Colloids and Surfaces, 36 (1989) 297–312
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

Streaming Potential as a Tool in the Characterization of Ultrafiltration Membranes

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(Received 28 July 1988; accepted 4 January 1989)

ABSTRACT

An apparatus for the measurement of streaming potential versus pressure relationships of ultrafiltration membranes is presented. Results for three types of membranes of various pore sizes at different pH, and ionic strengths are reported. The data have been used to calculate apparent values for zeta potentials of the membranes and the possibility to compare these values to the true zeta potentials is discussed. The influence of modification, the presence of small charged ions and charged polyelectrolytes on the apparent zeta potentials of the membranes has been measured. Finally the effects of the surface charges of the membranes, characterized by their apparent zeta potentials, are illustrated by ultrafiltration experiments performed with chlorolignin and whey protein.

INTRODUCTION

In ultrafiltration (UF) the permeate flux decline strongly depends on the adsorption of solute components on the membrane surface. This phenomenon often called fouling is usually caused by large molecules such as proteins [1,2] and promoted by small ones such as Ca^{2+} ions [3]. Fouling is most often an undesirable phenomenon as it decreases the flux of permeate through the membrane [4]. However, sometimes fouling may not be inconvenient, if the adsorbing component only builds up a thin modifying layer on the surface of the membrane. This layer may give the membrane such favorable properties as better retention, raised hydrophilicity or a more suitable surface charge density [5]. An important factor in UF is the strength and direction of the interaction forces between the macromolecules in solution and the surface layer of the membrane. The electrostatic component of these forces strongly depends on the charge density of the membrane surface and its pores, which is important to know in order to predict the amount of fouling caused by adsorption

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[6]. Surface charge density is related to the zeta potential of the membrane, which in principle can be calculated from streaming potential data.

The purpose of this paper is to present the construction of an inexpensive apparatus for streaming potential measurements of UF membranes equipped with all-electronic sensors analog-to-digital conversion of signals and digital signal processing implemented around an ordinary home computer, and to give and interpret the streaming potential data obtained for a number of commercial UF membranes. The measurements were carried out both with virgin and fouled membranes at different pH and ionic strengths.

THEORY

When electrolyte solution is forced to flow through a capillary or porous plug by means of hydraulic pressure, a streaming potential, ΔE, across the flow path is generated. The relation between this measurable quantity and the zeta potential, ζ, which is most often used to characterize the charge density of the steady interfacial layers, is given for a capillary by the well-known Helmholtz–Smoluchowski equation [7].

$$\frac{\Delta E}{\Delta P}=\frac{\epsilon_o \epsilon_r \zeta}{\eta \kappa} \tag{1}$$

In Eqn (1) ΔP is the hydraulic pressure across the capillary, ϵ_o the permittivity of vacuum, ϵ_r the relative dielectric constant of the solvent, η the viscosity and κ the conductivity of the solution.

Equation (1) can be applied only in an ideal case. In fact, a great number of phenomena interfere in the formation of the measured streaming potential. The influence of surface conductivity of the capillary was first studied by Stock [8], who introduced the correction term given in Eqn (2) where λ_s is the surface conductivity, and R the radius of the capillary.

$$\frac{\Delta E}{\Delta P}=\frac{\epsilon_o \epsilon_r \zeta}{\eta(\kappa+2\lambda_s/R)} \tag{2}$$

Later Rice and Whitehead [9] suggested, that at least for narrow capillaries, a correction in Eqn (1) should be made which takes into account the double layer thickness, r_{DH}, on the interface. As a result of solving the appropriate Poisson–Boltzmann equation they obtained

$$\frac{\Delta E}{\Delta P}=\frac{\epsilon_o \epsilon_r \zeta}{\eta \kappa_{cap}} \cdot F(R/r_{DH}) \tag{3}$$

In Eqn (3) κ_{cap} is the conductivity of the liquid in the capillary and the correction function F approaches the value 1 at the limit $R/r_{DH} \to \infty$. The proper correction of Eqn (1) should also depend on the fixed charge on the capillary

wall. However, Rice and Whitehead did not consider this fixed charge or the surface conductivity, in their derivation of Eqn (3). Later Oldham et al. [10] suggested a numerical solution of the same problem, which also takes into account these phenomena. The problem has subsequently been thoroughly studied by Levine et al. [11] and Anderson and Koh [12].

In addition Hildreth [13] has pointed out the importance of the presence of a distributed conductance across the capillary channel and the difference in the ionic mobilities of the co-ions and the counter-ions of the fixed charge.

Reports on streaming potential measurements of membranes are not abundant. Some work has been done with microfiltration (MF) membranes [14,15] and also with reverse osmosis (RO) membranes [16–18]. In the paper of Broz and Epstein [14] the zeta potentials were also calculated and corrected according to Rice and Whitehead, but the results suffer from difficulties caused by retardation effects due to high applied pressures. The authors of the other available reports on MF and RO do not try to calculate zeta potentials or base the calculations on the most simple equation, Eqn (1).

