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Tangential flow streaming potential measurements: Hydrodynamic cell characterization and zeta potentials of carboxylated polysulfone membranes

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Abstract

Computational fluid dynamics calculations were carried out to ensure that a self-made tangential flow mode streaming potential measurement cell meets the hydrodynamic stipulations of laminar, steady and established electrolyte flow necessary for reproducible electrokinetic measurements. The calculations show that the cell design meets all of these conditions.

Six carboxylated polysulfones with a range of different degrees of substitution (DS) from 0.26 to 1.74 carboxyl groups per polymer repeat unit were synthesized in a two-stage process of lithiation and carboxylation. Ultrafiltration membranes were made from both the unmodified polysulfone and these hydrophilic materials. The zeta potentials of these membrane surfaces were determined in 0.001 M KCl solution as a function of pH. The curves show the theoretically expected profiles for non-ionic and weakly acidic materials. The growing influence of the COOH dissociation on the surface charge formation is indicated by the flattening of the curves at low pH values. The magnitude of the negative zeta potentials plateau values ranged from –52 to –20 mV. While unmodified PSU has a plateau value of –52 mV this value decreases continuously with increasing DS to –20 mV for the PSU-COOH 1.74 material. It is suggested that this arises from a shift of the electrokinetic shear plane into the bulk electrolyte solution due to an extended swelling layer reflecting the enhanced hydrophilicity of these membrane surfaces. © 1998 Elsevier Science B.V.

Keywords: Streaming (zeta) potential measurements; Electrochemistry; Ultrafiltration; Carboxylated polysulfones; Computational fluid dynamics simulation

1. Introduction

Biomolecular fouling, a deposition of macromolecules on the membrane surface, is a severe problem in many microfiltration and ultrafiltration processes

resulting in a considerable reduction of transmembrane permeability, a loss of valuable product and consequently an increase in operating costs. The extent and nature of such fouling processes are strongly influenced by the surface charge properties of the species that interact (protein molecule and polymeric membrane surface in the simplest case). These are influenced or controlled by solution properties such as the nature of the ions, ionic strength and

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pH. It has been shown qualitatively that when the membrane is hydrophilic and carries an electric charge of the same sign as the biomolecule in solution, it resists fouling better [1,2]. Thus, tangential flow streaming potential measurements provide a useful quantitative measure of membrane surface charge in an environment close to its actual operating conditions.

Polysulfone-based membranes show outstanding oxidative, thermal and hydrolytic stability as well as good mechanical and film-forming properties. Both chloromethylation and lithiation of the commercial polymer have opened up a wide spectra of derivatives [3,4]. UF membranes manufactured from carboxylated polysulfone (PSU-COOH) have shown enhanced hydrophilicity over their unmodified polysulfone precursor. Different levels of functionality can be obtained from a two-stage process of lithiation, followed by carboxylation with dry ice [5].

In order to find out about the surface charge properties of such novel membrane materials and to understand the underlying mechanisms that control protein fouling it is necessary to explore the electrokinetic surface properties of these materials. Electrokinetic surface properties are of vital importance in many industrial, biological and medical applications; their determination has proven to be useful and non-invasive [6,7].

The objective of the present paper is to present zeta potential data on UF membrane surfaces made from unmodified polysulfone and six carboxylated polysulfones of a range of DS from 0.26 to 1.74. Problems concerned with surface conductivity will be discussed. A further objective was a thorough hydrodynamic characterization by computational fluid dynamics of a tangential flow cell for electrokinetic characterization which has been made at the institute in Essen.

2. Electrokinetic theory

The electrochemical double layer (EDL) which is formed at the phase boundary between a solid and a liquid determines the electrokinetic properties of solid materials. Several mechanisms account for the surface charge of polymeric membranes when contacted with aqueous solutions. These include dissociation (ionization) of surface functional groups, adsorption of ions

Fig. 1. Schematic representation of the charge distribution at the solid/liquid interface according to the GCSG model.

from solution, and adsorption of polyelectrolytes, ionic surfactants and charged macromolecules.

