CHAPTER 3
CHAPTER-3

PROPOSED METHOD FOR ANALYSIS OF ITC SPECTRUM

3.1 INTRODUCTION

In previous chapter we have discussed about different methods, as reported in literature, for the analysis of TSD or ITC spectrum. All these methods are based on different suggested mechanisms, as suggested by different workers engaged in the same work, for the appearance ITC spectrum. Most of the previously discussed methods focus on evaluation of dielectric relaxation parameters, only few methods are focused on order of kinetics parameter also. In all the discussed methods, there are some anomalies, like few of them are not concerned with order of kinetics, few of them are suitable only for monomolecular or first order kinetics, few of them have suggested different methods for different order of kinetics and most of them are not interested whether the evaluated values of dielectric relaxation parameters ($E_a$ and $\tau_0$) satisfies equation of peak temperature. Starting from the basic idea that ITC curve corresponding to monomolecular kinetics is very much similar to a TL glow curve involving monomolecular kinetics[10], and TL glow curves involving second and higher order kinetics [19,21,55 & 65] have already been reported in the literature, it was hence thought proper
to assess the involvement of second and higher order kinetics in ITC spectra also. With this aim in view, present work has been initiated and carried out. An attempt has been made to probe into the involvement of different order of kinetics in ITC measurements.

3.2 PROPOSED MODEL

In TSD processes, dielectric relaxation parameters $E_a$ and $\tau_o$ are usually evaluated following Bucci, Fieschi and Guidi (BFG) method [10]. Such evaluated values of $E_a$ and $\tau_o$ are expected to satisfy eq. (1.21). However, it has been observed that evaluated values of $E_a$ and $\tau_o$ do not satisfy eq. (1.21) in general. Such conclusion has been arrived at by Prakash and Nishad [66] while developing characteristic relaxation time for a lattice:dopant system. The same was unfortunately ignored and could not be then reported by the authors because of lack of vision, insight and proper explanation. Some representative data in support are presented in Table 1. It is obvious from the table that $T_m^2$ is different from $\left(\frac{b E_a \tau_m}{k}\right)$ which must have been equal as per eq. (1.21). Similar situation is observed in many other cases also. This clearly indicates and suggests the presence of a multiplying factor on the right hand side of eq. (1.21) such that the two sides of the equation become equal. It is anticipated that the multiplying factor may
include order of kinetics which when taken into account may lead to a situation when eq. (1.21) is satisfied. With this point in view a model has been developed for the occurrence of ITC spectrum.

