Preparation and Characterization of Porous Polysulfone Membranes with Spacer-Bonded N-Containing Groups

KLAUS RODEMANN and EBERHARD STAUDE*

Institut für Technische Chemie der Universität Essen, D-45117 Essen, Germany

SYNOPSIS

Ultrafiltration membranes were prepared from epoxidized polysulfone by the conventional phase separation procedure. For epoxidizing, the polymer was first lithiated and a reaction followed with glycidyl-4-oxohexylether providing an eight atomic spacer. The reaction of the epoxy group with N-containing substituents was performed heterogeneously using the ready membranes. The stability of the substituted membranes is visible by the fact that they are reacted under reflux conditions for 24 h. The reagents were trimethyl amine, diethylamine, *n*-butyl amine, and tauric acid. Thus, positively charged, negatively charged, and neutral membranes were obtained. The membranes were characterized via ultrafiltration using dextran solution as well as human albumin solutions. In addition, the streaming potential was measured in the presence and absence of the protein. By these measurements the obviously neutral membranes were surprisingly identified to be positively charged. This is related to subsequent reactions of the spacer-bonded epoxy groups with the amino groups.

INTRODUCTION

There are many ways to substitute polysulfone such that amino groups are attached to the polymeric backbone. Mostly, the aim is to create a positively charged polysulfone because of the interest in anion exchange membranes. A well-established reaction is the conversion with halogenated aliphatic ethers like halomethylalkylethers.[1,2] However, since the preparation of these ethers sometimes causes problems, the building of the ether *in situ* can also be employed using paraformaldehyde and HCl.[3,4] Once these reagents have been employed, the resulting substituted polysulfone must be dissolved in an appropriate solvent. After casting the membrane, it is reacted heterogeneously with an appropriate amine. Thus, it is fairly simple to prepare charged polysulfone membranes which are equipped with quaternary ammonia groups using ternary amines. This is the right way to manufacture anion exchange membranes for the ED.[1] Yet it has turned out that this group is not so stable during the ED process.[5] Therefore, more complex substituents were employed to overcome this disadvantage.[6] Other than for electrodialysis membranes, this lack of stability is less important for porous membranes used for ultrafiltration or microfiltration.

In these separation processes positively charged membranes do not have to experience very high pH. The preferred potential of their application lies in the treatment of solutions that are either handled in medical devices like artificial kidneys or in the pharmaceutical industry. In both cases, the positive charges serve to remove negatively charged ingredients like viruses or pyrogenes from the solutions. Normally, this goal is met with commercially available membranes made from polyamides. Yet positively charged polysulfone ultrafiltration membranes can also be successfully applied as was shown recently in laboratory scale with solutions that contain endotoxins stemming from *Escherichia coli*.[7]

The membranes for these experiments were obtained by conversion of the chloromethylated precursor as mentioned above (see also Ref. 7). Moreover, the halomethylation reaction is likewise appropriate for already prepared polysulfone mem-

* To whom correspondence should be addressed.

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branes.[8] According to the substituents used for this reaction, the ionogenic group is positioned rather closely to the polymer itself. The methylene group provides a nearly negligible length. For some circumstances, like for enzyme fixation, it is desirable that there exist a certain span between charge and the backbone of the polymer. This can be verified by introducing spacerlike substituents. One possibility offers the lithiation of the polysulfone[9] followed by epoxidation using glycidylethers.[10] Due to the length of the glycidylether applied, the length of the spacer can be selected.

In the experiments described in this paper only one type of epoxy spacer was used because the purpose of the investigation was to demonstrate how different N-containing substituents can be introduced via the epoxy group. In a preceding paper, the lithiation and the epoxidation of polysulfone membranes prepared in the laboratory scale as well as on commercially available membranes were shown.[11] Mainly, this paper contains the characterization method for porous charge-bearing membranes, namely, the streaming potential. This method became quite popular recently for membrane characterization.[12,13] In the latter article investigations are described using membranes supplied from a company. Most of them were "neutral" and some were modified by ultraviolet (UV) irradiation. However, the chemical outcome of this modification is not presented. Presumably, chain cleavage occurs and negative charges are established.

