

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231674864>

Hydration of a Polysulfone Anion-Exchange Membrane Studied by Vibrational Spectroscopy

ARTICLE *in* LANGMUIR · MARCH 2003

Impact Factor: 4.46 · DOI: 10.1021/la026290+

CITATIONS

20

READS

41

3 AUTHORS, INCLUDING:



Barbara Pałys

University of Warsaw

61 PUBLICATIONS 1,137 CITATIONS

SEE PROFILE



Claudine Buess-Herman

Université Libre de Bruxelles

86 PUBLICATIONS 1,363 CITATIONS

SEE PROFILE

Hydration of a Polysulfone Anion-Exchange Membrane Studied by Vibrational Spectroscopy

Sabine Vico,[†] Barbara Palys,^{*,‡} and Claudine Buess-Herman[†]

Université Libre de Bruxelles, Faculté des Sciences, Service de Chimie Analytique et Chimie des Interfaces, CP 255, 2 Boulevard de Triomphe, B-1050, Bruxelles, Belgium, and Warsaw University, Department of Chemistry, Pasteur Street 1, 02-093 Warsaw, Poland

Received July 24, 2002. In Final Form: February 12, 2003

The water sorption into a polysulfone membrane aminated with trimethylamine has been studied by means of attenuated total reflection Fourier transform infrared and Raman spectra. Spectra of model compounds diphenyl sulfone, diphenyl ether, diphenylisopropane, *p*-toluenesulfonyl chloride, and tetramethylammonium chloride are used to assign the sulfo, ether, and quaternary amine site contributions to infrared and Raman spectra. The polymer–water interaction causes systematic decrease of CH stretching intensities in both IR and Raman spectra. Intensity changes are explained by the ordering of water around quaternary amine sites and by the weakening of the interaction between the positively charged sites and the counterions. Sorption of water into the membrane also causes systematic changes of modes related to sulfo and ether groups. Slight shifts toward longer wavelengths and changes of the band shape are observed, indicating decrease of interchain interactions in the polysulfone membrane.

Introduction

Interaction of water with an organic interface exerts influence on many important phenomena such as polymer mechanical relaxation,^{1,2} conformational stability of biomolecules,^{3,4} formation of microemulsions,^{5,6} and properties of polymeric ion-exchange membranes. In particular, the hydrophilic–hydrophobic properties of the membrane and the state of absorbed water determine the permselectivity and the water flux through the membrane.^{7–18}

Numerous infrared and Raman studies have been devoted to the state of water structure in the membrane,

because the position and the shape of the OH stretching band (ν OH) of water are sensitive to hydrogen bonding.^{9–20} The analysis of relative intensities of ν OH components allows one to estimate the amount of “strongly” and “weakly” hydrogen bonded water, noninteracting with polymer. The strongly hydrogen bonded water corresponds to liquid water structure, and it is usually located in the large pores of the membrane. Membranes containing a large amount of bulk water are not ion-selective, but an insufficient amount of such water may lead to the precipitation of salts within the membrane. The water–polymer interaction disturbs the hydrogen-bond network, giving rise to weakly or “moderately” hydrogen bonded water. The presence of such disturbed water is crucial for the selectivity for ions. The water–polymer interaction can be tuned by introduction of polar (for example carbonyl) or hydrophobic (for example alkyl) groups. In this way, the selectivity for H⁺ over Na⁺ or NO₃[−] over Cl[−] can be influenced.^{7,8} Tetraalkylammonium ions are known to affect significantly the water structure and to promote ordering of water molecules, especially at low temperatures,^{21,22} giving rise to a clathrate-like structure.

The interest in polysulfone, as a membrane material, stems from its excellent thermal and mechanical stability, as well as its resistance to oxidizing agents. Polysulfone has been used as the base of ion-exchange membranes^{23–30}

* To whom correspondence should be addressed. E-mail: bpals@chem.uw.edu.pl.

[†] Université Libre de Bruxelles.

[‡] Warsaw University.

