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Ionic conductivity of perfluorinated ionomer solutions and gels

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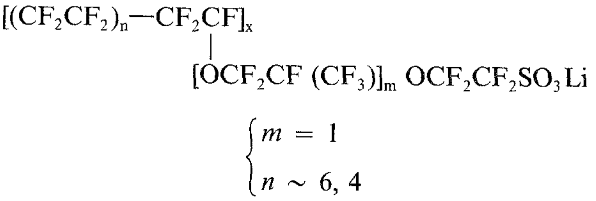
Conductivity measurements were made on stable solutions or gels of Li Nafion 1100 obtained by a recently reported process of solubilization of perfluorosulfonated ionomers in organic media. The influence of the solvent characteristics was shown by using *N*-methylformamide, propylene carbonate and triethylphosphate as solvents. The temperature, between 25 and 80° C, the concentration, in the 0.007–0.37 M range and water effects on the electrical properties were studied. The frequency dependence was measured in a 0.163 M solution in *N*-methylformamide from 15.6 Hz to 16 kHz. Conductivities at zero concentration are discussed using the treatment of simple salts and data from the literature. Li Nafion 1100 is well dissociated in *N*-methylformamide, giving a solution of higher conductivity ($\sim 10^{-3}\,\mathrm{S\,cm^{-1}}$) than in propylene carbonate and in triethylphosphate. The mobility of the $R-SO_3^-$ group is explained by the variation of the conductivity with frequency. Activation energies are interpreted as resulting from the viscous forces within the solutions.

1. Introduction

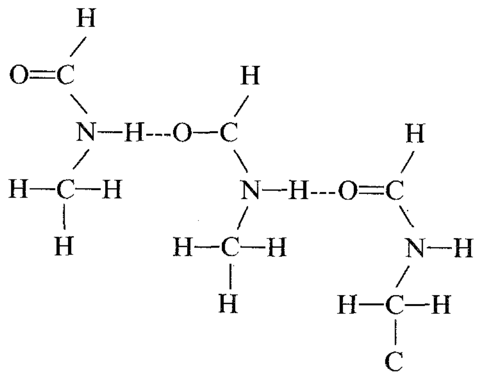
Because of their commercial importance, especially in the modern chlor-alkali industry, perfluorinated ionomers have been extensively studied as solid membranes. Processes for solubilization in water/alcohol mixtures of low exchange capacity membranes have been reported [1, 2]. Solutions and gels of Nafion 117 membranes (Dupont de Nemours trademark for its perfluorosulfonic acid membrane materials, equivalent weight 1100, exchange capacity 0.91 meq g^{-1}) in many polar solvents have been prepared [3] opening new ranges of applications. Due to their ionic properties, such solutions can be used in electrochemical devices mainly as room temperature electrolytes or composite materials. Depending on the nature of the solvent and on the concentration, they can result in stiff gels which present advantages such as lower contact resistances at the electrode interfaces and easier handling in technological applications when compared to liquids.

The aim of this work is to report results of ionic conductivity measurements of Li Nafion 1100 (I) solutions in organic media with relation to electrochemical applications. Measurements have been performed with very different solvents: *N*-methylformamide (NMF) (a), propylene carbonate (PC) (b) and triethylphosphate (TEP) (c). For each solvent the conductivity was measured as a function of the concentration of the Li Nafion 1100, the temperature, the frequency of the alternative current and the water content. This latter parameter is important since for most applications it is necessary to know the behaviour of the electrolytes when water is present. Nevertheless the structure of the solutions is not completely understood [4] and there is a lack of electrical measurements.

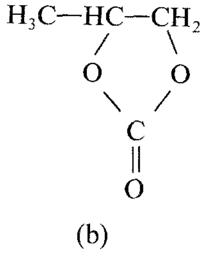


$$[(CF_2CF_2)_n-CF_2CF]_x \quad | \quad [OCF_2CF(CF_3)]_m\, OCF_2CF_2SO_3Li \qquad \begin{cases} m = 1 \\ n \sim 6, 4 \end{cases}$$

(I)



(a)



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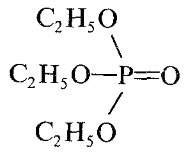

(c)

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* CNRS.