Neither the conditions in MF nor in RO resemble those in UF. In UF membranes the pores are very narrow and the thickness of the double layer may be even larger than the radius of the pore, which results in double layer overlapping. This is usually not the case with MF membranes. In UF we still have convective flow, which is not the case in RO.

The conditions inside an UF membrane somewhat resemble the conditions inside a bunch of ideal capillaries. However, a shape factor is often included in the calculation of the zeta potential to allow for the asymmetry of the pores. Some experimental work has been done with collodion (cellulose nitrate) membranes [19,20]. Zhukov and Fridrikhsberg have found that the values of the zeta potentials of pores of different sizes merge as the ionic strength increases [20]. The dependency of the zeta potential on the ionic strength clearly differs for pores with radii smaller than 25 nm (UF membranes) from that for pores with radii greater than 98 nm (MF membranes). In the first case the nominal value of the zeta potential increases with ionic strength and pore size, while in the latter case the zeta potential decreases with increasing ionic strength.

EXPERIMENTAL

Apparatus

The streaming potential measurements were carried out with the experimental setup depicted in Fig. 1. The streaming potential measurement cell (SPMC) was made of polycarbonate and it consisted of two parts between which the membrane was fixed by means of rubber seals. A pair of Ag/AgCl electrodes were located on both sides of the membrane. The first electrode was

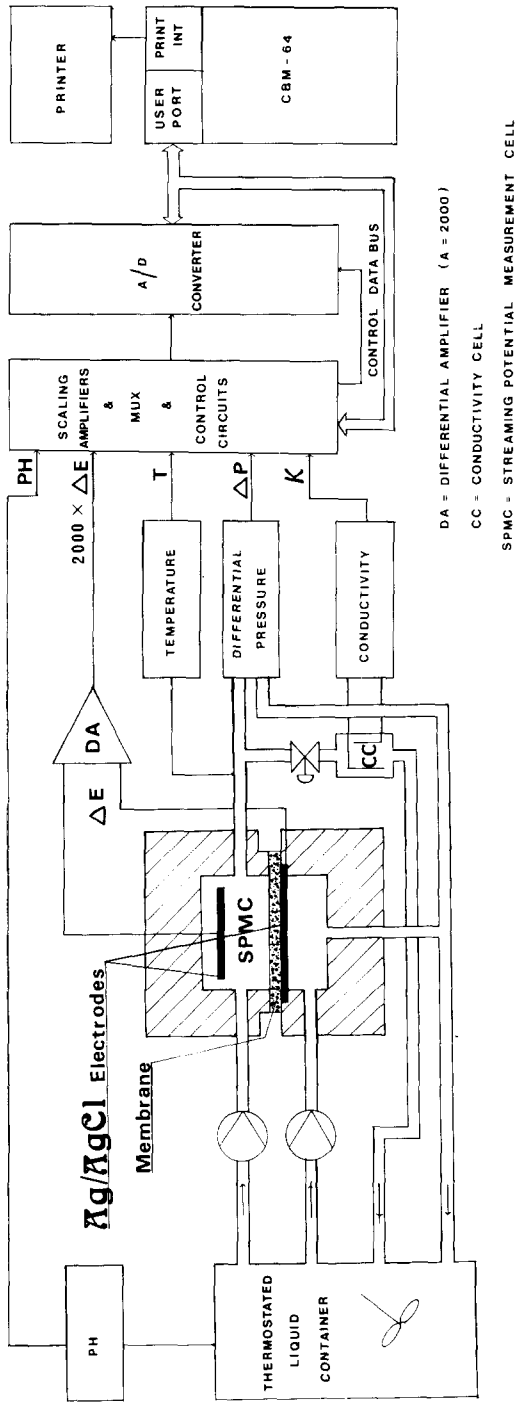

Fig. 1. Experimental setup for streaming potential measurements.

a perforated plate placed beneath the membrane as a support, the second one was a wire coil located above the membrane. The electrodes were prepared with anodic deposition of chloride on silver from 0.1 *N* HCl solution at a current density of 0.4 mA cm^{-2} [21].

Thermostated test solution was circulated on both sides of the membrane with a peristaltic pump. The pressure difference across the membrane, ΔP, (0–70 cm H_2O) was regulated manually by the valve shown in Fig. 1, and measured by means of a differential pressure sensor (Honeywell, 162 PC01D). Temperature was measured with a temperature sensor (Analog Devices Inc., AD 590 JH), pH with a pH-meter (Wissenschaftlich Technische Werkstätte, pH 521, Ingold U455 electrode) and conductivity with the flow-through conductivity cell CC.

The measured signals were amplified with circuits implemented with ordinary high quality operational amplifiers and converted to binary code with a 12-bit analog-to-digital converter in order to be further data processed. A Commodore 64 computer was used in data processing.

