$(K_2)^{1/2}(e^-)$ $(O_2)^{1/2}$ into equation (4), the rate equation can be rewritten as follows:

$$\frac{d(CO_2)}{dt}=k\,K_1\frac{(CO)\,(O^{2-}_{(latt)})}{(e^-)}K_2{}^{1/2}(e^-)\,(O_2)^{1/2}$$
$$=k\,K_2{}^{1/2}\,K_1(CO)\,(O_2)^{1/2}(O^{2-}_{(latt)})$$
$$=k'\,(CO)\,(O_2)^{1/2}$$

Thus, the suggested mechanism leads to the observed rate law, first order with respect to CO and 0.5 with respect to O_2. Therefore, the oxidation mechanism of CO on Ni-doped α-Fe_2O_3 can be suggested as follows:

$$2e^-+O_2 \rightleftharpoons 2O^-_{(ads)}$$
$$CO+O^{2-}_{(latt)} \rightleftharpoons CO^-_{2(ads)}+e^-$$
$$CO^-_{2(ads)}+O^-_{(ads)} \longrightarrow CO_2+O^{2-}_{(latt)}$$

With the conductivity data shown in Figures 3 and 4, we can find that the rate determining step is the chemisorption of CO on a lattice oxygen.

Acknowledgement. The authors are grateful to the Korean Trader's Scholarship Foundation for financial support.

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A Study of the Ionic Association of the Substituted N-Methyl Pyridinium Iodides (I).
N-Methyl Pyridinium Iodide in Ethanol-Water Mixture

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The ionic association constant (K) of N-methyl pyridinium iodide (NMPI) ion in several ethanol-water mixtures were determined by the combination of UV spectroscopy and conductance measurements using the Shedlovsky function as a correction factor. The measurement of electrical conductance and UV absorption were performed in 95, 90, 80 and 60 volume percentages of ethanol in the solvent mixture at 15, 25, 35 and 45 (±0.1) °C. The ion size parameter ($r_{A^+D^-}$) and the dipole moment ($\mu_{A^+D^-}$) of NMPI ion were obtained from the linear plots of $\ln K$ *vs.* $(1/D)$ and $(D-1)/(2D+1)$, respectively. These $\mu_{A^+D^-}$ values were in good agreement with the values of transition moment calculated from the equation, $\mu_{nm}=6.5168\times10^{-2}\times\left(\epsilon_{max}\frac{\bar{\nu}_{\frac{1}{2}}}{\bar{\nu}_{max}}\right)^{\frac{1}{2}}$ (Debye) which we have derived. The thermodynamic parameters indicate (1) that the water dipoles have an ordered rearrangement around the dipolar NMPI ions rather than the configuration existing in bulk free waters; and (2) that the equilibrium state between NMPI ion and its component ions are controlled by entropy.

Introduction

It has been observed by Kosower[1,2] that N-methyl pyridinium iodide(NMPI) gives rise to an ultraviolet charge transfer band in aqueous solution. This band arises due to a transfer of electron density from an occupied orbital of iodide into the lowest unoccupied orbital of the pyridinium ion.[3-5] Subsequently, it was shown that the concentration dependence of the charge transfer band could be employed to calculate the association constants (K) for the equilibrium state in which N-methyl pyridinium cation and iodide anion associated to form the N-methyl pyridinium iodide dipolar ion complex.

Paul Hemmes *et al.* have investigated the equilibrium and kinetics for the association of NMPI in water-alcohol mixtures by the combination of UV spectroscopy and conductance measurements using the Fuoss function as a correction factor.[6] These authors have not studied the thermodynamic variables, dipole moment and radius of the dipolar NMPI ion.

Therfore, we studied the ionic association of NMPI in ethanol-water mixture by a combination of UV spectroscopy and conductance measurements using the Shedlovsky function as a correction factor rather than the Fuoss function used by Hemmes.

