IONIC TRANSPORT IN THE
[xAgI:(1-x)AgCl]
MIXED-SYSTEM/SOLID SOLUTION
As mentioned earlier in Chapter 1, majority of Ag\textsuperscript{+} ion conducting 2-phase composite electrolyte systems, reported in the past, exhibited high conductivity enhancements at room temperature only when AgI has been used as first phase host matrix. AgI is well-known for its characteristic structural change at \(\sim 147^\circ\text{C}\). This corresponds to the transition from low conductivity (\(\sigma \sim 10^{-7} - 10^{-5} \text{ S.cm}^{-1}\)) \(\beta\)-phase to supersonic (\(\sigma \sim 10^{0} - 10^{-1} \text{ S.cm}^{-1}\)) \(\alpha\)-phase. As mentioned earlier, we have investigated a new compound: a quenched/annealed \([0.75\text{AgI}:0.25\text{AgCl}]\) mixed-system/solid solution which not only exhibited transport characteristics similar to AgI but has several transport parameters superior to the conventional host AgI. The \(\beta \to \alpha\)-like transition takes place at a substantially reduced temperature. This new compound has been used as an alternate host in place of AgI. This chapter deals in detail with the material and transport property characterization studies on \([\text{AgI}:\text{AgCl}]\) mixed-system/solid solution and the new host system.

Conductivity anomalies in the \([x\text{AgI}:(1-x)\text{AgCl}]\) mixed-system were recently studied by Lauer and Maier [1992a, b]. They prepared the samples by heating different molar compositions \(x\) well above the melting point, then annealed at \(\sim 200^\circ\text{C}\) for 24 h before cooling finally to room temperature. The maximum enhancement in the conductivity (\(\sigma \sim 3 \times 10^{-5} \text{ S.cm}^{-1}\) at \(27^\circ\text{C}\)) was reported for the composition \([0.75\text{AgI}:0.25\text{AgCl}]\). The conductivity enhancement was attributed to the increased Ag\textsuperscript{+} ion vacancy at the space-charge region of AgI/AgCl interface. However, detailed studies on several other ionic transport properties viz. ionic mobility, number of charge carriers, ionic transference number, ionic drift velocity etc. on this mixed-system were not done. Further, the effect of different thermal treatments on the conductivity was also not checked.

In the present work, detail investigations on this system are reported. The experimental studies carried out on \([x\text{AgI}:(1-x)\text{AgCl}]\) mixed-system/solid solution include:

(i) the effect of rate of thermal cooling (slow and rapid quenching) of the melt on the room temperature conductivity \(\langle \sigma \rangle\) as a function of molar ratio \(x\), to locate the optimum conducting composition;

(ii) XRD, IR and DTA studies for phase identification/material characterization and construction of phase diagram;
(iii) temperature variation of conductivity for different compositions;
(iv) determination of $\text{Ag}^+$ ion mobility ($\mu$) as a function of temperature;
(v) evaluation of mobile ion concentration ($n$) at different temperatures using $\sigma$ and $\mu$ data;
(vi) measurement of ionic transference number ($t_{\text{ion}}$) as a function of temperatures and evaluation of ionic drift velocity ($v_d$);

The sample preparation procedures and experimental techniques used have already been discussed in detail earlier in Chapter 2. By slow cooling we mean here that the molten sample was kept for annealing at $\sim 200^\circ$C for 24 h, then cooled slowly to room temperature. $\mu$, $n$, $t_{\text{ion}}$ and $v_d$ measurements were carried out on the optimum conducting composition only.

