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Permeability of pH-sensitive membranes grafted by Fenton-type reaction: An experimental and modeling study

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Abstract. Membrane modification by different concentrations of acrylic acid has been described. Grafting of acrylic acid to the surface of a polypropylene membrane was obtained by a Fenton-type reaction. Membrane permeability seemed to have been dependent on the value of pH in the solution. To explain tendency, a simple theoretical model was developed. The model incorporates explicitly statistical conformations of a polyacid chain grafted onto the pore surface. The charged capillary model with a varying diameter for porous membranes was then used to evaluate the permeability of the membrane. It has been shown both theoretically and experimentally that the permeability of a grafted membrane depends on the pH of the solution.

Keywords: ultrafiltration; acrylic acid; membrane grafting; membrane permeability; numerical modeling; pH-sensitive membranes

1. Introduction

Membrane separation technology has undergone intensive development during the last few decades. This has resulted in an increased number of applications, mainly in pharmaceutical and food industries wastewater and desalination processes.

Interest in chemical modifications of membrane surface has been growing recently. E.g., the loading of membrane surface with silver nanoparticles or silver compounds may lead to the antibacterial properties of such a membranes (Basri *et al.* 2011). The procedure of membrane grafting with molecules of various substances is usually used to prevent membrane fouling (Stengaard 1988, Kim *et al.* 1991, Ma *et al.* 2000a, b). It is also possible to use preadsorption of

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some simple molecules onto the membrane surface to improve its antifoulant properties (Wei *et al.* 2012). Such a method may be interpreted as a kind of membrane grafting where there are formed hydrogen bonding or van der Waals interactions instead of chemical bonding. However, it has been shown that the grafting of polyelectrolytes to membranes may also influence their permeability. Moreover, the permeability often depends on electrical and related properties of the solution e.g., pH or ionic strength (Kontturi *et al.* 1996, Ramırez *et al.* 2003). Such a grafting is the way to prepare variable permeability membranes (VPM) which may be used e.g., as chemical valves (Nishi and Kotaka 1986, Casolaro and Barbucci 1993).

There are many ways to obtain pH-switchable membranes. One of them is the deposition of silica onto the anodic aluminum oxide membrane through sol–gel method and then grafting polyelectrolytes on the membrane surface (Song *et al.* 2011). Another method, described in (Wang *et al.* 2012), uses a copolymer of poly(methyl methylacrylate-co-4-vinyl pyridine) (P(MMA–4VPy)) as an additive to the melted polymer during membrane production. Cheng *et al.* (2011) investigated the pH sensitivity of polyethersulfone hollow fiber membrane modified by blending an amphiphilic terpolymer poly(styrene–acrylic acid–N-vinylpyrrolidone). Hu and Dickson (2007) developed pH-sensitive membranes by means of *in situ* cross-linking poly(acrylic acid) inside poly(vinylidene fluoride) hydrophobic microporous substrate membranes.

Finally, there is a group of membrane modification methods by grafting of polyelectrolytes on their surface. However, due to their inertness and smooth surface, most polymers used as membrane templates (e.g., polyethylene (PE)) require an additional activation of their surface to obtain a sufficient grafting degree. The methods used to activate a polymer surface are: glow discharge (Suzuki *et al.* 1986), UV irradiation (Yang and Ranby 1999, Chun *et al.* 1999), corona discharge (Lei and Liao 2000) or *γ*-ray or other high-energy radiation methods (Dessouki *et al.* 1998, Kontturi *et al.* 1996). The methods have been also used lately to modify membrane surfaces. In works (Kontturi *et al.* 1996, Hautojarvi *et al.* 1996) the last method was used to graft poly(acrylic acid) (PAA) on poly(vinylidene fluoride) (PVDF) membranes. Grafting of membrane surface may result not only in surface properties modification but also play antifouling role. Kang *et al.* (2011) have shown that the grafting of polyelectrolytes on polyamide reverse osmosis membranes may results in decrease of fouling not only in protein but also in cationic surfactants solutions. Liu *et al.* (2011) present fabrication of a poly(vinylidene difluoride-*co*-chlorotrifluoroethylene) porous membrane via non-solvent induced phase inversion and subsequent hydrophilic modification using high efficient surface initiated atom transfer radical polymerization. The authors have observed the decrease of contact angle and significant degree of swelling that showed that the hydrophilicity was effectively improved by the immobilization of hydrophilic poly(ethylene glycol) monomethacrylate brushes.

