

에탄올-물 혼합용매내에서 2, 4, 6, N-Tetramethyl Pyridinium Iodide 의 회합에 대한 압력효과

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

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요 약. 부피 퍼센트 95%의 에탄올-물 혼합용매내에서 2, 4, 6, N-테트라메틸 피리디늄요오드 (TeMPI)의 이온회합 상수(K)를 수정한 자외선분광 및 전기 전도도 혼용법으로 온도범위 25~50°C, 압력범위 1~2,000bars에서 결정하였다. K 값은 압력이 증가함에 따라서 증가하였고 40°C에서 최대값을 나타내었다. 부분몰부피변화(ΔV)는 비교적 작은 음의 값이 있으며 ΔV 의 절대값은 40°C에서 최소값을 보여주었다. TeMPI의 이온 크기 변수(a)는 40°C에서 최대값을 가졌다. ΔH° 값은 40, 25°C 그리고 50°C에서 각각 영, 음수 및 양수로 나타났으며 엔트로피(ΔS°)와 자유에너지(ΔG°)와 같은 다른 열역학변수 값도 계산하였다. 이와 같은 실험결과로부터 우리들은 TeMPI가 압력증가에 대하여 안정화되고, 40°C까지는 온도증가에 따라서도 안정화됨을 보여주었다. 그러나 40°C에서는 TeMPI 두 분자에 있는 8개 메틸기의 분자간 소수성 상호작용으로 인하여 약한 이량체를 형성하고 50°C 이상에서는 다시 열적으로 분해된다는 결론을 얻게 되었다.

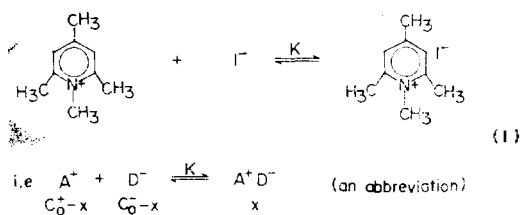
ABSTRACT. The ionic association constants(K) of 2, 4, 6, N-tetramethyl pyridinium iodide (TeMPI) in 95 volume percentage ethanol-water mixture were determined by a modified UV and conductance method at 25°C to 50°C under 1 to 2,000 bars. The K values increase with increasing pressure and have maximum value at 40°C. The partial molar volume change (ΔV) has relatively small negative value and the absolute values of ΔV are minimum at 40°C. The ion size parameter(a) 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 iodide 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:



where A^+ , D^- and A^+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 D^- , respectively and x the molar concentration of A^+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.

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

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

Letting $C_0^+ = C_0^- = C_0$ and taking the Shedlovsky correction of the degree of dissociation, $\gamma = (A/A_0)S$ in the nonaqueous system⁶ where A , A_0 and S are the equivalent conductance, limiting equivalent conductance of A^+D^- , and the Shedlovsky function, respectively, eq. (2) is rearranged by⁴

$$\frac{C_0^2 S}{A} = \frac{1}{\epsilon} [(1 + \gamma)C_0 S] + \frac{1}{K\epsilon} \quad (3)$$

And the following relation is given by

$$\epsilon = \frac{A}{C_0 - \gamma C_0} \quad (4)$$

Then the degree of dissociation, γ , is obtained by⁴

$$\gamma = \frac{(fC_0 - A/\epsilon)}{fC_0} \quad (5)$$

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

$$-\log f = \frac{1.290 \times 10^6 |z_1 z_2| (DT)^{-3/2} \sqrt{C\gamma}}{1 + \sqrt{C\gamma}} \quad (6)$$

where z_1 and z_2 are the ionic valencies 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

$$\frac{(fC_0)^2 S}{A} = \frac{1}{\epsilon} [1 + \gamma] fC_0 S + \frac{1}{K\epsilon} \quad (7)$$

The first correction of ϵ in the eq. (4) is obtained from the value of the relationship, $\gamma = (A/A_0)S$ obtained by conductivity method. Next, the γ value also can be corrected from the eq. (5) by using the first corrected ϵ 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 $|\epsilon_i - \epsilon_{i+1}| / \epsilon_i \leq 0.05$ by use of computer program.