3.2 Results And Discussion

3.2.1 Compositional variation of room temperature conductivity and effect of rate of cooling (slow and fast)

Fig. 3.1 shows the variation of room temperature conductivity as a function of molar wt. ratio $x$ for the slowly cooled (annealed) and rapidly cooled (quenched) melt of the $[x\text{AgI}:(1-x)\text{AgCl}]$ mixed-system/solid solution. Flat conductivity maxima were obtained for both the systems in the region of $x = 0.7-0.8$. The annealed samples were prepared in a similar manner to those of Lauer and Maier [1992a, b]. Theirs and the present conductivity variation with composition results are qualitatively similar but quantitatively different, due to different purity of starting materials used. No measurements on quenched samples exist in the literature and so direct comparison was not possible. It is obvious from Fig. 3.1 that quenched samples show high conductivity values. The composition $[0.75\text{AgI}:0.25\text{AgCl}]$ for both annealed and quenched samples exhibited the highest conductivity at room temperature and were used for different studies. The conductivity values for annealed and quenched samples are $\sim 1.3 \times 10^{-4}$ S.cm$^{-1}$ and $\sim 3.1 \times 10^{-4}$ S.cm$^{-1}$ respectively at 27°C. The quenched composition $[0.75\text{AgI}:0.25\text{AgCl}]$ has been referred to as the optimum composition. Fig. 3.2 shows the plot for room temperature conductivity values of the optimum conducting samples prepared using different quenching techniques viz. twin-roller, plate-plate, drop method. It can be obviously noted from the figure that the dif-
Figure 3.1: Compositional variation of room temperature conductivity for annealed and quenched $[x\text{AgI}:(1-x)\text{AgCl}]$ compositions.
Figure 3.2: Room temperature conductivity ($\sigma$) of the quenched optimum composition [0.75AgI:0.25AgCl] prepared using different quenching techniques: (A) Roller quencher; (B) Steel plates; (C) Repeated quenching (5 cycles) between steel plates; (D) Neutral bath.
different rates of quenching did not alter the conductivity significantly. However, we prepared all our samples by the twin-roller quenching technique. Lauer and Maier [1992a, b] explained the conductivity enhancement in their samples on the basis of increased mobile ion vacancy at the space-charge region of AgI/AgCl interface. We assign the similar reason for our samples also. However, the additional conductivity enhancement, in case of the quenched optimum composition, can be attributed to the formation of new disordered phases. The formation of new phases, along with the presence of fractional amorphity, was indicated in our XRD, IR and DTA studies, discussed below in the ensuing section.

3.2.2 Phase identification/material characterization

(i) X-ray diffraction (XRD): Fig. 3.3 depicts the XRD patterns for annealed and quenched optimum compositions [0.75AgI:0.25AgCl]. The filled (●) and open (○) dots mark the positions of characteristic reflection peaks (ASTM-data) of constituent compounds AgI and AgCl, respectively. Table 3.1 presents the summary of the results of XRD analysis. On comparing the XRD data of table, it can be noted that most of the observed XRD peaks of the new host (quenched/annealed) belong either to AgI or

Table 3.1: XRD data for AgI, AgCl and annealed & quenched optimum compositions: [0.75AgI:0.25AgCl]. Asterisk (*) indicates the data taken from ASTM card.

<table>
<thead>
<tr>
<th></th>
<th>AgI⁺</th>
<th>AgCl⁻</th>
<th>[0.75AgI:0.25AgCl]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Annealed</td>
<td>Quenched</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>l/l₀</td>
<td>d</td>
<td>l/l₀</td>
</tr>
<tr>
<td>3.98</td>
<td>60</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.75</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.51</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.73</td>
<td>17</td>
<td>2.83</td>
<td>20</td>
</tr>
<tr>
<td>2.30</td>
<td>85</td>
<td>2.23</td>
<td>40</td>
</tr>
<tr>
<td>2.12</td>
<td>30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.99</td>
<td>7</td>
<td>2.03</td>
<td>60</td>
</tr>
<tr>
<td>1.96</td>
<td>50</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 3.3: XRD patterns for optimum composition [0.75AgI:0.25AgCl].
AgCl. However, some reflections originally present in AgI and AgCl were found to be missing and some new reflections were observed in the new hosts. In addition to this, some reflections are found to become squatter. The results of XRD analysis indicate slight modifications in the structure of constituent compounds along with formation of a new compound/solid solution. If one can compares the XRD reflections of Fig. 3.3 carefully, several slight changes can be noted in the two patterns. These changes are introduced probably due to different rates of cooling were adopted during preparation of the hosts. Some of the well-defined peaks for the annealed host have been broadened in case of quenched host. The broadening of XRD peaks clearly indicates the presence of fractional amorphosity in the quenched host.

