Ion pair formation and its effect in PEO:Mg solid polymer electrolyte system

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Abstract

In poly(ethylene oxide) (PEO) based solid polymer electrolytes, the interaction between cations and the ether oxygen plays a major role in ion conductivity. Measurements with differential scanning calorimetry (DSC) illustrated clearly the modification of the PEO crystalline structure with increasing content of magnesium salt. FTIR spectral studies suggest interaction of Mg^{2+} cations with the ether oxygen of PEO, where a 1100 cm^{-1} broad band corresponds to COC stretching and severe deformation occurs. A spectral band at $\sim$623 cm^{-1} corresponds to the ClO_4^- anion and shows the growth of a shoulder at a higher wave number with increasing salt content. The apparent new envelope at $\sim$634.5 cm^{-1} clearly indicates ClO_4^-–Mg^{2+} ion pairing. Ionic conductivity increases with salt content, and is optimized at 15 wt.% Mg salt (O:Mg ratio 28:1). The decrease in ion conductivity at higher salt contents is due to ion–ion association, which leads to ion pair formation (i.e. aggregation of ionic salt) and retards the motion of ions. © 2002 Published by Elsevier Science B.V.

Keywords: Polymer electrolytes; FTIR studies; Differential scanning calorimetry; Ionic conductivity; Magnesium

1. Introduction

Investigation of the structural and transport properties of solid polymer complexes has attracted a high degree of attention. The main applications of solid polymer complexes as electrolytes are found in various electrochemical devices, such as energy conversion units (batteries/fuel cells), electrochemical display devices/smart windows and photo-electrochemical cell [1–5]. Structural modification of the polymer plays an effective role in enhancing its utility in the above-mentioned devices. Most of the studies reported to date have been conducted on mono-valent charged cationic salts in poly(ethylene oxide) (PEO) based polymers [6–21].

PEO is the most widely studied polymer system due to its exceptional solvating nature for a variety of ionic salts to form an electrolyte [22,23]. In PEO polymer, cations are coordinated with the oxygen atoms of the polyether chain. Changing the chemical composition can vary the physical properties. Particular materials can be designed for specific applications, as well as for fundamental studies of the ion-transport mechanism. Detailed understanding of the transport mechanism is greatly complicated by the presence of

significant ion–ion interactions at high salt content. The polymer electrolyte behaves as solvents for ions that deliver a liquid-like degree of freedom [24,25]. The ion-transport mechanism is assumed to be cation mobility (i.e. movement), in which polymer chain motion plays a significant role. Segmental motions of the chain is also one of the prime factors and depends on migration of unsolvated anions. Moreover, the concentration of charge carriers are important, which is a function of salt concentration in the polymer.

Earlier reports [26–30] suggested the formation of an ion-conducting solid polymer electrolyte with divalent ionic salts in PEO. It is expected that higher charged species with stronger coulomb interaction bears stronger structural and bonding implications in the formation of a solid polymer electrolyte which appears to be an attractive candidate for solid-state batteries in that the materials have lower cost and the metals are less reactive than lithium [27,28]. Our earlier report [30] shows that a Mg^{2+} divalent ionic salt effectively disrupts the PEO crystalline structure. An increase in the amorphous fraction leads to an increase in free-volume and to voids that enhance the ionic mobility (thus, ionic conductivity). The increase in conductivity is, however, restricted to a certain content of ionic salt. In the present investigation, we report critical evidence of ion-polymer and ion–ion interaction from FTIR spectroscopic, differential

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scanning calorimetry (DSC), and demonstrate their direct impact on ionic conductivity.

2. Experimental

Mg^{2+} ion-conducting polymer electrolyte films have been prepared by using PEO (M_W: 2×10^5, Aldrich) with magnesium perchlorate ($Mg(ClO_4)_2$) (Aldrich) salt at different weight ratios. The preparation scheme was carried out at 50 °C, as reported previously [30]. Initially, the polymer PEO was dissolved in methanol then $Mg(ClO_4)_2$ salt was added after 2 h the mixture was stirred for 12 h to form a homogeneous slurry, and sonication was applied for 30 min. Finally, the mixture was cast on Teflon dishes, evaporated slowly at 40 °C and dried under vacuum. Further drying is achieved in a dry box with a nitrogen environment to remove all traces of solvent.