For each ΔP all the parameters were measured 20 times and their averages recorded. This sequence was repeated every minute at least ten times. Then a new pressure, ΔP, was set manually and the procedure repeated. The program controlled automatically that $\Delta E/\Delta P$ had reached a steady value, and that the possible asymmetric potential between the Ag/AgCl electrodes did not change. If the deviation from linearity was small enough the best regression line for ΔE versus ΔP was calculated. From the slopes of these lines apparent zeta potentials were then calculated according to Eqn (1).

Before each sequence of measurements fresh solution was first circulated for at least 1 h on both sides of the membrane in order to stabilize the system.

The streaming potential strongly depends on the ionic and on the adsorption properties of the membrane material. Therefore, the membrane materials were studied at different pH. As only low values of ΔP were used, the streaming potential could not be measured accurately enough at pH values less than 2.5 because of the high ionic strength of such solutions. On the other hand, at pH values > 7 the Ag/AgCl electrodes suffered from the alkalinity of the solution. The actual range of pH in the measurements therefore was from 2.5 to 7.

Membranes

Unmodified membranes

Commercial membranes from De Danske Sukkerfabrikker (DDS) were studied. The characteristics and other available data for the membranes are given in Table 1.

Before experiments the membranes were cleaned to remove preservatives by filtering water through them until the conductivity of the permeate remained below 1 $\mu S\ cm^{-1}$.

TABLE 1

Properties of DDS membranes used in the experiments. Average pore radii are given by Jonsson [22,23]. The pore size distributions of the membranes were not known

Type	Material	Average pore radius (nm)	Cut-off	Character of the membrane
GR 51 PP	Polysulfone	< 10	50 000	hydrophobic, non-ionic
GR 61 PP	Polysulfone	2-6	20 000	
GR 81 PP	Polysulfone	2	6 000	
GS 61 PP	Sulfonated polysulfone	2-6	20 000	hydrophilic, ionic
GS 91 PP	Sulfonated polysulfone		1 500	
FS 61 PP	Modified polyvinylidene fluoride	2-6	20 000	slightly hydrophilic

Modified membranes

A polysulfone UF membrane (GR 61) was irradiated with UV light (Hanau, TNN15-32001721, E5) for 1 h in a solution of 0.2% chloroform in ethanol. Then the membrane was washed with water. After streaming potential measurements the modified membrane was further modified with an aqueous solution of polyethyleneimine (PEI) (50 ppm) by circulating the PEI solution only on the surface side of the membrane.

Chemicals

All the electrolytes used for regulation of ionic strength (KCl, NaCl) and pH (KOH, HCl) were of p.a. grade.

The water used was distilled, ion-exchanged, and ultrafiltered (GS 91) until its conductivity was less than 1 μS cm^{-1}.

Chlorolignin

The chlorolignin fraction used as a test sample in the experiments was isolated from pine kraft pulp bleach effluent, which was obtained from the first alkaline extraction stage, E_1, of Kymmene Co. Kaukas Mills, Lappeenranta. The details of the fractionation are described in an earlier publication [24]. Chlorolignin is a somewhat undetermined mixture of anionic polyelectrolytes, which contains a certain amount of carboxylic and other acidic groups. The point of zero charge of the test sample, p.z.c., was approximately at pH 3.5 and according to potentiometric titration dissociation of the acidic groups is complete at pH $\approx$ 9.

Polyethyleneimine

Polyethyleneimine (PEI) is a cationic polyelectrolyte. Its p.z.c. is at pH 10.8 and its association with H^+ ions is completed at pH $\approx$ 3. The stock PEI solution used in the experiments was supplied by BASF (Polymin SK, 25% solution, $\bar{M}_w = 1\,300\,000$ g mol^{-1}; $\bar{M}_n < 16\,000$ g mol^{-1}).

Whey protein

The whey protein used was WHEY PRO-80 supplied by Denmark Proteins A/S, Viby, Denmark. This is an undenaturated whey protein concentrate produced from whey by ultrafiltration and spray-drying. The isoelectric point of the major protein constituents of whey is in the pH range from 4.2 to 5.5.

RESULTS AND DISCUSSION

Streaming potentials at different ionic strengths and pore sizes

The typical ΔE versus ΔP curves obtained with the membranes tested at all different concentrations of KCl used indicate that no such retardation effects as those reported by Broz and Epstein [14] could be detected, presumably because the applied pressures, ΔP, remained low enough. The nominal values of the parameter $\Delta E/\Delta P$ increase monotonically as the electrolyte concentration decreases. This is in accordance with measurements carried out with other charged membranes [21]. The $\Delta E/\Delta P$ values and the corresponding apparent values of the zeta potentials [as calculated from Eqn (1)] are given in Table 2 for the GR 51 and the GS 61 membranes. One can see that the nominal values of the apparent zeta potentials of the polysulfone membrane (GR 51) increase

TABLE 2

Apparent zeta potentials of the GR 51 and the GS 61 membranes calculated from the corresponding streaming potential–pressure relationships according to Eqn (1) for different concentrations of KCl

