

FACTORS AFFECTING THE CONDUCTIVITY OF DIVALENT POLYMERIC ELECTROLYTES

M. A. G. MARTINS and C. A. C. SEQUEIRA*

Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisbon Codex (Portugal)

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Summary

The reported behaviour of a series of polymeric electrolytes, formed by poly(ethylene oxide) and salts of divalent metals, is reviewed. The effect of such factors as the choice of the anion, cation, casting solvent and stoichiometry on the observed performance of the electrolytes, is analysed. Consideration is given to the influence of chemical, physical and structural properties on the ionic conductivity of these solid materials. Suggestions are made for further studies aimed at elucidating or confirming aspects of these relationships.

1. Introduction

The substantial recent interest in polymeric electrolytes has been largely focussed on lithium systems because of the high energy densities that are potentially available from power sources involving Li^+ transport [1]. For certain applications, electrolytes involving cations other than Li^+ may be acceptable, or even preferred, since there are disadvantages associated with the use of lithium metal as an electrode material. These include the necessity to fabricate and handle lithium devices in a controlled atmosphere prior to encapsulation, and the tendency for lithium to migrate, which can lead to problems in devices in which Li is in direct contact with circuit boards.

In addition, a deeper understanding of the connection between structure and conductivity in polymeric electrolytes is being actively sought by many workers. Lithium systems are an inappropriate basis for certain types of studies of structure-conductivity relationships, *e.g.*, those involving X-ray techniques such as EXAFS [2].

For reasons including those cited above, there has been a steady interest in the behaviour of adducts or complexes formed between polymers such as poly(ethylene oxide), PEO, and salts of the divalent metals listed in Table 1. Such materials will be represented here as $\text{PEO}_n:\text{MX}_2$, where the

*Author to whom correspondence should be addressed.

TABLE 1

Ionic radii of cations and anions

Ion	Ionic radius (pm)	Ion	Ionic radius (pm)
Mg ²⁺	66	Cd ²⁺	97
Ca ²⁺	99	Hg ²⁺	110
Sr ²⁺	112	F ⁻	119
Ba ²⁺	134	Cl ⁻	167
Pb ²⁺	120	Br ⁻	182
Cu ²⁺	72	I ⁻	206
Zn ²⁺	74	ClO ₄ ⁻	236

stoichiometric number, n , refers to the ratio of the number of polymeric structural repeat units (*i.e.*, $-\text{CH}_2-\text{CH}_2-\text{O}-$) to each divalent metal ion M , and to each pair of monovalent anions, X . Thus $n = [\text{O}]/[\text{M}] = [\text{O}]/2[\text{X}]$.

The stoichiometric number merely represents the *overall* composition of the electrolyte; it should be borne in mind that polymeric electrolyte materials are not necessarily single phase, and the composition of individual regions or phases may deviate substantially from n . It is helpful to note that the use of the above formula may or may not imply the presence of a polymer-salt complex, as opposed to an adduct or solution. It is also to be recognised that the nominally denoted composition may be significantly incomplete, in that it does not indicate the possible presence of small amounts of water and/or trapped solvent which may have a noticeable effect on the observed behaviour. In fact, the presence of water in PEO electrolytes containing divalent cations can dramatically change the electrolyte conductivity and the observed transport numbers.

The earliest studies [3, 4] of $\text{PEO}_n:\text{MX}_2$ systems were on crystalline complexes of $\text{PEO}_4:\text{HgCl}_2$, $\text{PEO}_4:\text{HgBr}_2$, $\text{PEO}_5:\text{HgI}_2$ and $\text{PEO}_4:\text{CdCl}_2$. These, in fact, predate the seminal paper on PEO/alkali halide systems [5] from which the present day lithium and other monovalent systems were eventually developed.

Interest was then focussed on the detailed *trans* and *gauche* conformations of the polymer backbone within salt-rich (*i.e.*, low n) PEO/ HgCl_2 complexes [6].

