Swelling study of perfluorosulphonated ionomer membranes

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(*Received 29 October 1991; revised 23 April 1992*)

The swelling properties of perfluorosulphonated ionomer (PFSI) membranes have been studied as a function of the solvent, the counterion and the temperature. The expansion of PFSI membranes has been measured in numerous solvents. Different solvent parameters have been considered and the donor number of the solvent is proposed as the relevant parameter. The influence of counterion is shown to be related either to the softness parameter of the cations for a very polar solvent or to the size of the cations for other solvents. Very large solvent uptake can be obtained by increasing the temperature, which remains in the sample on cooling back to room temperature. The material begins to dissolve even with low solvent uptake. The dissolution of the membrane depends only on the degree of swelling.

(Keywords: swelling behaviour; perfluorosulphonated; ionomer)

INTRODUCTION

Since ionic polymers have different chemical structures, exchange capacities and degrees of crosslinking, they exhibit different swelling properties which depend on the solvent and the counterion[1,2]. The swelling studies of ionic polymers are only phenomenological because of the lack of an actual predictive theory. Perfluorinated ionomer membranes are used in many industrial electrochemical processes and especially in the chlor-alkali industry[3,4]. From the point of view of these applications and for the understanding of structure–property relationships, the swelling properties of these polymers are of crucial importance. It is indeed well known that swelling leads to an increase in the ionic conductivity and a decrease in the cation *versus* anion selectivity[5].

Structural investigations have been essentially restricted to the study of dry membranes and of membranes equilibrated either with water or aqueous electrolytes[5]. It is now generally accepted that ionic species aggregate to form ionic domains[6]. These clusters are surrounded by the hydrophobic fluorocarbon matrix. During the first steps of hydration, the clusters swell. A polymer reorganization occurs in order to keep the polymer–solvent interfacial area constant through an increase of the number of ionic groups per cluster[7]. The swelling equilibrium is obtained when the two opposed forces are equal: the matrix elastic forces and either the osmotic pressure[8] or the electrical forces[9]. Above 20% solvent content, adjacent clusters become connected by short channels. This percolation model explains both the ionic conductivity and the selectivity of these swollen membranes[10]. This connected network model can be applied up to 40% volume fraction of solvent. No model has yet been proposed for larger swelling which can easily be obtained with most of the polar solvents. The fact that these membranes are difficult to dissolve has been attributed to the existence of crystallites which are supposed to act as physical crosslinks[11–13].

The swelling properties of perfluorosulphonated ionomer (PFSI) membranes have primarily been studied in aqueous media because of the industrial applications of these membranes but water is not a good swelling agent for these membranes and consequently little information on swelling in other solvents is available. In a first study of the swelling of PFSI membranes performed with non-aqueous solvents[13,14], the solubility parameter was proposed as the best parameter to describe the swelling properties. A plot of the solvent uptake against the solubility parameter of solvents exhibits two swelling envelopes. The existence of two solubility parameter values in PFSI membranes was then deduced from this result: one is ascribed to the matrix whereas the other is attributed to the ionic domains. This feature has never been found for any other material whose solubility parameter has been reported[15]. It is also surprising that the solubility parameter attributed to the perfluorinated matrix is so different from that determined for poly(tetrafluoroethylene)[16] and is so sensitive to the counterion[14]. Finally, such correlation cannot be found with carboxylated ionomer membranes[14].

In the present work, systematic swelling experiments have been performed in order to define the solvent and counterion parameters which are relevant to the swelling properties. The effect of temperature has also been studied with the aim of obtaining information on the dissolution phenomenon.

EXPERIMENTAL

The PFSI membrane studied was Nafion 117 (E.I.

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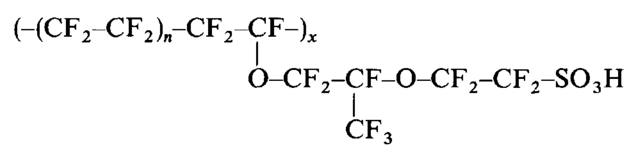
Du Pont de Nemours), with the chemical formula:



$$\text{(–(CF}_2\text{–CF}_2)_n\text{–CF}_2\text{–}\underset{\text{O–CF}_2\text{–}\underset{\text{CF}_3}{\text{CF}}\text{–O–CF}_2\text{–CF}_2\text{–SO}_3\text{H}}{\text{CF}}\text{–)}_x$$

$(n = 6.5)$

and an equivalent weight of 1100 g meq^{-1}. To obtain the neutralized form, the membrane was immersed in a 2 N chloride solution of the desired cation for at least 1 day. The membrane was then washed for 2 h several times in doubly distilled water.