KCl conc. (mol dm^{-3})	GR 51 membrane		GS 61 membrane		Calc. double layer thickness (nm)
	$\Delta E/\Delta P$ (mV m^{-1}H$_2$O)	ζ (mV)	$\Delta E/\Delta P$ (mV m^{-1}H$_2$O)	ζ (mV)	
$5\cdot10^{-5}$	−19.03	−1.15	-	-	43
$1\cdot10^{-4}$	−11.31	−2.15	-	-	30
$2.5\cdot10^{-4}$	− 5.76	−2.70	−10.35	− 4.8	19
$5\cdot10^{-4}$	− 2.80	−2.70	− 5.94	− 6.2	14
$1\cdot10^{-3}$	− 1.94	−3.75	− 4.26	− 8.7	10
$5\cdot10^{-3}$	− 0.39	−3.75	− 1.43	−13.0	4
$1\cdot10^{-2}$	− 0.19	−3.50	− 0.80	−14.0	3

with increasing concentration of KCl up to about 0.001 M KCl. Above this concentration they remain almost constant. This phenomenon can possibly be explained by the fact that at small ionic strengths the double layer is thicker than or at least of the same order of thickness as the radius of the pores and obviously no electroneutrality at all exists in the pore. At higher ionic strengths electroneutral channels in the pores are presumably formed.

The nominal values of the apparent zeta potentials of the GS 61 membrane increase monotonically with increasing ionic strength. Because the average cut-off value of the GS 61 membrane is smaller and the predicted net surface charge higher than those of the GR 51 membrane one can suppose that the conditions for electroneutral channel formation are not yet fulfilled at $C_{KCl} = 1 \cdot 10^{-2}$ mol dm^{-3}.

In Fig. 2 are depicted the results obtained for three polysulfone membranes of different cut-off values at $C_{KCl} = 5 \cdot 10^{-4}$ mol dm^{-3} and at constant pH and temperature. It is obvious that the nominal value of the ratio $\Delta E/\Delta P$ decreases along with the cut-off value. This phenomenon has been explained by the influence of surface conductivity in microcapillaries [8], but, according to the preceding discussion, is more likely due to double layer overlap.

One usually assumes that the true zeta potential of the membrane is independent of the pore size of the membrane and that it is determined only by the membrane material. In the experiments described above surface conductivity and the influence of the double layer were not taken into account. If the corrections predicted by Oldham [10] or Rice and Whitehead [9] are made the calculated true zeta potentials become some 10 times larger than those given in Table 2, and correspond better at higher electrolyte concentrations with the

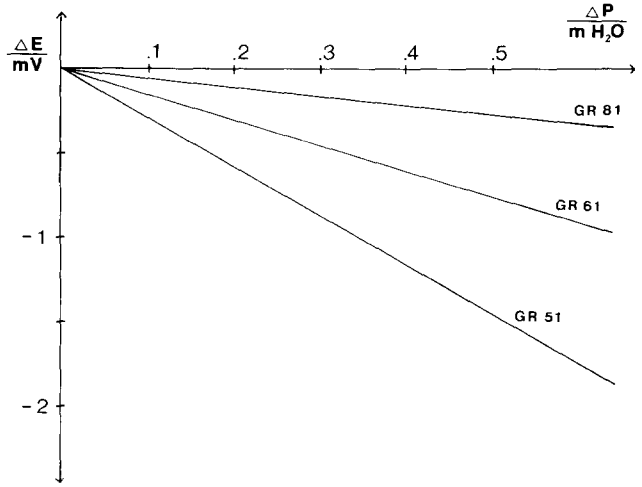

Fig. 2. Streaming potential, ΔE versus ΔP curves for polysulfone ultrafiltration membranes of different cut-off values. KCl concentration $= 5 \cdot 10^{-4}$ M; pH ≈ 5.5; T = room temperature.

values of the zeta potentials of the polymer materials used measured by other means [25].

Corrections resulting from surface conductivity influence the calculation of zeta potentials very little when the surface charges of the membranes remain low or the ionic strength of the solution is rather high. As the corrections mentioned above do not in fact take into account all the phenomena connected with measurements of zeta potentials in membrane pores of various sizes and do not explain the results fully, the zeta potentials given below were calculated from Eqn (1). Therefore they are not true zeta potentials and must be taken as apparent.

Apparent zeta potentials at various pH

Unmodified membranes

In Fig. 3 apparent zeta potentials are presented at various pH for the three different membrane materials studied. One can see that all the membranes studied possess either a negative zeta potential or none at all in the pH range studied. The sulfonated polysulfone membrane possesses an almost constant negative net zeta potential in the measured pH range, which can be explained by the almost fully developed dissociation of the sulfonic acid groups of the membrane material.