- (1) Sartor, G.; Johari, G. P. *J. Phys. Chem.* **1996**, *100*, 10450–10463.
- (2) McBrierty, V. J.; Keely, C. M.; Coyle, F. M.; Xu, H.; Vij, J. K. *Faraday Discuss.* **1996**, *103*, 255–268.
- (3) Ruffle, S. V.; Michalarias, I.; Li, J. C.; Ford, R. C. *J. Am. Chem. Soc.* **2002**, *124*, 565–569.
- (4) Finney, J. L. *Faraday Discuss.* **1996**, *103*, 1–18.
- (5) Bey Tamsamani, M.; Maeck, M.; El Hassani, I.; Hurwitz, H. D. *J. Phys. Chem. B* **1998**, *102*, 3335–3340.
- (6) Christopher, D. J.; Hills, B. P.; Belton, P. S.; Yarwood, J. *J. Colloid Interface Sci.* **1992**, *152*, 465.
- (7) Stachera, D. M.; Childs, R. F. *J. Membr. Sci.* **2001**, *187*, 213–225.
- (8) Sata, T. *J. Membr. Sci.* **2000**, *167*, 1–31.
- (9) Hirata, Y.; Miura, Y.; Nakagawa, T. *J. Membr. Sci.* **1999**, *163*, 357–366.
- (10) Dias, C. R.; Rosa, M. J.; De Pinho, M. N. *J. Membr. Sci.* **1998**, *138*, 259–267.
- (11) Sammon, C.; Mura, C.; Yarwood, J.; Everall, N.; Swart, R.; Hodge, D. *J. Phys. Chem. B* **1998**, *102*, 3402–3411.
- (12) Pereira, M. R.; Yarwood, J. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2731–2735.
- (13) Pereira, M. R.; Yarwood, J. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2737–2743.
- (14) Hajatdoost, S.; Yarwood, J. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1613–1620.
- (15) Laporta, M.; Pegoraro, M.; Zanderighi, L. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4619–4628.
- (16) Hietala, S.; Holmberg, S.; Nasman, J.; Ostrovskii, D.; Paronen, M.; Serimaa, R.; Sundholm, F.; Torell, L.; Torkkeli, M. *Angew. Makromol. Chem.* **1997**, *253*, 151–167.
- (17) Ostrovskii, D. I.; Brodin, A. M.; Torell, L. M. *Solid State Ionics* **1996**, *85*, 323–327.
- (18) Lowry, S. R.; Mauritz, K. A. *J. Am. Chem. Soc.* **1980**, *102*, 4665–4667.

(19) Zundel, G. *J. Membr. Sci.* **1982**, *11*, 240–274.

(20) Zundel, G. *Advances in Chemical Physics*; Prigogine, I., Rice, S. A., Eds.; Advances in Chemical Physics, Vol. 111; John Wiley & Sons: New York, 2000; pp 1–217.

(21) Kanno, H.; Ohnishi, A.; Tomikawa, K.; Yoshimura, Y. *J. Raman Spectrosc.* **1999**, *30*, 705–713.

(22) Wen, W. Y. In *Water and Aqueous Solutions*; Horne, R. A., Ed.; Wiley-Interscience: New York, 1972; Chapter 15.

(23) Eyal, A.; Kedem, O. *J. Membr. Sci.* **1988**, *38*, 101–111.

(24) Warshawsky, A.; Kedem, O. *J. Membr. Sci.* **1990**, *53*, 37–44.

(25) Hwang, G.-J.; Ohya, H. *J. Membr. Sci.* **1998**, *140*, 195–203; **1998**, *149*, 163–169.

(26) Hao, J. H.; Chen, C. X.; Li, L.; Yu, L. X.; Jiang, W. J. *J. Appl. Polym. Sci.* **2001**, *80*, 1658–1663.

(27) Cui, W.; Kerres, J.; Eigenberger, G. *Sep. Purif. Technol.* **1998**, *14*, 145–154.

(28) Kerres, J.; Cui, W.; Disson, R.; Neubrand, W. *J. Membr. Sci.* **1998**, *139*, 211–225. Kerres, J.; Cui, W.; Junginger, M. *J. Membr. Sci.* **1998**, *139*, 227–241.



Figure 1. Polysulfone structure.

or as ion-exchange coatings on other polymeric supports.³¹ Quaternary amine or sulfonate groups are introduced to transform polysulfone into an anion- or a cation-exchange membrane, respectively. The introduction of ionic exchange sites markedly modifies the polymer properties. Generally, it increases the swelling capacity and consequently the water flux, but it may lead to worse mechanical stability especially in the case of sulfonated polysulfones.³² Therefore, several cross-linking or blending procedures have been developed to reduce the swelling and to balance the membrane properties.^{25–29} Aminated polysulfone materials are usually mechanically stable and excellent for preparing self-supporting membranes.^{23,24}

In this paper, the sorption of water into the polysulfone membrane containing quaternary methylammonium sites is examined by both infrared and Raman spectra. On the basis of a detailed spectroscopic characterization of the polysulfone membrane, the water-induced changes in the polymer and the amine vibrational modes are discussed.

Experimental Section

Membrane Preparation. Membranes were cast from a solution of bromomethylated polysulfone in chloroform (pro analysis, Merck) onto glass plates of known surface area. The solvent was removed by evaporation at room temperature. The film thickness was controlled by using constant mass of the bromomethylated polymer.

The bromomethylation of polysulfone has been achieved by the procedure developed by Warshawsky et al.³³ The polysulfone substrate (Udel structure) is shown in Figure 1 in its aminated form. The chemicals used for the bromomethylation reaction are polysulfone (Aldrich), bromomethyl octyl ether (90%, Aldrich), tin(IV) chloride (99%, Acros Organics), 1,2-dichloroethane (99+%, A.C.S. reagent, Aldrich), and methyl alcohol (pro analysis, Acros Organics).

The amination was performed by immersing the bromomethylated membrane in a solution containing 27% trimethylamine (solution of 45% in water, for synthesis, Merck), 20% methyl alcohol (pro analysis, Acros Organics), and 53% deionized water. The membrane remained in the amine solution for 24 h. The aminated membrane was rinsed with 0.5 M HCl (hydrochloric acid, pro analysis, min 37%, Acros Organics) and deionized water. During rinsing with 0.5 M HCl, the Br[−] ions originally present in the membrane are probably exchanged into Cl[−].

