

Role of polyvinyl alcohol in the conductivity behaviour of polyethylene glycol-based composite gel electrolytes

S K PATEL¹, R B PATEL¹, A AWADHIA¹, N CHAND² and S L AGRAWAL^{1,*}

¹Solid State Ionics Laboratory, Department of Physics, A.P.S. University, Rewa 486 003, India

²Regional Research Laboratory, Hoshangabad Road, Bhopal 462 026, India

*Corresponding author. E-mail: sla_ssi@rediffmail.com

MS received 6 July 2006; revised 2 May 2007; accepted 8 June 2007

Abstract. An attempt has been made in the present work to combine gel and composite polymer electrolyte routes together to form a composite polymeric gel electrolyte that is expected to possess high ionic conductivity with good mechanical integrity. Polyethylene glycol (PEG) based composite gel electrolytes using polyvinyl alcohol (PVA) as guest polymer have been synthesized with 1 molar solution of ammonium thiocyanate (NH_4SCN) in dimethyl sulphoxide (DMSO) and electrically characterized. The ionic conductivity measurements indicate that PEG:PVA: NH_4SCN -based composite gel electrolytes are superior ($\sigma_{\text{max}} = 5.7 \times 10^{-2} \text{ S cm}^{-1}$) to pristine electrolytes (PEG: NH_4SCN system) and conductivity variation with filler concentration remains within an order of magnitude. The observed conductivity maxima have been correlated to PEG:PVA: NH_4SCN - and PVA: NH_4SCN -type complexes. Temperature dependence of conductivity profiles exhibits Arrhenius behaviour in low temperature regime followed by VTF character at higher temperature.

Keywords. Polymer blend; gels; polymer-based composite; conducting polymers.

PACS Nos 83.35.cd; 82.70.Gg; 81.05.Qk; 82.35.Cd

1. Introduction

Polymer electrolytes have become prominent electrolyte materials in different types of electrochemical devices owing to their special properties like easy mouldability, light weight, flexibility, good electrode–electrolyte contact and adhesive property [1,2]. It has been shown that ionic conductivity of polymer electrolytes, attributed to the presence of amorphous phases, can be enhanced by adding plasticizer or through incorporation of a filler in the polymer matrix or by soaking liquid electrolyte (acid/salt solution) inside the reticulated polymer network [1–7]. Amongst these routes, though addition of plasticizer and dispersal of organic/inorganic fillers in the pristine polymer electrolytes have resulted in significant improvement in

amorphous phase and thus the conductivity, these routes of conductivity modification have not been commercially acceptable for applications in different electrochemical devices. Among the other approaches, gel formation techniques have become popular in recent years, as they offer an approach to attain high conductivity value approaching that of liquid electrolytes. On account of properties like high ionic conductivity and good adhesion, gel electrolytes have attained precedence over conventional polymer electrolytes. Although these gel polymer electrolytes have enough mechanical strength, there still remains the exudation problem of liquid electrolyte due to phase separation between the polymer matrix and an encapsulated liquid electrolyte. Recently, modified copolymers with two or more functional monomers have been suggested as a solution to the leakage problem of liquid electrolyte and further improvement in mechanical strength of gel electrolytes [8]. Some of the reported gel systems belonging to this category are poly(VC-AN), poly(MMA-VC), poly(styrene-AN) and poly(styrene-butadiene) [8-11]. Within this framework, an attempt has been made in the present work to develop a polyethylene glycol-based polymer composite gel electrolyte, namely, polyethylene glycol-polyvinyl alcohol-NH₄SCN system. This system has been studied on account of the fact that both polyethylene glycol (PEG) and polyvinyl alcohol (PVA) are separately reported to form highly amorphous complexes and gels with salts and acids [11-14].

Further, these polymers possess properties to form good miscible blends [15]. Thus in the present investigation, the effect of PVA (used as the third component) on the electrical performance of the system has been investigated through XRD, DSC and conductivity studies.

