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Polymer electrolytes containing ionic liquids with acidic counteranion ($DMRImH_2PO_4$, R = ethyl, butyl and octyl)

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Abstract

Ionic liquids with acidic counteranion and having composition: 2,3-dimethyl-1-alkylimidazolium dihydrogenphosphate ($DMRImH_2PO_4$, R = ethyl, butyl, octyl) have been prepared and the effect of alkyl (R) sidechain length on the conductivity and viscosity behavior has been studied. $DMEtImH_2PO_4$ with highest conductivity (0.07 S/cm at 120 °C) has been incorporated in polyvinylidenefluoride-co-hexafluoropropylene (PVdF-HFP) to obtain polymer electrolytes in the membrane form. The conductivity of membranes has been found to depend upon the concentration of ionic liquid, phosphoric acid and temperature. Polymer electrolytes containing different ionic liquids are thermally stable up to 225 °C and can be used as high temperature membranes for fuel cells.

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1. Introduction

Room temperature ionic liquids containing various non-chloroaluminate anions, which are stable in air and moisture, are receiving much attention due to their potential applications in many diverse fields [1–4]. They generally comprise entirely of ions and are characterised by large window of electrochemical stability, high conductivity, wide operating temperature range, negligible vapor pressure, non-flammability, etc., which make them attractive candidates for various electrochemical devices including supercapacitors, batteries, fuel cells, dye sensitized solar cells, actuators, etc. [5–13]. They generally consist of a combination of organic cations such as imidazolium, pyridinium, pyrrolidinium, ammonium, sulfonium and phosphonium and bulky and soft anions, such as $CF_3SO_3^-$, $N(CF_3SO_2)_2^-$, PF_6^- and BF_4^- [1,14–20]. As a large number of combinations of cations and anions are possible, so the physicochemical properties of ionic liquids can be controlled by a suitable choice of the composition of ionic liquid. The physicochemical properties of different hydrophobic and hydrophilic ionic liquids based on imidazolium cations have been reported to depend upon the alkyl chain length of the imidazolium cation and nature of the anion [21,22]. The thermal stability of ionic liquids has also been reported to depend upon the nature of cation [23]. A change in viscosity, density, ion size and degree of dissociation also affects the conductivity of ionic liquid; however it is difficult to estimate the contribution of each parameter separately. The higher viscosity of ionic liquids is generally explained to be due to very strong coulombic forces between the ionic species present in ionic liquids. However, most of the studies are mainly on ionic liquids containing various fluoroanions and both cations and anions have been reported to be mobile in such ionic liquids. As electrolytes in the thin membrane form are generally preferred for their use in various electrochemical applications, so these ionic liquids have been incorporated in different polymers to obtain electrolytes in the gel and membrane form [24–27]. The effect of the addition of plasticizer and inert insulating phase on the properties of polymer electrolytes containing ionic liquids has also been reported [28–30].

Ionic liquids comprising of imidazolium cations and acidic counteranions are also important due to their capability of proton conduction by hopping mechanism.

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Polymer electrolytes containing ionic liquids with dihydrogenphosphate ($H_2PO_4^-$) and bisulfate (HSO_4^-) anions are receiving much attention due to their suitability as potential candidates for high temperature membranes for use in polymer electrolyte membrane fuel cells (PEMFCs) [31–33]. However, the effect of varying the composition of these ionic liquids on the conductivity and other physicochemical properties has not been fully explored, and the present work is a step in that direction.

In the present study, ionic liquids comprising of 2,3-dimethyl-1-alkylimidazolium ($DMRIm^+$) cation and dihydrogenphosphate ($H_2PO_4^-$) anion have been synthesized. The effect of alkyl (R) chain length on the conductivity and viscosity behavior of ionic liquids as well as on the thermal stability of membranes containing ionic liquids has been studied. Ionic liquid with highest conductivity has been incorporated in PVdF-HFP to obtain polymer electrolytes in the membrane form. The dependence of conductivity of membranes upon the concentration of ionic liquid, phosphoric acid and temperature has also been studied.