All the methods of membrane modifications mentioned above, e.g., grafting of polyelectrolytes on membrane surface, produce membranes whose permeability decreases with the value of pH of the solution. Kontturi *et al.* (1996) observed that the permeability of a grafted membrane is greater at a lower value of pH. They explained it as an effect of a lower dissociation degree of carboxyl groups in acid environment. Thus, PAA chains grafted inside pores collapse to increase their entropy. In contrast, at a higher value of pH, carboxyl groups start to dissociate and repulsive interactions between neighbouring groups come into play. That leads to chain extension, which means a decrease of pore effective diameter and finally a decrease of membrane permeability. The authors also observed changes in membrane as an effect of ionic strength of the solution. At a moderate pH value the permeability of the membrane appears to be a growing function of ionic strength of the solution.

Kontturi *et al*. (1996) present a simple theoretical description of membrane permeability at various pH values based on statistical thermodynamics formalism. Besides the study, hardly any papers tried to come up with a theoretical explanation of the behavior of pH-switchable membranes.

The main goal of this work is to report a new method of developing pH sensitive membranes by means of PAA grafting on the membrane surface. Contrary to Kontturi *et al*. (1996), the grafting was performed by means of a Fenton-like method. Details of the method are to be found in Section 2. Section 3 presents a simple theoretical model, which explains changes of membrane permeability. Finally, Section 4 contains discussion of presented results and conclusions.

2. Experimental

2.1 Membrane preparation

Porous polypropylene capillary membranes produced by MEMBRANA GmbH were modified. The inner and outer diameters of a single capillary were 1.8 mm and 2.8 mm, respectively. The mean pore diameter was 0.2 μm. The SEM image of the outside surface of membrane has been presented in Fig. 1.

Grafting of acrylic acid by a Fenton-type reaction is a two-step process (Barros *et al*. 2006). In the first step a polypropylene membrane is placed in a solution of ethylene glycol dimethacrylate (EGDMA) and cumenehydroperoxide (CHP) in hexane for a set amount of time. During this phase, EGDMA and CHP are adsorbed on the membrane surface. The second stage is the proper modification, when membranes are placed in a solution containing: iron chloride (II), ascorbic acid and an adequate amount of acrylic acid monomer (0.1, 0.5, 1, 5, 7, 10, 13 and 20%). This step begins with a radical reaction between CHP and iron ions. Peroxide present on the surface of polypropylene diffuses to an aqueous solution, where it is decomposed by the Fenton reaction, creating a large amount of free radicals. The free radicals present in the solution react with the modifying EGDMA (starting radical polymerization) and polypropylene – acrylic acid to form

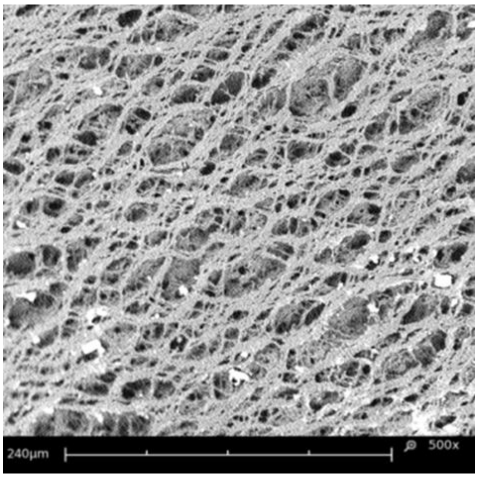


Fig. 1 SEM image of polypropylene membrane (MEMBRANA GmbH)

