CHAPTER - 3

ION TRANSPORT STUDY ON A NEW Ag⁺ ION CONDUCTING 2-PHASE COMPOSITE ELECTROLYTE SYSTEM: \((1-x)[0.75\text{AgI} : 0.25\text{AgCl}] : x\text{SiO}_2\)

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3.1 Introduction

This chapter deals with the ion transport characterization studies on a new Ag⁺ ion conducting 2-phase composite electrolyte system: \((1-x)[0.75 \text{ AgI} : 0.25 \text{ AgCl}] : x\text{SiO}_2\). The details on preparation sequences and the measurement procedures have been given earlier in Chapter 2. Nano size (~8nm) particles of insulating and insoluble SiO₂ were dispersed, as second phase dispersoid particles into the newly synthesized alternate first phase host compound: "a quenched/annealed \([0.75 \text{ AgI} : 0.25 \text{ AgCl}]\) mixed system/solid solution", in place of conventional host AgI. The composite electrolyte system \((1-x)\text{AgI} : x\text{SiO}_2\) of similar compositions were also prepared in the identical manner using AgI, just to enable a direct comparison of room temperature conductivity with those of newly synthesized composite systems. Shahi and Wagner [1982] also reported 2-phase electrolyte system: \((1-x)\text{AgI} : x\text{SiO}_2\) using different purity chemicals and dispersoid particle sizes. The composition: \(0.9[0.75 \text{ AgI} : 0.25 \text{ AgCl}] : 0.1\text{SiO}_2\), exhibited the highest enhancement (~\(10^4\)) in the room temperature conductivity (\(\sigma_{RT}\)) from that of the pure host and has been referred to as ‘Optimum Conducting Composition (OCC)’ with \(\sigma_{RT} \sim 10^{-3}\) S.cm⁻¹. The co-existence of constituent phases in OCC was confirmed by X-ray diffraction (XRD) and differential scanning calorimetry (DSC) studies. Various ionic transport parameters viz. conductivity (\(\sigma\)), mobility (\(\mu\)), mobile ion concentration (\(n\)), transference number (\(t_{\text{ion}}\)) and drift velocity (\(v_d\)) of the conducting ion were measured experimentally as a function of temperature. Thermoelectric power (TEP) measurements were also carried out on OCC which provided a further insight to understand the transport mechanism. The results have been explained on the basis of theories proposed for 2-phase composite electrolyte systems.

3.2 Results and Discussion

3.2.1 Compositional variation of room temperature conductivity: influence of preparation route and soaking time

Fig.3.1 shows the compositional variation of room temperature conductivity (\(\sigma\)) of the composite system: \((1-x)[0.75 \text{ AgI} : 0.25 \text{ AgCl}] : x\text{SiO}_2\) where \(x = 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5\) in molar weight fraction, prepared by adopting routes #1-3, discussed earlier in Section 2.2. A similar
Fig. 3.1: Compositional variation of room temperature conductivity for the composite electrolyte system: (1-x)[0.75AgI : 0.25AgCl] : 0.1 SiO₂ (□, △, □) and for (1-x)AgI : xSiO₂ (●). Number (#1-3) corresponds to preparation routes (see the text Section 2.2).
variation for the composite system: (1-x)AgI:xSiO₂, prepared by route #3, using the conventional salt AgI as host matrix, has also been plotted in Fig. 3.1, for direct comparison of room temperature conductivity values. The $\log \sigma$ vs x' variations are almost akin to those reported earlier for the composite systems: (1-x)[0.75AgI:0.25AgCl]:xAI₂O₃ & (1-x)[0.75AgI:0.25AgCl]:xSnO₂ [Agrawal and Gupta 1995, 1996, 1997]. Majority of the 2-phase composite electrolyte systems exhibit similar behavior i.e. the room temperature conductivity increases initially as the composition increases, attains a peak value then decreases and can be explained on the basis of percolation model [Bunde et al. 1985, 1986; Roman et al. 1985, 1986, Bunde 1995]. Some significant features of the present study are the following:

- Both the composite systems, prepared using new and conventional hosts, exhibited the conductivity enhancement at the same compositional ratio. However, a better enhancement has been achieved with the new host salt as obvious from Fig. 3.1. This is probably due to the fact that the new host exhibits superior transport properties than AgI, as reported by Agrawal & coworkers [Agrawal et al. 1994b, 1995]. Moreover, the dispersion of nano-size particles of SiO₂ in the new host salt yielded better solid electrolyte system as compared to other two dispersoids Al₂O₃ and SnO₂ reported earlier [Agrawal and Gupta 1995, 1996, 1997].