Solvation of the ionic salt with the PEO was investigated by means of an infrared (IR) spectroscopy technique. The IR spectra of all these films with KBr pellets were recorded with a Bio-Rad FTIR spectrometer (FTS-155). DSC studies were performed in the temperature range from 30 to 100 °C (Perkin-Elmer, DSC 7 series) at a heating rate of 5 °C min^{-1}. The sample weights were maintained in the range of 6–8 mg and all experiments were carried out under nitrogen flow.

Ionic conductivity of the solid polymer electrolyte films was investigated with a conductivity cell which consisted of two blocking, stainless-steel electrodes. Measurements were carried out over the frequency range 1 MHz to 10 Hz, with the help of a frequency analyzer AUTOLAB/PGSTAT 30 (potential/galvanostat) electrochemical instrument. The bulk resistance (R_b) was determined by equivalent circuit analysis by using a frequency response analyzer (FRA software) of complex impedance plots. The conductivity values (σ) were
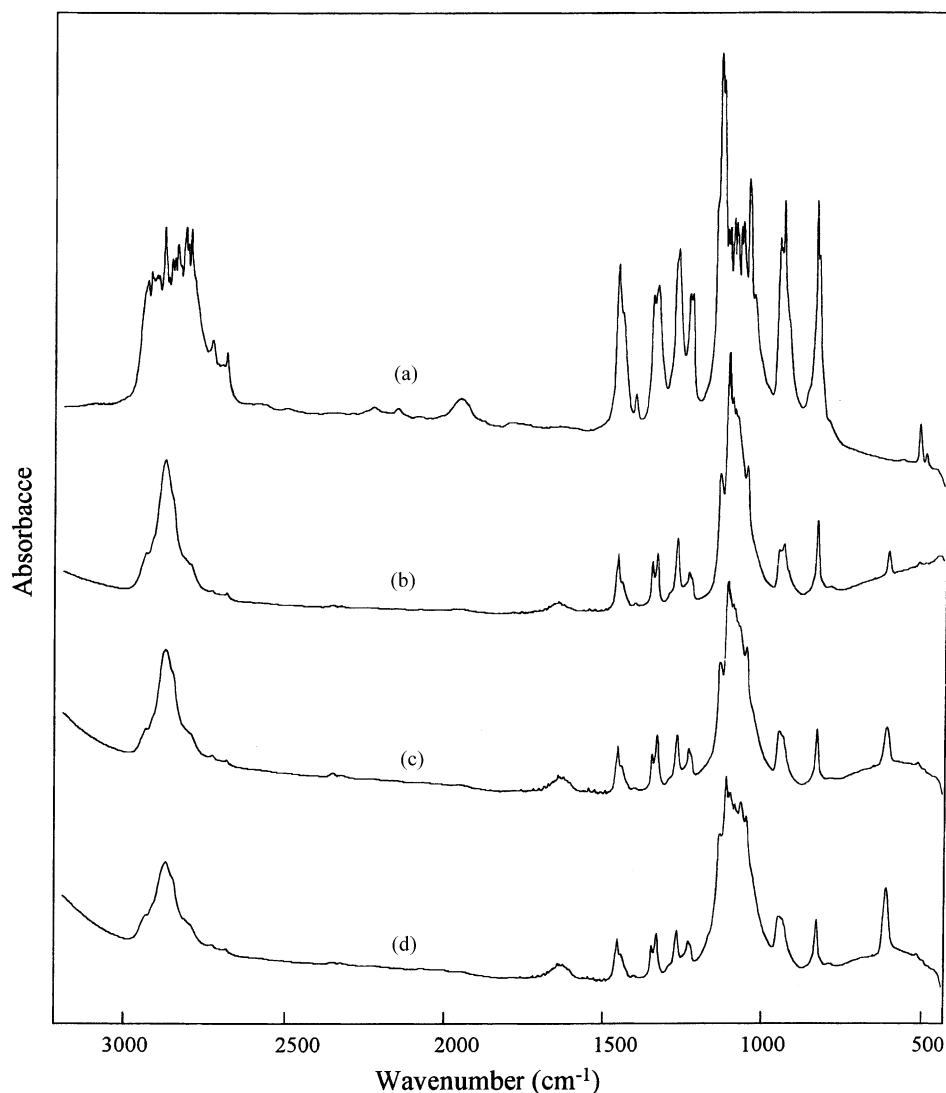

Fig. 1. FTIR spectra of (a) pure PEO; (b) 10; (c) 15 and (d) 20 wt.% Mg salt content to PEO.

calculated from the equation, $\sigma = (1/R_b)(t/A)$, where t is the thickness and A the area of the sample.

