A Study of the Ionic Association of the Substituted N-Methyl Pyridinium Iodide (II). 4, N-Dimethyl Pyridinium Iodide in Ethanol-Water Mixture

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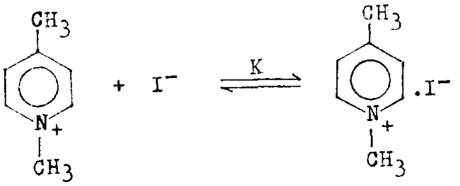
The electrical conductance and UV absorbance of 4,N-dimethyl Pridinium Iodide (NDMPI) were measured in the ethanol volume percentage, 95, 90, 80 and 60 of an ethanol-water mixture at 15, 25, 35 and 45°C. Ionic association constants(K) of NDMPI were evaluated in accordance with a combined method of conductance UV absorbance. The ion size parameter ($\gamma_{\pm}$) and dipole momemt ($\mu_{A^+D^-}$) of NDMPI were obtained from the values of K and dielectric constant. The $\mu_{A^+D^-}$ values were in good agreement with the values of transition moment(μ_{mn})which is calculated form the UV peak values. The large negative values of the electrical enthalpy (ΔH°_{el}) and entropy (ΔS°_{el}) have proved that NDMPI had a positive hydration. The positive values of entropy (ΔS°) means the formation of NDMPI ion goes with dehydration.

Introduction

In the previous study, the N-methyl pyridinium iodide (NMPI) gives rise to an ultraviolet charge transfer band in the ethanol-water mixture[1,2]. This band supposedly arises due to the transfer of electron density from the highest occupied orbital of an iodide to the lowest unoccupied orbital of an N-methyl pyridinium cation[3].

Recently, a thermodynamic investigation of the association process of NMPI in ethanol-water mixture was discussed by Paul Hemmes et al[4]. They did not study for the 4, N-dimethyl-pridinium iodide(NDMPI) and so we have obtained the thermodynamic variables, dipole moment and radius of the dipolar NDMPI ion according to a combined method which is consist of the UV spectroscopy and conductance measurement using the Shedlovsky function as a correction factor[3].

The ionic equilibrium relation ship of the NDMPI can be expressed.



(1)

$$i.e\ A^+ + D^- \overset{K}{\rightleftharpoons} A^+D^- \text{ (an abbreviation)}$$
$$C^+_e - x,\ C^-_e - x \qquad x$$

where A^+,D^- and A^+D^- represent 4, N-dimethyl pyridinium cation, iodic anion and the ionic complex, 4, N-dimethyl pyridinium iodide, respectively. C^+_0 and C^-_0 refer to the mole concentration of A^+ and D^-, and x the mole concentration of A^+D^- at equilibrium state.

Since the association constant, K depends upon NDMPI concentration, we had modified the Kosower equation[5,6] with the Shedlovsky function, S as follows[3]

$$\frac{(fC_0)^2S}{\Lambda}=\frac{1}{\epsilon}[(1+\gamma)fC_0S]+\frac{1}{K\epsilon} \qquad (2)$$

Where γ and f are the degree of dissociation and the activity coefficient given by

$$-\log f=\frac{1.290\times10^6|z_1z_2|(DT)^{-\frac{3}{2}}\sqrt{C\gamma}}{1+\sqrt{C\gamma}} \qquad (3)$$

This equation is called as Debye-Huckel limiting equation[7], where z_1 and z_2 represent ionic valences of the A^+ and D^-, and D and T the dielectric constant of solvent and the experimental temperature as Kelvin scale. The value of γ is expressed as

$$\gamma=\frac{\Lambda}{\Lambda_0}S=\frac{(fC_0-\Lambda/\epsilon)}{fC_0} \qquad (4)$$

Where the molar absorptivity (extinction coefficient)of A^+D^-, ϵ is given by

$$\epsilon=\frac{\Lambda}{\Lambda_0}S \qquad (5)$$

where Λ and Λ_0 are the equivalent conductance and the limiting equivalent conductance of A^+D^-.

The corrected values of ϵ, f, γ, K are calculated by the successive cyclic iteration from eq. (2) to eq. (5) using the computer program until $|\epsilon_i-\epsilon_{i+1}|/\epsilon\leq0.07$ is obtained.