(ii) Infrared (IR): Fig. 3.4 shows the IR spectra of AgI, AgCl and quenched optimum composition [0.75AgI:0.25AgCl]. One can not extract much information on comparing these IR spectra. However, the peaks for the quenched optimum composition are nothing but the modified/combined peaks of AgI and AgCl. Modifications/changes in the peak positions are indicative of the possible presence of new phases, as indicated also in XRD studies.

(iii) Thermal/phase diagram study on quenched system [xAgI:(1-x)AgCl]: Fig. 3.5 shows the DTA curves for [xAgI:(1-x)AgCl] quenched samples where x = 0, 0.1, ... 0.9, 1 in mol. wt. fraction. As x was increased, the following changes were observed in the DTA curves:

(i) The well-defined intense peak corresponding to melting of pure AgCl (x = 0) at ~455°C became squatter and gradually shifted towards the lower temperature region. The peak positions for x = 0.1, 0.2, 0.3 occurred at 417, 396 and 343°C, respectively. The peak finally disappeared for higher values of x. However, some new broad and deconvoluted small peaks started to appear in this temperature region, as indicated in the Fig. 3.5.

(ii) A relatively small, but well-defined, peak appeared at ~131°C for x = 0.1. The intensity of this peak increased as the fractional amount of AgI increased. This peak is similar to the β → α—transition of AgI with a reduced transition temperature. It should be noted that the AgI appeared to become modified in the quenched system, since the characteristic β → α—transition of pure AgI is ~147°C.

(iii) A new well-defined peak appeared at ~257°C for the composition of x = 0.3. The intensity of this peak increased as x increased to 0.5, then decreased for x = 0.6. This peak corresponded to the melting of a newly formed compound, AgI₂Cl₂.
Figure 3.1: IR spectra: (A) pure AgI, (B) pure AgCl; (C) quenched optimum composition [0.75AgI:0.25AgCl].
Figure 3.5: DTA curves for \([\text{xAgl:(1-x)AgCl}]\) quenched composition.
For higher compositions, small and broad deconvoluted peaks appeared in the higher temperature region, as indicated in the Fig. 3.5.

(iv) In the compositional region $0.7 < x < 0.9$ a very broad and diffused peak was observed just after the $\beta \rightarrow \alpha$-transition peak of modified AgI, as shown in Fig. 3.5. This broad peak was indicative of the presence of fractional amorphisity in this compositional region.

On the basis of above study, a phase diagram was drawn which is shown in Fig. 3.6. AgI was modified (denoted as AgI*), with a reduced $\beta \rightarrow \alpha$-transition temperature, as the AgCl content increased a new compound AgI$_2$Cl$_y$ was partially formed. The amorphisity in the compositional range $0.7 < x < 0.9$, as discussed in (iv) above, is shown in the diagram. It has been reported that the conductivity enhancement is directly related to the amorphisity in some glass systems [Angell 1986; Ingram 1987; Secco 1992], hence the enhancement in the conductivity from the constituent compounds is expected to be more in the above compositional region. Maximum enhancements with flat maxima in the ratios for $x = 0.7-0.8$, as shown earlier in Fig. 3.1, were obtained. Most of the features of the phase diagram of Fig. 3.6 are similar to those reported by Monkemeyer [1906] with only exceptions that AgI is modified with a reduced $\beta \rightarrow \alpha$-phase transition temperature, as reported also for the (AgI:AgBr) [Shahi and Wagner 1982a, b] and (AgI:AgCl) [Ihara et al 1984] 2-phase composite systems, and, the presence of amorphous region.