- The optimum conductivity value is obtained for the composition 0.9[0.75AgI:0.25AgCl]:0.1SiO₂. This is akin to that reported by Shahi and Wagner [1982] for 0.9AgI : 0.1SiO₂ composite system, although the room temperature conductivity value of their system is slightly different probably due to the reason that different purity of starting materials were used.

- No marked preparation-route-dependence in the room temperature conductivity values were observed. However, the composition : 0.9[0.75AgI:0.25AgCl]:0.1SiO₂, prepared by route #3 with 20 min soaking time, exhibited the highest conductivity ($\sigma_{27^\circ C} \sim 10^{-3}$ S.cm⁻¹) with an enhancement of $\sim 10$ times from the annealed host and $\sim 3$ times from the quenched host. This composition has been referred to as 'optimum conducting composition (OCC)'.

In the earlier studies [Uvarov et al. 1990; Shastry and Rao 1992; Agrawal and Gupta 1995, 1996, 1997], it was observed that the soaking time (i.e. time for which the sample is heated $\sim 700^\circ C$ during the preparation), influences the physical property and ionic conductivity.
of the composite system. To study the effect of soaking time on the conductivity, samples of OCC were prepared by route #3 for different soaking times. Fig. 3.2 shows the variation of room temperature conductivity as a function of soaking time. This variation is identical to those reported earlier for other two composite systems: 0.7[0.75AgI : 0.25AgCl] : 0.3Al2O3 & 0.8[0.75AgI : 0.25AgCl] : 0.2SnO2 [Agrawal and Gupta 1995, 1996, 1997], and can be explained on the similar lines. The conductivity increased as the soaking time increased, attained a peak value for 20 min soaking time, then decreased as the soaking time is increased further. The low conductivity values obtained at lower and higher soaking times are probably due to incomplete dispersal reaction and/or some stoichiometric changes.

3.2.2 Phase identification/material characterization: X-ray diffraction (XRD) and differential scanning calorimetric (DSC) analysis

It is well known that in a 2-phase composite system, the constituent phases coexist separately and the dispersal of the second phase dispersoid particle into the first phase host-matrix does not introduce any chemical and/or structural changes into either of the two phases. The existence of two separate phases has been confirmed by the phase identification/material characterization studies on OCC : 0.9[0.75AgI:0.25AgCl]:0.1SiO2 using XRD and DSC techniques, as mentioned in Section 2.2. Fig.3.3(a&b) shows the X-ray diffraction patterns of OCC : 0.9[0.75AgI:0.25AgCl] : 0.1SiO2 and fumed SiO2. The peaks in Fig. 3.3a correspond to the characteristic reflection peaks of pure quenched host : [0.75AgI:0.25AgCl], as reported earlier [Agrawal et al 1995; Agrawal and Gupta 1997]. The broad diffuse peak of Fig. 3.3b indicates the amorphous nature of fumed SiO2 of nano-size particles. Fig. 3.4 shows the DSC plot for OCC : 0.9[0.75AgI : 0.25AgCl] : 0.1SiO2. The endothermic peak at \( \sim 135 ^\circ C \) exactly corresponds to \( \beta \rightarrow \alpha \) like phase transition of the host as reported earlier by Agrawal & coworkers [Agrawal et al 1994b, 1995; Agrawal and Gupta 1997]. Hence, on the basis of XRD & DSC studies it can be obviously concluded that OCC : 0.9[0.75AgI : 0.25AgCl] : 0.1SiO2 is a 2-phase composite electrolyte system.
Fig. 3.2: Room temperature conductivity as a function of soaking time for optimum conducting composition $0.9[0.75\text{AgI} : 0.25\text{AgCl}] : 0.1\text{SiO}_2$ (prepared by route #3).
Fig 3.3: XRD diffraction patterns: (a) OCC: 0.9[0.75AgI:0.25AgCl]:0.1SiO₂ and (b) dispersoid compound: SiO₂ (fumed).