FTIR Measurements. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of polysulfone membranes were recorded by means of a Nicolet spectrometer equipped with a mercury cadmium telluride (MCT) liquid nitrogen cooled detector. A horizontal −12 reflections ATR accessory (Graseby-Specac) equipped with a ZnS crystal with an incident angle of 45° was used. The sample was pressed to the crystal by the Specac clamp-kit to ensure reproducible contact between the sample and the ATR crystal. Registration of a spectrum took 10 s.

(29) Koter, S.; Piotrowski, P.; Kerres, J. *J. Membr. Sci.* **1998**, *153*, 211–225.

(30) Kerres, J.; Cui, W.; Reichle, S. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 2421–2438.

(31) Messalem, R.; Mirsky, Y.; Daltrophe, N.; Saveliev, G.; Kedem, O. *J. Membr. Sci.* **1998**, *138*, 171–180.

(32) Johnson, B. C.; Yilgor, I.; Tran, C.; Iqbal, M.; Wightman, J. P.; Lloyd, D. R.; McGrath, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 721–737.

(33) Warshawsky, A.; Deshe, A. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1839.

The infrared spectrum of the water vapor in the cell compartment was measured immediately after the experiment and subtracted from the polysulfone spectrum. The water vapor contributions are located in two regions: 4000–3500 and 1900–1350 cm^{−1}.

FTIR spectra of the solid model compounds (diphenyl ether and diphenyl sulfone) were measured in KBr pellets. Spectra of liquid diphenylisopropane and the polysulfone solution in CHCl₃ were obtained with a ZnSe cell.

Raman Measurements. Raman spectra were recorded on a Perkin-Elmer FT-Raman spectrometer. The near-infrared 1064 nm line was used for excitation. For all presented spectra, a 200 mW laser power was used. For the swelling studies, 10 scans were collected in 15 s.

Swelling Measurements. The swelling degree was calculated as

$$S = \frac{m - m_d}{m_d} \times 100\%$$

where m_d is the mass of the membrane dried at 70 °C, and m stands for the mass of the swelled membrane.

The maximal mass increase due to water sorption for the studied membranes was equal to 18%, after immersion of the aminated polysulfone membrane in water for 24 h at room temperature.

Since the water content of the membrane may slightly decrease during the measurement of the IR or Raman spectrum, an average value of m has been considered by weighing the swelled membrane before and after the measurement.

Results and Discussion

Characterization of Polysulfone Membrane Spectra. Spectra of polysulfone and related polymers have been studied and assigned using general infrared and Raman tables.^{12,30,34–42} Although, the existing assignments are not always unequivocal. Some spectral differences might be introduced by various methods of membrane preparation or slight differences in chemical composition. Furthermore, contributions of quaternary amine sites are not included in proposed assignments. For these reasons, studies of model compounds corresponding to various fragments of the polysulfone backbone are useful for the interpretation. Detailed assignments, together with those taken from refs 35–41, of Raman and infrared modes are presented in Table 1.

Figures 2–4 illustrate relative contributions of various polysulfone fragments to infrared and Raman spectra. Comparison of polysulfone and model compound IR spectra indicates that the SO₂ and C–O–C contributions prevail between 1350 and 1000 cm^{−1} (Figure 2). The tetramethylammonium ions give rise to two strong infrared bands at 1489 and 951 cm^{−1} (Figure 2e). The 1489 cm^{−1} band overlaps with polysulfone modes, resulting in the single broad band in the membrane spectrum at 1484 cm^{−1}. The 951 cm^{−1} band corresponds to the triply degenerate

(34) Deimede, V.; Voyatzis, G. A.; Kallitsis, J. K.; Qingfeng, L.; Bjerrum, N. J. *Macromolecules* **2000**, *33*, 7609–7617.

(35) Kerres, J. A.; Van Zyl, A. J. *J. Appl. Polym. Sci.* **1999**, *74*, 428–438.

(36) Belfer, S.; Fainchtein, R.; Purinson, Y.; Kedem, O. *J. Membr. Sci.* **2000**, *172*, 113–124.

(37) Everall, N. J.; Chalmers, J. M.; Ferwerda, R.; Van der Maas, J. H.; Hendra, P. J. *J. Raman Spectrosc.* **1994**, *25*, 43–52.

(38) Briscoe, B. J.; Stuart, B. H.; Thomas, P. S.; Williams, D. R. *Spectrochim. Acta* **1991**, *47A*, 1299–1303.

(39) Pihlajamäki, A.; Vaisanen, P.; Nystrom, M. *Colloids Surf., A* **1998**, *138*, 323–333.

(40) Stuart, B. H. *Spectrochim. Acta A* **1997**, *53*, 107–110.

(41) Everall, N. J.; Lumsdon, J.; Chalmers, J. M.; Mason, N. *Spectrochim. Acta* **1991**, *47A*, 1305–1311.

