Chapter III

D C  IONIC CONDUCTIVITY STUDIES

3.1 INTRODUCTION

For increasing the ionic conductivity of glasses, different approaches were adopted. The addition of metal salts (halides, sulphates) to alkali glasses is found to increase the ionic conductivity [1-3]. The Tg usually decreases with the addition of salts [4]. The properties of borophosphate glasses have been studied by several workers [5, 6]. It was shown that [7] these glasses have relatively good chemical durability and comparatively high Tg on account of the presence of BPO$_4$ groups. The enhancement in the conductivity was explained on the basis of mixed glass former effect [8, 9]. Glasses with two glass formers generally increase conductivity. Due to mixed former effect, the presence of the two glass formers modifies the glass network making it favourable for alkali mobility. The host glass system contains BO$_4$, PO$_4$, BPO$_4$ tetrahedra and BO$_3$ triangles to which non-bridging oxygens are attached. Incorporation increases number of NBOs and ion expands the glass network increasing the ion mobility.

In order to study and understand the ionic transport mechanism, it is important to find a connection between the electrical ionic conductivity and the microscopic structure. Different ionic transport models were proposed to explain the ionic conductivity of glass systems [10-14]. Unlike in crystalline systems where an ion can hop to a neighbouring site only if the latter exists, in a glass, mobile ions are by themselves able to create vacant
sites for ion transport. Ionic conductivity in glasses arises mainly from the
dynamics of ion hopping. A diffusive mode contributes to the D.C. ionic
conductivity. In ion transport theories it is generally assumed that the
cations move into equivalent sites which are equivalent NBO environments
[15].

3.2 REVIEW OF EARLIER RESEARCH WORK

The ionic transport studies on the glass system NaF-Na$_2$O-B$_2$O$_3$–Tl$_2$O
were carried out by Rahman et al [16]. It was observed that the temperature
dependence of the d.c. electrical conductivity followed the Arrhenius
equation. The electrical conductivity was found to vary in a non-linear
manner with the compositional parameter. The charge transport was
mainly due to ionic. An electrochemical cell was fabricated using the
highest conducting glass as the solid electrolyte.

Nagaraja et al. [17] investigated the dc electrical conductivity of single
and mixed alkali doped cobalt-borate glasses in the temperature range 300-
550 K. The conductivity data was analyzed in the light of SPH model and
the activation energies were determined. In single alkali glasses the
variation of conductivity with Li$_2$O content indicated change over conduction
mechanism from electronic to ionic. In multi alkali glasses the conductivity
was attributed to mixed alkali effect.

Electrical and optical properties of sodium borate glasses containing
metal oxides like MgO, BaO were studied by Dawy and Salama [18]. The
activation energies and Tg values were evaluated. Addition of metal oxides have marked effect on the conductivity and optical absorption. The dc electrical conductivity of different glass system were compared.

The d.c. and a.c. conductivities containing two glass formers $A_2O$ ($A = \text{Li, Na, K}$)-$V_2O_5$-$P_2O_5$ glasses as a function of temperature and composition were studied by Barczynski et al [19]. It was observed that the dc conductivity decreased with increasing alkali content, and the decrease was more pronounced for larger alkali ions. The increase in the alkali content changes the structural units of vanadium atoms from square to tetrahedral. The ac conductivity exhibited a universal dynamic response.

The thermal analysis, hyperfine structure and electric transport properties of vanadium phosphate iron glasses were studied by Shapaan et al [20]. The glassy sample $40V_2O_5$-$40P_2O_5$-$20Fe_2O_3$ exhibited highest thermal stability. It was observed that increasing $V_2O_5$ content the d.c. conductivity increases while the activation energy decreases. It was observed that the conductivity strongly depends on $V_2O_5$ content. It was revealed that vanadium ions play the role of network modifier.

Devidas et al [21] prepared and investigated three different series of vanadium phosphate glasses. The glasses were prepared using melt quenching technique and their glassy nature was confirmed by XRD. The DC conductivity was measured in the temperature range 300-675 K. The data was analyzed under SHP model. The mixed alkali glasses have shown
higher activation energies and lower conductivities compared to single alkali doped glasses. This was attributed to a mixed alkali influence on the electrical conduction.