2. Experimental details

All samples were prepared and measurements were made in a dry box under argon atmosphere in order to prevent water adsorption. Solvents (high pressure liquid chromatography grade) were dehydrated: PC and TEP were distilled on sodium under an argon atmosphere; NMF was kept twice for 48 h on fresh molecular sieves, then pumped and distilled under reduced pressure. The viscosities of NMF and TEP were measured between 25 and 80° C using a Couette viscometer. Viscosity data of PC were taken from Ref. [5]. The water contents were measured in the dry box by the Karl–Fisher method using a Tacussel Aquaprocessor with a sensitivity of $\pm 0.1\,\mu g$. Soluble powders of Li Nafion 1100 were obtained as previously described [3], then dehydrated at 110° C under primary vacuum for at least 72 h. Complete dehydration of Li Nafion 1100 is difficult to achieve without modification of the polymer structure [6] since higher temperatures are needed. Gels were directly prepared in the measurement cells by mixing convenient proportions of Li Nafion powder and solvent. The mixtures were stirred and gently heated until the gels were obtained. A 24-h delay was observed before measurements in order to obtain homogeneous samples. The samples were introduced into a dry-bath thermostat especially designed for these experiments, and the temperature was controlled within ±0.05° C. Conductance measurements were performed using a Tacussel platinum platinized electrode (type CM 02 55 G) with a Tacussel CD 7N type conductimeter. The non-specified a.c. frequency was 1000 Hz. The other values used were 15.6 Hz, 62.5 Hz, 250 Hz, 4 kHz and 16 kHz.

Table 1 gives the specific conductance* and the water contents of the solvents. Table 2 gives the concentration range investigated. The limitations are due on one side to the specific conductance of the solvents and on the other side to the viscosity of the concentrated gels. Volume fractions are given as well as molar concentrations.

For the study of the water effect on conductivity, small amounts of water were gradually added using a microsyringe with a very thin needle (one drop ~ 4 μl) to the concentrated solutions (i.e. 0.204 M for NMF, 0.235 M for PC, 0.214 M for TEP). Measurements were performed after homogenization by stirring at moderate temperature (80° C).

Table 1. Specific conductances and water contents of the solvents

Solvent	σ_{sp} $(S\,cm^{-1})$	$[H_2O]$ $(mol\,l^{-1})$
NMF	23×10^{-6}	3.9×10^{-4}
PC	1.56×10^{-6}	3.4×10^{-5}
TEP	1.2×10^{-6}	2.5×10^{-4}

Table 2. Concentration ranges and corresponding volume fractions. I is a set of Li Nafion 1100 containing 1.35×10^{-2} H_2O/ionophore. II is a set containing 0.65×10^{-2} H_2O/ionophore. The concentration is expressed taking the molecular weight of the monomer as reference ($M = 1100$)

NMF			*PC*			*TEP*		
C (*M*)		*Volume fraction (%)*	C (*M*)		*Volume fraction (%)*	C (*M*)		*Volume fraction (%)*
0.327	I	18	0.371	I	20.4	0.274	I	15
0.263		14.5	0.304		16.7	0.214		11.7
0.203		11.22	0.237		13.1			
0.204	II	11.3	0.235	II	12.9	0.214	II	
0.128		7.02	0.175		9.6	0.133		7.3
0.077		4.22	0.067		3.71	0.081		4.4
0.018		0.99	0.019		1.05	0.019		1.07
0.007		0.40	0.009		0.5	0.007		0.4

3. Properties of the solvents

The classification given by Barthel *et al.* [7] shows that:

(i) *N*-methylformamide is a protophobic H-bond donor, with a very high dielectric constant and a moderate viscosity. It is a good solvent for Nafion 1100.

(ii) Propylene carbonate is an aprotic protophobic solvent with a dielectric constant close to that of water. It is a moderate solvent of Nafion 1100, but it is widely used in lithium batteries due to its electrochemical stability and its wide range of existence in the liquid state (−54.53 to 242° C).

(iii) Triethylphosphate belongs to the electron donor class with a low dielectric constant. However a very important swelling of native Nafion 1100 membrane was observed in this solvent, as well as a dissolution of the powder which gives rise to viscous solutions even in the dilute range.