Application of Conductance Theory. In non-aqueous systems, where the dielectric constant of the solvent is small, the degree of dissociation has been corrected by Shedlovsky as follows;

$$\gamma=\frac{\Lambda}{\Lambda_0}S(z) \tag{1}$$

where the equivalent conductance, Λ_0 is given by $\frac{1000K}{C}$; K being the specific conductance, C the equivalent concentration, and $S(z)$ the Shedlovsky[7] function as follows;

$$S(z)=\left(\frac{z}{2}+\sqrt{1+\left(\frac{z}{2}\right)^2}\right)^2 \tag{2}$$

The variable z is equal to $\alpha\Lambda_0^{-\frac{3}{2}}\sqrt{C\Lambda}$, and the Onsager coefficient is written as[8]

$$\alpha=8.204\times10^5\Lambda_0/(DT)^{3/2}+82.501/\eta(DT)^{1/2} \tag{3}$$

where D, η and T are the dielectric constant, the viscosity (poise) of solvent, and absolute temperature, respectively.

The activity coefficient(f) is given by the equation from the Debye-Hückel limiting equation;[9]

$$-\log f=\frac{\beta\sqrt{C\gamma}}{1+\sqrt{C\gamma}} \tag{4}$$

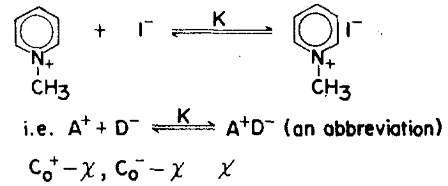
where β is the Debye-Hückel slope;

$$\beta=1.290\times10^6|z_1z_2|(DT)^{-3/2} \tag{5}$$

in which z_1 and z_2 are the ionic charges of the cation and anion, respectively.

A Modified UV Method with Conductance in the Determination of Association Constant. Let us consider the next general equation of the ionic equilibrium for the N-methyl pyridinium iodide and its *para*-amino, cyano, methyl substituted derivatives.

Equation(6) is the ionic equilibrium relationship for the N-methyl pyridinium iodide.



(6)

where A⁺, D⁻ and A⁺D⁻ are cationic electron acceptor, anionic electron donor and dipolar ionic complex, C_0^+ and C_0^- the initial concentration of A⁺ and D⁻, and χ the concentration of A⁺D⁻ at a equilibrium state.

We must modify the association constant K with the product of K and S which is the Shedlovsky function of the eq.(2) because K is the function of the ionic strength of the concentration of A⁺D⁻. Therefore, we can obtain from eq. (3).

$$KS=\frac{\chi}{(C_0^+-\chi)(C_0^--\chi)} \tag{7}$$

The absorbance (optical density), A of A⁺D⁻ is obtained from eq. (3) as follows;

$$A=\epsilon_\lambda^{A^+D^-}\chi=\epsilon\chi \tag{8}$$

where $\epsilon_\lambda^{A^+D^-}=\epsilon$ is the molar absorptivity (extinction coefficient) of A⁺D⁻ at the wavelength of measurement, λ.

If C_0^+ and C_0^- are equal to C_0, the degree of dissociation of the eq. (6), γ leads to the next expression.

$$\chi=C_0-\gamma C_0 \tag{9}$$

From eqs. (7), (8) and (9), we obtained the following equation.

$$\frac{C_0^2S}{A}=\frac{1}{\epsilon}[(1+\gamma)C_0S]+\frac{1}{K\epsilon} \tag{10}$$

Substitution eq. (8) into eq. (9) leads to the next equation.

$$\epsilon=\frac{A}{C_0-\gamma C_0} \tag{11}$$

In eqs. (10) and (11), we replace C_0 with fC_0 and rearrange to obtain the next results.

$$\gamma=\frac{(fC_0-A/\epsilon)}{fC_0} \tag{12}$$

$$\frac{(fC_0)^2S}{A}=\frac{1}{\epsilon}[(1+\gamma)fC_0S]+\frac{1}{K\epsilon} \tag{13}$$

The first corrected values of eq. (11) were obtained from the values calculated by the conductivity method which is shown in eq. (1). Next we obtain the corrected γ values from eq. (12) by using the corrected ϵ and f values which are evaluated from eq. (4). These corrected ϵ, γ and f values were used to calculate K value from eq. (13). This successive cyclic iterations was continued by using computer program until $|\epsilon_i-\epsilon_{i+1}|$ is less than 0.07.

