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ORIGINAL PAPER

Conductivity modification of proton conducting polymer gel electrolytes containing a weak acid (*ortho*-hydroxy benzoic acid) with the addition of PMMA and fumed silica

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Abstract Polymer gel electrolytes synthesized by dispersing nano size fumed silica in polymer gel electrolytes containing polymethylmethacrylate (PMMA), ortho-hydroxy benzoic acid (*o*-OHBA) and dimethylacetamide (DMA) have been studied by complex impedance spectroscopy, viscosity and pH measurements. The addition of acid, polymer and fumed silica has been found to result in an increase in conductivity and viscosity of gel electrolytes and gels with conductivity higher than the corresponding liquid electrolytes have been obtained. Nano dispersed polymer gel electrolytes show conductivity 2.95×10^{-4} S cm^{-1} and viscosity 1.74×10^{4} cP at 25 °C. Two maxima observed in the variation of conductivity of nano dispersed gels with fumed silica concentration have been assigned to the enhanced dissociation of weak acid and the formation of a high conducting interfacial region between fumed silica and gel electrolyte, respectively, which has also been supported by pH and viscosity studies. The small increase in conductivity of nano dispersed gels over the 20–100 °C temperature range and its constant value with time is suitable for devices.

Keywords Conductivity · Impedance spectroscopy · Viscosity · Polymethylmethacrylate

1 Introduction

Polymer gel electrolytes having some unique properties like high conductivity, wide range of composition and hence wider control of properties, ease of preparation, good electrode–electrolyte contacts etc. are technologically important materials [1–3]. Initially lithium ion conducting polymer gel electrolytes were studied due to their potential use in high energy lithium batteries [4–6]. Proton conducting polymer gel electrolytes are also gaining importance due to their potential use in various devices [7]. Non-aqueous proton conducting polymer gel electrolytes with high conductivity are suitable for applications at temperatures above 100 °C [8]. However, despite high conductivity, the poor mechanical properties of polymer gel electrolytes may restrict their use in devices. The addition of micron and nano size inert insulating materials to polyethylene oxide based polymer electrolytes is known to improve the mechanical properties of polymer films, in addition to modifying their conductivity [9–11]. Similar approach can be employed in the case of polymer gel electrolytes to improve their conductivity and mechanical properties. Thus, the dispersion of nano size insulating materials in polymer gel electrolytes and its effect on conductivity and viscosity will be an interesting study.

In the present work, fumed silica with average particle size 7 nm has been dispersed in polymer gel electrolytes containing PMMA, *ortho*-hydroxy benzoic acid (a weak aromatic carboxylic acid with dissociation constant 1.40×10^{-3}) and dimethylacetamide (DMA). The effect of addition of PMMA and fumed silica on the conductivity and viscosity behavior of gel electrolytes has been studied.

2 Experimental procedure

PMMA (Aldrich) with average molecular weight 15,000, 120,000 and 996,000; DMA (Merck) ($\varepsilon = 37.8$, $\eta = 1.937$ cP, M. P. $= -20$ °C, B.·P. $= 165$ °C), benzoic

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acid (C_6H_5COOH) (Lancaster), *ortho*-hydroxy benzoic acid (C_6H_4OH COOH) (Lancaster) and fumed silica (Aldrich) with surface area 380 m^2 g^{-1} and average grain size 7 nm were used as the starting materials. Polymer gel electrolytes were obtained by adding PMMA in different amounts (expressed as wt% of liquid electrolyte) to liquid electrolytes containing benzoic acid and *ortho*-hydroxy benzoic acid in DMA along with continuous stirring by magnetic stirrer. Nano dispersed gels were then prepared by dispersing fumed silica in different concentrations (expressed as wt% of polymer gel electrolytes) to the polymer gel electrolytes along with continuous stirring to ensure homogenization.