2. Experimental

2.1. Materials

Polyvinylidenefluoride-co-hexafluoropropylene (PVdF-HFP, $M_w = 130{,}000$, Aldrich), phosphoric acid (H_3PO_4, Aldrich), potassium dihydrogenphosphate (KH_2PO_4, Merck) 1,2-dimethyimidazole (Merck), 1-bromoethane (C_2H_5Br, Merck), 1-bromobutane (C_4H_9Br, Merck), 1-bromooctane ($C_8H_{17}Br$, Merck), ethyl acetate (SRL) and acetonitrile (Qualigens) were used as the starting materials.

2.2. Synthesis

2.2.1. DMRImBr

2,3-Dimethyl-1-alkylimidazolium bromide (DMRImBr, where R = ethyl, butyl, octyl) was prepared by the reaction of 1,2-dimethylimidazole with 1-bromoalkane and then 2,3-dimethyl-1-alkylimidazolium bromide was washed 2–3 times with dry ethylacetate to remove any starting material left in the reaction. Ethylacetate was then removed by evaporation under reduced pressure.

2.2.2. $DMRImH_2PO_4$

The anion exchange reaction of 2,3-dimethyl-1-alkylimidazolium bromide with potassium dihydrogen phosphate (KH_2PO_4) was carried out in acetonitrile and the solution was stirred for 48 hours at room temperature; precipitates of potassium bromide settled down and were filtered from the solution. A quantitative yield of 2,3-dimethyl-1-alkylimidazolium dihydrogenphosphate ($DMRImH_2PO_4$) was obtained after evaporating acetonitrile under reduced pressure. The absence of bromides in the ionic liquids was checked by bromide ion test.

2.2.3. Polymer electrolytes

Polymer electrolytes in the membrane form were prepared by dissolving stoichiometric quantities of polymer, ionic liquid and acid (H_3PO_4) in acetonitrile and the uniform solution was then poured in polypropylene dishes. The solvent was allowed to evaporate slowly and polymer electrolytes in the free standing film form were obtained

2.3. Measurements

2.3.1. NMR

^1H and ^{13}C NMR spectra of ionic liquids were recorded at room temperature with JEOL AL-300 MHz NMR spectrometer at 300 MHz and 75 MHz, respectively, in $CDCl_3$ with trimethylsilane (TMS) as internal standard. Chemical shifts were expressed as δ (ppm) downfield from TMS and the abbreviations used are s – singlet, d – doublet, t – triplet, m – multiplet, J – coupling constant. The mass spectra were recorded on LC-Agilent 100 series mass spectrometer.

2.4. Conductivity

The conductivity of ionic liquids has been measured by a.c. impedance spectroscopy with a computer interfaced Hioki 3532-50 LCR Hi-Tester using a cell with platinum electrodes. The conductivity of membranes was measured by using a cell with pressure contact stainless steel electrodes and the variation of conductivity with temperature was studied by placing the cell in a temperature controlled furnace.

2.5. Viscosity

Viscosity of the ionic liquids has been measured by Fungilab rotating viscometer (Visco Basic L) using a small sample adapter assembly and temperature was controlled within ±0.1 °C with a Julabo water circulator (F-12 EC).

3. Results and discussion

The formation of ionic liquids: 2,3-dimethyl-1-alkylimidazolium dihydrogenphosphate ($DMRImH_2PO_4$, where R = Et, Bu, and O) was checked by ^1H, ^{13}C NMR and mass spectra and the results are given below:

3.1. $DMEtImH_2PO_4$

^1H NMR ($CDCl_3$, 300 MHz); δ (ppm): 1.48–1.53 (t, 3 H, $-CH_3$); 3.37 (s, 3 H, $-CH_3$); 3.99 (s, 3H, $-NCH_3$); 4.29–4.34 (t, 2H, $-CH_2$); 7.61–7.62 (d, 1H, $J = 2.1$ Hz, ring proton); 7.67–7.68 (d, 1H, $J = 2.1$ Hz, ring proton).

