The Pressure Effect of the Association of 2, 4, 6, N-Tetramethyl Pyridinium Iodide in Ethanol-Water Mixture

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요 약. 루지 헤센트 95 %의 에탄올-물 혼합용매에서 2, 4, 6, N-테트라메틸 피리딘יום아로드 (TeMPI)의 이온화합 상수(K)를 수정한 자외선분광 및 전기 전도도 혼합용매로 운도범위 25 〜 50°C, 압력범위 1 〜 2,000 bars에서 결정하였다. K값은 압력이 증가함에 따라 증가하였고 40°C에서 최
대값을 나타내었다. 부분물질Density(1D)는 비교적 작은 음의 값이 있으며 ΔV의 최대값은 40°C에
서 최소값을 보여주었다. TeMPI의 이온 크기 반수(α)는 40°C에서 최대값을 가졌다. ΔH° 값은 40,
25°C 그리고 50°C에서 각각 4.0, 7.6 및 11.0 cal/mol로 나타났으며 엔트로피(ΔS°)의 자유에너지(ΔG°)와
같은 다른 열역학적수 값도 계산하였다. 이와 같은 실험결과로부터 우리들은 TeMPI가 압력증가에
대하여 안정화되고, 40°C까지는 운도증가에 따라서도 안정화를 보여주었다. 그러나 40°C에
서는 TeMPI 두 분자에 있는 8개 메틸기의 분자간 소수성 상호작용으로 인하여 약한 이원체를 형성
하고 50°C 이상에서는 다시 열적으로 분해된다는 결과를 얻게 되었다.

ABSTRACT. The ionic association constants(K) of 2, 4, 6, N-tetramethyl pyridinium iodide (TeMPI) in 95 volume percentage ethanol-water mixture were determined by a modified UV and conductance method at 23°C to 50°C under 1 to 2,000 bars. The K values increase with increasing pressure and have maximum value at 40°C. The partial molar volume change (ΔV) has relatively small negative value and the absolute values of Δ are minimum at 40°C. The ion size parameter(α) of TeMPI have maximum value at 40°C. ΔH° values are zero, positive and negative at 40°C, 25°C and 50°C respectively. Other thermodynamic parameters such as the changes of standard entropy(ΔS°) and free energy(ΔG°) were evaluated. From these experimental results, we came to conclusion that TeMPI is stabilized by the elevation of pressure and that of temperature below 40°C but weakly dimerized at 40°C because of the intermolecular hydrophobic interaction of eight methyl groups of two molecules. And it thermally decomposed above 50°C.
INTRODUCTION

It has been studied by Kosower\(^1,2\) that N-methyl pyridinium iodide(NMPI) gives rise to an ultraviolet charge transfer band in aqueous solution. Paul Hemmes et al. investigated the thermodynamics for the association of NMPI in water-alcohol mixtures.\(^3\) The extensive research for the association of the four para substituted pyridinium iodides in the same mixtures is also accomplished by J.G. Jee by means of a modified UV method with conductance and CNDO /2 scheme.\(^4\) The charge transfer band arises due to a transferral of electron density from an occupied orbital of the iodine anion to the pyridinium cation and it results in the formation of ionic dipolar complex salt.\(^4\)

In this paper, the pressure effect for the ionic association of the 2,4,6,N-tetramethyl pyridinium iodide(TeMPI) in the ethanol-water mixture was investigated by UV and conductance method and discussed by using of the thermodynamic parameter.\(^5\)

Equation (1) is the ionic equilibrium relationship for the TeMPI:

\[ A^+ + \mathbf{D}^- \rightarrow \mathbf{A}^+ \mathbf{D}^- \]  
\[ (\text{an abbreviation}) \]

where \( A^+ \), \( \mathbf{D}^- \) and \( \mathbf{A}^+ \mathbf{D}^- \) are a cationic electron acceptor, anionic electron donor and dipolar ionic complex, \( C_0^+ \) and \( C_0^- \) are the initial molar concentration of \( A^+ \) and \( \mathbf{D}^- \), respectively and \( x \) is the molar concentration of \( \mathbf{A}^+ \mathbf{D}^- \) at equilibrium state.

Since \( K \) is the function of the ionic strength depending upon the TeMPI concentration, we must modify the association constant\((K)\) with the Shedlovsky function, \( S \).\(^4\) Therefore, putting \( x = A/\epsilon \), the next equation is obtained.

\[ KS = \frac{A/\epsilon}{(C_0^+ - A/\epsilon)(C_0^- - A/\epsilon)} \]  
\[ (2) \]

where \( A \) and \( \epsilon \) are the absorbancy (optical density) and molar absorptivity (extinction coefficient) of \( \mathbf{A}^+ \mathbf{D}^- \) at absorption maxima, \( \lambda_{max} \).

