Infrared Investigations of Sulfonated Ionomer Membranes. I. Water–Alcohol Compositions and Counterions Effects

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SYNOPSIS

FT-IR spectra of Nafion 117, Raipore 1010, and PESS membranes loaded with different alkaline counterions and equilibrated with different liquid media were recorded by means of the attenuated total reflectance technique. The antisymmetric (ν_{as}) and especially the symmetric stretching vibrations (ν_s) of the sulfonate groups are affected by the presence of solvents in its local chemical environment. In the dry membrane the smaller the bare counterion, the higher the frequency of the symmetric vibration and the stronger the sulfonate–counterion interactions in the contacting ion pair. After equilibration with pure water, ethanol, and 2-propanol, the ν_s vibration shifts to a constant value corresponding to the solvated sulfonic grouping in the case of Nafion–Li$^+$ membrane. In the cases of PESS–Li$^+$ and Raipore–Li$^+$ membrane only water can cause a similar shift. The greater affinity of the Nafion membrane to alcohols can be attributed to the stronger acidity of the corresponding sulfonic acid. In water–alcohol mixtures the variation of ν_s with water content indicates that the ion pairs in the PESS–Li$^+$ membrane are progressively dissociated and solvated by increasing amounts of water in 2-propanol. Complete dissociation occurs at about 9 wt % water. Smaller shifts are observed with bigger cations, due to the weaker sulfonate–cation interactions.

INTRODUCTION

Over the last decade there has been an increasing interest in ionomer membranes. Ionomer membranes are ion-containing membranes that possess rather low ion exchange capacities (generally a few meq/g dry membrane). They are widely used in electrolysis cells and show high potential in many applications (gas dehydration, catalyses, electromembrane processes, pervaporation).

In pervaporation, one side of an ionomer membrane is put into contact with a water–organic solvent mixture. A permeate is extracted in vapor form from the other side by means of vacuum pumping or by sweeping with an inert gas or liquid. Due to the strong affinity of ionic sites to water and a certain inertness of polymer backbones to organic solvents, water is preferentially permeated. However, depending on the nature of the ionomer membrane and the mixture, different behaviors were observed.[1-7] The most important feature in pervaporation is the change in membrane characteristics in relation with the water content in the mixture and the pervaporation temperature. The flux and selectivity plots versus water content in various water–alcohol mixtures show different patterns for the same charged groups, e.g., for a crosslinked, sulfonated, styrene–butadiene base membrane,[1] polystyrene sulfonate grafted onto fluoropolymers,[5] and a perfluorosulfonated Nafion membrane.[2,6,7] The activation energy values for ethanol transport were also very different for a Nafion membrane and a sulfonated polyethylene film.[6] Moreover, when the counterions to the fixed charges were changed, the same membrane exhibited distinctly different characteristics to the same mixture.[1-3,5-7] Such properties could be advantageously used to "tailor" a suitable membrane for a given separation purpose without having to make unnecessary efforts to prepare chemically new membranes.

The aim of our study is to investigate the inter-

actions between membranes and water–organic solvent mixtures when the membranes are loaded with different counterions. It has been suggested that three categories of molecular interactions regulate the transport of a solvent through a dense membrane: polymer–polymer, polymer–solvent, and solvent–solvent.[8] In the case of a binary mixture, "ternary" interactions (e.g. polymer–solvent 1–solvent 2) should be considered in addition to all binary interactions.

The interactions at the molecular level between water vapors and ionomer membranes, including those successively loaded with different counterions, have been studied by several authors, generally by means of spectroscopic methods,[9-14] but also by calorimetric measurements.[6,15] It should be mentioned that a large number of studies have dealt with physical and ionic transport properties, as well as the superstructure of Nafion membranes.[16-20]

Very little attention has been paid to the interactions between ionomer membranes and organic solvents or water–organic solvent mixtures.[21-23] Cabasso et al.[6] have recently reported some preliminary results of the work undertaken in the group on the calorimetric study of the Nafion membrane–water–isopropanol system.

Infrared spectroscopy provides interesting information on the interactions at the molecular level between ionic sites and solvents. The vibration bands of the solvents can reveal the extent of sorption and the binding state of the solvents. The vibration bands of polar groups in polymer membranes can give information on the location and the strength with which solvent molecules are bound.

In the present work we focus our attention on the latter bands.