One of the topics of this investigation was to show how the adsorption of proteins influences the streaming potential of the membranes. The behavior of positively charged polysulfone membranes with respect to the streaming potential is shown in Ref. 7. In this investigation, protein as well as endotoxins were applied. Furthermore, the streaming potential can be used for analyzing the membrane, e.g., if the chemical modification has changed the surface charges and to what extent. This was demonstrated for homogeneously modified polysulfone membranes[14] as well as for heterogeneously modified ones.[8] In this study the preparation of porous polysulfone membranes is described which are fitted out with N-containing substituents differing in their charges. The starting point for all these membranes was an epoxidized polysulfone membrane with an eight atomic spacer. The ultrafiltration experiments were performed using dextran solutions and human serum albumin solutions as well. Besides these characterizations the streaming potentials of the different membranes were also determined.

EXPERIMENTAL

Membranes

The membranes were cast using a solution made from the following materials: 15% (by weight) of polysulfone fitted out with the glycidyl-4-oxohexylether and 85% (by weight) of triethylphosphate. The preparation of the polymer is described elsewhere.[10] In the following it is referred to as EPSU. The dope was cast onto a carefully cleaned glass plate using a casting device with a die width of 500 μm. After a residence time of about 15 s at ambient air, the plate was immersed in a water bath of 291 K. The membrane was stored in water containing 0.05% NaN_3 at 277 K until use. In order to introduce the N-containing substituents, the epoxidized membrane was immersed in a solution consisting of 69 mL H_2O, 33 mL methanol, and 0.2 mol of the corresponding N-containing substance. By adding HCl or NaOH to the reaction solution the pH was adjusted to 10. Keeping the solution at reflux temperature the membrane was reacted for 24 h. Figure 1 indicates the different reaction paths yielding the differently substituted membranes. It also contains the membrane nomenclature used hereafter.

Materials

The polysulfone type UDEL P-3500 were purchased from Amicon; diethylamine, *n*-butylamine, and tauric acid were purchased from Fluka, Heidelberg, Germany; and trimethylamine was purchased from Merck, Darmstadt, Germany. The dextrans differing in their molar masses from 4000 to 200,000 g/mol were obtained from Serva, Heidelberg, Germany, and from Pharmacia, Uppsala, Sweden. The human serum albumin (molar mass 65,000 g/mol) was received from ICN, Costa Mesa/CF. The analysis of the dextran in the UF experiments was carried out using a GPC unit from Waters (type 6000A). For analyzing the human serum albumin a method was practiced which is found elsewhere,[15] however in a slightly modified version.[16]

Experimental Setup and Measurements

The ultrafiltration experiments were carried out in a closed-loop ultrafiltration unit equipped with a 5-L feed tank, a membrane piston pump (0.4 L/min at 3 bars), four cells in series that were stirred magnetically, and a manometer of high accuracy. The temperature was set at 293 K. Before mounting in the UF cell each membrane having 40.7 cm^2 free