The electrical conductivity was measured by using WTW LF330 conductivity meter calibrated regularly with standard KCl solution and of gel electrolytes by complex impedance spectroscopy using a precision LCR meter (HP4284A) in the 20 Hz–1 MHz frequency range, with a cell having platinum electrodes. The viscosity was measured by rotating viscometer (Fungilab Visco Basic L) and temperature was maintained within ±0.1 °C with water circulator (Julabo F12-EC). pH of all the electrolytes was measured by Systronics 335 pH meter.

3 Results and discussion

The variation of conductivity for electrolytes containing *ortho*-hydroxy benzoic acid (*o*-OHBA) in DMA with acid concentration is given in Fig. 1. The acid upon dissociation provides free H^+ ions for conduction and as a result conductivity increases and reaches a value of 1.55×10^{-4} S cm^{-1} for electrolytes containing 1 M *o*-OHBA. Although the solvent (DMA) used has high dielectric constant ($\varepsilon = 37.8$ at 25 °C), yet some undissociated acid may be present in these electrolytes, as *o*-OHBA is a weak acid with dissociation constant (1.40×10^{-3}) less than one in an aqueous solution. Due to lower dielectric constant of DMA as compared with water ($\varepsilon \sim 80$), the amount of undissociated acid will be relatively more in electrolytes containing DMA.

The change in free H^+ ion concentration with the addition of *o*-OHBA was studied by pH measurements and the variation of pH with acid concentration is also included in Fig. 1. With an increase in acid concentration, pH decreases which is due to an increase in free H^+ ion concentration and it is also accompanied by an increase in conductivity. It is important to mention here that the aqueous pH values reported here for non-aqueous electrolytes do not give exact pH value but the change in pH gives information about the change in H^+ ion concentration. The results of pH measurements give qualitative support to the conductivity results. The addition of acid to DMA also results in a small increase in viscosity.

Although liquid electrolytes possess conductivity of the order of 10^{-4} S cm^{-1} at 25 °C yet they cannot be used in some devices due to their liquid nature. The immobilization of liquid electrolytes with the addition of a suitable polymer, resulting in gel electrolytes, can partly overcome this drawback of liquid electrolytes. The variation of conductivity of polymer gel electrolytes containing 0.5 M *o*-OHBA with the concentration of PMMA (av. mol. wt. 15,000), is given in Fig. 2. The conductivity shows an increase with the addition of PMMA, reaches a maximum value of 1.46×10^{-4} S cm^{-1} at 3 wt% PMMA, and then

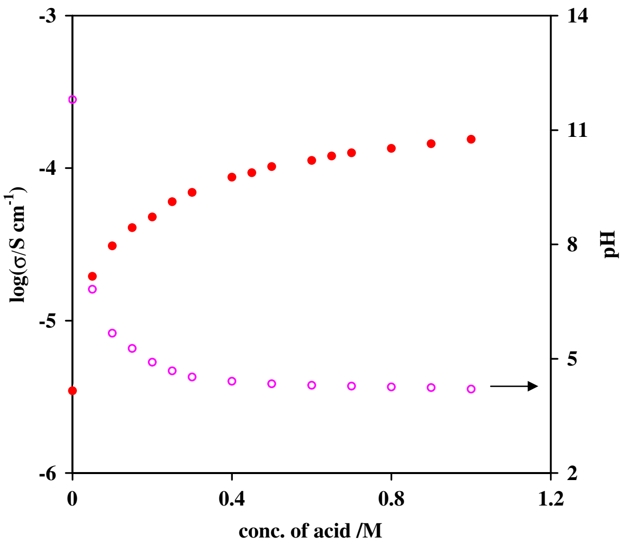


Fig. 1 Variation of log conductivity (●) and pH (○) with acid concentration for electrolytes containing *o*-hydroxy benzoic acid in DMA