Electrostatic Effects in Various Solvent Mixture. A theory for the influence of the dielectric constant of the medium on the free energy of a polar molecule has been given by Kirkwood.[10] By considering electrostatic forces only and neglecting van der Waal's forces, the difference in free energy of a dipole in a medium with dielectric constant D and with a dielectric constant of unity is given by

$$\Delta G_{el}^{\circ}=G_D^{\circ}-G_{D=1}^{\circ}=-\frac{\mu^2(D-1)}{\gamma^3(2D+1)} \tag{14}$$

where μ and γ are the dipole moment and radius of the molecule, respectively.

The thermodynamic relationship may next be considered.

$$\Delta G_{el}^{\circ}=G_D^{\circ}-G_{D=1}^{\circ}=-RT\ln K \tag{15}$$

From eqs. (6), (14) and (15), we obtain the next equation.

$$\ln K=\ln K_0-\frac{1}{RT}\left(\frac{\mu_{A^+}^2}{\gamma_{A^+}^3}+\frac{\mu_{D^-}^2}{\gamma_{D^-}^3}-\frac{\mu_{A^+D^-}^2}{\gamma_{A^+D^-}^3}\right)\frac{D-1}{2D+1} \tag{16}$$

where K and K_0 are the association constants in the medium of any dielectric constant D and $D=1$.

From eq. (16) and other thermodynamic relationships, we can also represent the following equations.

$$\Delta G_{el}^{\circ}=-RT(\ln K-\ln K_0) \tag{17}$$

$$\Delta S^{\circ}_{el} = -\left(\frac{\mu^2_{A^+}}{\gamma^3_{A^+}} + \frac{\mu^2_{D^-}}{\gamma^3_{D^-}} - \frac{\mu^2_{A^+D^-}}{\gamma^3_{A^+D^-}}\right)\frac{3D}{(2D+1)^2}\left(\frac{\partial \ln D}{\partial T}\right)_p \qquad (18)$$

$$\Delta H^{\circ}_{el} = \Delta G^{\circ}_{el} + T\Delta S^{\circ}_{el} \qquad (19)$$

When two ions of opposite charge form an ion pair, the resulting structure has a dipole moment, and electric dipole has an electrostatic energy which is a function of the dielectric constant of the surrounding medium. Therefore, the next equation results from the theoretical treatment of Denison and Ramsey,[11] Eigen,[12] and Fuoss[13] for ionic association.

$$K = \frac{4\pi Na^3}{3000}\exp\left(\frac{z_1 z_2 e^2}{\gamma_{\pm} DkT}\right) \qquad (20)$$

where N is Avogadro number, $\gamma_{\pm}$ is the ion size parameter, z_1 and z_2 are charges, e the unit electrostatic charge, and k the Boltzmann constant.

The other thermodynamic parameters associated with the ionic association constant (K) are given as

$$\Delta G^{\circ} = -RT\ln K \qquad (21)$$

$$\Delta H^{\circ} = -R\left(\frac{\partial \ln K}{\left(\partial \frac{1}{T}\right)}\right)_p \qquad (22)$$

$$\Delta S^{\circ} = \frac{1}{T}(\Delta H^{\circ} - \Delta G^{\circ}) \qquad (23)$$

Relationship between Dipole Moment and UV Maximum Peak. The dipole or oscillator strengths are given by the equation (24) when the transition from n to m take places.[14]

$$f_{nm} = \frac{C^2 m_e}{N_n \pi e^2}\int \epsilon(\bar{\nu})\, d\bar{\nu} \qquad (24)$$

where c, m_e, N_n, e, and $\bar{\nu}$ are the velocity of light, mass of electron, number of particles per unit volume, proton charge and wave number, respectively.