Later work extended the scope of polymer:divalent salt systems to include studies [7], especially on the glass transition temperature, of cellulose acetate, poly(methyl methacrylate), poly(vinyl acetate), poly(vinyl alcohol) and poly(methyl acrylate) with nitrates of Cu^{2+} , Zn, Ca and Cd (Table 2); of polyethers with a range of salts [8]; and of poly(propylene oxide), PPO, with ZnCl_2 [9]. More recent studies of the behaviour of a range of $\text{PEO}:\text{MX}_2$ systems have been carried out [10 - 14]; these are summarised in Table 3.

TABLE 2
Polymer:MX₂ systems

Polymer	Cation	Anion	Solvent	Type of study	Temperature range (°C)	Reference
Cellulose acetate	Ca ²⁺	NO ₃ ⁻	ethanol	DSC, infrared measurement	—	7
Poly(methyl acrylate)	Cd ²⁺	NO ₃ ⁻	ethanol	DSC, infrared measurement	—	7
Poly(methyl methacrylate)	Zn ²⁺	NO ₃ ⁻	ethanol	DSC, infrared measurement	—	7
Poly(vinyl acetate) and poly(vinyl alcohol)	Cu ²⁺	NO ₃ ⁻	ethanol	DSC, infrared measurement	—	7
Poly(tetramethylene glycol)	Zn ²⁺	Cl ⁻	ethanol	DSC and mechanical relaxation measurement	-100 to +100	9
Poly(propylene glycol)	Co ²⁺	Cl ⁻	ethanol	DSC and mechanical relaxation measurement	-100 to +100	9
	Fe ³⁺	Cl ⁻	ethanol	DSC and mechanical relaxation measurement	-100 to +100	9
	Sn ²⁺	Cl ⁻	ethanol	DSC and mechanical relaxation measurement	-100 to +100	9
	Hg ²⁺	Cl ⁻	ethanol	DSC and mechanical relaxation measurement	-100 to +100	9
	Cu ²⁺	Cl ⁻	ethanol	DSC and mechanical relaxation measurement	-100 to +100	9
	Zn ²⁺	Br ⁻	ethanol	DSC and mechanical relaxation measurement	-100 to +100	9
	Zn ²⁺	I ⁻	ethanol	DSC and mechanical relaxation measurement	-100 to +100	9
Poly(alkoxy phosphazene)	Ca ²⁺	SO ₃ CF ₃ ⁻	—	DSC, a.c. impedance, potentiostatic measurement	25 to 300	18
	Sr ²⁺	SO ₃ CF ₃ ⁻	—	DSC, a.c. impedance, potentiostatic measurement	25 to 300	18
	Zn ²⁺	SO ₃ CF ₃ ⁻	—	DSC, a.c. impedance, potentiostatic measurement	25 to 300	18