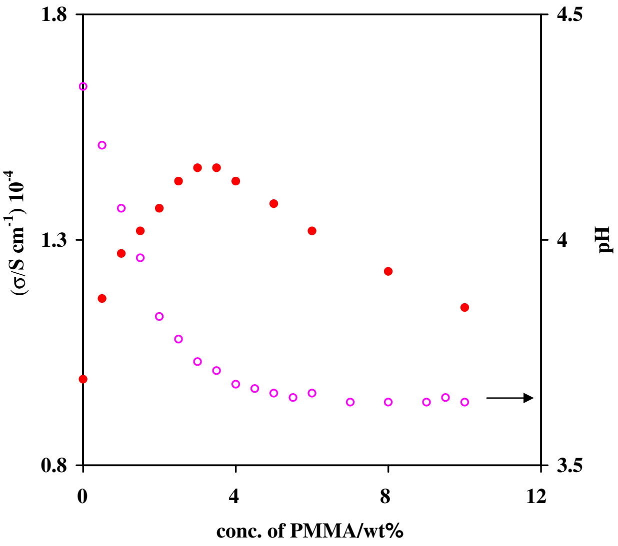


Fig. 2 Variation of conductivity (●) and pH (○) with PMMA concentration for polymer gel electrolytes containing 0.5 M *o*-hydroxy benzoic acid in DMA

decreases at higher PMMA concentrations. The conductivity of gel electrolytes has been found to be higher than the corresponding liquid electrolytes at all PMMA concentrations studied, i.e., up to 10 wt%. Similar behavior has also been observed for electrolytes containing 1 M *o*-OHBA. The addition of polymer generally enhances viscosity (η) of the electrolytes [12–14] which leads to lower ionic mobility, as mobility (μ) and viscosity are inversely related ($\mu = q/6\pi\eta r$), and secondly the addition of polymer also results in a net decrease in acid concentration, as no additional acid has been added along with PMMA. Both these factors—lower mobility and lower acid concentration should result in lower conductivity ($\sigma = nq\mu$). Despite this, the conductivity of liquid electrolytes has been found to increase with the addition of PMMA. Although the increase in conductivity is quite small yet it is significant in the sense that PMMA has been added to increase the viscosity of electrolytes and along with an increase in conductivity has also been observed. Similar results have also been reported for some other electrolytes [15–18]. The increase in conductivity with the addition of polymer has been generally explained to be due to an increase in free ion concentration, although the exact mechanism is still not very clearly understood. In the case of polymer gel electrolytes containing weak acids [16, 17, 19], a breathing polymeric chain model has been proposed to explain an increase in free ion concentration with the addition of polymer. Recently similar results (σ (gel) > σ (liquid)) have also been observed for some lithium ion conducting polymer gel electrolytes containing solvent with low value of dielectric constant [20].

The maxima observed in the variation of conductivity with PMMA concentration in Fig. 2 suggests the simultaneous presence of two competing processes—which in the present case are free ion concentration at low PMMA concentration and viscosity at high PMMA concentration [21]. This was checked by pH and viscosity measurements and the variation of pH of gel electrolytes, containing 0.5 M *o*-OHBA with PMMA concentration is given in Fig. 2. The decrease in pH at low PMMA concentrations (0–4 wt%) corresponds to an increase in free H$^+$ ion concentration, which results in an increase in conductivity. The increase in free ion concentration is possibly due to the dissociation of undissociated acid with the addition of PMMA [19]. The addition of PMMA also enhances the viscosity of electrolytes and decrease in conductivity observed in Fig. 2 at higher PMMA concentrations (4–10 wt%) is due to the dominant role played by viscosity, which lowers mobility and hence conductivity decreases.

The viscosity of polymer electrolytes also depends upon the molecular weight of polymer used and the polymer with different molecular weights shall affect the viscosity and conductivity by different amounts. This was checked in the present case by using PMMA with average molecular weight 15,000, 1,20,000 and 9,96,000. The variation of conductivity and viscosity of polymer gel electrolytes, containing PMMA having different molecular weights, as a function of PMMA concentration is given in Fig. 3. The increase in conductivity with PMMA addition has been found to depend upon the molecular weight of PMMA and is less for gels containing PMMA with higher molecular weight (9,96,000). However, the conductivity of gel electrolytes is more than the corresponding liquid electrolytes at all concentrations of PMMA having different molecular weights. This suggests that same type of mechanism is responsible for conductivity modification in these electrolytes.