The pH-dependency of the apparent zeta potentials of the polysulfone and the polyvinylidene fluoride membrane resemble each other. The net charges of both membranes are negative from about pH 3.5 to pH 7 and increase first with increasing pH but then level off at pH values > 5. As the membrane materials are not ionic in nature this effect most likely results from specific adsorption of negative ions on the membrane surface from the circulating solution.

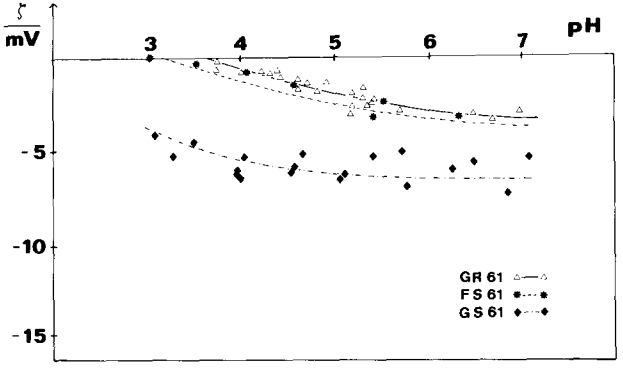

Fig. 3. Apparent zeta potentials versus pH for ultrafiltration membranes of different polymer materials calculated from streaming potential data according to Eqn (1). Polysulfone membrane, GR 61, polyvinylidene fluoride membrane, FS 61, and sulfonated polysulfone membrane, GS 61.

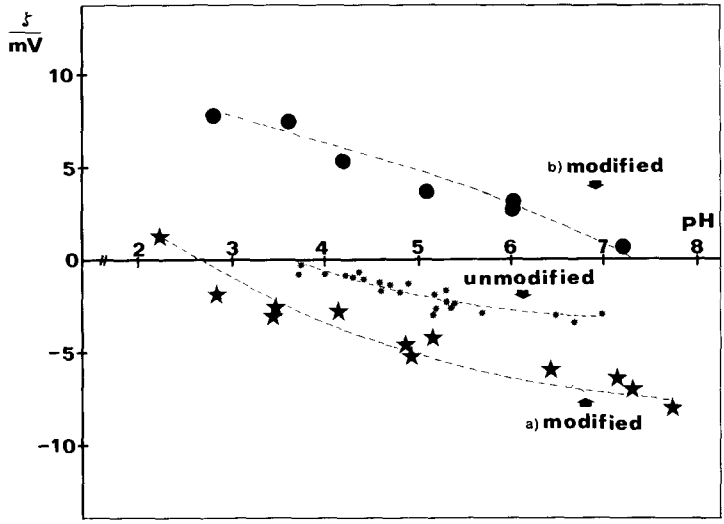

Fig. 4. Influence of modification on the apparent zeta potentials of ultrafiltration membranes. The apparent zeta potentials versus pH were calculated from streaming potential measurements by means of Eqn (1) for an unmodified polysulfone GR 61 membrane, (a) a GR 61 membrane modified with UV irradiation in a solution of 0.2% chloroform in ethanol and (b) the latter membrane further modified with 50 ppm PEI solution.

Modified membranes

In order to alter the surface charge of the UF membranes some modification experiments with the GR 61 membrane were carried out in the way described above. In Fig. 4 are depicted the apparent zeta potentials versus pH for the GR 61 membrane first modified in UV with chloroform in ethanol and then again with a 50 ppm PEI solution. For comparison also the curve of the unmodified membrane is given. One can see that the first modification lowers the apparent zeta potential of the membrane but the shape of the curve remains almost the same as with the unmodified membrane. This effect may result from pore size enlargement or formation of weak acidic groups during the irradiation period. No confirming spectroscopic analyses of the nature of the formed surface groups were made.

The curve of the membrane modified with PEI shows how the charge of the adsorbed PEI molecules determines the value of the zeta potential. The PEI molecule, being positively charged at pH < 10.8, contributes a net positive charge to the membrane, which increases along with pH decrease.

Influence of Ca^{2+} ions on the apparent zeta potentials

In order to see how small multivalent ions interact with the membranes at different pH values some experiments were carried out with solutions contain-

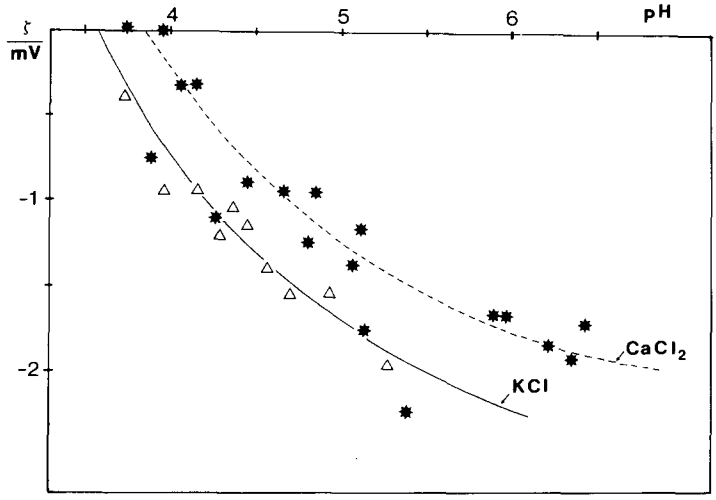

Fig. 5. Influence of Ca^{2+} ion adsorption at different pH on the apparent zeta potential of the polysulfone GR 61 membrane. Apparent zeta potentials versus pH were calculated from streaming potential measurements according to Eqn (1). (——) Reference curve, measurements made with $2.5 \cdot 10^{-4}$ *M* KCl solution. (— — —) Measurements made with $2.5 \cdot 10^{-4}$*M* $CaCl_2$ solution.