TABLE 3
PEO:MX₂(H₂O) systems

Cation	Anion	Hydrate	Solvent	Type of study	Temperature range (°C)	Reference
Ca ²⁺	SCN ⁻	4H ₂ O	methanol	DSC analysis	-100 to +200	10
Ba ²⁺	SCN ⁻	3H ₂ O	methanol	audio-frequency, DR	-267.5 to +27	10
Mg ²⁺	Cl ⁻	—	ethanol	DSC analysis	-100 to +260	10
				audio-frequency, DR	-267.5 to +27	10
				TGA, DSC analysis	25 to 320	11
				X-ray diffraction	~25	11
Pb ²⁺	Br ⁻	—	dimethyl sulfoxide	a.c. impedance analysis	25 to 300	11
				TGA, DSC analysis	25 to 320	11
				X-ray diffraction	~25	11
				a.c. impedance analysis	25 to 300	11
Cu ²⁺	ClO ₄ ⁻	—	isopropyl alcohol	CV, a.c. impedance	25 to 100	12
Zn ²⁺	Cl ⁻	—	isopropyl alcohol	CV, a.c. impedance	25 to 100	12
Cu ²⁺	Cl ⁻	—	isopropyl alcohol	CV, a.c. impedance	25 to 100	12
Zn ²⁺	Γ ⁻ /Cl ⁻	—	isopropyl alcohol	CV, a.c. impedance	25 to 100	12
Mg ²⁺	ClO ₄ ⁻	6H ₂ O	methanol	DSC studies	25 to 100	12
		4H ₂ O	methanol	DSC studies	-100 to 200	13
Ca ²⁺	ClO ₄ ⁻	6H ₂ O	methanol	DSC studies	-100 to 200	13
		3H ₂ O	methanol	DSC studies	-100 to 200	13
Zn ²⁺	ClO ₄ ⁻	6H ₂ O	methanol	DSC studies	-100 to 200	13
Sr ²⁺	ClO ₄ ⁻	6H ₂ O	methanol	DSC studies	-100 to 200	13
Mg ²⁺	ClO ₄ ⁻	6H ₂ O	methanol	DSC studies	-100 to 200	13
		4H ₂ O	methanol	a.c. impedance analysis	20 to 120	13
Ca ²⁺	ClO ₄ ⁻	6H ₂ O	methanol	a.c. impedance analysis	20 to 120	13
		3H ₂ O	methanol	a.c. impedance analysis	20 to 120	13
Zn ²⁺	ClO ₄ ⁻	6H ₂ O	methanol	a.c. impedance analysis	20 to 120	13
Sr ²⁺	ClO ₄ ⁻	6H ₂ O	methanol	a.c. impedance analysis	20 to 120	13
Pb ²⁺	Br ⁻	—	dimethyl sulfoxide	DSC, TGA, a.c. impedance	25 to 300	19
	Γ ⁻	—	dimethyl sulfoxide	DSC, TGA, a.c. impedance	25 to 300	19
	Cl ⁻	—	dimethyl sulfoxide	X-ray diffraction	~25	19
Mg ²⁺	Cl ⁻	—	ethanol	DSC, a.c. impedance	25 to 300	20
Zn ²⁺	Cl ⁻	—	—	DSC, dielectric TA	-100 to 150	21
Co ²⁺	Br ⁻	—	—	DSC, dielectric TA	-100 to 150	21
Ni ²⁺	Br ⁻	6H ₂ O	ethanol	TGA, a.c. impedance	20 to 250	22

2. Experimental

The sample preparation techniques used in all recent studies are essentially along the following lines. An appropriate amount of salt, sometimes hydrated, is dissolved in a suitable solvent, usually methanol, by stirring for some hours. Acetonitrile and PEO (sometimes as a solution and sometimes separately) are then added, and the solution is covered and stirred for about 24 h and then cast within a glass ring onto a PTFE or silicone paper base. Solvent evaporation then proceeds in a controlled manner over a period of several days, often in a desiccator over a 5A molecular sieve. Heating and/or vacuum may be applied, and the resultant films, typically 100 μm thick, are usually stored under moisture-free conditions, e.g., in a dry box.

Significant deviations from the above scheme, possibly giving rise to deviations in observed behaviour, will be noted at appropriate points within the discussion below.

The experimental methodology used to study the characteristics of the divalent polymeric electrolyte films embraces the following techniques, different combinations of which are used by the various workers. Morphological changes are observed using differential scanning calorimetry (DSC), variable temperature polarizing microscopy (VTPM) [15], scanning electron microscopy (SEM) and thermomechanical analysis (TMA). Compositional changes are studied by thermogravimetric analyses (TGA), energy dispersive X-ray analysis (EDX) and elemental analysis (EA). Electrochemical characteristics that are examined include conductivity as a function of temperature, $\sigma(T)$, and ionic transport numbers t_+ and t_- , both usually obtained from frequency-dependent complex plane analysis; cell discharge measurements, usually expressed in terms of voltage as a function of time, $V(t)$; cyclic voltammograms (CV), to provide evidence for redox reactions involving candidate species; and dielectric relaxation (DR).

It is customary to carry out the above investigations for several stoichiometries, normally in the range $4 < n < 30$.

3. Comparison of systems

The observed behaviour of $\text{PEO}_n:\text{MX}_2$ systems is found to depend very significantly on a range of factors including:

- (i) nature of cation
- (ii) nature of anion
- (iii) stoichiometry
- (iv) temperature
- (v) thermal history
- (vi) preparation conditions

Similar observations have been made for lithium systems [15, 16], apart from the obvious difference that the cation is invariant.

To facilitate analysis of these factors and to aid the subsequent elucidation of their effect, certain key differences between different systems will now be highlighted.