The integral of eq. (24) is transformed into[15,16]

$$A = \int \epsilon(\bar{\nu})\, d\bar{\nu} = 1.0645\, \epsilon_{max}\bar{\nu}_{1/2} \qquad (25)$$

where ϵ_{max} and $\bar{\nu}_{1/2}$ are the peak value of the molecular extinction coefficient at the maximum wavelength λ_{max} and the half-width of the peak in wave number unit, respectively.

The integrated absorption coefficient A has been given by[17]

$$A = \frac{8\pi^3 N}{3hC(1000)}\bar{\nu}_{max}|\mu_{nm}|^2 \qquad (26)$$

where N, h, μ_{nm}, and $\bar{\nu}_{max}$ are the Avogadro number, Planck constant, transition moment, and the frequency in cm^{-1} at λ_{max}, respectively.

From eqs. (24), (25) and (26), we have

$$\mu_{nm} = 6.5168\times 10^{-2}\left(\epsilon_{max}\frac{\bar{\nu}_{1/2}}{\bar{\nu}_{max}}\right)^{1/2} \qquad (27)$$

We will compare the $\mu_{A^+D^-}$ values with μ_{nm} values of eqs. (16) and (27) respectively in the section on results and discussion.

TABLE 1: Dielectric Constants of Ethanol–Water Mixtures

% EtOH	15 °C	25 °C	35 °C	45 °C
95	28 80	27.19	25.68	24.09
90	31.60	29.88	28.27	26.59
80	37.20	35.27	33.45	31.58
60	48.41	46.04	43.80	41.56

TABLE 2: Viscosities ($\eta\times 10^2$ poise) of Ethanol–Water Mixtures

% EtOH	15 °C	25 °C	35 °C	45 °C
95	1.317	1.089	0.901	0.757
90	1.307	1.078	0.892	0.748
80	1.289	1.057	0.873	0.731
60	1.251	1.016	0.834	0.697

TABLE 3: Limiting Equivalent Conductances Λ_0 ($cm^2\cdot mho\cdot mol^{-1} \pm 0.05$) of NMPI in Ethanol–Water Mixtures

% EtOH	15 °C	25 °C	35 °C	45 °C
95	53.8	65.0	77.0	93.2
90	54.2	66.3	79.2	101
80	69.8	85.3	107	127
60	85.0	109	137	173

TABLE 4: Degree of Dissociation (γ) of NMPI in Ethanol–Water Mixtures

% EtOH	$C\times 10^4$ ($mole\cdot l^{-1}$)	15 °C	25 °C	35 °C	45 °C
95	5.35	0.532	0.533	0.534	0.550
	3.62	0.622	0.634	0.561	0.620
	1.55	0.733	0.734	0.756	0.759
	0.79	0.873	0.869	0.881	0.875
90	4.79	0.581	0.589	0.611	0.570
80	5.52	0.376	0.406	0.401	0.419
60	6.83	0.324	0.351	0.369	0.390

TABLE 5: Activity Coefficients (f) of NMPI in Ethanol–Water Mixtures

% EtOH	$C\times 10^4$ ($mole\cdot l^{-1}$)	15 °C	25 °C	35 °C	45 °C
95	5.35	0.935	0.933	0.930	0.929
	3.62	0.943	0.940	0.937	0.936
	1.55	0.959	0.958	0.956	0.954
	0.79	0.968	0.967	0.966	0.964
90	4.79	0.944	0.942	0.939	0.039
80	5.52	0.962	0.959	0.958	0.956
60	6.83	0.973	0.972	0.970	0.968

TABLE 6: Molar Extinction Coefficients ($\epsilon\times 10^{-4}\cdot l\cdot mole^{-1}cm^{-1}$) of NMPI in Ethanol–Water Mixtures