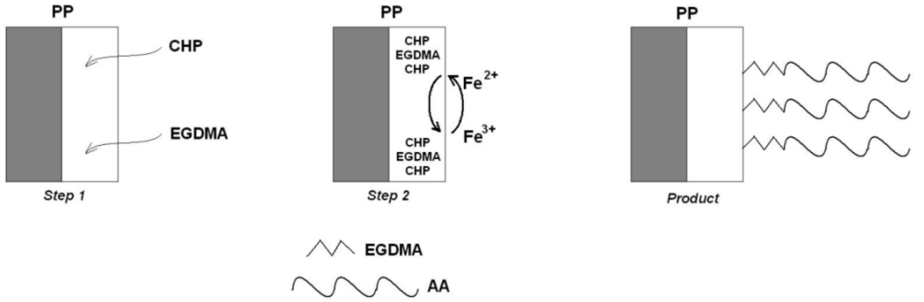


Fig. 2 Scheme of acrylic acid grafting on the polypropylene membrane using Fenton-type reaction (Butruk *et al*. 2012)

macroradicals. EGDMA is used as a cross- linking agent, which aims to improve the bond between polypropylene and a layer of acrylic acid. Also in the second step, iron ions are consumed during the Fenton reaction, and then regenerated using ascorbic acid present in the modifying solution (Butruk *et al*. 2012). The final step is to remove the unreacted acrylic acid and other compounds from the surface of modified membranes by sodium dodecyl sulfate (SDS) followed by rinsing of the membranes with RO water. The whole process is schematically presented in Fig. 2.

2.2 Membrane characterization

Modified membranes were analyzed by FT – IR analysis to identify functional groups present on the surface of modified membranes. Thanks to FT – IR spectra it was possible to confirm the presence of acrylic acid on the surface of modified membranes. An analysis of FT – IR was performed on a NICOLET 6700 whose wave number range was from 400 to 4000 cm^{-1}.

The contact angle of modified membranes was measured on Kruss K121 tensiometer. Contact angle of capillary membranes was measured by the dynamic Wilhemy method. During the experiment, samples were immersed in water, which surface tension σ was equal to 72.8 mN/m. Sample was dipped to a depth of 3 mm, then measurement was stopped for 2 seconds (automatic) and then the sample emerged from the liquid. In a result of the experiment advancing contact angle may be determined.

In order to determine the amount of carboxyl groups grafted with acrylic acid at the membrane surface the test with toluidine blue – o was performed. Nominal length of the modified membrane was placed in 20 ml of a 0.5 mM solution of toluidine blue at pH = 10 for 6 h at 30°C. After a set time the membrane was removed and rinsed with sodium hydroxide solution of pH = 9 in order to remove unbound toluidine blue from the surface of the membrane. Then membrane was placed in a 20 ml of 50% acetic acid solution in which toluidine blue was released from the membrane surface. Then, the prepared sample was examined spectrophotometrically at a wavelength of 630 nm. The content of carboxyl groups was assessed on the basis of the standard curve, assuming that the molar ratio of carboxyl groups to the amount of dye is 1:1 (Gupta *et al*. 2002). This procedure has been run only for the case of the membrane modified by 10% acrylic acid..

2.3 Permeability testing

Small laboratory modules were tested on a specially designed installation shown in Fig. 3.

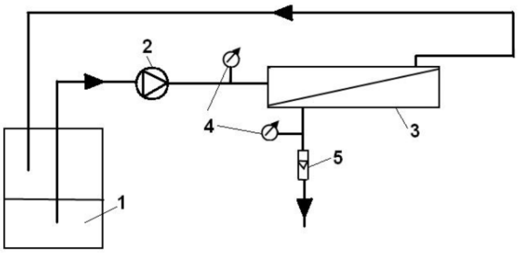


Fig. 3 Scheme of installation prepared for permeability measurements. (1) feed; (2) peristaltic pump; (3) membrane module; (4) pressure gauges; (5) rotameter

During the permeability measurement feed (RO water with different pH), a solution was pumped by means of peristaltic pump (2) from the feed container (1) to the membrane module (3), then the retentate was recycled back to the feed tank, and the permeate was collected in a separate tank (not shown).

