

Study of enhanced dissociation of aliphatic dicarboxylic acids with PVdF addition in polymer gel electrolytes

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The ionic conductivity of non-aqueous polymer gel electrolytes containing weak aliphatic dicarboxylic acids has been found to depend upon the dissociation constant of the acid used and conductivity of $(1-2) \times 10^{-3}$ S/cm has been obtained at 25°C. The addition of polyvinylidene fluoride (PVdF) to the solution electrolytes containing different dicarboxylic acids results in an increase in conductivity, which depends upon the concentration of polymer and acid present in these electrolytes. The enhancement of conductivity with PVdF addition has been explained to be due to the dissociation of undissociated acid present in the electrolytes which results in an increase in free H⁺ ion concentration and has been studied by pH measurements. The variation of viscosity with acid and polymer concentration and temperature has also been studied and viscosity increases exponentially at high PVdF concentrations and plays a dominant role at high PVdF concentrations.

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1. Introduction

Polymer gel electrolytes are technologically important materials due to their high conductivity ($\sim 10^{-3}$ S/cm) and suitability for applications in display devices [1–3], supercapacitors [4, 5], solid state batteries [6–10] etc. Gel electrolytes are generally prepared by dissolving salt/acid in an organic polar solvent and then this solution is immobilized with the addition of a suitable polymer [11]. The solvent used should have low viscosity, high dielectric constant, low freezing point and high boiling point. If a single solvent with suitable properties is not available then a solvent mixture having the desired properties could be used [12–14]. The choice of polymer depends upon the end use of the corresponding gel electrolytes like PMMA based gel electrolytes are highly transparent in the visible region and are suitable for smart windows/electrochromic devices, whereas PVdF and PVdF-HFP based gel electrolytes have better mechanical properties and are generally used in solid state batteries. Lithium ion conducting polymer gel electrolytes containing various lithium salts have been widely studied due to their suitability for high energy density lithium batteries [15–21]. Proton conducting polymer gel electrolytes are also gaining importance due to their potential use in fuel cells and other devices [22]. In lithium ion conducting polymer gel electrolytes the addition of polymer generally results in a small decrease in conductivity which is explained to be due to an increase in viscosity which lower

ionic mobility and hence conductivity decreases. However recently it has been reported that in the case of proton conducting polymer gel electrolytes containing weak acids, the addition of polymer results in an enhancement in conductivity [23, 24]. This conductivity enhancement with polymer addition is not fully understood and is the motivation for the present work.

In the present work, non-aqueous polymer gel electrolytes containing simple aliphatic dicarboxylic acids (COOH-(CH₂)_n-COOH) with $n=0$ (oxalic acid), $=1$ (malonic acid), $=2$ (succinic acid) and with PVdF as the gelling polymer has been studied. The dependence of conductivity on acid concentration, dissociation constant of acid, polymer concentration and temperature has been studied. The viscosity of the electrolytes has also been measured as a function of acid and polymer concentration. The change in free ion (H⁺) concentration in the electrolytes has been examined by pH measurements.

2. Experimental details

High purity polyvinylidene fluoride (PVdF) (Fluka, $M_w = 534,000$), ethylene carbonate (EC), propylene carbonate (PC), dimethylacetamide (DMA) (all Merck) and oxalic acid, malonic acid and succinic acid (Qualigen, AR) have been used as the starting materials. Liquid electrolytes were prepared by dissolving acid in different concentrations (expressed as molar values)

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in ternary solvent mixture of EC, PC and DMA taken in 2:2:1 volume ratio. Gel electrolytes were prepared by adding PVdF in different amounts (expressed as wt% of liquid electrolyte) to the liquid electrolyte along with continuous stirring to obtain homogenous gels. The electrical conductivity was measured with HP4284A precision LCR meter operating in the 20 Hz–1 MHz frequency range using a cell with platinum electrodes. The details of the method has been reported earlier [25]. The viscosity of electrolytes was measured by Fungilab rotating viscometer model Visco Basic L and pH was measured by using Systronics pH meter model 315.