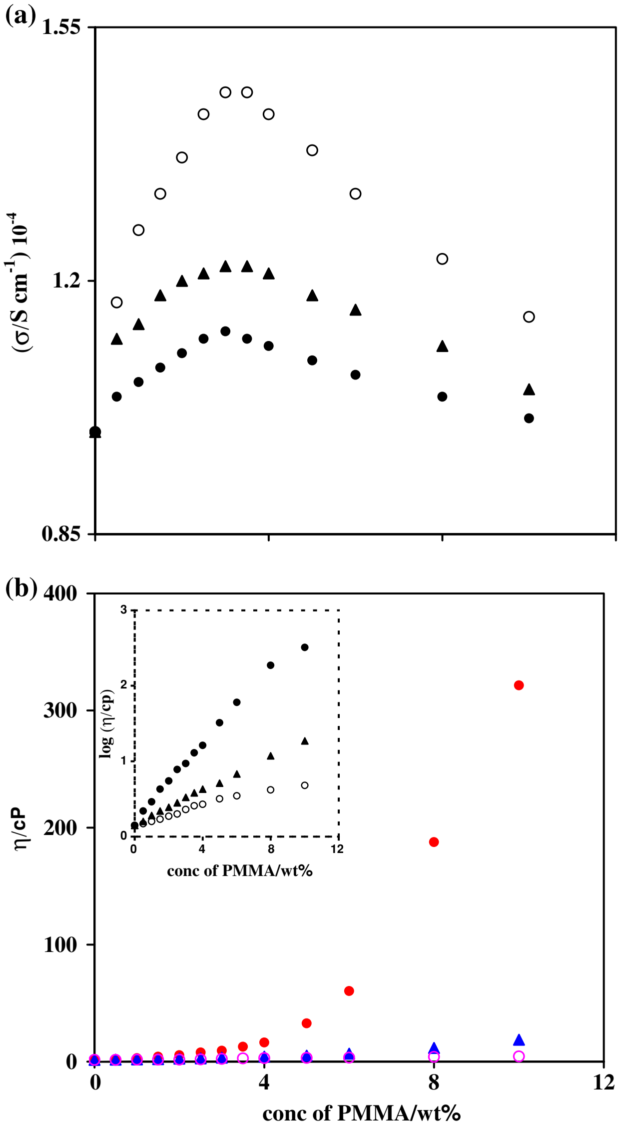


Fig. 3 Dependence of conductivity (**a**) and viscosity (**b**) upon PMMA (av. mol. wt. 15,000 (○), 120,000 (▲) and 996,000 (●)) concentration for polymer gel electrolytes containing 0.5 M *o*-hydroxy benzoic acid in DMA (Inset shows the variation of log viscosity with PMMA concentration)

The viscosity of polymer gel electrolytes depends upon the molecular weight of PMMA and is higher for gels containing high molecular weight PMMA. At low PMMA concentration, the viscosity is very low for each gel, whereas at high PMMA concentration, the viscosity is large and plays a dominant role and results in a decrease in conductivity as observed in Fig. 3. Polymer gel electrolytes containing PMMA with molecular weight 9,96,000 show highest viscosity but the increase in conductivity is lowest as compared with gels containing PMMA with average molecular weight 1,20,000 and 15,000. However, the difference in conductivity is small and all gels show conductivity of the same order ($\sim 10^{-4}$ S cm^{-1}) at 25 °C. Although these polymer gel electrolytes show high conductivity as well as high viscosity yet further improvement in their mechanical properties is required for their use as electrolyte in various devices.