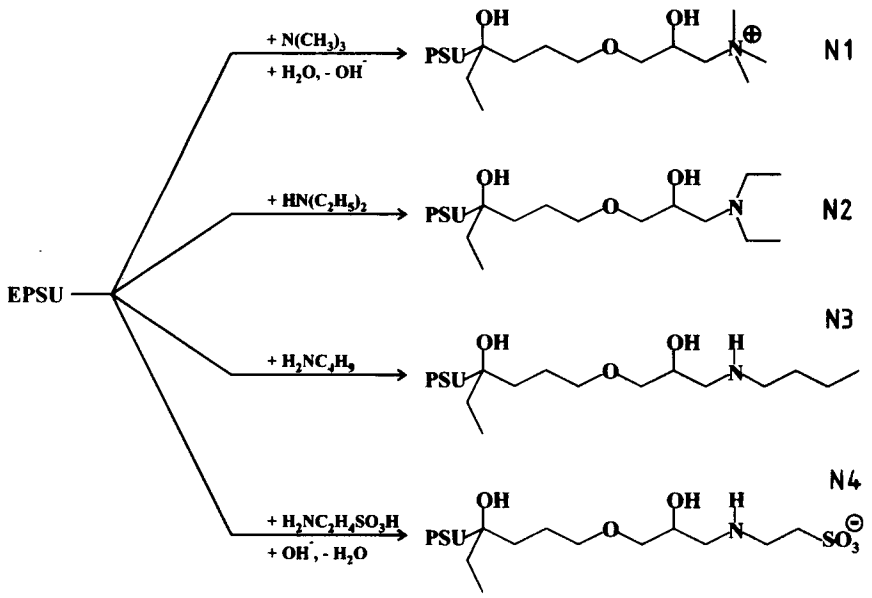

Figure 1 Chemical formula of the derivatives made from epoxidized polysulfone (EPSU).

area was conditioned at 3 bars for 24 h using desalted and filtered (0.2 μm) water. The runs were made with pure water and a 1% solution of dextrans of different molar masses as well. The solution of human serum albumin contained only 11.78 μmol/L. At this low concentration the membrane fouling by a noteworthy gel layer could be nearly excluded. The pH was adjusted to 7 using 20 mmol/L sodium phosphate buffer. To avoid any nonspecific adsorption of the protein, 58.4 g NaCl were added per 1 L of solution. The setup for the streaming potential is shown in detail elsewhere.[11] As electrolyte a KCl solution of 10^{-3} mol/L was used in all experiments. In this unit also the experiments were carried out for determining the influence of human serum albumin upon the streaming potential. In these cases the protein concentration was only 2.3 μmol/L.

RESULTS AND DISCUSSION

Ultrafiltration Experiments

The results of the investigations of the membranes' ultrafiltration properties are listed in Table I. The presented values were obtained at a pressure of 1 bar. From the data evaluated from the experiments using the dextran solution, the molecular weight cutoff for all membranes was determined to 155,000 g/mol. Despite the degree of substitution of 0.3 for all membranes, the pure water volume flow is different according to the chemical character of the substituents. The fixed charges contribute much to the volume flow increase, as may be seen for the EPSU-N1 and EPSU-N4 membranes compared to the EPSU master membrane. The latter has the

Table I Membrane Characterization at 1 Bar

Membranes	J_W L m^{-2} d^{-1}	J'_W L m^{-2} d^{-1}	J_D L m^{-2} d^{-1}	J'_D L m^{-2} d^{-1}	J_{HSA} L m^{-2} d^{-1}	R %
EPSU	6800	5640	720	650	4450	43
EPSU-N1	9200	6440	770	680	3540	60
EPSU-N2	7900	5920	740	650	3370	55
EPSU-N3	8300	6200	760	670	3600	53
EPSU-N4	8900	8200	780	740	6560	38

J_w pure water volume flow, J'_W pure water volume flow after membrane treatment with HSA solution, J_D volume flow for 1% dextran solution, J'_D volume flow for 1% dextran solution after membrane treatment with HSA solution, J_{HSA} volume flow of a HSA solution (11.76 μmol/L), R rejection of a HSA solution (11.76 μmol/L).

lowest volume flow which is associated with the highest degree of hydrophobicity. Just the interactions between water and the membrane polymer are accountable for the membrane's fouling predisposition. The feasible influence of fouling-prone ingredients was tested by using a protein solution (11.78 μmol/L) that was circulated for 2 h in the UF unit. After that, the volume flow was checked using pure water. Even if a very diluted protein solution was applied, a flow reduction differing from 10 to 30% is found. Typically, this is the consequence of the buildup of a fouling layer normally found on top of a membrane. Yet, because of the moderate rejection of the protein, an adsorption of the protein at the capillary walls within the membranes by reason of any interaction forces may not be excluded. Inasmuch as the negatively charged N4 membrane has only a 9% decline, the positively N1 suffers a 30% one. Even the other substituted membranes are more sensitive to protein "fouling" than the "neutral" EPSU master membrane. This experimental result needs to be proved by other means.