We have obtained the next equation from the Kirkwood equation[8] which refers to the influence of the dielectric constant of the medium on the free energy of a polar molecule in solution[3].

$$\ln K=\ln K_0-\frac{1}{RT}\left(\frac{\mu^2_{A^+}}{\gamma_{A^+}^3}+\frac{\mu^2_{D^-}}{\gamma^3_{D^-}}-\frac{\mu^2_{A^+D^-}}{\gamma_{A^+D^-}^3}\right)\frac{D-1}{2D-1} \qquad (6)$$

where K, K_0 and μ are the association constants of A^+D^- in the medium of a dielectric constant, D and $D=1$ and dipole moment of A^+D^- respectively.

From the eq. (6) and other thermodynamic relationships, several equations were given in the form:

$$\Delta G_{el}^{\circ}=-RT(\ln K-\ln K_0) \qquad (7)$$

$$\Delta S^{\circ}_{el} = -\left(\frac{\mu^2_{A^+}}{\gamma^3_{A^+}} + \frac{\mu^2_{D^-}}{\gamma_{D^-}{}^3} - \frac{\mu^2_{A^+D^-}}{\gamma^3_{A^+D^-}}\right)\frac{3D}{(2D+1)^2}\left(\frac{\partial \ln D}{\partial T}\right)_p \qquad (8)$$

$$\Delta H^{\circ}_{el} = \Delta G^{\circ}_{el} + T\Delta S^{\circ}_{el} \qquad (9)$$

where superscript,o and subscript, el represent the equilibrium state and "electrostriction" respectively.

Assuming that ions with opposite charges z_1e and z_2e can be considered to form ion-pair when they come within a contact distance $\gamma_{\pm}$ of each other, Denison and Ramsey[9], Eigen[10] and Fuoss[11] derived the association constant for ion-pairs, A^+D^- in the form

$$K = \frac{4\pi N\gamma^3_{\pm}}{3000}\exp\left(\frac{z_1z_2e^2}{\gamma_{\pm}DkT}\right) \qquad (10)$$

where N and k are Avogadro's number and Boltzmann constant respectively.

The common thermodynamic parameters associated with the ionic association constant (K) are given by ΔG°,ΔH° and ΔS°.

On the other hand we have published the transition moment, μ_{nm} from n to m electronic state of the A^+D^- complex in the previons study[3].

$$\mu_{nm} = 6.5168\times10^{-2}\left(\frac{\epsilon_{max}\tilde{\nu}_{1/2}}{\tilde{\nu}_{max}}\right)^{\frac{1}{2}} \qquad (11)$$

where ϵ_{max}, $\tilde{\nu}_{max}$ and $\tilde{\nu}_{1/2}$ are the peak value of the molecular extinction coefficient (unit: 1 mol^{-1} cm^{-1}), the frequency and the half-width of the peak in wave number unit of the A^+D^- complex. We will compare the $\mu_{A^+D^-}$ values of eq. (6) with this μ_{nm} values in the part of result and discussion.

Experimental

Chemicals; 4, N-dimethyl pyridinium iodide (NDMPI) was prepared by the way which 4-methyl pyridine and methyl iodide were refluxed in absolute ethanol from Merck, West Germany, and twice recrystallized from the absolute ethanol to give white crystal. The NDMPI was stored in a desicator filled with $CaCl_2$ and measured its melting point to be 152°C. It's structure was identified by use of NMR and IR spectroscopy.

The preparation of stock solution and measuring apparatus were conducted as the same way of our previous paper[3].

The ethanol volume percentage in ethanol-water mixtures were 95, 90, 80, and 60. The experimental temperature was controlled in the range of 15, 25, 35, and 45°C (±0.1°C).

Result and Discussion

The values of dielectric constant and viscosity of the ethanol-water mixture which are requisite to calculate the γ and f values were taken from the data in our paper[3].