Swelling was measured through determining the expansion along three directions. The laminating direction was indicated by the manufacturer on each membrane. Small rectangular pieces of membrane were cut with respect to the parallel and perpendicular laminating directions. Samples were then dried at 110°C for at least overnight. The dimensions of each piece (2 cm × 1 cm × 175 μm) were then quickly determined using a comparator for thickness ($\pm 1\,\mu$m) and a vernier eyepiece microscope for the other directions ($\pm 10\,\mu$m). The samples were then soaked in the swelling agent and measured daily until the dimensions were constant. For high vapour pressure solvents, the expansion was measured with the samples immersed in the solvent to prevent evaporation.

Swelling rates were very different from one solvent to another. For example, the steady state was reached in <2 days for alcohols and 2 weeks or more were necessary for solvents such as propylene carbonate, glycerol or pyridine. Nevertheless the swelling was always found to be faster along the thickness. This is probably due to the fact that the solvent penetrates the membrane from the surface so that swelling is faster along the thickness which is only 175 μm and it then takes longer to equilibrate along the other directions.

The classical method was used for determining the effect of temperature. Pieces of dried membrane were weighed (~ 0.1 g) and immersed in the swelling agent kept in a thermostatically controlled bath at the desired temperature for 12 h. When the desired temperature was higher than the boiling point of the solvent, an autoclave was used. After swelling, samples were quickly wiped between two filter papers and weighed. The samples were then dried overnight at 110°C. The dry weight difference before and after swelling gave the quantity of polymer dissolved during the swelling procedure. When swelling was performed in an autoclave, opening the autoclave was only possible when the temperature was <50°C. It is assumed that the swelling remains the same after cooling the membrane to room temperature which means that an 'irreversible' deformation occurs. Two results confirm this assumption: swelling curves *versus* temperature exhibit continuous behaviour from atmospheric pressure to higher pressure experiments and such hysteresis is always verified in atmospheric pressure experiments, for instance, those performed under reflux with high boiling point solvents, such as amides or phosphates.

RESULTS AND DISCUSSION

Effect of solvents

The swelling of Li$^+$ neutralized membranes has been measured in numerous solvents, such as alcohols, amides, phosphates, etc. A list of these solvents with some physical constants[17–19] is given in *Table 1*. The Li$^+$ and H$^+$ forms of the PFSI membranes exhibit higher swelling compared to other cationic forms; Li$^+$ has been chosen and not H$^+$ because of the specific catalytic properties of the acidic form. *Table 2* lists the expansions along the parallel and perpendicular laminating directions ($\Delta l_{\parallel}/l_{\parallel}$ and $\Delta l_{\perp}/l_{\perp}$, respectively), along the thickness ($\Delta e/e$), the calculated volume increase ($\Delta V/V$) and the number of solvent molecules per SO$_3^-$ ($N_{\mathrm{SO}_3^-}$). $N_{\mathrm{SO}_3^-}$ is easily obtained if the density of Nafion 117 is assumed to be 2 g cm^{-3}:

$$N_{\mathrm{SO}_3^-} = \frac{1100 d_0}{2M_0}\left\{\left[\left(\frac{\Delta l_{\perp}}{l_{\perp}}+1\right)\left(\frac{\Delta l_{\parallel}}{l_{\parallel}}+1\right)\left(\frac{\Delta e}{e}+1\right)\right]-1\right\}$$

where d_0 is the solvent density and M_0 its molecular weight. The values obtained with water are comparable with those obtained previously[2].

It can be seen from *Table 2* that expansions are identical along the thickness and along the perpendicular laminating direction for all solvents except phosphates. The ratio of the expansion along the perpendicular and parallel laminating directions is almost 1.4, but this anisotropy varies from one piece of membrane to another. A value close to 1.2 was found with another piece of membrane. The swelling anisotropy of the membranes can be attributed to the laminating conditions as has already been suggested in a previous paper[20]. The determination of the expansions allows the expected weight increase to be calculated, which is found to be equal to the measured value. Since $\Delta l_{\parallel}/l_{\parallel}$ is not constant for a given solvent from one membrane to another, the total solvent uptake measurement is not an absolute determination and therefore the determination of $\Delta l_{\perp}/l_{\perp}$ is preferable when comparing the swelling properties of different types of membrane.

It is surprising that quasi non-polar solvents like the phosphates exhibit such an important swelling. When going from trimethylphosphate (TMP) to tributylphosphate (TBP), the dielectric constant decreases and the swelling increases. In fact $N_{\mathrm{SO}_3^-}$ is found to be constant, so the swelling increase from TMP to TBP is only due to the increase of the molecular volume of the solvent. The values of $N_{\mathrm{SO}_3^-}$ are <8 which is rather small compared to those obtained with other good swelling agents of PFSI. The fact that swelling along the thickness is larger than along the perpendicular laminating direction for all the phosphate solvents is still unexplained. The highest values for the solvent uptake are obtained with hexamethylphosphotriamide which is both a phosphate and an amide solvent, so this solvent has been used to dissolve PFSI membrane under reflux[21].