TABLE 1

REPRESENTATIVE DIELECTRIC RELAXATION DATA OF SOME DOPED ALKALI HALIDE SYSTEMS SUPPOSEDLY INVOLVING FIRST ORDER KINETICS

<table>
<thead>
<tr>
<th>System</th>
<th>b (Ks(^{-1}))</th>
<th>T(_{m}) (K)</th>
<th>E(_a) (eV)</th>
<th>(\tau_0) (s)</th>
<th>(T^2_{m}) (K(^2))</th>
<th>(\frac{bE_A\tau_m}{K}) (K(^2))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl:Mn(^{2+})</td>
<td>0.1</td>
<td>214.3</td>
<td>0.67</td>
<td>9.1 \times 10^{-15}</td>
<td>45925</td>
<td>40989</td>
<td>[67]</td>
</tr>
<tr>
<td>NaCl:Mg(^{2+})</td>
<td>0.067</td>
<td>206</td>
<td>0.49</td>
<td>8.8 \times 10^{-11}</td>
<td>42436</td>
<td>32962</td>
<td>[68]</td>
</tr>
<tr>
<td>NaCl:NCO(^-)</td>
<td>0.012</td>
<td>65</td>
<td>0.192</td>
<td>2.0 \times 10^{-13}</td>
<td>4225</td>
<td>4176</td>
<td>[69]</td>
</tr>
<tr>
<td>NaCl:NO(_2^-)</td>
<td>0.022</td>
<td>18.9</td>
<td>0.04</td>
<td>7.0 \times 10^{-10}</td>
<td>357</td>
<td>335</td>
<td>[70]</td>
</tr>
<tr>
<td>KCl:Mg(^{2+})</td>
<td>0.1</td>
<td>189</td>
<td>0.49</td>
<td>3.85 \times 10^{-12}</td>
<td>35721</td>
<td>25799</td>
<td>[71]</td>
</tr>
<tr>
<td>KCl:Mn(^{2+})</td>
<td>0.1</td>
<td>192</td>
<td>0.49</td>
<td>6.2 \times 10^{-12}</td>
<td>36864</td>
<td>25959</td>
<td>[71]</td>
</tr>
<tr>
<td>KCl:Yb(^{3+})</td>
<td>0.1</td>
<td>215</td>
<td>0.67</td>
<td>1.1 \times 10^{-14}</td>
<td>46225</td>
<td>44025</td>
<td>[71]</td>
</tr>
<tr>
<td>KCl:AsO(_2^-)</td>
<td>0.1</td>
<td>58.3</td>
<td>0.161</td>
<td>1.6 \times 10^{-13}</td>
<td>3399</td>
<td>2505</td>
<td>[12]</td>
</tr>
<tr>
<td>KBr:AsO(_2^-)</td>
<td>0.01</td>
<td>60</td>
<td>0.169</td>
<td>2.4 \times 10^{-13}</td>
<td>3600</td>
<td>748</td>
<td>[12]</td>
</tr>
<tr>
<td>KBr:Se(^{2-})</td>
<td>0.05</td>
<td>230</td>
<td>0.72</td>
<td>2.0 \times 10^{-14}</td>
<td>52900</td>
<td>50691</td>
<td>[73]</td>
</tr>
<tr>
<td>KBr:Se(^{2-})</td>
<td>0.14</td>
<td>41</td>
<td>0.119</td>
<td>2.0 \times 10^{-13}</td>
<td>1681</td>
<td>1663</td>
<td>[69]</td>
</tr>
<tr>
<td>KBr:Cu(^{2+})</td>
<td>0.184</td>
<td>70.2</td>
<td>0.196</td>
<td>1.0 \times 10^{-13}</td>
<td>4928</td>
<td>4995</td>
<td>[74]</td>
</tr>
<tr>
<td>KI:Pb(^{2+})</td>
<td>0.059</td>
<td>201.2</td>
<td>0.61</td>
<td>4.5 \times 10^{-14}</td>
<td>40481</td>
<td>36287</td>
<td>[68]</td>
</tr>
<tr>
<td>KI:Se(^{2-})</td>
<td>0.046</td>
<td>215</td>
<td>0.64</td>
<td>1.3 \times 10^{-13}</td>
<td>46225</td>
<td>45249</td>
<td>[75]</td>
</tr>
<tr>
<td>KI:AsO(_2^-)</td>
<td>0.016</td>
<td>60.5</td>
<td>0.172</td>
<td>3.5 \times 10^{-13}</td>
<td>3660</td>
<td>2410</td>
<td>[12]</td>
</tr>
<tr>
<td>KI:Te(^{2-})</td>
<td>0.066</td>
<td>217</td>
<td>0.62</td>
<td>4.0 \times 10^{-14}</td>
<td>47089</td>
<td>4828</td>
<td>[76]</td>
</tr>
</tbody>
</table>

It has already been mentioned that depolarization current starts appearing when frozen-in polarized dipoles depolarize or disorient. The depolarization current density or ionic thermocurrent density \( J \) depends on
the rate of depolarization of IV dipoles and is expressed by eq. (1.5). The rate of depolarization, however, depends on the characteristic features of the system. As reported in the literature it depends on the remaining polarization \( P \) present at that time and on the relaxation time \( \tau \) at the corresponding temperature \( T \). It has been proposed here that it also depends on the order of kinetics \( \ell \) involved. Thus, the rate of depolarization is proposed to be expressed by

\[
-\frac{dP}{dt} = \left( \frac{1}{\ell} \right) \left( \frac{P}{\tau} \right)
\]

(3.1)

It is obvious that for \( \ell = 1 \), eq. (3.1) changes to conventional equation reported in the literature [5]. Eqs. (1.5) and (3.1) result into

\[
J = \left( \frac{1}{\ell} \right) \left( \frac{P}{\tau} \right)
\]

(3.2)

Now, eq. (3.1) can be solved to give

\[
P = P_o \exp \left[ -\left( \frac{1}{\ell} \right) \left( \frac{\ell}{\tau} \right) \right]
\]

(3.3)

where \( P_o \) is the maximum polarization or initial polarization at \( t = 0 \) i.e. the polarization at the start of the experiment. Isothermal decay of polarization for a hypothetical system for different order of kinetics evaluated using eq. (3.3) is shown in Fig.9.
FIG. 9: ISOTHERMAL DECAY OF POLARIZATION FOR A HYPOTHETICAL SYSTEM WITH $\tau = 50$ s. NUMBER ON THE CURVE REPRESENTS THE ORDER OF KINETICS.
It is obvious from the figure that the decay is fastest for first order kinetics. The decay becomes slower and slower with increasing order of kinetics. Thus, eq. (3.2) represents the mechanisms inherent in the ITC processes. With the help of eq. (1.3), one can write down eq. (3.3) as

\[ P = P_0 \exp \left[-\left(\frac{1}{\ell}\right)\left(\frac{t}{\tau_0}\right)\exp\left(\frac{E_a}{kT}\right)\right] \] (3.4)