The charge distribution at the solid/liquid interface is different from that in the bulk solution. The generally accepted Gouy–Chapman–Stern–Grahame (GCSG) model [8] describes this charge distribution (Fig. 1). The material's surface has the surface potential ψ_0 (and hence surface charge density σ_0) which is experimentally inaccessible. It is followed by the inner Helmholtz plane (IHP) that is made up of dissociated functional groups of the solid surface and partially hydrated, specifically adsorbing ions (mostly anions). The outer Helmholtz plane (OHP), compensating for the IHP charge, contains fully hydrated ions of opposite charge. These two layers form the electrical double layer. Extending into the bulk phase from the OHP is the diffuse Gouy and Chapman layer which allows diffusion of ions through thermal motion. The potential, ψ , decreases linearly from ψ_{IHP} to ψ_{OHP} , and then decays exponentially to zero in the diffuse layer. The zeta potential, ζ , is defined as the potential at the shear plane, so called because any relative movement of the surface with respect to the solution will cause some of the counter-ions to be

sheared off, that is, layers inside the shear plane are adsorbed and immobile. The zeta potential ζ is commonly used as the electrokinetic value that describes the surface charge properties and is used to compare materials. Although this potential is somewhat different from the actual surface potential it gives a realistic magnitude of electrical surface charge that interacts with its surroundings.

The relative motion between an electrolyte solution and a charged solid surface can result in one of the four electrokinetic effects: (1) electrophoresis, (2) electroosmosis, (3) sedimentation potential, or (4) streaming potential. The induced electrokinetic effects depend on the driving force and the nature of the solid and liquid phases. In the case of flat surfaces such as polymeric membranes, electroosmosis and streaming potential measurements are most appropriate for studying a stationary solid phase and a mobile liquid phase. Measuring streaming potentials is the most practical and convenient technique for flat surfaces or porous membranes, and superior to electroosmosis [9].

When an electrolyte solution is forced, by means of external pressure, through a capillary system (perpendicular flow through porous membrane) or across a flat channel (tangential flow across membrane), a streaming potential develops between the ends (Fig. 2). The hydraulic pressure causes movement of liquid and thus ions are stripped off along the shear plane, and a streaming current I_s is formed, Fig. 2(b). Due to a charge accumulation at the downstream side, an electrical field E is generated that causes a backflow of ions I_b (Fig. 2(c)) until a steady state is reached where $I_s - I_b = 0$ (Fig. 2(d)). The measurable potential difference between the two ends of the capillary system, the streaming potential E_s , gives direct information about the electrostatic charge at the EDL shear plane. The fundamental equation relating the measured streaming potential to the zeta potential is given by the well-known Helmholtz–Smoluchowski equation [8]:

$$\zeta = \frac{E_s}{\Delta p} \cdot \frac{\eta}{\varepsilon_r \cdot \varepsilon_0} \cdot \left(\kappa + \frac{2 \cdot \lambda_s}{r} \right), \quad (1a)$$

where E_s is the streaming potential, Δp the hydrodynamic pressure difference along the capillary, η the liquid viscosity, κ the liquid conductivity, ε_r the liquid permittivity, ε_0 the permittivity of free space, λ_s the surface conductivity and r the capillary radius.

The various terms in Eq. (1a) are known or must be measured. The ratio $E_s/\Delta p$ is determined by direct measurement of the streaming potential for a given, experimentally measured pressure drop. It has been suggested to measure the potential as a function of continuously increasing Δp for a significant increase in precision and repeatability of detection [10]. The values of η , ε_r and ε_0 are constant for the liquid used at a constant temperature. Eq. (1a) can be simplified for surfaces with low surface conduction by eliminating the surface conductivity term:

$$\zeta = \frac{E_s}{\Delta p} \cdot \frac{\eta \cdot \kappa}{\varepsilon_r \cdot \varepsilon_0}. \quad (1b)$$