In ion–solvent interactions the solvent is characterized by its bulk and molecular properties. Table 3 gives some bulk properties of the solvents together with their electron donor and acceptor abilities. Density (ϱ), viscosity (η) and relative permittivity or dielectric constant (ε) are the main relevant bulk properties. They are the only parameters involved in the Debye–Hückel theory of dilute electrolytes. The number of dissociated ions increases with permittivity, and the lower the viscosity the more conductive is the electrolyte. The importance of these parameters decreases when the concentration of the solute is increased. Association and solvation of ions are related, on a molecular scale, to the donor/acceptor abilities of the solvents. Many polarity scales have been proposed for the description of these abilities. One of the most commonly used for the donicity is the Gutmann donor number DN. It is defined as the molar enthalpy ($kcal\,mol^{-1}$) corresponding to the

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* The specific conductance (or conductivity), σ_{sp} $(S\,cm^{-1})$ is the conductance divided by the cell constant k (cm) = A $(cm^2)/L$ (cm), where A is the surface of the electrodes and L is the distance between them. The equivalent conductivity is the specific conductance divided by the concentration: σ_{eq} $(S\,cm^2\,eq^{-1}) = \sigma_{sp}$ $(S\,cm^{-1})/C$ $(10^{-3}\,eq\,l^{-1})$. In our case: σ_{eq} $(S\,cm^2\,eq^{-1}) = \sigma_{eq}$ $(S\,cm^2\,mol^{-1})$.

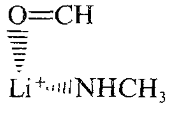
Table 3. Properties of solvents and water

Solvent	*B.p.** (°*C*)	ϱ^{25*}	η† (10^{-3} Pa s)	ε†	*DN*†	*Et*†
NMF	180.5	0.9980	1.65	182.4	1.26‡	0.72
PC	242	1.2069	2.513	66.1	0.39	0.49
TEP	215	1.065	1.55	13.3	0.67	0.34
H_2O	100	1.00	0.890	78.39	0.85	1.00

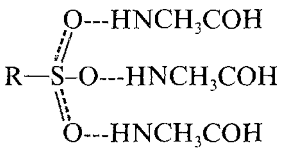
* 'Handbook of Chemical Physics' (65th edition).
† 'Ion Solvation' by Y. Marcus, Wiley, New York (1985) pp. 141–144.
‡ 0.60 is another value from I. Persson, M. Sandström and P. L. Coggin, *Inorg. Chim. Acta* **129** (1987) 183.

interaction of the solvent with $SbCl_5$ used as a reference electron acceptor in a 10^{-3} M solution of dichloromethane. The DN scale of Table 3 is normalized (DN = (DN/kcal mol^{-1})/38.8) assigning the value DN = 1.00 to hexamethylphosphoric triamide and DN = 0.00 to 1, 2 dichloromethane [8]. The electron-pair acceptance represents the ability of a solvent to solvate a negative charge and has received many definitions. In Table 3 Et is the lowest energy transition (kcal mol^{-1}) of an indicator (2,6-diphenyl-4-(2′,4′,6′-triphenyl-1-pyridino)phenoxide) dissolved in the studied solvent [9] and is scaled by assigning Et = 1.00 to water [8].

NMF, which is an H-bond donor, can easily solvate small cations like Li^+, according to Scheme II and can solvate anions according to Scheme III [10].



II



III

The solvation of Li^+ cations by PC is well known [7, 8], and their solvation by TEP is probably stronger since the DN of the TEP is superior to the DN of PC. Conversely the TEP appears to solvate the sulfonyl group poorly because of its moderate electron-pair acceptance. But an aprotic dipolar solvent like PC can solvate large anions more strongly than protic solvents, especially when anions have delocalized charge [11]. The major contribution in that solvation phenomenon is the electrostatic dipole–dipole interaction between the solvent and the solute. For a given solute, correlations with the dielectric constant, the molar polarization, the dipole moment and the structure of the solvent have been attempted [12]. In solvent mixtures, generally selective solvation occurs with one of the components. In mixtures with water, cations are preferentially solvated by water. The mobility of ions and the conductive properties of the electrolyte are then modified not only by the change in the bulk properties of the medium, but also by the ability of the negative atom in the anion to accept hydrogen bonding.