Probably another type of experiments can help to answer the question of whether adsorption of protein influences the transmembrane transport and how. Obviously, not only the different water sorption of the membrane polymer plays a role, but also the charge of the membranes causes different degrees of fouling when proteins are involved. Another set of experiments was carried out using a 1% dextran solution at different pressures. In any case, the experiments were performed such that a steady state was achieved. Then the membranes were carefully washed with pure water. As in the former investigation, a circulation of a 11.78 μmol/L human serum albumin solution was applied for 2 h. Subsequently, the unit was rinsed with pure water and once again a dextran solution was used. The experimental findings are shown in Figure 2 as well as for the 1 bar experiments in Table I. Likewise as in the former investigation, the volume flow is reduced and the protein is accountable for this result. Analogously, the positively charged N4 and the neutral EPSU master membrane are fairly resistant to protein adsorption, the volume flow reduction is 5 and 9%, respectively. Contrarily, the volume flows for the other membrane types drop down at about 12%. From the chemical point of view this seems astonishing since N1 is positively charged whereas both the other membranes are neutral (Fig. 1). It may be assumed that mainly charges play a dominant role. Accomplishing UF experiments with the protein solution of the mentioned concentration, a volume flow reduction was also observed. The corresponding results are shown in Table I. The differences in the volume flows (see column 2 and 5) result from the different process conditions. In the former case only a 2-h run was set, however, in the latter a fully established stationary state was attained before measuring.

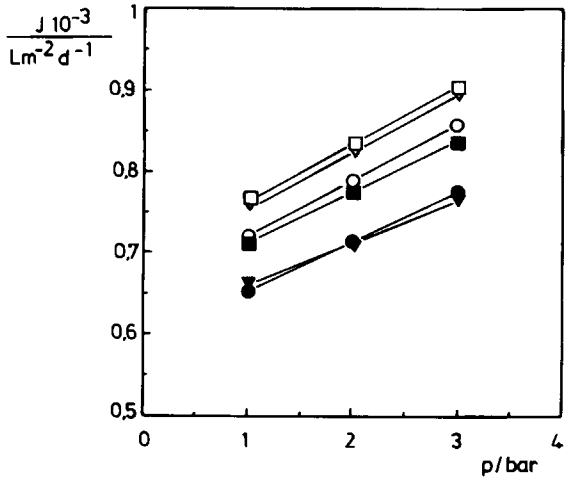

Figure 2 Influence of human serum albumin on dextran volume flow as a function of pressure for different membranes. Membranes: (○) EPSU, (▽) EPSU-N1, (□) EPSU-N4; dextran solution 1%, open symbols: before, filled symbols: after a two hour treatment with 11.78 μmol/L human serum albumin solution containing 58.4 g/L NaCl, pH 7, temp.: 293 K.

Nonetheless, the aforementioned differences in the membranes' performances are also reflected by the protein ultrafiltration. Table I also presents the rejection values of the protein at 1 bar. Their pressure dependency is shown in Figure 3. Like in the foregoing experiments, the various types of substituents disclose their different influence upon the membrane performance. Also here the normally expected picture is lacking. Rejection almost increases with increasing pressure. As can be seen from the figure, this is sound for the neutral EPSU membrane and the EPSU-N4 membrane that possesses negative charges because of the sulfonic acid groups. Yet, the findings for the membranes carrying amino groups of different quality are not in accord with the common ones. With increasing pressure the rejection drops from higher to lower values. Due to the relatively high NaCl concentration in the solutions applied, a nonspecific adsorption should be excluded. Then the effect comes from the substituents. The membranes fitted out with amino groups presumably bear positive surface charges that will be partially slipped off with increasing pressure resulting in a diminished repulsion of the protein mole-