Fig 3.4: DSC plot for OCC: 0.9[0.75AgI:0.25AgCl]:0.1SiO₂.
3.2.3 Temperature dependence of ionic parameters: \( \sigma', \mu', n', \theta' \) studies

3.2.3a \( \sigma'- \) measurement

Fig. 3.5 shows log \( \sigma \) vs 1/\( T \) Arrhenius plots for different compositions \( x' \) of composite electrolyte system: \((1-x)[0.75\text{AgI} : 0.25\text{AgCl}] : x\text{SiO}_2\), prepared by route #3. Similar plot for pure annealed/quenched host: \([0.75\text{AgI} : 0.25\text{AgCl}]\) has been reproduced from the earlier work [Agrawal et al. 1994b] for direct comparison. The regions (I & II) in the figure refer to the stable \( \beta^- \) & \( \alpha^- \)-like phases of the host salt separated by an unstable transition region. The linear variations of Fig. 3.5 can be expressed by following Arrhenius equation (eq. 1.7):

\[
\sigma(T) = \sigma_a \exp\left(-\frac{E_a}{kT}\right)
\]

where \( \sigma_a \) is the pre-exponential factor and \( E_a \) is the activation energy. The activation energy \( (E_a) \) values were computed from the slopes of \( \log \sigma \) vs 1/\( T \) plots in the temperature region (27-110 °C) using least square fitting method and plotted as an inset in this figure for different compositions. It can be noted that \( E_a \) is minimum for OCC. Some significant features of this study are:

- The conductivity variation at room temperature for different composition \( x' \) is akin to \( \sigma' \) vs \( x' \) variation of Fig. 3.1 which is clearly visible in the region - I. Maximum enhancement in the conductivity is exhibited for 2-phase composite electrolyte system: \((1-x)[0.75\text{AgI} : 0.25\text{AgCl}] : x\text{SiO}_2\) and is achieved only at room temperature. This has been referred to as OCC. The magnitude of enhancement decreased as the temperature increased.

- \( \log \sigma \) vs 1/\( T \) variation of OCC is almost identical to those of the host salts (annealed & quenched) in both the temperature regions (I & II).

- In the temperature region (region-II), the conductivity values of OCC as well as other compositions have been substantially reduced as compared to those for the pure host salt. This is again a usual behavior observed in majority of 2-phase composite electrolyte systems and reason for lowering of the conductivity is attributed to the blocking effect of dispersoid particles.

These features are very common and witnessed in the majority of two-phase composite electrolyte systems [Agrawal and Gupta 1999]. The high room temperature conductivity with low
Fig. 3.5: 'Log $\sigma$ vs $1/T$' Arrhenius plots for various compositions of composite electrolyte system: $(1-x)[0.75\text{AgI}:0.25\text{AgCl}] : x\text{SiO}_2$ prepared by route #3. $(x = 0.05(\Delta), 0.1(\circ), 0.15(\square), 0.2(\triangledown), 0.3(\times), 0.4(\blacktriangle), 0.5(\blacktriangledown)$ and pure annealed (X)/quenched (●) host].

Inset: variation of activation energy ($E_a$) as a function of $x$ in temperature region-I.
activation energy for OCC: 0.9 [0.75AgI:0.25AgCl]: 0.1 SiO₂ is indicative of an easy ion transport. The reason for the conductivity enhancement at room temperature can be attributed either to the increased mobile ion concentration at the host/dispersoid double-layer interface or to the increased ionic mobility as a result of creation of conducting paths inter-connecting the different phase boundaries [Jow and Wagner 1963; Maier 1985; Dudney 1985; Bunde et al. 1985; Uvarov et al. 1992; Shaju and Chandra 1995; Agrawal and Gupta 1999].

3.3.2b ‘μ’ & ‘n’ measurements
To identify the exact reason for the conductivity enhancement in OCC at room temperature, a direct determination of ionic mobility (μ) has been done using transient ionic current (TIC) technique. Subsequently, mobile ion concentration (n) has been evaluated by substituting ‘σ’ and ‘μ’ data in the eq. (1.6): σ = n.q.μ. The details on TIC technique have already been discussed in Chapter 2. ‘σ’, ‘μ’ and ‘n’ values obtained for OCC at room temperature are listed in the Table 3.1 along with those for the pure host-salt. On comparing these parameters one can obviously note that the ionic mobility of OCC is approximately an order of magnitude higher than that of the host-salt while the mobile ion concentration for both composite electrolyte and host-salt are almost same. This is indicative of the fact that the increase in ‘μ’ is predominantly responsible for the enhancement in the room temperature conductivity of OCC. This seems logical also. Due to nano-size particles of SiO₂ with very large surface area (~325 m² gm⁻¹), the space-charge interface regions are also large which resulted into intergrain connectivity and/or creation of high conducting paths, and in turn increase in the ionic mobility.