### 3.2.3 Temperature dependence of conductivity

Fig. 3.7 shows the Log $\sigma$ vs $1/T$ plots for quenched compositions [xAgI:$(1-x)$AgCl], where $x = 0.2, 0.4, 0.6, 0.7, 0.75, 0.8, 0.9$. Similar plots for pure AgI, AgCl and annealed optimum composition [0.75AgI:0.25AgCl] are also drawn in the figure to enable direct comparison. The conductivity of quenched compositions increased slowly with temperature initially, then abrupt jumps occurred at $\sim 130-136^\circ C$, identical to $\beta \rightarrow \alpha$-transition behaviour of AgI. The conductivity remained stable afterwards. The annealed optimum composition also exhibited similar behaviour with $\beta \rightarrow \alpha$-like phase transition at $\sim 140^\circ C$. The Log $\sigma$ vs $1/T$ variations of Fig. 3.7 can be expressed by Arrhenius type equations in both the regions of temperature (I & II). These variations are similar to those reported earlier for 2-phase composite systems: (AgI:AgBr) [Shahi and Wagner 1982a, b] and (AgI:AgCl) [Lauer and Maier 1992a, b]. In the present study, the quenched composition [0.75AgI:0.25AgCl] exhibited high-
Figure 3.6: Phase diagram of \([x \text{AgI} : (1-x) \text{AgCl}]\) quenched compositions.
Figure 3.7: Log $\sigma$ vs $1/T$ Arrhenius plots for $[x\text{AgI}:(1-x)\text{AgCl}]$ quenched system where $x = 0.2 (\otimes), 0.4 (\times), 0.6 (+), 0.7 (\triangle), 0.75 (\bigcirc), 0.8 (\square), 0.9 (\triangledown)$ along with similar plots for AgI (■), AgCl (▼) and annealed optimum composition [0.75AgI:0.25AgCl] (●). Activation energy ($E_a$) as a function of $x$ for the above compositions in the temperature Region-I (27-120°C).
est conductivity (σ = 3.1 × 10⁻⁴ S·cm⁻¹ at 27°C) as compared to other systems. As mentioned earlier, the maximum enhancement in the room temperature conductivity for the quenched optimum composition can be attributed due to the combined effects such as formation of new disordered phase (e.g. AgI⁺, a new compound AgI₄Cl) and presence of fractional amorphisity in addition to increased mobile ion vacancies at the space-charge region of AgI/AgCl interface [Lauer and Maier 1992a, b]. The activation energy (E_a) values for all compositions were computed in both the Regions (I & II). E_a-values, computed in Region-I, are plotted with x in the inset of Fig. 3.7. No significant changes in the E_a-values were noted for different compositions. E_a: ~0.234, 0.233, 0.290, 0.235 eV were obtained for the quenched, annealed (optimum compositions), AgI & AgCl respectively [Agrawal et al 1992, 1994]. For the annealed and quenched optimum compositions: [0.75AgI:0.25AgCl] activation energy values are relatively lower as compared to that of AgI. This is indicative of the fact that the transport of mobile ion in these systems takes place with relative ease.

3.2.4 Temperature dependence of ionic mobility and mobile ion concentration

Ag⁺ ion mobility (µ) at different temperatures were measured for the quenched optimum composition using transient ionic current (TIC) technique, discussed earlier in section 2.3.2. A dc potential of ~0.5 V was applied across the cell in the following configuration for sufficiently long time:

\[
C / [0.75\text{AgI}:0.25\text{AgCl}] \text{ quenched optimum composition} / C.
\]

Graphite (C) acted as blocking electrode for the mobile Ag⁺ ions. The cell was first polarized completely, then the polarity of the field was reversed and the current was recorded with time simultaneously. A peak was obtained in the current vs time plot which corresponded to the time of flight τ i.e. the time taken by the Ag⁺ ion to cross the thickness d of the sample. Hence, the ionic mobility was determined using eq.(2.5):

\[
\mu = \frac{d^2}{V \cdot \tau}, \mu \sim (2.4 \pm 1) \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}
\]

was obtained at room temperature (27°C) for this composition. To check the reliability of the obtained mobility value, TIC measurements were carried out on sample pellets of different thicknesses and with different values of applied dc voltages (<0.7 V). Fig. 3.8(a & b) shows µ as a function of thickness and applied voltage. It can be obviously noted from the figure that µ remained almost unaltered within the experimental error range. We have
Figure 3.8: Room temperature mobility ($\mu$) of $\text{Ag}^+$ ion for quenched optimum composition [0.75Ag:0.25AgCl] as a function of (a) pellet thickness and (b) applied voltage.
Table 3.2: Comparison of some important transport parameters of AgI, AgCl and annealed & quenched optimum compositions: [0.75AgI:0.25AgCl].

