<table>
<thead>
<tr>
<th><strong>Title</strong></th>
<th>Dielectric Behavior of Ethylenediamine Oligomer (Physical and Inorganic Chemistry)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Author(s)</strong></td>
<td>Ikada, Eiji</td>
</tr>
<tr>
<td><strong>Citation</strong></td>
<td>Bulletin of the Institute for Chemical Research, Kyoto University (1968), 45(4-5): 352-362</td>
</tr>
<tr>
<td><strong>Issue Date</strong></td>
<td>1968-01-20</td>
</tr>
<tr>
<td><strong>URL</strong></td>
<td><a href="http://hdl.handle.net/2433/76206">http://hdl.handle.net/2433/76206</a></td>
</tr>
<tr>
<td><strong>Type</strong></td>
<td>Departmental Bulletin Paper</td>
</tr>
<tr>
<td><strong>Textversion</strong></td>
<td>publisher</td>
</tr>
</tbody>
</table>

Kyoto University
Dielectric Behavior of Ethylenediamine Oligomer

Eiji Ikada
(Koizumi Laboratory)

Received September 18, 1967

Dielectric properties of the ethylenediamine oligomer, \( H_2NC_2H_4(HNC_2H_4)_{n-1}NH_2 \) (\( n=1, 2, 3, \) and 4) were studied in order to elucidate the molecular behavior in liquid and supercooled states.

Dielectric measurements have been made at frequencies from 7.5 Hz to 5 MHz over the temperature ranges of \(-78.5\) to \(+60^\circ\text{C}\) in ethylenediamine and triethylenetetramine, and of \(-100\) to \(+60^\circ\text{C}\) in diethylenetriamine, respectively. Some related physical constants of these compounds were determined. It has been found that in these oligomers the static dielectric constants were related to the dipole moments by the Onsager equation and that the temperature dependence of the dielectric constants was well represented empirically by the equation

\[ \varepsilon = a + \frac{b}{T}, \]

where \( a \) and \( b \) are empirical constants and \( T \) the absolute temperature.

In supercooled state the oligomers exhibited a dielectric relaxation which was interpreted as superposition of the circular arc and the skewed arc relaxations.

INTRODUCTION

It is well known that some hydrogen-bonded liquids such as water and \( n \)-alcohol show a large primary dielectric relaxation which is expressed by Debye's equation or a semi-circle\(^1\) and that the strong intermolecular hydrogen bonding between the end OH groups plays an important role in the relaxation. In the ethylene glycol oligomer\(^2\) the dielectric behavior also exhibited the evidence of strong hydrogen bonding between OH groups and showed some distribution of relaxation times which was due to the local orientation of part of the molecule in addition to the orientation of the molecules as a whole.

Although the NH\(_2\) groups are capable of hydrogen bonding formation, the dielectric behavior of compounds having the NH\(_2\) and NH groups are not extensively studied yet. In the present work dielectric studies of the ethylenediamine oligomer, \( H_2NC_2H_4(HNC_2H_4)_{n-1}NH_2 \) (\( n=1, 2, 3, \) and 4), were undertaken in connection with the contribution of hydrogen bond to the dielectric behavior of this oligomer. Also an interest was taken in dielectric relaxation of these non-rigid molecules.

This paper reports the static dielectric constant and their relation to the intermolecular hydrogen bonding and also dielectric relaxations in the supercooled liquid state.

EXPERIMENTAL

Materials

The oligomer samples used are ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), and tetraethylenepentamine (TEPA) which

*英之茂

(352)
Dielectric Behavior of Ethylenediamine Oligomer

were prepared by fractional distillation of commercial products from Union Carbide Corporation. Commercial ethylenediamine was dried over sodium and fractionally distilled three times at a reduced pressure of nitrogen; b.p. 32° (22 mm); m.p. 10.65°. Other commercial oligomers were purified by drying over Drierite and by successive fractional distillations under reduced nitrogen atmosphere. Diethylenetriamine: b.p. 65° (1.7 mm); m.p. −39.7°. Triethyleneteramine: b.p. 111° (1.4 mm). Tetraethylenepentamine: b.p. 152° (1.7 mm). Purified samples were kept under dry nitrogen atmosphere.