3. Results and discussion

In order to confirm whether a membrane modification did in fact take place, a FTIR analysis based on the correlation table was performed. It confirmed the introduction of specific carboxyl groups to acrylic acid. Fig. 4 shows a spectrum obtained for the different concentrations of acrylic acid. The presence of groups characteristic for AA was confirmed in all modifications. There were peaks the regions responsible for –O–H bond - 3500 – 3000 cm^{-1}, between 1760 and 1650 cm^{-1} ^{t}he peak was responsible for the carbonyl group (–C = O). However, in the area 1550 – 1610 cm^{-1} a small peak is also responsible for the carbonyl group, but most likely one derived from carboxylates. In addition, in the vicinity of 1100 cm^{-1} the peak is responsible for the C–O– bond, probably from ester groups. FTIR spectrum analysis clearly showed the presence of acrylic acid grafted onto the membrane surface.

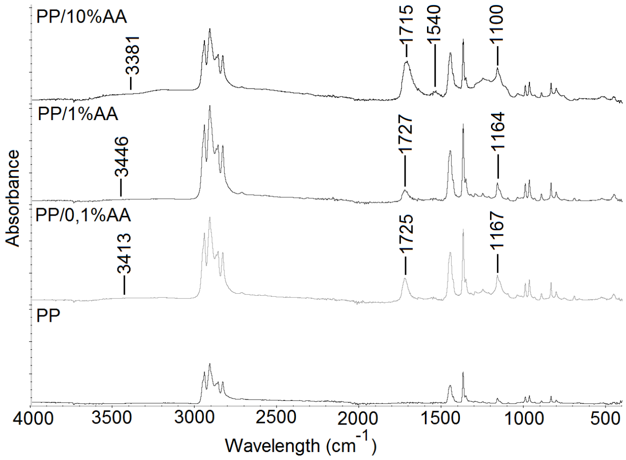


Fig. 4 FT IR analysis for unmodified membrane (bottom) and membranes modified by means of solutions with different concentrations of acrylic acid (from top to bottom 10%, 1% and 0.1 % acrylic acid)

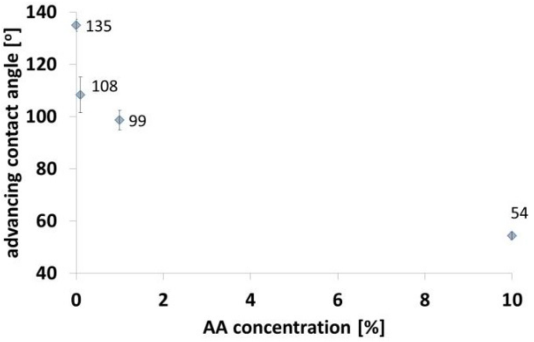
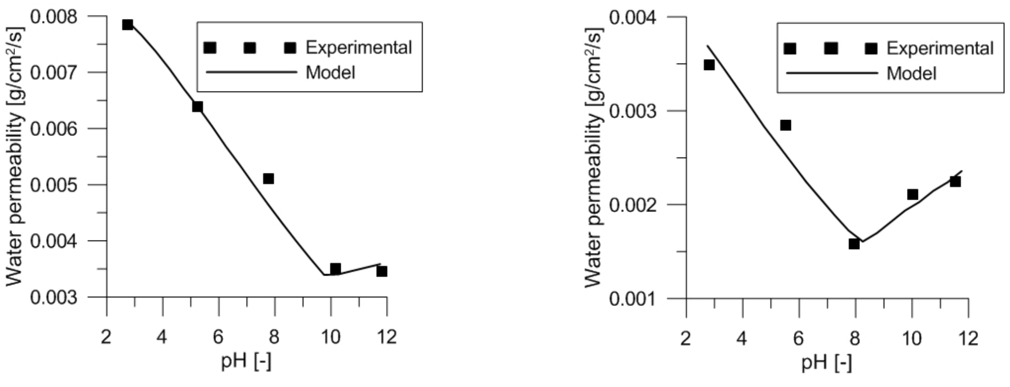