ing small amounts of calcium ions. The results are depicted in Fig. 5. As expected, most probably some adsorption of Ca^{2+} ions takes place, which increases the value of the zeta potential. This adsorption seems to take place in the whole pH range studied and therefore explains the importance of calcium removal in the UF of, e.g., whey protein [3], where the adsorbed positive calcium ions promote fouling. The experiments with the Ca^{2+} ions were carried out before the measurements with pure KCl. The results therefore ensure that the adsorption of calcium is reversible as the apparent zeta potential of the membrane returns to its normal value after Ca^{2+} ion removal.

Influence of chlorolignin on the apparent zeta potentials

The UF behavior of chlorolignin is of great practical importance in the possible color removing treatment of bleach effluents. The size of the chlorolignin molecule is so small that it should pass the pores of the UF membranes studied but according to UF experiments the retention of chlorolignin is surprisingly good especially in the pH range where it is fully dissociated.

In this study some experiments were carried out where streaming potentials of membranes in contact with solutions of different concentrations of chlorolignin and KCl were determined. The results from such experiments with a sulfonated polysulfone membrane (GS 61) are depicted in Fig. 6. From this figure one can deduce that the chlorolignin strongly lowers the apparent zeta

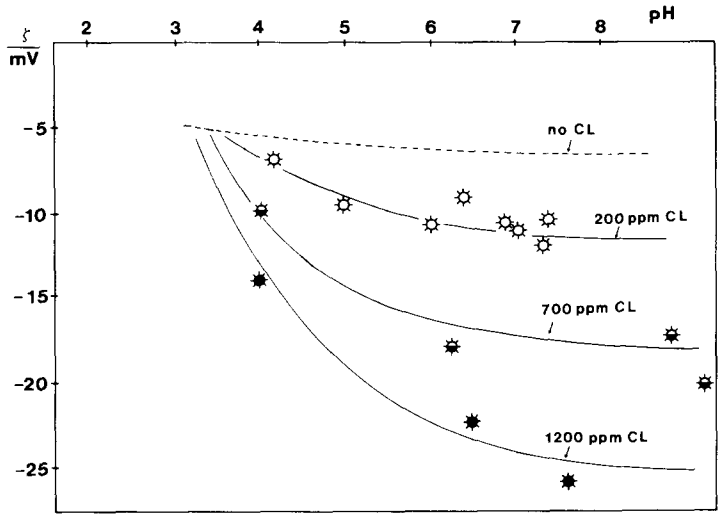

Fig. 6. Apparent zeta potential versus pH of a sulfonated polysulfone membrane, GS 61, at different concentrations of chlorolignin (CL) in the solution. Apparent zeta potentials were calculated from streaming potential measurements according to Eqn (1). pH and concentration of chloride ions ($5 \cdot 10^{-5}$ *M*) were adjusted by KCl and HCl or KOH.

potential of the membrane in the pH range where chlorolignin itself is negatively charged. The adsorption of chlorolignin on polysulfone membranes has been verified to decrease at higher pH values by in situ adsorption measurements with a quartz crystal microbalance [24] as the negative net charge of the chlorolignin molecules increases, although the apparent nominal zeta potential of the membrane increases with pH. This is most probably also the case with sulfonated polysulfone membranes. The fact that the apparent zeta potential of the sulfonated polysulfone membrane decreases considerably when chlorolignin is present, most probably results from the fixed negative charge of the small number of slowly moving chlorolignin molecules, which are able to penetrate into the pores of the membrane and give raise to a higher steady negative charge inside the pore.

