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Protonic polymer gel electrolytes based on carboxylic acids: ortho and inductive effects

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The conductivity of polymer gel electrolytes containing three aromatic and three aliphatic carboxylic acids has been studied, viz. (i) ortho-, meta- and para-hydroxybenzoic acids and (ii) oxalic, malonic and succinic acids. Polymeric gels were prepared by adding different wt% of polymer poly(methylmethacrylate) (PMMA) in solutions of respective acids in high dielectric constant organic solvent mixtures of propylene carbonate, ethylene carbonate and dimethylformamide. The highest conductivity in the first of the above group of acids is for *o*-hydroxy benzoic acid and oxalic acid in the second group of acids. Results have been explained on the basis of "ortho" and/or "inductive" effects which depend upon the relative positions of the substituted hydroxyl (–OH) and carboxyl (–COOH) group or that of the two carboxylic groups. *© 2002 Kluwer Academic Publishers*

1. Introduction

Polymer gel electrolytes due to their high value of conductivity are currently of great interest [1–6] commercially as they are seen as better alternative to the solvent-free polymer electrolyte or polymer-salt complexes. The gel electrolytes are generally prepared by dissolving a salt in a polar liquid and then the macroscopic immobilization of the liquid solvent is achieved by increasing the viscosity of the liquid electrolytes [7] by adding a soluble polymer like poly(methylmethacrylate) (PMMA), polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVdF) etc.. The low molecular weight solvents used in the gel electrolytes are carbonate esters such as propylene carbonate and ethylene carbonate having high permittivity (but reasonably low viscosity). Other high dielectric constant solvents being used in polymer gel electrolytes include N, N-dimethyl formamide and γ-butyrolactone [8]. These solvents are miscible with a wide range of polymers and are non-volatile. The high value of conductivity observed for polymer gel electrolytes has been found to depend upon the physical properties of the solvent used such as viscosity, dielectric constant and the concentration of salt in the electrolyte [9]. The high dielectric constant of the solvents like ethylene carbonate and propylene carbonate increases the level of salt dissociation whereas their low viscosity value leads to high ionic mobility-thus optimising the conductivity value. The earlier work on polymer gel electrolytes has been mainly with different lithium salts [10–15], but recently proton conducting polymer gel electrolytes have attracted attention due to their potential technological applications in fuel cells and othe devices [16].

Proton conducting polymer gel electrolytes of polyacrylamide (PAAM) based hydrogels doped with H_3PO_4 and H_2SO_4 have been studied and their conductivity has been reported to depend upon the concentration of acid, water, crosslinking and gelation agents [17]. The decrease in conductivity of gels containing high concentration of H_2SO_4 at temperatures exceeding 60°C has been explained to be due to the dehydration of the hydrogels or from the degradation of the polymer matrix which occurs in the presence of a strong inorganic acid. This type of behaviour has not been observed with H_3PO_4. The presence of water in hydrogels is a severe limitation for their applications in devices containing water sensitive materials like electrochromic windows. The aqueous and nonaqueous protonic gels incroporating H_3PO_4 have been studied using propylene carbonate and dimethyl formamide as solvents and conductivity value of 10^{-3} S/cm has been reported at room temperature. The high conductivity value of hydrogels PAAM-H_2SO_4 has been explained to be due to the protonation capability of the amide groups.

The use of organic acids in proton conducting polymer gel electrolytes has been reported recently [18]. The salicylic acid or paratoluenesulfonic acid is used in a highly plasticized PMMA matrix and it is reported that the conductivity of these gel electrolytes is independent of the relative humidity conditions and these electrolytes are reported to be thermally stable up to very high temperatures.

In the case of organic acids [19], the acidity of derivatives of aromatic carboxylic acids depends upon the position of the derivative group relative to the carboxyl

(—COOH) group. As the distance between the two groups increases or in other words as we go from ortho to meta and para position, the acidity decreases. The acidity is maximum in the ortho case known as the "ortho effect". Similarly in the case of aliphatic dicarboxylic acids of the type HOOC—$(CH_2)_n$—COOH, the acidity constant value depends upon the distance between the two carboxyl groups and it decreases with an increase in the distance between the two groups-generally known as the "inductive effect". The change in acidity should result in a corresponding change in the conductivity value but so far no systematic study has been carried out for proton conducting polymer gel electrolytes.

In the present work, we report the synthesis and properties of protonic polymeric gel electrolytes containing aromatic carboxylic acids and aliphatic dicarboxylic acids. The first set of protonic polymer gel electrolytes were prepared by using ortho-, meta- and para-hydroxybenzoic acids; propylene carbonate, ethylene carbonate and dimethyl formamide as the 'solvent'; and PMMA as the gelling 'polymer'. In the second set of polymeric gels, aliphatic dicarboxylic acids used are oxalic acid (OA), malonic acid (MA) and succinic acid (SA) with formula HOOC—$(CH_2)_n$—COOH having $n = 0$, 1 and 2.