4. Composition of maximum conductivity

It has been observed for both hydrated and dehydrated salts that isotherms of $\log(\sigma/S \text{ cm}^{-1})$ against stoichiometry number, n , are usually irregular [11, 13]. Consequently isopleths of $\log(\sigma/S \text{ cm}^{-1})$ against $1000K/T$ vary in gradient, and may cross each other. In some systems, *e.g.*, $\text{PEO}_n:\text{Ca}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, the conductivity maximum appears to lie at concentrations of salt that are more dilute (*i.e.*, $n > 18$) than those studied. This apparently curious finding of an inverse relationship between conductivity and salt content is also observed [17] for $\text{PEO}_n:\text{LiClO}_4$.

In Table 4, the compositions for maximum conductivity, n_{max} , are tabulated as a function of temperature for a range of systems. Since n_{max} for Li systems is close to 8, an *a priori* estimate for divalent systems might be:

- (i) 8, if the number of cation carriers is the relevant factor;
- (ii) 16, if the number of charges carried (by anion or cation), or alternatively the number of carriers, is more significant.

Inspection of Table 4 reveals that n_{max} varies substantially with anion, cation and temperature, from below 8 to above 16. The observed limits of the variation, *i.e.*, 4 - 24, may be artificially narrow and merely reflect the truncated range chosen by individual authors.

Values of n_{min} are presented in Table 5. Although also irregular, it can be seen that, except for some hydrated salt systems near room temperature, $n_{\text{min}} < n_{\text{max}}$. Inspection of Tables 4 and 5 in conjunction with Table 1 clearly reveals that n_{max} and n_{min} do not correlate with cationic radius (or charge density), although at certain temperatures it has been noted that conductivity at fixed n decreases with increase in cationic radius [13]. As can be seen in Table 6, the conductivity results for $\text{PEO}-\text{X}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ complexes, where $\text{X} = \text{Mg}^{2+}, \text{Zn}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}$, are in accord with that observation, too.

There appears to be some ambiguity regarding the choice of the anion that will yield maximum conductivity with a given cation, or *vice versa*. Further significant observations can be reported, however, as discussed below.

Linford and co-workers [13] have found that the polyether electrolytes of divalent cation perchlorates are generally better conductors than the corresponding thiocyanates. Table 6 shows results for the Mg and Ca systems confirming this observation, which seems to be also valid for other salts (*e.g.*, the conductivity of $\text{PEO}:\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ complexes is higher than the conductivity of $\text{PEO}:\text{MgCl}_2$ complexes). The fact that $\text{PEO}:\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ complexes [13] present lower maximum conductivities than $\text{PEO}:\text{ZnCl}_2$ complexes [12] may be due to the different preparation

TABLE 6
Maximum conductivities of the PEO:salt complexes, in $(-\log \sigma)$ values

Salt	Temperature ($^{\circ}\text{C}$)											Reference
	20	30	40	50	60	70	80	90	100	110	120	
$\text{Ca}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	8.0	7.2	6.2	5.2	4.8	4.7	4.4	4.1	4.0	3.9	3.8	13
$\text{Ca}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$	8.8	8.2	7.5	6.6	5.8	5.5	5.3	5.2	5.0	4.9	4.8	13
$\text{Cu}(\text{ClO}_4)_2$	4.7	4.3	4.0	3.4	3.2	3.0	3.0	2.9	2.8			12
MgCl_2	9.4	8.8	8.0	7.2	6.5	5.7	5.5	5.2	5.0	4.9	4.7	11, 20
$\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	6.4	5.6	5.0	4.7	4.3	4.1	4.0	3.9	3.8	3.7	3.6	13
$\text{Mg}(\text{SCN})_2 \cdot 4\text{H}_2\text{O}$	9.2	8.3	7.0	6.2	5.9	5.6	5.4	5.1	5.0	4.8	4.7	13
PbBr_2	9.0	8.6	8.2	7.8	7.4	7.0	6.0	5.9	5.8	5.7	5.5	11, 19
$\text{Sr}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$		7.5	6.8	6.3	5.7	5.3	5.0	4.7	4.4	4.2	3.9	13
ZnCl_2	5.3	4.7	4.4	4.1	4.0	4.0	3.7	3.6	3.4			12
$\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	7.6	6.7	5.8	4.9	4.6	4.3	4.0	3.8	3.8	3.7	3.6	13
PbI_2		9.6	9.2	8.4	7.4	6.5	6.4	6.3	6.2	6.1	5.9	19
PbCl_2	9.4	9.1	8.7	8.2	7.6	6.7	6.5	6.4	6.3	6.3	6.2	19