In order to find a parameter that can be used to predict the swelling of PFSI membranes, the linear expansion along the perpendicular laminating direction, $\Delta l_{\perp}/l_{\perp}$, has been plotted *versus* different solvent parameters: the dielectric constant (*Figure 1a*); the solubility parameter, which is defined as the square root of the cohesive energy density (*Figure 1b*); the surface tension coefficient which is representative of the matrix–solvent interaction (*Figure 1c*); and finally the donor number, DN, which can be used to define the ability to solvate the cations (*Figure 1d*).

Non-polar solvents are poor swelling agents of PFSI membranes so ion dissociation ability of the solvent is an important parameter but it is clearly seen from *Figure 1a* that the swelling properties cannot be described using

Table 1 Density, ρ, molecular weight, M, dielectric constant, ε, solubility parameter, δ, air–solvent surface tension, γ, and donor number, DN, of solvents[21–24]

Solvent	ρ (g cm^{-3})	M (g mol^{-1})	ε	δ (J$^{1/2}$ cm$^{-3/2}$)	γ ($\times 10^{-2}$ N m^{-1})	DN[a] (kcal mol^{-1})
Water	1.00	18.02	78.4	47.9	7.18	(18)
Methanol	0.791	32.04	32.7	29.3	2.21	(30)
Ethanol	0.789	46.07	24.6	26.0	2.19	(32)
2-Propanol	0.785	60.11	19.9	23.7	2.12	(36)
1-Butanol	0.810	74.12	17.5	23.3	2.42	(29)
1-Pentanol	0.814	88.15	13.9	22.4	2.52	(25)
Glycerol	1.261	92.11	42.5	33.7	6.30	(19)
Ethylene glycol	1.109	62.07	37.7	32.4	4.80	(20)
Formamide	1.133	45.04	111.0	39.6	5.79	(24)
N-methylformamide	1.011	59.07	182.4	32.9	3.87	(25)
N,*N*-dimethylformamide	0.949	73.39	36.7	24.1	3.52	26.6
N,*N*-diethylformamide	0.908	101.15		20.4		30.9
N,*N*-dimethylacetamide	0.937	87.12	37.8	23.3	3.315	27.8
N,*N*-diethylacetamide	0.913	115.18				32.2
Trimethylphosphate	1.197	140.08	22.3	21.1		23.0
Triethylphosphate	1.072	182.16	13.3	16.4	3.06	(26)
Tributylphosphate	0.979	266.32	8.1	15.3	2.72	23.7
Hexamethylphosphotriamide	1.024	179.20	30.0	19.1	3.38	38.8
Dimethylsulphoxide	1.101	78.13	46.7	26.6	4.29	29.8
N-methylpyrrolidinone	1.026	99.13	32.0	23.6	4.05	27.3
Cyclohexanone	0.948	98.15	18.2	19.7	3.45	19.4
2-Ethoxyethanol	0.930	90.12	29.6	21.4	2.82	
Tetrahydrofuran	0.889	72.12	7.6	19.0	2.64	20.0
Propylene carbonate	1.189	102.09	66.1	21.8	4.14	15.1
Butyl acetate	0.882	116.16	5.1	17.6	2.45	11.0
Dioxane	1.034	88.12	2.2	19.7	3.30	14.8
Pyridine	0.982	79.10	12.3	21.7	3.66	33.1
Hydrazine	1.004	32.05	52.9	37.1	7.53	44.0
Acetonitrile	0.786	41.05	37.5	24.1	2.76	14.1

[a] Values in parentheses are uncertain

Table 2 Expansions along the perpendicular ($\Delta l_{\perp}/l_{\perp}$) and parallel ($\Delta l_{\parallel}/l_{\parallel}$) laminating directions and thickness ($\Delta e/e$). $\Delta V/V$ is the volume increase and $N_{SO_3^-}$ is the number of solvent molecules per charge