Jamal et al. [22] investigated the quaternary glass system NaI-Na$_2$O-V$_2$O$_5$-B$_2$O$_3$ emphasizing the influence of two glass formers on the transport properties. The existence of two glass formers V$_2$O$_5$ and B$_2$O$_3$ was found to have considerable influence on the ionic conductivity and activation energy. The variation of conductivity with composition exhibited two maxima indicating mixed former effect.

Aldomagistris et al. [23] studied the high ionic conductivity in AgI-Ag$_2$O-B$_2$O$_3$ glass system at room and high temperatures. They have investigated the effect of the glass modifier to the former ratio on the ionic conductivity. It was observed that with the increase in the modifier content the conductivity increased.

Levasseur et al. [24-26] synthesized lithium haloborate glasses containing F, Cl, Br and I. It was found that the conductivity increased with total Li$^+$ content. They observed largest conductivity enhancement upon addition of LiI. The conductivity was found to increase with increasing the size of halide ion, which was attributed to the enlarging diffusion path.

Shelby and Ortolana [27] investigated the Tg, viscosity, refractive index and electrical conductivity of NaF-Na$_2$O-B$_2$O$_3$ glasses over a wide
range of compositions. Even though these glasses appear to be cation conductors, there was a small mixed anion effect in the conductivity, Tg and viscosity.

The mixed glass former effect in lithium boroarsenate glasses was reported by Chowdari and Akther [28]. The dependence of conductivity on the temperature was found to obey the Arrehenius equation. It was clearly indicated that the effect of adding second glass former to the binary system of Li$_2$O-B$_2$O$_3$ increased the conductivity, Tg, density and oxygen packing density.

Siddu et al. [29], Govindraj and Bhaskaran [30] and Satyanarayana et al [31] have studied the effect of mixed glass formers on the conductivity of silver ion in ternary and quaternary glassy materials.

Castantani et al. [32] studied the effect of substitution of B$_2$O$_3$ and P$_2$O$_5$ network formers on Tg and electrical conductivity of silver based phosphate glasses. The results were interpreted on the basis of a structure composed of AgI micro domains in a phosphate or borophosphate matrix and on the basis of diffusion path model for ionic conduction.

The effect of adding network modifiers and dopant salts (halides) on the structural and conducting properties of borate glasses was studied with the aid of Raman and IR spectroscopy by Balkanski et al. [33]. They also used theoretical models using network dynamics and lattice dynamic
calculations. The effect of the dopant salts LiX \([X = F, Cl, Br, I]\) and Li\(_2\)SO\(_4\) and also the effect of modifier Li\(_2\)O were discussed. The network modifier H\(_2\)O was found to change the structure of the glass matrix through which the lithium ions supplied by the dopant salts must diffuse. These structural modifications were analyzed and discussed with reference to their effect on the ionic conductivity.

The ternary glass system AgX-Ag\(_2\)O-B\(_2\)O\(_3\) \((X = I, Br, Cl)\) were synthesized and studied by Minami et al. [34]. The transport properties of these glasses were discussed. The glasses were found to contain BO\(_3\), BO\(_4\) and B-O-B groups regardless their composition. It was observed that BO\(_3\)X groups were present in the glasses when the mole ratio Ag\(_2\)O/B\(_2\)O\(_3\) was greater than unity. A structure was proposed to explain the Ag\(^+\) ion transport.

Yuhuwang et al [35] studied the effect of halide ions on Li\(^+\) ionic conductivity for the glass system Li\(_2\)X–Li\(_2\)O–B\(_2\)O\(_3\) \((X=F,Cl,Br)\) where Li\(_2\)O was replaced by Li\(_2\)X with the total Li content kept constant. It was observed that the conductivity with the increase of halide content was found to decrease for F glasses and increase for Cl and Br glasses which was due to increase in the activation energy for F glasses and decrease for Cl and Br glasses. The analysis of the activation energy in terms of the Anderson Stuart model indicated that with the increase LiX the electrostatic energy \((\Delta E_b)\) increases for F glasses where as the strain energy \((\Delta E_s)\) and \(\Delta E_b\) decreases for Cl and Br glasses. The effect of the halide ions were attributed
to a stronger interaction between Li and F and to expanded and weakened glass network due to accommodation of Br and Cl ions.

