ions present in actual process solutions. Experimental data were obtained for the zeta potential of both standard and positively-charged polyethersulfone ultrafiltration membranes in the presence of a variety of monovalent and multivalent buffer ions. The zeta potential of the positively-charged membrane was very strongly dependent upon the buffer, with the adsorption of di- and tri-valent anions causing a large reduction in the zeta potential. Changes in buffer composition also caused long transients in the membrane zeta potential under some conditions due to the slow kinetics for the displacement of strongly bound ions from the membrane surface. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Streaming potential; Buffer effects; Membrane charge; Zeta potential; Ultrafiltration

1. Introduction

There has been considerable recent interest in evaluating the surface charge characteristics of ultrafiltration membranes. For example, Nyström et al. [1] showed that changes in membrane charge (evaluated from streaming potential data) could be used to study the rate and extent of protein adsorption and fouling during ultrafiltration. Nabe et al. [2] used membrane charge as a tool for studying the effectiveness of different surface modification techniques. Several investigators have used the membrane surface charge as a correlating parameter to study the fouling characteristics of different ultrafiltration membranes [3,4], with the greatest fouling typically seen under conditions where the solute and membrane have opposite net charge. Nakao et al. [5] and van Reis et al. [6] showed that the membrane surface charge can be exploited to improve the selectivity of protein separation processes by adjusting the magnitude of the electrostatic interactions between charged proteins and the charged membrane.

The most common technique for evaluating the membrane surface charge is to determine the streaming potential as a function of the applied pressure. Data can be obtained with the flow either through the pores or along the membrane surface. The streaming potential develops because of the excess convective flux of oppositely charged counterions through the membrane pore. This is discussed in more detail subsequently. In order to simplify the data analysis, all of the studies mentioned above were performed using solutions of simple monovalent salts. KCl is used most extensively since the mobilities of the K^+ and Cl^- are nearly identical. However, the actual surface

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charge of a polymeric membrane arises not only from the dissociation of specific ionizable groups on the base polymer, but also from the preferential adsorption of specific ions from the bulk electrolyte solution. Data obtained with KCl solutions are unable to provide any information on the different extents of ion adsorption that may occur with the wide range of salts encountered in commercial ultrafiltration systems.

The effects of ion adsorption on the electrical properties of colloidal materials has been studied quite extensively for more than 50 years [7]. Fig. 1 shows a schematic of a typical ion distribution near a positively-charged surface. The Stern surface (also referred to as the outer Helmholtz plane) is drawn through the center of those ions which are effectively adsorbed to the surface [8]. The extent of ion adsorption is determined by electrical and other long-range interactions between the individual ions and the membrane surface. The ions outside of the Stern layer form the diffuse double layer, which is also referred to as the Gouy–Chapman layer. The surface of shear defines the region at which the fluid becomes mobile and is coincident with or just beyond the outer Helmholtz plane [8]. The electrical potential at the surface of shear is defined as the zeta potential, ζ, and this is the value that is typically used to characterize the electrical properties of the surface.

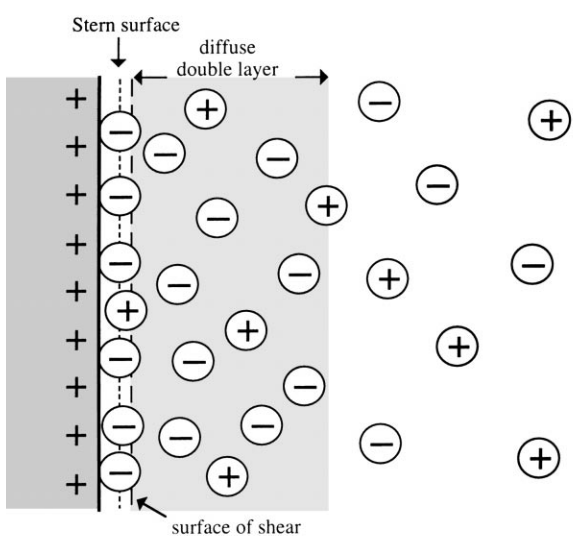

Fig. 1. Schematic representation of ion distribution near a positively-charged surface.

