

4	2	$\pm 2$	-1	4 $d_{xy}$	$(128\zeta^6/45\pi^2)^{1/2} r^2 (2\zeta r - 5) r^{-\nu} \sin^2\theta \sin\phi \cos\phi$
4	3	0	0	4 $f_z$	$(16\zeta^7/45\pi^2)^{1/2} r^3 e^{-\nu r} \cos\theta (4\cos^2\theta - 3)$
4	3	$\pm 1$	1	4 $f_{xz}$	$(16\zeta^7/45\pi^2)^{1/2} r^3 e^{-\nu r} \sin\theta (4\cos^2\theta - 1) \cos\phi$
4	3	$\pm 1$	-1	4 $f_{yz}$	$(16\zeta^7/45\pi^2)^{1/2} r^3 e^{-\nu r} \sin\theta (4\cos^2\theta - 1) \sin\phi$
4	3	$\pm 2$	1	4 $f_{zx^2-y^2}$	$(128\zeta^7/45\pi^2)^{1/2} r^3 e^{-\nu r} \sin^2\theta \cos\theta (\cos^2\phi - \sin^2\phi)$
4	3	$\pm 2$	-1	4 $f_{xyz}$	$(512\zeta^7/45\pi^2)^{1/2} r^3 e^{-\nu r} \sin^2\theta \cos\theta \sin\phi \cos\phi$
4	3	$\pm 3$	1	4 $f_x$	$(128\zeta^7/225\pi^2)^{1/2} r^3 e^{-\nu r} \sin^3\theta \cos\phi (\cos^2\phi - 3\sin^2\phi)$
4	3	$\pm 3$	-1	4 $f_y$	$(128\zeta^7/225\pi^2)^{1/2} r^3 e^{-\nu r} \sin^3\theta \sin\phi (\sin^2\phi - 3\cos^2\phi)$
5	0	0	0	5 $s$	$(2\zeta/9)^{1/2} (2\zeta^4 r^4 - 16\zeta^3 r^3 + 36\zeta^2 r^2 - 24\zeta r + 3) e^{-\nu r}$

\*d value; 0.1 and -1 stand for having zero, cosine and sine combination in the transformation of the complex wave functions into the real functions.

improved the conventional STO's and obtained the orthonormalized STO's which are closest in form to the hydrogenic orbitals. These new orbitals,  $\chi_{nlm}(r, \theta, \phi)$  shall be extensively utilized in LCAO-MO procedures in the near future.

## Reference

- (1) C.C.J. Roothaan, *Revs. Modern Phys.* **23**, 69 (1951).
- (2) R.K. Nesbet, *Proc. Roy. Soc.* **A230**, 312 (1955).
- (3) C.C. J. Roothaan, *Revs. Modern Phys.* **32**, 179 (1960).
- (4) C. Allen, *J. Chem. Phys.* **34**, 1156 (1961).
- (5) E. Clementi, Roothaan, C.C. J. and Yoshimine, *M., Phys. Rev.* **127**, 1618 (1962).
- (6) J.C. Slater, *Phys. Rev.*, **36**, 57 (1930).
- (7) E. Clementi and D.L. Raimondi, *J. Chem. Phys.* **38**, 2686 (1963).
- (8) I.G. Csizmadia, *Progress in theoretical organic chemistry* Vol. 1. P17. (Elsevier Scientific Pub. Comp. Amsterdam-Oxford-New York (1976))
- (9) S.F. Boys, and I. Shavitt, *Proc. Roy. Soc.* **A254**, 487 (1960).
- (10) Shavitt, I., and Karplus, M., *J. Chem. Phys.* **36**, 550 (1962).
- (11) J.M. Foster and S.F. Boys, *Rev. Mod. Phys.* **32**, 303 (1960).
- (12) J.A. Pople, *Acc. Chem. Res.* **3**, 217 (1970)
- (13) Ref. 8, P15.
- (14) Ira N. Levine, *Quantum Chemistry* and edition P113, Table 6.2 (Allyn and Bacon, Inc. Boston. London. Sydney 1974).
- (15) Ref. 12, P313, Table XII-2.