Fusco et al. [36] have investigated the ionic conductivity, Tg and densities of a number of glasses in the system RCl-R2O-B2O3 [R=Li,Na,K]. They observed that increasing the RCL content resulted in sharp increase in alkali ion conductivity and decrease in Tg and density. This was attributed to changes in the network structure.

El-Damrawi [37] studied the mixed former effect in lead-chloroborate glasses PbCl2–PbO-B2O3-P2O5. It was observed that addition of dopant PbCl2 and the mixed glass former enhanced the d.c. conductivity. The decrease in glass transition temperature, increase in molar volume with increasing PbCl2 support the idea of expansion of glass network by Cl2 ions.

The effect of mixing two glass formers in the glass system AgI-Ag2O-B2O3-MoO3 was investigated by Sarma and Radhakrishna [38]. The ratio of glass modifier and the total glass former content was fixed at 0.75. In the plot room temperature conductivity vs. B2O3/B2O3+MoO3, two maxima were observed. It was attributed to the opening of channels for the mobile species to move faster in the glass matrix thus causing increase in mobility and in turn in conductivity.

Sathyasainath Prasad et al. [39] investigated the effect of variation of two glass formers (B2O3 and AS2O3) on the transport properties of AgI-Ag2O-
B$_2$O$_3$-AS$_2$O$_3$ glass system. The mixed glass former effect was discussed based upon the ionic radius, field strengths and valency state of the glass forming cations.

The electrical conductivity of Li$_2$O-B$_2$O$_3$-P$_2$O$_5$-Li$_2$SO$_4$ glass system was studied by Deshpande et al [40]. The observed conductivity results were explained by dividing the compositions in two regions.

The lithium ion transport in Li$_2$O-LiCl-CaO-B$_2$O$_3$ glasses were discussed by Shue and Tuller [41]. The influence of CaO in Li$_2$O-B$_2$O$_3$-4Cl on the conductivity was discussed. It was observed that CaO addition decrease ionic conductivity. The results were discussed in terms of a number of transport models applicable to glass system.

Jamal et al. [42] discussed the ionic transport and battery characterization of the ternary glass system NaI-Na$_2$O-B$_2$O$_3$. It was observed that the conductivity increased in a non-linear manner with NaI/Na$_2$O ratio. When the concentration of NaI and Na$_2$O were equal the conductivity attained a maximum value. When NaI/Na$_2$O > 1 the conductivity was found to decrease. Conductivity maximum was envisaged by the incorporation of NaI.

3.3 EXPERIMENTAL

The glass samples used for the investigation of electrical conductivity studies were prepared by using the melt quenching method discussed in
Chapter-II. The composition of the glasses studied are given in Tables 3.1 to 3.5. Glasses in the form of circular discs were ground and polished on both sides to achieve uniform thickness and painted both sides with silver paint for ionic conductivity measurements. The ionic conductivity was measured at different temperatures using the conductivity set up described in Chapter-II. The currents were measured using digital Keithly electrometer. The error in the measurement of current is about ±1 µA.

3.4 RESULTS AND DISCUSSION

3.4.1 DC Ionic Conductivity Studies on xKR-(30-x)K₂O-35B₂O₅-35P₂O₅

\[ \text{[R} = \text{Cl, Br and I]} \]

The glass samples with the general composition xKR-(30-x)K₂O-35B₂O₅-35P₂O₅ [x = 1, 2, 3, 4, 5 mole % and R = Cl, Br, & I] were prepared using the melt quenching method described in Chapter-II. Tables 3.1 to 3.3 present the details of the glass system studied.

In the glass systems studied the content of the network formers B₂O₃ and P₂O₅ were kept constant, while the contents of network modifier K₂O and the halide salts (KCl, KBr and KI) were varied. The ionic conductivity was measured below the glass transition temperature using the experimental set up described in Chapter II. For the measurement of currents keithley digital electrometer model 614 was used.