Rutgers and de Smet [9] evaluated the zeta potential of glass capillaries in different electrolyte solutions using both streaming potential and electro-endosmosis data. The zeta potential in 0.1 mM salt solutions ranged from −115 mV in KCl to +145 mV in $Th(NO_3)_4$. This charge reversal was attributed to the strong adsorption of the tetravalent thorium ion to the glass surface, which led to a positive charge at the surface of shear even though the glass itself was negatively charged. Rosenberg et al. [10] observed similar behavior for the surface charge of ion exchange membranes determined from measurements of water transport in response to an applied voltage. The membrane charge increased monotonically with increasing cation valence, with a charge reversal seen between trivalent lanthanum and tetravalent thorium. Beg and Saxena [11] reported large changes in the surface charge of ion exchange membranes made from manganese ferrocyanide impregnated parchment paper in the presence of both divalent (barium, calcium, and magnesium) and trivalent (chromium, aluminum, and lanthanum) cations.

These studies of ion interactions were focussed on the behavior of multivalent cations because of the importance of these interactions in ion exchange systems for water deionization. However, multivalent anions like phosphate and citrate are of much greater importance in bioprocessing and food applications because of their buffering capacity. The only reported data on the zeta potential of ultrafiltration membranes in different buffers is the study by Lee and Hong [12] on the electroosmobility of polysulfone membranes. Zeta potential data in acetate and tris, both of which are monovalent anions, showed no statistically significant differences. Anion-binding interactions have, however, been studied quite extensively in chromatographic systems. For example, Jenke [13] determined the retention times for monovalent (tris), divalent (phthalate), and trivalent (citrate) anions in a Dionex AS-1 anion exchange column as 1.0, 3.8, and 6.3 min, respectively. The increase in retention time with increasing ion valence suggests a stronger interaction between the positively-charged resin and the multivalent anions. Sosimenko and Haddad [14] reported retention times on a functionalized polymethacrylate anion exchange resin of 6.22 min for acetate, 9.47 min for chloride, and 19.41 min for chlorate (all monovalent anions), and 32.14 min for the trivalent phosphate. The different results for the monovalent anions is likely due to specific chemical interactions between the different anions and the base polymer.

The objective of this study was to obtain quantitative data for the effect of different ionic species, and in particular different multivalent anions in biologically significant buffers, on the surface charge characteristics of polyethersulfone ultrafiltration membranes. Polyethersulfone ultrafiltration membranes were examined since this polymer is used quite extensively for both food and bioprocessing applications. Data were obtained with both negatively- and positively-charged membranes, each produced from the same base polymer, with the zeta potential evaluated from streaming potential measurements using different electrolyte solutions. The results show large differences in zeta potential in the presence of different ionic species, even for data obtained at the same pH and solution ionic strength, with these differences arising from the different affinity of the ions for the membrane surface.

2. Materials and methods

KCl solutions were prepared by dissolving pre-weighed amounts of KCl (EM Science, Gibbstown, NJ) in deionized distilled water obtained from a Nanopure water purification system (Barnstead, Dubuque, IA) with conductivity less than 5.6×10^{-5} mS/cm. Solutions were buffered at the desired ionic strength by adding pre-weighed amounts of potassium hydrogen phthalate, potassium phosphate monobasic, sodium borate, sodium acetate, sodium citrate (Fisher Scientific, Pittsburgh, PA), or tris(hydroxymethyl)aminomethane (Sigma Chemical Co., St. Louis, MO). LiCl, NaCl, and $CaCl_2$ were obtained from Fisher Scientific. The solution pH was measured to within 0.01 pH units using an Acumet 915 pH meter (Fisher Scientific) and adjusted by addition of small amounts of either 10 mM HCl or 10 mM KOH solutions as required. Solution conductivity was then measured using an ES-12 conductivity meter (Horiba, Kyoto, Japan). All solutions were prefiltered through 0.2 μm pore size Supor®-200 membranes (Gelman Sciences, Inc., Ann Arbor, MI) to remove any particles prior to use.

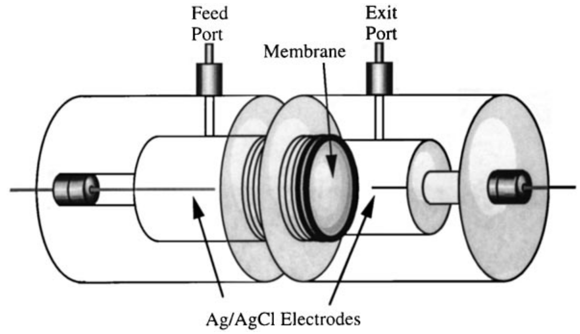

Fig. 2. Schematic drawing of the streaming potential apparatus.

