Thermodynamics of 2, N-Dimethyl Pyridinium Iodide in Ethanol-Water Mixture under High Pressure

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The ionic association constants (K) of 2, N–dimethyl pyridinium iodide (2NDMPI) in 95 volume percentage ethanol–water mixture were determined by a modified UV and conductance method at 20°C~50°C under 1 to 2000 bars. The K values increase with increasing pressure and decrease with temperature. The total partial molar volume change (ΔV) has relatively small negative value and the absolute ΔV value decrease with increasing pressure and temperature. The ion size (a) and solvation number (n) of 2NDMPI were about 5 Å and changed from 1 to 3 with decreasing temperature. Other thermodynamic parameters such as enthalpy ($\Delta H°$) and entropy ($\Delta S°$) for the equilibrium of the 2NDMPI were evaluated. From all the parameters mentioned above, we came to conclusion that the electrostriction effect of 2NDMPI in the ethanol–water mixture is enhanced with increasing pressure and decreasing temperature.

Introduction

It has been studied by Kosower[1,2] that N–methylpyridinium 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 was also accomplished by Jong–Gi Jee by using a modified UV and conductance method and CNDO/2 scheme[4]. The charge transfer band arises due to a transferral of electron density from an occupied orbital of the pyridinium ion and result in the formation of ionic dipolar complex salt.[4]

In this paper, the pressure effect for the ionic association of the 2,N-dimethyl pyridinium iodides (2NDMPI) in the ethanol–water mixture, which has not been studied, was investigated by UV and conductance method and its result will be discussed by using of the thermodynamic parameters.

Equation (1) is the ionic equilibrium relationship for the 2, N–dimethyl pyridinium iodide:

$$i.e \quad A^+ + D^- \overset{K}{\rightleftharpoons} A^+D^- \qquad \text{(an abbreviation)}$$
$$C_0^+ - x \quad C_0^- - x \qquad x$$
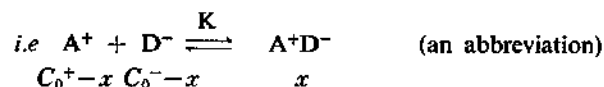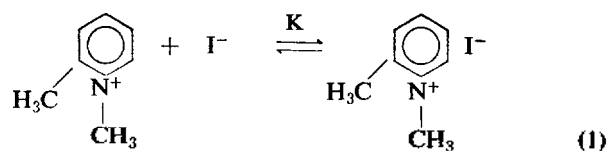
where A^+, D^- and A^+D^- are a cationic electron acceptor, anionic electron donor and dipolar ionic complex, C_0^+ and C_0^- are the initial molar concentration of A^+ and D^-, and x the molar concentration of A^+D^- at equilibrium state.

Since K is the function of the ionic strength that depens upon the 2NDMPI concentration, we must modify the association constant (K) with the product K and the Shedlovsky function S[4,5]. Therefore, putting $x = A/\epsilon$, the following equation is obtained.

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

where A and ϵ are the absorbance (optical density) and molar absorptivity (extinction coefficient) of A^+D^- at maximum absorbance wavelength, λ.

Letting $C_0^+ = C_0^- = C_0$, eqn. (2) is rearranged as follows.

$$\frac{C_0^2 S}{A} = \frac{(2C_0 - x) S}{\epsilon} + \frac{1}{K\epsilon} \qquad (3)$$

where x can be defined by

$$x = C_0 - \gamma C_0 \qquad (4)$$

where γ is the degree of dissociation of the eqn. (1), which can be defined as follows in nonaqueous system.[5]

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

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

Substitution of the eqn. (4) into the eqn. (3) leads to the next result.

$$\frac{C_0^2 S}{A} = \frac{1}{\epsilon} [(1 + \gamma) C_0 S] + \frac{1}{K\epsilon} \qquad (6)$$

And the following relation is given by the eqn. (4) and $x = A/\epsilon$

$$\epsilon = \frac{A}{C_0 - \gamma C_0} \qquad (7)$$

Then the degree of dissociation, γ, is obtained by replacing C_0 with fC_0 in the eqn. (4).

$$\gamma = \frac{(fC_0 - A/\epsilon)}{fC_0} \qquad (8)$$

where f is the activity coefficient given by the following relationship from the Debye–Hückel limiting equation.[6]

$$-\log f = \frac{1.290 \times 10^6 |z_1 z_2| (DT)^{-\frac{3}{2}} \sqrt{C\gamma}}{1 + \sqrt{C\gamma}} \qquad (9)$$