4. Results

Figure 1 shows the change of the specific conductance with concentration of the Li Nafion 1100 solutions in NMF between 25 and 80°C. Figure 2 shows the specific conductances in PC and TEP. Figures 3, 4 and 5 give the specific conductance of Li Nafion 1100 gels in PC, TEP and NMF, respectively when water is present. Figure 6 shows the temperature dependence of the conductivity at different frequencies from 15.6 Hz to 16 kHz for a solution of 0.163 M Li Nafion 1100 in NMF. The variations of the conductivity with frequency are much smaller in PC and TEP.

5. Discussion

The main result which emerges from these measurements is that at room temperature the conductivity of Li Nafion 1100 gets is much higher (about 50 times) in NMF than in PC and TEP. The value of a solution 0.26 M in NMF (4 × 10^{-3} S cm^{-1}) is comparable to that of a lithium perchlorate solution 0.3 M in PC.

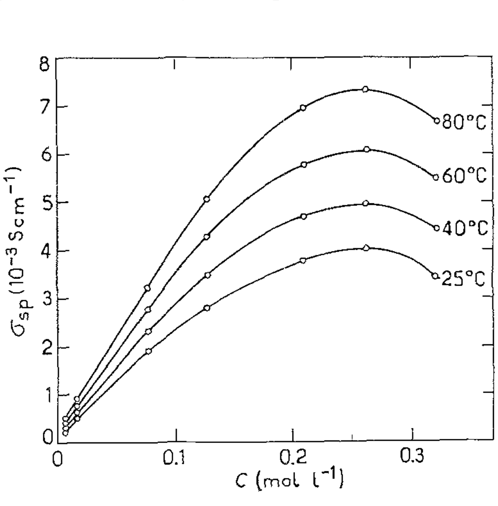


Fig. 1. Specific conductance of the Li Nafion 1100 solutions in NMF (sets I and II of Table 2) vs concentration at various temperatures.

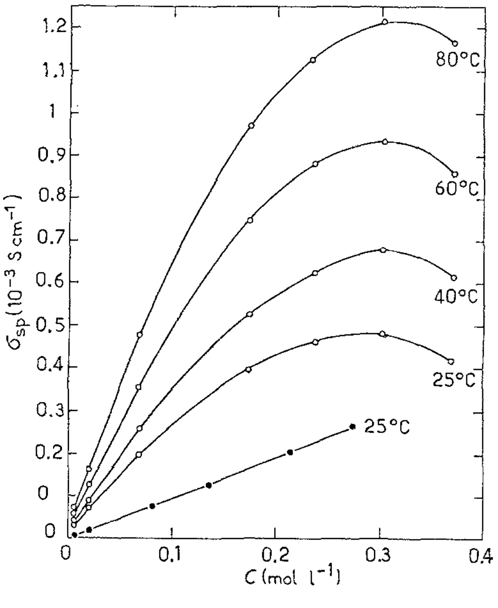


Fig. 2. Concentration dependence of the specific conductance of Li Nafion 1100 solutions. ○ in PC (sets I and II of Table 2) from several temperatures; ● in TEP (sets I and II of Table 2) at 25°C.

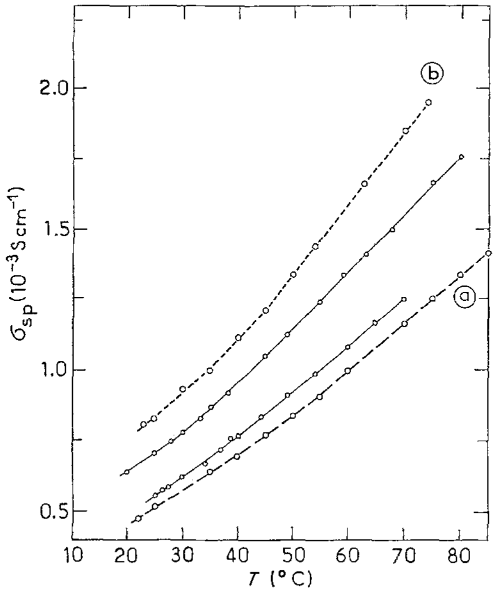


Fig. 3. Specific conductance vs temperature of a Li Nafion 1100 gel 0.235 M in PC with different amounts of water: (a) 10^{-2} H_2O/ionophore; (b) 5 H_2O/ionophore.