The DC ionic conductivity was found to increase with increasing temperature. The variation of conductivity with temperature can be represented by the Arrhenius equation
Table 3.1: Glass Composition of xKCl-(30-x)K₂O-35B₂O₃-35P₂O₅

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Glass System</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>KCKBP1</td>
<td>1KCl-29K₂O-35B₂O₃-35P₂O₅</td>
</tr>
<tr>
<td>2.</td>
<td>KCKBP2</td>
<td>2KCl-28K₂O-35B₂O₃-35P₂O₅</td>
</tr>
<tr>
<td>3.</td>
<td>KCKBP3</td>
<td>3KCl-27K₂O-35B₂O₃-35P₂O₅</td>
</tr>
<tr>
<td>4.</td>
<td>KCKBP4</td>
<td>4KCl-26K₂O-35B₂O₃-35P₂O₅</td>
</tr>
<tr>
<td>5.</td>
<td>KCKBP5</td>
<td>5KCl-25K₂O-35B₂O₃-35P₂O₅</td>
</tr>
</tbody>
</table>
Table 3.2 : Glass Composition of xKBr-(30-x)K$_2$O-35B$_2$O$_3$-35P$_2$O$_5$

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Glass System</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>KBKBP1</td>
<td>1KBr-29K$_2$O-35B$_2$O$_3$-35P$_2$O$_5$</td>
</tr>
<tr>
<td>2.</td>
<td>KBKBP2</td>
<td>2KBr-28K$_2$O-35B$_2$O$_3$-35P$_2$O$_5$</td>
</tr>
<tr>
<td>3.</td>
<td>KBKBP3</td>
<td>3KBr-27K$_2$O-35B$_2$O$_3$-35P$_2$O$_5$</td>
</tr>
<tr>
<td>4.</td>
<td>KBKBP4</td>
<td>4KBr-26K$_2$O-35B$_2$O$_3$-35P$_2$O$_5$</td>
</tr>
<tr>
<td>5.</td>
<td>KBKBP5</td>
<td>5KBr-25K$_2$O-35B$_2$O$_3$-35P$_2$O$_5$</td>
</tr>
</tbody>
</table>
Table 3.3: Glass Composition of $x$KI-(30-$x$)K$_2$O-35B$_2$O$_3$-35P$_2$O$_5$

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Glass System</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>KIKBP1</td>
<td>5KI-25K$_2$O-35B$_2$O$_3$-35P$_2$O$_5$</td>
</tr>
<tr>
<td>2.</td>
<td>KIKBP2</td>
<td>10KI-20K$_2$O-35B$_2$O$_3$-35P$_2$O$_5$</td>
</tr>
<tr>
<td>3.</td>
<td>KIKBP3</td>
<td>15KI-15K$_2$O-35B$_2$O$_3$-35P$_2$O$_5$</td>
</tr>
<tr>
<td>4.</td>
<td>KIKBP4</td>
<td>20KI-10K$_2$O-35B$_2$O$_3$-35P$_2$O$_5$</td>
</tr>
<tr>
<td>5.</td>
<td>KIKBP5</td>
<td>25KI-5K$_2$O-35B$_2$O$_3$-35P$_2$O$_5$</td>
</tr>
</tbody>
</table>
### Table 3.4: Glass Composition of xNaCl-(30-x)Na₂O-35B₂O₃-35P₂O₅

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Glass System</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>NCNBP1</td>
<td>1NaCl-29Na₂O-35B₂O₃-35P₂O₅</td>
</tr>
<tr>
<td>2.</td>
<td>NCNBP2</td>
<td>2NaCl-28Na₂O-35B₂O₃-35P₂O₅</td>
</tr>
<tr>
<td>3.</td>
<td>NCNBP3</td>
<td>3NaCl-27Na₂O-35B₂O₃-35P₂O₅</td>
</tr>
<tr>
<td>4.</td>
<td>NCNBP4</td>
<td>4NaCl-26Na₂O-35B₂O₃-35P₂O₅</td>
</tr>
<tr>
<td>5.</td>
<td>NCNBP5</td>
<td>5NaCl-25Na₂O-35B₂O₃-35P₂O₅</td>
</tr>
</tbody>
</table>
Table 3.5: Glass Composition of xNaBr-(30-x)Na<sub>2</sub>O-35B<sub>2</sub>O<sub>3</sub>-35P<sub>2</sub>O<sub>5</sub>