Substituting C_0 with fC_0 in the eqn. (6), the result is

$$\frac{(fC_0)^2 S}{A} = \frac{1}{\epsilon}\left[(1+\gamma)\ fC_0\ S\right] + \frac{1}{K\epsilon} \tag{10}$$

The first correction of ϵ in the eqn.(7) is obtained from the γ value of the eqn(5). obtained by conductivity method. Next, the γ value can also be corrected from the eqn.(8) by using the first corrected ϵ value and f value obtained from the eqn. (9). These corrected values are used to calculate K value from the eqn.(8). This cyclic procedure continues until the successive iterations $|\epsilon_i - \epsilon_{i+1}|/\epsilon_i \leq 0.05$ come out by use of computer program.

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

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V}{RT} \tag{11}$$

where ΔV is the total partial molar volume change of the dissolved species when they are in the equilibrium state.
The discussion for the ΔV will be presented in the part of the results and discussion.

Experimental

Materials. 2, N-dimethyl pyridinium iodide (2NDMPI) was prepared in the following way that the extra pure 2-methyl ypridine and methy iodide were refluxed in absolute ethanol from Merck, Germany, and four times recrystallized from the absolute ethanol to give white crystal. The 2NDMPI crystal was stored in a desiccator filled with silica gel and its melting point measured was 225 °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 were prepared by dissolving weighted sample of 2NDMPI in the 95 volume % 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.l^{-1}. These series of concentration were taken within suitable limits to keep the measuring UV absorbancy[7].

Apparatus and measurements. The conductance and absorbancy for the ionic solution of 2NDMPI were measured withconductivity bridge (♯ PM-70CB, Barnstead Sybron Co) and double beam spectrophotometer (SHIMADZU-210A).

During the experimental process, the experimental temperature and pressure were controlled in the range of 20, 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,[8] is composed of two parts.

One part, acts as conductance cell, is consisted of a glass globe of about 5 cm³ in volume where two Pt rectangular plate electrodes were sealed and the other part, pressure conductor, has two branched teflon tube of 7 cm long and 0.4 cm in diameter. The cell is set in the pressure vessel and the pressure measurement system was described elsewhere[9].

Dielectric constants[10,11] and viscosities[12] of the ethanol-

TABLE 1: Dielectric Constants (D) of 95% Ethanol-Water Mixture at Various Temperatures and Pressures

P (bars) T (°C)	1	500	1000	1500	2000
20	27.47	28.61	29.57	30.33	30.91
30	25.87	27.20	28.05	28.62	29.29
40	24.18	25.69	26.64	27.11	27.88
50	22.59	24.10	25.14	25.61	26.28

TABLE 2: Viscosities ($\eta \times 10^2$ poise) of 95 % Ethanol-Water Mixture at Various Temperature and Pressures

P (bars) T (°C)	1	500	1000	1500	2000
20	1.360	1.427	1.735	2.053	2.497
30	0.996	1.264	1.556	1.829	2.247
40	0.872	1.114	1.310	1.621	1.976
50	0.754	0.954	1.187	1.400	1.717

water mixture were calculated in the ratio of volume percentage by use of tabulated data. These results were listed in Table 1 and 2.

The maximun absorption of 2NDMPI occurs at 266 nm around room temperature and atmospheric pressure.

Results and Discussion

Limiting equivalent conductance. The limiting equivalent conductance (Λ_0) were obtained from the extrapolation of the plot of equivalent conductance (Λ) *vs.* the concentration (C) of 2NDMPI as shown in Figures 1, 2, 3 and 4. The results are listed in Table 3. These Λ_0 values increase with increasing temperature and decrease with pressure.