In situations where surface conduction becomes important (i.e. at low electrolyte concentrations or/and charged surfaces) surface conduction must be considered. The concentration of ions in the electrical double layer is greater than their concentration in the diffuse layer. In situations when the electrolyte concentration is low or/and the surface charge is high the electrical resistance of the measurement liquid reaches a value comparable to that of the membrane surface. Thus, part of the back current flows over the surface which is not desirable (Fig. 2(e)). According to Briggs [11] and Fairbrother and Mastin [12] the conductivity term of Eq. (1a) can then be replaced by

$$\kappa + \frac{2 \cdot \lambda_s}{r} = \frac{k^h \cdot R^h}{R}, \quad (2)$$

where R^h is the Ohmic resistance across the capillary when the cell is filled with a liquid of high salt concentration (i.e. when the surface conduction can be assumed negligible, usually a 0.1 M KCl solutions is used), κ^h is the conductivity of this liquid and R is the measured resistance when the cell is filled with the measurement solution. $R^h \cdot \kappa^h$ can be considered to be the cell constant expressing l/A where l is the length of the capillary, and A its cross-sectional area. R is measured using an AC bridge. Eq. (3) is a combination of Eq. (1a) and Eq. (2):

$$\zeta = \frac{E_s}{\Delta p} \cdot \frac{\eta}{\varepsilon_r \cdot \varepsilon_0} \cdot \frac{\kappa^h \cdot R^h}{R}. \quad (3)$$

One of the prerequisites of Eq. (1a) is that the ratio of the capillary radius (when dealing with membrane surfaces this is equal to the pore radius) to the electrical double layer thickness must be large, which is

Fig. 2. Schematic representation of the development of the streaming potential at the solid/liquid interface along a membrane pore under pressure driven liquid flow.

not the case for many ultrafiltration membranes. The applicability of streaming potential measurements was substantially extended from the characterization of capillary surfaces (through pore or perpendicular flow measurements) to flat surfaces (across surface or tangential flow measurements) by the work of Van Wagenen and Andrade [14] who developed a flat plate flow system. Later a commercial system was developed on this basis (A. Paar GmbH, Graz, Austria). Assuming that the surface properties inside a mem-

brane pore are the same as on the outer surface, the tangential flow eliminates the drawback of the requirement for large pores. Fig. 3 shows a schematic representation of the tangential flow cell system that is used for streaming potential measurements. The streaming channel of well-defined and uniform dimensions is formed by a teflon spacer. The film material under investigation is placed above and below the spacer. The channel can be visualized to be an idealized macropore. The geometrical dimensions l/A of the

Fig. 3. Schematic diagram of the streaming potential measurement system (top) and cell principle (bottom).

teflon spacer cannot be used for calculation replacing $R^h \cdot \kappa^h$ in Eq. (2) because it has been shown previously that the geometrical dimensions of the streaming channel are sensitive towards the force that is used to clamp the cell halves together, as the teflon spacer is slightly compressible [13]. When zeta potentials are determined at different pH values, characteristic curves can be obtained for different types of materials as shown in Fig. 4.

3. Flow simulation inside tangential flow cell by a computational fluid dynamics simulation

3.1. General

For accurate streaming potential measurements Poiseuille flow is required, i.e. flow must be steady,

incompressible, laminar, and established. To verify the intended developed laminar flow characteristics of the cell being used for streaming potential measurements, a numerical simulation in two dimensions of its hydrodynamics was undertaken. The flow through the cell was simulated using a finite difference code based on the TURCOM package [15].

The version employed here is the same as detailed in a previous paper [16] where it was tested against various analytical results, and was able to obtain matching results under specific benchmark conditions. The code is based on the following governing equations expressed in tensor notation:

$$\text{Mass : } \frac{\partial p}{\partial t} + (\rho u)_{jj} = 0, \quad (4)$$

$$\text{Momentum : } \frac{\partial (\rho u)_i}{\partial t} + ((\rho u)_j u_i)_j = -p_{,i} + \tau_{ij,j}. \quad (5)$$

Fig. 4. Schematic representation of typical zeta potential profiles as a function of pH for different types of materials according to [5,8].

Above, $\tau_{ij,j}$ is obtained from

$$\tau_{ij,j} = \eta \cdot (u_{i,j} + u_{j,i}) - \frac{2}{3} \cdot \eta \cdot u_{k,k} \cdot \delta_{ij}. \quad (6)$$

Above, ρ and η are, respectively, the fluid density and viscosity, u_i is its i -direction velocity component, p is pressure, t is time, δ_{ij} is the Kronecker delta function and i, j and k are directional indices. The fluid was considered to be water at 25°C. The boundary conditions were determined based on the maximum volumetric flow rate of 0.8 ml/s. Any irregularities in the flow would be greatest at this highest flow rate. A simulation at 0.1 ml/s, the lowest operating flow rate within the applied pressure range from 30 to 400 mbar, was run and analyzed for completeness.