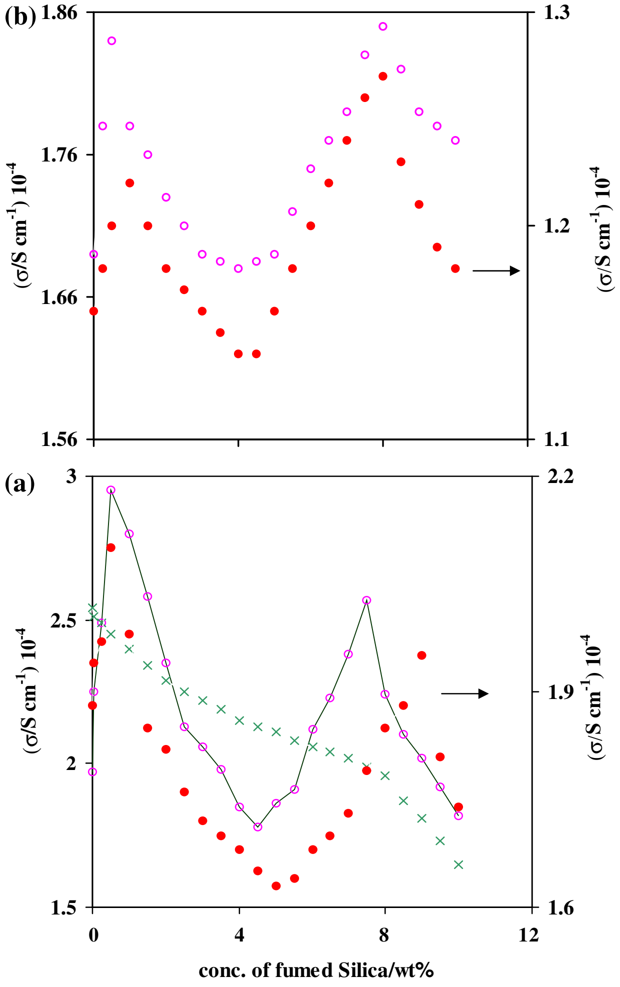
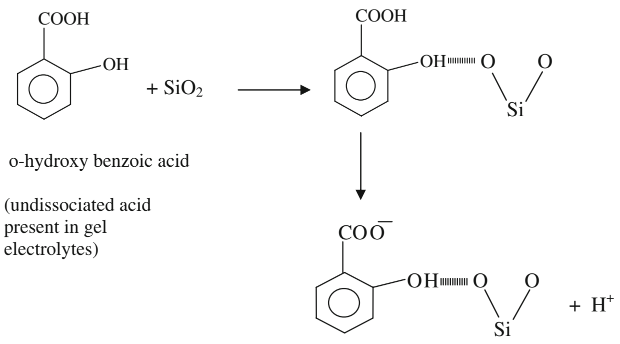


Fig. 4 **a** Conductivity variation with fumed silica concentration for nano dispersed polymer gel electrolytes containing 4 wt% PMMA in the solution of 0.5 M (●) and 1 M (○) *o*-hydroxy benzoic acid and 1 M benzoic acid (×) in DMA. **b** Conductivity variation with fumed silica concentration for nano dispersed polymer gel electrolytes containing 10 wt% PMMA in the solution of 0.5 M (●) and 1 M (○) *o*-hydroxy benzoic acid in DMA

The addition of an insulating material (Al_2O_3) to a poor ionic conductor (LiI) has been reported to result in an increase in conductivity [22], which was later found to depend upon the particle size and concentration of the insulating material (increase in conductivity was more for particles of smaller size) [10, 23]. Later on, the addition of insulating particles to polymer electrolytes was also found to result in an improvement in the mechanical properties along with an increase in conductivity [9–11, 24]. Similar results have also been reported for some lithium ion conducting polymer gel electrolytes [20, 25]. In view of these results, the effect of addition of fumed silica (with average particle size in the nanometer range) on the conductivity and viscosity of proton conducting polymer gel electrolytes has been studied.