The limiting equivalent conductance (Λ_0) was obtained from the extrapolation of the plot of equivalent conductance (Λ) *vs.* the concentration(C) of NDMPI as shown in Figure 1, which is a typical one (% EtOH = 90) of the 4 volume percentages of the solvent mixtures. These Λ_0 values in Table 1 ascend with increasing temperature and decreasing ethanol percentage of the solvent mixture. It can be explained by the facts that the degree of dissociation of NDMPI increases with elevating temperature but the viscosity of the solvent mixture decreases to raise the number of the free ions of NDMPI. The dielectric constant increases as the ethanol content decreases, which enlarges the dissolving ability of the solvent.

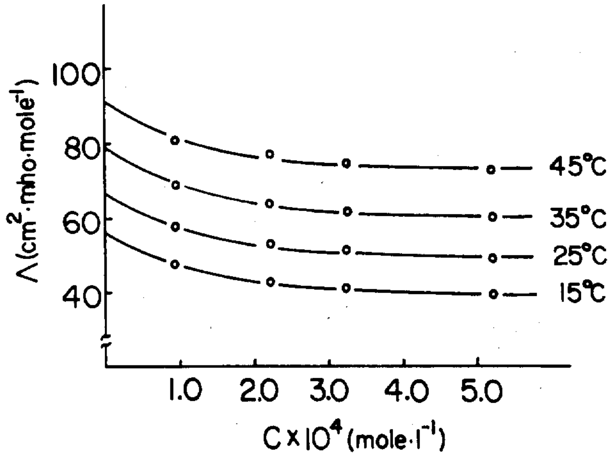


Figure 1. The plot of Λ *vs.* C for NDMPI in 90% EtOH.

TABLE 1: Limiting Equivalent Conductances Λ_0 (cm^2. mho mol^{-1}) of NDMPI in Ethanol-Water Mixtures

% EtOH	15°C	25°C	35°C	45°C
95	55.4	65.7	75.3	88.5
90	56.1	66.2	78.2	91.2
80	58.2	74.1	91.8	114
60	81.4	109	138	167

TABLE 2: Degree of Dissociation (γ) of NDMPI in Ethanol-Water Mixtures

% EtOH	$C\times10^4(mol.1^{-1})$	γ			
		15°C	25°C	35°C	45°C
95	5.10	0.625	0.648	0.694	0.704
	3.20	0.666	0.691	0.731	0.736
	2.18	0.680	0.703	0.740	0.742
	0.90	0.864	0.883	0.926	0.933
90	5.20	0.634	0.686	0.736	0.769
80	5.10	0.538	0.539	0.547	0.537
60	5.52	0.373	0.403	0.425	0.450

The value of the degree of dissociation (γ) of NDMPI as shown in Table 2 diminishes because of descending of the dissociable capacity of the solvent mixture with increasing its ethanol content.

The values of the activity coefficient(f) of NDMPI could be evaluated in various solvent mixtures as listed in Table 3. The f values advanced with the increase of the water content of the solvent mixture and temperature. This phenomenon is contrasted with γ values mentioned above. It is natural that the less the number of free ions, the more f values.

The values of molar absorption coefficient (ϵ) of NDMPI as shown Table 4 were elevated with increasing temperature

TABLE 3: Activity Coefficients (*f*) of NDMPI in Ethanol-Water Mixtures

% EtOH	C×10⁴(mol.1⁻¹)	*f*			
		15 C°	25°C	35°C	45°C
95	5.10	0.932	0.929	0.924	0.920
	3.20	0.944	0.941	0.937	0.934
	2.18	0.953	0.951	0.948	0.943
	0.90	0.966	0.965	0.963	0.961
90	5.20	0.940	0.936	0.932	0.927
80	5.10	0.957	0.955	0.954	0.952
60	5.52	0.974	0.973	0.971	0.970

TABLE 4: Molar Absor ptoin Coenfficients ($\epsilon \times 10^{-4}$l. mol^{-1}.cm^{-1}) of NDMPI in Ethanol-Water Mitxures

% EtOH	15°C	25°C	35°C	45°C
95	1.238	1.329	1.550	1.787
90	1.091	1.276	1.524	1.754
80	1.041	1.062	1.081	1.050
60	0.707	0.723	0.746	0.784