Degree of dissociation. The γ values of 2NDMPI in the solvent mixture were calculated after 5 iterations as mentioned in the last part of the introduction and put down in
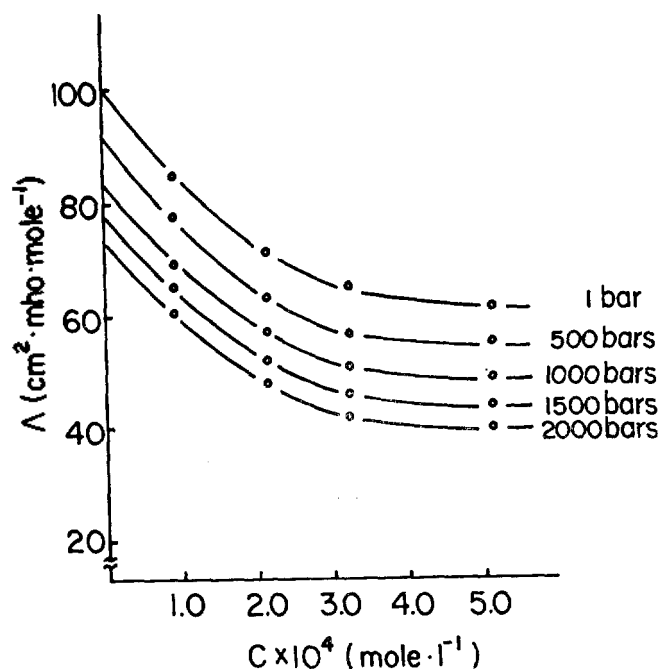

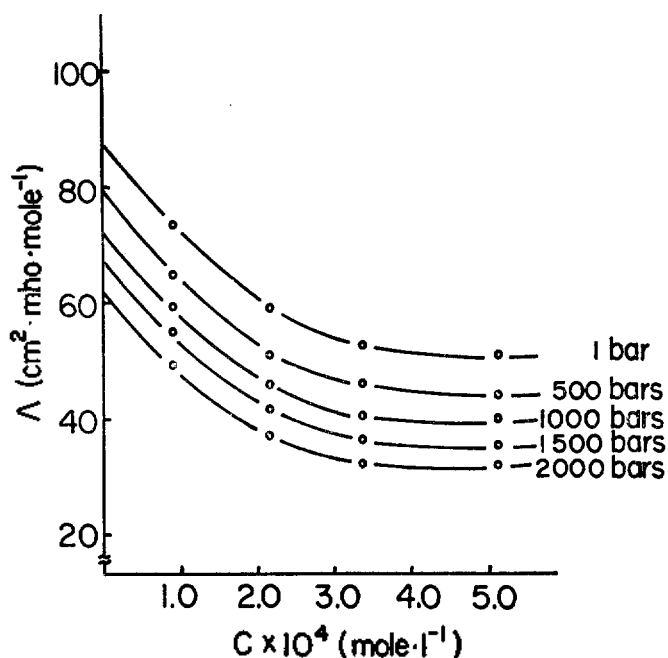**Figure 1.** The Plot of Λ *vs.* C for 2NDMPI in 95 % Ethanol-Water Mixture at 20 °C.

Figure 2. The Plot of Λ vs. C for 2NDMPI in 95 % Ethanol–Water Mixture at 30 °C.

Figure 3. The Plot of Λ vs. C for 2NDMPI in 95 % Ethanol–Water Mixture at 40 °C.

Figure 4. The plot of Λ vs. C for 2NDMPI in 95 % ethanol–water mixture at 50 °C.
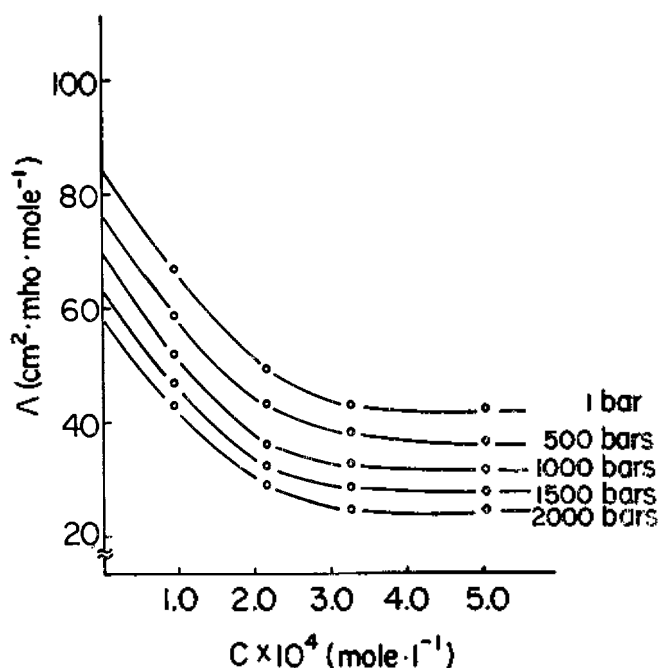
TABLE 3: Limiting Equivalent Conductances (Λ_0 cm^2.mho.mole^{-1}) of 2NDMPI in 95 % Ethanol–Water Mixture