Asymmetric polyethersulfone Biomax™ membranes were provided by Millipore Corporation (Bedford, MA) with nominal molecular weight cutoffs of 30, 100 and 300 kD. Limited data were also obtained with Omega 100 kD membranes provided by Filtron Technology Corp. (Northborough, MA). Detailed information on the nature of any fixed charge groups on these polyethersulfone membranes is not available. Prototype positively-charged polyethersulfone membranes were also supplied by Millipore. These membranes were prepared by chemical attachment of quaternary amine groups to the base Biomax™ membrane. All membranes were flushed with 100 l/m^2 distilled water to remove wetting agents prior to use.

Streaming potential measurements were performed using the device shown in Fig. 2, which consisted of two Plexiglas chambers, each 2 cm in diameter and approximately 2.4 cm in length. The ends of the chambers were threaded so that they could be screwed together to give a tight seal. Ag/AgCl electrodes were screwed tightly into the ends of the chambers to ensure reproducible placement relative to the membrane surface. The electrodes were sealed using O-rings to prevent leakage. The Ag/AgCl electrodes were first prepared by placing a 1 mm diameter silver wire (Sigma) and a reducing electrode in a 1M KCl solution. The wire and electrode were connected to a DC power source, and the current was maintained at 10 mA for approximately 20 min to deposit a uniform Ag/AgCl layer on the wire surface.

The device was assembled with the membrane carefully sealed between the two chambers. The chambers were slowly filled with the desired salt solution taking care to remove any entrapped air bubbles. A feed reservoir, containing the same buffer solution, was then attached to one of the chambers, with the exit from the second chamber directed to the drain. The system was pressurized by adjusting the height of the feed reservoir or by air pressurization. The system was allowed to stabilize for approximately 30 min at which point the transmembrane voltage (E_z) was measured using a high impedance 8060A True RMS Multimeter (Fluke Corporation, Everett, WA) connected to the two electrodes. Streaming potential measurements were obtained at several discrete pressures up to 35 kPa with the system allowed to equilibrate at each pressure. Wilbert et al. [15] have shown that this approach gives more accurate and reproducible data than using a continuous pressure ramp as employed in most commercial zeta potential devices. The entire apparatus was then emptied and thoroughly rinsed with a new buffer solution to evaluate the zeta potential in different salts.

3. Results

Fig. 3 shows typical experimental data for the measured streaming potential (E_z) as a function of the transmembrane pressure (ΔP) for a Biomax™

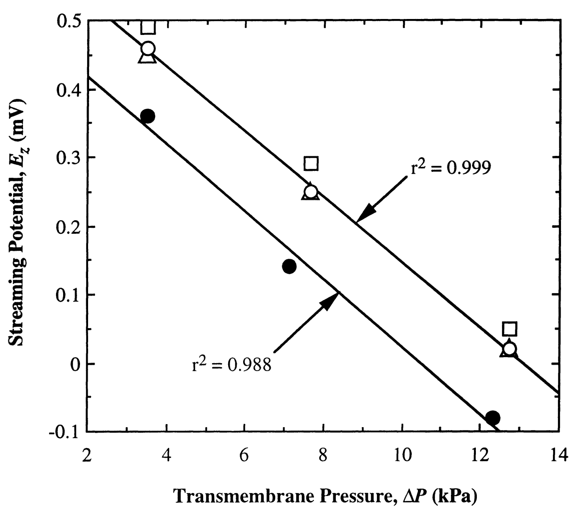

Fig. 3. Sample data for the streaming potential of a Biomax™ membrane in a 10 mM KCl solution at pH 6.5. The open symbols represent repeat measurements with a single membrane. The closed symbols represent data for a second Biomax™ membrane under identical conditions.

100 membrane in 10 mM KCl at pH 6.5. The surface charge on the membrane causes an accumulation of counterions in the double layer within the pore. Fluid flow through the pore thus initially generates a net excess flux of counterions through the membrane. The accumulation of these counterions at the pore exit causes an electrical (streaming) potential to develop across the membrane. This streaming potential then produces an electrophoretic flux of counterions back through the membrane. At steady state, these ion fluxes are exactly in balance so that the entire system maintains electroneutrality.

The streaming potential data in Fig. 3 are for two separate Biomax™ membranes (open and filled symbols). Repeat measurements with the same membrane were highly reproducible with only a small constant displacement in the data due to a shift in the zero pressure intercept. The displacement of the zero pressure intercept is due to small asymmetries in the Ag/AgCl electrodes and thus varied in magnitude from run to run. The electrodes were recoated whenever the absolute value of this zero pressure intercept was greater than 3 mV. Somewhat greater deviations in the results were seen between different membrane samples due to the inherent variability in membrane properties. However, in each case the data are highly linear (correlation coefficients of r^2>0.98) with slopes differing by less than 20%.