^{13}C NMR ($CDCl_3$, 75 MHz): δ (in ppm) = 10.78 (CH_3), 15.18 (CH_3); 44.0 ($-NCH_3$); 50.24 ($-CH_2$); 120.5, 122.9, 143.5

Mass spectra (ESI) $m/z = 125.2$ ($DMEtIm^+$), 97.3 ($H_2PO_4^-$).

3.2. $DMBuImH_2PO_4$

^1H NMR ($CDCl_3$, 300 MHz); δ (ppm): 0.94–0.99 (t, 3H, $–CH_3$); 1.36–1.44 (m, 2H, $–CH_2$); 1.76–1.86 (m, 2H, $–CH_2$); 2.82 (s, 3H, $–CH_3$); 4.02 (s, 3H, $–NCH_3$); 4.20–4.25 (t, 2H, $–CH_2$); 7.50-7.51 (d, 1H, $J = 2.1$ Hz, ring proton); 7.72–7.73 (d, 1H, $J = 2.1$ Hz, ring proton).

^{13}C NMR ($CDCl_3$, 75 MHz): δ (in ppm) = 10.83 ($–CH_3$), 13.40 ($–CH_3$); 19.45 ($–CH_2$); 31.66 ($–CH_2$); 36.08 ($–CH_2$); 48.64 ($–NCH_3$); 121.06, 122.94, 143.55

Mass spectra (ESI) $m/z = 153.1$ ($DMBuIm^+$), 97.3 ($H_2PO_4^-$).

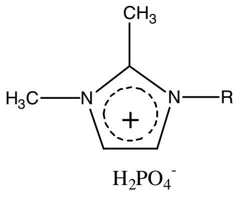
3.3. $DMOImH_2PO_4$

^1H NMR ($CDCl_3$, 300 MHz); δ (ppm): 0.85–0.90 (t, 3H, $–CH_3$); 1.26–1.32 (m, 8H, $–CH_2–CH_2–CH_2–CH_2$); 1.80–1.89 (m, 4H, $–CH_2–CH_2$); 2.81 (s, 3H, $–CH_3$); 4.16 (s, 3H, $–NCH_3$); 4.16–4.21 (t, 2H, $–CH_2$); 7.41–7.42 (d, 2H, $J = 2.1$ Hz, ring proton); 7.69–7.70 (d, 1H, $J = 2.1$ Hz, ring proton).

^{13}C NMR ($CDCl_3$, 75 MHz): δ (in ppm) = 10.99 ($–CH_3$), 14.00 ($–CH_3$); 22.51 ($–CH_2$); 26.33 ($–CH_2$); 28.93 ($–CH_2$); 28.96 ($–CH_2$); 29.78 ($–CH_2$); 31.61 ($–CH_2$); 31.20 ($–CH_2$); 49.1 ($–NCH_3$); 120.90, 123.03, 143.74

Mass spectra (ESI) $m/z = 209.1$ ($DMOIm^+$), 97.3 ($H_2PO_4^-$).

On the basis of above NMR results, the following structure of ionic liquids is proposed:



(where R- Ethyl (Et), Butyl (Bu), Octyl (O))