TABLE 7
Transport numbers in $\text{PEO}_n\text{:MX}_2$ systems

Salt	t_c	t_a	Type of study	Temperature range ($^{\circ}\text{C}$)	Reference
$\text{PbBr}_2(\text{PEO})_{20}$	0.6 - 0.7	0.4 - 0.3	d.c. polarisation	140	11
$\text{CuCl}_2(\text{PEO})_6$	≈ 0.5	≈ 0.5	d.c. polarisation	20 - 80	12
$\text{ZnCl}_2(\text{PEO})_4$	≈ 0.9	≈ 0.1	d.c. polarisation	20 - 80	12
$\text{ZnCl}_2(\text{PEO})_8$	≈ 0.9	≈ 0.1	d.c. polarisation	20 - 80	12
$\text{ZnCl}_2(\text{PEO})_{12}$	≈ 0.9	≈ 0.1	d.c. polarisation	20 - 80	12
$[\text{Zn}(\text{SO}_3\text{CF}_3)_2](\text{MEEP})_6^a$	≈ 0.01	≈ 0.99	d.c. polarisation	61.6	18
$\text{ZnI}_2(\text{PEO})_{12}$	≈ 0.19	≈ 0.81	a.c. impedance	120	23
$\text{ZnI}_2(\text{PEO})_{12}$	≈ 0.23	≈ 0.77	a.c. impedance	100	23
$\text{PbBr}_2(\text{PEO})_{20}$	0.6 - 0.7	0.4 - 0.3	a.c. impedance	140	11, 19
$\text{MgCl}_2(\text{PEO})_{16}$	< 0.005	> 0.995	d.c., a.c. studies	100	20
$\text{NiBr}_2(\text{PEO})_8$	≈ 0.0	≈ 1.0	d.c., a.c. studies	20 - 140	22

^aPoly(alkoxy phosphazene) electrolyte.

procedures of the polymers (different water content trapped in the polymer films), apart from the larger size of the ionic carriers. The hypothesis of ion-pairing between ClO_4^- and Zn^{2+} can also be advanced, but evidence for this hypothesis requires experimental confirmation. The high cationic transference numbers for ZnCl_2 complexes, reported in Table 7, show that there is no ion-pairing in the ZnCl_2 complex.

As far as the effect of the different anions on the conductivity is concerned, Table 7 shows that

$$\sigma_{\text{PEO:PbBr}_2} > \sigma_{\text{PEO:PbCl}_2} > \sigma_{\text{PEO:PbI}_2} \quad (T < 60^\circ\text{C})$$

$$\sigma_{\text{PEO:PbBr}_2} = \sigma_{\text{PEO:PbI}_2} > \sigma_{\text{PEO:PbCl}_2} \quad (T = 60^\circ\text{C})$$

$$\sigma_{\text{PEO:PbI}_2} > \sigma_{\text{PEO:PbCl}_2} > \sigma_{\text{PEO:PbBr}_2} \quad (T = 70^\circ\text{C})$$

$$\sigma_{\text{PEO:PbBr}_2} > \sigma_{\text{PEO:PbI}_2} > \sigma_{\text{PEO:PbCl}_2} \quad (T > 70^\circ\text{C})$$

Comparing these sequences with the values of the ionic radii for the ions Cl^- , Br^- and I^- (Table 1), it can be concluded that there is no relationship between maximum conductivities and anionic radii.