Figures 1 and 2 show maxima of the conductivity for Li Nafion 1100/NMF and PC solutions, but a linear variation in the case of TEP solutions. As in the case of simple salts, the plot of the equivalent conductivities vs the square root of the concentrations is observed to be linear (Figs 7 and 8). In Table 4, the experimental slopes, $-k$, are compared with the Onsager coefficient, S, calculated from the solvent parameters and from the values of the equivalent conductivities at zero concentration, σ_0, extrapolated from the graphs of Figs 7 and 8. Table 4 gives also the values of the equivalent conductivity, σ_0, found in the literature for lithium salts in NMF [13] and in PC [14].

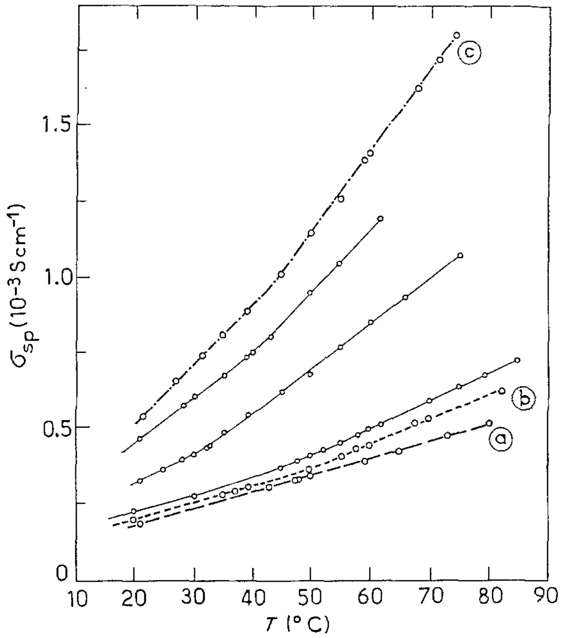


Fig. 4. Specific conductance vs temperature of a Li Nafion 1100 gel 0.214 M in TEP with different amounts of water: (a) 10^{-2} H_2O/ionophore; (b) 5 H_2O/ionophore; (c) 57 H_2O/ionophore.

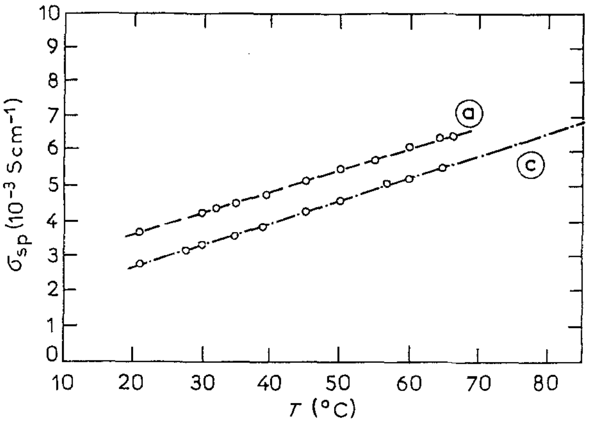


Fig. 5. Specific conductance vs temperature of a Li Nafion 1100 gel 0.204 M in NMF with different amounts of water: (a) 10^{-2} H_2O/ionophore; (c) 57 H_2O/ionophore.

5.1. *Case of the Li Nafion 1100 gels in NMF*

We observed a negative deviation of the slope from the Onsager coefficient and a value of σ_0 close to the value given for LiCl/NMF solution [13], 34.15 S cm^2 mol^{-1} compared to 35.10 S cm^2 mol^{-1}. The literature reports both the negative deviation of the slope and the validity of Kohlrausch's law of independent ion migration in highly polar solvents [13–15]. Since the σ_0^+ in LiCl/NMF solution is equal to 15 S cm^2 mol^{-1}, this result shows that at 1 kHz the anions contribute to the conductivity even in the case of Li Nafion 1100 solutions.