Fig. 5 Dependence of this contact angle on the AA concentration in solution used to modification of the membranes

According to our research, we observed some differences in grafting degree for different AA concentration. In some cases we obtained better results for smaller concentration of acrylic acid (e.g., for 0.1% AA we obtained more pronounce peaks in FT IR spectrum, than for 1% of AA). At this point of research, it is very difficult to explain such phenomenon. In our opinion, this fact might be caused by different routes of reaction, changes in local pH which can affect grafting or possible detachment of polymer chain fragments. Similar results were observed by You *et al.* (2006). They, however, have not interpreted this phenomenon.

The dependence of this contact angle on the AA concentration in solution used to modification of the membranes is presented in Fig. 5. The decrease of contact angle as a function of this concentration is clearly seen that means that the membrane surface becomes more hydrophilic. This is an effect of appearance of hydrophilic carboxyl groups on and near the surface of the membrane.As to the concentration of carboxyl groups, it has been found that the membrane modified by 10% acrylic acid contains 1.05 μg COOH groups per square centimeter of membrane what is equivalent to about 23.3 nmol/cm^2 of COOH groups.



(a) Membrane modified with 10% solution of acrylic acid

(b) Membrane modified with 7% solution of acrylic acid

Fig. 6 Dependence of permeability of the PAA-grafted membrane on pH of the solution – experimental (dots) and theoretical (line) results

Modules with membranes modified by 10% AA and 7% AA (the membranes modified by means of less concentrations of AA have not exhibited the clear pH-dependent permeability) were tested in a different pH of the feed solution (from 2 to 11), tests were carried out for 15 min. During measurements, the intermembrane pressure was set at the value of 0.75 Pa. On the basis of these measurements the permeate flux was calculated. Results are presented in Fig. 6.

We may observe that the permeate flux and thus the permeability of the membrane is in general a decreasing function of pH. The shallow minimum appears for pH equal to about ten. Comparing the results of our experiment with the results presented by Kontturi *et al.* (1996) a conclusion can be drawn that permeability decrease being an effect of pH growth is now much weaker than in the case of membranes modified by radiation-induced grafting. While the latter exhibit the decrease of permeability about two orders of magnitude – here we observe an approximately twofold reduction. The numerical model presented in the next section is going to provide an explanation.

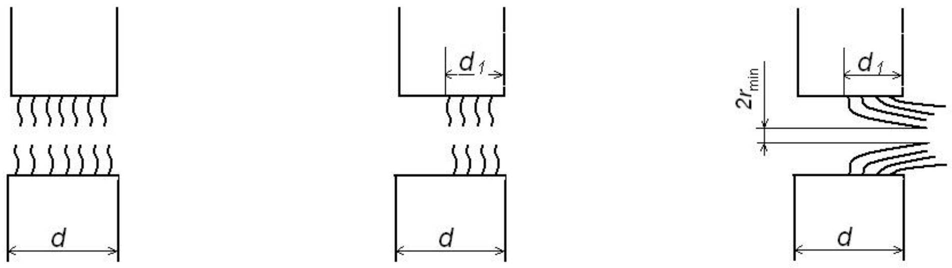
4. Numerical modeling

The permeability of a polyelectrolyte membrane will be modeled by a method similar to those presented by Kontturi *et al.* (1996). According to their results, the first step of calculating membrane permeability is the flow analysis in a single pore. Let us assume that the pore is a straight tube with a radius equal to r and the length equal to membrane thickness d. Then the gradient of the pressure is given by means of Poiseulle equation.

The permeability changes when grafted polyelectrolite chains are present on the surface of the membrane and inside pores. The polyelectrolytes grafted on the surface cause the increase of effective membrane thickness. Those present inside the pores result in decreasing the pore radius as shown in Fig. 7(a). This decrease is more significant at a high pH as a result of higher length of polyelectrolyte chains in this condition. Thus, membrane permeability generally decreases with the value of pH.