The parameter \( (\ell \, \tau_0) \) can be named as the effective fundamental relaxation time. With increasing order of kinetics, \( (\ell \, \tau_0) \) will increase leading to increased value of effective relaxation time \( (\ell \, \tau) \) which will consequently lead to decrease the rate of depolarization in accordance with eq. (3.1). This statement is also supported by Fig.9. It would be justified to mention that the Arrhenius eq. (1.3) will remain unchanged because the relaxation time \( \tau \) changes to \( (\ell \, \tau) \) due to effective fundamental relaxation time \( (\ell \, \tau_0) \). Thus, the fundamental relaxation time of the system is \( \tau_0 \) but the effective fundamental relaxation time of the system is \( (\ell \, \tau_0) \). In the situations when \( \ell = 1 \), fundamental relaxation time becomes equal to effective fundamental relaxation time. It is this effective fundamental relaxation time which when taken into consideration may probably lead to satisfy eq. (1.21). It is due to experimental conditions prevailing during polarization and rate of rapid cooling that the fundamental relaxation time \( \tau_0 \)
of the system under investigation appears as \((\ell \tau_0)\). It is a well established fact that characteristic dielectric relaxation parameters \(E_a\) and \(\tau_0\) are fixed for the system under investigation and are independent of the experimental conditions of polarization. Thus in ITC runs recorded on a specimen, \(\ell\) is a representative of the experimental conditions of polarization and rapid cooling rate leaving \(E_a\) and \(\tau_0\) unaffected. Non-isothermal form of eq. (3.4) can be written as

\[
P = P_0 \exp \left[-\left(\frac{1}{t_0}\right) \int_0^t \exp \left(-\frac{E_a}{kT}\right) dt\right] \quad (3.5)
\]

When the system is heated following a constant linear heating rate \(b\) in accordance with eq. (1.9), one gets from eq. (3.5)

\[
P = P_0 \exp \left[-\left(\frac{1}{b t_0}\right) \int_{t_0}^T \exp \left(-\frac{E_a}{kT}\right) dT'\right] \quad (3.6)
\]

Eqs. (1.3) and (3.6) when substituted in eq. (3.2) result into

\[
J = \left(\frac{P_0}{\ell \tau_0}\right) \exp \left[-\left(\frac{E_a}{kT}\right) - \left(\frac{1}{b t \tau_0}\right) \int_{t_0}^T \exp \left(-\frac{E_a}{kT}\right) dT'\right] \quad (3.7)
\]

Eq. (3.7) in terms of current \(I\) can be written as

\[
I = \left(\frac{Q_0}{\ell \tau_0}\right) \exp \left[-\left(\frac{E_a}{kT}\right) - \left(\frac{1}{b t \tau_0}\right) \int_{t_0}^T \exp \left(-\frac{E_a}{kT}\right) dT'\right] \quad (3.8)
\]
where \( Q_o \) is the total charge released during ITC run and equals to \( P_o \cdot A \) where \( A \) is the cross-sectional area of the crystal specimen.

Eq. (3.8) represents the generalized equation for ITC spectrum involving \( \ell \)th order of kinetics. It is obvious that for \( \ell = 1 \), eq. (3.8) changes to eq. (1.14) corresponding to an ITC spectrum involving monomolecular or first order kinetics. Equations for ITC spectra involving second and higher order kinetics can be obtained from eq. (3.8) after substituting the corresponding values of \( \ell \) into it. It would be justified to mention just for the sake of reference that an equation similar to eq. (3.8) for TL studies has been developed by Prakash et. al. [21,77] where number of simplifying assumptions has been taken into account. Eq. (3.8) is, however, free from any assumption and is simpler and convenient in nature. It can be realized, however, from eq. (3.8) that for a fixed value of \( (\ell \cdot \tau_o) \), same ITC spectrum is reproduced which poses a problem in deciding the order of kinetics involved and in evaluating the values of dielectric relaxation parameters. However, in actual systems \( \ell \cdot \tau_o \) rarely happens to be the same particularly because of the fact that \( \tau_o \) is different for different systems and \( \ell \) depends on experimental conditions of polarization which ought to have been different in different ITC runs.
3.3 ITC PEAK