$DMRImH_2PO_4$

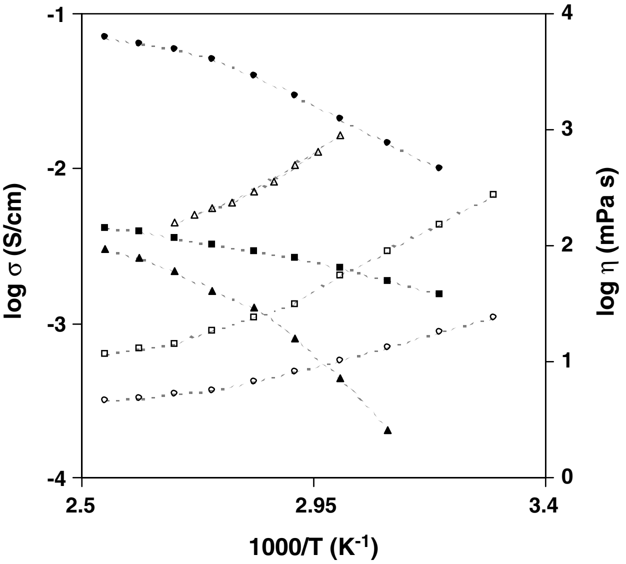


Fig. 1. Variation of log conductivity (solid symbols) and log viscosity (hollow symbols) with reciprocal temperature for the ionic liquids $DMRImH_2PO_4$ with R = ethyl (●, ○), butyl (■, □) and octyl (▲, △).

The contaminant bromides in the ionic liquids were checked by bromide ion test and negative test indicates their absence. Some important physicochemical properties of different ionic liquids are given in Table 1. The conductivity of ionic liquids decreases with an increase in the alkyl (R) chainlength whereas viscosity shows an increase. The conductivity of ionic liquids having composition $DMRImH_2PO_4$ (with R = ethyl, butyl and octyl) was measured at different temperatures and the variation of conductivity with temperature is given in Fig. 1. The conductivity of ionic liquids has been observed to depend upon the chainlength of alkyl (R) group in the imidazolium cation and shows the trend, ethyl > butyl > octyl at all temperatures. The curved nature of the conductivity vs temperature plot for all the ionic liquids suggests the highly viscous nature of electrolytes and the conductivity variation has been explained by VTF behavior. The VTF equation for conductivity is

$$\sigma = \sigma_o \exp[-B/(T - T_o)],$$

where σ_o (S/cm), B (K) and T_o (K) are constants and adjustable parameters. The best-fit parameters were calculated and are listed in Table 2. Ionic liquid containing ethyl group ($DMEtImH_2PO_4$) shows maximum conductivity, which reaches a value of 7.0×10^{-2} S/cm at 120 °C. As viscosity of ionic liquids also depends upon the chain length of the alkyl (R) group, so viscosity of ionic liquids was measured at different temperatures and the variation of viscosity with temperature is also given in Fig. 1. The dependence of viscosity upon the alkyl chain length shows the variation, which is opposite of that observed for conductivity and varies as octyl > butyl > ethyl at all temperatures in the 20–120 °C range. The viscosity results have been

Table 1
Some important physicochemical properties of the ionic liquids: $DMRImH_2PO_4$, with R = ethyl, butyl and octyl

Ionic liquid	σ (mS/cm) at 50 °C	η (mPa s) at 60 °C	Density (gm/cm^3)
$DMEtImH_2PO_4$	14.5	10.4	1.26
$DMBuImH_2PO_4$	1.9	55.2	1.17
$DMOImH_2PO_4$	0.2	902.9	1.08

Table 2
VTF equation parameters of ionic conductivity data for ionic liquids $DMRImH_2PO_4$

Ionic liquid	σ_o (S/cm)	B (K)	T_o (K)	$100R^2$
$DMEtImH_2PO_4$	1.28	281.9	184.9	98.7
$DMBuImH_2PO_4$	0.18	130.6	189.9	99.7
$DMOImH_2PO_4$	0.17	86.22	278.8	99.9

explained by the VTF behavior and the VTF equation for viscosity is

$$\eta = \eta_o \exp[B/(T - T_o)]$$

where η_o (mPa s), B (K) and T_o (K) are adjustable parameters. The best-fit parameters for different ionic liquids are listed in Table 3. As viscosity (η) and mobility (μ) (and hence conductivity ($\sigma = nq\mu$)) are inversely related to each other ($\mu = q/6\pi r\eta$, where q is the charge and r is radius of the ion), so the higher value of viscosity leads to lower conductivity and vice versa. The different behavior observed for conductivity and viscosity results is possibly due to the difference in bulk or macroviscosity – which is measured experimentally and local or microviscosity – which is related to mobility and conductivity. The relation $\sigma = k/\eta$ is not obeyed over the different alkyl (R) chains in the salt due to an increase in the non-polar part on the imidazole. The ionic liquid with octyl group (DMOImH$_2$PO$_4$) has maximum viscosity, whereas the ionic liquid with ethyl group (DMEtImH$_2$PO$_4$) possesses maximum conductivity, as given in Fig. 1. The length of alkyl group in the imidazolium cation thus affects the conductivity and viscosity of the resulting ionic liquid. However, the exact contribution of alkyl group on the modification of conductivity of ionic liquids can not be estimated, as some other parameters such as ion size, degree of dissociation etc also affect the conductivity of ionic liquid. The ionic liquid with ethyl group, DMEtImH$_2$PO$_4$, shows maximum value of ionic conductivity and was chosen for the preparation of polymer electrolyte membranes.