3. Results and discussion

3.1. IR spectroscopic studies

Polymer complexes with ionic salts have been characterized by IR spectroscopy [13,16,18,31–34]. This technique provides a powerful means to characterize the organic and inorganic components and their composite formation. The IR spectra of pure PEO and its blending with $Mg(ClO_4)_2$ are given in Fig. 1. Marked changes are found when PEO is blended with Mg ionic salt. The regions of particular interest in the current study are the features observed at the C–H, C–O and ClO_4^- bands, where the changes in intensity, shape and position of these bands are associated with polyether–$Mg(ClO_4)_2$ interaction. The aliphatic C–H stretching vibrational band (ca. 2900 cm^{-1}) found in PEO decreases in width and intensity with increasing Mg salt concentration. This behavior is similar to that reported for mono-valent ionic salts, such as lithium, and sodium. Though direct evidence is not yet available, it is believed acid–base coordination between Mg^{2+} cations and the oxygen of the ether of PEO comprises the major interaction.

The interaction is expected to influence directly the COC stretching and deformation ranges. In Fig. 2, IR spectra in the range 1000–1200 cm^{-1} are summarized for pure PEO and PEO blended with Mg^{2+} ionic salt. It is apparent that COC stretching and the deformation broad band width and intensity around 1100 cm^{-1} is decreased with increasing salt content in PEO, and suggests coordination/complexation of the salt with the polymer. The interaction of pure PEO with alkali metal and divalent ionic salts has been studied extensively [13,16,18,32,34,35]. Here, the vibrational spectroscopic results show that alkali earth metal also undergo a similar association with PEO.

IR spectra of PEO blended with Mg^{2+} ionic salt in the range 600–650 cm^{-1} are presented in Fig. 3. This band has been assigned to the stretching of ClO_4^- ions. At a salt content of 10 wt.% and above (Fig. 3b), additional high frequency bands develop with increasing salt content. For simplicity, the asymmetric IR line shapes can be deconvoluted into two components. These peaks are assigned to two major ClO_4^- species associated with different conformations: one is free ClO_4^- ions with maxima at ∼623 cm^{-1} (denoted as band 'i'), the other is due to a different degree of association of ClO_4^- ions with the cation Mg^{2+} at ∼634.5 cm^{-1} (denoted as band 'ii'). The agreements of the fit are superimposed with the spectrum for 20 wt.% $Mg(ClO_4)_2$, see Fig. 3d. The intensity of the band 'ii' increases with markedly increasing salt content in PEO. This analysis suggests that ClO_4^- ions favor re-association with Mg cations above 10 wt.% salt content in PEO. It is important to note that the re-association of ions or the
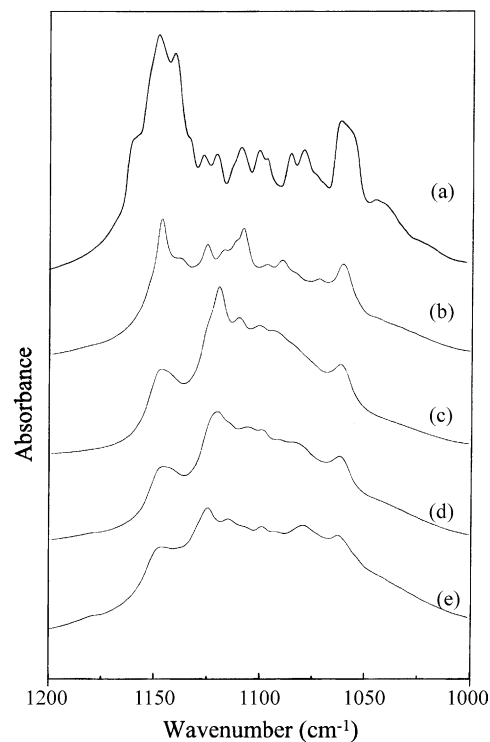

Fig. 2. IR spectra of (a) pure PEO; (b) 8; (c) 10; (d) 15 and (e) 20 wt.% Mg salt content to PEO.