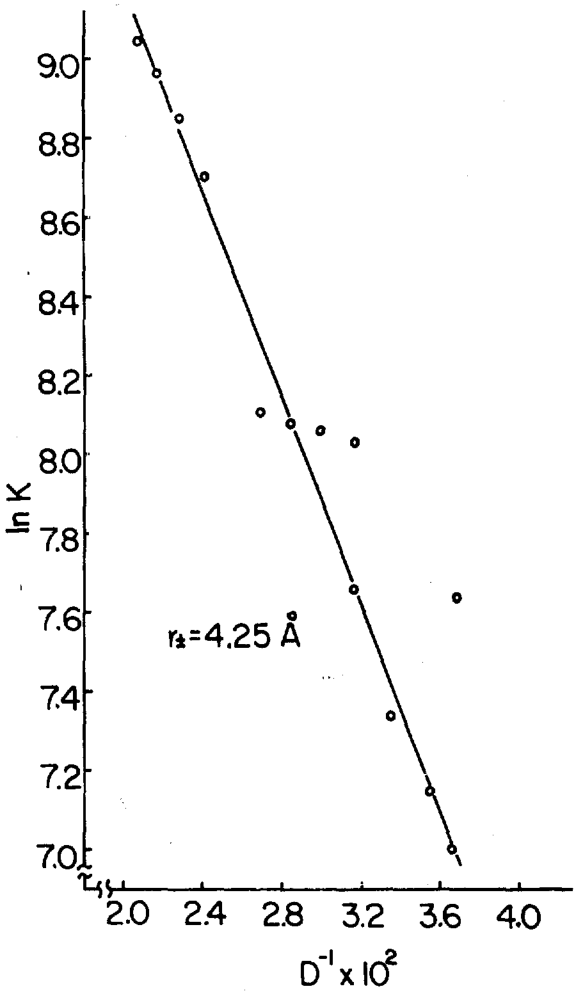


Figure 2. The plot of lnK *vs.* D^{-1} for NDMPI at 25°C.

and diminished with decreasing the ethanol content. This fact agreed with the case of the transition moment as listed in Table 6.

The values of association constants of NDMPI which resulted in Table 5 increased as the ethanol content decrease and descended with rising temperature. This result is interpreted by the fact that the complex A^+D^- is more stable due to more hydration at lower temperature.

TABLE 5: Association Constants (*K*, 1.mol⁻¹) of NDMPI in Ethanol-Water Mixtures

% EtOH	15°C	25°C	35°C	45°C
95	2.44	2.09	1.51	1.24
90	2.13	1.54	1.28	1.03
80	3.32	3.22	3.16	3.06
60	8.56	7.48	7.07	6.09

TABLE 6: Transition Moments in Debye Unit of NDMPI in Ethanol-Water Mixtures

% EtOH	15°C	25°C	35°C	45°C
95	24.7	25.6	27.7	29.7
90	23.2	25.1	27.4	29.4
80	22.7	22.9	23.1	22.8
60	18.7	18.9	19.2	19.7

TABLE 7: Electrical Thermodynamic Parameters of NDMPI in Ethanol-Water Mixtures at 25°C

% EtOH	ΔH°_{el}(kcal.mol⁻¹)	ΔS°_{el}(*e.u.*)	ΔG°_{el}(kcal.mol⁻¹)
95	−55.4	−16.8	−50.4
90	−55.1	−14.9	−50.7
80	−54.8	−12.5	−51.1
60	−54.1	−8.44	−51.6

TABLE 8: Thermodynamic Parameters of NDMPI in Ethanol-Water Mixtures at 25°C

% EtOH	ΔH°(kcal.mo⁻¹)	ΔS°(*e.u.*)	$\Delta^{\circ}G$(kcal·mol⁻¹)
95	−4.11	1.41	−4.53
90	−3.90	1.51	−4.35
80	−3.21	5.30	−4.79
60	−2.41	9.73	−5.31

The plot of lnK *vs.* D^{-1} was represented in Figure 2. From this plot, the ionsize parameter (contact distance), $\gamma_{\pm}$ of NDMPI was evaluated to be 4.25 A.

Next we ploted lnK *vs.* $(D-1)/(2D+1)$ by using eq.(6) in Figure 3. Assuming that the dipole moment of nonpolar ion of A^+ and D^- is zero because they have a spherical symmetry by their hydration, we could obtain the value of the dipole moment of dipolar NDMPI ion, $\mu_{A^+D^-}=23.8$D.