EXPERIMENTAL

Membranes

The chemical structure and some characteristics of the membranes used are given in Table I. None of the membranes were backed.

In order to avoid any slow structural changes during the experiments, the samples of the Nafion membrane first underwent a standard pretreatment consisting of boiling with distilled water for 30 min. The PESS membrane was expanded at 50°C for 4 h. Samples in a given ionic form were obtained by an immersion for 24 h in $1 M$ solution of the appropriate hydroxide (Li^+, Na^+, K^+, or Cs^+), followed by repeated rapid washes to remove the excess of caustic solutions. Care was taken to obtain a correctly dried sample for spectroscopy: The samples were first dried under a 10^{-2} torr vacuum at 95°C for 24 h and quickly mounted under an infrared lamp. They are referred to as "dry membranes," although very small amounts of strongly sorbed water may still be present in the membranes. A complete drying under severe conditions was not undertaken, as it could damage or change the structure of the membrane.

Infrared Spectra (IR)

IR spectroscopic measurements were carried out by the attenuated total reflectance (ATR) mode on the

Table I   Physico-chemical Properties of the Membranes Investigated

Membrane	Chemical Structure	Thickness (μm)	Ion Exchange Capacity (meq/g)
PESS[a]	Interpenetrating network of polyethylene and sulfonated polystyrene-co-divinylbenzene	180	2.10
Nafion 117	Poly (tetrafluoroethylene-co-perfluoro-3,6-dioxa-4-methyl-7-octen-sulfonic acid)	170	0.91
Raipore 1010	Polystyrene sulfonate grafted onto PTFE films	50	1.2

[a] The PESS membrane was prepared at Technical University of Wroclaw (Poland) in the Laboratory of Prof. Trochimczuk.[24]

FT-IR Bruker spectrometer. Usually 128 interferograms were co-added and the Fourier transform was calculated at an apodized resolution of 2 cm^{-1}. All spectra were recorded in the range of 4000–400 cm^{-1} at 20°C.

ATR–IR spectroscopy is a surface technique with a penetration depth of the evanescent wave of 3–20 μm, depending on the incident angle; and it is assumed that the spectra observed are representative of the bulk sample. With this technique films of any thickness may be used by simply clamping them between the internal reflectance crystal and the back plate. A selenium zinc internal reflection crystal mounted at an incident angle of 45° was used in all experiments.

The spectra were collected both for membranes in the dried form and for membranes equilibrated in pure solvents and various water–alcohol mixtures.

RESULTS AND DISCUSSION

General Features of the Spectra

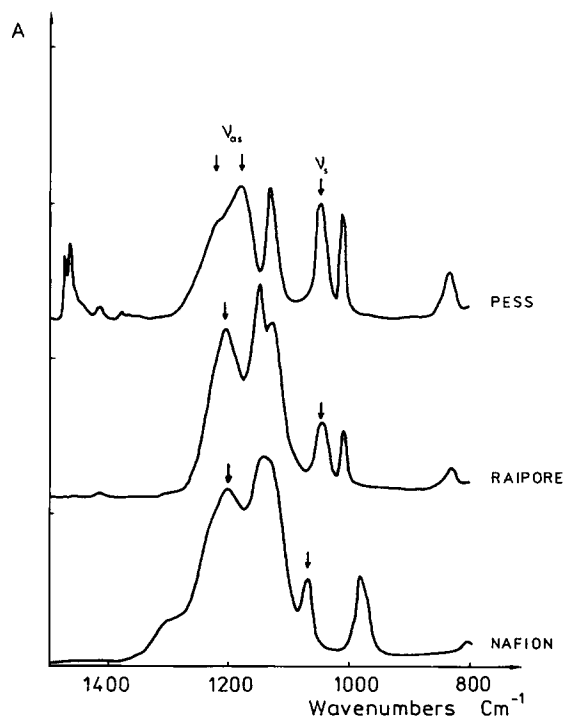Figure 1 gives the infrared spectra of dry Nafion, Raipore, and PESS membranes in the lithium form.

Figure 1 ATR-IR spectra of Nafion, Raipore and PESS membranes (Li$^+$ form, dry). ν_s, ν_{as}—symmetric and antisymmetric—stretching vibration bands of sulfonic groups.