Figure 9 shows that the equivalent conductivity of a 0.163 M Li Nafion 1100 solution in NMF decreases at low frequency, and that the extrapolated value at zero frequency is consistent with that of the cations only. This result may be explained in the following way: the maximum displacement of an ion during one cycle from its equilibrium position is $a_i = v_i/4\nu$ where v is the mean velocity and ν the frequency. The velocity is related to the mobility, μ, by $v_i = \mu_i V_{eff}/d$ where V_{eff} is the maximum effective potential, d is the distance between electrodes and μ is related to the equivalent conductivity, σ_i, by $\sigma_i = |z_i| F\mu_i$. Combining these

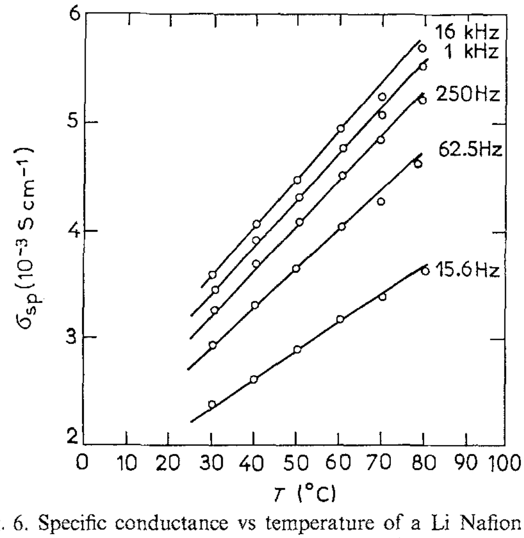


Fig. 6. Specific conductance vs temperature of a Li Nafion 1100 solution 0.163 M in NMF at different frequencies.

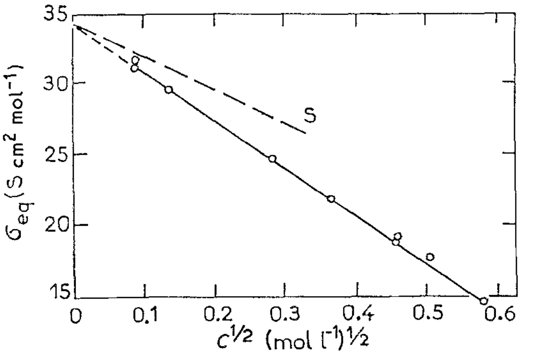


Fig. 7. Equivalent conductance at 25° C vs the square root of the concentration of Li Nafion 1100 solutions in NMF (set II of Table 2). The dotted line (S) is the Onsager limit law calculated from the solvent parameters.

relations and using the experimental values, we found that in NMF, a varies from 2.5 Å at 1000 Hz to 120 Å at 15 Hz. These values should be compared with the length of a stretched side chain in Nafion ($L \sim 8$ Å) at the extremity of which the SO_3^- is attached. At 1 kHz, $a < L$, the SO_3^- is free to move and participate in the conductivity. At 15 Hz, $a > L$, and the SO_3^- ions can be considered as bound to the polymer.

5.2. *Case of the Li Nafion 1100 gels in PC*

The experimental slope and the σ_0^+ are smaller than the values given for salts in the Debye–Hückel model [14]. Two factors can reduce the conductivity. On one hand, Li Nafion could be weakly dissociated in this concentration range in spite of the high dielectric constant of the PC. On the other hand the moderate swelling of Nafion in this solvent associated with its high viscosity may explain a low mobility of the ions.

5.3. *Case of the Li Nafion 1100/TEP solutions*

We observed (Fig. 2) a linear variation of the conductivity with the concentration in the investigated range. Since gel viscosity was high, it was not possible to prepare gels with concentrations greater than 0.214 M in order to observe a maximum in conductivity as with the other solvents. The dissolution of ions is weak. It is probable that multiplets complexed by TEP may exist. Fuoss and Accassina indicate highly associated forms in low permittivity solvents [16]. This could be related to the important swelling of Nafion membranes which is observed in this solvent.