% EtOH	15 °C	25 °C	35 °C	45 °C
95	1.305	1.331	1.324	1.401
90	1.279	1.327	1.378	1.288
80	1.060	1.129	1.156	1.187
60	0.694	0.726	0.746	0.747

Experimental

Chemicals. N-methyl pyridinium iodide was prepared by refluxing methyl iodide and pyridine in absolute ethanol from Merck, West Germany, and twice recrystallizing from the absolute ethanol to give white crystals. The NMPI was stored in a desiccator over $CaCl_2$; its melting point was found to be 118 °C. The structure of NMPI was confirmed by use of NMR and IR spectroscopy.

Preparation of Stock Solution. Each solution was freshly prepared at room temperature before measuring the conductance and absorption spectrum. Solutions were prepared by dissolving weighed samples of NMPI as 95, 90, 80, and 60 volume percentage of ethanol in ethanol-water mixture. The typical concentrations of the solution were 5.10, 3.20 2.18 and 0.90×10^{-4} mole·l^{-1}. These series of concentration were taken within suitable limits to keep the measuring UV absorbancy[18].

Apparatus and Measurements. The conductance and absorbance of the ionic solutions of NMPI were measured with conductivity bridge (# PM-70CB, Barnstead Sybron Co.) and double beam spectrophotometer (SHIMADZU-210A). During the process, the experimental temperature was controlled in the range of 15, 25, 35, and 45 °C (±0.1 °C). The conductance cell was a dipping type and the cell constant was determined employing KCl. Solvent properties, dielectric constants[19-21] and viscosities[22], were taken from the literature as shown in Table 1 and 2.

The absorbance of the stock solution of NMPI was determined to have a λ_{max} at 260 nm.

Result and Discussion

Limiting Equivalent Conductance, The limiting equivalent conductance (Λ_0) was obtained from the extrapolation of the plot of equivalent conductance (Λ) *vs.* the concentration (C) of the NMPI as shown in Figure 1 which is the typical one (% EtOH=90) of 4 plots for the NMPI. These values in Table 3 increase with increasing temperature and decreasing ethanol percentage of the solvent mixture. It can be explained by the facts that the degree of dissociation of the NMPI increases with increasing temperature but viscosity (η) decreases, and dielectric constant increases as the ethanol percentage of the solvent mixture as listed decreases.

Degree of Dissociation, We obtained the value of the degree of dissociation (γ) of NMPI in the various solvent mixtures after five iterations, as mentioned in the last part of the introduction, and they are presented in Table 4.

From Table 4, we know that the values diminish with decreasing ethanol percentage of the solvent mixture and slightly increase with temperature.

Activity Coefficient, The activity coefficients (f) of the NMPI could be evaluated in the various solvent mixtures as listed in Table 5. The f values become larger as the water content of the solvent mixture and the temperature increase.

Molar Extinction Coefficient, The molar extinction coefficient (ϵ) of NMPI in the solvent mixture are shown in Table 6. The values were elevated by increasing temperature and diminished by decreasing the ethanol content. These phenomena were in agreement in the case of the transition moment as listed in Table 8.

Association constants (K) of eq. (6) in the solvent mixtures could be evaluated by the five iterative method as mentioned above to result in Table 7. The K values increase as the ethanol content of the solvent mixture decreases, and diminish with temperature.

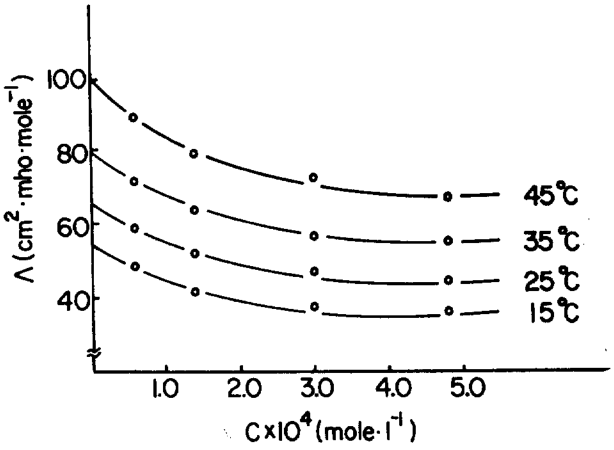


Figure 1. The plot of Λ *vs.* C for NMPI in 90 % EtOH.