Measurements

A Type TR-1-A Transformer Bridge from Ando Electric Company was employed for measurements of capacitance and conductance which worked over a frequency range from 7.5 Hz to 5 MHz. The dielectric cell consisted of concentric platinum cylinders; the cell constant was determined by use of standard liquids. For dielectric measurements below dry ice temperature the temperature control bath was filled with a non-flammable mixture and cooled by liquid nitrogen. An Au-Co versus Cu thermocouple was convenient for measurements of low temperature.

Density measurements were made with a pycnometer of the Lipkin type and refractive indices were measured by a Pulfrich refractometer. Refractive indices and densities of the oligomers are tabulated together with literature values in Tables 1 and 2, respectively.

The samples were transferred into the cell and the pycnometer in a dry box filled with nitrogen to avoid the contamination by moisture and carbon dioxide.

Table 1. Refractive indices \( n_0 \) of ethylenediamine oligomers.

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>EDA ( \text{lit.}^4 )</th>
<th>DETA</th>
<th>TETA</th>
<th>TEPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.45677</td>
<td>1.45677</td>
<td>1.48443</td>
<td>1.49847</td>
</tr>
<tr>
<td>25</td>
<td>1.45418</td>
<td>1.4513</td>
<td>1.48216</td>
<td>1.49640</td>
</tr>
<tr>
<td>30</td>
<td>1.45169</td>
<td>1.47980</td>
<td>1.49224</td>
<td>1.49788</td>
</tr>
<tr>
<td>40</td>
<td>1.44881</td>
<td>1.47523</td>
<td>1.49018</td>
<td>1.49788</td>
</tr>
</tbody>
</table>

Table 2. Densities of ethylenediamine oligomers in g/ml.

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>EDA ( \text{lit.}^4 )</th>
<th>DETA ( \text{lit.}^6 )</th>
<th>TETA ( \text{lit.}^5 )</th>
<th>TEPA ( \text{lit.}^5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.8978</td>
<td>0.8977</td>
<td>0.9517</td>
<td>0.9525</td>
</tr>
<tr>
<td>25</td>
<td>0.8934</td>
<td>0.9478</td>
<td>0.9751</td>
<td>0.9939</td>
</tr>
<tr>
<td>30</td>
<td>0.8885</td>
<td>0.9436</td>
<td>0.9711</td>
<td>0.9864</td>
</tr>
<tr>
<td>40</td>
<td>0.8792</td>
<td>0.9352</td>
<td>0.9632</td>
<td>0.9787</td>
</tr>
<tr>
<td>50</td>
<td>0.8697</td>
<td>0.9267</td>
<td>0.9553</td>
<td>0.9715</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Static Dielectric Constant

Static dielectric constants of EDA, DETA, TETA, and TEPA are listed in Table 3. These ethylenediamine oligomers showed relatively small dielectric constants in comparison with strongly hydrogen-bonded liquids such as \( n \)-alcohols and polyethylene glycols. The larger the molecule in this homolog, the smaller was the dielectric constants, because of a decrease in concentration of the end NH\(_2\) group with increasing the molecular dimension. DETA, TETA, and TEPA are easily supercooled down to about \(-80^\circ C\). No discontinuity was observed in the curve of dielectric constant versus temperature between liquid and supercooled liquid states as shown in Fig. 1. This indicates that these three compounds have the freedom of dipole orientation in the supercooled state. The dielectric constant of EDA dropped abruptly at the melting point, showing a small value in the crystalline solid state.