The fundamental equation for the effect of pressure on the ionic equilibrium of the eq. (1) is

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V}{RT} \quad (8)$$

where ΔV 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 0.91×10^{-4} mole/liter. These were varied within suitable limits

to keep the measuring UV absorbancy for any one measuring system.⁸

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 ($\pm 0.01^\circ\text{C}$) and 1, 500, 1000, 1500, 2000 bars respectively.

The conductivity cell, the schematic drawing of which has been shown elsewhere⁹, 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.¹⁰

Dielectric constants and viscosities of the ethanol-water mixture were used by the data of our previous paper.⁵

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 (A_0) were obtained from the extrapolation of the plot of equivalent conductance (A) 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 γ values of

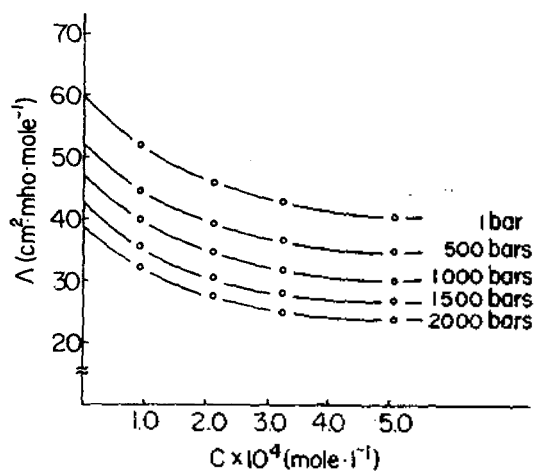


Fig. 1. The plot of Λ vs. C for TeMPI in 95 % ethanol-water mixture at 25°C.

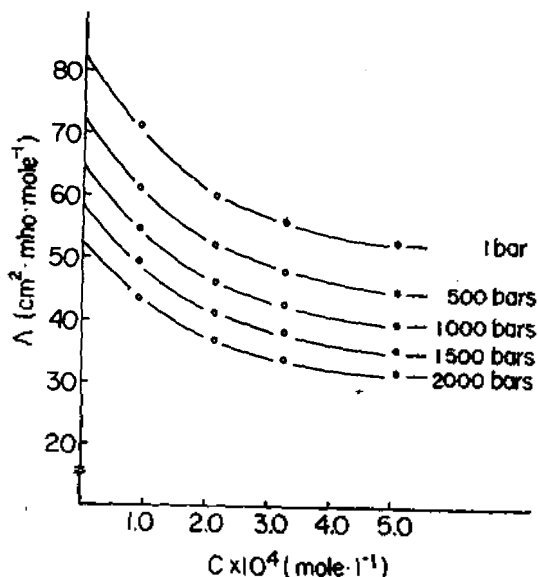


Fig. 3. The plot of Λ vs. C for TeMPI in 95 % ethanol-water mixture at 40°C.

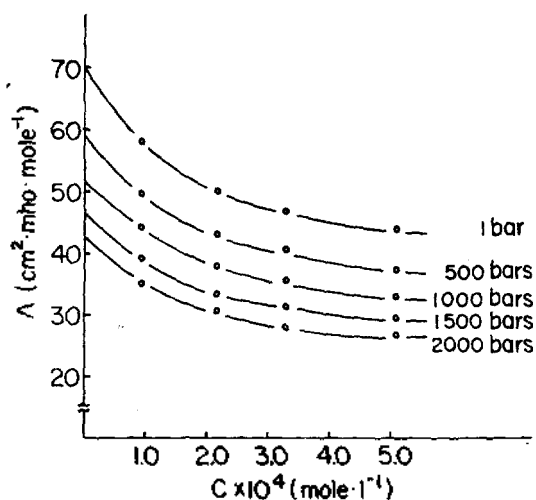


Fig. 2. The plot of Λ vs. C for TeMPI in 95 % ethanol-water mixture at 30°C.