Solvent	$\Delta l_{\perp}/l_{\perp}$ (%)	$\Delta l_{\parallel}/l_{\parallel}$ (%)	$\Delta e/e$ (%)	$\Delta V/V$ (%)	$N_{SO_3^-}$
Water	14	10	14	43	13.1
Methanol	51	36	50.5	209	28.4
Ethanol	45	32	47	181	17.1
2-Propanol	32	22	33	114	8.2
1-Butanol	45	30.5	45	174	10.5
1-Pentanol	44.5	31.5	45	176	8.9
Glycerol	17	12	16.5	52	4.0
Ethylene glycol	28	20	28	97	9.5
Formamide	28.5	20.5	28.5	99	13.7
N-methylformamide	51	37	54	219	20.6
N,*N*-dimethylformamide	53	38	52	221	15.8
N,*N*-diethylformamide	53	37	53.5	222	10.9
N,*N*-dimethylacetamide	68	49	70	326	19.3
N,*N*-diethylacetamide	74	53	75	366	16.0
Trimethylphosphate	40	28	49	167	7.8
Triethylphosphate	46	33	66	222	7.2
Tributylphosphate	65	46	91	360	7.3
Hexamethylphosphotriamide	98	73	143	732	26.2
Dimethylsulphoxide	45.5	32.5	45	180	13.9
N-methylpyrrolidinone	53	37	54	223	12.7
Cyclohexanone	21	15	20.5	68	3.6
2-Ethoxyethanol	36	25	37	133	7.5
Tetrahydrofuran	20.5	14.5	20	66	4.7
Propylene carbonate	18	13	18.5	58	3.7
Butyl acetate	15.5	11	17	50	2.1
Dioxane	15	11	16	47	3.0
Pyridine	36.5	26	38	137	9.4
Hydrazine	14	10	15	44	7.6
Acetonitrile	16.5	11	16	50	5.3

the dielectric constant. This result has been predicted by Dreyfus[9] who suggested that the electrostatic energy variation during swelling is proportional to the difference between the inverse of the dielectric constants of the solvent and of the matrix. The dielectric constant of the solvent can therefore be neglected provided it is significantly greater than those of the matrix ($\simeq 2$).

A plot of the expansion *versus* solubility parameters does not corroborate the PFSI dual cohesive energy densities theory[13,14] but appears to be very scattered (*Figure 1b*). The discrepancy with the previous results[13,14] can be attributed to their limited choice of solvents (especially alcohols). There is no clear evidence of a penetration of the solvent in the perfluorinated matrix while an actual phase separation has been proved in the case of water[22]. Therefore the solvent–matrix interaction has to be considered in terms of interfacial energy rather than in terms of the solubility parameter. The surface tension coefficient is indeed confirmed to be a relevant parameter for values $>4.5\times10^{-2}$ N m^{-1} (*Figure 1c*) while no correlation exists for lower values. A similar result has been obtained for the structural study of perfluorinated ionomer solutions[23,24] in which the radii of the rod-like structures are shown to depend on the surface tension coefficient only for values >0.045 N m^{-1}.

Since the dielectric constant does not play any role in the swelling, another solvent parameter has to be involved in the ion dissociation to create the driving force. This parameter could be the DN which has been shown to be very important in ion solvation[18]. The DN of Guttman is defined as $\Delta H_{D.SbCl_5}$ with $D + SbCl_5 \leftrightarrows D.SbCl_5$ in 1,2-dichloroethane where D is the solvent. Despite the fact that some values are uncertain or have not been measured directly, it is clear from *Figure 1d* that a correlation exists between the swelling of PFSI and DN parameter of the solvent. There is still some uncertainty about the DN values >32 kcal mol^{-1} because of the

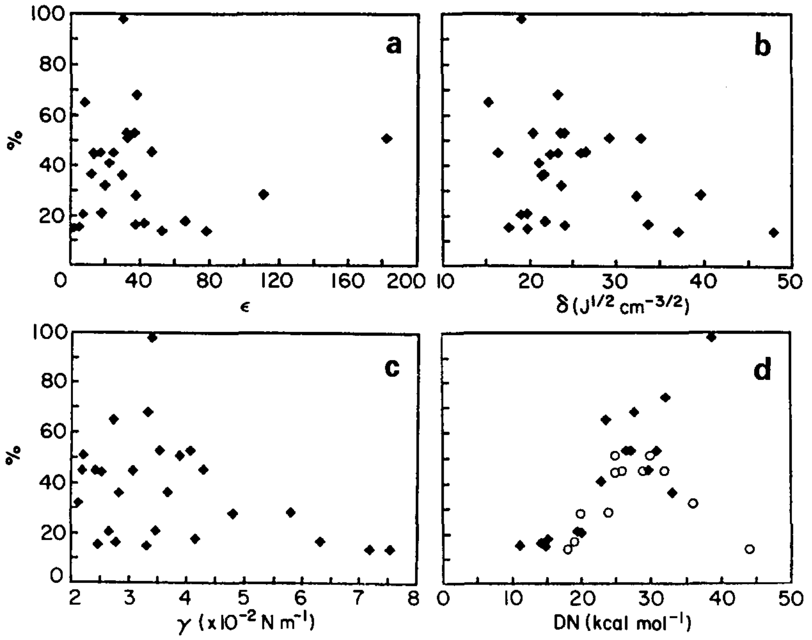


Figure 1 Expansion along the perpendicular laminating direction of Nafion 117 Li *versus* solvent parameters: (a) dielectric constant, ε; (b) solubility parameter, δ; (c) interfacial energy, γ; (d) donor number, DN. The open circles refer to uncertainty in the values of DN