In order to rigorously evaluate the membrane zeta potential from the streaming potential data one would need to account for: the overlap of electrical double layers within the cylindrical pore [16,17], the effects of surface conduction [18,19], the change in conductivity due to ion exclusion from the charged pore [20], the presence of a significant pore size distribution [21], and the detailed morphology and connectivity of the pore structure. Since detailed information on these phenomena are largely unavailable, the data were analyzed in terms of the apparent zeta potential (ζ_a) which was calculated from the streaming potential using the Helmholtz–Smoluchowski equation [8]:

$$\left(\frac{\mathrm{d}E_z}{\mathrm{d}\Delta P}\right) = \frac{\varepsilon_o \varepsilon_r \zeta_a}{\eta \Lambda_o} \tag{1}$$

where η is the solution viscosity, Λ_o is the solution conductivity, ε_o is the permittivity of free space, and ε_r is the dielectric constant of the solution. The data in Fig. 3 for the three repeat runs with the same membrane yielded ζ_a from −9.2 to −9.4 mV, while the data for the second Biomax™ membrane yielded ζ_a=−9.3±0.2 mV. Similar reproducibility was obtained under other solution conditions, although the variability between membrane samples could be as large as 20%.

Experimental data for the apparent zeta potential of the different standard polyethersulfone membranes are shown in Fig. 4. The data were obtained using 10 mM KCl solutions buffered with 1 mM phthalate (for pH 2.2–5.8), 1 mM phosphate (pH 5.8–8), 1 mM tris (pH 8–9), or 1 mM borate (pH 9–10). The polyethersulfone membranes all have a negative zeta potential for pH>2.4, with the absolute value of the zeta potential increasing with increasing pH. This behavior is very similar to that reported previously by Nyström et al. [3], Hinke and Staude [22], and Causserand et al. [23] for other polyethersulfone membranes. The data for the different molecular weight cut-off Biomax™ membranes are very similar, with only a small discrepancy seen with the Biomax™ 300 at the lowest pH values. This discrepancy is likely due to the greater ratio of the pore radius to the double layer thickness and/or the greater error involved in measuring the streaming potential for this larger pore size membrane. The data for the polyethersulfone Omega 100,000 MWCO (Filtron Technology Corp., Northborough, MA) membrane were similar to the results for the Biomax™ membranes, suggesting that this pH dependence is an inherent property of the polyethersulfone membranes.

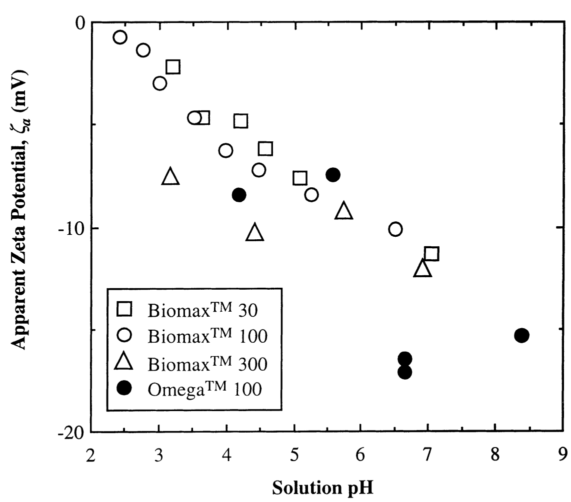

Fig. 4. Apparent zeta potential for different standard polyethersulfone membranes in buffered 10 mM KCl solutions.

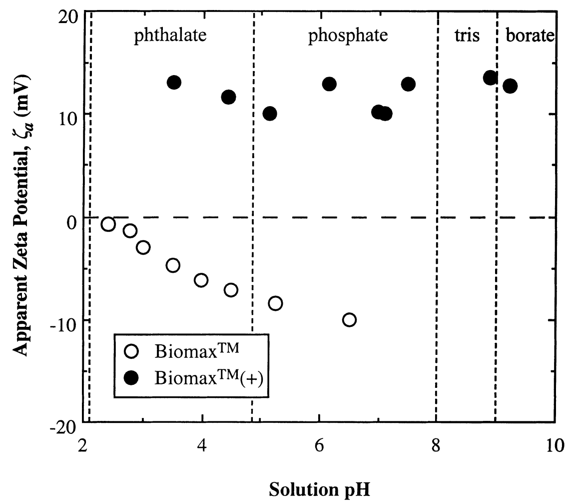

Fig. 5. Apparent zeta potential for the Biomax™ and Biomax™(+) membranes in buffered 10 mM KCl solutions. The dashed lines delineate the buffers used in each pH region.