Table II Frequencies (in cm^{-1}) of the Symmetric (ν_s) and Antisymmetric (ν_{as}) Stretching Vibrations of the S—O Band in Different Sulfonated Membranes (K$^+$ Form)

Membrane	ν_s	ν_{as}	
		l	h
Nafion	1058	1206	Obscured
PESS	1036	1178	1204
Raipore	1036	1151	Obscured

The detailed assignment of the vibrational bands of the backbone of these membranes has already been presented by several authors.[9,10,13]

For this study the most important bands are the vibration bands of the sulfonic groups. The sulfonic anions have two active stretching vibrations: (1) a symmetric stretching vibration (ν_s) at 1030–1070 cm^{-1} and (b) an antisymmetric stretching vibration (ν_{as}) at about 1200 cm^{-1}.

An isolated SO$_3^-$ ion possesses a pyramidal structure with C_{3v} symmetry, and its ν_{as} vibration is doubly degenerate. However, in the membrane, an approaching cation polarizes one of the S—O bonds and the ν_{as} band occurs as a doublet.[11] This splitting increases with increasing electrostatic field of the cation.

Table II presents the positions of the symmetric (ν_s) and antisymmetric (ν_{as}) stretching vibrations of sulfonic groups in membranes equilibrated with water.

The position of the symmetric stretch differs for each membrane, and this difference may reflect the ionic strength of the sulfonic groups in the membranes due to the chemical environment.[11] The sulfonic groups linked to either aromatic or aliphatic segments (Raipore, PESS) have symmetric stretching frequencies significantly lower than those linked to perfluorinated vinyl ether (Nafion). Thus, sulfonic groups in the Nafion membrane have the strongest acidic character. This behavior can be explained by the strong electro-attractive effect of the fluor atoms, which accentuates the polarization of S—O links.

The antisymmetric stretching vibration band shows a doublet structure for all the membranes presented in Figure 1. From this fact one can conclude that the asymmetric attachment of cations to sulfonate ions is a general feature, as was discussed by Zundel,[11] who also put forward that the bond energy is greater when the center of cationic charge

is on the S—O bond axis than if the counterion affects all three S—O bonds.

In the cases of the Nafion and Raipore membranes, only the lower frequency part of the doublet is seen in the spectra because of the very strong —CF— band in the same region.[16,25] Therefore, we will mainly focus our discussion on the symmetric stretching vibration.

Changes in the Symmetric Stretching Vibrations in Dry Membranes

For a given membrane the position of the symmetric stretching vibration band of the sulfonic group is affected by changes in its local chemical environment. The detailed studies of the effects of hydration and counterion type on this band have been performed by Lowry and Mauritz (Nafion membrane)[9] and by Zundel (polystyrene sulfonate membrane).[11]

Table III groups the frequencies of ν_s band for PESS and Nafion membranes in different cationic forms and different solvents. The results concerning the Raipore 1010 membrane, which exhibits a very similar behavior to that of the PESS membrane, are not shown here.

For all dry membranes the frequency ν_s shifts toward higher wave numbers when the counterion is changed from Cs^+ to Li^+, that is, when the radius of the nonsolvated counterion decreases. This frequency increase has already been observed,[9,10] and was explained by stronger induced polarization of the S—O dipole by the stronger electrostatic field of smaller bare cations (Table IV). Therefore, whatever the nature of the "backbone," a decrease

Table III   Frequency of the Symmetric Stretching Vibration Band ($\nu_s SO_3^-$) (cm^{-1}) in PESS and Nafion Membranes

Ionic Form	Dried	H_2O	EtOH	isoPrOH
PESS				
Li^+	1046.3	1035.7	1046.3	1044.0
Na^+	1039.6	1035.7	1040.5	1039.6
K^+	1037.6	1035.7	1037.6	1036.7
Cs^+	1033.8	1035.7	1034.8	1034.8
Nafion				
Li^+	1070.4	1057.9	obscured	1055.0
Na^+	1063.7	1057.9	obscured	1055.8
K^+	1059.8	1057.9	1056.9	1057.9
Cs^+	1054.0	1055.0	1054.0	1054.0

Table IV   Values of Ionic Radius and Electrostatic Field for Alkaline Cations

Cation	Ionic Radius (Å)	Electrostatic Field (10^{-6} ESU/cm^2)
Li^+	0.68	3.18
Na^+	0.97	2.08
K^+	1.33	1.36
Rb^+	1.47	1.18
Cs^+	1.67	0.98

in the sulfonate–cation binding strength is observed with increasing size of the bare cations in the contact ion pair.