Polymer electrolytes in the membrane form were prepared by incorporating the ionic liquid with ethyl group (DMEtImH$_2$PO$_4$) in PVdF-HFP and the variation of conductivity (at 30 °C) as a function of the concentration of ionic liquid is given in Fig. 2. The addition of inert polymer to the ionic liquid results in a decrease in conductivity by one order of magnitude, as the polymer does not contribute to the conductivity of electrolyte [30]. The conductivity of membranes has been found to increase by a small factor with an increase in the concentration of ionic liquid and membranes with different weight ratios of the polymer and ionic liquid show conductivity of the order of 10^{-4} S/cm at 30 °C. However, the presence of high concentration of ionic liquid can lead to deterioration in the mechanical properties of membranes. Membranes having composition PVdF-HFP + DMEtImH$_2$PO$_4$ in equal weight ratio and possessing conductivity of the same order as other membranes along with reasonably good mechanical properties were used for further studies. Phosphoric acid (H$_3$PO$_4$), which has the same anion as the ionic liquids (DMRImH$_2$PO$_4$) used in the present work, was added to polymer electrolytes containing PVdF-HFP and DMEtImH$_2$PO$_4$ in equal weight ratio and the variation of conductivity (at 30 °C) as a function of H$_3$PO$_4$ concentration is given in Fig. 3. The addition of phosphoric acid results in an increase in conductivity of the membranes and membranes containing 1 M H$_3$PO$_4$ show conductivity of 2.32×10^{-4} S/cm at 30 °C. Phosphoric acid upon dissociation provides free H$^+$ ions, which contribute to the conductivity of these electrolytes. An improvement in the physical stability of the membranes containing ionic liquid was also observed with the addition of phosphoric acid. However, the concentration of phosphoric acid, ionic liquid and

Table 3
VTF equation parameters of viscosity data for ionic liquids DMRImH$_2$PO$_4$

Ionic liquid	η_o (mPa s)	B (K)	T_o (K)	R^2
DMEtImH$_2$PO$_4$	1.01	106.2	227.1	99.6
DMBuImH$_2$PO$_4$	0.85	194.0	229.1	99.4
DMOImH$_2$PO$_4$	3.51	84.5	283.5	99.7

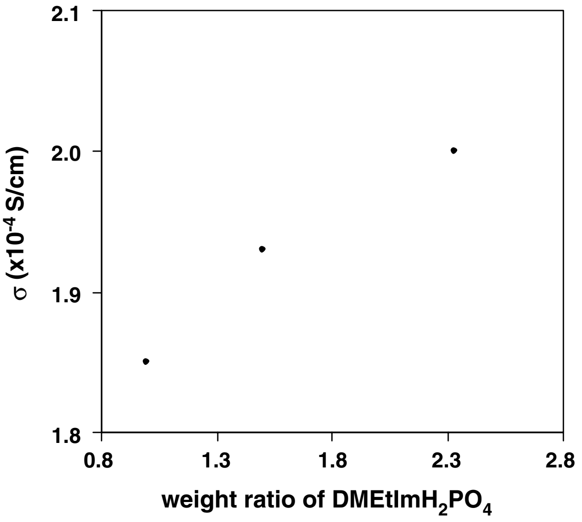


Fig. 2. Dependence of conductivity upon the concentration of ionic liquid for PVdF-HFP + DMEtImH$_2$PO$_4$ polymer electrolytes.