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Glass System</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>NBNBP1</td>
<td>1NaBr-29Na&lt;sub&gt;2&lt;/sub&gt;O-35B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-35P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
</tr>
<tr>
<td>2.</td>
<td>NBNBP2</td>
<td>2NaBr-28Na&lt;sub&gt;2&lt;/sub&gt;O-35B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-35P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
</tr>
<tr>
<td>3.</td>
<td>NBNBP3</td>
<td>3NaBr-27Na&lt;sub&gt;2&lt;/sub&gt;O-35B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-35P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
</tr>
<tr>
<td>4.</td>
<td>NBNBP4</td>
<td>4NaBr-26Na&lt;sub&gt;2&lt;/sub&gt;O-35B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-35P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
</tr>
<tr>
<td>5.</td>
<td>NBNBP5</td>
<td>5NaBr-25Na&lt;sub&gt;2&lt;/sub&gt;O-35B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-35P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
</tr>
</tbody>
</table>
\[ \sigma = \frac{\sigma_0}{T} e^{-\frac{E_a}{kT}} \]  

... (3.1)

where \( \sigma_0 \) is the pre-exponential factor, \( T \) is the absolute temperature, \( K \) is the Boltzmann constant and \( E_a \) is the activation energy.

Fig.3.1 presents the variation of \( \log \sigma T \) with \( \frac{10^3}{T} \) for the \( xKCl-(30-x)K_2O-35B_2O_3-35P_2O_5 \) glass system. From the plots activation energies were evaluated. The variation of activation energies with KCl content is presented in Fig.3.2. The isothermal conductivity plots at 408 K, 508 K and 608 K are plotted as a function of KCl content in Fig.3.3. The variation of conductivity as a function of KCl is non-linear (Fig.3.3). The conductivity was found to be maximum for 3 mole% of KCl, while for 4 mole% of KCl the conductivity was found to be minimum. The activation energy was found to be minimum at 3 mole% of KCl. As the KCl content was increased from 1 mol% to 2 mol% the conductivity decreases, then attains maximum at 3 mole%. Again the conductivity decreases at 4 mole % of KCl. Further, increase of KCl mole % resulted in the increase of conductivity. The glass system \( xKCl-(30-x)K_2O-35B_2O_3-35P_2O_5 \) exhibited inflections in the conductivity plot due to halide ion effect.

The dc ionic conductivity studies on the second glass system \( xKBr-(30-x)K_2O-35B_2O_5-35P_2O_5 \) were carried out. In this glass system the content of KBr and \( K_2O \) are varied. The dc conductivity was measured at different temperatures. Fig.3.4 shows the variation of \( \log \sigma T \) with \( 10^3/T \). The
Fig 3.1 Variation of $\log T$ vs 1000/T with KCl composition
Fig 3.2 Activation energy variation with KCl composition
Fig 3.3 Variation of conductivity isotherms with KCl composition
Fig 3.4 Variation of $\log T$ vs $1000/T$ with KBr composition
variation of conductivity can be represented by Arrenius equation (Eqn. 1). The isothermal conductivity plots as a function of KBr content are drawn in Fig.3.5 while Fig.3.6 presents the variation of activation energy with KBr content. The conductivity variation was found to be non-linear with KBr content variation. The conductivity maximum occurred at 3 mole% of KBr, while the minimum was observed at 4 mole%. Inflections were observed in the conductivity plots. Activation energy minimum was observed at 3 mole% of KBr. The variation of activation energy with KBr content was found to be non-linear.

Fig.3.7 presents the log $\sigma T$ vs. $10^3/T$ plots of the glass system $x$KI-(30-$x$)K$_2$O-35B$_2$O$_5$-35P$_2$O$_5$. In this glass system the contents of network modifier and the halide salt are varied. The variation of conductivity with temperature was found to obey the Arrhenius relation. The conductivity was found to increase with increase of temperature. The isothermal conductivity plots as a function of KI are presented in Fig.3.8. From these plots it was observed that the variation of conductivity was non-linear with KI content. The variation of activation energy with KI content was also found to be non-linear (Fig.3.9).