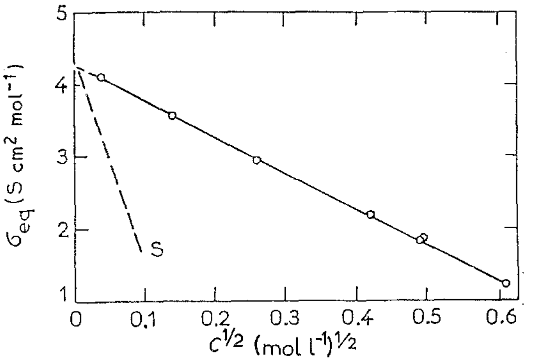


Fig. 8. Equivalent conductance at 25° C vs the square root of the concentration of Li Nafion 1100 solutions in PC (set II of Table 2). The dotted line (S) is the Onsager limit law calculated from the solvent parameters.

Table 4.

Solvent	$-k$*	S*	$\sigma_{0\,\mathrm{obs}}$†	$\sigma_{0\,\mathrm{lit}}$†	$\sigma_{0\,\mathrm{lit}}^+$
NMF	37.4	23.71	34.15	35.10†	15.0‡
PC	4.4	24.57	4.03	27.34§	8.89§

* Units are S cm^2 mol$^{-3/2}$ l$^{1/2}$.
† Units are S cm^2 mol^{-1}.
‡ For LiCl in NMF from Ref. [13].
§ For LiClO$_4$ in PC from Ref. [14].

5.4. *Effect of water on conductance*

When plotting the logarithm of the specific conductance versus T^{-1} for two sets of samples in each solvent, we obtained linear variations from which activation energies, E_A, could be deduced. Table 5 gives the values of E_A compared with the activation energies E_η obtained from the plots of the logarithm of the viscosity vs T^{-1} for the pure solvents. We believe that E_A, an average of the migration energy of ions, is representative of the viscous forces acting on the ions during their motion. It depends both on the viscosity of the solvent and on the size of the solvated ions. For NMF, E_A is significantly lower than E_η. In this structured solvent, the activation energy E_A could be lowered by a process of destructuration of the solvent by lithium [15] in such a manner that the local viscosity around the cations could be smaller than the viscosity of the pure solvent. In the case of TEP, E_A is higher than E_η, showing the solvation of the ions by this solvent. In the case of PC, the similar values for E_A and E_η could be interpreted as a poor solvation of the ions, or as a water effect if E_η has not been determined under anhydrous conditions.

We determined also the quantity E_A for a very dry solution of lithium perchlorate in PC (Table 6) and for

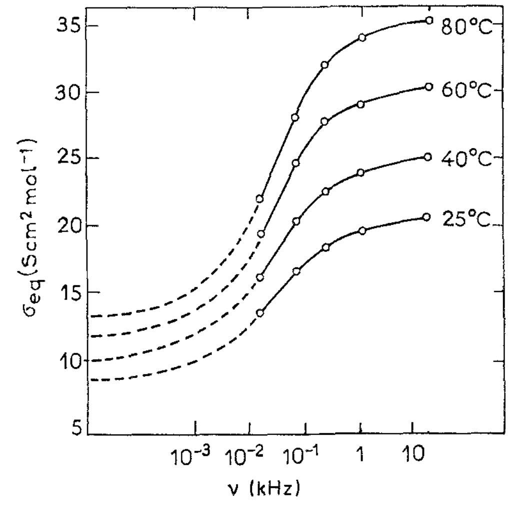


Fig. 9. Equivalent conductivity vs frequency of a Li Nafion 1100 solution 0.163 M in NMF. The dotted lines are possible extrapolations for zero frequency.

Table 5. Activation energies of Li Nafion 1100 solutions of Table 2. Accuracy of E_A is ± 0.25 kcal mol^{-1}

NMF		*PC*		*TEP*	
C (*M*)	E_A (*kcal mol^{-1}*)	C (*M*)	E_A (*kcal mol^{-1}*)	C (*M*)	E_A (*kcal mol^{-1}*)
	I/II		I/II		I/II
0.327	2.4	0.371	3.9	0.274	3.6
0.263	2.2	0.304	3.6	0.214	3.5
0.204	1.8/2.4	0.235	3.6/3.7		–
0.128	2.3	0.175	3.6		–
0.077	2.1	0.067	3.4		–
0.118	2.1	0.019	3.6		–
0.007	1.9	0.009	3.4		–
E_η (kcal mol^{-1})	3	$E_\eta = 3.55$		$E_\eta = 2.81$	

Li Nafion 1100 solutions also in PC with different amounts of water (Table 7). From these data we observed that the activation energy is minimum for the dry solution, and increases with the increasing addition of water to the gels. When added to the solution, water immediately solvates the ions, therefore increasing the hydrodynamic size of the moving ions.