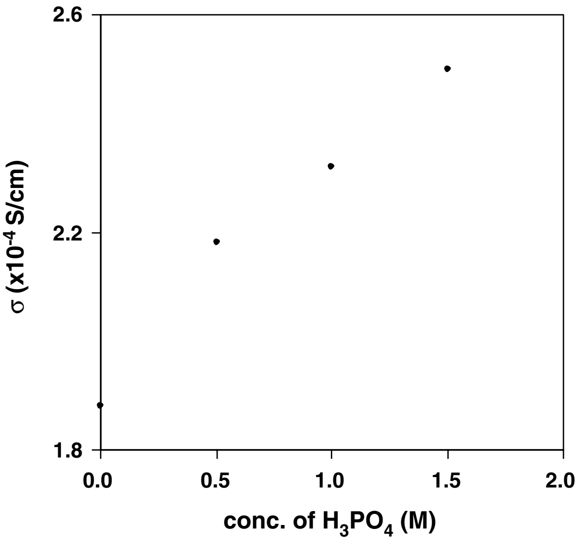


Fig. 3. Dependence of conductivity upon the concentration of phosphoric acid for polymer electrolytes having composition PVdF-HFP:DMEtImH$_2$PO$_4$ (1:1) + x (M) H$_3$PO$_4$.

polymer have to be optimized so that membranes with best combination of ionic conductivity and mechanical strength are obtained.

The conductivity of different membranes having composition PVdF-HFP:DMEtImH_2PO_4 (1:1) + x(M) H_3PO_4 with $x = 0$ and 1 was measured at different temperatures and the variation of conductivity with temperature is given in Fig. 4. The conductivity variation for the neat ionic liquid (DMEtImH_2PO_4) has also been included in Fig. 4 for comparison. The curved nature of plots has been explained by the VTF behavior and the best-fit parameters are given in Table 4. The conductivity of membranes containing H_3PO_4 is higher than for the corresponding membranes without H_3PO_4, but is less than for the neat ionic liquid by nearly one order of magnitude. Membranes containing the ionic liquid and with conductivity higher than 10^{-3} S/cm above 50 °C can find potential use in various electrochemical devices. However, for their use in PEMFCs, the conductivity has to be improved by more than one order of magnitude and secondly protons should be the mobile species. Although cations and anions are the main mobile species in ionic liquids yet the presence of acidic counteranion ($H_2PO_4^-$) and phosphoric acid (H_3PO_4) suggests that protons also contribute to the conductivity of these polymer electrolyte membranes. It is important for their future use as proton conducting membranes in polymer electrolyte membrane fuel cells. However, more experimental studies are required to establish the nature of mobile species in these membranes containing ionic liquids.

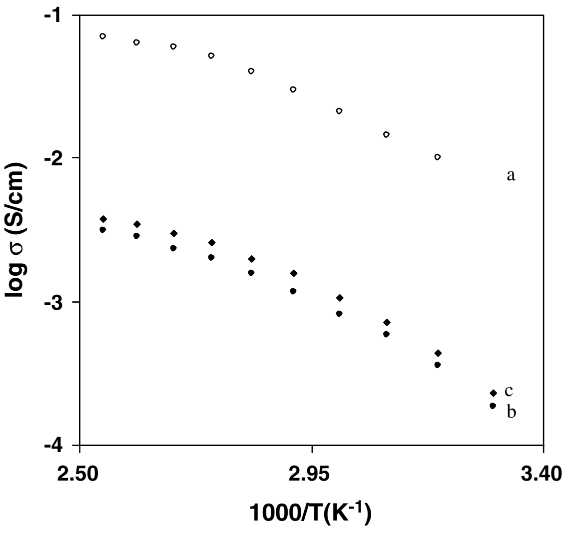


Fig. 4. Variation of log conductivity with reciprocal temperature for electrolytes having composition: (a) DMEtImH_2PO_4, (b) PVdF-HFP:DMEtImH_2PO_4 (1:1) and (c) PVdF-HFP:DMEtImH_2PO_4 (1:1) + 1 M H_3PO_4.