2. Experimental

2.1 Synthesis

In the present investigation, PEG (MW: 10000, Aldrich make), PVA (average MW: 85000-146000, Aldrich make), ammonium thiocyanate (NH₄SCN), AR grade, sd fine chem make and aprotic solvent dimethyl sulphoxide (DMSO) AR grade, sd fine chem make were used for synthesis of composite gels. PVA was dispersed in different stoichiometric ratios in pristine electrolyte (PEG:NH₄SCN system) keeping the molarity of liquid electrolyte (solution of NH₄SCN in DMSO) fixed at 1 M. Addition of the polymer to liquid electrolyte was carried out very slowly to form the homogeneous gel. After syneresis, gels in the form of thick films were taken out and dried at room temperature for few days to obtain stable gel electrolytes. The resulting gel films were stored carefully to avoid further exudation of solvent.

2.2 DSC studies

Differential scanning calorimetry of pristine materials as well as few gel electrolyte samples were performed with a scanning rate of 5 K min⁻¹ in a nitrogen purged

cell in the temperature range 298–523 K to assess their thermal behaviour and morphology.

2.3 X-ray diffractogram

X-ray diffractograms were obtained using Philips make diffractometer with Cu-K α ($\lambda = 1.544 \text{ \AA}$) radiation used for X-ray analysis of gel films to assess complexation behaviour and morphology.

2.4 Electrical measurements

The gel electrolytes were sandwiched between two platinum electrodes and electrical conductivity measurements were performed on a Hioki make LCR meter (Model 3520) in the frequency range 40 Hz–100 kHz at various temperatures ranging between 287 and 373 K.

3. Results and discussion

3.1 XRD analysis

Figure 1 depicts the XRD patterns of pristine materials PEG, PVA and NH₄SCN together with that of pure blend (65 : 35). The figure also shows the XRD pattern of PEG : NH₄SCN : PVA composite electrolytes for variable concentrations of PVA in the pristine complex (PEG : NH₄SCN). All the XRD patterns exhibit background modulation, generally observed in the case of polymeric systems. The relatively sharp characteristic peak at $2\theta = 19.6^\circ$ (curve c) in DMSO-casted PVA [11,16] and two peaks around $2\theta = 21^\circ$ and 22° related to pure PEG (curve b) were noticed. When the two components were added to form PEG : PVA blend (65 : 35 ratio), a relatively intense peak at $2\theta = 11.2^\circ$ was observed (curve d) showing interaction amongst components leading to occurrence of this peak and not assignable to components. Thus the presence of peak around 11.2° can be correlated to the formation of blend. Moreover, appearance of peak at lower 2θ value is probably on account of the affinity of PEG with PVA which makes it a good plasticizer for PVA [17,18]. When PVA is added to pristine PEG : NH₄SCN gel electrolyte to form composite gel system, the observed peaks appear to broaden upon increase of PVA content, signifying enhanced amorphous nature of gel film or the presence of excess liquid trapped within polymer blend matrix. It is further noticed that as the fraction of PVA in the pristine gel enhances, though there is insignificant change in 2θ value corresponding to characteristic peak of PEG, d -spacing increases slightly. This can be correlated to loosening of the macromolecular chains in the presence of PVA. PVA is known to form complexes with NH₄SCN [12,18]. Thus, a slight shift in 2θ values could be associated to interaction among components leading to the formation of PVA : NH₄SCN complex. The crystallite sizes related to pure PEG were evaluated [19] using the well-known Scherrer equation to assess the morphology of