Eq. (3.2) when differentiated with respect to time gives

\[ \dot{J} \tau + J \dot{\tau} = \left( \frac{1}{\ell} \right) \dot{p} \]  

(3.9)

Now at the peak of the ITC spectrum, the value of \( \dot{J} \) is zero and hence one gets with the help of eq. (1.5)

\[ J \left[ \dot{\tau} + \left( \frac{1}{\ell} \right) \right] = 0 \]  

(3.10)

Using the value of \( \dot{\tau} \) from eq. (1.3) one can get

\[ T_m^2 = \frac{\ell b E_a s_m}{k} \]  

(3.11)

It can be seen that eq. (3.11) changes to eq. (1.21) for \( \ell = 1 \) corresponding to monomolecular kinetics. Eq. (3.11) happens to be a general equation wherefrom equations corresponding to different order of kinetics can be obtained after substituting the values of \( \ell \). It is obvious that the location of \( T_m \) is independent of concentration of dipoles as expected and appears at the same location when \( b \) is kept fixed.

3.4 METHOD OF ANALYSIS OF ITC SPECTRUM

Eq. (1.5) with the help of eq. (1.9) can be arranged to give
\[ P_o = \frac{1}{b} \int_{r_o}^{\infty} J(T')dT' \]  \hspace{1cm} (3.12)

which gives the value of \( Q_o \) through

\[ Q_o = \frac{1}{b} \int_{r_o}^{\infty} I(T')dT' \]  \hspace{1cm} (3.13)

The same expression has been mentioned already as eq. (1.13) and represents the total charge released during ITC run and equals to the area enclosed in the ITC spectrum.

Eq. (1.5) can also be rearranged to give

\[ P = \frac{1}{b} \int_{T}^{\infty} J(T')dT' \]  \hspace{1cm} (3.14)

where \( P \) is the polarization remaining at the temperature \( T \). Corresponding value of \( Q \) (= \( P A \)) at \( T \) is given by

\[ Q = \frac{1}{b} \int_{T}^{\infty} I(T')dT' \]  \hspace{1cm} (3.15)

where \( Q \) is the charge remaining at the temperature \( T \) and equals to the area of the ITC spectrum enclosed within the temperature range \( T \) to \( \infty \). Thus, \( Q_o \) and \( Q \) can be obtained from ITC spectrum using eqs. (1.13) and (3.15), respectively. In the quest of establishing a methodology for the analysis of ITC spectrum with a view to evaluate the values of dielectric
relaxation parameters and order of kinetics, considerations of mechanisms inherent in the ITC processes may probably be helpful.

It is obvious from eq. (1.5) that the depolarization current density $J$ depends on the rate of depolarization or decay of polarization. If decay of polarization is fast, the magnitude of $J$ will obviously be large. Fig. 9 suggests that decay of polarization becomes slower and slower with increasing order of kinetics leading to consequent decreased value of $J$. This conclusion finds a support through Fig. 10, where ITC curves of hypothetical systems involving different order of kinetics evaluated using eq. (3.8) are shown. However, such a conclusion only provides a qualitative explanation. The decay of polarization as per eq. (3.1) depends on $P$, $\tau$ and $\ell$. It is found that $\tau_0$ depends on the characteristic feature of the system and $\ell$ depends on the experimental conditions of polarization. Consequently for a given ITC run of a system, $\tau_0$ and $\ell$ will behave as a constant quantity. Thus, isothermal decay of polarization for a system becomes proportional to $P$. More $P$ means faster decay of polarization leading to large magnitude of $J$. However, such a conclusion only provides a qualitative explanation. The decay of polarization as per eq. (3.1) depends on $P$, $\tau$ and $\ell$. 
FIG. 10: ITC spectra involving different order of kinetics for a hypothetical system with $E_a = 0.60$ eV, $\tau_0 = 5.0 \times 10^{13}$ s, $Q_0 = 3.0 \times 10^{11}$ C and $b = 0.05$ Ks$^{-1}$. The number on the curves represents the involved order of kinetics.
It is found that $\tau_0$ depends on the characteristic feature of the system and $\ell$ depends on the experimental conditions of polarization. Consequently for a given ITC run of a system, $\tau_0$ and $\ell$ will behave as a constant quantity. Thus, isothermal decay of polarization for a system becomes proportional to $P$. More $P$ means faster decay of polarization leading to large magnitude of $J$. Less value of $P$ means slower decay of polarization leading to small magnitude of $J$. In a hypothetical system with same value of $P$ but involving higher order of kinetics say $\ell = 2$, the effective remaining polarization $P$ becomes half leading to smaller magnitude of $J$. Thus, involvement of higher order of kinetics means slower decay of polarization. Had first order kinetics been involved, the decay of polarization would have been faster leading to higher magnitude of $J$. However, the characteristic features i.e. dielectric relaxation parameters $E_a$ and $\tau_0$ of the system shall not change. Involvement of higher order of kinetics means slower decay of polarization which will only decrease the magnitude of $J$ but the dielectric relaxation parameters $E_a$ and $\tau_0$ will remain unchanged. Thus, a system with lesser $P_0$ means a system having slower decay of polarization. Dipole-dipole interaction may be the reason for the involvement of higher order of kinetics. Fastest decay or exponential decay of polarization of Fig. 9 for first
order kinetics corresponds to Debye relaxation suitable for the cases having no dipolar interaction. In the presence of dipole-dipole interaction the decay of polarization becomes non-exponential leading to slower and slower decay of polarization. Thus, it is obvious that the nature of decay of polarization decides the order of kinetics involved. The dielectric relaxation parameters $E_a$ and $\tau_o$, however, remain unaffected. Mechanism responsible for non-exponential decay of polarization is discussed elsewhere [5,20,55].