3.2. Cell geometry and simulation conditions

The feed section of the system under consideration is depicted schematically in Fig. 5. The entire cell is 165 mm long, with an exit configuration symmetric with the entrance shown in the figure. Of interest is the comparatively large tubular entry and exit channel of diameter 10 mm, which feeds into a narrow slit channel of cross-section 0.3 mm $\times$ 10 mm. The entry region

Fig. 5. Schematic of streaming potential cell geometry (top), and CFD boundary conditions (bottom).

will produce the largest vorticity since the fluid will accelerate substantially at constant volumetric flow rate.

For preliminary calculations a hydraulic Reynolds number Re_H can be used to describe the flow state in the narrow slit channel. A volumetric flow rate of 0.8 ml/s translates to an average velocity, $\bar{u} = 0.266$ m/s.

$$Re_H = \frac{D_H \cdot \bar{u} \cdot \rho}{\eta}. \quad (7)$$

For water, $\rho = 1000$ kg/m³ and $\eta = 0.001$ Pa s at 25°C. D_H is the hydraulic diameter, defined as, $D_H = 4A/P$ where A is the cross-sectional area of the channel, and P is the length of its perimeter. Thus, at $Re_H = 158$, the flow will be clearly laminar, and it is sufficient to simulate it as such.

In two dimensions, a horizontal plane simulation will not be able to show any meaningful entrance effects. The vertical cross-section however, shown in Fig. 5 can provide some useful information characterizing the flow properties of the different regions in the cell. The boundary conditions employed in the simulation and the flow region are depicted here. The cross-section of the feed tube is over 26 times larger than the narrow slit channel, and as such, the Reynolds number will be still lower. Thus, a fully developed parabolic laminar profile was imposed at the top side inlet. Such a profile follows the form

$$U = U_{MAX} \cdot \left(1 - \frac{r^2}{R^2}\right) \quad (8)$$

with r and R being the radius and tube radius, shown in Fig. 5. For such a profile, $U_{\text{MAX}} = 2\bar{U}$. Along the top surface, the above equation can be transformed to the tube width w , cut at an angle parallel to the x -axis. Thus,

$$U(x) = U_{\text{MAX}} \cdot \left(1 - \frac{(x - w/2)^2}{(w/2)^2} \right). \quad (9)$$

The x and y components are thus, $u(x) = U(x) \sin \phi$, and $v(x) = -U(x) \cos \phi$, where $\phi = 45^\circ$. The no-slip condition was applied to walls ($u=0$, $v=0$), and the zero-gradient condition of $\partial u / \partial x = 0$ was imposed at the exit. In two dimensions the cross-sectional area of the inlet tube was 33.3 times larger than that of the narrow-slit channel, so the value of U_{MAX} used was adjusted with this ratio.

A 42×32 grid was used to partition the flow field (not shown here). Additional grid lines are included over the narrow slit channel region to provide some flow field resolution there. The domain modeled included a 15 mm length of the inlet tube, the junction region and the 5 mm slit region behind the junction, as well as a 15 mm length of the narrow slit channel downstream from the junction. The transition effects of the flow passing from the wide inlet tube to the narrow slit channel are demonstrated in simulation results from this flow-field region.

3.3. Results

In Fig. 6 (top), a vector plot of the velocity field of the entire flow field is shown. There is a substantial acceleration into the narrow slit channel, proportional to the cross-sectional areas of the two regions. The velocities near the walls and in the slit region behind the junction are too small to show any vectors in Fig. 6 (top). The raw numerical data for the simulation shows that a back flow current exists in the narrow slit region behind the inlet tube, but at negligible velocities. The lead side exit produces a small leftward drift of the main flow stream in the inlet tube.