<table>
<thead>
<tr>
<th>Material</th>
<th>Ionic conductivity $\sigma_{25^\circ C}$ S cm$^{-1}$</th>
<th>Ionic mobility $\mu_{25^\circ C}$ cm$^2$ V$^{-1}$ s$^{-1}$</th>
<th>Mobile ion concentration $n_{25^\circ C}$ cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgI</td>
<td>$2.5 \times 10^{-5}$</td>
<td>$(2.5 \pm 1) \times 10^{-2}$</td>
<td>$6.0 \times 10^{15}$</td>
</tr>
<tr>
<td>AgCl</td>
<td>$1.0 \times 10^{-6}$</td>
<td>$(3.1 \pm 1) \times 10^{-3}$</td>
<td>$2.0 \times 10^{15}$</td>
</tr>
<tr>
<td>[0.75AgI:0.25AgCl] (Annealed)</td>
<td>$1.0 \times 10^{-4}$</td>
<td>$(1.5 \pm 1) \times 10^{-2}$</td>
<td>$4.0 \times 10^{16}$</td>
</tr>
<tr>
<td>[0.75AgI:0.25AgCl] (Quenched)</td>
<td>$3.1 \times 10^{-4}$</td>
<td>$(2.4 \pm 1) \times 10^{-2}$</td>
<td>$8.0 \times 10^{16}$</td>
</tr>
</tbody>
</table>

obtained identical results for the composite electrolyte systems discussed later in the Chapters 4 & 5.

Subsequently, the mobile ion concentration ($n$) was calculated using conductivity ($\sigma$) and mobility ($\mu$) data with the help of expression (eq.1.1): $n = \sigma \cdot \mu$, as discussed earlier in section 2.3.2. $\mu$ and $n$ values for the annealed optimum composition were also determined in the similar way at room temperature only.

Table 3.2 lists the room temperature values of ionic conductivity, mobility and mobile ion concentration for annealed and quenched optimum composition [0.75AgI:0.25AgCl] as well as for constituent compounds AgI and AgCl. On comparing these values one can obviously note that for the [0.75AgI:0.25AgCl] system, $n$ has been increased by one order of magnitude compared to that of AgI, whereas $\mu$ remained almost unchanged. This is indicative of the fact that the increase in $n$ is predominantly responsible for the room temperature enhancement in $\sigma$ of annealed as well as quenched systems.

Fig. 3.9 shows the plots for temperature variation of $\mu$ and $n$ for the quenched composition [0.75AgI:0.25AgCl]. Log $\sigma$ vs $1/T$ plot of Fig. 3.7 for this composition is redrawn in Fig. 3.9. One can note an increase ($\sim 10^5$) in the mobility from the
Figure 3.9: Arrhenius plots of $\log \mu$ vs $1/T$ (○) and $\log n$ vs $1/T$ (▽) for quenched optimum composition [0.75AgI:0.25AgCl]. Plot $\log \sigma$ vs $1/T$ (●) of Fig. 3.7 is redrawn.
room temperature value, as the temperature was increased to ~100°C, then it decreased sharply afterwards by more than two orders of magnitudes. Whereas, mobile ion concentration n remained almost constant initially up to ~100°C, then an abrupt jump (~10^4) was observed. The onsets of the abrupt changes occurred well ahead of the β → α-like transition temperature (~135°C) of the system. The reason for this may be assigned as pretransition effects. The decrease in the mobility may be due to the structural-volume contraction [Secco 1992], also observed by us earlier for pure AgI after β → α-transition [Agrawal et al 1992, 1994]. This has resulted into the space narrowing for ion migration. The abrupt increase in mobile ion concentration is because of the transition to an entirely new structure (assigned as α-phase, analogous to the average structure of α-AgI) where a large number of equinergetic Ag^+ ions become available for conduction. Hence, an apparent decrease in σ, due to the decrease in μ, has been more than compensated by the large number of mobile Ag^+ ions present in the α-like phase of the system. The Arrhenius equations governing the variation of μ and n in the two temperature regions (I & II), above and below the phase transition, can be expressed as:

\[
\begin{align*}
\mu &= 3.3 \times 10^1 \exp(-0.17/kT) \\
n &= 9.3 \times 10^{17} \exp(-0.07/kT)
\end{align*}
\]