(42) Gordeyev, S. A.; Nikolaeva, G. Y.; Prokhorov, K. A.; Withnall, R.; Dunkin, I. R.; Shilton, S. J.; Pashinin, P. P. *Laser Phys.* **2001**, *11*, 82–85.

Table 1. Frequencies and Assignments of IR and Raman Bands

IR/cm ⁻¹		Raman/cm ⁻¹	assignment
dry	swelled		
3094, 3056	3094, 3066	3070	CH stretch – benzene
3021	3034	3034	CH stretch – benzene CH stretch – CH ₃ of quaternary amine groups
2963	2969		CH stretch – CH ₃ of polysulfone backbone CH stretch – CH ₃ of quaternary amine groups
<i>a</i>	2931, 2914		CH stretch – CH ₃ of polysulfone backbone
2924, 2852	2852		CH stretch – CH ₂ of quaternary amine groups: $-(CH_2)N^+(CH_3)_3$
2871	2871	2972–2877	CH stretch – CH ₃ of polysulfone backbone CH stretch – CH ₃ of quaternary amine groups
		1610/1586	in-plane benzene ring deformation
1579	1579		benzene C–C deformation
1484 (broad)	1484 (broad)		benzene C–C deformation CH ₃ , CH ₂ deformation quaternary amine groups
		1450 (broad)	CH ₃ , CH ₂ deformation of polysulfone backbone and quaternary amine groups
1409	1409		benzene mode
1386, 1365	1386, 1365		CH ₃ deformation of polysulfone backbone
1319/1291	1319/1291	~1297 (weak)	SO ₂ asym stretching
		1244	benzene C–H in-plane
1225	1231	1209	asymmetric C–O–C stretching
1169	1169		benzene C–H in-plane
		1150	ring-breathing mode of benzene coupled with C–S and C–O motions
1144	1144		SO ₂ sym stretching
		1108, 1075	benzene C–H in-plane
1099, 1070, 1007	1099, 1070, 1012		benzene C–H in-plane coupled with C–S motions
971, 918	975, 922		asym C–N stretching of quaternary amine groups
874, 856	874, 856		out-of-plane CH of benzene
		795	out-of-plane CH of benzene

^a Covered by the 2924 cm⁻¹ band.

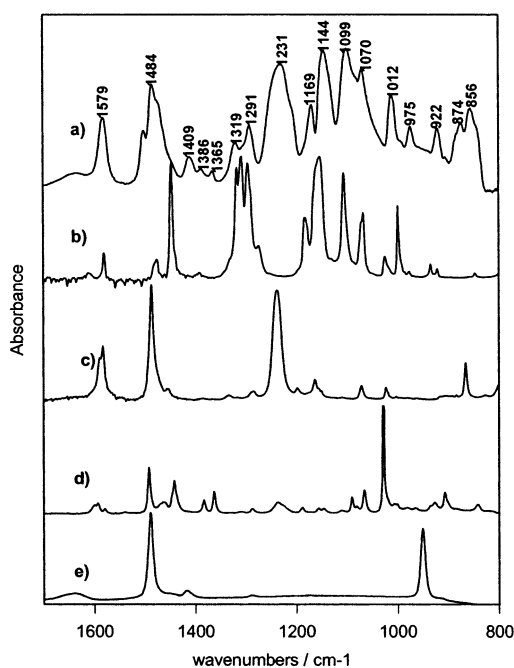


Figure 2. FTIR spectrum of a polysulfone membrane in the 1700–800 cm⁻¹ range compared with spectra of model compounds: (a) polysulfone membrane; (b) diphenyl sulfone; (c) diphenyl ether; (d) diphenylisopropane; (e) tetramethylammonium chloride.

asymmetric C–N stretching mode. Since the symmetry of quaternary amine groups fixed on the polymer matrix is lower than the symmetry of the $N(CH_3)_4^+$ ion, the 951 cm⁻¹ band splits into two components at 975 and 922 cm⁻¹ in the membrane spectrum.

Contrary to the infrared, the Raman spectrum of polysulfone is dominated by benzene modes. The contributions of SO₂ and C–O–C groups are difficult to identify, because it is difficult to find bands that are present solely

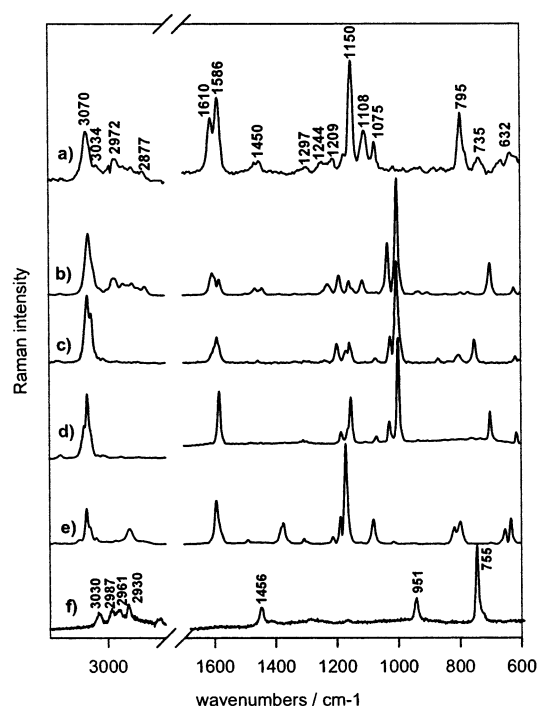


Figure 3. Raman spectrum of a polysulfone membrane compared with spectra of model compounds: (a) polysulfone membrane; (b) diphenylisopropane; (c) diphenyl ether; (d) diphenyl sulfone; (e) *p*-toluenesulfonyl chloride; (f) tetramethylammonium chloride.