Kimura, Toshiyasu, and Fujishiro\(^7\) and Okamoto et al\(^8\) studied the dipole moment of this particular oligomer and found that the observed dipole moments in benzene solutions were in good agreement with those calculated under the assumption of free rotation around the C-C and C-N bonds. The Kirkwood equation correlates the static dielectric constant with the dipole moment\(^9\)

\[
\varepsilon_0 = \varepsilon_\infty + \frac{3\varepsilon_\infty + 2}{2\varepsilon_\infty + \varepsilon_\infty} \left( \frac{\varepsilon_\infty + 2}{3} \right)^2 \cdot \frac{4\pi N \mu_0 g}{3kT},
\]

where \( \varepsilon_0 \) is the static dielectric constant, \( \varepsilon_\infty \) the dielectric constant at infinite frequency, \( \mu_0 \) the molecular dipole moment in vacuum, \( N \) the number of dipoles in cubic centimeter, \( g \) Kirkwood's correlation factor, \( Z \) the number of the nearest neighbor, \( \langle \cos \theta \rangle \) the average of cosine of the angle between the reference dipole
Dielectric Behavior of Ethylenediamine Oligomer

Fig. 1. Plots of static dielectric constants of ethylenediamine oligomers versus reciprocal of absolute temperature.

and its $Z$ neighbors, and $k$ and $T$ have the usual significance.

The values of $g$ for these compounds obtained from the dielectric constants

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>EDA</th>
<th>DETA</th>
<th>TETA</th>
<th>TEDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>-60</td>
<td>...</td>
<td>1.34</td>
<td>...</td>
<td>1.20</td>
</tr>
<tr>
<td>-50</td>
<td>...</td>
<td>1.33</td>
<td>1.19</td>
<td>1.19</td>
</tr>
<tr>
<td>-40</td>
<td>...</td>
<td>1.32</td>
<td>1.18</td>
<td>1.18</td>
</tr>
<tr>
<td>-30</td>
<td>...</td>
<td>1.31</td>
<td>1.17</td>
<td>1.17</td>
</tr>
<tr>
<td>-20</td>
<td>...</td>
<td>1.29</td>
<td>1.15</td>
<td>1.15</td>
</tr>
<tr>
<td>-10</td>
<td>...</td>
<td>1.23</td>
<td>1.13</td>
<td>1.13</td>
</tr>
<tr>
<td>0</td>
<td>1.22</td>
<td>1.26</td>
<td>1.13</td>
<td>1.14</td>
</tr>
<tr>
<td>10</td>
<td>1.21</td>
<td>1.24</td>
<td>1.12</td>
<td>1.12</td>
</tr>
<tr>
<td>20</td>
<td>1.21</td>
<td>1.24</td>
<td>1.11</td>
<td>1.11</td>
</tr>
<tr>
<td>30</td>
<td>1.20</td>
<td>1.22</td>
<td>1.09</td>
<td>1.10</td>
</tr>
<tr>
<td>40</td>
<td>1.20</td>
<td>1.21</td>
<td>1.08</td>
<td>1.09</td>
</tr>
<tr>
<td>50</td>
<td>1.18</td>
<td>1.19</td>
<td>1.07</td>
<td>1.08</td>
</tr>
</tbody>
</table>

Table 4. Kirkwood $g$ factors of ethylenediamine oligomers.
and the dipole moments\(^{10}\) are nearly equal to 1 as shown in Table 4. This means
that the short range interaction such as hydrogen bonding is rather weak in the
ethylenediamine oligomer and that the N-H intermolecular hydrogen bond does
not contribute much to the static dielectric constant. It was found that the ethyl-
enediamine oligomer exhibits the behavior similar to non-hydrogen bonded polar
liquid, as far as the static dielectric constant is concerned. Trouton’s constant
also indicates that the intermolecular interaction in this oligomer is weak, com-
pared with the ethylene glycol oligomer, as shown in Table 5.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>EDA 25.73</td>
<td>Ethylene</td>
</tr>
<tr>
<td>DETA 25.36</td>
<td>Diethylene</td>
</tr>
<tr>
<td>TETA 24.40</td>
<td>Triethylene</td>
</tr>
<tr>
<td>TEPA 23.88</td>
<td>Tetraethylene</td>
</tr>
</tbody>
</table>

Table 5. Comparison of Trouton’s constants of ethylenediamine\(^{10}\) and
ethylene glycol\(^{11}\) oligomers.