3. Results and discussion

The conductivity of liquid electrolytes containing three simple aliphatic dicarboxylic acids namely oxalic acid (OA), malonic acid (MA) and succinic acid (SA) in the ternary solvent mixture of EC, PC and DMA taken in 2:2:1 volume ratio was measured at different acid concentrations and the results are given in Fig. 1. The ternary solvent mixture composition used in the present study show higher conductivity as reported earlier [26]. The conductivity of electrolytes depends upon the dissociation constant of the acid used and is higher for electrolytes containing OA than those containing MA and SA at all acid concentrations and varies as:

$$\sigma(\text{OA}) > \sigma(\text{MA}) > \sigma(\text{SA})$$

This behaviour can be attributed to be due to the higher first dissociation constant (K_1) of OA (5.4×10^{-2}) as compared to MA (1.40×10^{-3}) and SA (6.4×10^{-5}) which also varies as $K_1(\text{OA}) > K_1(\text{MA}) > K_1(\text{SA})$. The higher value of the dissociation constant of OA shall lead to relatively better dissociation of the acid in the electrolyte which contribute to higher conductivity as compared with electrolytes containing MA and SA.

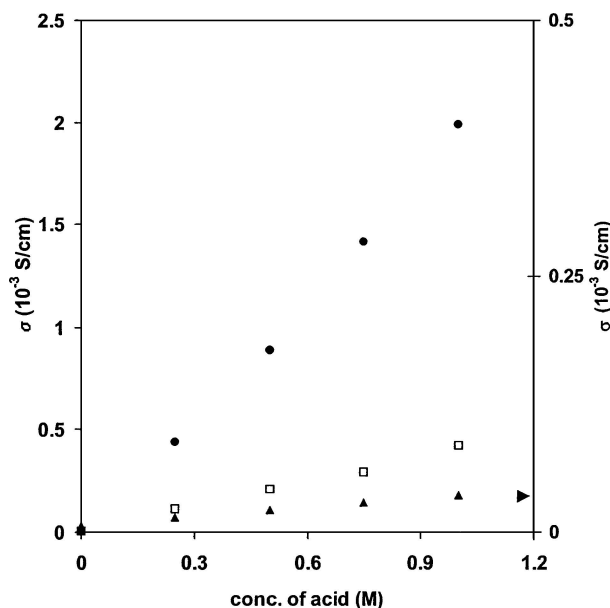


Figure 1 Variation of conductivity with acid concentration for liquid electrolytes containing: OA (●), MA (□) and SA (▲) in ternary solvent mixture.

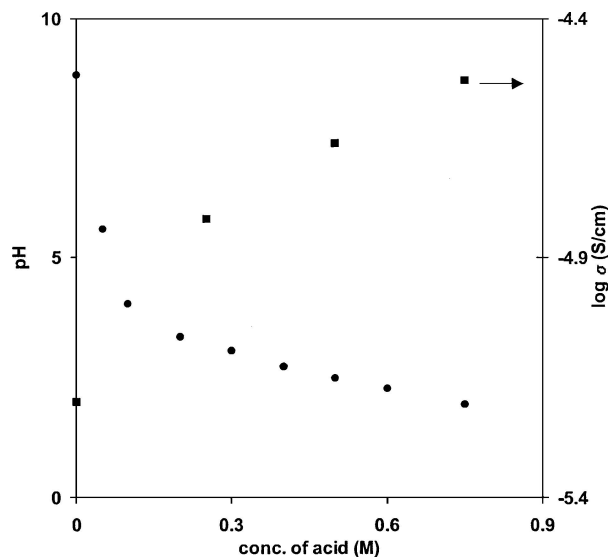


Figure 2 Variation of pH (●) and log conductivity (■) with acid concentration for liquid electrolytes containing SA.

Although the dissociation constant of OA is relatively higher yet it is less than one and as a result some undissociated acid will also be present in these electrolytes. Electrolytes containing MA and SA with still lower dissociation constant will contain more undissociated acid.

An increase in acid concentration results in higher H^+ ion concentration and hence conductivity increases as given in Fig. 1. The change in free H^+ ion concentration has also been studied by pH measurements which is related to free H^+ ion concentration by the relation $\text{pH} = -\log_{10} [\text{H}^+]$. pH of liquid electrolytes containing SA was measured at different acid concentrations and the variation is given in Fig. 2. For comparison the variation of log conductivity with acid concentration for liquid electrolytes containing SA is also included in the figure. pH of liquid electrolyte decreases with an increase in SA concentration and the rate of decrease of pH is small at high acid concentration. The decrease in pH which is due to an increase in free H^+ ion concentration is accompanied by an increase in conductivity of the electrolyte. The addition of acid shall also increase the viscosity of the electrolytes and the variation of viscosity with SA concentration is given in Fig. 3 and viscosity increases with an increase in acid concentration, although the increase is small. As the increase in viscosity with the addition of acid is very small so it will not result in a large change in conductivity.