in the diphenyl sulfone or diphenyl ether spectra and are repeated in the membrane spectrum, as visible in Figure 3. Furthermore, the 1350–1000 cm⁻¹ range, where the SO₂ and C–O–C are expected, looks similar for all model compounds containing monosubstituted benzene, suggesting that substitution-dependent benzene modes prevail in the concerned part of the spectrum. Raman bands of tetramethylammonium ions are very weak in the

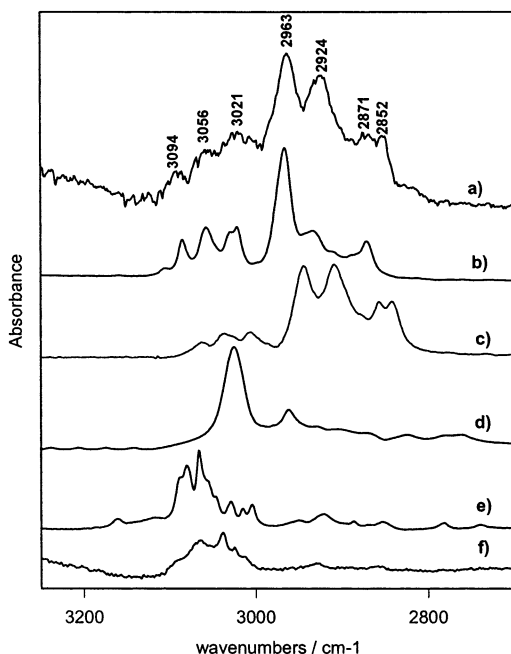


Figure 4. FTIR spectrum of a polysulfone membrane in the 3250–2700 cm^{-1} range compared with spectra of model compounds: (a) polysulfone membrane; (b) diphenylisopropane; (c) bromomethylated membrane; (d) tetramethylammonium chloride; (e) diphenyl sulfone; (f) diphenyl ether.

membrane spectrum, as SO_2 and $\text{C}-\text{O}-\text{C}$. They could be identified as shoulders within the 1450 and 795 cm^{-1} bands.

The strongest band in the membrane Raman spectrum is observed at 1149 cm^{-1} (Figure 3a). A band of similar intensity occurs at 1150 cm^{-1} in the spectrum of *p*-toluenesulfonyl chloride (Figure 3e) and at 1000 cm^{-1} in spectra of diphenylisopropane, diphenyl ether, and diphenyl sulfone (Figure 3b–d, respectively). Despite the big frequency difference, we suppose that both 1000 and 1149 cm^{-1} bands involve the ring-breathing mode of benzene, including possibly the $\text{C}-\text{O}$ and $\text{C}-\text{S}$ motions.

As illustrated in Figure 4, the infrared CH stretching region of the membrane is composed of many overlapping bands. Bands due to CH_3 groups of quaternary amines at 3020 and 2963 cm^{-1} are difficult to discern in the membrane spectrum, because they overlap with the aromatic CH and CH_3 of diphenylisopropane modes, respectively. Two intense bands in the membrane spectrum at 2924 and 2852 cm^{-1} match typical frequencies of CH_2 groups. Consequently, these bands could originate from the CH_2 of quaternary amine sites. Alternatively, these bands could be related to unreacted CH_2Br groups, because they are observed in the spectrum of the membrane prior to the amination (Figure 4c). Although, such a hypothesis is rather improbable, because the reaction of bromomethyl groups with trimethylamine proceeds with high efficiency.⁸

Effect of Hydration. *Changes in IR Spectra Caused by Hydration: CH Stretching Intensities.* Typical ATR-FTIR spectra in the $\text{C}-\text{H}$ stretching range obtained for aminated polysulfone membranes at various water contents are presented in Figure 5.

Swelling of polysulfone membranes by water introduces apparent changes in the spectral region of CH stretching bands (Figure 5). The CH_2 bands at 2924 and 2852 cm^{-1} decrease visibly with the increasing water content. Although, the thorough examination of the concerned region reveals that also bands related to CH_3 groups

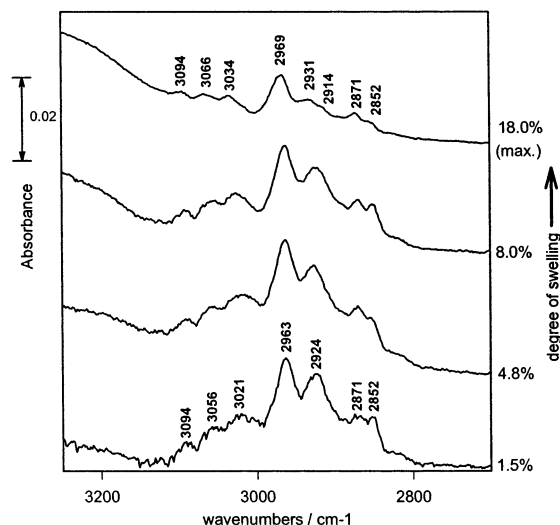


Figure 5. FTIR spectra of the polysulfone membrane at various degrees of swelling in the 3250–2700 cm^{-1} range.