Another effect of water addition to the gels is to modify the values of their specific consequences. The specific conductance rises significantly (~ 70% at room temperature) when $5H_2O$/ionophore are added to PC solutions (Fig. 3b), in spite of the dilution (3% in volume). This mixture (1 mol H_2O/9 mole PC) exhibits slight but significant changes of its bulk properties, i.e. the permittivity and the viscosity. The increase of conductivity could be due to the solvation of both anions and cations by water and also probably to the local decrease of the viscosity around cations. Furthermore water and PC separate out when water reaches ~ 10% by volume. This effect arises from the large difference between the solvating properties of the two solvents.

Large amounts of water (57 H_2O/ionophore or 2.3 mole H_2O/1 mole TEP) are necessary to noticeably enhance the conductivity in TEP solutions (Fig. 4c). To a first approximation the dielectric constant of the mixture rises from 13 to 58, increasing the ion dissociation and hence the conductance. The hydrophilic character of TEP leads to homogeneous mixtures with water in all proportions.

On the contrary the specific conductance decreases when 57 H_2O/ionophore are added to NMF solutions (Fig. 5c) since both the concentration and the dielectric constant of the mixture decrease. This confirms that the Li Nafion 1100 is well dissociated in NMF.

6. Conclusion

In view of applications, the most interesting quantity to consider is the specific conductance. We found that room temperature values for Li Nafion 1100 solutions are of the same order of magnitude as simple salts in organic solvents. Compared to the best conductive ionic solid polymers that are known at the present time, such as for instance doped polyoxyethylene [17], there is a difference of two orders of magnitude (~ 10^{-5} S cm^{-1} compared to 10^{-3} S cm^{-1}). NMF could be the most interesting solvent but it cannot be used at room temperature in electrochemical devices because of its protic nature. Conductivities in TEP and especially in PC could probably be enhanced by using mixtures of solvents as is actually done in numerous electrolytes for batteries.

From a fundamental point of view, little is known about the structure of the solutions. The rod model of the polyelectrolytes [18] could be more adequate than

Table 6. Comparison between Li Nafion 1100 and $LiClO_4$ solutions in PC

Solute in PC	C (*M*)	E_A (*kcal mol^{-1}*)	[H_2O] (*mol l^{-1}*)
$LiClO_4$	0.2	2.9	10^{-4}
	0.1	2.9	$5\ .10^{-5}$
	0.05	2.9	2.5×10^{-5}
Li Nafion 1100	0.23	3.7	1.5×10^{-3}
	0.175	3.6	1.1×10^{-3}
	0.067	3.4	4.3×10^{-3}

*Table 7. Activation energies of Li Nafion 1100 solutions containing water. The water concentrations are * 10^{-2} H_2O/ionophore; † 5.2 H_2O/ionophore; ‡ 57 H_2O/ionophore. Accuracy of E_A is ± 0.25 kcal mol^{-1}*

Solvent	C (*M*)	E_A (*kcal mol^{-1}*)		
		[H_2O]*	[H_2O]†	[H_2O]‡
NMF	0.204	1.8		3.2
	0.263	2.2		3.0
	0.327	2.4		3.6
PC	0.235	3.6	3.6	
	0.304	3.6		
	0.371	3.9	3.8	
TEP	0.214	3.5	4.0	4.6
	0.274	3.6		4.6

the Debye–Hückel model of a continuous distribution of the charges. It will be interesting to measure the transference number of lithium in NMF because of its high dissociating power and in TEP since the swelling of Nafion is very important in this solvent. Further measurements of the osmotic pressure and determination of the activity coefficients are necessary to obtain a better understanding of the Li Nafion 1100 solutions.

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