3.4.2 DC ionic conductivity studies on xNaR-(30-$x$)Na$_2$O-35B$_2$O$_3$-35P$_2$O$_5$

[where R = Cl and Br]

The dc electrical conductivity studies were carried out on the glass system xNaR-(30-$x$)Na$_2$O-35B$_2$O$_3$-35P$_2$O$_5$ | $x = 1, 2, 3, 4, 5$ mol% and R = Cl
Fig 3.5 Variation of conductivity isotherms with KBr composition
Fig 3.6 Activation energy variation with KBr composition
Fig 3.7 Variation of $\log T$ vs $1000/T$ with KI composition
Fig 3.8 Variation of conductivity isotherms with KI composition
Fig 3.9 Activation energy variation with KI composition
and Br]. The composition of the glass systems studied are given in Tables 3.4 and 3.5.

The dc ionic conductivity of the glass system xNaCl-(30-x)Na₂O-35B₂O₃-35P₂O₅ was measured at different temperatures below the glass transition temperatures. Fig.3.10 shows the log σT vs. 10³/T plots for the glass system. The conductivity was found to increase with increase in temperature and followed the Arrhenius equation. In Fig.3.11 variation of isothermal conductivity is plotted against NaCl content at 473 K, 523 K and 573 K. The conductivity was found to vary in a non-linear manner with NaCl content. The conductivity exhibited maximum at 1 mole% NaCl content while at 2 mole% there was minimum conductivity. From 2 mole% onwards the conductivity was found to increase with NaCl content. The activation energy variation with NaCl content is shown in Fig.3.12. The variation was found to be non-linear.

The conductivity plots of xNaBr-(30-x)Na₂O-35B₂O₅-35P₂O₅ (log σT vs. 10³/T) are shown in Fig.3.13. The conductivity was found to increase with increase in temperature and followed Arrhenius relation. The variation of isothermal conductivity at 408 K, 483 K and 558 K with NaBr content is given in Fig.3.14. The conductivity variation was found to be non-linear with NaBr content and maximum conductivity was observed at 3 mole% of NaBr. The variation of activation energy with NaBr content is shown in Fig.3.15. Minimum activation energy was observed at 3 mole% of NaBr.
Fig 3.10 Variation of log $T$ vs 1000/T with NaCl composition
Fig 3.11 Variation of conductivity isotherms with NaCl composition
Fig 3.12 Activation energy variation with NaCl composition
Fig 3.13 Variation of \( \log T \) vs 1000/T with NaBr composition
Fig 3.14 Variation of conductivity isotherms with NaBr composition
Fig 3.15 Activation energy variation with NaBr composition
In all the glass systems of $x\text{KR}-(30-x)\text{K}_2\text{O}-35\text{B}_2\text{O}_3-35\text{P}_2\text{O}_5$ ($R = \text{Cl, Br, I}$) and $x\text{NaR}-(30-x)\text{Na}_2\text{O}-35\text{B}_2\text{O}_3-35\text{P}_2\text{O}_5$ [$R = \text{Cl, Br}$], it was observed that the variation of conductivity and activation energy with KCl, KBr, KI, NaCl and NaBr content was found to be non-linear. As we proceed from chloride to iodine in the glass series, the ionic radius increases. Hence, K/Na-R electrostatic binding energy becomes weaker. The polarizability of halide increases the mobility of the mobile ion. It was observed from Raman spectroscopy and other experimental studies that the halide do not react with boron, phosphorous and oxygen network. The halide ions are not sufficient to break the B-O bond. The halide ions are merely assimilated into interstices of the network in contrast with the alkali oxide. An additional free volume is created by the halide ions. A small portion of cation can at any time breakaway in a pure alkali oxide glass. By the addition of alkali halide, excess of cations can be created over the oxide binding sites and expect these to be mobile. However, the extent of mobility will be determined by the size of the ion, structure of the glass, and relative to the size and continuity of the interspatial space between large anions.

As observed in the present work, the glass systems containing halide ions show dependence of the conductivity and activation energy on the halide ion content. This may give information regarding the structural changes in the glass network. In all the isothermal conductivity graphs of the halide systems the variation with halide content was found to be non-linear. In the glass systems studied the alkali halide content was increased and at the same time the alkali oxide (K$_2$O/Na$_2$O) content was decreased. In
the glass system the total potassium/sodium concentration is the sum of K\(^+\)/Na\(^+\) ion concentration from the alkali halide and alkali oxide. A significant variation in conductivity was observed with the variation of alkali halide content. It was observed from the similar studies of alkali glasses, that the glass network is not strongly modified by the addition of halide salt [33]. The results obtained may be explained on the basis of Diffusion Path Model (DPM) [43]. The fact that some alkali ions contribute to the conduction and the mobility is dependent on the glass composition may be explained in terms of the large potential energy difference resulting from the coexistence of two types of anions, halide and oxide.