formation of ion pairs will affect other property characteristics. Variation in the two populations of ClO_4^- ion species shows an interesting trend. The relative population of ion pairs of ClO_4^- anions with Mg cations is calculated as the ratio of the area under the ∼634.5 cm^{-1} modes to the total area under the ClO_4^- envelope, and is depicted in the inset of Fig. 7. Wieczorek et al. [36] and Salomon et al. [37] have also attributed the 623 cm^{-1} band to free anions ClO_4^- and
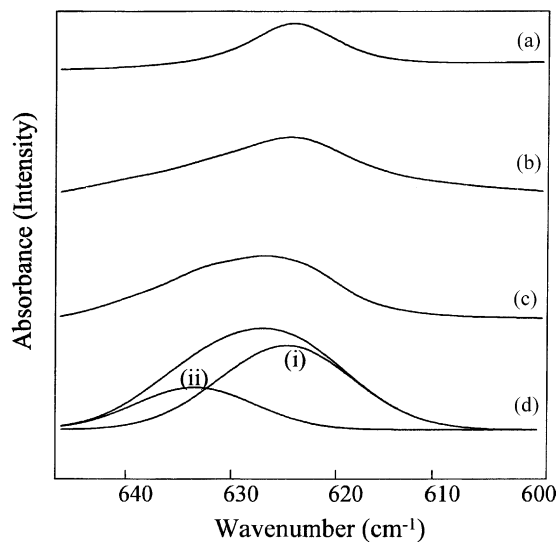

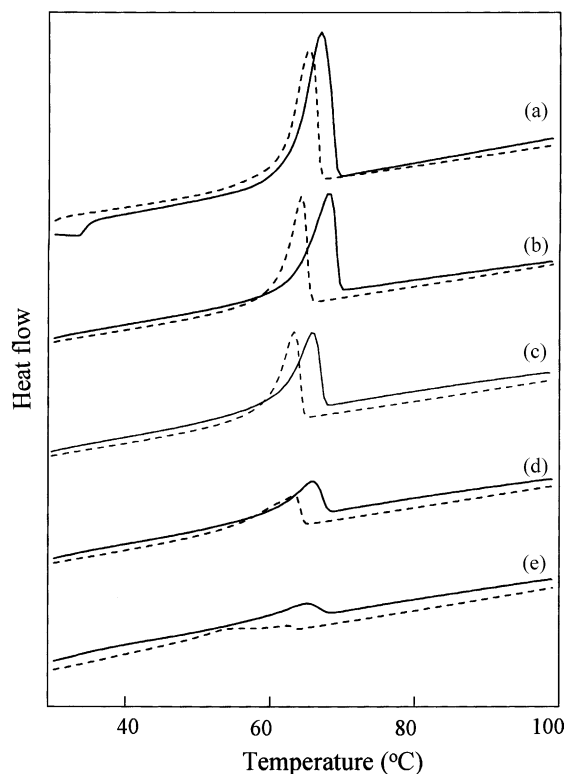Fig. 3. IR spectra of (a) 8; (b) 10; (c) 15 and (d) 20 wt.% Mg salt content to PEO.

Fig. 4. DSC thermograms of first (—); second (- - -) heating scan of (a) pure PEO; (b) 5; (c) 10; (d) 15 and (e) 20 wt.% Mg salt content to PEO.

and the melting temperature (T_m) decrease with increase in salt content to the PEO. In addition, the melting endotherm becomes broader. Both the reduced melting temperature and the broadening of the melting endotherm are consistent with the notion of PEO interaction with Mg^{2+}, which leads to smaller PEO crystallites. The relative crystalline (χ) percentage has been calculated from the second heating scan, taking that of pure PEO as 100%, by means of the equation $\chi = \Delta H_f / \Delta H_f^0$, where ΔH_f^0 is the heat of fusion of pure PEO and ΔH_f is related to complexed PEO. The crystallinity (χ), and melting temperatures (T_m) are listed in Table 1 and also depicted in Fig. 5. It is interesting to note that χ is suppressed more effectively due to disruption of the PEO crystallinity. At a high salt content (i.e. ~25 wt.%) the system is completely amorphous as no heat of fusion (i.e. $\Delta H_f = 0$) is observed.