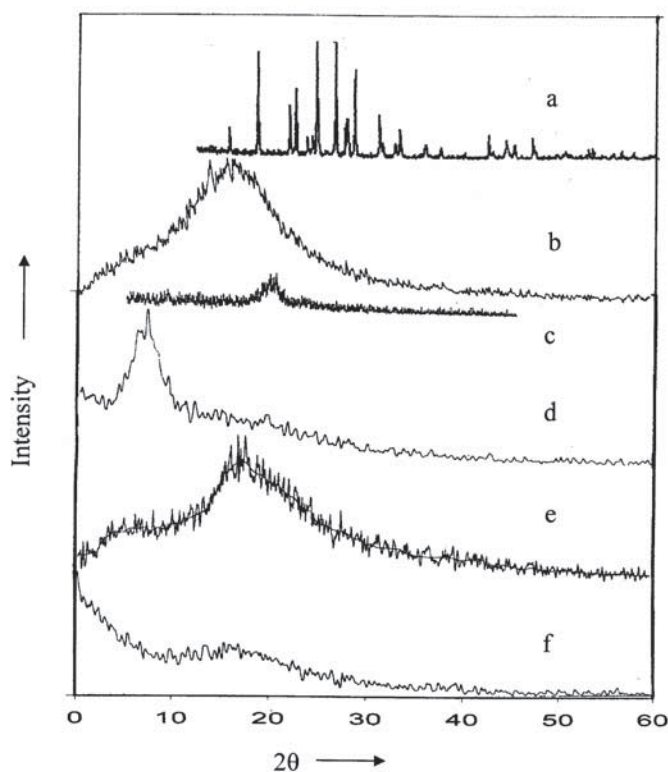


Figure 1. X-ray diffractograms of (a) NH_4SCN , (b) pure PEG, (c) DMSO casted PVA gel film, (d) PEG:PVA blend and gel electrolyte films of PEG-PVA- NH_4SCN with PEG-PVA ratio of (e) 70:30 and (f) 60:40.

gel electrolytes and listed in table 1. Low value of crystallite size (table 1) clearly advocates for highly amorphous nature of gel electrolytes under investigation.

3.2 DSC studies

Polymeric materials are known to exhibit both crystalline and amorphous phases simultaneously in variable amounts. One of the pertinent factors for miscibility of polymers to form compatible blends is that one of the components should be highly crystalline while the other highly amorphous [15]. Within this framework, polyethylene glycol being mostly crystalline is expected to show compatibility with polyvinyl alcohol. Figure 2 represents the DSC thermograms for NH_4SCN along with pure blend and synthesized composite gel electrolytes. Two shoulders (318 and 464 K) and two strong (324 and 411 K) melting endotherms were witnessed in the thermogram of PEG-PVA blend besides the appearance of a shoulder endotherm around 458 K related to the presence of unreacted DMSO in the samples (B.P. of DMSO = 453 K). The occurrence of shoulder around 318 K can be correlated

Table 1. Crystallite size and d -spacing of composite gels along with salt.

Sample	2θ	Crystallite size (Å)	d -spacing (Å)
Ammonium thiocyanate	14.6	50.8	6.07
Pure PEG	22	5.7	4.04
PVA film casted in DMSO	19.6	21.2	4.52
PEG:PVA Composite	11.2	16.06	7.89
Gel electrolyte containing 70:30 wt. ratio of PEG:PVA	21	7.13	4.22
Gel electrolyte containing 60:40 wt. ratio of PEG:PVA	20	5.97	4.23

to interaction of DMSO with PVA in the process of gel formation and has also been reported in the case of PVA–NH₄SCN–DMSO gels by Agrawal and Awadhia [14]. The observed endotherm at 324 K is on account of the melting of unblended PEG [11]. The broad endotherm around 411 K can be associated to the melting of PVA–DMSO gel mass as well as PVA–DMSO–PEG mass probably on account of interaction of PEG with both PVA and DMSO [18]. A small endotherm at 464 K is on account of the formation of PVA–PEG composites in small amounts. The disappearance of strong PVA melting peak suggests complete absorption of PVA in PEG matrix. However, careful examination of DSC curve (b) shows a slight shift of base line with the tendency of endothermic transition to suggest the presence of uncomplexed PVA in traces. Since composite polymer gel electrolytes are characterized by salt solution trapped within the polymeric network, thermal behaviour of gel electrolytes is expected to be affected on account of interaction between components and is evidenced in the present study as well. When 10 wt% of polymer (PEG+PVA) was added in the ratio 65:35 to 1 M ammonium thiocyanate electrolyte to form composite gel electrolyte, the endothermic transition in low temperature range 373–493 K become broad and shift towards higher temperature. Thus the observed broadness (393–433 K) can be assigned to co-existence of uncomplexed NH₄SCN, PEG–PVA–NH₄SCN–DMSO and PEG–PVA–DMSO gel mass discussed earlier. The broad endothermic transition around 493 K indicates the melting of PEG–PVA–NH₄SCN complex, along with melting of uncomplexed PVA. The disappearance of low temperature endothermic transitions represents complete solvation of PEG with NH₄SCN/PVA leading to the formation of single phase system.