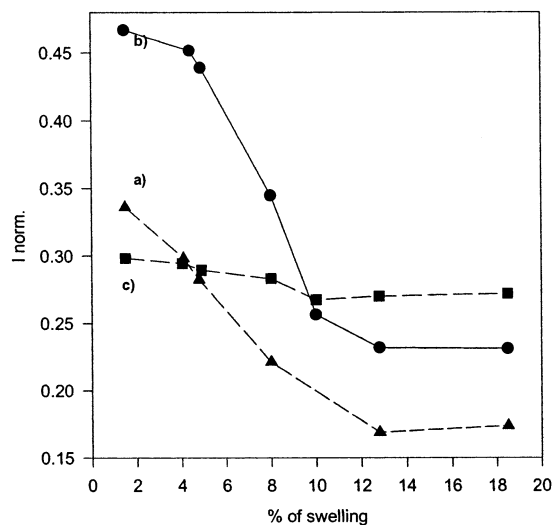


Figure 6. Dependence of the normalized infrared intensity of (a) the CH stretching modes of CH_3 groups (integration limits: 2990–2800 cm^{-1}) (\blacktriangle), (b) the total CH stretching range (3150–2800 cm^{-1}) (\bullet), and (c) the benzene deformation band (1579 cm^{-1}) (\blacksquare) on the swelling of the membrane. Intensities have been normalized to the integrated intensity of benzene and $\text{C}-\text{H}$ deformation modes 1530–1350 cm^{-1} . Before the integration, the baseline correction was made to obtain the horizontal baseline.

diminish upon water sorption into the membrane. The highest band in the concerned region, related to CH_3 groups (2963 cm^{-1} in the dry membrane), decreases systematically as well as the intensity of the whole CH stretching range (3150–2800 cm^{-1}), as visualized in Figure 6. Remaining bands in the spectrum, for example, the benzene deformation mode at 1579 cm^{-1} , do not reveal intensity changes due to the membrane swelling (see Figure 6).

As follows from the study of model compounds, the amine part is difficult to discern from the whole CH stretching range. So, we suppose that the observations refer to the CH included in the amine sites. To support this affirmation, we have studied infrared spectra of tetramethylammonium chloride and benzyl-trimethylammonium chloride in KBr pellets. We compared spectra of dry pellets with spectra after exposure of pellets to the water vapor. The intensity of the CH stretching range (3150–2800 cm^{-1}) normalized in a similar way as in Figure

6 changes from 1.5 for the dried samples to 0.5 for samples exposed to the water vapor. This indicates that the decrease of the CH stretching intensity is solely an effect of the hydration of quaternary amine groups.

Among numerous factors influencing the infrared intensity, the method of measurement plays a role and therefore requires here some immediate comment. In the ATR technique, the penetration depth of the infrared beam depends on the polarization. According to formulas in ref 42, in the experimental configuration used in this work, the light polarized parallel to the incident plane enters a membrane layer whose thickness is twice that examined with light polarized perpendicularly to the plane.

The change of relative intensities in the infrared spectrum shown in Figure 6 could suggest a reorientation or disordering in the membrane introduced by water. Although, such a suggestion is rather improbable, since polysulfone is known to be an amorphous polymer.

Recently, Gussoni and Castiglioni⁴⁴ thoroughly discussed factors influencing the intensity of CH bands and suggested the use of CH stretching intensities as a tool for chemical diagnosis.^{44–48} According to arguments presented in ref 44, the decrease of CH intensity indicates more positive charge on the H atom and possible modification of the intra- or intermolecular interactions between CH groups and their surroundings due to the hydration of the membrane. In the dry membrane, the quaternary amine sites interact with counterions, which are Cl^- . The Cl^- ions are able to share partially the lone pair of electrons with the hydrogen of a CH group implicated in the amine site. So, this kind of interaction causes a decrease of the positive charge on the concerned hydrogen and high intensity of amine CH stretching modes. With hydration of the membrane, the quaternary amine sites are surrounded by water molecules, which break the amine site–counterion interaction, as a result causing the decrease of CH intensity. Formation of hydrogen bonds between quaternary amine sites and water molecules is rather unlikely, because hydrogen bonding increases the intensity. Such a conclusion is supported by the fact that the water molecules are forming clathrate structures around tetraalkylammonium ions.²² These water molecules interact strongly with each other by hydrogen bonds but not significantly with the encapsulated species, tetraalkylammonium ions being indeed quasi totally unhydrated. To verify this specific behavior of water in the membrane, we compare the infrared OH band of water in the aminated polysulfone membrane with the band of pure liquid water (Figure 7). A great fraction of strongly hydrogen bonded water is expected to give intense low-wavenumber components in the νOH band of water. Figure 7 shows that the intensity of the low-wavenumber components is clearly higher in the case of water in the membrane, corroborating strong ordering of water molecules around the quaternary amine sites.