Changes in the Symmetric Stretching Vibration in Membranes Equilibrated with Pure Water

In pure water all counterions lead to the same frequency of the S—O symmetric stretch. This behavior, which has already been observed for ionomer membranes exposed to high relative humidity,[9,10] means that the same immediate environment was obtained for the sulfonic group, whatever the counterion. This immediate environment probably corresponds to water molecules that are bound to the oxygen atoms by hydrogen bonds (shift of ν_s toward the lowest frequency). One can consider that all the types of alkaline sulfonates undergo dissociation and hydration, and that the sulfonate group is shielded from the influence of the electrostatic field of the cation. The biggest relative shift of the symmetric stretching frequency observed in the hydration of any membrane in the Li^+ form is consistent with the explanation that the strongest polarization of the sulfonate group by the Li^+ cation field in a contact ion pair disappears on hydration. The Cs^+ ion, because of the weakest electrostatic field (Table IV), has a negligible polarization effect in a contact ion pair, and consequently practically no shift occurs on hydration. This model of electrostatic polarization of sulfonate groups by a cation field in a contact ion pair, advocated by Mauritz[9] in the case of the Nafion membranes, is substantiated by our results for other membranes with different polymer matrix.

However, the IR data based on observations of sulfonate vibrations do not allow us to form an opinion on the total water uptake by different membranes and counterion forms: despite their same ν_s values, the different membranes show quite different water uptake (Table V). This is due to the fact that, once the primary hydration "shells" around the ions

Table V   Water Sorption in Membranes

Membrane	Water Sorption			
	[g H_2O/g dry membr.]		[mole H_2O/ mole SO_3^-]	
	Li^+	K^+	Li^+	K^+
PESS	0.78	0.48	20.6	12.7
Nafion	0.21	0.09	12.8	5.5
Raipore	0.43	0.27	19.9	12.5

are completed, subsequent water molecules are incorporated in the polymer through hydrogen bonding with the strongly bound water molecules of the primary shells, and with each other. The secondary bound water molecules may have an influence on the vibrations of O—H bands, but a negligible influence on the S—O vibrations. The water uptake depends on: (i) the interaction potential, (ii) elasticity of the polymer matrix permitting the additional volume, and (iii) the entropy for the redistribution of different species.

The smaller cation has stronger interactions with water, and it also leaves more "space" for water molecules to be housed in the solid for a given amount of energy necessary to deform the polymer network. The results of water uptake (Table V) are consistent with this statement: The Li^+ form absorbs more water than the K^+ form. Similar behavior was found for ion exchange resins made of cross-linked polystyrene sulfonate.[26] One might also expect that water sorption decreases with decreasing exchange capacity of the membrane, and with increasing rigidity of the polymer network.

Changes in the Symmetric Stretching Vibration in Membranes Equilibrated with Pure Alcohols

It can be seen from Table III that after equilibration with pure alcohols, the position of the ν_s band in PESS–Li^+ remains close to that in the dry membrane, while in the Nafion–Li^+ membrane it shifts to the same value as that obtained with the hydrated membrane. In general, the symmetric stretching of the PESS membrane in different forms remains closer to that in the dry membrane, while that of the Nafion membrane experiences a frequency-lowering effect from the alcohol molecules.

Lowry and Mauritz[9] suggested that the solvation of ion pairs is different according to the strength of the interactions that exist between the ion pair and the solvent molecules. Starting from the case of an

ion pair in the dry state where the two ions are in close electric contact, there is first an "inner-sphere" complex, then an "outer-sphere" contact, followed by the formation of an ion pair at the contact of an undisturbed primary hydration shell, and finally independently solvated ions.

Our results show that the lithium (or sodium) sulfonate ion pairing in the PESS membrane was practically unmodified by alcohol molecules, i.e., the solvation, if any, affected only the outer atmosphere of the ion pair (Table III). On the other hand the sulfonate group in the Nafion membrane behaves similarly in alcohols and in water, i.e., the sulfonate groups are shielded from its counterion electrostatic field by one or several alcohol molecules (Table III). Distinct behavior is therefore noted in these conditions for the Nafion and the PESS membranes in 2-propanol solvent on the one hand, and for the PESS membrane in water and 2-propanol on the other hand.