3.3 Conductivity studies

The variation of ionic conductivity of liquid electrolytes as a function of salt concentration is shown in figure 3. The optimum conductivity of liquid electrolyte was found to be 1.5×10^{-2} S cm⁻¹ for 1 M solution. Dimethyl sulphoxide is a highly aprotic solvent and ammonium thiocyanate is likely to dissociate into respective ions in this solution [20] which is reflected by the high conductivity value. The

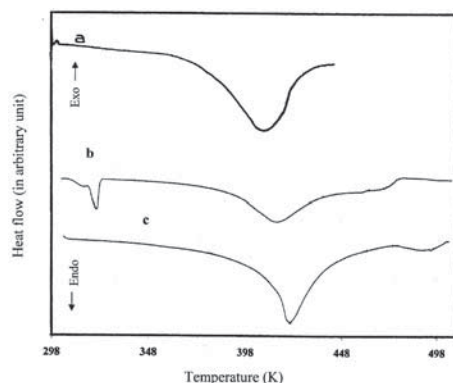


Figure 2. DSC thermograms of (a) ammonium thiocyanate, (b) gel films of PEG : PVA blend and (c) PEG : PVA : NH_4SCN composite gel electrolyte.

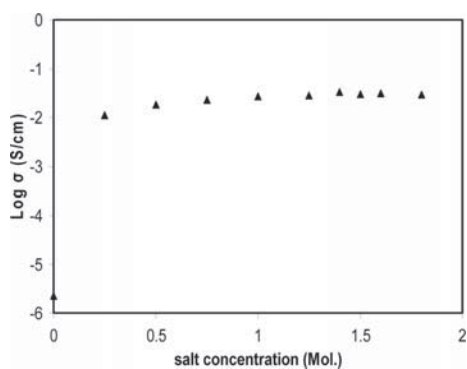


Figure 3. Variation of ionic conductivity of liquid electrolyte as a function of salt concentration.

behaviour of liquid electrolyte can be best described by the well-known Walden's rule [16]. The initial increase can be related to significant increase in the number of ions as a result of dissociation of salt. However, after the conductivity optimum, the observed fall in conductivity is due to increase in viscosity of the system.

PEO-based composite polymer electrolyte with dispersed inorganic/organic fillers have been extensively studied by Wiczorek and coworkers in recent years [5,6]. It is concluded from their investigations that the dispersed filler in the composite polymer electrolyte not only serves the purpose of phase modifier but also actively participates in the complexation process on account of ion-dipole interactions between the salt ions and the heteroatom on the filler following Lewis acid-base theory. Similar observations have also been reported for PVA-PVAc- NH_4SCN composite electrolytes by Shukla and Agrawal [7]. In the present system, PVA used as a soft filler forms partially miscible blend with host PEG as discussed earlier. Further, both PEG and PVA have been reported to form complexes with NH_4SCN [12,21]. It is recently observed [22] that PVA also forms coordinating complex with DMSO. This may lead to the formation of four types of complexes in the system, namely,

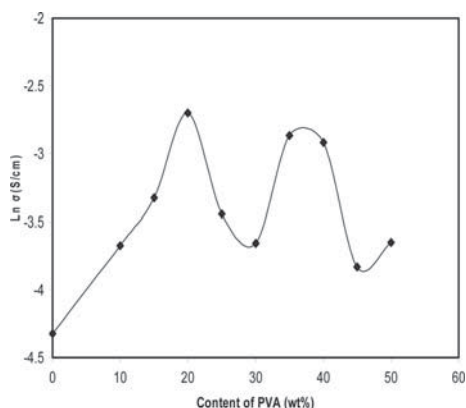


Figure 4. Variation of ionic conductivity of composite gel electrolyte as a function of PVA concentration in wt%.