The main difference between the analysis presented in (Kontturi *et al.* 1996) and our own paper is the distribution of polyelectrolyte chains inside pores. In radiation-induced grafting the distribution of chains inside pores may be treated as uniform as was done by Kontturi *et al.* (1996). In grafting by means of a Fenton-type reaction, polyelectrolyte chains are present mainly in the vicinity of the inlet of the pores.

To give a mathematical description we assume that there is a pore segment where polyele-



(a) Polyelectrolyte chains at the whole length of the pore

(b) Polyelectrolyte chains near the inlet of the pore only

(c) Polyelectrolyte chains near the inlet of the pore with deflection

Fig. 7 Scheme of the pore in membrane with polyelectrolyte chains ctrolyte chains are uniformly distributed and a segment where they are not present at all. The length of the first segment is denoted as $d_1 < d$. Moreover, we do not take into account the presence of bridges between chains as they are assumed to have a marginal influence on the mean length of a single polyelectrolyte chain. The computation results presented below confirm this assumption. A schematic of the model of a single pore is presented in Fig. 7(b).

To compute membrane permeability, we first estimate the mean length of polymer chains at a given pH, similarly as in (Hill 1986). Following the method developed in (Kontturi *et al.* 1996) we assume that every monomer building a polymer chain may appear in one of three states: the neutral state (without charge - let us call it state 1), the short charged state (state 2) and the long charged state (state 3). Each state has an assigned length and the total length of a polyelectrolyte chain is the sum of the lengths of every unit. Thus, to compute the total length of a chain we have to know the number of units (monomers) in every state. Following the procedure presented in (Kontturi *et al.* 1996), we obtain numbers minimizing free energy of a single chain.

The main parameter of the method is the partition function assigned to every possible state of a monomer. Based on the method developed in (Hill1986) we assume, without the loss of generality, that the partition function of the monomer in the uncharged state as well as in the short charged state is 1 while for the long charged state we have $q > 1$ (Kontturi *et al.* 1996). The total partition function of the polymer chain can be given by

$$Z = \frac{N!}{n_1!(N-n_1)!} q^{n_1+n_2} \exp\left(- \frac{\varpi_{22} n_2^2 + \varpi_{33} n_3^2 + 2\varpi_{23} n_2 n_3}{NkT} \right) \tag{1}$$

where N denotes the mean total number of monomers in a single polyelectrolyte chain, n_i (with i equal to 1, 2 or 3) – the number of monomers in state i, ϖ_{ij} - the interaction energy between two neighboring monomers in state i and j, and k is the Boltzmann constant.

The number of monomers in all three states may be found by solving three equations. The first one expresses the equality of the chemical potential of the monomers in the short and long charged states and has a form

$$\mu_2 = -kT \frac{\partial \ln Z}{\partial n_2} = -kT \frac{\partial \ln Z}{\partial n_3} = \mu_3 \tag{2}$$

The second is the equation between the chemical potentials of hydrogen ions in -COOH groups and in the solution

$$\mu_{COOH} = -kT \frac{\partial \ln Z}{\partial n_1} = \mu^0_{H^+} + kT \ln\left[\mathrm{H_3O^+}\right] = \mu_{H_3O^+} \tag{3}$$

where $\mu^0_{H^+} = kT \cdot pK_a$, K_a is a negative logarithm of acidity constant (it is assumed to be equal to 3.5 for carboxyl groups in PAA (Kontturi *et al.* 1996)) and $[H_3O^+] = 10^{-pH}$. Finally, the last equation simply takes the form

$$n_1 + n_2 + n_3 = N \tag{4}$$

A solution of the system of three equations gives us three numbers n_1, n_2, n_3 and, in consequence, the length of a polymer chain. This length is given by the formula

$$l = n_1 l_1 + n_2 l_2 + n_3 l_3 \tag{5}$$

where l_i is the length of a monomer in state i. The values for PAA are assumed as equal to (Kontturi *et al.* 1996): $l_1 = 0.3$ nm, $l_2 = 0.35$ nm and $l_3 = 0.6$ nm.