The difference between the influence of water and 2-propanol resides in the ability of each to dissociate contact ion pairs. In fact, the dissociation process involves the separation of the contact ion pair (an endothermic process) and the solvation of the ions (an exothermic process). Due to their low dielectric constant, alcohols as solvents are known to possess lower dissociation ability. The absence of dissociation of lithium styrene sulfonate in alcohols means that the interactions between the solvents and the ions are not powerful enough to overcome the attractive energy in the contact ion pairs. In the case of the Nafion membrane, the stronger acidic character, i.e., the stronger innate tendency to dissociation of the tetrafluoroethylene sulfonic acid, explains the easier dissociation of its salts in alcohols.

As already observed in the case of weak acids in aqueous media, the stronger the acidity, the better the dissociation of the corresponding salts in the medium. Thus the salts of tetrafluoroethylene sulfonic acid in the Nafion membrane must dissociate more easily than those of normal sulfonic acids in 2-propanol (in which sulfonic acids rather behave as weak acids).

Changes in the Symmetric Stretching in Membranes Equilibrated with Water–Alcohol Mixtures

The situation is much more complex in the cases of membranes equilibrated with water–alcohol mixtures. As both solvents are active in hydrogen bonding, there should be a composition dependence competition between different hydrogen bond acceptors

present in the system, i.e., water and alcohol molecules, and sulfonate sites, in addition to the different ion solvation ability of the two species. The counterions again modify the polarization of the sulfonate groups and contribute to the solvents uptake through their solvation.

In the case of the PESS–Li$^+$ membrane, the position of ν_s (frequency of the symmetric vibration of the S—O band) is unchanged until the water content (in isopropanol) exceeds 3 wt %; then it decreases progressively to a stable value when the water content exceeds 9 wt % (Fig. 2). Since for this membrane there is negligible dissociation of the ion pairs by the alcohols, these results suggest that at about 3 wt % of water in the mixture, there was enough water activity to promote a hydration by insertion of water molecules between sulfonic groups and their counterion. The separation between the anion and the cation appears to be complete at about 9 wt % of water. Subsequent solvent uptake would supply the space around the ions with water and alcohol molecules, which are bound to the early bond water molecules by hydrogen bonding, and at longer distances, structured solvent mixtures similar to that in the bulk media.

Results obtained with the other salts of PESS membranes suggest that the larger counterions in the contact ion pairs require less water activity in the mixtures for the solvent to be inserted in the ion pairs.

This behavior is reminiscent that observed by Mauritz,[9] where the water activity in vapor phase in contact with the Nafion membrane needed for separation of contact ion pairs decreases as the radius of bare counterions increases. As proposed by Mauritz, this behavior can be attributed to the difference in hydration number and in energetics of
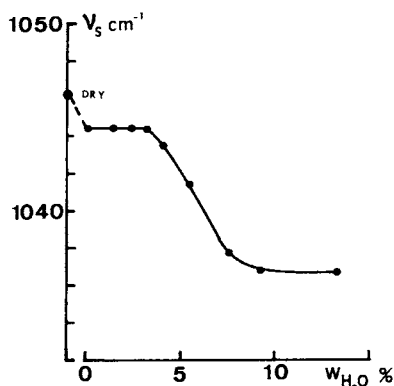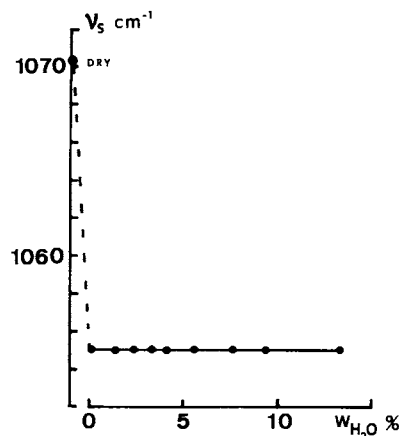

Figure 3   Position of the symmetric stretch band of sulfonic groups (ν_s) vs. water content in the external water–isopropanol mixture (Nafion–Li$^+$ membrane).

solvation of ions. Schematically, one can say that the interactions in the contact ion pairs with Li$^+$ are stronger so the higher total energy of solvation (by water or alcohol molecules) is required for the dissociation of the ion pairs.