2. Experimental

High molecular weight (996,000) poly (methylmethacrylate) (PMMA) (Aldrich), oxalic acid (OA), malonic acid (MA), succinic acid (SA), *o*-hydroxybenzoic acid (*o*-OHBA), *m*-hydroxybenzoic acid (*m*-OHBA), *p*-hydroxybenzoic acid (*p*-OHBA), propylene carbonate, ethylene carbonate and dimethyl formamide were used as the starting materials in the present study. All the starting materials were dried before use. A ternary mixture of propylene carbonate, ethylene carbonate and dimethyl formamide in equal volume ratio was used as the solvent in the present study. Liquid electrolytes were prepared by dissolving acid in appropriate stoichiometric ratio in the solvent. Gel electrolytes were prepared by adding the polymer i.e. PMMA to the liquid electrolytes. PMMA was added slowly alongwith continuous stirring at a temperature of around 60°C so that the gel formation takes place.

Table I lists the properties of different carboxylic acids used in the present study. The ionic conductivity of all the liquid and gel electrolytes was measured at room temperature as well as in the 275–355 K temperature range by using WTW conductivity meter LF-330 and HP 4284 Precision LCR meter operating in the 20 Hz–1 MHz frequency range. The conductivity in the liquid electrolyte can easily be estimated from a single frequency measurement where electrode-electrolyte interface impedance is not significant. However for separating on electrode-electrolyte impedance from bulk impedance, which is necessary for gel or polymeric electrolytes, there the method of complex impedance plot (i.e. impedance spectroscopy) is required [20, 21]. Hence measurement of real and imaginary parts of impedance were made by the HP 4284 LCR meter in a wide frequency range.

TABLE I Dissociation/acidity constants of different aliphatic and aromatic carboxylic acids used to prepare gel electrolytes

Acid	Dissociation or acidity constant $\times 10^5$
(A) Aromatic carboxylic acids	
o-OHBA	105 (K_1)
(Ortho-hydroxybenzoic acid)	
m-OHBA	8.3 (K_1)
(Meta-hydroxybenzoic acid)	
p-OHBA	2.6 (K_1)
(Para-hydroxybenzoic acid)	
(B) Aliphatic carboxylic acids	
HOOC—COOH	5400 (K_1)
(Oxalic Acid (OA))	5.2 (K_2)
HOOC—CH_2—COOH	140 (K_1)
(Malonic Acid (MA))	0.20 (K_2)
HOOC—$(CH_2)_2$—COOH	6.4 (K_1)
(Succinic acid (SA))	0.23 (K_2)

3. Results and discussion

3.1. Conductivity of hydroxybenzoic acid based electrolytes

Hydroxybenzoic acids with the substitution of the hydroxyl (—OH) group at the ortho-, meta- and para-positions has been used as the proton conductor in the first set of polymeric gel electrolytes. Due to the different positions of the hydroxyl group relative to the carboxyl (—COOH) group, these acids have different properties as given in Table I. Fig. 1 shows the variation of the room temperature conductivity of liquid electrolytes containing *o*-, *m*- and *p*- hydroxy benzoic acids in a ternary solvent mixture of propylene carbonate, ethylene carbonate and dimethyl formamide in equal volume ratio. The following features follow from Fig. 1:

(i) The conductivity increases initially, almost linearly with the molar concentration of the acid added but later at higher concentrations the rate of increase is much slower than the rate of increase of concentration. This effect is more pronounced for *o*-OHBA (which has highest acidity constant, see Table I) as compared to *m*- and *p*-OHBA. This can be understood in terms of ion-association and/or Debye-Huckel-Falkenhagen shielding effects [22]. It may be noted here that the possibility of these effects is more for materials where

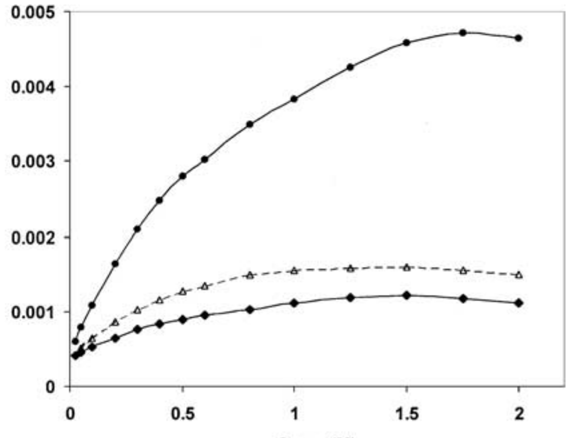

Figure 1 Variation of conductivity of ortho (●), meta (♦) and para (Δ) hydroxybenzoic acid containing electrolytes with concentration at 30°C.