lack of high donor solvents. A maximum appears for DN$\simeq$25–30 kcal mol^{-1} (*Figure 1d*) if hexamethylphosphotriamide (DN$\simeq$38.8 kcal mol^{-1}) is considered as a special solvent for PFSI membranes as shown above. Amines are the strongest donor solvents (DN$>$50) and lead to very low degrees of swelling[13,14] which confirms our conclusion. One would expect a maximum in the swelling curve *versus* the DN of solvents because when DN increases there is better solvation of cations but poorer solvation of anions.

Mixtures of solvents

Swelling data in mixtures of solvents have been reported previously[25]. The results with water–2-propanol, water–cellosolve and water–diglyme mixtures indicate for the first time that a maximum in the swelling can be obtained for a mixture compared to the pure solvents, for example, five times larger for the water–diglyme mixture.

Water–ethanol, water–2-propanol, cyclohexanone–2-propanol and water–formamide mixtures have been studied. Different results have been obtained depending on the solvent mixture: either a maximum is reached for the mixture compared to the pure solvent or a monotonic increase from one to the other with a plateau near one of the solvents (water for water–formamide and ethanol for water–ethanol). Such experiments can only be qualitatively interpreted because of preferential solvation. This phenomenon is probably responsible for the existence of a plateau for some solvent mixtures. The main result is that some solvent mixtures exhibit a maximum in swelling data compared to pure solvents. This feature shows that either a parameter reaches an optimum value or that two parameters are involved and the conditions are more favourable in the mixture compared to the pure solvents. The second hypothesis is unlikely since no two parameters have been found which act in the opposite way to the pure solvents. For the first hypothesis, if the swelling data are plotted *versus* a parameter assuming a linear combination for the mixture, the maximum obtained with different mixtures of solvents should be located in the same place for all the mixtures studied and should be coherent with swelling data obtained for pure solvents. This behaviour can be obtained with DN as a parameter (*Figure 2*) while totally erratic behaviour is obtained for other parameters. The position (25–30 kcal mol^{-1}) and intensity ($\simeq$60%) of the maximum corroborate the data obtained with pure solvents (*Figures 1d* and *2*).

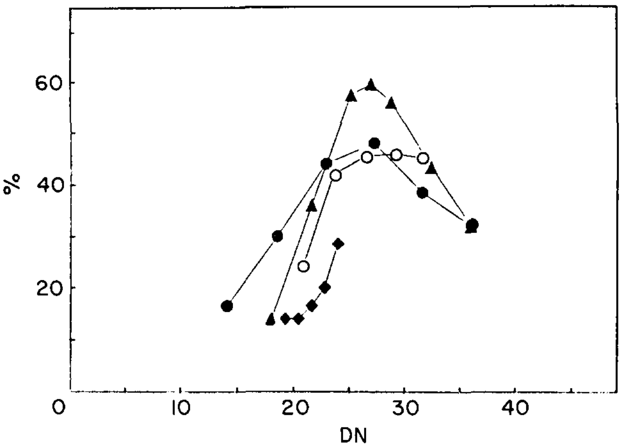


Figure 2 Expansion along the perpendicular laminating direction of Nafion 117 Li *versus* donor number, DN, of mixed solvents: (▲) water–2-propanol; (○) water–ethanol; (◆) water–formamide; (●) cyclohexanone–2-propanol

Effect of counterions

Four typical swelling agents of PFSI membranes have been chosen to define the effect of counterions (water, ethanol, *N*-methylformamide, triethylphosphate). The water swelling measurements have been taken from Du Pont commercial product information[26] where swelling has been performed using boiling water.

Table 3 Softness parameter, σ, and size of cations, r

Cation	Li^+	Na^+	Ca^{2+}	Ba^{2+}	K^+	Rb^+	Cs^+	UO_2^{2+}	Mg^{2+}	Ni^{2+}	Fe^{2+}	H^+	Cu^+	Cu^{2+}
$\sigma (\times 10^2)$	−95	−75	−65	−60	−53	−49	−46	−38	−37	−11	−6	0	26	39
$r (\times 10^3 \text{ nm})$	60	95	99	135	133	148	169	73	65	70	75	(0)	96	70