Letting \( C_0^+ = C_0^- = C_0 \) and taking the Shedlovsky correction of the degree of dissociation, \( \gamma = (A/C_0)S \) in the nonaqueous system\(^6\) where \( A, C_0 \) and \( S \) are the equivalent conductance, limiting equivalent conductance of \( \mathbf{A}^+ \mathbf{D}^- \), and the Shedlovsky function, respectively, eq. (2) is rearranged by\(^4\)

\[ \frac{C_0^+S}{A} = \frac{1}{\epsilon}(1 + \gamma)C_0S + \frac{1}{K \epsilon} \]  
\[ (3) \]

And the following relation is given by

\[ \epsilon = \frac{A}{C_0 - \gamma C_0} \]  
\[ (4) \]

Then the degree of dissociation, \( \gamma \), is obtained by\(^4\)

\[ \gamma = \frac{(fC_0 - A/\epsilon)}{fC_0} \]  
\[ (5) \]

where \( f \) is the activity coefficient given by the following relationship from the Debye-Hückel limiting equation.\(^7\)

\[ -\log f = 1.290 \times 10^6 |z_1z_2| (DT)^{-3/2} \sqrt{C_0} \]  
\[ 1 + \sqrt{C_0} \]  
\[ (6) \]

where \( z_1 \) and \( z_2 \) are the ionic valancies \( D \) the dielectric constant of the solvent and the other parameter have the conventional physical meaning.

Substituting \( C_0 \) with effective concentration \( fC_0 \) in the eq. (3), the result is

\[ \frac{(fC_0)^3S}{A} = \frac{1}{\epsilon}(1 + \gamma) fC_0S + \frac{1}{K \epsilon} \]  
\[ (7) \]
The first correction of \( \varepsilon \) in the eq. (4) is obtained from the value of the relationship,
\[
\gamma = (\Delta/\rho_0)S
\]
where \( \gamma \) value can be corrected from the eq. (5) by using the first corrected \( \varepsilon \) value and \( f \) value obtained from the eq. (6). These corrected values are used to calculate \( K \) value from the eq. (7). This cyclic procedure continues until for the successive iterations \( |\varepsilon - \varepsilon_{i-1}|/\varepsilon_i < 0.05 \) by use of computer program.

The fundamental equation for the effect of pressure on the ionic equilibrium of the eq. (1) is
\[
\left( \frac{\partial n K}{\partial P} \right)_T = -\frac{\Delta V}{RT}
\]
where \( \Delta V \) is the partial molar volume change of the dissolved species when they are in the equilibrium state.

**EXPERIMENTAL**

**Materials.** 2, 4, 6, N-tetramethyl pyridinium iodide (TeMPI) was prepared by the way which the extra pure 2, 4, 6-trimethyl pyridine and methyl iodide were refluxed in absolute ethanol from Merck, Germany, and four times recrystallized from the absolute ethanol to give white crystal. The TeMPI crystal was stored in a desiccator over silica gel and measured its melting point to be 209°C. Its structure was confirmed by use of NMR spectrometer.

**Preparation of Stock Solution.** Each measuring solution was freshly prepared at room temperature before measuring the conductance and absorption spectrum. Solutions was prepared by dissolving weighed sample of TeMPI in 95 volume percent ethanol-water mixture. The concentrations of the measuring solution which was diluted by ten times of the stock solution were 5.08, 3.25, 2.14, and 0.91 \times 10^{-4} \text{ mole/liter}. These were varied within suitable limits to keep the measuring UV absorbancy for any one measuring system.

**Apparatus and Measurements.** The conductance and absorbancy for the ionic solution of TeMPI were measured with conductivity bridge model PM-70CB PAT. No. 3, 576, 491 BARNSTEAD SYBRON CO. BOSTON, MASS. 02132, in U.S.A and double beam spectrophotometer, SHIMADZU210A, in Japan.

During the experimental process, the experimental temperature and pressure were controlled in the range of 25, 30, 40, 50°C(±0.01°C) and 1, 500, 1000, 1500, 2000 bars respectively.

The conductivity cell, the schematic drawing of which has been shown elsewhere, is composed of two parts. One part as conductance cell, is consisted of a glass globe of about 5cm³ in volume where two Pt rectangular plate electrodes were sealed and the other part, pressure conductor, has two branched teflon tube of 7cm long and 0.4cm in diameter. The cell is set in the pressure vessel and the pressure measurement system was described elsewhere.

Dielectric constants and viscosities of the ethanol-water mixture were used by the data of our previous paper.

The maximum absorption of TeMPI occurs at 270nm in the range of room temperature and atmospheric pressure.