Fig. 6 (center) is an expanded view of the narrow channel entry region. Uniform flow is established in a short distance (~ 12 mm) along the narrow channel, with a laminar parabolic profile. The flow rates are sufficiently low that eddies, back flow or swirling regions are not created. Viscous mixing can possibly

Fig. 6. Vector plots as obtained from the CFD simulation.

be reduced at lower mean velocities, so a simulation was run at 0.1 ml/s, which is the low end of the operating range of this cell. The results are qualitatively nearly identical, and compared to the high end flow rate, uniform flow is established at a shorter distance of about 8 mm along the narrow channel. At the far right of the simulation domain, the velocity profiles in the narrow slit channel are also given in Fig. 6 (bottom). A parabolic profile exists here, with $u_{\text{MAX}} = 0.545$ m/s, a 2.4% deviation from the precise laminar condition of $U_{\text{MAX}} = 2\bar{U}$. Grid refinement, which was not attempted here, would no doubt reduce this discrepancy. For the purposes of validating the streaming potential measurements obtained in this cell, such a velocity profile satisfactorily demonstrates the fully developed laminar flow characteristics in the narrow slit channel. Of course, the cell is physically three-dimensional, so increased precision with a two-dimensional simulation is somewhat moot.

4. Zeta potentials of carboxylated polysulfone membranes

4.1. Experimental

4.1.1. Polymer modification and characterization

Udel P-3500 polysulfone was obtained from Amoco Performance Products, Netherlands and used as a

starting material in all carboxylations. Carboxylic acid polysulfone derivatives with degrees of substitution of 0.26, 0.51, 0.86, 1.00, 1.19 and 1.74 were prepared by a two-stage process of lithiation and carboxylation with dry ice as previously described [5]. The chemical structure and value of DS for modified polymers was determined by preparing methyl ester derivatives and using $^1\text{H-NMR}$ spectroscopy.

4.1.2. Membrane fabrication

Polymers were dried at 60°C under vacuum for at least 12 h. Casting solutions were made by preparing 20 wt% polymer solutions in 1-methyl-2-pyrrolidone (NMP), which was obtained from Aldrich and used as received. Ultrafiltration membranes were cast on an automated casting machine that allowed precise control of casting conditions. The solutions were cast onto a nonwoven polyethylene backing using a round bar having a $200\text{ }\mu\text{m}$ gap. The casting speed was 5.08 cm/s . The pregelled membranes were exposed to air (humidity $<15\%$, $T=20^\circ\text{C}$) for 20 s and then gelled into RO water at 3°C . Membranes were characterized by pure water flux and multiple solute permeation tests to determine their molecular weight cut-off separation performance. These results will be reported later.

4.1.3. Equipment and measurements procedure

A variable-speed pump drive (model 75225-05) with a cavity-style pump head (120 series) by Cole Parmer, USA, was used to generate a pulseless driving pressure to generate an electrolyte flow through the streaming channel, recirculating the feed. Pressure was measured using a pressure transducer (model 280 E, accuracy 1 mbar) by Setra, USA. Ag/AgCl electrodes were from Sensortechnik Meinsberg, Germany. A conductance meter (model 32) by YSI, USA, was used to measure conductivity and Ohmic resistance. The pH of the 0.001 M KCl solutions (all chemicals used were of pure analytical grade) was adjusted by adding small amounts of 1 M HCl or KOH and measured using a pH-meter by Orion (model 230A), USA. A thermostat maintained the feed electrolyte solution at 25°C . A digital voltmeter by Voltcraft, Germany, was used to measure the streaming potential.

The membrane under investigation was always soaked overnight in 0.001 N KCl solution to equilibrate it with the measuring solution. The polymeric

films were placed above and below the $300\text{ }\mu\text{m}$ teflon spacer with the membrane top surfaces facing the flow channel. After clamping the cell halves together firmly, the electrolyte solution was pumped through the cell and an equilibrium streaming potential was reached after about 2 min. A minimum of 10 pressures differences was used to cover a pressure range from 50 to 300 mbar to generate the streaming potential versus pressure curve and obtain the value of $E_s/\Delta p$ from linear regression. After the pure 0.001 N KCl measurement, the pH was always adjusted to the basic end of the pH scale under investigation, followed by a stepwise lowering of the pH. R was measured for each pH when there was no liquid flow using an AC bridge. At the end of each measurement series the cell was filled with 0.1 M KCl solution to measure R^h and κ^h of the cell for the Fairbrother/Mastin correction. All measurements were repeated at least three times. Results were reproducible within 10%.