Thus, the efficient pore radius in the part covered by the polyelectrolyte is equal to

$$r_{eff} = r_0 - l \tag{6}$$

It should be also taken into account that when the mean length of a polyelectrolyte chain appears to be comparable with the pore radius, repulsive interactions between different chains start to play a more significant role. As a result, the deflection of a polyelectrolyte chain appears to have the shape shown in Fig. 7(c).

The interchain interactions have not been fully explained as yet. In the present paper we take them into account by assuming that there is a minimum pore radius $r_{\min}$. When the effective radius computed by means of (6) gives a value lower than $r_{\min}$, we put $r_{eff} = r_{\min}$ and finally we obtain

$$r_{eff} = \min(r_0 - l, r_{\min}) \tag{6a}$$

The pressure drop for the flow in a pore presented in Figs. 5(b) and (c) is assumed to be equal to the sum of pressure drop values for the capillaries with radius and length equal to r_{eff}, d_1, r_0 and $d - d_1$ respectively. This assumption seems to be valid when the inlet phenomena can be neglected i.e. when the pore diameter is smaller than its length. As long as membrane pores have a very low diameter equal to 0.2 μm, the condition mentioned above seems to be valid. Then, membrane permeability is expressed as follows

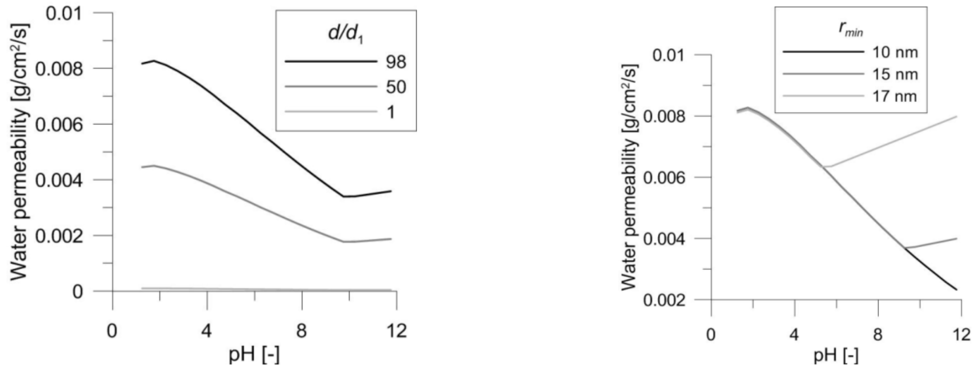
$$\dot{V} = \frac{\varepsilon r_{eff}^2 \Delta p}{8 \mu d} \cdot \frac{1}{1 + \left(\frac{r_{eff}}{r_0}\right)^4 \left(\frac{d}{d_1} - 1\right)} \tag{7}$$

where ε is a porosity of the membrane and μ - the viscosity of water.

To predict the permeability of a membrane, we have to know the values of a few parameters, which cannot be measured by means of typical experimental methods. These are: the mean number of monomers in a single polymer chain N, the value of partition function for the monomer in state 3 q, grafting depth d_1 and the minimum permitted effective radius $r_{\min}$. The influence of the first two parameters N and q has been discussed at length in (Kontturi *et al.* 1996). In the present paper we would like to analyze in depth the influence of the grafting depth and minimum effective radius, as they were not taken into account in the paper mentioned above.

Fig. 8(a) presents plots showing the dependence of membrane permeability on the pH for three values of grafting depth. We observe that membrane permeability is a decreasing function of d_1 (or an increasing function of the ratio d/d_1). We recognize that at the higher value of the ratio d/d_1 the mean water permeability is greater. Moreover, we find that the dynamics of permeability change is less than it has been reported in (Kontturi *et al.* 1996). The reason is that the membranes investigated by Kontturi *et al.* (1996) have over four times higher value of mean pore diameter. That enables the higher range of effective radius changes and higher range of permeability in result.