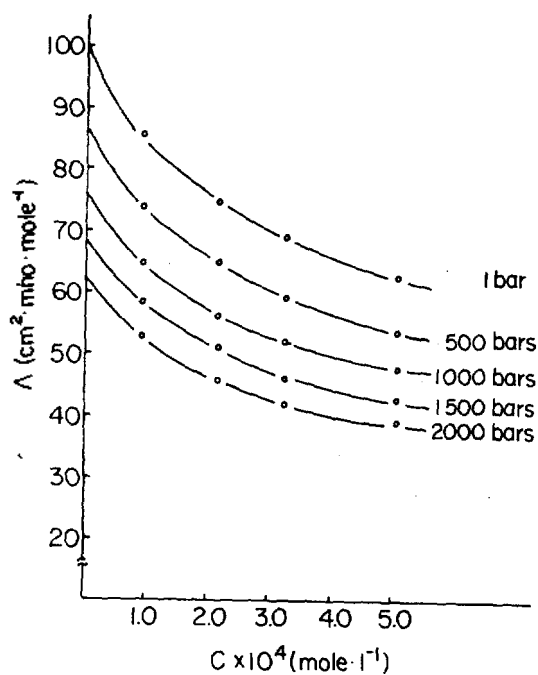


Fig. 4. The plot of Λ vs. C for TeMPI in 95 % ethanol-water mixture at 50°C.

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 γ 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 γ 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 (ϵ) of TeMPI in ethanol-water mixture is evaluated from the eq. (7) using the

Table 1. Limiting equivalent conductance (Λ_0 cm²·mho·mole⁻¹) of TeMPI in 95 % ethanol-water mixture

T(°C)	P(bars)				
	1	500	1000	1500	2000
25	60.0	52.1	46.9	42.8	38.6
30	70.1	59.5	52.2	46.6	43.0
40	85.1	72.9	64.8	58.6	53.0
50	100.2	86.8	76.0	69.1	63.2

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

C×10 ⁴ (mole·l ⁻¹)	P(bars)				
	1	500	1000	1500	2000
5.08	0.573	0.569	0.547	0.528	0.523
3.25	0.656	0.645	0.621	0.597	0.586
2.14	0.721	0.708	0.682	0.651	0.653
0.91	0.862	0.846	0.831	0.819	0.811

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

C×10 ⁴ (mole·l ⁻¹)	P(bars)				
	1	500	1000	1500	2000
5.08	0.930	0.935	0.939	0.942	0.944
3.25	0.940	0.945	0.948	0.949	0.953
2.14	0.949	0.953	0.956	0.958	0.960
0.91	0.964	0.966	0.968	0.970	0.971

previous values. ϵ 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 ΔV 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.*¹¹⁻¹³ have shown that the ΔV of the eq. (8) can be estimated quite reliably from Fuoss's theory of ionpair formation.¹⁴

Table 4. Molar extinction coefficients ($\epsilon \times 10^{-4}$ l·mole⁻¹·cm⁻¹) of TeMPI in 95 % ethanol-water mixture.

T(°C)	P(bars)				
	1	500	1000	1500	2000
25	2.51	2.41	2.22	2.05	2.03
30	2.19	2.17	2.17	2.15	2.01
40	1.96	1.97	1.97	1.92	1.87
50	2.22	2.14	2.19	2.05	1.99

Table 5. Association constants ($K \times 10^{-3}$ l·mole⁻¹) of TeMPI in 95 % ethanol-water mixture

T(°C)	P(bars)				
	1	500	1000	1500	2000
25	2.57	2.77	3.22	3.52	3.91
30	3.13	3.40	3.39	3.73	3.99
40	4.23	4.28	4.27	4.47	4.73
50	3.43	3.61	3.79	3.88	4.14

Table 6. Partial molar volume change ($-\Delta V$ cm³·mole⁻¹) and ionpair size ($a \times 10^8$ cm) of TeMPI in 95 % ethanol-water mixture

T(°C)	25	30	40	50
$-\Delta V$	5.24	3.71	1.15	2.60
$a \times 10^8$	4.27	5.50	10.5	6.80

Table 7. Thermodynamic parameters of TeMPI in 95% ethanol-water mixture at 25°C*

P(bars)	1	500	1000	1500	2000
ΔG° (kcal·mole ⁻¹)	-4.65 (-5.23)	-4.70 (-5.26)	-4.79 (-5.29)	-4.84 (-5.30)	-4.90 (-5.35)
ΔH° (kcal·mole ⁻¹)	12.05 (-6.11)	10.56 (-5.63)	6.82 (-4.00)	6.63 (-4.20)	5.24 (-3.20)
ΔS° (e. u.)	56.0 (-2.72)	51.2 (-1.14)	38.9 (3.99)	38.5 (3.40)	34.0 (6.65)

*The unparenthesized and parenthesized data are values of 25°C and 50°C, respectively.