The zeta potential data for the standard polyethersulfone membrane and the positively-charged version are compared in Fig. 5. The surface modified positively-charged Biomax™(+) membrane (prepared by chemical attachment of quaternary amine groups to the base Biomax™ membrane) shows a positive zeta potential that is relatively independent of solution pH for 3.5<pH<9.5. However, the data show considerable scatter, which appears to be at least partially attributable to the use of different buffers over the different pH ranges. The effect of different buffers on the membrane zeta potential is examined in more detail in Table 1. Results are shown at pH

Table 1
Apparent zeta potential of Biomax™ and Biomax™(+) membrane at pH 5 and 7 in 10 mM KCl solutions with 1 mM ionic strength buffer

Buffer	Biomax™, ζ_a (mV)		Biomax™(+), ζ_a (mV)	
	pH 5	pH 7	pH 5	pH 7
No buffer	−5.6±0.3	−15.1±0.8	10.7±0.3	8.9±0.5
Tris	−5.2±0.3	−12.9±0.6	9.5±0.2	8.9±0.3
Acetate	−4.9±0.2	−14.0±0.3	9.9±0.2	9.0±0.2
Phosphate	−5.0±0.3	−13.9±0.2	8.9±0.1	5.9±0.5
Phthalate	−7.4±0.4	−11.6±0.5	7.7±0.3	4.5±0.1
Citrate	−5.1±0.3	−16.0±0.4	10.0±0.2	4.1±0.2

5 and 7 for a single standard and a single surface modified membrane. Data were again obtained using 10 mM KCl with 1 mM of the appropriate buffer. The apparent zeta potential for the standard Biomax™ membrane was relatively independent of the buffer, varying from −4.9±0.2 mV to −5.6±0.3 mV at pH 5 and −12.9±0.6 mV to −16.0±0.4 mV at pH 7 for the phosphate, tris, acetate, and citrate buffers. The one exception was phthalate which yielded a somewhat less negative zeta potential at pH 7 but a more negative potential at pH 5. The results for the positively-charged membrane show a much greater variation in zeta potential for the different buffer solutions, with the values in citrate, phthalate, and phosphate at pH 7 being well below the values in pure KCl, tris, and acetate. The variations in zeta potential were smaller at pH 5, although the phthalate buffer again yielded a smaller zeta potential. These differences in zeta potential were not due to changes in either the solution conductivity (which varied by less than 10%) or the ionic strength, but were instead likely associated with different extents of ion binding by the positively-charged membrane.

Table 2 shows the pK_a values of the different anions examined in this study. At pH 7 citrate is present primarily in trivalent form, phthalate is almost entirely divalent, phosphate exists as a mixture of mono- and di-valent ions, acetate is almost entirely monovalent, and tris is largely uncharged. The zeta potentials in tris (neutral) and acetate (monovalent) buffers were almost identical to that measured in unbuffered KCl (which has monovalent chloride ions). In contrast, the presence of the divalent or trivalent ions (phosphate, phthalate, and citrate) causes a significant reduction in the zeta potential at pH 7, with the magnitude of this reduction being directly related to the anion valency. This behavior is likely attributable to the reduction in the positive charge on the membrane caused by the adsorption or binding of the di- and tri-valent anions. The data for the positively-charged membrane at pH 5 show a weaker dependence on the buffer anion since none of the anions are fully di- or tri-valent at this pH. The lowest zeta potential at pH 5 is found with phthalate which is about 28% in divalent form at this pH (phosphate and citrate have less than 10% divalent ions). The large change in valence of the citrate ion (from primarily trivalent at pH 7 to primarily monovalent at pH 5) causes a large increase in charge in going from pH 7 where ζ_a=4.1±0.2 mV to pH 5 where ζ_a=10.0±0.2 mV.