**RESULTS AND DISCUSSION**

**Limiting equivalent conductance.** The limiting equivalent conductance (\( \Lambda_0 \)) were obtained from the extrapolation of the plot of equivalent conductance (\( \Lambda \)) vs. the concentration (C) of TeMPI as shown in Figs. 1~3 and 4. The results were listed in Table 1. These values increase with increasing temperature and decrease with pressure.

**Degree of Dissociation.** The \( \gamma \) values of
Fig. 1. The plot of $\Lambda$ vs. $C$ for TeMPI in 95% ethanol-water mixture at 25°C.

Fig. 2. The plot of $\Lambda$ vs. $C$ for TeMPI in 95% ethanol-water mixture at 30°C.

TeMPI in the solvent mixture were calculated after 5 iterations as mentioned in the last part of the introduction to be written in the Table 2. The $\gamma$ values at 25°C decrease with increasing pressure, this tendency corresponds to the variation of the limiting equivalent conductance with pressure.

Activity Coefficient. The activity coefficients ($f$) of TeMPI in the solvent mixture at 25°C were also obtained from the eq. (6) using the above $\gamma$ values. The results were shown in Table 3. Generally, the $f$ values decrease with increasing pressure and concentration. The rea-
son is correlated to the fact that the ideality of the solution is inversely proportional to pressure because the interaction such as ionpair-ionpair, ionpair-dipole etc occurs more vigorously at higher pressure and concentration. But the result in Table 3 is contradictory to the fact in the pressure effect. This phenomena can be explained with which the effect for the dimerization of TeMPI is promoted by the increment of the pressure.

**Molar Extinction Coefficients.** Molar extinction coefficients ($\epsilon$) of TeMPI in ethanol-water mixture is evaluated from the eq. (7) using the previous values. $\epsilon$ values decrease with increasing pressure but are minimum at 40°C under all pressure range as shown in Table 4.

The effect of pressure on the dipolar ionic complex. Table 5 is shown the effect of pressure and temperature on the association constants (K) of the dipolar ionic charge transfer complex of the eq. (1).

The $\Delta V$ values were calculated from the eq. (8), Fig. 5 and the $K$ values in Table 5. This results were summarized in the Table 6.

On the other hand, Hamann et al.11-12 have shown that the $\Delta V$ of the eq. (8) can be estimated quite reliably from Fuoss's theory of ionpair formation.14

**Table 1.** Limiting equivalent conductance ($A_e$ cm$^2$ mho$^-1$ mole$^-1$) of TeMPI in 95% ethanol-water mixture.

<table>
<thead>
<tr>
<th>$T{(^\circ C)}$</th>
<th>P(bars)</th>
<th>1</th>
<th>500</th>
<th>1000</th>
<th>1500</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>60.0</td>
<td>52.1</td>
<td>46.8</td>
<td>42.8</td>
<td>39.6</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>70.1</td>
<td>69.5</td>
<td>52.2</td>
<td>46.8</td>
<td>43.0</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>88.1</td>
<td>72.8</td>
<td>64.8</td>
<td>58.8</td>
<td>53.0</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>100.2</td>
<td>86.8</td>
<td>76.0</td>
<td>69.1</td>
<td>63.2</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.** Degree of dissociation ($\gamma$) of TeMPI in 95% ethanol-water mixture at 25°C

<table>
<thead>
<tr>
<th>$C\times10^4$ (mole$^-1$)</th>
<th>P(bars)</th>
<th>1</th>
<th>500</th>
<th>1000</th>
<th>1500</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.08</td>
<td>0.573</td>
<td>0.589</td>
<td>0.514</td>
<td>0.528</td>
<td>0.532</td>
<td></td>
</tr>
<tr>
<td>3.25</td>
<td>0.656</td>
<td>0.645</td>
<td>0.621</td>
<td>0.597</td>
<td>0.586</td>
<td></td>
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<tr>
<td>2.14</td>
<td>0.721</td>
<td>0.708</td>
<td>0.682</td>
<td>0.651</td>
<td>0.653</td>
<td></td>
</tr>
<tr>
<td>0.91</td>
<td>0.862</td>
<td>0.846</td>
<td>0.831</td>
<td>0.819</td>
<td>0.811</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.** Activity coefficients ($f$) of TeMPI in 95% ethanol-water mixture at 25°C

<table>
<thead>
<tr>
<th>$C\times10^4$ (mole$^-1$)</th>
<th>P(bars)</th>
<th>1</th>
<th>500</th>
<th>1000</th>
<th>1500</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.08</td>
<td>0.930</td>
<td>0.935</td>
<td>0.939</td>
<td>0.942</td>
<td>0.944</td>
<td></td>
</tr>
<tr>
<td>3.25</td>
<td>0.940</td>
<td>0.945</td>
<td>0.948</td>
<td>0.949</td>
<td>0.953</td>
<td></td>
</tr>
<tr>
<td>2.14</td>
<td>0.954</td>
<td>0.953</td>
<td>0.956</td>
<td>0.958</td>
<td>0.960</td>
<td></td>
</tr>
<tr>
<td>0.91</td>
<td>0.964</td>
<td>0.966</td>
<td>0.968</td>
<td>0.970</td>
<td>0.971</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.** Molar extinction coefficients ($\epsilon\times10^4 l$ mole$^-1$ cm$^-1$) of TeMPI in 95% ethanol-water mixture.