As already mentioned in Chapter 1, the ionic transport parameters σ, n, μ are temperature dependent quantities and can be related with each other as in eq. (1.6) [Agrawal and Gupta 1999]. The thermally activated behavior of ‘σ’ is expressed by the eq. (1.7), while those of ‘n’ & ‘μ’ can be expressed by Arrhenius type equations (eqs. 1.8 & 1.9):

\[
n(T) = n_0 \exp\left(\frac{-E_r}{kT}\right)
\]

\[
μ(T) = μ_0 \exp\left(\frac{-E_m}{kT}\right)
\]

where \(n_0\) & \(μ_0\) are the pre-exponential factors, ‘\(E_r\)’ & ‘\(E_m\)’ are the energies involved in the two different thermal activated processes. ‘\(E_r\)’ & ‘\(E_m\)’ defined as energies of formation ‘and
migration of mobile ions respectively, can be related with \( E_s \) by following energy equation (1.10):

\[
E_s = \pm E_r \pm E_m
\]

As mentioned, the (-)ve & (+)ve signs in the arguments of above exponentials correspond to the increase & decrease respectively of the factors on the left hand side of the equations with the increase in temperature. 'E_m' & 'E_r' have been experimentally evaluated from the temperature dependent studies on 'n' & 'n'. Fig. 3.6 shows 'log \( \mu \) vs 1/T' and 'log n vs 1/T' Arrhenius plots for OCC : 0.9 [0.75AgI : 0.25AgCl] : 0.1 SiO_2. 'Log \( \sigma \) vs 1/T' plot of OCC in Fig. 3.5 for the OCC has been reproduced in Fig. 3.6. One can obviously note that both '\( \mu \)' & 'n' increased very slowly initially with increasing temperature upto \(-100^\circ C\) in region-I, followed by rapid decrease in '\( \mu \)' and increase in 'n' in the transition region, and then both remained almost independent of temperature in region-II. Variations of analogous nature were reported by Agrawal and coworkers earlier for composite systems : 0.7[0.75AgI : 0.25AgCl] : 0.3Al_2O_3 & 0.8[0.75AgI:0.25AgCl]:0.2SnO_2 [Agrawal and Gupta 1995, 1997]. The rapid change in '\( \mu \)' & 'n', well ahead of \( \beta \rightarrow \alpha \)-like phase transition temperature (~135 \( ^\circ C \)) of the host, has been attributed to as pre-transition effect, as before. The decrease in '\( \mu \)' in region-II is due to the structural narrowing of the \( \alpha \)-like phase of the host as well as the blocking effect of dispersoid particles, while increase in 'n' is due to the availability of a large number of equienergetic mobile Ag ions in the \( \alpha \)-like phase of the host. The increase in 'n' not only compensated the decrease in '\( \mu \)' but resulted in an overall increase in \( \sigma \) in the region-II.

The linear variations of '\( \mu \)' & 'n' in Fig. 3.6 give following Arrhenius equations:

\[
\mu = 7.8 \times 10^{11} \exp(-0.037/kT) \text{ [cm}^2\text{V}^{-1}\text{s}^{-1}] \text{ Region-I}
\]

\[
n = 2.5 \times 10^{17} \exp(-0.053/kT) \text{ [cm}^3 \text{]} \text{ (27-100 \( ^\circ C \))}
\]

\[
\mu = 1.3 \times 10^{13} \exp(0.083/kT) \text{ [cm}^2\text{V}^{-1}\text{s}^{-1}] \text{ Region-II}
\]

\[
n = 8.1 \times 10^{21} \exp(-0.253/kT) \text{ [cm}^3 \text{]} \text{ (180-215 \( ^\circ C \))}
\]

where \( E_m \sim 0.037 \text{ eV} \) & \( E_r \sim 0.053 \text{ eV} \) in \( \beta \)-like phase (region-I) and \( E_m \sim -0.083 \text{ eV} \) & \( E_r \sim -0.253 \text{ eV} \) in \( \alpha \)-like phase (region-II). The energy values along with relevant pre exponential factors are
Table 3.1: Room temperature conductivity, ionic mobility and mobile ion concentration of pure (annealed & quenched) host and optimum conducting composition (OCC): \[0.9(0.75\text{AgI}: 0.25\text{AgCl}) : 0.1\text{SiO}_2\].