Table 2
pK_a values for buffer ions

Buffer	p$K_{a,1}$	p$K_{a,2}$	p$K_{a,3}$
Tris [24]	8.0	–	–
Acetate [24]	4.76	–	–
Phosphate [24]	2.12	7.21	12.67
Phthalate [25]	2.95	5.41	–
Citrate [24]	3.13	5.93	6.38

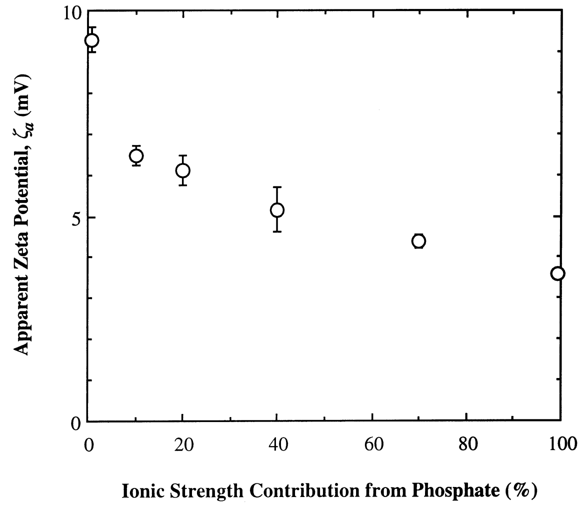

Fig. 6. Apparent zeta potential of a Biomax™(+) membrane at pH 7 measured in 10 mM ionic strength solutions prepared with different amounts of KCl and phosphate.

All of the data in Table 1 were obtained with 10 mM KCl using 1 mM concentration of the added buffer. Fig. 6 shows experimental data for the positively-charged membrane at pH 7 using mixtures of potassium chloride and potassium phosphate with 10 mM total ionic strength but with different amounts of chloride and phosphate. In each case the ionic strength, I, was calculated as:

$$I = \sum C_i z_i^2 \qquad (2)$$

The concentrations of the charged phosphate ions were determined from the Henderson–Hasselbalch equation:

$$[A^{-n}] = [H_{3-n}A^{-(n+1)}] \times 10^{pH-pK_{a,n}} \qquad (3)$$

where A is the phosphate anion concentration, $H_{3-n}A$ is the hydrated phosphate anion concentration, and n is the anion valence. The pK_a values for the different anion valencies are given in Table 2 [24,25]. The results are plotted as a function of the percentage of the total ionic strength associated with the phosphate ions. The zeta potential in pure KCl (ζ_a=9.3±0.3 mV) was consistent with that seen for the membrane used for the experiment in Fig. 5 and Table 2. The zeta potential decreases with increasing phosphate concentration, approaching a value of approximately 3.5 mV when the percentage of the ionic strength due to phosphate reaches 100%. Similar behavior was seen with phthalate and citrate, with the zeta potential decreasing from about 14 mV in 10 mM ionic strength KCl to 2.5 mV in 10 mM ionic strength phthalate and 0.2 mV in citrate. The much greater effect of the phthalate and citrate anions on the zeta potential is again consistent with the greater valency of these anions at pH 7.

The large effect of citrate on the zeta potential of the Biomax^{TM}(+) membrane is examined in more detail in Fig. 7 which shows ζ_a as a function of pH in a pure citrate solution of 10 mM ionic strength. In sharp contrast to the data in Fig. 5 (which were obtained in buffered KCl solutions), the zeta potential in citrate decreases from slightly more than 6 mV at pH 4 (where citrate is present in about 87% monovalent form) to a value of −0.7 mV at pH 8 (where citrate is present in 97% trivalent form). Thus, at high pH the adsorption/binding of the trivalent citrate ion completely masks the positive charge of the quaternary amine groups, giving the membrane a small net negative charge in 10 mM citrate compared to the +13 mV measured at this same pH in 10 mM KCl. This charge reversal cannot be accounted for by purely electrostatic interactions, but instead suggests the presence of specific attractive interactions between the citrate ion and the positively-charged membrane surface [7].

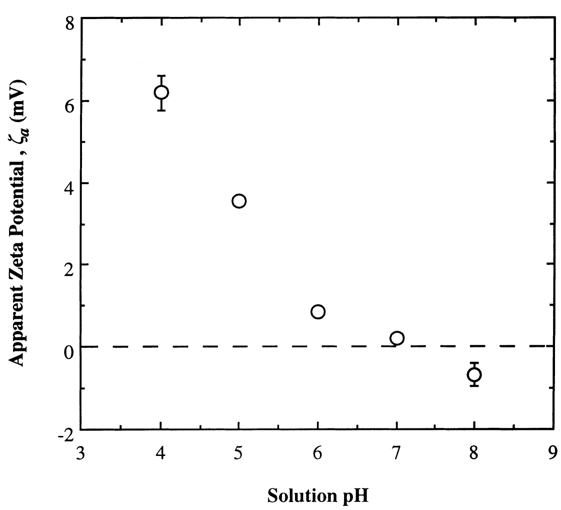

Fig. 7. Apparent zeta potential of a Biomax^{TM}(+) membrane in 10 mM ionic strength solutions of sodium citrate as a function of solution pH.