On the other hand, the values of the transition moment, nm of the complex A^+D^- calculated from eq. (14) with $\lambda_{max} = 256$ nm were shown in Table 6. These μ_{nm} values are in agreement with $\mu_{A^+D^-}$ value mentioned above. The μ_{nm} values deacrease as the ethanol content diminishes and increase with the elevation of temperature, the former can be explained with the more reduction of the charge of the NDMPI ion by its more hydration in the more water content and the latter with its less hydration because of the larger thermal motion of NDMPI ions and solvent molecules in the higher temperature.

The values of the electrical thermodynamic parameters of NDMPI ion were calculated from the association constant

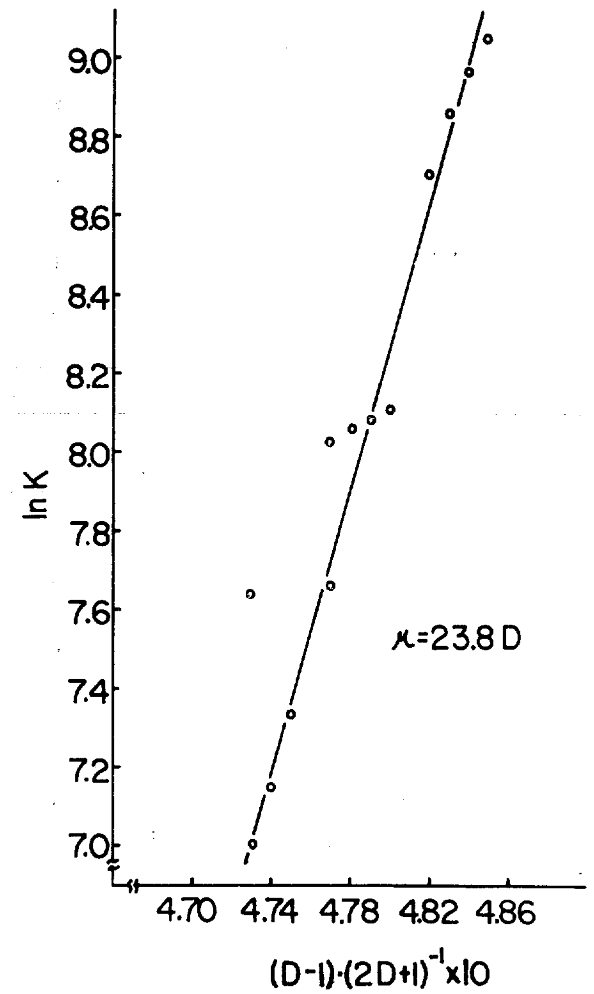


Figure 3. The plot of lnK *vs.* (D-1) (2D+1) for NDMPI at 25°C.

listed in Table 5 by use of eqs. (7), (8), and (9) to result in Table 7. The large negative values of ΔH°_{el}. and ΔS°_{el} proved that the water molecules became more ordered around the NDMPI ions by their hydration.

Thermodynamic properties evaluated from eqs. (11), (12), and (13) were tabulated in Table 8. The fact that ΔS° values are positive means the formation of NDMPI ion goes with dehydration. The ΔS° values increased as the water content ascended, which proved that the equilibrium of eq. (1) is controlled by entropy when water content rises.

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Synthesis and Properties of Thermotropic Compounds with Two Terminal Mesogenic Units and a Central Spacer (VI). Homologous Series of α, ω-Bis [4-(*p*-substituted benzoyloxy)benzoyloxy]alkanes*

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The thermal and optical properties of two new series of thermotropic, liquid crystalline compounds were studied by differential scanning calorimetry and on the hot-stage of a polarizing microscope. The first series contained two identical mesogenic units, 4-(*p*-phenylbenzoyloxy) benzoate moieties, at both ends of the polymethylene spacer of varying lengths and the second series, mesogenic units with different substituents and the hexamethylene group as the central spacer. A thermodynamic analysis of the phase transitions of the compounds was made and the results were discussed in relation to their chemical structures.