<table>
<thead>
<tr>
<th>Material</th>
<th>Ionic conductivity (\sigma_{27^\circ C}) (S.cm(^{-1}))</th>
<th>Ionic mobility (\mu_{27^\circ C}) (cm(^2).V.s(^{-1}))</th>
<th>Mobile ion conc. (n_{27^\circ C}) (cm(^{-3}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Host compound</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[0.75AgI : 0.25AgCl] (annealed)</td>
<td>1.0x10(^{-4})</td>
<td>(1.5±1)x10(^{-2})</td>
<td>4.0x10(^{16})</td>
<td>Agrawal et al. 1994b</td>
</tr>
<tr>
<td>[0.75AgI : 0.25AgCl] (quenched)</td>
<td>3.1x10(^{-4})</td>
<td>(2.4±1)x10(^{-2})</td>
<td>8.0x10(^{16})</td>
<td>Agrawal et al. 1994b</td>
</tr>
<tr>
<td>Composite system</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.9[0.75AgI:0.25AgCl]:0.1SiO(_2)</td>
<td>1.0x10(^{-3})</td>
<td>(1.4±1)x10(^{-1})</td>
<td>4.4x10(^{16})</td>
<td>present study</td>
</tr>
</tbody>
</table>

Fig. 3.6 ‘Log \(\mu\) vs 1/T’ and ‘log \(n\) vs 1/T’ Arrhenius plots for OCC: \[0.9(0.75\text{AgI}: 0.25\text{AgCl}) : 0.1\text{SiO}_2\]. ‘Log \(\sigma\) vs 1/T’ plot of Fig. 3.5 for the OCC has been reproduced.
listed in Table 3.2. Both $E_m$ and $E_r$ values for the OCC are substantially lower than those of the host salt ($E_m = -0.17 \text{ eV}$ & $E_r = -0.07 \text{ eV}$ [Agrawal et al. 1994b]). Hence, it further substantiates our argument that the transport of mobile ions occur with relative ease in the composite electrolyte as compared to the pure host salt. Substituting ‘$E_m$’ & ‘$E_r$’ values in the above energy equation, we obtain $E_s = -0.09 \text{ eV}$ (region-I) & $-0.17 \text{ eV}$ (region-II) which are in close agreement with the $E_s$-values obtained from ‘log $\sigma$ vs $1/T$’ plot of the OCC (Fig. 3.5) in the temperature regions I & II respectively.

### 3.2.3c $t_{\text{ion}}$ & $v_{\text{d}}$ measurements

The above experimental results are well supported by temperature dependent studies on ionic transference number ‘$t_{\text{ion}}$’ using Wagner’s dc polarization method. As discussed earlier in Chapter 2, the transference number gives a quantitative measure of the ionic and electronic contributions to the total conductivity in a system. A dc potential ($-0.5 \text{ V}$) was applied across the pellets of OCC sandwiched between blocking (graphite) and non-blocking (silver-metal) electrodes and the current was monitored with time. Since, this system exhibits $\beta \rightarrow \alpha$- like phase transition, the study was carried out in both the temperature regions (I & II). Fig. 3.7 shows the ‘current vs time’ plots recorded at various temperatures. Some important features of these studies are:

- The initial value of total current ($I_T$) approaches zero which is indicative of the fact that the system remained purely ionic ($t_{\text{ion}}=1$) at all temperatures of measurement.

#### Table 3.2: Pre-exponential factors ($\sigma_o$, $\mu_o$, $n_o$) and energy values ($E_s$, $E_m$, $E_r$) for the optimum composition (OCC) : $0.9[0.75\text{AgI:0.25AgCl}]\cdot0.1\text{SiO}_2$.