the acidity constant (and hence ionic carrier concentration) is higher as observed by us. This will also have a bearing on the relative conductivity values of these acid based gels as given below:

(ii) For all the concentration values, the conductivity of electrolytes with *o*-, *m*- and *p*-hydroxybenzoic acids varies in the following order: *o*-OHBA > *m*-OHBA, *p*-OHBA. The higher value of conductivity of *o*-OHBA in comparison to that for *m*- and *p*-OHBA based electrolytes at all acid concentrations has been found to show the well known "ortho effect" due to which the value of acidity constant for *o*-OHBA is higher than for the *m*-OHBA and *p*-OHBA [19]. With the substitution of the hydroxyl (—OH) group at different positions relative to the (—COOH) group, the distance between the two groups increases in going from *o*- to *m*- and *p*-positions. As a result, it leads to a decrease in the acidity constant value and hence the conductivity value also decreases. So the ortho effect is also observed in the conductivity behaviour of *o*-, *m*- and *p*-substituted hydroxy benzoic acids based electrolytes.

(iii) The ortho-effect is also reflected in "polymeric gelled" systems. The gel electrolytes were prepared by adding different wt% of PMMA to the 1 M solution of *o*-, *m*- and *p*-hydroxybenzoic acids in the ternary solvent mixture. The relative values of conductivity of liquid electrolyte and that of the gel electrolyte with 10 wt% PMMA is given in Table II for different temperatures. From Table II, it is clear that at each temperature the conductivity of gels for different hydroxybenzoic acids follows the sequence σ(ortho) > σ(meta), σ(para) confirming the ortho-effect in polymeric gels also. Further, σ(liquid) < σ(gel). This difference is more for *o*-OHBA than for the other two acids with smaller values of acidity constants. Earlier, it has been found for lithium salts that σ(liquid) > σ(gel), but our present systematic studies on many protonic acids point to the contrary. Similar observation for a gel electrolyte has been reported by Grillone *et al.* [18]. An explanation to this effect is briefly given below.

Normally, σ depends on the number of charge carriers (n) and mobility (μ) as $\sigma = n.q.\mu$. The number of charge carriers depend upon the acidity constant (or dissociation energy U involved) and the dielectric constant $\in$ as

$$n \propto \exp(-U/\in k\,T) \qquad (1)$$

With the addition of PMMA, $\in$ would decrease as the dielectric constant of the solvent PC + EC + DMF is higher than that of the added polymer. This means that due to a decrease in $\in$, n ought to have decreased leading to a decrease in conductivity. Roughly, the proportionality of σ with $\in$ can be written as

$$\sigma \propto \in^{x} \qquad (2)$$

Further, addition of PMMA increases the viscosity as gelling progresses. This would decrease mobility and hence conductivity. In other words, conductivity is an inverse function of viscosity (η) as

$$\sigma \propto 1/\eta^{y} \qquad (3)$$

The exponents x and y of Equations 2 and 3 are not yet known theoretically but are taken as positive numbers to explain the expected trend of variation of σ. Both Equations 2 and 3 suggest a decrease in the conductivity on gellification induced by PMMA. However, we observe a slight increase in σ on gelling for the present proton conducting benzoic acid system[§]. However the earlier [7] data on lithium gels does not show any increase. On the contrary, it is marked by a small decrement in σ. But this decrement is also much less than what is expected due to an increase in viscosity on gellification. Therefore, one has to think of a mechanism which can counter the normally expected decrement in σ due to addition of PMMA. This has been explained by us on the basis of a "Breathing Polymer Chain Model" [23]. The essence of the model is based on a gross pictorial situation of the polymeric gel electrolyte consisting of ions, ion pairs and polymer chains dispersed in the gel as depicted in Fig. 2. The polymer (P) is supposed to breathe in- and-out by folding and unfolding up of its loop/chain. This leads to density or pressure fluctuations at a microscopic level assisting the motion of ions as well as the dissociation of any ion pairs leading to an effect which causes conductivity to increase.

TABLE II Comparative values of conductivity (σ) of liquid and gel electrolytes based on hydroxy benzoic acids. The concentration of gelling polymer PMMA was 10 wt%

	$\sigma \times 10^3$ (S/m) at temperature							
	10°C		30°C		60°C		80°C	
Acid	Liquid	Gel	Liquid	Gel	Liquid	Gel	Liquid	Gel
o-OHBA	2.66	6.74	4.38	10.33	9.07	17.69	18.03	27.7
m-OHBA	1.206	1.912	1.757	2.866	4.065	5.653	9.442	11.778
p-OHBA	1.25	1.18	1.96	2.01	3.58	3.58	6.15	5.42

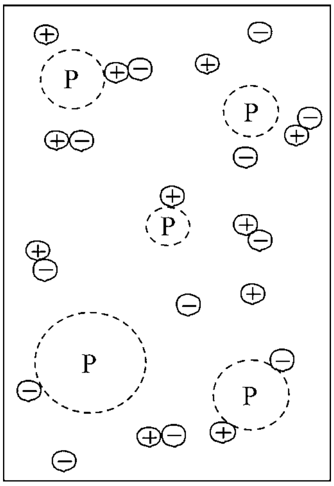

Figure 2 Schematic model of polymer gel electrolytes.