Polymer gel electrolytes were prepared by adding PVdF to the solutions of 0.25 M OA, 0.5 M MA and 1.0 M SA in ternary solvent mixture and the variation of conductivity with PVdF concentration (expressed as wt% of liquid electrolyte) is given in Fig. 4. The results show that in each case conductivity increases with the addition of PVdF, reaches a maxima and then shows a decrease at higher PVdF concentrations. The presence of maxima is indicative of the simultaneous presence of two competing phenomena. The increase in conductivity with PVdF addition is despite the fact that the addition of polymer shall increase the viscosity, which shall lower mobility and secondly it also leads to a net

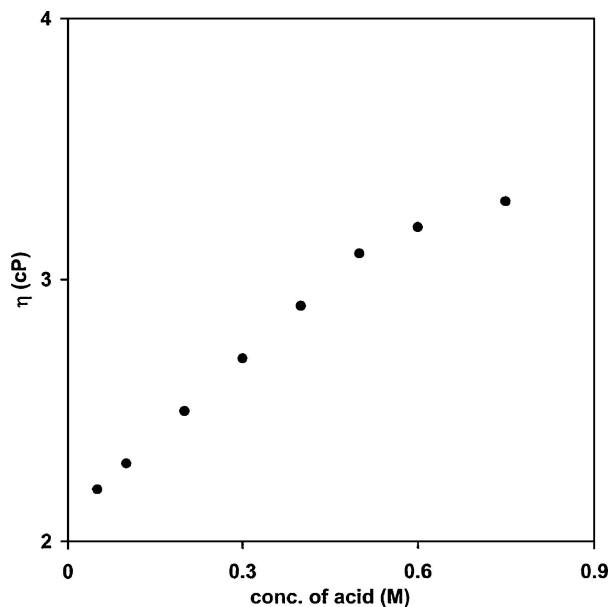


Figure 3 Variation of viscosity for liquid electrolytes with SA concentration.

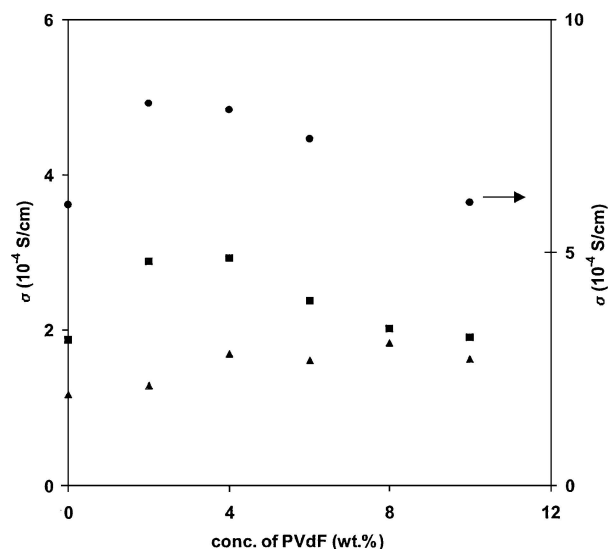


Figure 4 Conductivity variation with PVdF concentration for gel electrolytes containing: 0.25 M OA (●), 0.5 M MA (■) and 1 M SA (▲).

decrease in acid concentration as no new acid is added and both these factors shall decrease conductivity. As undissociated acid is present in all the electrolytes so the addition of PVdF may result in the dissociation of undissociated acid, which leads to higher free H^+ ion concentration, and as a result conductivity increases. However at high PVdF concentrations, the viscosity of gel electrolytes shall be much higher and shall play a dominant role resulting in a decrease in conductivity.