Influence of the membrane charges on the UF results

Knowing the charge of an UF membrane is of great practical importance when one has the possibility to choose between a number of candidate membranes and adjust the pH of the solution to be ultrafiltered. Strong electrostatic repulsion between membrane and solute molecules enhances retention and permeate flux. In Fig. 7 are depicted curves for flux reduction [1− (flux of permeate)/(flux of pure water)] and retention [1− (conc. of chlorolignin in permeate)/(conc. of chlorolignin in bulk solution)] versus pH in ultrafiltra-

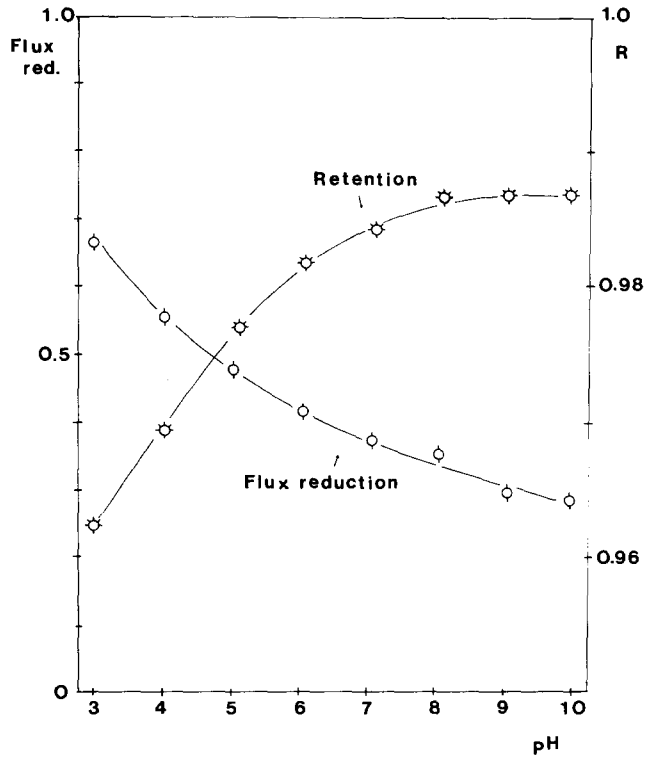

Fig. 7. Flux reduction and retention versus pH in ultrafiltration of an aqueous solution of 0.3% chlorolignin with the sulfonated polysulfone membrane, GS 61. $\Delta P = 3$ bar, $T = 25\,^{\circ}$C.

tion of chlorolignin with the anionic GS 61 membrane, at the pressure 3 bar in a plane UF module described in detail elsewhere [24]. As both the chlorolignin molecules and the membrane are negatively charged above pH 3.5 electrostatic repulsion prevails between them. Flux reduction takes the smallest values at pH > 9 where chlorolignin is completely dissociated. At pH values < 6 the electrostatic repulsion diminishes and flux reduction increases gradually to a rather high value at pH 3 as the chlorolignin molecules become neutral and the negative charge on the GS 61 membrane diminishes as well. Also retention is influenced by this phenomenon. When the chlorolignin molecules are completely dissociated the surface and pores of the membrane repel them and the molecules can scarcely pass the pores, although the molar mass of chlorolignin is smaller than the nominal cut-off value of the membrane. On the contrary, the neutral molecules can pass the membrane rather easily as the electroviscous effect is small and the molecules are more compact due to the lack of opening of the chains by electrostatic repulsion.

In Fig. 8 the influence of whey protein adsorption on flux for the GS 61 and

GR 61 membranes at different pH is illustrated. The experiments were performed in a standard circular ultrafiltration batch cell (2.5 cm in diameter) described in detail elsewhere [26] at $P=2.5$ bar and $T=25\,^{\circ}C$. Flux was measured for pure buffer solution before and after the membranes had been exposed to protein solutions (0.4 g protein/100 ml) at different pH for 1 h in a depressurized batch cell. The reduction in flux due to adsorption of proteins is presented in terms of relative flux reduction [1 – (flux after adsorption)/(flux before adsorption)].

Above pH 5, where both the protein and the membranes are negatively charged, relative flux reduction is not as high for the GS membrane as for the GR one. This could be explained by the fact that the GS membrane has a higher negative charge density in this pH range (see Fig. 3) and is therefore less prone to adsorption due to stronger electrostatic repulsion compared with the GR membrane.

On the other hand, at lower pH (pH 3–4), where the proteins below their isoelectric points are positively charged, the apparent zeta potentials from Fig.

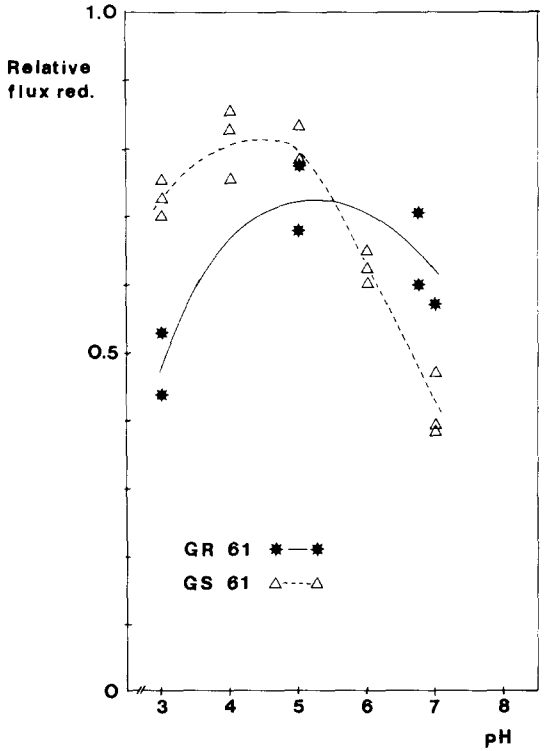

Fig. 8. Relative flux reduction versus pH in ultrafiltration of buffer solution after adsorption of whey protein from an aqueous 0.15 M NaCl solution (0.4 g protein/100 ml) on a sulfonated polysulfone membrane, GS 61, and on a polysulfone membrane, GR 61. $\Delta P=2.5$ bar; $T=25\,^{\circ}C$.