3.2. Conductivity of aliphatic dicarboxylic acid based electrolytes

Aliphatic dicarboxylic acids with composition HOOC—$(CH_2)_n$—COOH for $n = 0, 1, 2$ has been

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[§] The decrement effect caused by enhanced viscosity does show up if PMMA concentration is higher [18] than what is used in the present study.

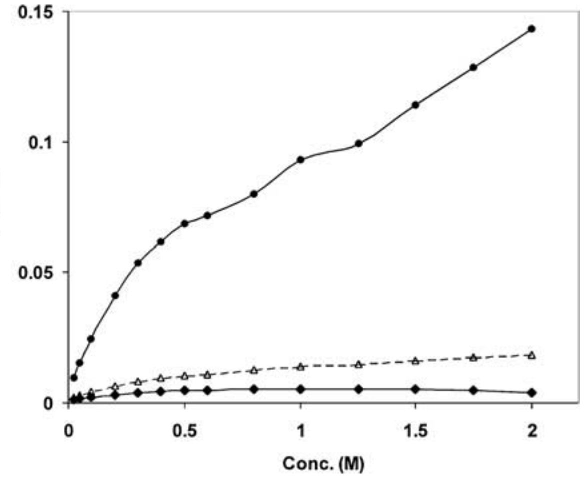
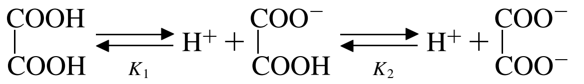


Figure 3 Variation of conductivity with concentration for electrolytes containing oxalic acid (●), malonic acid (△) and succinic acid (♦) at 60°C.

chosen to study the effect of increase in the distance between the two carboxyl (—COOH) groups on the conductivity of the electrolytes because of the change in their acidity constants as given in Table I. In the case of dicarboxylic acids containing more than one ionizable hydrogen, ionization of the second carboxyl group occurs less readily than ionization of the first group ($K_1 > K_2$) because more energy is required to separate a positive hydrogen ion from the doubly charged anion than from the singly charged anion:



$$\begin{array}{c}\mathrm{COOH}\\|\\\mathrm{COOH}\end{array} \underset{K_1}{\rightleftharpoons} \mathrm{H}^+ + \begin{array}{c}\mathrm{COO}^-\\|\\\mathrm{COOH}\end{array} \underset{K_2}{\rightleftharpoons} \mathrm{H}^+ + \begin{array}{c}\mathrm{COO}^-\\|\\\mathrm{COO}^-\end{array}$$

As K_2 is very less than K_1 as given in Table I, so only K_1 values are relevant for discussing the relative values of conductivity.

The conductivity of liquid electrolyte for this system as a function of concentration is given in Fig. 3 and the relative values of conductivity of liquid electrolytes and one of its typical polymeric gel is given in Table III. As discussed earlier for the case of hydroxybenzoic acid, the ion-association and shielding effects at higher concentration is also seen for this system. Further, the conductivity sequence is $\sigma(\mathrm{OA}) > \sigma(\mathrm{MA}) > \sigma(\mathrm{SA})$ following the relative values of acidity constants for these acids. The reason for this sequence of acidity constants in these acids is the well-known "Inductive Effect" as described in the Introduction of this paper.

TABLE III Comparative values of conductivity (σ) of liquid and gel electrolytes based on aliphatic dicarboxylic acids. The concentration of gelling polymer PMMA was 20 wt%

	$\sigma \times 10^3$ (S/m) at temperature							
	10°C		30°C		60°C		80°C	
Acid	Liquid	Gel	Liquid	Gel	Liquid	Gel	Liquid	Gel
OA	32.6	49.6	53.4	93.0	101.2	206.0	188.0	284.0
MA	4.86	10.08	8.06	15.97	15.27	28.9	24.8	39.8
SA	–	–	5.45	5.51	9.31	10.05	14.44	14.45

The results given in Table III are similar to that given in Table II for the set of benzoic acids in both respects i.e. (a) higher acidity constant leads to higher conductivity in polymeric gels also and (b) $\sigma_{\mathrm{gel}} > \sigma_{\mathrm{liquid}}$. Therefore, the same explanation applies as given earlier for hydroxybenzoic acids.

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