## The Pressure Effect on the Ionization of *m*-chloroanilinium Ion in Sodiumacetate Buffer Solution

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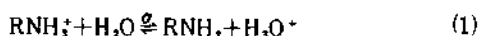
The dissociation constants ( $K$ ) of *m*-chloroanilinium ion in water-ethanol mixture, where the volume percentage of water is 89.5%, were evaluated by UV-spectroscopic method at 20~50°C, up to 1500 bars with changing ionic strength from 0.04 to 0.10 mol kg<sup>-1</sup> by use of acetate buffer.  $K$  values enhance with increasing ionic strength and temperature, but decrease with elevating pressure. From  $K$  values, we obtained the partial molar volume change and some other thermodynamic parameters. From the values of enthalpy, entropy and isoequilibrium temperature (649 K), we concluded that the dissociation of *m*-chloroanilinium ion mentioned above is controlled by enthalpy.

## Introduction

To observe the more direct phenomena of the solution, one must measure the effect of pressure on the volumes of different concentrations because pressure is the conjugated thermodynamic variable of volume which is more direct and visual parameter than entropy conjugated to temperature.

The influence of pressure on the ionization of some substituted anilinium ions had already been studied.<sup>1</sup> But *m*-chloroanilinium ion has not been done, so the authors measured its optical coefficients up to 1500 bars at several pH's and temperatures in water-ethanol mixture.

To extend the study to ionization reaction of some similar types, let us consider the next equation.



where  $\text{RNH}_3^+$  stands for anilinium ion from aniline ( $\text{RNH}_2$ ) in an acidic solution.

Putting the degree of dissociation of eq. (1)  $\alpha$ , one can write the optical density of the buffer solution containing the anilinium ion,  $A$  as follows:

$$A = (1 - \alpha) A_{\text{RNH}_3^+} + \alpha A_{\text{RNH}_2} \quad (2)$$

where  $A_{\text{RNH}_3^+}$  and  $A_{\text{RNH}_2}$  are the absorbance of the  $\text{RNH}_3^+$  and  $\text{RNH}_2$  respectively.

From the eq's.(1) and (2), we simplified the dissociation constant,  $K$  of anilinium ion to be the exact relationship.<sup>2-4</sup>

$$K = \frac{\alpha}{1 - \alpha} \frac{\gamma_{\text{RNH}_2} \gamma_{\text{H}_3\text{O}^+} m_{\text{H}_3\text{O}^+}}{\gamma_{\text{RNH}_3^+}} \quad (3)$$

where the  $\gamma_i$  denotes activity coefficients of chemical species,  $i$  and  $m_{\text{H}_3\text{O}^+}$  represents the molality of hydronium ions, by

making the usual assumption that  $\gamma_{\text{RNH}_3^+} = 1$ , and assuming the addition that  $\gamma_{\text{H}_3\text{O}^+} + \gamma_{\text{RNH}_3^+} \approx 1$ . Although the latter approximation may not be valid at high ionic strengths, it is nevertheless likely that the pressure dependence of  $\gamma_{\text{H}_3\text{O}^+} / \gamma_{\text{RNH}_3^+}$  is small and that the ratio  ${}^P K / {}^1 K$  in eq. (6) is less in error than the absolute values of  ${}^P K$  and  ${}^1 K$ . Therefore, we obtain the next equation.

$$K \approx \frac{\alpha}{1-\alpha} m_{\text{H}_3\text{O}^+} \quad (4)$$

The fundamental equation for the pressure effect on the equilibrium constant of a reaction is

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V^\ominus}{RT} \quad (5)$$

where  $\Delta V^\ominus$  and  $R$  represent the change of partial molar volume for the ionization (1) at the absolute temperature  $T$ , and the gas constant.

The partial molar volume change for the reaction (1) at atmospheric pressure and zero ionic strength is given by<sup>1</sup>

$$\Delta V^\ominus = -RT \left(\frac{\partial \ln K}{\partial P}\right)_{T,P=1} = -RT \left(\frac{1+b(P-1)}{(P-1)}\right) \ln \left(\frac{{}^P K}{{}^1 K}\right) \quad (6)$$

where the symbols  ${}^1 K$  and  ${}^P K$  denote the dissociation constants of the anilinium ions at 1 bar and  $P$  bars, and  $b$  represents an experimental constant.

The other thermodynamic parameters ( $\Delta H^\ominus$ ,  $\Delta G^\ominus$ , and  $\Delta S^\ominus$ ) are obtained from the well-known relationships.

Denison and Ramsey<sup>5</sup>, Eigen<sup>6</sup>, and Fuoss<sup>7</sup> have derived eq. (7) from a theoretical treatment when two ions of opposite charge form an ion pair in an electrolytic solution.<sup>8-12</sup>

$$\ln K = \ln \frac{3000}{4\pi\rho N\gamma^3} \frac{|Z_1 Z_2| e^2}{\gamma kT} \left(\frac{1}{D}\right) \quad (7)$$

where  $\rho$ ,  $N$ ,  $\gamma$  and  $k$  stand for the density of solvent, Avogadro's number, the size of ion-pair, and Boltzmann constant, respectively.