Region - I (27 - 105°C)

and

\[
\begin{align*}
\mu &= 1.1 \times 10^{-5} \exp(+0.18/kT) \\
n &= 1.9 \times 10^{24} \exp(-0.24/kT)
\end{align*}
\]

Region - II (170 - 205°C)

The energy of migration (E_m) and the energy of formation (E_f), defined earlier in Chapter 1, obtained from the above equations respectively are: 0.17 & 0.07 eV in the Region-I and -0.18 & 0.24 eV in the Region-II. The activation energy (E_a) values were calculated in these two temperature regions by substituting E_m & E_f in the energy equation (eq.1.17): E_a = ±E_m ± E_f. It was observed that the obtained E_a values were very close to the values computed earlier from Log σ vs 1/T plot in the same Regions (I & II).

3.2.5 Temperature dependence of ionic transference number and ionic drift velocity

The results obtained in the μ and n studies were well supported by the temperature dependence of ionic transference number (t_on) carried out with the help of Wagner's
Section 3.2.5

de polarization method. The experimental details of the Wagner's method has already been discussed earlier in preceding chapter (section 2.3.3). Fig. 3.10 shows the current vs time plots for the quenched optimum composition [0.75Agl:0.25AgCl], recorded at various temperatures in Regions (I & II). Some notable features of this study are summarized below:

(i) The initial value of the total current \(I_T\) approached to zero with time at all temperatures of our measurements. This is indicative of two facts: (a) the system remains purely ionic in the entire temperature range; (b) \(Ag^+\) ions are the sole charge carriers in this system. Since \(I_T \approx I_{on}\), the ionic transference number \(t_\text{ion}\) extremely close to unity. \(I_{on}\) vs temperature plot for this system is shown as an inset in Fig. 3.10.

(ii) The polarizing time \((t)\), for which the total current \(I_T\) approached to zero, increased as the sample temperature was increased. This is an expected behaviour. At higher temperatures the mobile ions are thermally more agitated, hence, they need longer time to get polarized at a fixed value of applied dc potential as compared to the time required at lower temperatures.

(iii) The magnitude of initial current \(I_T\) also increased with increasing temperatures. An abrupt jump \((\sim 10^2)\) in the \(I_T\) was observed in the Region-II, after \(\beta \rightarrow \alpha\)-like transition.

The increase in \(I_T\) may be either due to the increase in number of mobile ions \((n)\) or ionic drift velocity \((v_d)\) or both as obvious from the eq.(1.18): \(I_T = n q v_d A\).

For the present system, the increase in \(I_T\) with temperature is obviously due to the increase in \(n\), as observed earlier in \(\text{Log} n \text{ vs} 1/T\) variation. Knowing the values of \(I_T\) and \(n\), drift velocity \(v_d\) of mobile \(Ag^+\) ions were calculated at various temperatures for the quenched optimum composition [0.75Agl:0.25AgCl].

Fig. 3.11 shows the \(\text{Log} v_d \text{ vs} 1/T\) plot for the quenched optimum composition [0.75Agl:0.25AgCl]. The thermally activated behaviour of \(v_d\) in Regions (I & II) can be expressed by following Arrhenius type equations:

\[
v_d = 3.5 \exp(-0.186/kT) \quad \text{Region - I} \quad (27 - 105^\circ C)
\]

\[
v_d = 7.2 \times 10^{-9} \exp(+0.189/kT) \quad \text{Region - II} \quad (170 - 205^\circ C)
\]