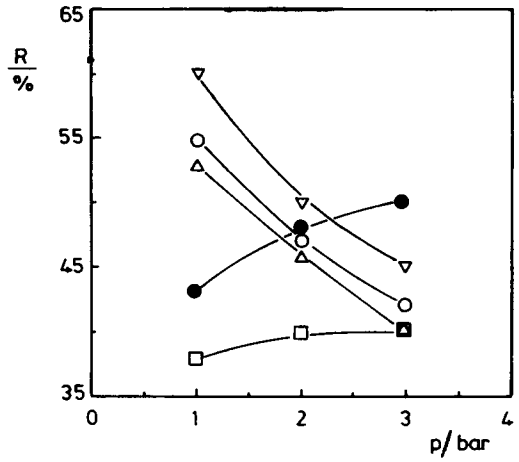

Figure 3 Human serum albumin rejection as a function of pressure for different membranes. Membranes: (●) EPSU, (▽) EPSU-N1, (○) EPSU-N2, (△) EPSU-N3, (□) EPSU-N4; solution: human serum albumin 11.78 μmol/L, pH 7.0, NaCl 58.5 g/L; temp.: 293 K.

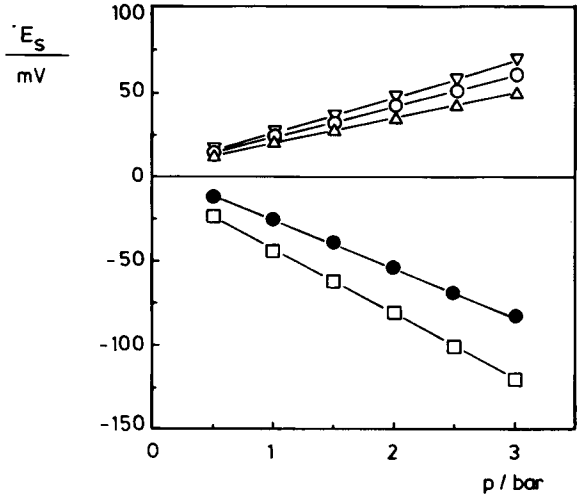

Figure 4 Streaming potential E_s as a function of pressure for different membranes. Membranes: (●) EPSU, (▽) EPSU-N1, (○) EPSU-N2, (△) EPSU-N3, (□) EPSU-N4; solution: 10^{-3} mol/L KCl, pH 6.3, temp. 293 K.

cules. This suggestion is supported by the observations concerning the volume flow. Membranes with positive charges interact with negatively charged ingredients in the solution like proteins provided the solutions' milieu has the right pH. This is the case here. Ultimately, a more detailed information on the membrane behavior can be obtained by measuring the surface charges. For that purpose electrokinetic investigations were performed.

Electrokinetic Measurements

The streaming potential which gives information on the surface charges of any solid medium in aqueous solutions is also essential for investigating the surface properties of membranes. This is shown as a function of pressure for the different membranes in Figure 4. The starting membrane EPSU is in the negative segment of the potential because the neutral membrane polymer takes up negative ions from the solution. This is an adsorptive accomplishment. The EPSU-N4 membrane is more negative. It has fixed charges in form of the sulfonic acid groups. These promote an increase of the absolute values of the streaming potential. In addition, the plot has a steeper slope. The streaming potential plots of the other membranes substituted with nucleophilic amines are located in the positive segment of the diagram. This is unquestionably correct for the N1 membrane with the positively fixed charges in the form of the quaternary ammonium groups. Contrary to this, for both the other membranes bearing secondary (N2) and tertiary (N3) amino groups, respectively, the plots should not be found in this positive range. However, taking into account the protonation of the N atom at the pH applied, then the findings are in accord with the position of the plots in the diagram. The N2 membrane possesses the stronger basic N atom than the N3 membrane that is reflected by the stronger slope of the streaming potential plot. Anticipating the explanation's correctness, the streaming potential of both these membranes that are in the protonated state at higher pH (6.8) should show a dependency as a function of pH. The results, however, shown in Figure 5, do not support this assumption. Mainly the N3 mem-