## Experimental

**Materials.** All materials were used extra-pure and first-grade reagents.

**Preparation of stock solution:** Stock solution was prepared by dissolving weighted *m*-chloroaniline in the water-ethanol mixture in which the volume percentage of water was 89.5%. The measuring solutions were obtained from dilution of the stock solution, and a typical concentration was  $1.74 \times 10^{-4}$  mol  $\text{kg}^{-1}$ .

**Apparatus and measurements.** The absorbance of *m*-chloroanilinium ion at  $\lambda_{\text{max}} = 287$  nm was measured with UV-spectrometer (Shimadzu-210A) which had been installed Lentz cell (Hofer, Germany).

The pressure generated by the hand pump (Nova, Swiss) was delivered into the Lentz cell through the liquid-separator which was made in this laboratory.

Throughout the measurements, the ionic strengths of the buffer solution were controlled with 0.04, 0.06, 0.08 and 0.10 mol  $\text{kg}^{-1}$ .

During the experimental processes, the experimental temperature and pressure were controlled in the range of 20, 30, 40, 50°C ( $\pm 0.01^\circ\text{C}$ ) and 1, 500, 1000, 1500 bars, respectively.

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

T(°C)	P (bars)			
	1	500	1000	1500
20	74.4	76.2	78.0	79.8
30	71.0	72.8	74.5	76.3
40	67.7	69.5	71.3	73.0
50	64.7	66.4	68.1	69.8

TABLE 2: Absorbance of the *m*-chloroanilinium Ion in the Acetate Buffer Solution

T(°C)	Soln	P (bars)			
		1	500	1000	1500
20	NaOH + A	0.71	0.73	0.75	0.77
	HCl + A	0.44	0.43	0.42	0.41
	0.04 + A	0.59	0.57	0.56	0.53
	0.06 + A	0.60	0.59	0.58	0.57
	0.08 + A	0.60	0.60	0.59	0.58
30	0.10 + A	0.62	0.61	0.60	0.60
	NaOH + A	0.71	0.73	0.75	0.77
	HCl + A	0.44	0.43	0.42	0.41
	0.04 + A	0.59	0.58	0.56	0.55
	0.06 + A	0.60	0.59	0.58	0.58
40	0.08 + A	0.60	0.61	0.59	0.59
	0.10 + A	0.62	0.62	0.61	0.60
	NaOH + A	0.72	0.74	0.76	0.78
	HCl + A	0.44	0.43	0.42	0.41
	0.04 + A	0.60	0.59	0.57	0.56
50	0.06 + A	0.61	0.60	0.59	0.58
	0.08 + A	0.62	0.61	0.60	0.59
	0.10 + A	0.63	0.63	0.62	0.61
	NaOH + A	0.73	0.75	0.77	0.79
	HCl + A	0.44	0.43	0.42	0.42
	0.04 + A	0.61	0.60	0.58	0.57
	0.06 + A	0.62	0.61	0.59	0.59
	0.08 + A	0.64	0.62	0.61	0.60
	0.10 + A	0.65	0.63	0.63	0.62

A denotes *m*-chloroanilinium ion.

Dielectric constants of water-ethanol mixture were calculated in the ratio of volume percentage by use of tabulated data.<sup>13,14</sup> The result was listed in Table 1.

The measured absorbance of the *m*-chloroanilinium ion were given in Table 2.