Table 4
VTF equation parameters of conductivity data for polymer electrolytes

Polymer electrolyte	σ_o (S/cm)	B (K)	T_o (K)	R^2
PVdF-HFP:DMEtImH_2PO_4 (1:1)	0.215	152.1	233.4	99.9
PVdF-HFP:DMEtImH_2PO_4 (1:1) + 1 M H_3PO_4	0.214	131.3	240.6	99.8

The effect of alkyl chain length on the thermal stability of membranes containing ionic liquids with acidic counteranion was also studied. The simultaneous DSC/TGA/DTG thermograms of polymer electrolyte membranes containing DMRImH_2PO_4 (R = ethyl, butyl, octyl) and PVdF-HFP in equal weight ratio, recorded in the 20-600 °C temperature range under nitrogen atmosphere are given in Fig. 5. The DSC thermogram of membrane containing ionic liquid with ethyl group shows an endothermic peak at 62 °C, which corresponds to the transition of polymer (PVdF-HFP) to the polar form [34] and this peak shifts to 61 and 57 °C for membranes containing ionic liquid with butyl and octyl group, respectively. The TGA thermograms for all the membranes show a weight loss by 3% only up to 225 °C, which indicates that these membranes are thermally stable up to this temperature. The onset of weight loss takes place between 225 and 250 °C for all the electrolytes. In the case of electrolytes containing ionic liquid with ethyl group two endothermic peaks at 253 and 300 °C in the DSC thermogram have accompanied this weight loss. This is also reflected in the different values of the rate of weight loss observed at 255 °C (0.65 mg/min) and 299 °C (0.53 mg/min) in the DTG plot for this electrolyte. This weight loss is due to the decomposition/evaporation of electrolyte and the rate is slow and takes place over a wide (225–400 °C) temperature range. However, for electrolytes containing ionic liquid with butyl and octyl group, the DSC thermogram shows only a single peak at 290 and 283 °C, respectively, and this is accompanied by a single rate of weight loss observed at 265 (1.05 mg/min) and 270 °C (1.46 mg/min), respectively. The rate of weight loss has been found to increase with an increase in the chain length of alkyl group (R) and it takes place over relatively narrow temperature ranges of 225–325 °C and 225–300 °C, respectively, for electrolytes containing ionic liquids with butyl and octyl groups. The char weight remaining at 600 °C also decreases with an increase in the chain length, from above 30% to 25% and 22% for membranes containing ionic liquids with ethyl, butyl and octyl group, respectively. The rate of weight loss has been observed to depend upon the length of alkyl group (R) and increases with an increase in the length of alkyl chain group in the imidazolium cation of ionic liquid. The above results show that these polymer electrolytes containing ionic liquids with different alkyl groups are thermally stable up to 225 °C and can be safely used in different electrochemical devices, including proton exchange membrane fuel cells, up to 175–200 °C. The thermal stability of membranes containing phosphoric acid may be slightly lower as phosphoric acid is unstable above 200 °C, and further studies in this direction are in progress.