The variation of conductivity (at 25 °C) with fumed silica concentration for nano dispersed polymer gel electrolytes containing 4 and 10 wt% PMMA (average molecular weight 15,000) in the 0.5 and 1 M solution of *o*-OHBA in DMA is given in Fig. 4a, b. These compositions were selected in order to study the effect of different free ion concentrations (by using electrolytes containing 0.5 and 1 M *o*-OHBA) and different viscosities (by using electrolytes containing 4 and 10 wt% PMMA) on the conductivity behavior of nano dispersed gels. Figure 4a, b shows the presence of two maxima—one at very low (<1 wt%) concentration and second at ~8 wt% fumed silica. Two maxima in the conductivity behavior have earlier been reported for composite polymer electrolytes based on polyethylene oxide [26–28] but such results are not common for polymer gel electrolytes. The presence of two maxima in Fig. 4a, b could be explained as follows:

The presence of first maxima at very low concentrations is possibly due to enhanced dissociation of weak acid with the addition of fumed silica. Due to the charged surface of fumed silica particles, the H of hydroxyl group (–OH) in *o*-hydroxy benzoic acid will be attracted towards the oxygen of fumed silica. This will lead to an increase in the inductive effect, which shall result in an increase in the dissociation constant of acid [29]. This leads to an enhanced dissociation of the acid as given below:



The dissociation of *o*-OHBA will increase the free H^+ ion concentration and as a result an increase in conductivity has been observed. However, one could miss these maxima if measurements are not taken at very low concentrations of fumed silica. This maxima has been observed in each of the four gel compositions containing different amounts of *o*-OHBA and PMMA.

If above explanation is correct, then the first conductivity maxima should not be present in electrolytes containing benzoic acid (C_6H_5COOH)—which does not contain any hydroxyl group (–OH). To check this, the variation of conductivity as a function of fumed silica concentration for nano dispersed gel electrolytes containing 10 wt% PMMA in the 1 M solution of benzoic acid in DMA was also studied and the results are given in Fig. 4a. In this case, the conductivity does not show any maxima at very low concentration of fumed silica and no change in pH has been observed. Thus, the addition of fumed silica does not enhance the dissociation of benzoic acid as observed in the case of electrolytes containing *o*-OHBA. This supports the explanation as proposed above.

The presence of second conductivity maxima at ~8 wt% fumed silica in Fig. 4a, b is due to the interlocking of fumed silica particles within the PMMA chains, which increases viscosity along with promoting composite nature of the electrolytes and as a result the formation of a high conducting interfacial layer between the particles of fumed silica and PMMA gel. As the grain size of fumed silica used in the present work is quite small (~7 nm), so conductivity maxima is observed at low concentration (8 wt%) of fumed silica, whereas in the case of composite electrolytes containing micron size Al_2O_3, the maxima is generally observed at relatively higher concentration (20–30 wt%) of insulating material due to the relatively small surface area of the particles.

The increase in free H^+ ion concentration, due to the enhanced dissociation of *o*-OHBA with the addition of fumed silica at low concentrations was also examined by pH measurements and the variation of pH with the concentration of fumed silica for electrolytes containing 4 and 10 wt% PMMA in 0.5 and 1 M *o*-OHBA solutions in DMA are given in Fig. 5a. The pH shows a decrease at low concentrations of fumed silica and reaches saturation value for electrolytes containing more than 4 wt% fumed silica, and similar behavior has been observed for all the gels. The decrease in pH indicates an increase in acidity due to an increase in free H^+ ion concentration, which is due to the enhanced dissociation of undissociated acid, as proposed above while explaining conductivity results. The saturation value of pH at higher fumed silica concentration suggests that the second maxima is not related to a change in free H^+ ion concentration as proposed above.