TABLE 7: Association Constants(K, l·mole^{-1}) of NMPI in Ethanol-Water Mixtures

% EtOH	15 °C	25 °C	35 °C	45 °C
95	2.89	2.84	2.66	2.62
90	2.90	2.88	2.78	2.43
80	6.81	5.72	5.29	5.15
60	11.0	9.05	8.38	8.14

TABLE 8: Dipole Moments in Debye Unit of NMPI in Ethanol-Water Mixtures

% EtOH	15 °C	25 °C	35 °C	45 °C
95	27.5	27.8	28.3	28.5
90	27.3	27.8	28.0	28.4
80	24.8	25.6	25.9	26.3
60	20.1	20.5	20.8	20.8

TABLE 9: Electrical Thermodynamic Parameters of NMPI in Ethanol-Water mixtures at 25 °C

% EtOH	ΔH°_{el}(kcal·mole^{-1})	ΔS°_{el}(e.u.)	ΔG°_{el}(kcal·mole^{-1})
95	−32.6	−9.87	−29.7
90	−32.4	−8.77	−29.8
80	−32.3	−7.37	−30.1
60	−31.9	−3.97	−30.4

TABLE 10: Thermodynamic Parameters of NMPI in Ethanol-Water Mixtures at 25 °C

% EtOH	ΔH°(kcal·mole^{-1})	ΔS°(e.u)	ΔG°(kcal·mole^{-1})
95	−0.55	14.0	−4.71
90	−0.55	14.0	−4.70
80	−1.75	11.2	−5.08
60	−2.78	8.79	−5.40

The larger the dielectric constant of solvent, the more stable the dipolar ionic complex due to the interaction of solvent and ionic complex.

So the content of water in solvent increases, the equilibrium constant increases and the dissociation constant decreases

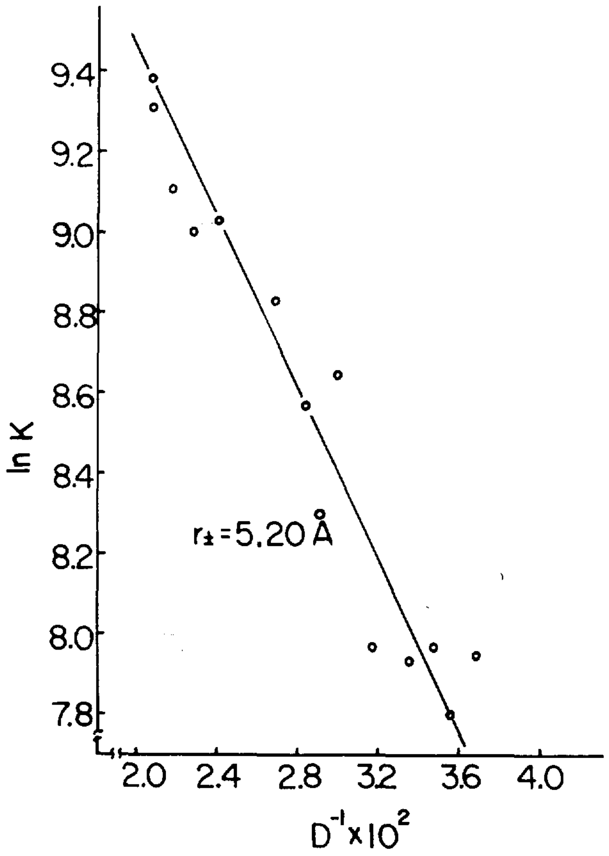


Figure 2. The plot of ln K vs. D^{-1} for NMPI.