P (bars) T (°C)	1	500	1000	1500	2000
20	83.5	76.5	70.0	63.0	58.0
30	87.0	79.0	72.0	67.0	62.5
40	100	92.0	84.0	78.0	74.0
50	116	106	98.0	90.0	83.0

TABLE 4: Degree of Dissociation (γ) of 2NDMPI in 95 % Ethanol–Water Mixture

C×10^4 (mole.l^{-1})	P (bars) T (°C)	1	500	1000	1500	2000
5.08	20	0.348	0.325	0.308	0.308	0.291
	30	0.445	0.396	0.421	0.394	0.371
	40	0.479	0.477	0.460	0.435	0.405
	50	0.543	0.529	0.508	0.498	0.494
3.25	20	0.389	0.386	0.345	0.342	0.329
	30	0.515	0.485	0.458	0.433	0.410
	40	0.550	0.518	0.507	0.489	0.466
	50	0.577	0.568	0.552	0.532	0.525
2.14	20	0.501	0.471	0.429	0.423	0.410
	30	0.603	0.576	0.561	0.553	0.511
	40	0.669	0.632	0.613	0.602	0.582
	50	0.682	0.675	0.658	0.639	0.618
0.91	20	0.790	0.744	0.719	0.725	0.717
	30	0.833	0.815	0.809	0.808	0.765
	40	0.839	0.821	0.811	0.816	0.805
	50	0.859	0.863	0.845	0.842	0.838

Table 4. The γ values increase with increasing temperature and decrease with pressure, this tendency corresponding to the variation of the limiting equivalent conductance with temperature and pressure but not to the dielectric constant (D) and viscosity of the ethanol–water mixture.

Activity coefficients. The activity coefficients (f) of 2NDMPI in the solvent mixture is also obtained from the eqn. (9) using the above γ values. The results were shown in Table 5. The f values decrease with increasing temperature and decreasing pressure. The reason is associated with the fact that the ideality of the solution is inversely proportional to temperature because the interaction such as ion pair–ion pair, ion pair–dipole
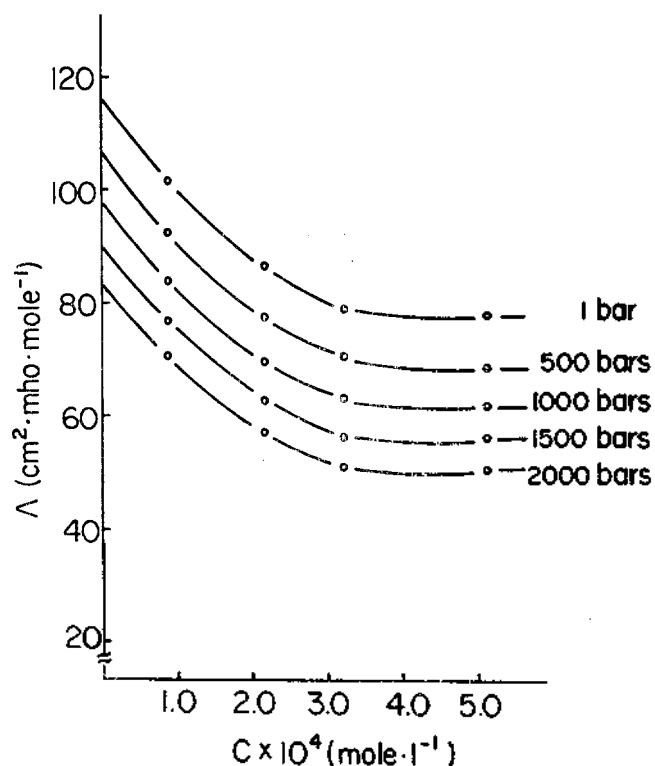
etc. occurs more vigorously at higher temperature and the effect for the dimerization of 2NDMPI elevates at higher