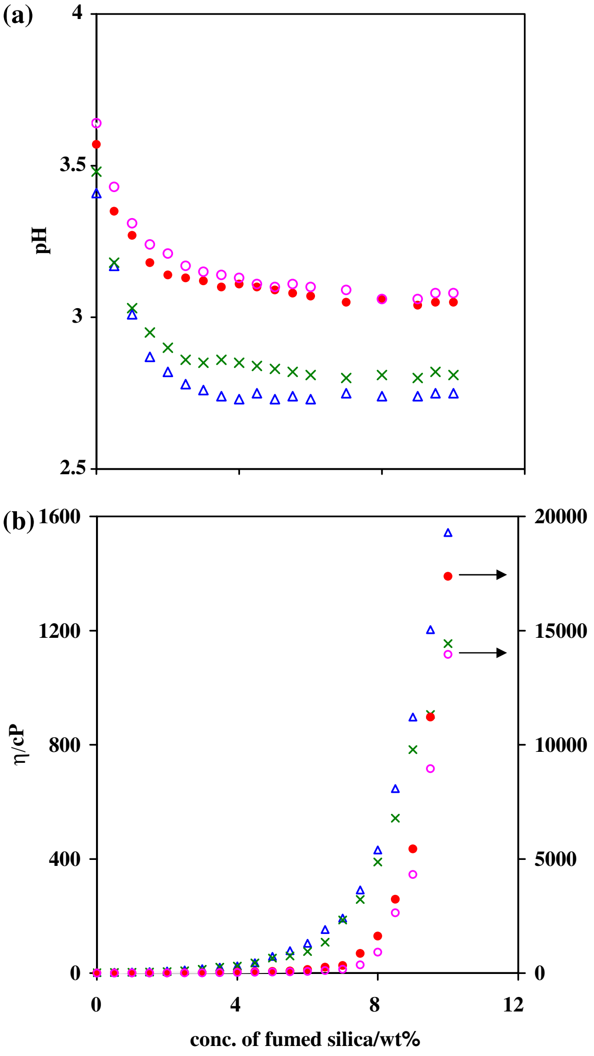


Fig. 5 Change of (**a**) pH and (**b**) viscosity with fumed silica concentration for nano dispersed polymer gel electrolytes containing 4 wt% PMMA in the 0.5 M (×) and 1 M (Δ) solution of *o*-OHBA in DMA and 10 wt% PMMA in the 0.5 M (○) and 1 M (●) solution of *o*-OHBA in DMA

The change in viscosity of nano dispersed polymer gel electrolytes as a function of fumed silica concentration is given in Fig. 5b, for electrolytes containing 4 and 10 wt% PMMA and 0.5 and 1 M *o*-OHBA. The viscosity of electrolytes containing 10 wt% PMMA is higher than those containing 4 wt% PMMA and electrolytes containing 1 M *o*-OHBA also show higher viscosity than those with 0.5 M *o*-OHBA at all fumed silica concentrations. The viscosity of all nano dispersed gel electrolytes is quite large at higher fumed silica concentrations (>8 wt%), which plays a dominant role in conductivity modification. The decrease in conductivity observed for electrolytes containing more than 8 wt% fumed silica concentration is possibly due to the dominant role of viscosity.