where 0.186 & -0.189 eV are energy \((E_d)\) values involved in the above thermally activated processes. It is well-known that \(v_d\) is directly proportional to \(\mu\) at a fixed value of applied dc field. Hence, \(\text{Log} v_d \text{ vs} 1/T\) variation would be identical to \(\text{Log} \mu \text{ vs} 1/T\)
Figure 3.10: Current vs time plots at various temperatures (given in parenthesis) for the measurement of ionic transference number $t_{ion}$ on the quenched optimum composition $[0.75\text{AgI}:0.25\text{AgCl}]$. Inset: $t_{ion}$ as a function of temperature.
Figure 3.11: Log $v_d$ vs $1/T$ Arrhenius plot for the quenched optimum composition [0.75AgI:0.25AgCl].
\( \mu \) vs \( 1/T \) variation, in principle. Thus, \( E_x \)-value should be equal to the \( E_m \)-value obtained from \( \log \mu \) vs \( 1/T \) Arrhenius plot. On comparing the two energy values \( (E_x, E_m) \) in both the Regions (I & II), we note that they are in close agreement with each other. A little deviation may probably due to the experimental limitation of measuring the value of initial current accurately by the x-y-t recorder used in the present study. We would like here to point out that due to some finite (although small) response time of the pen of the x-y-t recorder, it would not be possible to estimate \( I_T \) accurately at \( t = 0 \) s. Hence, an error might be introduced during computing \( u_d \) using eq.(1.18). In the calculation of \( u_t \), we also assumed that the initial current \( I_T \) is directly proportional to the applied dc potential \( V \) and Ohm's law is valid. However, this may not probably be true as the applied dc field may instantly cause build-up of polarization cloud right at the initial stage of the measurement. To check this phenomenon, we carried out \( I_T \) vs \( V \) study by keeping the applied dc field below the decomposition potential of the sample material. Fig. 3.12 shows \( I_T \) vs \( V \) plot for the quenched optimum composition \([0.75\text{AgI}:0.25\text{AgCl}]\). It can be obviously noted that this variation is linear and the Ohm's law seems to obey well. Hence, on the basis of this study it can be concluded that the effect of instant polarization charge build up by applied dc field has been negligibly small in the present measurement of \( I_T \).

### 3.3 Conclusion

On the basis of various studies carried out on \([x\text{AgI}:(1-x)\text{AgCl}]\) mixed-system/solid solution, following conclusion may be drawn:

High ionically \( \text{Ag}^+ \) ion conducting compositions can be prepared by rapidly quenching the molar compositions of \([x\text{AgI}:(1-x)\text{AgCl}]\) system. \( \beta \rightarrow \alpha \)-transition of AgI gets modified and some new phases appear in the compositional phase diagram. The quenched composition \([0.75\text{AgI}:0.25\text{AgCl}]\) exhibits the optimum room temperature conductivity. Detailed investigations on transport properties of quenched composition \([0.75\text{AgI}:0.25\text{AgCl}]\) revealed that the mobility of \( \text{Ag}^+ \) decreases sharply on going from \( \beta \rightarrow \alpha \)-like phase (analogous to \( \beta \rightarrow \alpha \)-transition of AgI) while a large increase in the mobile ion concentration not only compensates the decrease in mobility but essentially results into a net increase in ionic conductivity. The temperature dependence studies on ionic transference number, hence drift velocity, espoused these results well. The conductivity results are explained on the basis of phase diagram. Further, based on the results obtained from various studies it is suggested
Figure 3.12: $I_t$ vs $V$ plot for the quenched optimum composition [0.75AgI 0.25AgCl].
that the quenched and/or annealed composition \([0.75 \text{AgI}: 0.25 \text{AgCl}]\) can be a better substitute of AgI for preparing AgI nan conducting superionic solids especially at amorphous/glassy and composite phases. In the next Chapters (4 & 5) to follow, preparation of two new 2-phase composite electrolyte systems using this quenched and/or annealed composition \([0.75 \text{AgI}: 0.25 \text{AgCl}]\) as first phase host-matrix will be discussed along with various transport property studies on the optimum conducting composition of the composite systems.