Changes in IR Spectra Caused by Hydration: The 1700–800 cm^{-1} Range. The width of infrared $-\text{SO}_2-$ and $\text{C}-\text{O}-\text{C}$ bands changes systematically during swelling (1350–900 cm^{-1} range in Figure 8). They are very broad for the dry membrane and become narrow as the water content is

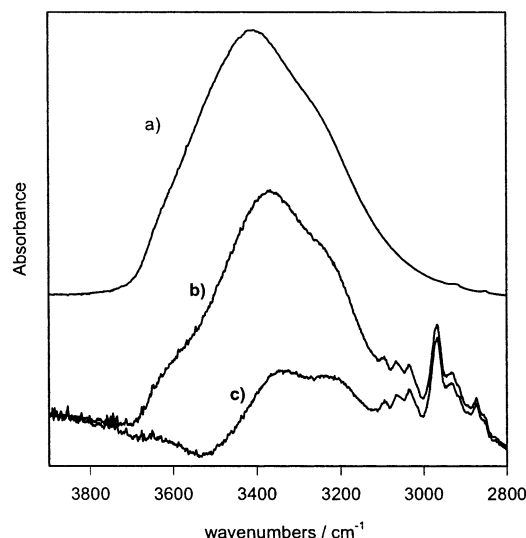


Figure 7. The νOH band of water in the membrane (a) compared with the νOH band of pure liquid water (b) and the difference of the water band in the membrane minus the water band of pure water (c).

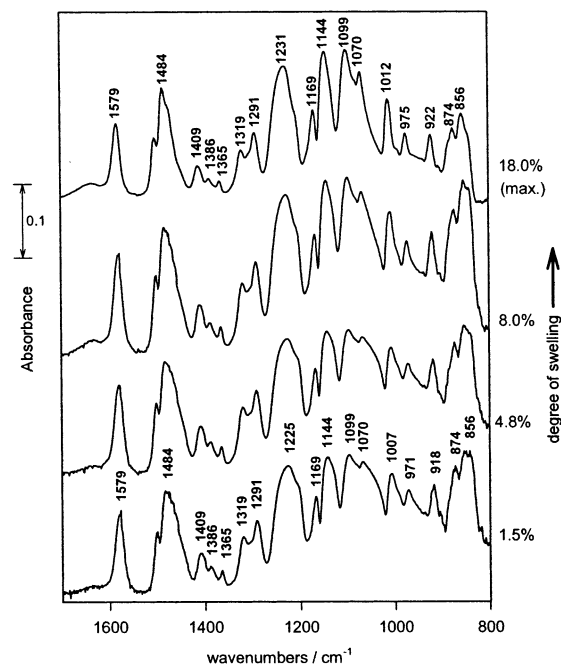


Figure 8. FTIR spectra of the polysulfone membrane at various degrees of swelling in the 1700–800 cm^{-1} range.

increased. Simultaneously, slight shifts (from 2 to 6 cm^{-1}) toward longer wavenumbers are observed. Similar spectral changes have been reported in studies of polystyrene-sulfonic acid¹⁸ and sulfosuccinate reverse micelle hydration.^{49,50} In these reports, the exchange of cations interacting with the SO_3^- groups was responsible for the change of bandwidth and position of the sulfonate bands.

It has been demonstrated that the full width at half-maximum of the SO_3^- group symmetric stretching band is directly related to the strength of the cation– SO_3^- interaction.

On the basis of the above observations, we conclude that sorption of water into the polysulfone membrane

(43) Harrick, N. J. *Internal Reflection Spectroscopy*; John Wiley & Sons: New York, 1967; p 43.

(44) Gussoni, M.; Castiglioni, C. *J. Mol. Struct.* **2000**, 521, 1–18.

(45) Gussoni, M.; Castiglioni, C.; Zerbi, G. *J. Phys. Chem.* **1984**, 88, 600.

(46) Rui, M.; Ramos, M. N.; Castiglioni, C.; Gussoni, M.; Zerbi, G. *Mol. Cryst. Liq. Cryst.* **1990**, 187, 275.

(47) Coleman, M. M.; Painter, P. C. *Appl. Spectrosc. Rev.* **1984**, 20, 255.

(48) Stanghellini, P. L.; Rossetti, R. *Inorg. Chem.* **1990**, 29, 2047.

(49) Moran, P. D.; Bowmaker, G. A.; Cooney, R. P.; Bartlett, J. R.; Woolfrey, J. L. *J. Mater. Chem.* **1995**, 5, 295–302.

(50) Moran, P. D.; Bowmaker, G. A.; Cooney, R. P.; Bartlett, J. R.; Woolfrey, J. L. *Langmuir* **1995**, 11, 738–743.