TABLE 5: Activity Coefficients (f) of 2NDMPI in 95 % Ethanol-Water Mixture

$C \times 10^4$ (mole.l^{-1})	P (bars) T (°C)	1	500	1000	1500	2000
5.08	20	0.945	0.950	0.953	0.955	0.958
	30	0.936	0.947	0.945	0.948	0.951
	40	0.931	0.937	0.941	0.944	0.948
	50	0.923	0.931	0.936	0.938	0.941
3.25	20	0.954	0.957	0.961	0.962	0.964
	30	0.946	0.953	0.954	0.957	0.959
	40	0.941	0.948	0.951	0.953	0.956
	50	0.936	0.943	0.947	0.949	0.951
2.14	20	0.958	0.962	0.965	0.966	0.968
	30	0.952	0.959	0.959	0.961	0.963
	40	0.947	0.954	0.956	0.958	0.960
	50	0.944	0.949	0.953	0.955	0.957
0.91	20	0.966	0.969	0.971	0.972	0.973
	30	0.964	0.968	0.968	0.969	0.971
	40	0.962	0.965	0.967	0.968	0.970
	50	0.959	0.963	0.965	0.966	0.968

pressure.

Molar extinction coefficients. Molar extinction coefficients (ε) of 2NDMPI in ethanol-water mixture is evaluated from the eqn.(10) using the previous values. ε values increase with increasing temperature and decrease with pressure as shown in Table 6.

The effect of pressure on the dipolar ionic complex. Table 7 shows the effect of pressure and temperature on the association constants (K) of the dipolar ionic charge tranfer complex of the eqn. (1). It can be summarized that the association constants of 2NDMPI decrease in proportion as the temperature and the pressure increase.

We checked the following equation by the least-mean-squares method in order to evaluate the total partial molar volume change (ΔV) of the 2NDMPI in 95 % ethanol-water mixture.

$$\ln K = 9.241 + 3.099 \times 10^{-4} P - 2.589 \times 10^{-8} P^2 \text{ (at 20 °C)}$$
$$\ln K = 8.078 + 1.603 \times 10^{-4} P - 1.190 \times 10^{-10} P^2 \text{(at 50 °C)}$$

$$(12)$$

The ΔV values claculated from the eqn.(11), (12) and Table 7 were shown in Table 8. The absolute ΔV values decrease with increasing pressure and temperature. And the extent of decrease is smaller in the range of higher pressure. In order to interpret this phenomena, let us consider the next equation from the eqn.(1).

$$\Delta V = [V_{A \cdot D^-} - (V_{A^-} + V_{D^-})] - n(V_0 - V)$$
$$= \Delta V_{in} + \Delta V_{el} \quad (13)$$

where $V_{A \cdot D^-}$, V_{A^-}, and V_{D^-} are the molar volume of $A^+ D^-$, A^+ and D^-, and V_0, V and n are the molar volume of free solvent, molar volume of compressed solvent due to solvation, and solvation number for all the ionic species of the eq. (1) respectively. Intrinsic volume (ΔV_{in}) and electrostriction volume (ΔV_{el}) can be defined by[13]

$$\Delta V_{in} = V_{A \cdot D^-} - (V_{A^-} + V_{D^-}) \quad (14)$$

TABLE 6: Molar Extinction Coefficients ($\epsilon \times 10^{-4}$ l.mole^{-1}.cm^{-1}) of 2NDMPI in 95 % Ethanol-Water Mixture

P (bars) T (°C)	1	500	1000	1500	2000
20	1.51	1.35	1.25	1.25	1.22
30	1.90	1.69	1.69	1.65	1.45
40	2.06	1.86	1.79	1.78	1.69
50	2.28	2.28	2.09	2.03	1.97

TABLE 7: Association Constants ($K \times 10^{-3}$ $l \cdot$mole^{-1}) of 2NDMPI in 95 % Ethanol-Water Mixture

P (bars) T (°C)	1	500	1000	1500	2000
20	10.3	12.0	13.7	15.4	17.3
30	5.09	6.43	6.54	7.42	9.12
40	4.01	4.68	5.05	5.55	6.48
50	3.25	3.39	3.81	4.15	4.40

TABLE 8: Total Partial Molar Volume Change ($-\Delta V$ cm$^3 \cdot$mole^{-1}) of 2NDMPI in 95 % Ethanol-Water Mixture

P (bars) T (°C)	1	500	1000	1500	2000
20	7.45	6.83	6.21	5.58	4.96
30	5.62	5.19	4.93	4.72	4.50
40	5.37	5.15	4.77	4.34	4.24
50	4.25	4.25	4.24	4.24	4.24

$$\Delta V_{el} = -n(V_0 - V) \quad (15)$$

The ΔV value is the sum of ΔV_{in} and ΔV_{el}, in which the former is the volume change of reactant particles themselves when they form the product complex (structral effect) and the latter, the corresponding volume change caused by interactions between these particles and solvent molecules (solvent effect).