These static dielectric constants in liquid and supercooled liquid states increase
linearly with the reciprocal of absolute temperature, as is the case with some
other liquids, (Fig. 1) and can be expressed by the empirical relation

\[ \varepsilon_0 = a + \frac{b}{T}, \]

where \(a\) and \(b\) are empirical constants. Numerical values of \(a\) and \(b\) are shown
in Table 6.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>EDA</td>
<td>-6.547</td>
</tr>
<tr>
<td>DETA</td>
<td>-7.364</td>
</tr>
<tr>
<td>TETA</td>
<td>-5.460</td>
</tr>
<tr>
<td>TEPA</td>
<td>-3.825</td>
</tr>
</tbody>
</table>

Table 6. The numerical values \(a\) and \(b\) for the equation \(\varepsilon = a + b/T\).

Dielectric relaxation

Of these four compounds studied, only EDA crystallized easily at the melting
point and the dielectric constant dropped to a small value. Solid EDA showed
the wedge-type dispersion\(^{12}\) which is often observed for ionic crystals, hydrogen-
bonded organic solids and some solid systems with ionic impurity. Figure 2 shows
the frequency dependence of the dielectric constant in the crystalline solid of EDA.
The dispersion in this case may be caused by the ionic space charge due to the
weak hydrogen bonding in the solid. With decreasing temperature, the intensity
of this polarization decreased. This would be due to the decreased mobility of
charge carrier. Other three compounds remained in the supercooled liquid state
Dielectric Behavior of Ethylenediamine Oligomer

Fig. 2. Plots of log $\varepsilon'$ in the wedge type dispersion of EDA against frequency.

even at dry ice temperature and exhibited dielectric relaxation. The dielectric dispersion and absorption in DETA at various temperature are shown in Figs. 3 4, respectively. Figures 5 and 6 illustrate the frequency dependence of the dielectric constant and loss in TETA, respectively. As seen from Figs. 4 and 6, the curves of the dielectric loss versus logarithm of frequency are not symmetrical in these compounds.

Fig. 3. Frequency dependence of dielectric constant of DETA.

In many cases the dielectric relaxation can be fitted by one of the following equations:

$$
\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\tau}
$$

Debye type; 13

Cole-Cole or circular arc type; 14

Davidson-Cole or skewed arc type, 15

where $\varepsilon'$ is the real part of complex dielectric constant, $\varepsilon''$ the imaginary part of complex dielectric constant or the dielectric loss, $\varepsilon_0$ the static dielectric constant,
The dielectric loss of diethylenetriamine is shown in Fig. 4.

Dielectric constant of TETA is shown in Fig. 5.

The expression is given by:

\[ \varepsilon = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega \tau} \]

where \( \varepsilon_\infty \) is the limiting dielectric constant at high frequency, \( \tau \) the mean relaxation time, \( \omega \) the angular frequency, and \( \alpha \) and \( \beta \) are parameters for the distribution of relaxation time.

With these polyethyleneimines except EDA the relaxation may be interpreted in terms or superposition of two types of relaxation. A typical example of overlapping of the absorption regions are shown for DETA in Fig. 7. The superposition of the relaxation regions is illustrated with DETA and TEPA in the complex plane plots in Fig. 8 and 9. With DETA and TETA the low-frequency relaxation was fitted by the Debye type and the high frequency one by the relaxation of...
Dielectric Behavior of Ethylenediamine Oligomer

Fig. 6. Frequency dependence of dielectric loss of TETA.