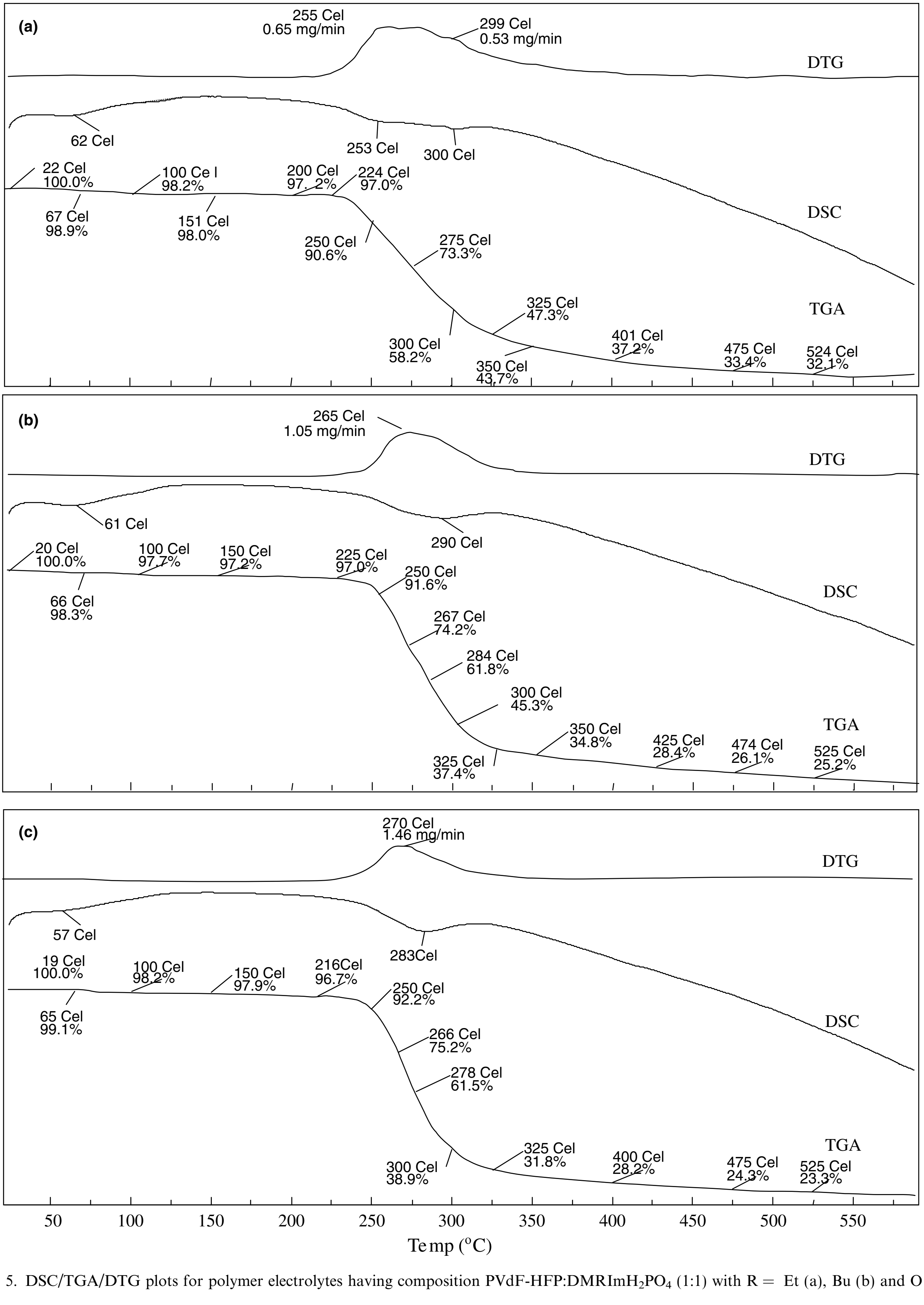


Fig. 5. DSC/TGA/DTG plots for polymer electrolytes having composition PVdF-HFP:DMRImH$_2$PO$_4$ (1:1) with R = Et (a), Bu (b) and O (c).

4. Conclusions

The conductivity and viscosity of ionic liquids containing acidic counteranion: 2,3-dimethyl-1-alkylimidazolium dihydrogenphosphate ($DMRImH_2PO_4$) have been found to depend upon the chain length of alkyl (R) group and ionic liquid with ethyl group ($DMEtImH_2PO_4$) show maximum conductivity of 0.07 S/cm at 120 °C. The conductivity of polymer electrolytes containing $DMEtImH_2PO_4$in a polymer (PVdF-HFP) matrix has been found to depend upon the concentration of ionic liquid, phosphoric acid and temperature. Polymer electrolytes containing different ionic liquids are thermally stable up to 225 °C and are suitable as high temperature membranes in proton exchange membrane fuel cells under non-humid conditions.

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