In view of above explanation the addition of PVdF increases the free H^+ ion concentration and hence it should also result in a change in pH of the gel electrolytes. This was examined by measuring the pH of the electrolytes containing SA as a function of PVdF concentration and the results are given in Fig. 5. For comparison the variation of conductivity of gel electrolytes containing SA is also included in Fig. 5. The addition of PVdF results in a decrease in pH at low

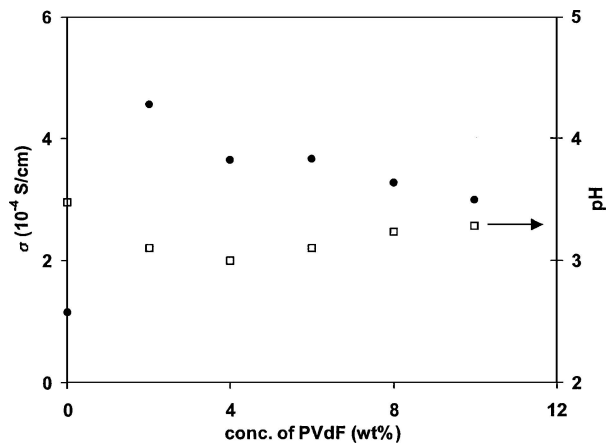


Figure 5 Variation of conductivity (●) and pH (□) with PVdF concentration for gel electrolytes containing 0.25 M SA.

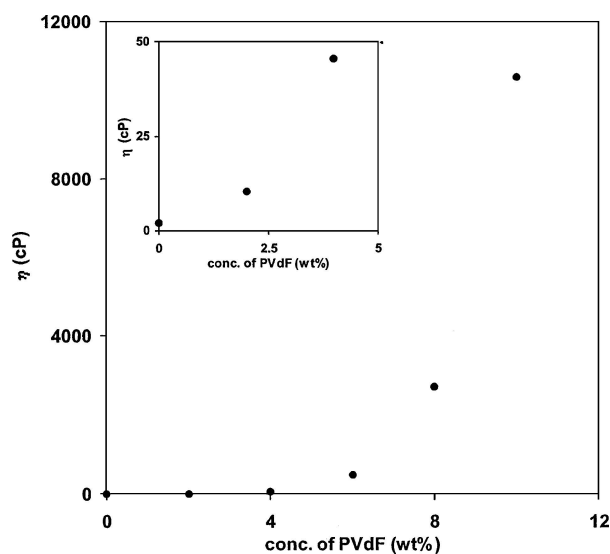


Figure 6 Variation of viscosity with PVdF concentration for gel electrolytes containing 0.25 M SA. Inset shows variation of viscosity at low PVdF concentrations.

PVdF concentration which is accompanied by an increase in conductivity which suggests that the polymer increases the free H^+ ion concentration by dissociating undissociated SA present in the electrolytes. However at high PVdF concentrations viscosity plays a dominant role and results in a decrease in conductivity as discussed earlier.

The role of viscosity of gel electrolytes at high PVdF concentrations was also studied by measuring the viscosity of electrolytes containing 0.25 M SA and the variation of viscosity with PVdF concentration is given in Fig. 6. The viscosity of gel electrolytes is quite low (<50 cP) at low polymer concentrations (1–5 wt%) as given in the inset of Fig. 6 and it rises exponentially at high PVdF concentration and attains a value of 1.05×10^4 cP at 10 wt% PVdF. The much higher viscosity at high PVdF concentrations results in a decrease in mobility and hence conductivity decreases whereas at low PVdF concentrations the viscosity is relatively low and does not play a dominant role. Thus from the variation of pH, viscosity and conductivity with PVdF concentration for gel electrolytes it has been

TABLE I Variation of conductivity with PVdF addition

Conc. of acid (M)	Change in conductivity with PVdF addition for gel electrolytes containing		
	Oxalic acid (OA)	Malonic acid (MA)	Succinic acid (SA)
0.10	+	+	+
0.25	+	+	+
0.50	-	+	+
1.00	-	-	+

(+)—increase in conductivity with PVdF addition.

(-)—decrease in conductivity with PVdF addition.

observed that the addition of PVdF results in an increase in free H^+ ion concentration at low PVdF concentrations which increases conductivity whereas at high PVdF concentrations, the viscosity is very high and results in a decrease in conductivity.

From above results it has been observed that the increase in conductivity of polymer gel electrolytes at low PVdF concentrations is due to an increase in free H^+ ion concentration due to the dissociation of undissociated acid present in these electrolytes. As the increase in conductivity with PVdF addition is related to the presence of undissociated acid in polymer gel electrolytes containing weak dicarboxylic acids so it was further studied by taking polymer gel electrolytes containing different concentrations (0–1 M) of OA, MA and SA i.e., containing different amounts of undissociated acids. The variation of conductivity of these gel electrolytes as a function of PVdF concentration was studied and the results are summarized in Table I. From the table, it has been observed that conductivity of gel electrolytes containing 0.1 and 0.25 M OA; 0.1, 0.25 and 0.5 M MA and 0.1, 0.25, 0.5 and 1 M SA increases with the addition of PVdF whereas at higher concentrations of these acids the conductivity shows a decrease with PVdF addition.