## Result and Discussion

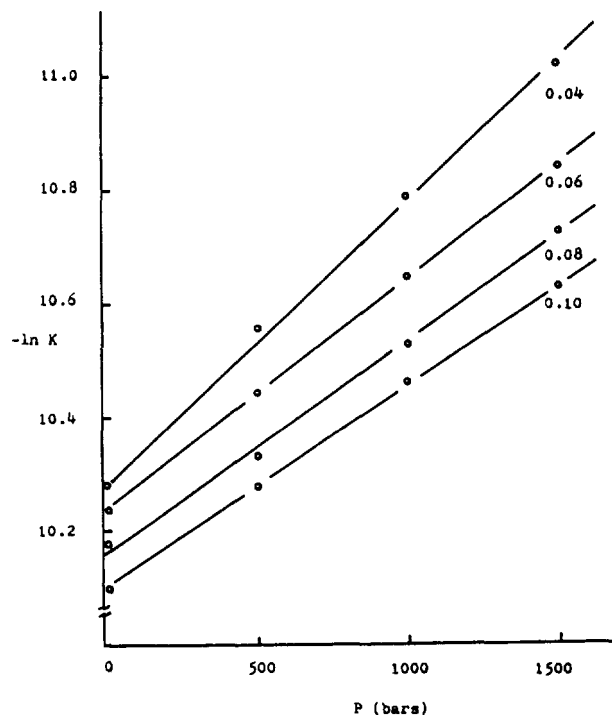
The dissociation constants,  $K$  of *m*-chloroanilinium ion were evaluated from the eq. (4) and listed in Table 3.  $K$  values enhance with increasing ionic strength because the more the protons of acetate buffer increase, the more the  $-\text{NH}_2$  group of *m*-chloroaniline convert into the  $-\text{NH}_3^+$ . Also  $K$  values increase with increasing temperature but decrease with enhancing pressure. The former can be explained using the fact that the  $-\text{NH}_3^+$  group dissociate into the  $-\text{NH}_2$  group and the hydronium ion by the higher thermal motion and the latter using the fact that the backward reaction is more favorable than the forward reaction in eq. (1) under higher pressure.

TABLE 3: Dissociation Constants ( $K \times 10^4$ ) of *m*-chloroanilinium Ion in Water-Ethanol Mixture

T(°C)	I(mol kg <sup>-1</sup> )	p (bars)			
		1	500	1000	1500
20	0.04	3.50	2.57	2.06	1.63
	0.06	3.56	2.90	2.37	2.02
	0.08	3.78	3.25	2.66	2.18
	0.10	4.15	3.44	2.80	2.43
30	0.04	3.58	2.78	2.12	1.76
	0.06	3.64	3.12	2.40	2.12
	0.08	3.86	3.47	2.76	2.34
	0.10	4.53	3.86	2.95	2.53
40	0.04	3.65	2.88	2.20	1.92
	0.06	3.79	3.26	2.44	2.15
	0.08	4.53	3.54	2.84	2.40
	0.10	4.98	4.00	3.14	2.65
50	0.04	3.81	2.98	2.35	1.99
	0.06	4.39	3.33	2.54	2.18
	0.08	5.07	3.59	2.88	2.46
	0.10	6.01	4.07	3.28	2.71

TABLE 4: Partial Molar Volume Changes ( $\Delta V^{\ominus}$  cm<sup>3</sup> mol<sup>-1</sup>) of *m*-chloroanilinium Ion

T(°C)	Soln 0.04	I(mol kg <sup>-1</sup> )		
		0.06	0.08	0.10
20	12.42	9.43	8.58	7.80
30	12.24	9.62	8.78	9.82
40	12.16	9.94	11.05	11.43
50	11.72	12.58	13.15	14.37

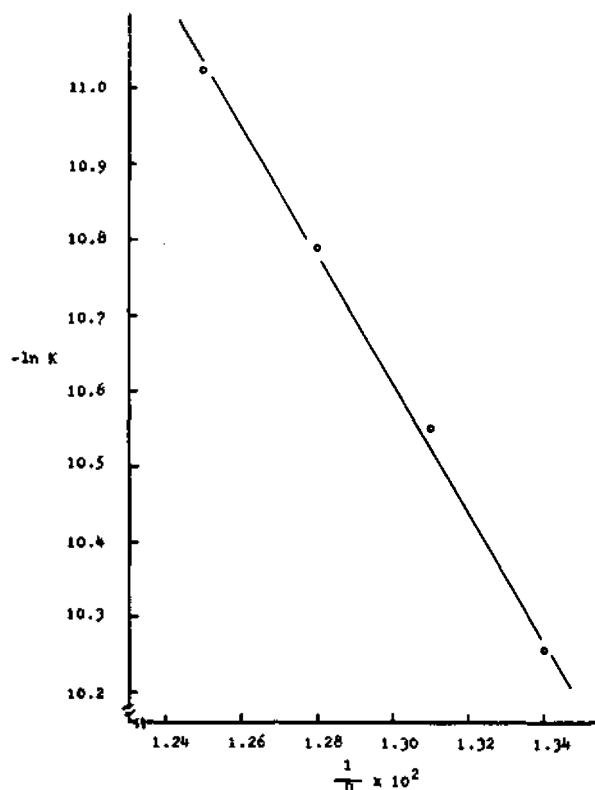
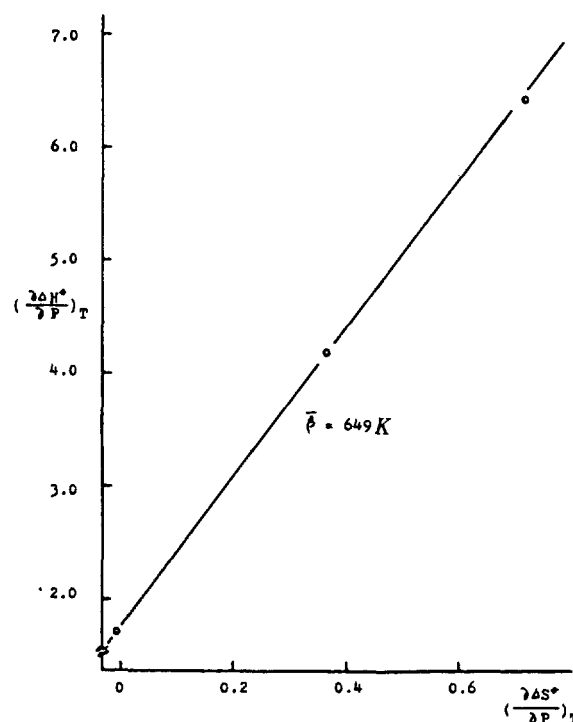
Figure 1. The plot of  $\ln K$  vs.  $p$  for *m*-chloroanilinium ion at  $I = 0.04$  mol kg<sup>-1</sup> and  $T = 20^\circ\text{C}$ 