If we consider a fixed value of n , we can see that the increase in conductivity is a direct function of the increase of the cationic mobility. For example, the ionic radii for Sr^{2+} , Ca^{2+} , Zn^{2+} , and Mg^{2+} , decrease in the order (Table 1): $\text{Sr}^{2+} > \text{Ca}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+}$ and the opposite should occur with the corresponding mobilities. Indeed, Table 6 shows that at 30°C , for example, the maximum conductivity for the corresponding complexes increases in the order: $\text{PEO}_{12}:\text{Sr}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} < \text{PEO}_{12}:\text{Ca}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} < \text{PEO}_{12}:\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} < \text{PEO}_{12}:\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$.

An obvious exception to this rule is shown by complexes like $\text{PEO}:\text{Cu}(\text{ClO}_4)_2$ and $\text{PEO}:\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. The ionic radius of Cu^{2+} is higher than that of Mg^{2+} , so the $\sigma_{\text{Mg complex}}$ should be higher than the $\sigma_{\text{Cu complex}}$. However, this is not the case, which can easily be understood on the basis of the fact that Mg^{2+} mobile ions are surrounded by their hydration shells. Moreover, the Mg^{2+} ions are apparently trapped in strong electrostatic bonds with the ether linkages on the polymer chains. Further conclusions about the conductivity relationships for fixed n and temperature values can be derived from analysis of Table 8. For example, for $n = 8$ and $T = 25^\circ\text{C}$,

$$\sigma_{\text{PEO:ZnCl}_2} > \sigma_{\text{PEO:CuCl}_2}$$

$$\sigma_{\text{PEO:Cu}(\text{ClO}_4)_2} > \sigma_{\text{PEO:CaCl}_2}$$

although the radius of the involved ions increases in the orders:

$$\text{Cu}^{2+} < \text{Zn}^{2+}$$

$$\text{Cl}^- < \text{ClO}_4^-$$

Papke *et al.* [24] have found that PEO-alkali metal salt complexes exhibit no detectable crystallisation for the larger cations such as Rb^+ and

TABLE 8
Conductivities of some divalent metal-salt-PEO complexes

Salt	PEO _n :salt ratio	Conductivity, -log($\sigma/S\text{ m}^{-1}$)	Temper- ature (°C)	Type of study	Refer- ence
Cu(ClO ₄) ₂	12	7.21	25	a.c. impedance	12
	8	4.70	25	a.c. impedance	12
	4	7.60	25	a.c. impedance	12
ZnCl ₂	12	8.75	25	a.c. impedance	12
	8	5.28	25	a.c. impedance	12
	4	5.70	25	a.c. impedance	12
CuCl ₂	8	8.92	25	a.c. impedance	12
MgCl ₂	24	5.10	80	a.c. impedance	20
	16	5.00	80	a.c. impedance	20
	12	5.20	80	a.c. impedance	20
	8	6.10	80	a.c. impedance	20
	4	8.00	80	a.c. impedance	20
KI·2ZnCl ₂	4	7.27	25	a.c. impedance	12
Ba(SCN) ₂ ·3H ₂ O	6.5	11.30	27	audio-frequency, electrical relaxation	10
Ca(SCN) ₂ ·4H ₂ O	6.5	11.0	27	audio-frequency, electrical relaxation	10

Cs⁺, while Na⁺ salt complexes showed a high degree of crystallinity. A similar observation was noticed for PEO:metal salt complexes with larger anions. Furthermore, Watanabe and Ogata [25] also reported that the larger the cation radius, the higher were the conductivity values for PPO-SCN(alkali metals) electrolytes. Accepting that this phenomenon can be applied to PEO:divalent metal salt complexes also, we can assume that large cations and/or anions favour the production of complexes possessing large proportions of amorphous regions, which explains the higher conductivities obtained experimentally.

For the same complex, at a certain temperature, and variable n , we can observe that usually the conductivity increases as the salt concentration increases (n decreases), then it attains a maximum for intermediate n values, and finally it decreases for higher salt concentrations. This behaviour is typical of, for example, PEO_n:Cu(ClO₄)₂, PEO_n:ZnCl₂ and PEO_n:MgCl₂ complexes (Table 8).