Literature reports on the variation of conductivity of polymer gel electrolytes containing various lithium salts as a function of polymer concentration shows that the addition of polymer increases the viscosity of gel electrolytes which lowers ionic mobility and as a result conductivity decreases [27]. The decrease in conductivity is generally small and is by a factor only not an order, which suggests that the polymer plays a passive role and acts as a stiffener only. However recent results on proton conducting polymer gel electrolytes containing weak acids show that the addition of polymer results in an increase in conductivity [23, 24, 28]. In such cases the polymer plays an active part in the conduction process and has been reported to enhance the free ion concentration by dissociating undissociated acid/ion aggregates present in these electrolytes. The conductivity results given in Table I could be explained as follows:

In the case of polymer gel electrolytes containing low concentrations (0.1 and 0.25 M) of OA, the acid is better dissociated due to relatively higher value of dissociation constant alongwith the presence of some undissociated acid. The addition of PVdF results in an increase in free H^+ ion concentration by dissociating undissociated OA alongwith a small increase in vis-

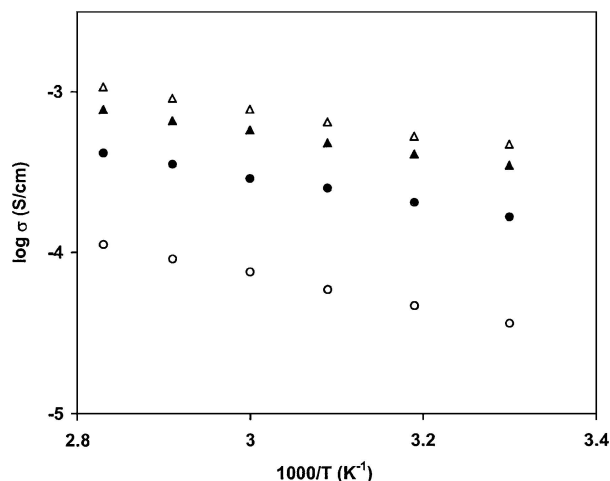


Figure 7 Variation of conductivity with temperature for liquid electrolytes containing 1 M OA (Δ) and 1 M SA (\circ) and corresponding gel electrolytes OA (\blacktriangle) and SA (\bullet) containing 10 wt% PVdF.

cosity. As viscosity at low PVdF concentrations is low so free ion concentration plays a dominant role and results in an increase in conductivity. However in the case of electrolytes containing high concentrations (0.5 and 1 M) of OA, the concentration of free H^+ ions is already large and the increase in free H^+ ion concentration by PVdF addition alongwith large increase in viscosity results in a net decrease in conductivity. The variation (increase/decrease) in conductivity of polymer gel electrolytes containing MA and SA could also be explained on similar lines. Thus results given in Table I indicate that the increase in conductivity with PVdF addition depends upon the concentration and dissociation constant of the dicarboxylic acid and the concentration of PVdF.

The variation of conductivity and viscosity of gel and the corresponding liquid electrolytes containing OA and SA was also measured as a function of temperature over the 20 to 80°C temperature range and the results are given in Fig. 7. The conductivity of gel electrolytes containing 1 M OA is lower than the corresponding liquid electrolytes whereas the conductivity of gel electrolytes containing 1 M SA is higher than the corresponding liquid electrolytes. The variation of conductivity with temperature for gel electrolytes is similar to that for liquid electrolytes which suggests liquid like behaviour of these gel electrolytes and the small increase in conductivity observed over the operational range of temperature is desirable from device point of view.

4. Conclusions

Polymer gel electrolytes containing weak aliphatic dicarboxylic acids show high conductivity of $\sim 10^{-3}$ S/cm at 25°C which depends upon the dissociation constant of the acid used. The addition of polymer (PVdF) results in an increase in conductivity which has been explained to be due to the dissociation of undissociated acid present in these electrolytes. The increase in free H^+ ion concentration with PVdF addition is also monitored by pH measurements. Viscosity has been found to play a dominant role at high PVdF concentrations.

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