On the contrary, the ν_s frequency of the sulfonate in the Nafion–Li$^+$ membrane, which is already solvated by pure alcohols with at least one alcohol molecule inserted in the ion pair, is not affected by the water enrichment in the external liquid phase (Fig. 3). The constancy of the ν_s frequency in the whole composition range (0–100 wt % of water) indicates that the strength of the hydrogen bonding of the sulfonate grouping with either alcohols or water molecules is nearly identical. However, this does not necessarily mean that the sorbed liquid has the same composition as the external phase. Although the same frequency of the solvated sulfonate ions was obtained for the Nafion membrane loaded with different counterions, the extent of sorption and the composition of the absorbed phase for a mixture at given composition vary largely with the nature of the counterion.[6] This is due to the fact that the ν_s frequency reflects mainly the immediate environment of the SO_3^- group.

Changes in the Antisymmetric Stretching Vibrations

A closer examination of the behavior of the antisymmetric stretch (ν_{as}) confirms the conclusions of the previous sections.

In the Figures 4 and 5 are presented spectra of the PESS–Li$^+$ and the Nafion–Li$^+$ membranes in the dry state and membranes equilibrated with water, ethanol, and isopropanol.

Figure 2   Position of the symmetric stretch band of sulfonic groups (ν_s) vs. water content in the external water–isopropanol mixture (PESS–Li$^+$ membrane).
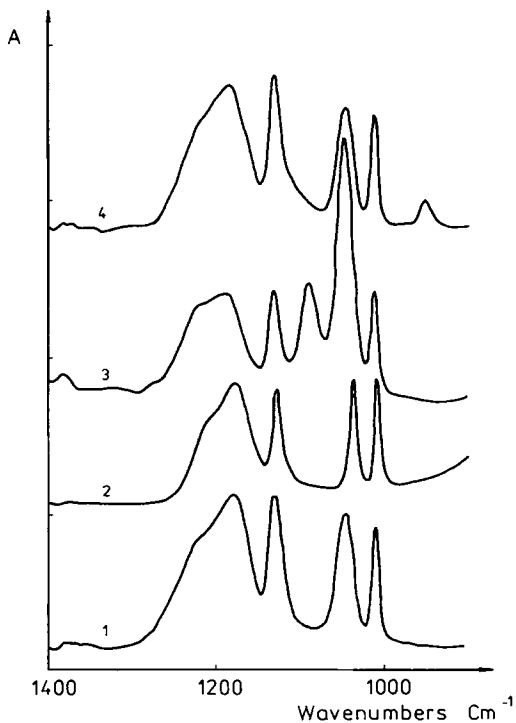
Figure 4 ATR–IR spectra of 1400–800 cm^{-1} region of PESS–Li$^+$ membrane: (1) dry; (2) equilibrated with water; (3) equilibrated with ethanol; (4) equilibrated with isopropanol.

Figure 5 ATR–IR spectra of 1400–800 cm^{-1} region of Nafion–Li$^+$ membrane: (1) dry; (2) equilibrated with water; (3) equilibrated with ethanol; (4) equilibrated with isopropanol.

For the PESS–Li$^+$ membrane the magnitude of splitting of the antisymmetric stretch follows the order:

Dry membrane > EtOH $\cong$ isoPrOH $\gg$ H$_2$O

With increasing water concentration in the external solution, the magnitude of the splitting ($\Delta\nu_{as}$) is constant up to 3 wt % of H$_2$O and then decreases (Fig. 6). This is in accordance with our previous suggestion that the dissociation of the ion pairs in PESS–Li$^+$ membrane is caused only by water molecules. Indeed, as the splitting is caused by the removing of the degeneracy due to the sulfonate–cation interactions, the more important the splitting, the greater the influence of the field of the asymmetrically attached cation. According to the results shown in Figure 5, the SO$_3^-$–Li$^+$ ion pairing in the PESS–Li$^+$ membrane should remain essentially unmodified by the water–isopropanol mixture up to 3 wt % of water: after that the cation–anion bond should loosen in a multistage equilibrium process.[11]