4.2. Results and discussion

For evaluation of the surface properties of the membranes made from polysulfone and carboxylated polysulfones of different degrees of substitution, the zeta potentials were determined as a function of pH in 0.001 M potassium chloride solution. The zeta potentials were calculated using both Eq. (3) and Eq. (1b), i.e. considering surface conduction in the former case and neglecting it in the latter. Fig. 7 shows the zeta potential versus pH curves for all the materials under investigation using Eq. (3).

A discussion of the results must consider both the profiles of the curves obtained and the magnitude of the zeta potential values. Plain, unmodified polysulfone exhibits the characteristic profile for non-ionic surfaces (see Fig. 4). The surface charge of the plain PSU samples is slightly positive at pH values <4 and increasingly negative with growing pH until it reaches a plateau value of -52 mV between pH 8 and 10. A pH value of 4.0 is the isoelectric point of this PSU membrane surface in this particular ionic system. This reflects the higher ionic adsorption potential of anions resulting in preferential anionic adsorption due to their weaker hydration. Specific ionic adsorption is the only process possible for surface charge formation of the PSU samples as PSU has no dissociable functional groups. The magnitude of the zeta potentials obtained

Fig. 7. Zeta potentials calculated with Eq. (3) considering surface conduction as a function of pH for UF membranes made from carboxylated polysulfones (PSU-COOH) of different functionality, measured in 10^{-3} M KCl, $p=50\text{--}300$ mbar.

for this material by the tangential flow technique is somewhat larger than values obtained by others from perpendicular flow streaming potential measurements of commercial polysulfone UF membranes [9,17]. As mentioned above, the influence of small pores is most likely responsible for this behavior and leads to an underestimation of the true zeta potential of the surface. For a 0.001 M KCl solution, the Debye length of the electrical double layer is 10 nm on each wall side of a cylindrical pore. The radii of UF membrane pores are fairly narrow ranging from 2 to 10 nm diameter and it is very likely that the thickness of the electrical double layer is larger than the radius of the pore. This results in double layer overlapping. Therefore the streaming potential cannot fully develop and the true surface charge is underestimated by the perpendicular flow streaming potential measurement technique. This is supported by new results [18,19] which demonstrate the dependence of electrokinetic results on the pore size using the perpendicular flow measurement technique.

The profiles of the ζ -pH-curves for the PSU-COOH samples are typical for weakly acidic materials (Fig. 4) and they are in accordance with former results [20]. All values are negative and show plateau values in the basic pH region between -48 mV for the lowest DS and -20 mV for the highest DS investigated. All curves show plateaus at basic pH values. At the acidic end of the pH scale the ζ -potential curves become more flat as the DS increases, reflecting the expected growing control of the COOH group over the membrane's electrokinetic behavior. Besides specific ionic adsorption the dissociation of the COOH group plays an important role in the formation of surface charge of these materials. Both processes are competitive. With increasing degree of substitution the dissociation becomes increasingly important which is reflected by the flattening of the curves at low pH values. It is interesting to note that the sign of charge of these materials cannot be reversed at low pH values in contrast to the PSU sample. Two possible explanations can be given for this. On one hand this shows the different adsorption potential of the present electrolyte ions towards these modified surfaces. One must not forget that a different composition of the electrochemical double layer will always result in different zeta potentials. Apparently it takes higher concentrations of cations (especially hydronium ions) to displace adsorbed anions. However, it is more likely that the negative surface charge of these materials at low pH values is caused by dissociated COOH groups. This may be surprising from a chemical standpoint.

However, Edwards et al. [21], in studying the acidity of NOM (natural organic matter), found the deprotonation of COOH groups to be more complex than it appears. They found that strongly acidic functional groups (COOH groups that are still deprotonated at pH 3.0) are a significant portion of the total acidity in samples of organic matter. These groups are considered to be COOH groups whose acidity is enhanced by adjacent functional groups. Other COOH groups remained protonated up to pH values as high as pH 8.0. This "staggered" deprotonation can easily be assumed for the PSU-COOH samples with the adjacent SO_2 group that is a known functional group to increase acidity of adjacent dissociable groups.

Another finding is more difficult to explain: the zeta potential plateau values of the PSU-COOH samples obtained from Eq. (3) show decreasing absolute

values with increasing DS as shown in Fig. 8. Jacobasch et al. [22] found a similar result for sulfonated polyethersulfone hemodialysis membranes. The four

Fig. 8. Zeta potential plateau values considering surface conduction as a function of degree of substitution for membranes made from polysulfone (○ DS=0) and carboxylated polysulfones (■ PSU-COOH).