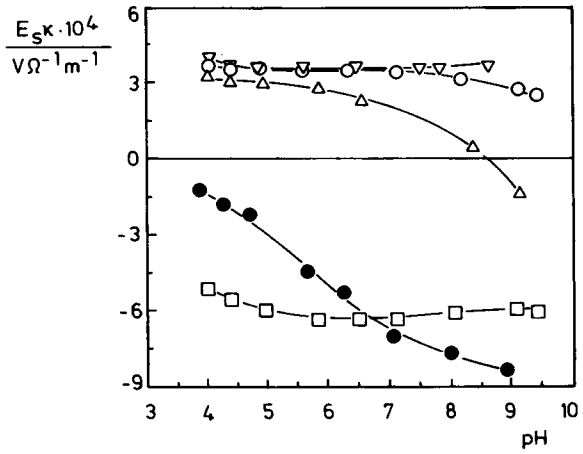

Figure 5 Streaming potential $E_s\kappa$ as a function of pH for different membranes. Membranes: (●) EPSU, (▽) EPSU-N1, (○) EPSU-N2, (△) EPSU-N3, (□) EPSU-N4; solution: 10^{-3} mol/L KCl, pressure 1 bar, temp. 293 K.

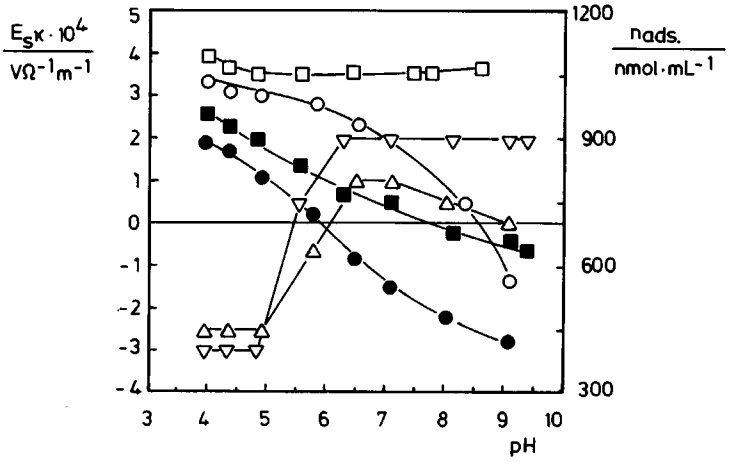

Figure 6 Influence of human serum albumin (HSA) on the streaming potential as a function of pH for EPSU-N1 and EPSU-N3 membranes. Streaming potential: (□) EPSU-N1 membrane without HSA, (■) with HSA, (○) EPSU-N3 membrane without HSA, (●) with HSA, HSA amount: (▽) EPSU-N1 membrane, (△) EPSU-N3 membrane. Solution: 10^{-3} mol/L KCl with 2.37 μmol/L HSA, pressure 1 bar, temp. 293 K.

brane, but also within a distinct limit also the N2 membrane, demonstrate a pH-independent behavior. This is not to be expected from the structure of the corresponding substituents. Moreover, nearly identical shapes of the curves are presented when comparing the curve of the N2 membrane with that of the N1 membrane. The streaming potential of the latter remains constant over the range investigated due to the quaternary ammonium ion that does not react on a pH change. The pH independence of both the former membranes (N2 and N3, resp.) has presumably its rationale in an existing quaternary ammonium ion. This yields from a consecutive reaction of an additional epoxide with a tertiary amine already built. In the case of the secondary amine, two epoxides are required, which is not as likely as the reaction with one epoxide. Therefore the streaming potential of the N3 membrane is more pH-dependent than that of the N2 membrane. This assumed reaction can only occur in the case where the active sites are spacer-bonded, which provides a discrete mobility of these specially needed reagents. This explanation finds support by the investigations on chloromethylated PSU membranes reacted with different N-containing nucleophiles.[14] The various membranes have pronounced pH dependency on the streaming potential. There is no potential for forming a quaternary ammonium ion as spacer-like substituents were not used in these experiments. In the negative range the N4 plays a similar role as the N1 in the positive one. The N4 membrane contains a sulfonic acid substituent that dissociates almost completely over the whole pH range applied. Therefore, the graph is nearly independent of the pH. The unsubstituted EPSU master membrane is considered neutral. The streaming potential as a function of pH prevails satisfactorily this prospect. With increasing pH the concentration of OH ions increases and accordingly the membrane's negative charge rises as expected.