The partial molar volume changes,  $\Delta V^{\ominus}$  which were calculated from eq. (5) were listed in Table 4.

The plot of  $\ln K$  versus pressure at constant ionic strength is independent of pressure as shown in Figure 1, therefore the

TABLE 5: Ion Size of *m*-chloroanilinium Ion ( $\gamma \times 10^8$  cm) in Water-Ethanol Mixture at  $I = 0.04$  mol kg<sup>-1</sup>

T(°C)	20	30	40	50
( $\times 10^8$ cm)	6.8	7.6	8.9	9.5

Figure 2. The plot of  $\ln K$  vs.  $(1/D)$  for *m*-chloroanilinium ion at  $I = 0.04$  mol kg<sup>-1</sup> and  $T = 20^\circ\text{C}$ .Figure 3. The plot of  $(\partial\Delta H^{\ominus}/\partial p)_T$  vs.  $(\partial\Delta S^{\ominus}/\partial p)_T$  at  $20^\circ\text{C}$  and  $I = 0.04$  mol kg<sup>-1</sup>.

$\Delta V^{\ominus}$  values in eq. (5) equal to the  $\Delta^{\circ}V^{\ominus}$  values in eq. (6). The  $\Delta V^{\ominus}$  values were positive instead of negative. The reason lies in the fact that *m*-chloroanilinium ion is merely replaced by hydronium ion. The fact that  $\Delta V^{\ominus}$  values are not zero, but

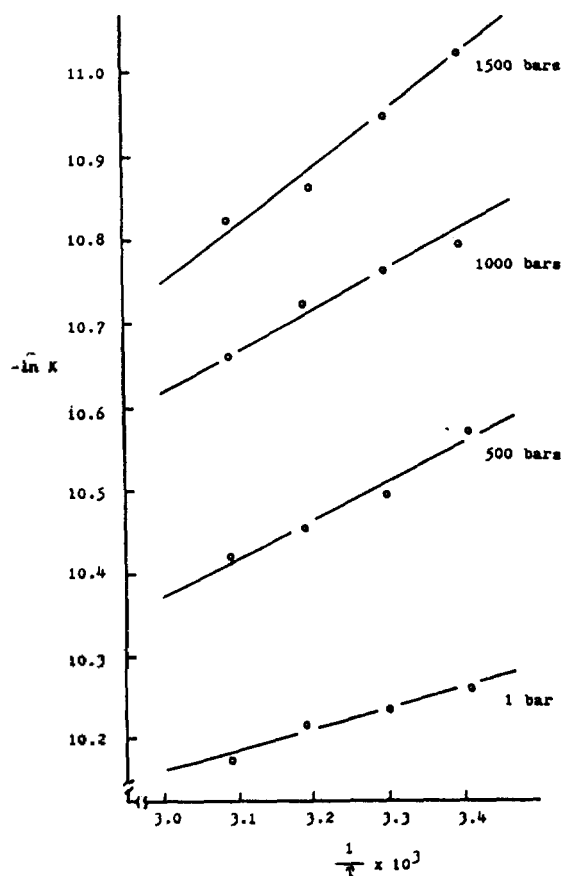


Figure 4. The plot of  $\ln K$  vs.  $(1/T)$  for *m*-chloroanilinium ion at  $I=0.04 \text{ mol kg}^{-1}$ .

positive, for eq. (1) indicates that a proton is more effective in causing electrostriction when it is attached to an amino group than when it is freely dissolved in water-ethanol mixture (that is true of amines in general<sup>15</sup> not just of *m*-chloroaniline).