High salt concentrations have four main effects: (a) favour the formation of the PEO:salt complex, leaving a film depleted in free PEO [20]; (b) hinder the complete salt dissociation; (c) facilitate the formation of ionic multiplets, such as triplets ($X^-M^+X^-$, $M^+X^-M^+$) and quartets ($M^+X^-M^+X^-$), which are less mobile than free ions, and, in addition,

decrease their effective concentration [26]; (d) diminish the number of vacancies available for ionic transport [27]. These effects explain the low conductivities observed at higher salt concentration.

The low conductivities measured at low salt concentrations ($n \geq 12$) are to be expected, due to the reduced number of available charge carriers.

Cation-anion interactions inside the polymer electrolyte, such as the phenomenon of 'ion-pairing' [28], can explain conductivity variations over the whole range of temperatures and stoichiometries used. Salts whose anions are large, easily polarizable, and weak Lewis bases, *i.e.*, bases whose conjugate acids are strong, have a reduced tendency for ion-pairing, and their incorporation in the polymeric material leads to higher conductivity complexes.

5. Glass transition temperatures

From Table 9 we can see that, in general, the glass transition temperature, T_g , of divalent metal salt-polymer electrolytes increases considerably as the metal salt concentration increases.

The elevation of T_g of the polyether (host polymer) obtained by addition of metal salts, has been studied by several techniques such as infrared, DSC and X-ray techniques, and has been interpreted by Whetton and co-workers [9] in terms of the presence of strong ion-dipole interactions between the polymer and the metal salt reducing the average mobility of the polymer chain.

The most probable chemical interactions which occur in polyether-salt complexes are those between the lone electron pair on the ether oxygen atoms and the metal cation of the salt. Such interactions would result in the formation of coordinate bonds between the polymer chain and the metal salt. At high concentration of metal salt, all the available oxygen atoms in the polyether are able to coordinate to the salt, thus approaching the 'limit of solubility' of the salt in the polymer and the 'limiting value' of T_g [9]. Below this limit, the salt may be molecularly dispersed into the polymer, and above the solubility limit, excess salt will coexist as a second phase, without further elevation of T_g [9].

Apart from the size, the polarity of the metal salt molecule also affects T_g . The former influences chain flexibility and the latter influences intermolecular forces.

The effect of T_g on the cation mobility or, in other words, on the polymer ionic conductivity at high salt concentrations can be explained by means of the Williams-Landel-Ferry (WLF) equation:

$$\log \frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)}$$

where C_1 and C_2 are constants, and $\sigma(T)$ and $\sigma(T_g)$ are ionic conductivity values at temperatures T and T_g . This equation points out that the main term affecting the ionic conductivity is $T - T_g$.

TABLE 9

Glass transition temperatures of the PEO:MX₂(H₂O) systems

Salt	(PEO) _n :salt ratio	T _g (°C)	Reference
Mg(ClO ₄) ₂ ·6H ₂ O	20.0	-2	13
	15.1	-4	13
	12.0	0	13
	9.0	0	13
	6.0	1	13
Mg(SCN) ₂ ·4H ₂ O	18.0	11	13
	15.0	13	13
	12.0	4	13
	9.0	12	13
	6.0	14	13
Ca(ClO ₄) ₂ ·6H ₂ O	18.0	7	13
	15.0	0	13
	12.0	3	13
	9.0	23	13
	6.0	11	13
Ca(SCN) ₂ ·3H ₂ O	18.1	6	13
	15.0	13	13
	12.0	17	13
	9.2	6	13
	6.0	26	13
Zn(ClO ₄) ₂ ·6H ₂ O	18.0	-6	13
	15.0	-3	13
	12.0	-3	13
	9.0	2	13
	6.0	4	13
Ca(SCN) ₂ ·4H ₂ O	16.5	35	10
Ba(SCN) ₂ ·3H ₂ O	16.5	55	10
MgCl ₂	24.0	20	20
	12.0	20	20
	8.0	10/120	20
	4.0	70	20

6. Conclusions and future needs

The actual mechanism of ion transport in polymer electrolytes continues to be a matter of controversy, although several models have been proposed [1, 20, 24, 28 - 32], particularly for PEO-alkali salt complex polymer electrolytes.