In the Nafion membrane the big shift of the peak at about 1200 cm^{-1} is observed in alcohols compared
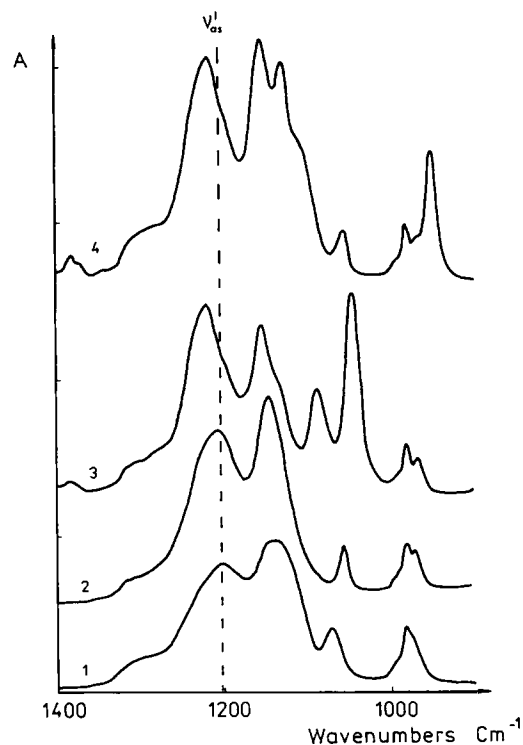
with that of the dry membrane (Fig. 7). This suggests that the peak at this position is a lower frequency part of the antisymmetric stretch of sulfonic groups ν_{as}^l SO$_3^-$ (overlapped partially by the strong
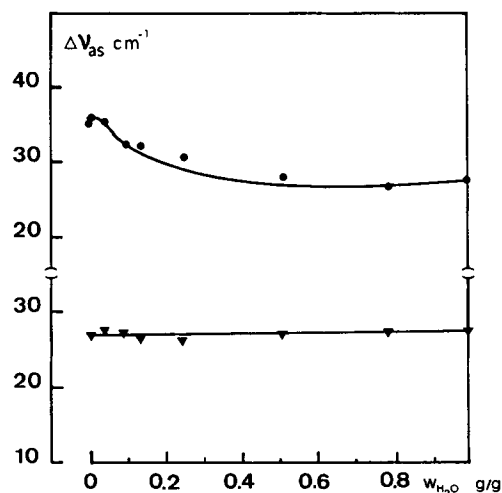

Figure 6 Splitting of the antisymmetric stretch band of sulfonic groups in PESS membranes ($\Delta\nu_{as}$) vs. water content in the external water–isopropanol mixture.
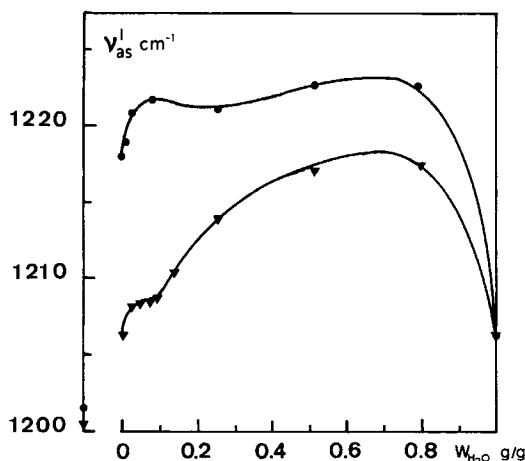
Figure 7 Position of the lower frequency part of the antisymmetric stretch band of sulfonic groups in Nafion membrane (ν_{as}^l) vs. water content in the external water–isopropanol mixture.

—CF_2— stretch).[16,25] The higher frequency part of $\nu_{as}SO_3^-$ is suggested to be about 1300 cm^{-1}.[25] In all spectra a shoulder is observed at this position, but it is difficult to locate it exactly (Fig. 5).

The position of ν_{as}^l in Nafion changes significantly with the state of membrane, shifting to the higher wavenumber in the order.

$$\text{Dry membrane} < H_2O < EtOH \cong isoPrOH$$

From that we can conclude again that pure solvents like alcohols can cause the ion pairs dissociation in Nafion membranes.

Figure 7 presents the position of $\nu_{as}SO_3$ in Nafion membrane with increasing water content in the external mixture. The $\nu_{as}^l SO_3^-$ band passes through the maximum at water concentration about 55 wt %, indicating a very strong synergetic effect in Nafion membrane.[2]

Cabasso et al.[6] suggest that this synergetic effect is due to the interactions of isopropanol molecules with less hydrophilic sections of the membrane, i.e., fluoroether domains. However, our results suggest that also the ionic domains should participate to the synergetic mechanism of sorption, probably via the aggregates of molecules linked by multiple hydrogen bonds.