<table>
<thead>
<tr>
<th>$\sigma = \sigma_o \exp(-E_s/kT)$</th>
<th>$\mu = \mu_o \exp(-E_m/kT)$</th>
<th>$n = n_o \exp(-E_r/kT)$</th>
<th>Temp. range</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_o$</td>
<td>$E_s$ (eV)</td>
<td>$\mu_o$</td>
<td>$E_m$ (eV)</td>
</tr>
<tr>
<td>0.04</td>
<td>0.096</td>
<td>7.8x10^{-4}</td>
<td>0.037</td>
</tr>
<tr>
<td>10.09</td>
<td>0.152</td>
<td>1.3x10^{-3}</td>
<td>-0.053</td>
</tr>
</tbody>
</table>
Fig. 3.7: 'Current vs time' plot at various temperatures (given in the parenthesis) for OCC: 0.9[0.75AgI:0.25AgCl]: 0.1SiO$_2$
• The magnitude of initial current \( I_T \) increases as the temperature is increased. This, in turn, indicates that \( n \) increases with increasing temperature, hence, supports our result on \( \log n \) vs \( 1/T \) variation.

• The polarization time (i.e. the time at which the total current approaches to zero) increased with increasing sample temperature. This is an expected behavior. At higher temperatures, the mobile ions are relatively more thermally agitated than at lower temperatures; hence, longer time duration would be required for them to get polarized at a constant fixed potential as compared to those at lower temperatures.

• An abrupt jump in the \( I_T \) was observed in region-II i.e. after \( \beta \rightarrow \alpha \)-like phase transition. This may either due to an abrupt increase in \( n \) or ionic drift velocity \( v_d \) as obvious from the following equation (eq.1.11):

\[
I_T = n q v_d A
\]

where \( A \) is the cross sectional area of the sample pellet and \( q \) is the charge on the mobile ion. Substituting \( n \) (from Fig.3.6) and initial total current \( I_T \) (from Fig. 3.7) in the above equation, \( v_d \)-values have been calculated at various temperatures. Fig.3.8 shows \( \log v_d \) vs \( 1/T \) plot for the OCC. The equation governing the thermally activated behavior of \( v_d \) in the temperature regions I \& II can be expressed as :

\[
v_d = 1.2 \times 10^{-1} \exp(-0.040/kT) \quad \text{[cm.s}^{-1}] \quad \text{Region-I (27-100 °C)}
\]

\[
v_d = 5.0 \times 10^{-6} \exp(+0.082/kT) \quad \text{[cm.s}^{-1}] \quad \text{Region-II (165-210 °C)}
\]

where 0.040 and -0.082 eV in the arguments of two exponentials correspond to the energy \( (E_d) \)-values involved in the above thermally activated process in the temperature regions (I \& II) respectively. At a constant dc electric field across the sample, the ionic drift velocity is directly proportional to the ionic mobility. Thus, \( \log v_d \) vs \( 1/T \) variation should be identical to \( \log \mu \) vs \( 1/T \) and the energies \( E_d \) and \( E_m \) involved in the two separate thermal processes would be same. On comparing the plots of Figs. 3.6 \& 3.8, one can obviously note that the two variations are almost analogous and \( E_d \)-values are very close to \( E_m \)-values in both the regions (I \& II).

A little deviation in the two values can be attributed to the reasons that due to the finite response time of the x-y-t recorder the initial current can not be measured accurately at \( t = 0 \) s. Similar results were obtained earlier for number of \( Ag^+ \) ion conducting systems [Agrawal and Kumar 1994, 1996; Agrawal et al. 1996a,b, 1998a; Agrawal and Gupta 1997]. It is also obvious once
again from Fig. 3.7 that an abrupt increase in the initial current and hence, in \( \sigma' \), after \( \beta \rightarrow \alpha \)-like phase transition is predominantly due to increase in \( 'n' \).

While calculating \( 'v_d' \) it was assumed that the initial total current \( 'I_I' \) is directly proportional to the applied dc voltage (V) and the Ohm's law is valid for the fast ion conducting systems also. This probably need not be true, as the applied dc field may cause an instant build-up of a polarization cloud right at the initial stage of the measurement. To check this, \( 'I_I \) vs V' study was carried out keeping applied dc voltage below 0.687 V, the decomposition potential of AgI. Fig. 3.9 shows \( 'I_I \) vs V' plot for OCC. One can note that the current varies linearly with voltage, hence, the Ohm's law seems to obey well for this system. This, in turn, indicates the fact that the effect of the instant build up of polarization due to the applied dc voltage is negligibly small and the measured \( 'I_I' \) values correspond approximately to the true values.