The average size,  $\gamma$  or *m*-chloroanilinium ion which is the nearest distance between two ions were calculated from eq. (7) and Figure 2, and the results are listed in Table 5. The values of  $\gamma$  increase from 6.8 Å to 9.5 Å in the range of this experimental temperature.

The isoequilibrium temperature,  $\bar{\beta}$  evaluated from the relation<sup>16</sup>  $(\Delta H_p^\ominus - \Delta H_1^\ominus) = \bar{\beta} (\Delta S_p^\ominus - \Delta S_1^\ominus)$ , where subscripts 1 and p stand for 1 and p bars, respectively, and Figure 3 was 649 K. It turned out that the ionic equilibrium of *m*-chloroaniline in acetate buffer solution is controlled by enthalpy.<sup>17</sup> These fact is supported by the phenomena that values calculated from Figure 4 increase with enhancing pressure but  $\Delta S^\ominus$  values are

TABLE 6: Thermodynamic Parameters of *m*-Chloroanilinium Ion in Water-Ethanol Mixture at 20°C and  $I=0.04 \text{ mol kg}^{-1}$

p (bars)	1	500	1000	1500
$\Delta H^\ominus$ (kcal mol <sup>-1</sup> )	0.53	0.71	0.96	1.20
$\Delta G^\ominus$ (kcal mol <sup>-1</sup> )	5.98	6.16	6.29	6.24
$\Delta S^\ominus$ (e.u.)	-18.6	-18.6	-18.1	-17.8

nearly constant as shown in Table 6.

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## References

- (1) S.D. Hamann and M. Linton, *J. Chem. Soc. Faraday*, **1**, **71**, 485 (1975).
- (2) H. Von Halban and L. Ebert, *Z. Phys. Chem.*, **112**, 359 (1924).
- (3) R.A. Robinson, "The Structure of Electrolyte Solutions," ed p. 253. W.J. Hamer(Wiley, New York, 1959).
- (4) S.D. Hamann and M. Linton, *J. Chem. Soc. Faraday*, **1**, **70**, 2239 (1974).
- (5) J.T. Denison and J.B. Ramsey, *J. Am. Chem. Soc.*, **77**, 2615 (1955).
- (6) M. Eigen, *Z. Phys. Chem. (Frankfurt am Main)*, **1**, 176 (1954).
- (7) R.M. Fuoss, *J. Am. Chem. So.*, **88**, 664 (1966).
- (8) S.D. Hamann, P.J. Pearce and W.J. Strauss, *J. Phys. Chem.*, **68**, 375 (1964).
- (9) S.D. Hamann, *Aust. J. Chem.*, **28**, 639 (1975).
- (10) J.G. Jee, Ph. D. Thesis, Univ. of Han Yang, Seoul, Korea (1981).
- (11) J.G. Jee, Y.H. Lee, E.H. Woo and K.H. Lee, *Bull. Korean Chem. Soc.*, **4**, 115 (1983).
- (12) J.G. Jee, Y.H. Lee, K.H. Lee and O.C. Kwun, *Bull. Korean Chem. Soc.*, **5**, 112 (1984).
- (13) N.E. Danforth, *Phys. Rev.*, **38**, 1224 (1931).
- (14) B.B. Owen, R.C. Miller, C.E. Milner, *J. Phys. Chem.*, **65**, 2065 (1961).
- (15) S. Cabani, G. Conti and L. Lepri, *J. Phys. Chem.*, **78**, 1030 (1974).
- (16) B.S. El'yanov and E.M. Vasylytskaya, "Modern Aspects of Physical Chemistry at High Pressure," ed., p. 180. J. Osugi (The Physico-Chemical Society of Japan, Kyoto, 1980).
- (17) J.U. Hwang, S.D. Yoh and J.G. Jee, *J. Korean Chem. Soc.*, **24**, 405 (1980).