To evaluate ΔV_{el} from a sound electrostatic theory of the contraction of solvent around an ion, let us consider the following Born's formula for the molar free energy of solvation of ions.[14]

$$\Delta G_{el} = -\frac{N|z_1 z_2|e^2}{2a}\left(1 - \frac{1}{D}\right) \quad (16)$$

where a is the ionpair size $i.$ $e.$ the distance between the center of ions in an ionpair, z_1 and z_2 are the valences of ions, N and e Avogadro's number and the electronic charge, D the dielectric constant of the solvent. Krichevskii[15] obtained the next expression for ΔV_{el} by differentiating the eqn. (16) with respect to pressure

$$\Delta V_{el} = -\frac{N|z_1 z_2|e^2}{2aD^2}\left(\frac{\partial D}{\partial P}\right)_T \quad (17)$$

On the other hand, Hamann et al[16~18] have shown that the ΔV of the eqn.(13) can be estimated quite reliably from Fous-s's theory of ion pair formation.[19]

$$\Delta V = \frac{N|z_1 z_2|e^2}{a}\left(\frac{\partial D^{-1}}{\partial P}\right)_T + RT\left(\frac{\partial \ln \rho}{\partial P}\right)_T \quad (18)$$

From the eqn. (11), (12) and (18), we obtained the ion pair

TABLE 9: Ion Pair Size ($a \times 10^8$ cm) and Solvation Number (n) of 2NDMPI in 95 % Ethanol–Water Mixture

		1 bar	500 bars	1000 bars	1500 bars	2000 bars
a	20 °C	3.24	3.48	3.77	4.10	4.50
	50 °C	4.93	4.93	4.93	4.94	4.94

	20 °C	30 °C	40 °C	50 °C
n	2.95	2.40	1.63	0.95

TABLE 10: Thermodynamic Parameters of 2NDMPI in 95 % Ethanol–Water Mixture at 30 °C and Various Pressures

P (bars)	1	500	1000	1500	2000
ΔG° (kcal·mole^{-1})	−5.14	−5.28	−5.30	−5.37	−5.49
ΔH° (kcal·mole^{-1})	−4.35	−4.63	−5.03	−5.48	−6.88
ΔS° (e.u.)	2.62	2.14	0.89	−0.36	−4.59

size (a) of 2NDMPI in the ethanol–water mixture by using the data of D in Table 1 and the density (ρ) of the mixture were calculated to the mole ratio of ethanol and water from the published density of ethanol[10,11] and water[20] at various pressure at 20°C and 50°C. The results are listed in Table 9.

The next equation is given by differentiation of the eqn.(13) with respect to V_0 assuming that n and V are independent of external pressure as the electrostriction effect of ionic reactions is dependent on only the nature of ions and solvents over the pressure range studied.

$$\left(\frac{\partial \Delta V}{\partial V_0}\right)_T = \left(\frac{\partial \Delta V_{in}}{\partial P}\right)_T \left(\frac{\partial P}{\partial V_0}\right) - n \tag{19}$$

A similar equation for kinetics under high pressure was introduced by Goniberg and El'yanov.[21] The calculated solvation number (n) were summarized in Table 9.

The free energy of reaction (ΔG°), enthalpy of reaction (ΔH°) and entropy of reaction (ΔS°) for the equilibrium of the eqn.(1) were calculated at 30°C from the plot of ln K vs. 1/T and shown in Table 10.

The ionpair size (a) increases with increasing pressure at 20°C but are independent of pressure at 50°C. This phenomena can be explained by the fact that the electrostriction effect of 2NDMPI at 20°C is larger than that at 50°C since the solva-

tion number (n) decreases with increasing temperature and increases with increasing pressure, because the negative ΔH° value increases with pressure and ΔS° value decreases with pressure.

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