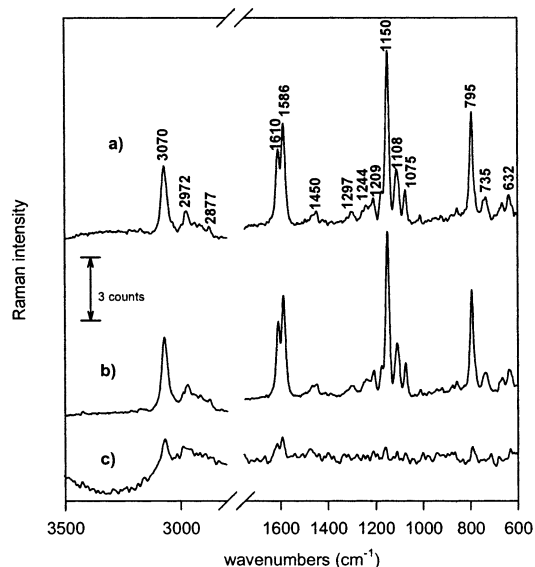


Figure 9. Raman spectra of the polysulfone membrane: (a) at the maximum degree of swelling; (b) dry membrane; (c) the difference spectrum between dried and swelled membrane.

enlarges distances between polymer chains and destroys possible interchain interactions involving SO_2 and $\text{C}-\text{O}-\text{C}$ groups. Since both sulfo and ether groups are strongly electronegative and probably are negatively charged, they might interact with positive amine sites.

Effect of Hydration in Raman Spectra. Raman spectra of the dry and hydrated membrane differ only by relative intensities of CH stretching modes, as illustrated in Figures 9 and 10. The intensity integrated over the whole CH stretching range diminishes with increasing water content in the same way as in infrared spectra (compare Figure 6 and Figure 10) and can be similarly explained as a result of hydration of quaternary amine sites, since Raman intensities are influenced by the surroundings of the H atom similarly to infrared intensities.⁵¹

The ordering or reorientation can be easily excluded from possible reasons of observed intensity changes, because they are expected to change intensity ratios between bands of different symmetry. The $1610/1586\text{ cm}^{-1}$ band of polysulfone corresponds to the E_g benzene deformation mode,⁵² and possible reorientation in the polymer film should change its intensity with respect to totally symmetric vibrations, for example, the 1150 cm^{-1} band. As visualized in Figure 10, the intensity of the $1610/1586\text{ cm}^{-1}$ band divided by that of the 1150 cm^{-1} band is not influenced by the water content in the membrane, so

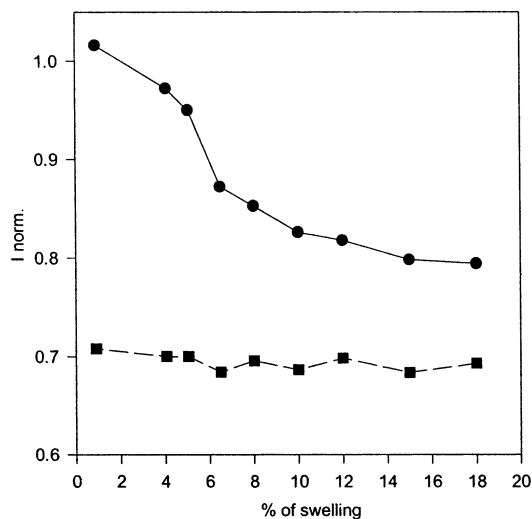


Figure 10. Dependence of the normalized Raman intensity of the CH stretching range ($3150\text{--}2800\text{ cm}^{-1}$) (●) and the benzene deformation band (doublet, $1610/1586\text{ cm}^{-1}$) (■) on the swelling of the membrane. Intensities have been normalized to the integrated intensity of benzene and C–H deformation modes $1190\text{--}1040\text{ cm}^{-1}$.

a reorganization of the polymer backbone cannot be a significant reason for the observed intensity changes.

The hydration of the membrane does not influence significantly the $1350\text{--}900\text{ cm}^{-1}$ range in Raman spectra of the membrane (Figure 9), while in infrared spectra changes of bandwidth and small shifts of positions were observed. This discrepancy can be rationalized, since the concerned spectral range of the infrared spectrum involves significant SO_2 and COC contributions, while in the Raman spectrum it is dominated by benzene motions, which are unaffected by interchain interactions.

Conclusions

Hydration of quaternary amine sites in the polysulfone anion-exchange membrane influences clearly both infrared and Raman spectra of the polymer. Changes concern relative intensities of CH stretching modes coming from quaternary amine sites and bandwidths and positions of infrared modes involving SO_2 and COC contributions. The spectral results are consistent with hydration models of tetraalkylammonium ions, assuming formation of water clathrates surrounding the quaternary amine ions, where water molecules interact strongly with each other by hydrogen bonds but not significantly with the quaternary amine sites.

Acknowledgment. B. Palys thanks the Government of the Brussels Capital Region for making possible her stay in Brussels.

LA026290+

(51) Gussoni, M. J. *Mol. Struct.* **1984**, *113*, 323–340.

(52) Varsanyi, G. *Vibrational Spectra of Benzene derivatives*; Akademiai Kiado: Budapest, 1969; pp 232–238.