<table>
<thead>
<tr>
<th>$T{(^\circ C)}$</th>
<th>P(bars)</th>
<th>1</th>
<th>500</th>
<th>1000</th>
<th>1500</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>2.51</td>
<td>2.41</td>
<td>2.22</td>
<td>2.05</td>
<td>2.03</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>2.19</td>
<td>2.17</td>
<td>2.17</td>
<td>2.15</td>
<td>2.01</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>1.96</td>
<td>1.97</td>
<td>1.97</td>
<td>1.92</td>
<td>1.87</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>2.22</td>
<td>2.14</td>
<td>2.19</td>
<td>2.05</td>
<td>1.99</td>
<td></td>
</tr>
</tbody>
</table>

**Table 5.** Association constants ($K\times10^{3} V$ mole$^-1$) of TeMPI in 95% ethanol-water mixture.

<table>
<thead>
<tr>
<th>$T{(^\circ C)}$</th>
<th>P(bars)</th>
<th>1</th>
<th>500</th>
<th>1000</th>
<th>1500</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>2.57</td>
<td>2.77</td>
<td>2.22</td>
<td>3.52</td>
<td>3.91</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>3.13</td>
<td>3.40</td>
<td>3.39</td>
<td>3.73</td>
<td>3.99</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>4.23</td>
<td>4.28</td>
<td>4.27</td>
<td>4.47</td>
<td>4.73</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>3.43</td>
<td>3.61</td>
<td>3.79</td>
<td>3.88</td>
<td>4.14</td>
<td></td>
</tr>
</tbody>
</table>

**Table 6.** Partial molar volume change ($-\Delta V$ cm$^-3$ mole$^-1$) and ionpair size ($a\times10^6$ cm) of TeMPI in 95% ethanol-water mixture.

<table>
<thead>
<tr>
<th>$T{(^\circ C)}$</th>
<th>25</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-\Delta V$</td>
<td>5.24</td>
<td>3.71</td>
<td>1.45</td>
<td>2.60</td>
</tr>
<tr>
<td>$a\times10^6$</td>
<td>4.27</td>
<td>5.50</td>
<td>10.5</td>
<td>6.80</td>
</tr>
</tbody>
</table>
Table 7. Thermodynamic parameters of TeMPI in 95% ethanol-water mixture at 25°C.

<table>
<thead>
<tr>
<th>$P$ (bars)</th>
<th>1</th>
<th>500</th>
<th>1000</th>
<th>1500</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G^\circ$ (kcal/mole$^{-1}$)</td>
<td>-4.65</td>
<td>-4.70</td>
<td>-4.79</td>
<td>-4.84</td>
<td>-4.90</td>
</tr>
<tr>
<td>$\Delta H^\circ$ (kcal/mole$^{-1}$)</td>
<td>12.65</td>
<td>10.56</td>
<td>6.82</td>
<td>6.63</td>
<td>5.24</td>
</tr>
<tr>
<td>$\Delta S^\circ$ (e. u.)</td>
<td>-8.72</td>
<td>-1.14</td>
<td>3.99</td>
<td>3.40</td>
<td>6.65</td>
</tr>
</tbody>
</table>
| \[ \text{The unparenthesized and parenthesized data are values of 25°C and 50°C, respectively.} \]

From the Table 5~7 and Fig. 8, we obtained the interesting phenomena as follows:

1. $K$ values increase with increasing pressure and have maximum value at 40°C.
2. $\Delta V$ values are negative and the absolute $\Delta V$ values are minimum at 40°C.
3. The values of the ionsize parameter ($a$)
are maximum at 40°C.

(4) $\Delta H^\circ$ values are zero, positive and negative at 40°C, 25°C, and 50°C respectively.

(5) $\Delta S^\circ$ values at 25°C are large positive and decrease with increasing pressure but those at 50°C are small negative at lower pressure range, small positive at higher pressure range and increase with increasing pressure.

From these contributions, we can infer a conclusion that TeMPI is stabilized by the elevation of pressure and that of temperature below 40°C but weakly dimerized at 40°C because of the intermolecular hydrophobic interaction of bulky methyl groups of two molecules, and thermally decomposed above 50°C.

ACKNOWLEDGEMENTS

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