Table 3 shows data for the effect of different cations (Li^+, K^+, Na^+, and Ca^{+2}) on the apparent zeta potential of the Biomax^{TM} and Biomax^{TM}(+) membranes at pH 7. The zeta potential for the Biomax^{TM} membrane was very similar in the LiCl, KCl, and NaCl, which is consistent with the absence of any significant ion-binding interactions for these monovalent salts. The zeta potential in the $CaCl_2$ solution was slightly less negative than that in the other salts, which could be due to the depression of the electrical double layer and/or to the adsorption/binding of the divalent cation. The zeta potential for the Biomax^{TM}(+) membrane shows a stronger dependence on the salt type, with the zeta potential ranging from 8.3 mV in KCl to 16.1 mV in $CaCl_2$. The high zeta potential in $CaCl_2$ is likely due to the lower chloride concentration since the 10 mM ionic strength $CaCl_2$ solution only has a 6.7 mM concentration of Cl^- compared to the 10 mM concentration of Cl^- with the monovalent salts.

All of the data presented up until this point were obtained after the membrane had equilibrated with the given buffer solution. Fig. 8 shows data for the apparent zeta potential of the Biomax^{TM}(+) membrane as a function of time after a 24 h storage of the membrane in either hydrochloric or phosphoric acid at pH 2.5. The zeta potential was measured using 10 mM KCl buffered with 1 mM tris at pH 7. The time axis refers to the time after removal of the membrane from the acid storage solution evaluated at the midpoint of the zeta potential determination. The first data point is at t=30 min due to the time required to fill the solution chambers, set the transmembrane pressure, and then evaluate the streaming potential at four different pressures (required to calculate ζ_a from Eq. (1)). The initial zeta potential measured after storage in phosphoric acid was +39 mV. The zeta potential decayed to +20 mV after 120 min and eventually to +13 mV

Table 3
Apparent zeta potential of Biomax^{TM} and Biomax^{TM}(+) membranes measured in 10 mM ionic strength solutions with different cations

Salt	Λ_o (mS/cm)	[Anion] (mM)	[Cation] (mM)	Biomax^{TM}, ζ_a (mV)	Biomax^{TM}(+), ζ_a (mV)
KCl	1.41	10.0	10.0	−7.8±0.3	11.2±0.2
NaCl	1.18	10.0	10.0	−7.7±0.4	11.7±0.1
LiCl	1.05	10.0	10.0	−7.6±0.1	8.3±0.1
$CaCl_2$	0.71	6.7	3.3	−5.1±0.1	16.1±0.5

after 16 h. This final asymptote is in good agreement with the data in Fig. 5, which were obtained on a fresh membrane without any exposure to either phosphoric or hydrochloric acid. In contrast to the data obtained after storage in phosphoric acid, the zeta potential measured after storage in HCl was nearly constant at a value of +12.1±0.2 mV. This value is essentially identical to the steady-state value obtained after storage in the phosphoric acid indicating that the membrane surface charge and surrounding double layer eventually attain equilibrium with the 10 mM KCl solution. Thus, the very different behavior observed after storage in hydrochloric or phosphoric acid was not due to any irreversible alteration in the membrane surface chemistry or pore structure. Instead, the slow transient seen after storage in phosphoric acid may be due to the slow kinetics of Cl^- adsorption to the positively-charged membrane in this system. Another

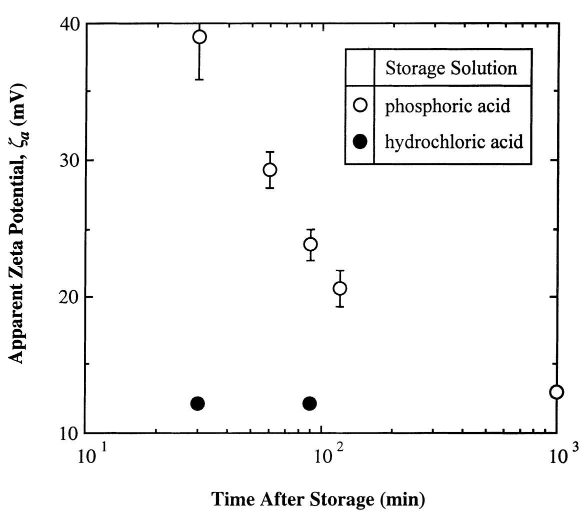

Fig. 8. Apparent zeta potential of a Biomax^{TM}(+) membrane in 10 mM KCl buffered with 1 mM tris after 24 h adsorption in either phosphoric or hydrochloric acid.

factor that could affect the observed behavior is the partitioning of unionized phosphoric acid into the pore during storage at pH 2.5. The unionized phosphoric acid within the pore will tend to deprotonate upon exposure to the pH 7 KCl solution, releasing positively-charged H^+ ions into the pore. The reduction in zeta potential with time would thus be the result of a transient ion-exchange phenomenon. Small transients were also seen upon switching between some buffer solutions, although the zeta potential generally equilibrated to its steady-state value within 30 min.