Influence of adsorbed human serum albumin on the streaming potential

As aforementioned in the section dealing with UF experiments, an adsorption of human serum albumin was considered the explanation for the reduced volume flow. In order to verify this assumption, streaming potential measurements were carried out using very dilute protein solutions. These experiments, associated with the analytical determination of the amount of protein adsorbed, should give information on the membrane's surface properties. In Figure 6, the results for the EPSU-N1 and EPSU-N3 membranes are presented. In addition, the gravimetric amount of adsorbed protein is drawn. The former membrane with the positively fixed ion binds increasing numbers of protein molecules with increasing pH because of ion interactions. This yields an augmenting loss in positive surface charges, hence the streaming potential moves straight toward zero. The analytically determined amount of protein is in conjunction with the electrokinetic behavior. After the IEP of the protein is surpassed, the now negative protein molecules interact with the positive ammonium ions of the membrane, causing a noteworthy

protein uptake. The other membrane is fitted out with secondary amino groups which result from the reaction using a primary amine. In addition, as also revealed in Figure 5, some quaternary ammonium groups are responsible for the pH dependence of this membrane. However, since the concentration of these fixed charges is low, as explained above, the protein adsorption is correspondingly lower. As the plot shows, the protein amount picked up by the membrane decreases when the curve of the streaming potential drops sharply at increasing pH. In Figure 7 the results of the influence of protein adsorption on the streaming potential are shown for the neutral EPSU membrane and the membrane substituted with tauric acid (EPSU-N4) as well. For both these membranes, the streaming potential lies in the negative section. Despite the negative fixed charges at the N4 membrane, the curve of the streaming potential after treatment with protein as well as the curve of the adsorbed mass of protein are similar to the corresponding curves of the neutral membrane. The explanation is as follows. At low pH the negative charges at the membrane are almost compensated for by the positive protein molecules causing a jump of the streaming potential toward zero. Due to this charge neutralization, the membrane acts like the EPSU. The slightly higher mass adsorbed on the N4 membrane may be due to its ionic groups. Past the IEP the amount of adsorbed protein diminishes at increasing pH, and the remaining human serum albumin at the membranes surface now seemingly is kept by hydrophobic interactions rather than by coulombic interactions.

CONCLUSION

Epoxidized polysulfone membranes obtained via polysulfone lithiation and subsequent conversion using glycidyl-4-oxohexylether can be reacted with many reagents which can benefit from the reactivity of the epoxy group. Because of the spacerlike glycidylether, the substituents were somewhat distant from the polymer matrix. In the experiments described herein, three different amino groups were applied, namely primary, secondary, and tertiary ones. Hence, the reactions yielded polysulfone membranes fitted out with secondary amines, tertiary amines, and quaternary ammonium ions. This means two membranes were considered neutral and one is bearing charges. Moreover, a further N-containing substituent was the tauric acid resulting in a negatively charged polysulfone membrane. Under ultrafiltration conditions using protein solutions, the different substituents should employ their fouling preventing behavior with respect to their charges. Neutral membranes made from hydrophobic polymers like polysulfone (EPSU) or from polysulfone substituted with neutral molecules (EPSU-N2 and EPSU-N3) are expected to possess a higher fouling potential than hydrophilic membranes (EPSU-N1 and EPSU-N4). Yet the results were somewhat contradictory. The EPSU-N1 membrane fitted out with quaternary ammonium groups is more susceptible to protein fouling than the neutral EPSU master membrane. Hence, it is not the state of water at the membrane surface that is the clue for protein fouling but the membrane's surface charge. Then,