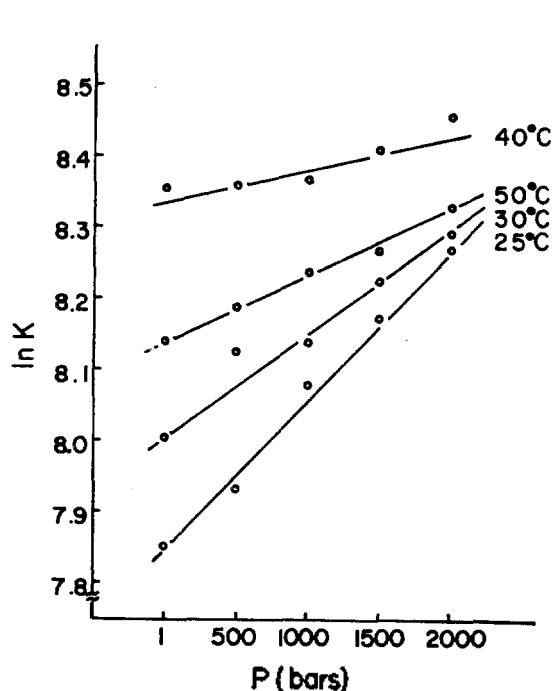


Fig. 5. The plot of $\ln K$ vs. pressure at various temperature.

$$\Delta V = \frac{N|z_1 z_2|e^2}{a} \left(\frac{\partial D^{-1}}{\partial P} \right)_T + RT \left(\frac{\partial \ln \rho}{\partial P} \right)_T \quad (9)$$

From the eq. (8) and (9), we obtained the ionpair size (a) of TeMPI in the ethanol-water mixture by using of the data of dielectric constant (D) in our paper⁵, and the density (ρ) of which is calculated according to the mole ratio of ethanol and water from the published density of ethanol^{15,16} and water¹⁷ at various pressure and at 25, 30, 40 and 50°C. The values of the ionpair size were listed in Table 6.

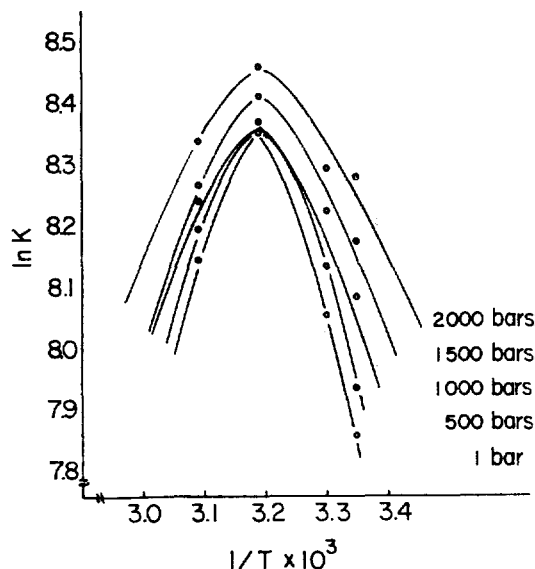


Fig. 6. The plot of $\ln K$ vs. $1/T$ at various pressure.

The changes of standard free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) of the eq. (1) were calculated at 25° and 50°C by use of the well known thermodynamic relations from the plot of $\ln K$ vs. $1/T$ in Fig. 8 which has the maximum value at 40°C. These thermodynamic parameters were listed in Table 7.

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) ΔV values are negative and the absolute ΔV values are minimum at 40°C.
- (3) The values of the ionsize parameter (a)

are maximum at 40°C.

(4) ΔH° values are zero, positive and negative at 40°C, 25°C, and 50°C respectively.

(5) ΔS° 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.

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