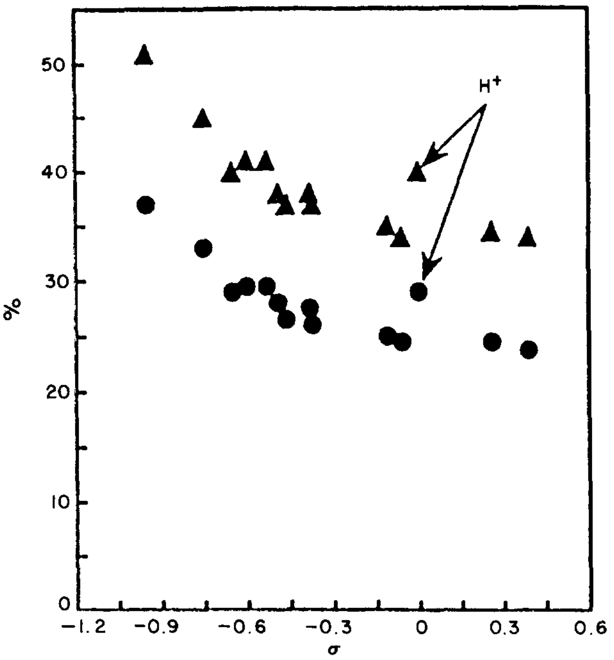


Figure 3 Expansion along the perpendicular (▲) and parallel (●) laminating directions of Nafion 117 in *N*-methylformamide *versus* softness parameter, σ, of the counterions

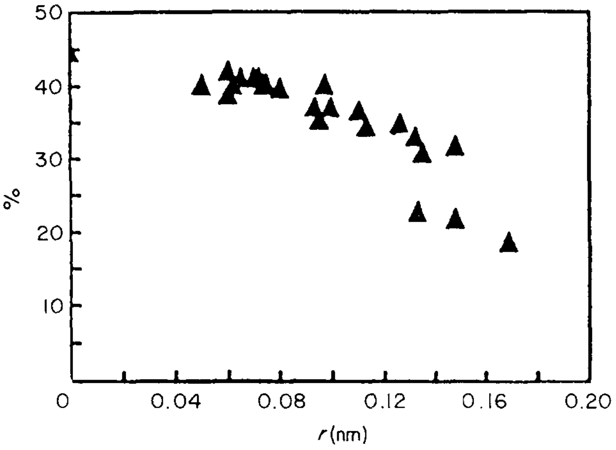


Figure 4 Volume increase of Nafion 117 in boiling water *versus* cation size, r

The electron pair donation ability of solvents has been shown to be the relevant parameter for the solvents. This result suggests that to study the effect of cations their electron pair acceptance capability should be considered. There are no generally accepted criteria for measuring this property. Marcus[17] proposes 'softness' as a measure of the tendency of ions to undergo covalent bonding and expects that some combination of the square of the crystal ionic radii and the softness parameter would express the electron pair acceptance capability of the cations. The softness parameter is defined as the difference between the ionization potential of the gaseous atom to form the cation and the enthalpy of hydration of the latter, normalized by subtraction of and division by the corresponding difference for the hydrogen ion. Softness parameters and crystal ionic radii of cations are given in *Table 3*.

With *N*-methylformamide, a very polar solvent ($\varepsilon = 182$), the solvent uptake is related to the softness parameter of cations except for the proton (*Figure 3*). With water, the effect of counterions upon swelling cannot be attributed to the softness parameter, but to the size of the cations (*Figure 4*). The same behaviour was obtained with ethanol. Yeo and Cheng[14] found that the counterion influences the solvent uptake of the membrane drastically for all the solvents used (especially alcohols) except formamide ($\varepsilon = 111$). The counterions used (H^+, Li^+, Na^+, K^+) have very different sizes but similar softness parameters. These data are in agreement with our conclusions: the counterion effect is mostly due to the size of the cation except very polar solvents for which the softness parameter has to be considered. If the two parameters proposed by Marcus[17] are relevant, the expected combination would have not been dependent on the solvent as it has been found.

With triethylphosphate, a quasi non-polar solvent, the swelling rate could be also related to the size of the cations. A better description of swelling is to use the number of molecules of solvent per charge, we find that this number is the same for H^+, Li^+, Na^+, and half for divalent cations and for K^+ and almost zero for Rb^+ and Cs^+ (*Figure 5*). An identical trend was obtained with TMP. A phenomenon of solvation coupled with an effect of size of the cations is necessary to explain such results.

Effect of temperature

The swelling of the lithium form PFSI membranes *versus* temperature has been studied in water, ethanol and water–ethanol (50/50) mixtures. The swelling remains after cooling the samples back to room temperature. If the swollen samples are dried overnight, even at 100°C, and then soaked in the swelling agent at room temperature, the solvent uptake is found to be the same as that performed at high temperature. This hysteresis can be eliminated by drying the samples at a temperature $> 150°C$. A similar result was obtained for solution-cast films[19]: the evaporation of a PFSI solution at room temperature leads to a highly soluble membrane but thermal treatment applied to this film restores the swelling properties of the as-received membrane. The elementary structure is largely modified during the swelling procedure (or the dissolution) and it is then necessary to bring sufficient energy to the system to allow it to return the original structure; heating to a temperature greater than the glass transition of the perfluorinated matrix is necessary for this. Such a hysteresis which induces a lower conductivity and a higher conductivity can be of crucial importance for applications.