3.2.3d \( '\theta' \) measurement

Temperature dependent studies on ionic transport parameters viz. \( \sigma, \mu, n, \tau_{\text{ion}}, v_d \) give a direct information of the magnitude of energies involved in various thermally activated processes in an insight to understand the ion transport mechanism is the, temperature dependence thermoelectric power (\( \Theta \)), as mentioned earlier in Chapter 2. This experiment can be performed very conveniently on AgI-based systems due to relatively high Ag\(^+\) ion conduction as well as readily availability of silver-metal reversible electrodes [Coleman 1979]. Fig. 3.10 shows \( '\Theta' \) vs 1/T plot for the composite electrolyte system : 0.9[0.75AgI: 0.25AgCl]:0.1SiO\(_2\) in two temperature regions I & II. \( '\Theta' \) decreases with increasing temperature in both the regions. This is a legitimate and usual phenomenon observed in majority of fast Ag\(^+\) ion conducting systems [Shahi 1977; Agrawal and Gupta 1999]. The values of heat of Ag\(^+\) ion transport \( (q^*) \sim -0.113 \) & 0.145 eV, computed from the slopes of the straight line portions in the two regions (I & II), are fairly close to the activation energy \( (E_a) \sim 0.096 \) & 0.153 eV obtained earlier from 'log \( \sigma \) vs 1/T' Arrhenius plot (Fig. 3.5) in the same temperature regions (I & II) respectively. This, in turn, indicates that the new fast Ag\(^+\) ion conducting 2-phase composite electrolyte possesses an average structure and Rice & Roth's 'free-ion-like' states exist in the system. Fig. 3.10 also shows that the sign of \( '\Theta' \) always
Fig 3.8: 'Log \( v_d \) vs \( 1/T \) ' Arrhenius plot for the OCC: 0.9[0.75AgI: 0.25AgCl]:0.1SiO₂.

Fig 3.9: 'Iₜ vs V' plot for the OCC: 0.9[0.75AgI: 0.25AgCl]:0.1SiO₂.
remained negative in the entire range of temperature which is indicative of the fact that the positive (Ag⁺) ions are the sole charge carriers in the system [Colman 1979].

3.3. Conclusion

An enhancement of an order of magnitude in the room temperature conductivity has been achieved in a new Ag⁺ ion conducting two-phase composite electrolyte system: 0.9[0.75AgI : 0.25AgCl] : 0.1SiO₂, and referred to as ‘Optimum Conducting Composition (OCC)’. The conventional first phase host matrix salt AgI has been replaced by an alternative host compound: ‘a quenched/annealed: [0.75AgI:0.25AgCl] mixed system/solid solution’, recently investigated in the present laboratory. The phase identification/ material characterization studies confirmed the existence of the two separate phases. The electrical conductivity (σ) and ionic mobility (μ) measurements on OCC were carried out as a function of temperature by impedance spectroscopy (IS) and transient ionic current (TIC) technique, respectively. Subsequently, mobile ion concentration (n) was evaluated with the help of ‘σ’ & ‘μ’ data. On the basis of these studies, it has been concluded that the enhancement in the room temperature conductivity of OCC is predominantly due to increase in the ionic mobility. The temperature dependence studies of ionic transference number on OCC revealed the fact that the system remained purely ionic in the whole temperature range of measurement i.e. 27-215 °C. The ionic drift velocity (v₉) was determined at various temperatures with the help of initial total current ‘Iₒ’ and ‘n’ data. The results have been explained on the basis of proposed theories on 2-phase composite electrolyte systems. The thermoelectric power measurements have also been carried out which provided an additional insight to understand the ion transport mechanism in this system. TEP studies revealed an average structure as well as the existence of Rice & Roth’s ‘free-ion-like’ states in the system.
Fig. 3.10. $\theta$ vs $1/T$ plot for the OCC: 0.9[0.75AgI : 0.25AgCl] : 0.1SiO$_2$. 