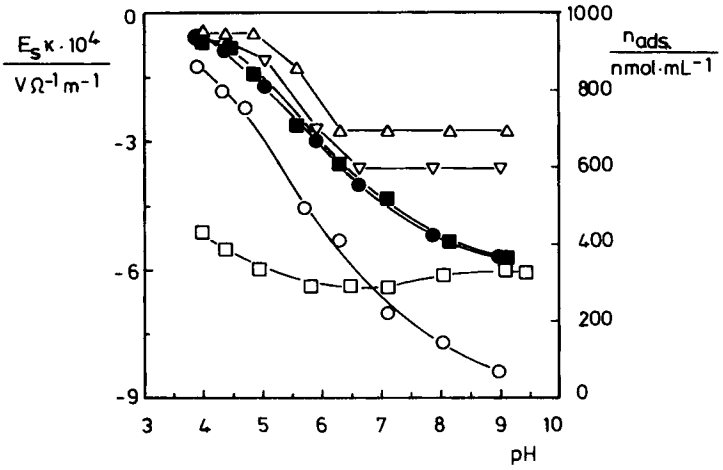

Figure 7 Influence of human serum albumin (HSA) on the streaming potential as a function of pH for EPSU-N4 and EPSU membranes. Streaming potential: (○) EPSU membrane without HSA, (●) with HSA, (□) EPSU-N4 membrane without HSA, (■) with HSA, HSA amount: (▽) EPSU membrane, (△) EPSU-N4 membrane. Solution: 10^{-3} mol/L KCl with 2.37 μmol/L HSA, pressure 1 bar, temp. 293 K.

however, the membrane characterization by ultrafiltration is a necessary but not sufficient means. An additional tool is required. Charges on porous membranes can be made easily discernible by electrokinetic investigations. For that purpose streaming potential measurements were carried out with these membranes, and the original epoxidized membrane was also included in these investigations. The latter membrane demonstrates the normal behavior of neutral materials in aqueous solutions. It picks up OH ions and the streaming potential lies in the negative section. With increasing pH the OH ion concentration increases, and due to this the streaming potential becomes more negative. The membranes bearing amino groups should exhibit the same behavior, yet they did not. Their streaming potentials are found increasingly positive with respect to the pressure applied. As to the pH dependence of the streaming potential, the experimental findings for the N2 membrane are comparable to those of the N1. This indicates the presence of a fair concentration of fixed ions that are supposed to be ammonium ions. These may originate by the reaction of the tertiary amine with a second epoxy group that seems to be a disadvantage of the glycidylether spacer. The same is apparent for the N3 membrane that, however, needs two epoxy groups. This is more unlikely; hence this membrane possesses fewer ammonium ions. The streaming potential curve is not constant over the entire pH range measured, clearly indicating the lower concentration of the positive charges. Even if this assumption is not yet proved by chemical means, nonetheless its indirect support is achievable by adding human serum albumin to the solution. The master membrane, from its origin presumably neutral, is negatively charged because of being supplied with OH ions from the aqueous solution. Therefore, at low pH the positive protein is attracted. Surpassing the IEP the amount of bonded protein decreases since the ionic interactions do not hold longer. The now negative protein contests with the OH ions with increasing pH, and eventually a discrete amount of the protein remains at the membrane's surface. Conversely, regarding the protein uptake, the obvious neutral membranes (N2 and N3) behave like the positively charged N1 membrane. However, they respond to the lower amount of their ionogenic groups. The positive charges at these membranes are additionally accentuated by measuring the streaming potential. The experimentally obtained values clearly hint at the above-mentioned consecutive reaction. Once again, it turns out that electrokinetic investigations are feasible for characterizing membrane surfaces. Obviously, while spacers are useful for preventing steric effects because of their more pronounced mobility, at least they should not be as reactive as in the case described in this study.

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