The position of the maximum of ν_{as}^l is in accordance with the maximum of the total solvent uptake.[7] Results in Figure 7 point out also that the alcohol molecules are released from the solvation shells only at the water concentration higher than 60 wt %.

REFERENCES

1. A. Wenzlaff, K. Hattenbach, and K. W. Boddeker, *J. Membr. Sci.*, **22**, 333 (1985).
2. I. Cabasso and Z. Z. Liu, *J. Membr. Sci.*, **24**, 101 (1985).
3. I. Cabasso, E. Korngold, and Z. Z. Liu, *J. Polym. Sci. Polym. Lett. Ed.*, **23**, 577 (1985).
4. J. Nieuwenhuis, Y. Y. Tan, and G. O. R. Alberda van Ekenstein, *Ang. Makrom. Chemie*, **147** 83 (1987).
5. R. François, T. Q. Nguyen, and J. Neel, *Makromoleculare Chemie, Symp.*, **23**, 421 (1989).
6. I. Cabasso, Z. Z. Liu, and T. Mekenzie, *J. Membr. Sci.*, **28**, 109 (1986).
7. W. Kujawski, T. Q. Nguyen, and J. Néel, in R. Bakish Ed., *Proceedings of the Third International Conference on Pervaporation Processes in the Chemical Industry*, Bakish Materials Corp. Publ., NJ, 1988, pp. 355–363.
8. J. R. Scherer, G. F. Bailey, S. Kint, R. Young, D. P. Malladi, and B. Bolton, *J. Phys. Chem.*, **89**, 312 (1985).
9. S. R. Lowry and K. A. Mauritz, *J. Am. Chem. Soc.*, **102**, 4665 (1980).
10. S. Quezado, J. C. T. Kwak, and M. Falk, *Can. J. Chem.*, **62**, 958 (1984).
11. G. Zundel, *J. Membr. Sci.*, **11**, 249 (1982).
12. D. J. Barres, in Pineri M. and Eisenberg A., Eds., *Structure and Properties of Ionomers*, NATO ASI Series, *C198*, D. Reidel Publ., Dortrecht, 1987, pp. 501–510.
13. L. Y. Levy, A. Jenard, and H. D. Hurwitz, *J. Chem. Soc., Faraday I*, **76**, 2558 (1980).
14. J. Ostrowska and A. Narębska, *Colloid Polymer Sci.*, **261**, 93 (1983).
15. M. Escoubes and M. Pineri, in Pineri M. and Eisenberg A., Eds. *Structure and Properties of Ionomers*, NATO ASI Series *C198*, D. Reidel Publ., Dortrecht, 1987, pp. 341–359.
16. K. A. Mauritz, C. J. Hora, and A. J. Hopfinger, *ACS Symp. Ser.* **187** (*Ions Polym.*), 123 (1980).
17. J. Ceynowa, *Polymer*, **19**, 73 (1978).
18. Z. Twardowski, H. L. Yeager, and B. O'Dell, *J. Electrochem. Soc.*, **129**, 328 (1982).
19. A. Narębska, S. Koter, and W. Kujawski, *J. Membr. Sci.*, **25**, 153 (1986).
20. A. Narębska, W. Kujawski, and S. Koter, *J. Membr. Sci.*, **30**, 125 (1987).
21. J. L. Pauley, D. D. Vietti, C. C. Ou-Yang, D. A. Wood, and R. D. Shervil, *Anal. Chem.*, **41**, 2047 (1969).
22. R. G. Fessler and H. A. Strobel, *J. Phys. Chem.*, **67**, 2562 (1963).
23. J. A. Sinegra and G. Carta, *Ind. Eng. Chem. Res.*, **26**, 2437 (1987).
24. G. Poźniak and W. Trochimczuk, *Ang. Makromol. Chemie*, **127**, 171 (1984).
25. C. Heitner-Wirguin, *Polymer*, **20**, 371 (1979).
26. F. G. Helfferich, in Helfferich F. G., Ed., *Ion Exchange*, McGraw-Hill, New York, 1962, pp. 100–107.