As far as monovalent polymer electrolytes are concerned ionic conduction in both the crystalline and amorphous regions of the divalent polymer requires the mobility of the polymer chain [24]. This is true even for highly crystalline polymer-salt complexes, where configurational

motions of the backbone chain or side chains are indispensable for ionic pathways to be opened up.

Papke *et al.* [24] suggested that strong cation–oxygen interaction energies provide the driving force for conformational changes of the polymer. Moreover, they pointed out that the ionic transport depends on (i) the multiple association of carrier ions to polymer segments, (ii) the segmental motion with associated ions, and (iii) the dissociation of such ions. In the polyethers, changes in the polymer conformation and translation of chains are very important for rapid ion transport.

The conductivity of divalent polymer electrolytes depends on several factors, namely: nature of the anion, nature of the cation, stoichiometry and thermal history of the complex, preparation conditions (for example, the kind of solvent, dry or wet conditions, solvent cast or hot pressed, etc.) and temperature. These factors are so significant that, for example, an optimised choice of anion and stoichiometry for a given divalent cation species can lead to an improvement in conductivity by two orders of magnitude [13]. For all the factors, except temperature, there is no easy rule to predict their effect on the conductivity, but some general findings are being observed from analysis of works reported in the open literature.

Accordingly, it can be said that the conductivity of any PEO–salt complex always increases when the temperature increases, because the percentage of the elastomeric phase also increases, and this is the principal phase responsible for the ionic conductivity in these materials.

At T_g the large amplitude segmental polymer motions are frozen out and the conductivity is very low, dropping essentially to zero as the temperature drops towards T_g . At temperatures well above T_g the ion motion usually occurs more slowly inside the crystalline regions than inside the amorphous regions [26].

For the highly crystalline PEO–salt complexes, an Arrhenius behaviour is usually observed, while for the amorphous regions, a Vogel–Tamman–Fulcher (VTF), or Williams–Landel–Ferry (WLF), behaviour is commonly verified. There are also some particular systems that do not follow either the VTF or the WLF mechanism [25].

It can be concluded from the above considerations that several aspects need to be actively studied in the near future including those mentioned below.

In the area of transport number determination, it is necessary to obtain more data for divalent salt polymers, as well as a better correlation between values reported in the literature which have been obtained by different techniques and different researchers. At the time of writing, cationic transport numbers for a certain system range from 0.03 to 0.95, and the explanation for these discrepancies is unclear.

For some systems, the anionic transference numbers are higher than those for cations. It is well known that the anionic transference number is intimately connected with the anion mobility, which depends on factors such as the hydrogen bonding ability, the ion size and the ion polarity,

among others. Studies on these aspects are very scarce and require further research.

New polymer electrolytes, possessing high- and single-ionic conductivity, need to be synthesized. In this context, attention should be paid to the enhancement of the conductivity by mixed salts relative to the single-salt systems, which may be considered to be a result of the topological disorder induced into the system by the mixing of salts different in size and type.

The establishment of less empirical models for ion conduction in divalent polymers, and of the effect of several parameters on their behaviour, is an urgent requirement. In fact, apart from the academic interest, the development of many polymer systems of practical importance, and their commercialisation, is largely dependent on the understanding of the ion transport mechanism in the polymer.

In addition to the preparation of new polymers, substituted polymers and copolymers should be prepared and characterised, since some of them have already shown promising results [33]. Moreover, the structure of present-day polymers should be modified by means of crosslinking agents, plasticisers, and/or fillers, in order to achieve soft materials with high ionic conductivity, and good mechanical, chemical and electrochemical stability. These materials will have great application in solid state batteries, solar cells, electrochromic displays, microelectronic ion sensors and other advanced devices.

It should also be noted that perhaps one of the most important fields requiring future research is concerned with the quality of the experimental techniques (in terms of precision and significance of the results) used to characterise the polymer electrolytes, such as DSC, VTPM, a.c. impedance analysis, complex plane analysis, d.c. polarization, infrared, Raman, NMR, radio-tracer techniques, EXAFS, TGA, TMA, EA, SEM, EDX, vibrational spectroscopy, dielectric relaxation and cross-polarization magic angle spinning NMR [34]. This view is corroborated by recent conferences on the topic of conducting polymers [35 - 37].

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