Fig. 9. Zeta potentials calculated considering surface conduction (filled symbols) and neglecting it (open symbols) as a function of pH for UF membranes made from polysulfone and carboxylated polysulfones (PSU-COOH) of different low DS, measured in 10^{-3} M KCl, $p=50$ –300 mbar.

different sulfonated samples (very low degrees of substitution from 0.075% up to 1.050%) they studied showed decreasing absolute values with increasing DS over the entire pH range from 3 to 10. They assume that the extraordinary hydrophilicity of the sulfonic acid groups increases the thickness of the swelling layer concerned with the membrane's surface. As a result, the shear plane is moved towards the solution bulk and, thus, eventually a lower zeta potential is measured. This could well be an explanation for our findings, too. The hydrophilicity of the carboxylated samples is beyond any doubt. This is supported by water absorption measurements on a wide range of carboxylated polysulfones [5]. It was demonstrated that the introduction of the carboxyl groups increased the water take up of the entire set of samples with varying DS, PSU-COOH 1.90 showed a 12-fold increase in water absorption compared to unmodified PSU. Thus, this increasing hydrophilicity and extension of the swelling layer leads to a shift of the electrokinetic shear plane resulting in lower zeta potential plateau values with increasing DS.

Fig. 10. Zeta potentials calculated considering surface conduction (filled symbols) and neglecting it (open symbols) as a function of pH for UF membranes made from carboxylated polysulfones (PSU-COOH) of different high DS, measured in 10^{-3} M KCl, $p=50$ –300 mbar.

The necessity of using Eq. (3) is clearly indicated in Figs. 9 and 10. It is instructive to compare both the zeta potentials that were calculated considering surface conduction (values calculated with Eq. (3)) and those that were computed by neglecting this effect using Eq. (1b). Even for unmodified polysulfone, a significant surface conduction contribution can be observed. Eq. (1b) gives smaller absolute zeta potential values for all materials. From Fig. 2(e) it becomes clear that I_b and therefore E_s would be smaller if the surface conducted a significant portion of the ions back to the high pressure end and thus ζ would be underestimated. It is also evident that the relative difference between the corrected and the uncorrected values is smaller at low pH values. The reason is that most of the COOH groups are not dissociated at low pH values and the resistance of the surface should be higher resulting in a smaller fraction of the back current flowing over the surface. Surface conduction is more pronounced when all COOH groups are in the ionic state, and thus, electrical surface resistance is low.

5. Conclusions

Given the cell geometry and operating conditions together with preliminary calculations and numerical simulation results, it can be confidently stated that the unit operates in a fully developed laminar flow regime along the narrow slit channel, at distances greater than about 12 mm from the inlet and outlet tubes. The maximum volumetric flow rate of 0.8 ml/s which passes the measurement streaming channel was employed for these tests. At flow rates less than this, the flow behavior is very similar, and the length over which laminar flow becomes fully established is shorter.

The zeta potentials of membranes made from polysulfone and carboxylated polysulfones of six degrees of substitution ranging from 0.26 to 1.74 were determined in a tangential flow mode cell. The zeta potentials of all membranes for pH 3–10 were negative except for the unmodified material that showed a positive surface charge at low pH. While the zeta potentials of unmodified PSU exhibit a clear pH-dependency this becomes less and less pronounced for the carboxylated samples with increasing DS. This

is attributed to the growing influence of COOH dissociation and a decreasing specific ion adsorption process on the surface charge formation. The fact that some COOH groups are still deprotonated is explained with a complex deprotonation process. The zeta potential plateau values in the basic pH region ranged from –20 to –52 mV. They decrease continuously with increasing DS. It is suggested that this could be attributed to a shift of the electrokinetic shear plane into the bulk electrolyte solution due to an extended swelling layer for higher DS polymers reflecting their enhanced hydrophilicity. Therefore the profile of the ζ versus pH curves and the magnitude of the plateau values generated by streaming potential measurements can give valuable hints about the chemical nature and the hydrophilicity of membrane surfaces.

Evaluation of the link between increased hydrophilicity and ultrafiltration behavior of these membrane surfaces will be reported separately.

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