4. Discussion

Although the effects of ion adsorption/binding on the surface charge of colloidal materials are well appreciated, there has been almost no work on the effects of specific buffer ions on the charge characteristics of ultrafiltration membranes. Data obtained in this study with the surface-modified Biomax^{TM}(+) membrane yielded zeta potentials at pH 7 that varied by more than a factor of 2 even in the presence of only 1 mM buffer (with 10 mM KCl) due to the strong adsorption/binding of the di- and tri-valent anions to the surface of the positively-charged membrane. Even more dramatic effects were seen using 10 mM ionic strength solutions of citrate. In this case, the zeta potential for the Biomax^{TM}(+) membrane at pH 8 in citrate was −0.7 mV compared to +13 mV in pure KCl or KCl buffered with 1 mM tris at this same pH. This type of charge reversal has been seen with multivalent cations on ion exchange materials [9,10], but has never been reported for the type of ultrafiltration membranes examined in this study.

The very different behavior seen with the standard and positively-charged polyethersulfone membranes is due to the difference in the potential-determining ions for these membrane systems. The surface charge of the standard Biomax^{TM} membrane is determined by the presence of ionogenic groups on the membrane surface (probably weakly acidic carboxylic or phenolic groups), with the extent of ionization of these groups a strong function of the local hydrogen ion concentration (i.e. the solution pH). Multivalent anions (like phosphate and citrate) have little effect on the surface charge of the Biomax^{TM} membranes since these anions are largely excluded from the double layer. In contrast, the charge on the Biomax^{TM}(+) membranes is due to the attached quaternary amine groups, with the extent of ionization (and thus the net charge) being independent of pH (as seen in Fig. 5). Multivalent anions will be potential-determining ions for these membranes due to the strong adsorption of these anions to the positively-charged surface. Thus, the pH dependence of the zeta potential for the Biomax^{TM}(+) membrane seen in Fig. 7 is really an indirect effect associated with the change in the valence of the citrate ion (as opposed to a direct protonation of charged groups on the membrane surface).

A detailed study of the effects of ion adsorption on the performance of ultrafiltration membranes is beyond the scope of the current investigation. However, Godjevargova and Dimov [26] showed that albumin adsorption on positively-charged acrylonitrile copolymer membranes (4.7 mg/m^2) was much larger than that on a negatively-charged version of the same membrane (0.7 mg/m^2). The data obtained in this study would indicate that these levels of adsorption might be dramatically altered by switching buffer anions, with the use of a trivalent anion like citrate leading to a significant reduction in the extent of adsorption of the negatively-charged albumin to the positively-charged membrane surface. Zydney and Pujar [27] theoretically evaluated the effects of membrane charge on protein transport by accounting for the free energy of interaction between the charged protein and the charged membrane pores. The protein selectivity at low ionic strength was much greater for a membrane with very low surface charge density since protein transport under these conditions was determined primarily by the deformation of the electrical double layer around the charged protein [27]. The results presented in this study clearly demonstrate that one can effectively titrate the membrane charge by adjusting the composition of the bulk electrolyte solution, even for membranes with fixed charged groups like the positively-charged quaternary amines on the Biomax^{TM}(+) membrane. The effects of membrane charge on protein transport will be examined in more detail in a forthcoming study [28].

The data obtained with the Biomax^{TM}(+) membrane also showed the presence of a long transient in the zeta potential upon switching from phosphoric acid (pH 2.5) to 10 mM KCl buffered with 1 mM tris at pH 7. This transient was apparently due to some type of ion exchange phenomenon involving the phosphoric acid. This type of transient could have a significant effect on membrane performance during diafiltration processes used for buffer exchange [29]. In addition, phosphoric acid (among a number of other strong acids and oxidizing agents) is often used as a storage agent to prevent bacterial growth. The results obtained in this study indicate that under some conditions it could take as much as 6–10 h for the membrane surface charge to equilibrate with the process buffer after prolonged storage in these chemical solutions. The resulting changes in membrane charge could have profound effects on membrane fouling as well as solute transmission during ultrafiltration processes.

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