In an alkali halide matrix having IV dipoles, $P_o$ at the polarization temperature $T_p$ is given by

$$P_o = \frac{N p^2 E}{3 k T_p} \quad (3.16)$$

where $N$ is the number of IV dipoles per unit volume each of dipole moment $p$ and $E$ is the polarizing electric field. In a given system, $P_o$ is proportional to $N$ provided $E$ and $T_p$ are kept constant. Obviously, $P_o$ will be more if $N$ is more leading to faster decay of polarization which results into higher magnitude of $J$. It has been observed experimentally that concentration of dipoles $N$ does not change the values of dielectric relaxation parameters $E_a$ and $\tau_o$ but the depolarization current density increases proportionally. Thus, involvement of higher order of kinetics means
that a sample of the same system with lesser value of $N$ has been considered. It is hence obvious that experimental conditions of polarization and rate of rapid cooling are the prime parameters which decide the involvement of different order of kinetics in ITC spectrum. However, the analysis of such an ITC spectrum will ultimately give the same values of $E_a$ and $\tau_o$ because the experiment is carried out on a sample of the same system. Had monomolecular kinetics been involved, $J$ would have been more without affecting the values of $E_a$ and $\tau_o$. Thus, the evaluated values of $E_a$ and $\tau_o$ correspond to an ITC spectrum involving monomolecular or first order kinetics and remain unaffected with either $N$ or $\ell$. It is thus obvious that $\ell$ does not represent in any way the characteristic feature of the system under investigation. Experimental data recorded in KCl: Sr$^{2+}$ single crystals [10] presented in Fig. 5 following initial rise method support this statement. Parallel lines suggest that $E_a$ is same. The intercepts are different for different parallel lines because of changed value of $N$ which ultimately results into the same value of $\tau_o$. Thus, $E_a$ and $\tau_o$ are the characteristic dielectric relaxation parameters of the system and are found to be independent of the order of kinetics and experimental conditions. Hence, dielectric relaxation parameters $E_a$ and $\tau_o$ can be obtained from eq. (3.8) after
substituting \( \ell = 1 \) in it. In such a case eq. (3.8) with the help of eqs. (3.6) and (3.7) for \( \ell = 1 \) can be written as

\[
I = \frac{Q}{\tau_o} \exp \left( -\frac{E_a}{kT} \right)
\]  

(3.17)

which can be rearranged as

\[
\ln \left( \frac{Q}{I} \right) = \ln(\tau_o) + \frac{E_a}{kT}
\]  

(3.18)

It is obvious that \( \ln \left[ \frac{Q}{I} \right] \) when plotted against \( \frac{1}{T} \) will give a straight line in accordance with eq. (3.18). The slope and intercept of the straight line give the values of \( E_a \) and \( \tau_o \), respectively. This is effectively BFG method of analysis [10] written in a changed form. Knowing the values of \( E_a \) and \( \tau_o \), order of kinetics can be obtained from eq. (3.11). \( \ell \) can also be obtained from eq. (3.8) through iteration after substituting the evaluated values of \( E_a \) and \( \tau_o \). The value of \( N \) can also be estimated using eq. (3.16). Due to uncertainty in the value of \( T_p \) [78,79], eq. (3.16) gives the approximate value of \( N \). Thus, the values of \( E_a, \tau_o, \ell \) and \( N \) can be obtained with the help of the suggested methodology conveniently and easily.

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