3 show that the GS 61 membrane has almost the same negative charge density as before while the GR 61 membrane has almost none at all. In this area the GS membrane has a higher relative flux reduction than the GR membrane as a consequence of higher adsorption due to attractive forces between the negatively charged membrane and the positively charged protein molecules.

CONCLUSIONS

It is possible to determine an apparent value for the zeta potential of UF membranes by measuring streaming potentials. As the pores of the UF membranes are very narrow the models used for the calculation of the true zeta potential from streaming potential data do not apply well. However, the apparent values obtained by using the well-known Helmholtz–Smoluchowski equation for calculations are reproducible for the same piece of membrane. These results give important information for the prediction of adsorption, fouling, flux and retention in ultrafiltration of solutions, especially if the solutions themselves contain macromolecules of ionic nature.

ACKNOWLEDGEMENTS

The authors are indebted to Nordisk Industrifond, The Finnish Academy of Sciences, Icelandic Science Foundation, and Maj and Tor Nessling Foundation for financial support.

REFERENCES

1 B. Sivik and B. Hallström, in B. Hallström, D.B. Lund and Ch. Trägårdh (Eds), Fundamentals and Applications of Surface Phenomena Associated with Fouling and Cleaning in Food Processing, Reprocentralen, Lund, Sweden, 1981, p. 10.
2 E. Matthiasson, in D. Lund, E. Plett and C. Sandu (Eds), Fouling and Cleaning in Food Processing, University of Wisconsin-Madison Extension Duplicating, Madison, WI 53706, U.S.A., 1985, p. 429.
3 J. Patocka and P. Jelen, J. Food Sci., 52 (1987) 1241.
4 P. Aimar and V. Sanchez, in D. Lund, E. Plett and C. Sandu (Eds), Fouling and Cleaning in Food Processing, University of Wisconsin-Madison Extension Duplicating, Madison, WI 53706, U.S.A., 1985, p. 466.
5 M.S. Le, Membrane Ultrafiltration Fouling and Treatment, Ph.D. Thesis, Dept. of Chem. Eng., University College of Swansea, 1982.
6 W. Norde, Adv. Colloid Interface Sci., 25 (1986) 367.
7 J. Perrin, J. Chim. Phys., 2 (1904) 601.
8 J. Stock, Bull. Intern. Acad. Pol. Sci. Lett. A, (1912) 635.
9 C.L. Rice and R. Whitehead, J. Phys. Chem., 69 (1965) 4017.
10 I.B. Oldham, F.J. Young and J.F. Osterle, J. Colloid Sci., 18 (1963) 328.
11 S. Levine, J.R. Marriott, G. Neale and N. Epstein, J. Colloid Interface Sci., 52 (1975) 136.
12 J.L. Anderson and W.-H. Koh, J. Colloid Interface Sci., 59 (1977) 149.

13 D. Hildreth, J. Phys. Chem., 74 (1970) 2006.
14 Z. Broz and N. Epstein, J. Colloid Interface Sci., 56 (1976) 605.
15 J. Benavente and C. Fernandez-Pineda, J. Membr. Sci., 23 (1985) 121.
16 M.G.A. Khedr, S.M. Abd el Haleem and A. Baraka, J. Electroanal. Chem., 184 (1985) 161.
17 G. Tanny, E. Hoffer and O. Kedem, Experientia, suppl., 18 (1971) 619.
18 N. Kaneko and Y. Yamamoto, J. Chem. Eng. Jpn., 9 (1976) 158.
19 T. Cserfalvi, T. Meisel and E. Pungor, J. Electroanal. Chem., 74 (1976) 377.
20 P.N. Zhukov and D.A. Fridrikhsberg, Kolloidn. Zh., 12 (1950) 25.
21 M. Tasaka, S. Tamura, N. Takemura and K. Morimoto, J. Membr. Sci., 12 (1982) 169.
22 G. Jonsson, personal communication.
23 G. Jonsson, Pure Appl. Chem., 58 (1986) 1647.
24 M. Lindström, M. Nyström and M. Laatikainen, Sep. Sci. Technol., 23 (1988) 703.
25 M. Laatikainen, Publication 7/84, LTKK, Lappeenranta University of Technology, Dept. of Chem. Technol., Lappeenranta, Finland, 1984 (in Finnish).
26 E. Matthiasson, J. Membr. Sci., 16 (1983) 23.