The exponential effect of temperature on swelling requires a plot of solvent uptake *versus* temperature on a logarithm linear scale (*Figure 6*). No measurements are presented for volume ratios of solvent to polymer (V_s/V_p)

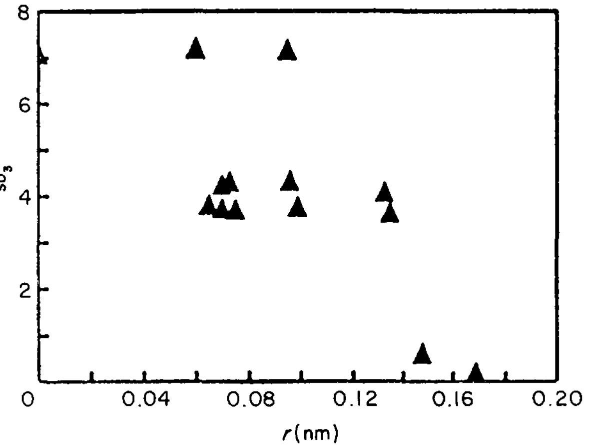


Figure 5 Number of triethylphosphate molecules per charge, $N_{SO_3^-}$, *versus* cation size, r

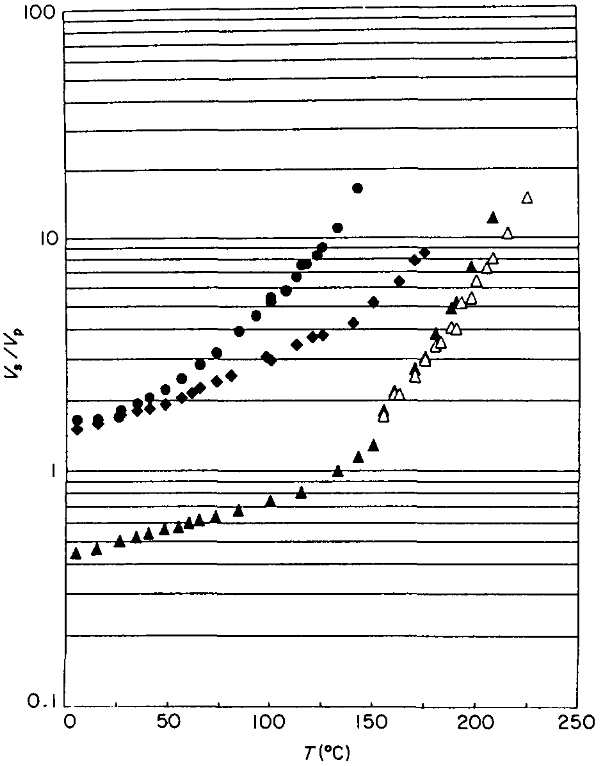


Figure 6 Ratio of solvent volume to dried residual polymer volume, V_s/V_p, *versus* temperature, T, after swelling for 12 h: (▲) water; (◆) ethanol; (●) water–ethanol mixture; (△) calculated using the polymer volume measured before swelling

of >20 because the swelling is no longer homogeneous: macroscopic domains of solvent are detectable in the membrane. With water as the swelling agent, the slope increase in the 120–140°C range can probably be attributed to the glass transition of the perfluorinated matrix[12]. The weights of the samples dried overnight at 100°C were measured before and after swelling. The difference between these two values allows the quantity of PFSI dissolved during the swelling procedure to be calculated. This quantity *versus* swelling is presented in *Figure 7*. It appears that the quantity dissolved does not depend on the solvent, the temperature or the counterion but it is only related to the degree of swelling. The linear behaviour suggests that this dissolution phenomenon cannot be interpreted as the dissolution of the low molecular weight part of the polymer.

When a highly water swollen membrane is immersed at room temperature in, for example, ethanol, the degree of swelling increases by a factor of two. This swelling increase is reversible. While no homogeneous swelling with $V_s/V_p > 20$ can be obtained at high temperature, it is possible to obtain a homogeneously swollen membrane with $V_s/V_p \simeq 40$ by swelling the membrane in water at $V_s/V_p \simeq 20$, and then changing the solvent. Another interesting point in this method is that while high temperature swelling leads to partial dissolution, this swelling increase due to a change of solvent at room temperature is not accompanied by any dissolution. Based on a previous work on perfluorinated ionomer solutions[23,24,27], the highly swollen membrane can be considered as a connected network of cylinders. The change of solvent leads to a modification of the radii as evidenced in the solutions[23,24,27] without changing the connectivity. Therefore, due to the conservation of the volume, decreasing the radius leads to an increase in the length between crosslinks and consequently the macroscopic dimensions.