Fig. 7. Dielectric loss of DETA. Dashed curves represent calculated curves for the Debye type and the skewed arc relaxation of $\beta = 0.35$ and circles $\ominus$ show the residual dielectric loss when the Debye type absorption is subtracted from the total loss.

the skewed arc type (Fig. 8). However in the case of TEPA the observed relaxation was separated into the circular arc and the skewed arc types as shown in Fig. 9. Therefore it was found that the dielectric relaxation in these oligomers was expressed

$$
\varepsilon^* = \varepsilon_{\infty} + \frac{\varepsilon_{\infty 1} - \varepsilon_{\infty 1}}{1 + (j\omega \tau_1)^{\alpha - 1}} + \frac{\varepsilon_{\infty 2} - \varepsilon_{\infty 2}}{(1 + j\omega \tau_2)^{\beta}}
$$

where $\varepsilon^* (\varepsilon = \varepsilon' - j\varepsilon'')$ is the observed complex dielectric constant; subscripts 1 and 2.

(359)
Fig. 8. Complex dielectric constants of TETA. Solid and dashed curves show observed and calculated curves, respectively.

Fig. 9. Complex dielectric constants of TETA.

2 mean the low- and high-frequency relaxation regions, $\epsilon_{\infty} = \epsilon_{\infty 1}$, $1 > \alpha > 0$ and $1 > \beta > 0$.

It has been reported that the supercooled state exhibits the skewed arc relaxation in some compounds such as glycols$^{15,16,22}$ and alkyl halides$^{23}$. Other types of dielectric relaxation$^{18,19}$ have been discussed concerning the distribution of relaxation times. The superposition of two different types of relaxation as is the case with the present work has been suggested for a few examples$^{20,21}$.

Meinnel and Martin$^{22}$ studied the dielectric relaxation of alkyl halides in the supercooled state and found that the dipole relaxation depended on the rate of
Dielectric Behavior of Ethylenediamine Oligomer

solidification and might be explained by conformational isomerism of non-rigid molecules. They also suggested that in general at least two dispersions might appear at the supercooled state for organic compounds and that the activation energy was greater than 1 eV and the entropy was about 100 e.u.\(^2\). The relaxation times in low- and high-frequency regions of DETA, TETA and TEPA are listed in Table 7. Logarithm of the relaxation times are plotted against reciprocal of the absolute temperature in Fig. 10. The activation enthalpy and entropy obtained for these oligomers are 25 kcal/mole and 100 e.u in both low- and high-frequency relaxations. These results are very similar to those of 2- methyl pentanediol 2, 4\(^2\).

Table 7. The relaxation times of ethylenediamine oligomers.

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>Low frequency</th>
<th>High frequency</th>
<th>Low frequency</th>
<th>High frequency</th>
<th>Low frequency</th>
<th>High frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>−60</td>
<td></td>
<td>3.54×10(^{-5})</td>
<td>7.96×10(^{-7})</td>
<td>3.98×10(^{-5})</td>
<td>3.98×10(^{-6})</td>
<td></td>
</tr>
<tr>
<td>−70</td>
<td></td>
<td>8.61×10(^{-8})</td>
<td>1.45×10(^{-5})</td>
<td>1.68×10(^{-3})</td>
<td>1.59×10(^{-4})</td>
<td></td>
</tr>
<tr>
<td>−78.5</td>
<td>7.96×10(^{-6})</td>
<td>1.59×10(^{-6})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>−90</td>
<td>3.98×10(^{-4})</td>
<td>9.10×10(^{-5})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>−95</td>
<td>3.98×10(^{-3})</td>
<td>7.96×10(^{-4})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 10. Plots of logarithm of relaxation time versus reciprocal absolute temperature.

The molecular mechanism of these two relaxations have not been made clear. However it may be considered that the low-frequency relaxation is attributed to the dipole orientation of the molecule as a whole and that the high-frequency...
Eiji Ikada

relaxation from the segmental motion of the molecule.

ACKNOWLEDGMENT

The author wishes to express sincere thanks to Professor Naokazu Koizumi and Associate Professor Tetsuya Hanai for many helpful discussions and criticism during the course of this study. He is also grateful to Nagase and Company Ltd., for supplying samples used in this investigation.

REFERENCES

(3) American Institute of Physics, "Temperature" (Reinhold publishing Co.) (1941) p. 208.
(8) H. Okamoto and N. Koizumi, unpublished.
(22) J. Meinnel and G. Martin, ibid., p. 56.