It is interesting to note that the second heating traces resemble the initial scan, but the melting temperatures have all been shifted slightly to lower temperatures with lower heats of fusion compared with the first one. This behavior is also shown by PEO complexed with lithium salts, implies that more Mg ions are released upon heating to form an acid–base complex with PEO which results in further disruption of the PEO crystallinity. Prolonged heating at even higher temperatures (above 120 °C) leads however to the formation of stable crystalline complex phases between PEO and Mg ions, similar to that in the lithium salt as reported previously [30].

3.3. Ionic conductivity

The variation in conductivity (σ) as a function of the salt concentration of Mg added to PEO is displayed in Fig. 6 at ambient temperature. The conductivity data are presented in Table 1. The results indicate that the room temperature conductivity of pure PEO is about 10^{-10} S cm^{-1} [38] and increases sharply to 10^{-8} S cm^{-1} with 2 wt.% Mg salt added to PEO. The charge transport in PEO solid polymer complexes involves dissociation of the cation from its coordinating oxygen to an adjacent site. The high ionic conductivity in an electrolyte is attributed to increased ionic mobility and

the 635 cm^{-1} envelope to ion pair formation or contact of ClO_4^- anions with lithium.

3.2. DSC studies

DSC has been employed to determine the thermal behavior of the PEO:Mg polymer complexed system. The DSC curves of pure PEO and PEO:Mg films are shown in Fig. 4, where the two traces represent the first and second heating scans, respectively. The second heating is performed immediately after the samples have been cooled to room temperature following the first heating. The heat of fusion (ΔH_f)

Table 1
Melting temperature (T_m), crystalline percentage, χ (%) and ionic conductivity of PEO:Mg(ClO$_4$)$_2$ SPE system

Mg(ClO$_4$)$_2$ (wt.%)	O:Mg ratio	T_m (°C)		χ (%)	Conductivity (S cm^{-1})
		First scan	Second scan		
0	–	68.3	66.3	100	2.96×10^{-10}
2	248	67.9	65.1	82.9	4.36×10^{-8}
5	96	67.1	64.4	74.1	6.17×10^{-8}
8	58	66.7	64.0	66.2	2.91×10^{-7}
10	46	66.4	63.9	61.6	3.30×10^{-7}
15	28	66.3	62.5	32.2	1.42×10^{-6}
20	20	65.4	53.9	8.6	1.14×10^{-7}

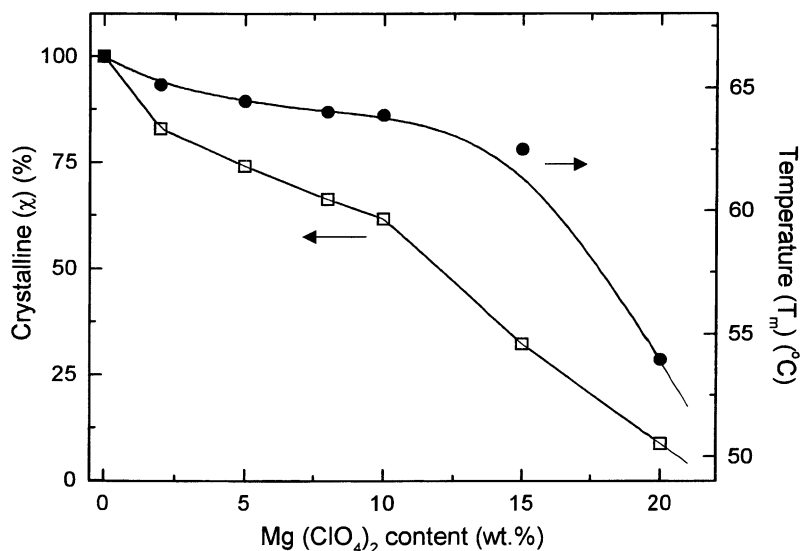Note: crystalline (χ) are calculated from second scan of heating.