Figure 3.16 (a, b and c) shows the schematic representation of the potential energy. This figure presents the schematic representation of various possible combinations of interaction potentials with distance. In the figure three types of combinations are shown. They are: (i) shallow-shallow (halide=halide) (3.16a), (ii) shallow deep (halide-oxide) (3.16b), (iii) (deep-deep (oxide-oxide) (3.16c).

The wide-shallow potential is formed by the interaction of cations (K\(^+\)/Na\(^+\)) with halide (Cl, Br, I) ions. The narrow deep one is formed by the interaction of cations with oxide ions. As the glass structure is of disorder type, a random distribution of potential energy among the potentials formed only by halide or oxide ions must be present. The potential curves are to be considered to involve the random distribution of potential energy formed by each anion. The alkali ions which are trapped in deep potential wells will be
Fig. 3.16: Schematic representation of the Potential energy with distance – (a) Shallow-Shallow, (b) Shallow-Deep and (c) Deep-Deep
less mobile than those in shallow wells. Therefore, the carrier concentration will depend on the number of alkali ions which are in shallow potential wells. The mobility will depend on how long the shallow wells are connected (Fig. 3.16a). If the shallow potential wells are connected for a long period, they form a favourable path for the ion transport. This type of path is referred to as diffusion path. Therefore, the conductivity will mainly be controlled by the nature and presence of the diffusion path in the glass system containing two different anions i.e., halide and oxide. Therefore, this kind of transport was called as the diffusion path model [44, 45]. This diffusion path model claims the presence of two types of alkali (K⁺/Na⁺) ions which are referred to as mobile and immobile (45-49). The mobile K⁺/Na⁺ ions interact with halide (Cl, Br, I) ions and should be located in potential wells as shown in Fig.3.16a. The mobile ions interact with oxide ions and will be located in potential wells shown in Fig.3.16c. Due to the random structure of the glasses the potential wells connected as in Fig.3.16b must be present in the glasses. As shown in Fig.3.16b K⁺/Na⁺ ions in the shallow wells can pump into the adjacent site, but those in the deep wells will find it more difficult to jump. The K⁺/Na⁺ ions located as shown in Fig.3.16b (shallow) are observed to be less mobile than those in the wells like Fig.3.16a (shallow-shallow) than those in the wells like Fig.3.16c (deep-deep). The presence of potential wells as shown in Fig.3.16b (shallow-deep) will make the difference obscure between mobile and immobile K⁺/Na⁺ ions. Also the EXAFS results support the existence of two types of K⁺/Na⁺ ions surrounded by halide and by oxide ions [50]. Computer simulation experiments [51] also reported the presence of the diffusion path favourable
for ion transport. This explains the non-linear variation of conductivity in the glasses studied.

3.5 CONCLUSIONS

DC ionic conductivity of the glasses xKR-(30-x)K₂O-35B₂O₃-35P₂O₅ [R = Cl, Br, I] and xNaR-(30-x)Na₂O-35B₂O₃-35P₂O₅ [R = Cl, Br] were measured at different temperatures and composition (x) values. Activation energies were evaluated from the conductivity plots (log \( \sigma T \) vs. \( \frac{10^3}{T} \)). The isothermal conductivity plots (log \( \sigma T \) vs. alkali halide composition) were also drawn. The conductivity was found to increase with increasing temperature and obeyed the Arrhenius equation. In all the glass systems the conductivity was found to vary in a non-linear manner with the alkali halide content. The variation of activation energy was also found to vary in a non-linear manner with alkali halide content. The present glass systems containing halide ions showed a dependence of the conductivity and activation energy on the halide ion content. The results obtained were explained using the diffusion path model. The non-linear variation was explained in terms of large potential energy difference resulting from the coexistence of the two types of anions i.e., halide and oxygen.
3.6 REFERENCES