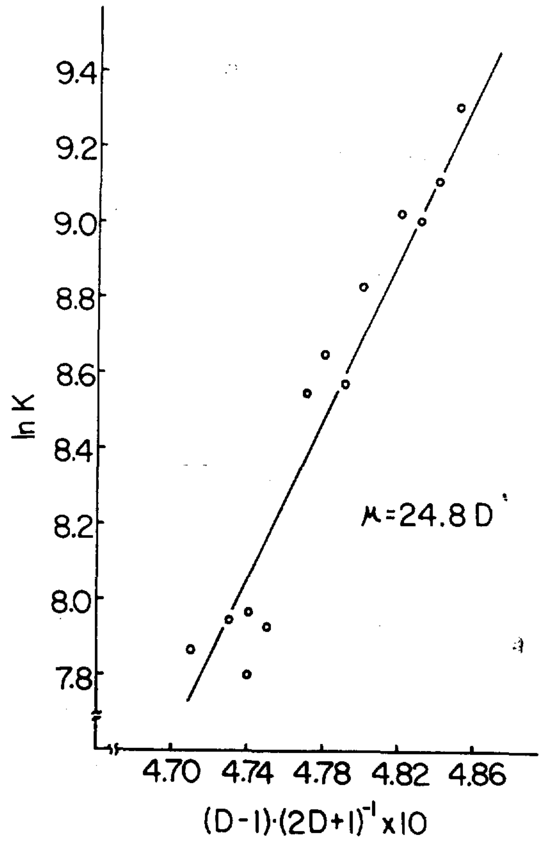


Figure 3. The plot of ln K vs. $(D-1)/(2D+1)$ for NMPI.

as shown in Table 4, Table 7 and Figure. 2.

Ion Size Parameter and Dipole Moment, Now we will evaluate the correlation between the association constant and the polarity of solvent mixture which is described in terms of the dielectric constant and dipole moment in this paper. The polarity of a solvent is determined by its solvation behavior which in turn depends on the action of intermolecular forces between the solvent and solute.[23]

Accordingly, we will represent the plot of ln K vs. D^{-1} in Figure 2. by use of eq. (20). From this plot, the ion size parameter ($\gamma_{\pm}$) of NMPI was evaluated to be 5.20Å.

Next we can plot ln K *vs.* $(D-1)/(2D+1)$ by using eq. (16) to show in Figure 3. Assuming that the dipole moment of nonpolar ion of A^+ and D^- are zero because of their spherical symmetry, we obtained the value of the dipole moment of dipolar NMPI ion,

$$\mu_{A^+D^-}=24.8\,D.$$

On the other hand, the μ_{nm} values calculated from the eq. (27) and the experimental UV peak values were shown in Table 8. These values are in agreement with $\mu_{A^+D^-}$ previously mentioned value. We can also know from Table 8 that the μ_{nm} values decrease with diminishing the ethanol content of the solvent mixture and increase with the elevation of temperature, the former can be explained as being due to the reduction of the charge of the dipolar NMPI ion by its more extensive hydration in solutions of larger water content and the latter by its lesser hydration at the higher temperature.

Thermodynamic Functions. The values of free energy and entropy of the NMPI ion were calculated from the association constant listed in Table 7 by use of eqs. (17), (18), and (19). These results were summarized in Table 9. The large negative value of ΔH°_{el} and ΔS°_{el} proves that the water molecules of hydration become more ordered around the dipolar pyridinium iodide ions.

From eqs. (21), (22), and (23), we obtained the various thermodynamic parameters for eq. (6) tabulated in Table 10. The ΔS° values are positive and large as compared with the ΔH° and ΔG° values. The former ($\Delta S^{\circ}>0$) means that the formation of dipolar NMPI ion is favored by dehydration, the latter (ΔS° is large) shows that the equilibrium of eq. (6) is controlled by entropy.

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