(i) Type-I: PVA : DMSO complex, (ii) Type-II: PVA : NH_4SCN complex, (iii) Type-III: PEG : NH_4SCN complex and (iv) Type-IV: PEG : PVA : NH_4SCN complex. The formation of Type-I and Type-II complexes in PVA : DMSO : NH_4SCN gel electrolytes have been studied by Agrawal and Awadhia [14]. DSC studies of composite gel electrolyte have not revealed the presence of Type-III complex in the composite system in the range of temperatures scanned. Hence only Type-I, II and IV complexes are expected to contribute to ionic conduction. Figure 4 depicts the isothermal variation in conductivity of (PEG : NH_4SCN) : PVA composite polymer gel electrolytes with PVA concentration in the complex for a fixed molarity of salt. It has been shown by Awadhia [23] that there is a significant increase in the conductivity of PVA–DMSO complex. However, this enhancement is not significant enough to explain the appearance of two conductivity maxima with further increase in the order of magnitude noticed in figure 4. Therefore, the observed behaviour of σ_{RT} can be explained on the basis of Type-IV and II complexes. PVA is known for its solvent swollen characteristics [17]. Due to this character, the solvent holding capacity of gel electrolytes is enhanced in PVA-rich regions of the gel. As a consequence, conductivity of as-synthesized gel is quite likely to augment. However, beyond 20 wt% of PVA in the gel, a dip is noticed which can be associated to the increase in viscosity of system as well as buildup of tortuous path for the otherwise conducting ionic specie. Beyond 30 wt% of PVA in the composite gel again an increase is observed that can be linked to the formation of PVA– NH_4SCN complex. Thus the second conductivity maxima is probably associated to the behaviour of PVA– NH_4SCN complex plasticized by PEG.

3.4 Temperature dependence of conductivity

Figure 5 shows the temperature dependence of conductivity of composite gel electrolytes (CGE) prepared in 1 M NH_4SCN solution and containing different wt% of PVA. All the curves display similar behaviour, i.e. a combination of VTF and Arrhenious behaviour. Arrhenious region is noticed in low temperature regime while

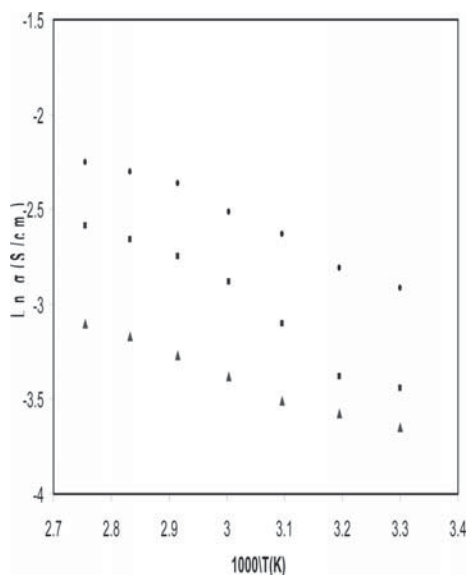


Figure 5. Temperature dependence of composite gel electrolytes with (■) 25 wt%, (●) 40 wt%, (▲) 50 wt% PVA content with respect to total polymer content.

VTF nature is exhibited at higher temperature. The low-temperature Arrhenius behaviour is possibly due to the presence of liquid electrolyte encapsulated by the blend matrix, i.e. effect of temperature on conductivity of liquid electrolytes. As the temperature of the system is raised further beyond 313 K, polymeric nature starts affecting conductivity leading to VTF nature described by the relation

$$\sigma = \sigma_o \exp\left(\frac{-B}{T - T_o}\right), \quad (1)$$

where σ_o is the pre-exponential factor, B is a constant related to activation energy and $T_o (= T_g - 60^\circ\text{C})$ is the quasi-equilibrium glass transition temperature.