Fig. 5. Melting temperature and crystalline percentage (from second scan of heating) of PEO:Mg(ClO$_4$)$_2$ system.

increased ionic charge carrier concentration. The motion of ions in solid polymer electrolytes is a liquid-like mechanism, by which the movement of ions through the polymer matrix is assisted by the large amplitude of the polymer segmental motion [24,25]. The enhancement of ionic conductivity of PEO complexed with Mg ionic salt content is presented in Fig. 7. The conductivity increases with increasing salt concentration and maximum value at 15 wt.%. The
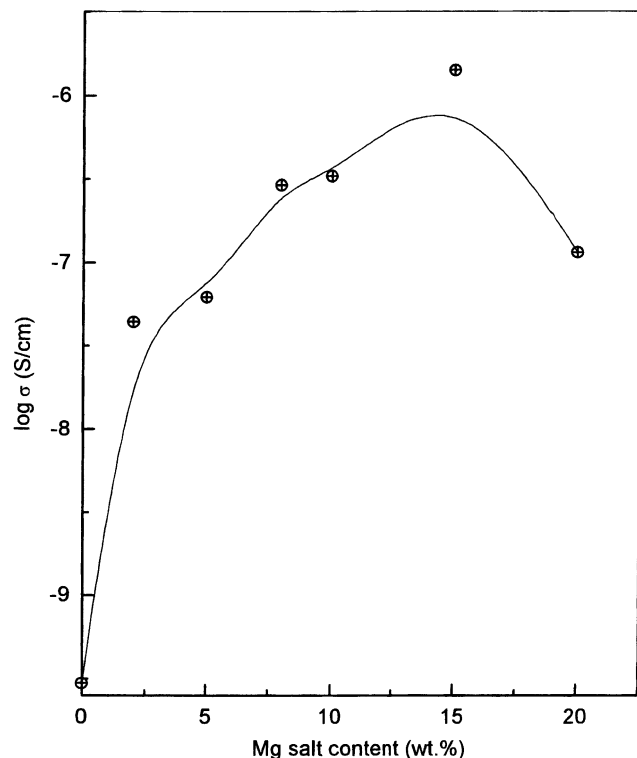
fraction of paired ions calculated from IR studies is also displayed in the insect in Fig. 7, for comparison. Clearly, the decrease in conductivity at high salt concentration is due to a decrease in free ions due to the formation of ion–ion pairing. A similar trend was reported by various researchers in studies on lithium salt in PEO-based polymer electrolyte systems using the concept of ion association and the formation of charge multiplets [39–41]. The decrease in conductivity at higher magnesium salt contents agree with the earlier concept. Doeff et al. [42] have explained this type of behavior in terms of a trade-off between an increasing number of charge carriers and ion aggregation and increased viscosity due to ionic cross-linking, which lowers the conductivity as the salt concentration passes a critical value. Dupon et al. [43] have interpreted the dependence ionic conductivity on salt composition as strong ion pairing may effectively trap the mobile cations, which significantly reduces the ionic conductivity relative to non-ion-paired complexes of the similar structure.