The value of $r_{\min}$ on the other hand influences the depth of minimum of membrane permeability as a function of pH as it has been shown in Fig. 8(b). When this value is equal to 10 nm or less (at



(a) Various values of grafting depth d_1 (b) Various values of minimum effective radius $r_{\min}$

Fig. 8 Modeling results of membrane permeability as a function of pH

given pore diameter r_0 and monomers number N) the permeability is continuously decreasing function of pH at pH higher than 2. For greater values of $r_{\min}$ the minimum membrane permeability appears and it is an increasing function of $r_{\min}$. The minimum was observed also by Kontturi *et al.* (1996). That paper, however, did not give a theoretical explanation of this observation. For $r_{\min}$ greater than 19 nm the minimum is not observed and the membrane permeability is growing function of pH.

Following the considerations above, we may fit the model parameter values to the experimental results presented in Fig. 6. As a result, for the case of 10% AA we obtain the following values: the number of monomers in a single chain $N = 268$, the value of maximum partition function of the monomer $q = 1.2$, grafting depth $d_1 = 10.2\ \mu$m and minimum radius of the pore $r_{\min} = 13.74$ nm. Fore the case of 7% AA we have obtained the same values of N and q, but the grafting depth were equal to 25.0 μm and minimum radius of the pore 15.0 nm.

The interpretation of the results above is as follows. At the lower concentration of AA the reaction runs more slowly. This results in deeper penetration of reagents into the pores and, finally, higher grafting depth. Simultaneously, the density of polymer chain is less what leads to stronger deflection and, in a result, higher value of $r_{\min}$.

Basing of these results, we may estimate the mean distance between two neighboring polyelectrolyte chains for the case of 10% AA. Assuming that the membrane surface is covered with pores with very high density (see Fig. 1) we find the number of pores equal to about $6.4\cdot10^8$ pores per square centimeter. Following that, the amount of COOH groups is equal to $3.6\cdot10^{-17}$ mol/pore that is $2.2\cdot10^6$ COOH groups/pore. Taking into account the value of N reported above we find that the number of PAA chains is equal to about $8.23\cdot10^4$ chains/pore. The surface grafted with polyelectrolyte chains per single pore is equal to

$$S = \pi d_{pore} d_1 \tag{8}$$

where d_{pore} denotes the (initial) pore diameter. We obtain 6.4 m^2/pore. Following that the effective density of PAA chains is equal to $1.28\cdot10^4$ chains/m^2. What gives the mean distance between two neighboring chains as equal to 8.82 nm. We find that this is over ten time greater than the length of single monomer in any state so we may recognize this value as quite realistic.

5. Conclusions

We have developed a new method of grafting membranes by means of poly(acrylic acid). The method utilizes the Fenton reaction. Contrary to the radiation-induced grafting method presented in (Kontturi *et al.* 1996), the present method triggers polyelectrolyte chains appearing on the membrane surface and in a relatively short distance inside the pores. This results in a smaller reduction of membrane permeability than that for membranes obtained by means of radiation-induced grafting. A conclusion can be drawn that while the last method enables obtaining membranes very efficient as chemical valves, the Fenton reaction based grafting produces membranes more suitable to filtrating solutions with a broad range of pH. The presence of grafted polyelectrolytes may then prevent membrane colloidal fouling. The experimental and theoretical investigations in this field are now in progress.

The theoretical model presented in this work was used to explain the dependence of membrane permeability on the pH of a solution. Contrary to the model presented in (Kontturi *et al.* 1996), the shallow minimum of this dependence was also reconstructed.

Future work will focus on the application of the method of membrane modification for fouling prevention. We may expect that PAA chains on the surface of a membrane will weaken surface blocking during colloid suspension filtration. The possibility of configuration changes of polyelectrolyte chains (e.g., during membrane washing at different pH) may play a role as an additional antifoulant factor. Further work on the subject is in progress.

Acknowledgments

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