4. Conclusion

A new type of polymeric gel electrolyte based on polymer composites has been reported in the present work, viz. PEG-PVA-NH₄SCN. The XRD and DSC studies reveal complexation of salt with the polymer with increase in amorphous nature (extremely small value of crystallite size) upon the addition of polymer. The ionic conductivity studies indicate that NH₄SCN-based composite gel electrolytes are superior ($\sigma_{\text{max}} = 5.7 \times 10^{-2} \text{ S cm}^{-1}$) to pristine electrolytes with the wide temperature window.

Acknowledgements

Authors are grateful to UGC, New Delhi for the financial support in the form of a minor research project. Authors are thankful to the University of Hyderabad for providing XRD facility.

References

- [1] F M Gray, *Solid polymer electrolytes*, in: *Fundamentals and technological applications* (VCH, New York, 1991)
- [2] W Wieczorek, K Such, S H Chung and J R Stevens, *J. Phys. Chem.* **98**, 9047 (1994)
- [3] S S Sekhon, *Bull. Mater. Sci.* **26**, 321 (2003)
- [4] A Chandra and S Chandra, *Bull. Electrochem.* **11**, 88 (1995)
- [5] W Wieczorek, K Such, Z Florjanczyk and J R Stevens, *Electrochim. Acta* **40**, 2417 (1995)
- [6] W Wieczorek, K Such, S H Chung and J R Stevens, *J. Phys. Chem.* **98**, 6840 (1994)
- [7] S L Agrawal and P K Shukla, *Ionics* **6**, 312 (2000)
- [8] B Oh, Y K Sun and D W Kim, *Bull. Korean Chem. Soc.* **22**, 1136 (2001)
- [9] M Yamazaki, Y Soji, S Yoshimura, K Nishio and T Saito, Sanyo Electric Co., Japanese Patent Publication, No. 07, 320781 (1995)
- [10] T Ichino, Y Takeshima, M Takeshima and S Nishi, NTT Co., Japanese Patent Publication, **07**, 335258 (1995)
- [11] Th Joykumar Singh and S V Bhat, *Bull. Mater. Sci.* **26**, 707 (2003)
- [12] P K Shukla and S L Agrawal, *Ind. J. Pure Appl. Phys.* **38**, 53 (2000)
- [13] P N Gupta and K P Singh, *Proc. 10th International Conference on Solid State Ionics* edited by B V R Chowdari (North Holland, Amsterdam, 1995) p. 317
- [14] S L Agrawal and Arvind Awadhia, *Bull. Mater. Sci.* **27**, 523 (2004)
- [15] D R Paul and S Newman (Eds), *Polymer blends* (Academic Press, New York, 1978) Vol. 1
- [16] A Awadhia, S K Patel, R B Patel and S L Agrawal, *Electroactive polymers: Materials and devices* edited by N Khare, S A Hashmi, Amita Chandra and Amreesh Chandra, Series ed. Suresh Chandra (Allied Publishers, New Delhi, 2006) vol. 1, p. 115
- [17] C A Finch, *Polyvinyl alcohol, properties and applications* (Wiley & Sons, New York, 1973)
- [18] Ke-cheng Gong and Huang Shou-Cai, *Mat. Res. Soc.* **135**, 377 (1989)
- [19] B D Cullity, *Elements of X-ray diffraction* (Wesley Publishing Company, Inc., London, 1978)
- [20] M Deepa, N Sharma, Pradeep Varshney, R Chandra and S A Agnihotry, *Ion conducting materials: Theory and applications* edited by A R Kulkarni and P Gopalan (Narosa Publishing House, New Delhi, 2001) p. 74
- [21] Nader Binesh and S V Bhat, *Extended abstract*, SSI-10, Singapore 235 (1995)
- [22] Arvind Awadhia and S L Agrawal, *Solid State Ionics* **178**, 951 (2007)
- [23] A Awadhia, *Studies on ion conducting polymer gel electrolytes*, Ph.D. Thesis, A.P.S. University, Rewa (2006)