The deterioration of conductivity in the present study occurs at a much higher PEO:Mg ratio (O:Mg = 28:1). In the case of lithium salts conductivity deteriorates at a O:Li ratio of about O:Li = 8:1, for various anions. The doubly charged Mg cation introduces at least two important different factors in comparison with that of lithium. First, it exhibits a stronger lattice energy in the salt and, second, it gives a stronger acid–base interaction (and solvation energy) with the polymer substrate, PEO. Therefore, the tendency to form an ion pair is stronger, but at the same time the interaction with the ether oxygen is also stronger; compared with lithium. Competition of both factors leads to a decrease in the free Mg^{2+} ion fraction in the PEO at higher salt uptake, where the conductivity deteriorates. The results also suggest that both Mg–PEO association, and ion-pairing complexes disrupt PEO crystallinity.
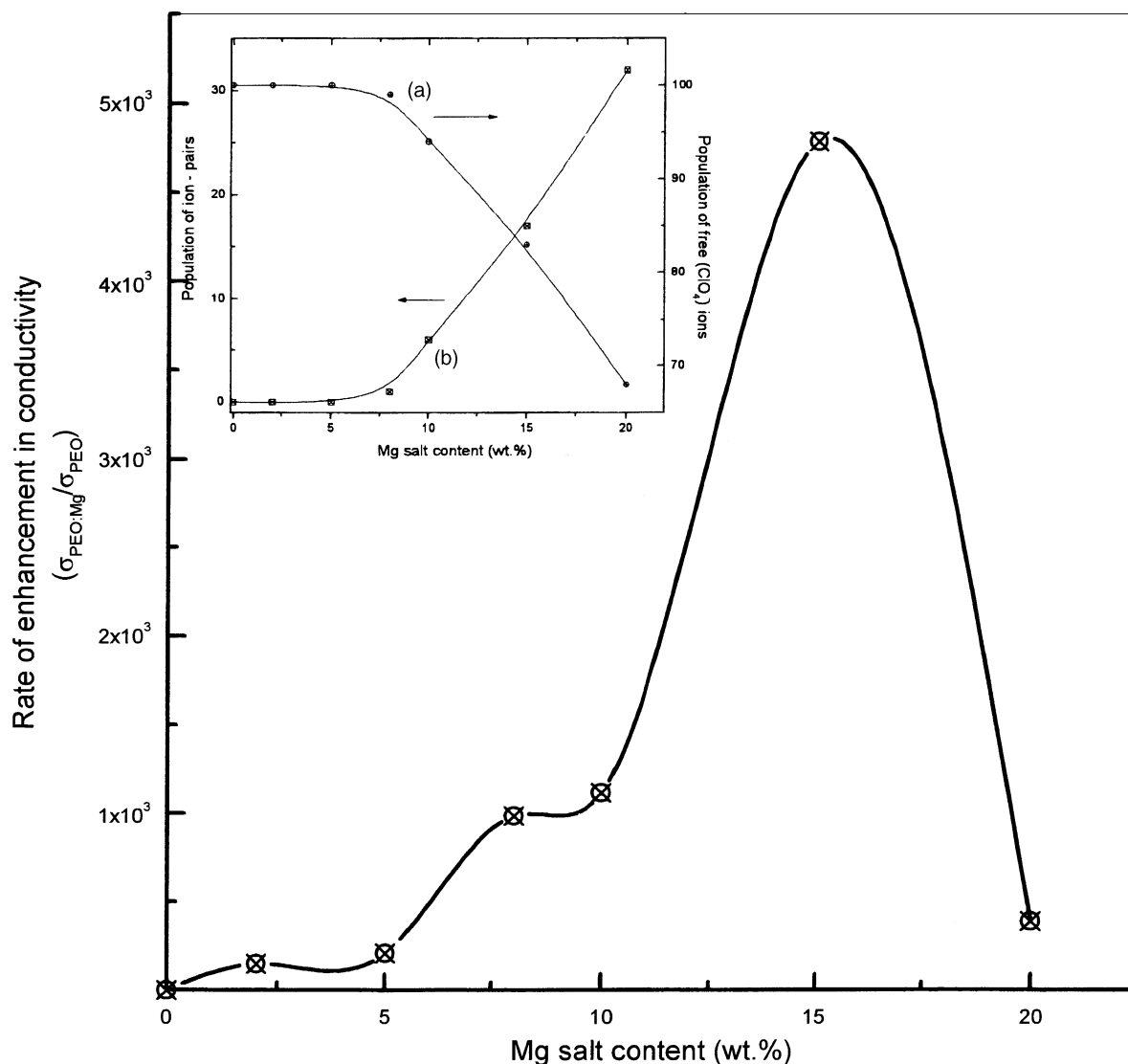

Fig. 6. Compositional conductivity of PEO:Mg(ClO$_4$)$_2$ system.

Fig. 7. Enhancement in ionic conductivity of PBO:Mg solid polymer electrolyte system. Inset: (a) ClO_4^- free ions and (b) $Mg–ClO_4^-$ ion pair population with salt content.

4. Conclusions

Divalent ion Mg^{2+} in PEO demonstrates acid–base interaction between the cation and the ether oxygen of PEO, and shows a compositional dependency of ion conductivity. The DSC measurements indicate directly the modification of PEO crystalline structure with increasing salt content. The IR spectra provide direct evidence of the interaction of cation Mg^{2+} with the other oxygen of PEO, where a broad band corresponds to COC stretching and there is a severe effect on the deformation range. On the other hand, a band which corresponds to ClO_4^- anion grows with increasing salt content and a new envelope develops at a higher wave number. The apparent new envelope at 634.5 cm^{-1} corresponds to association of ClO_4^- anions with the cation Mg^{2+} and this suggests ion–ion interaction. The optimum value of ionic conductivity is found at 15 wt.% salt. The subsequent decrease in ion conductivity is due to consumption of free Mg ions through the ion pair association of Mg cations and ClO_4 anions, which retards the ion mobility.

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