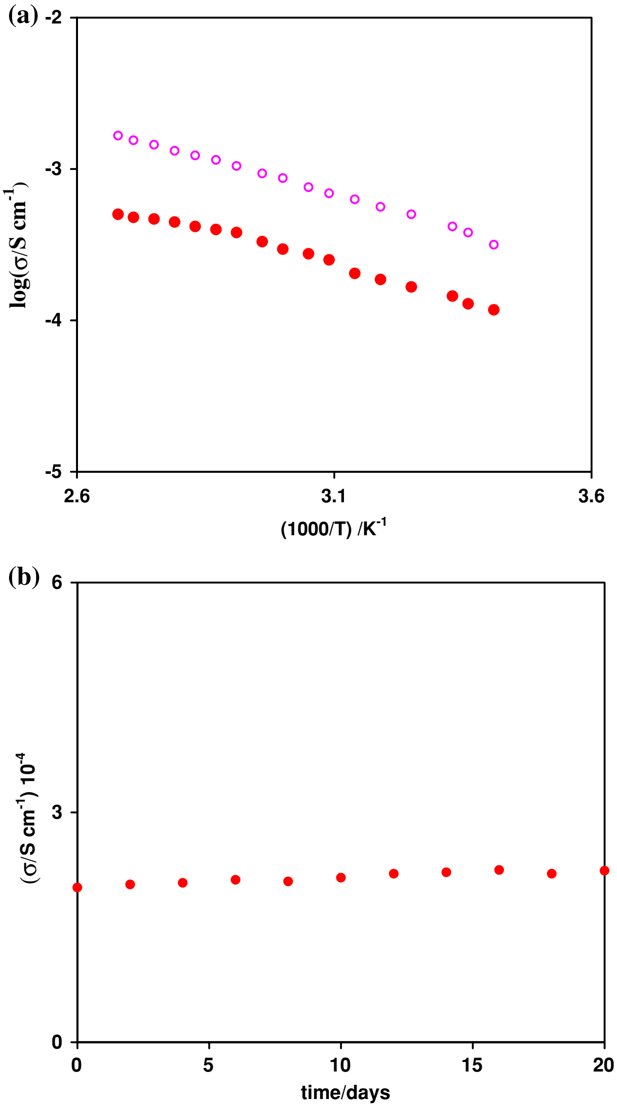


Fig. 6 **a** Conductivity as a function of temperature for gel electrolytes (●) containing 10 wt% PMMA in the solution of 1 M *o*-hydroxy benzoic acid in DMA and nano dispersed gel electrolyte (○) containing 10 wt% fumed silica. **b** Conductivity as a function of time for nano dispersed gel electrolyte (●) containing 10 wt% fumed silica

The variation of conductivity with temperature for polymer gel electrolytes containing 10 wt% PMMA in the 0.5 M solution of *o*-OHBA in DMA and the corresponding nano dispersed polymer gel electrolytes containing 10 wt% fumed silica is given in Fig. 6a. At all temperatures in the 20–100 °C range, the conductivity of nano dispersed gels is higher than for the corresponding polymer gel electrolytes, however, the change in conductivity with temperature is quite small. The conductivity of nano dispersed gels was also measured as a function of time and results are given in Fig. 6b. The conductivity does not show any appreciable change over a limited period of 3 weeks. However, more studies are needed to check the long term stability of these electrolytes from device point of view.

From above studies it has been observed that nano dispersed gels containing a weak acid (*o*-hydroxy benzoic acid) show high conductivity (10^{-4} S cm^{-1}) along with large viscosity (10^4 cP) at 25 °C. The conductivity of nano dispersed gels does not change with time and also show only a small change over the operational range of temperature.

4 Conclusions

Nano dispersed polymer gel electrolytes with conductivity $\sim 10^{-4}$ S cm^{-1} at 25 °C along with high viscosity have been obtained. The enhanced dissociation of *o*-hydroxy benzoic acid with the addition of PMMA results in an increase in conductivity and σ (gel) > σ (liquid) has been observed. The increase in conductivity and viscosity of polymer gel electrolytes with the addition of PMMA has been found to depend upon the molecular weight of PMMA. The addition of nano size fumed silica to polymer gel electrolytes also results in conductivity enhancement and two maxima have been observed along with an increase in viscosity. The first maxima at low fumed silica concentration has been explained to be due to the enhanced dissociation of acid whereas the second maxima at relatively higher fumed silica concentrations is due to the formation of a high conducting interfacial layer between the particles of fumed silica and polymer gel electrolytes. Only a small change in conductivity of nano dispersed gels with temperature and time is observed.

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