The difficulties encountered for PFSI membrane dissolution have been attributed to the existence of crystallites which are supposed to act as physical crosslinks[11–13]. This idea is based on several points: (1) low equivalent weight membranes are non-crystalline and soluble; (2) higher equivalent weight increases the crystallinity and decreases solvent uptake; (3) the dissolution temperature has to be higher than the melting point of the crystallites; and (4) quenched samples exhibit larger degrees of swelling. The solubility and the crystallinity are both related to the quantity of charge along the polymer chain but they are probably not related to each other. In a previous publication about PFSI solution-cast membranes[19], we have shown that membranes with the same equivalent weight and very different crystallinity index can exhibit the same swelling behaviour. A calorimetric study of very similar perfluorinated ionomers[28] shows that the melting temperature of the crystallites is close to 360°C which is significantly higher than the dissolution temperature (≃200°C). As to the last point, before being quenched, the samples are heated at very high temperatures (≃360°C) and two transitions have occurred[12]. These transitions have been attributed[12] to matrix and cluster glass transitions. To our knowledge,

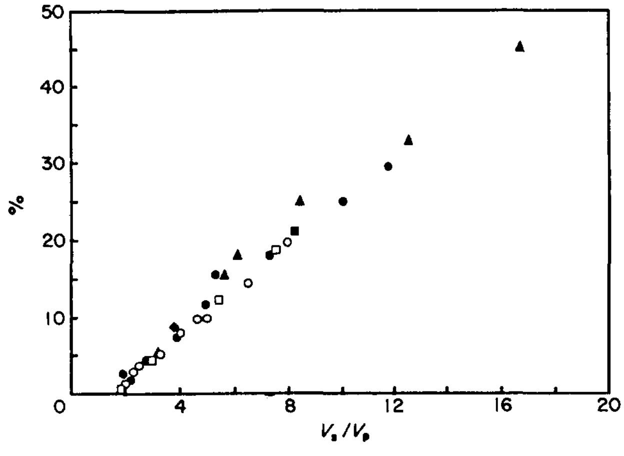


Figure 7 Percentage of dissolved membrane *versus* V_s/V_p: (▲) Nafion 117 H-water; (●) Nafion 117 Li-water; (◆) Nafion 117 Na-water; (■) Nafion 117 K-water; (○) Nafion 117 Li-ethanol; (□) Nafion 117 Li-water-ethanol

it has not been shown that this swelling increase due to quenching does not exist for non-crystalline materials. Finally, according to Starkweather[29], the crystallites are described as only two layers of perfluorinated chains. Such crystallites can probably not resist the swelling pressures which are of the order of several hundreds of atmospheres. We attribute the difficulties of swelling to the fact that significant structural modifications are necessary with a highly hydrophobic matrix. The structure of swollen membranes goes from 'reverse' spherical micelles to direct cylinders and such a transformation requires a large amount of energy.

CONCLUSIONS

The swelling properties of PFSI membranes have been shown to depend on the solvent, the counterion and the temperature. The swollen membranes can be described by the two-phase model where the swelling agent is contained by the clusters. The driving force for swelling is the solvation of the charges and the opposing force is the elastic deformation of the perfluorinated matrix[8,9].

In such a description of the swelling, the solubility parameter concept defined for non-charged polymers to describe the solubility of the polymer chain in the solvent is probably inadequate since the polymer matrix and the solvent form separate phases. The solvent–matrix interactions are better described by the interfacial energy and the charge solvation requires a solvent parameter such as the dielectric constant or DN. We have shown that the solubility parameter actually leads to erratic behaviour, that the effect of interfacial energy is only significant for the larger values and that the best description of swelling is obtained by using the DN.

The fact that the counterion drastically influences the solvent uptake of the membrane confirms that cation solvation has to be considered as the driving force of swelling. In most of the solvents, the effect is due to the differences in the size of the cations, but with very polar solvents such as formamide or *N*-methylformamide it is related to the softness parameter of the cations.

The effect of temperature is also very important and it has been shown that dissolution begins when the volume of solvent contained in the membrane is twice the volume of the dried membrane. This dissolved part is independent of the solvent and of the counterion which means that these membranes can be dissolved in almost all the swelling agents if the temperature is sufficiently high. The swelling hysteresis can be considered as a plastic deformation which can be suppressed with thermal treatment.

ACKNOWLEDGEMENTS

We thank P. Stevens for his help and the Atochem Company for financial support.

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