The Review of Physical Chemistry of Japan Vol. 48 No. 1 (1978)

# EFFECT OF PRESSURE ON IONIZATION OF TRIETHYLAMINE IN METHANOL

BY HISAYUKI INOUE, KIMIHIKO HARA AND JIRO OSUGI

The ionic dissociation constants of ionization of triethylamine in methanol were determined from the measurements of electrical conductivities over the range of 1–2000 kg cm$^{-2}$* at 25°C and 1–1600kg cm$^{-2}$ at 30 and 40°C. The ionization constants were obtained by the Shedlovsky equation which contains the equivalent conductivity of weak electrolyte and the limiting equivalent conductivity of strong electrolyte. The data were treated by the Fuoss-Onsager equation for potassium chloride, triethylammonium chloride, and potassium methoxide to determine the limiting equivalent conductivities after the justification of the Onsager limiting equation at high pressure. The ionic dissociation constant at 25°C increased from $0.502\times10^{-6}$ mol kg$^{-1}$ at 1 atm to $5.78\times10^{-6}$ mol kg$^{-1}$ at 2000kg cm$^{-2}$, and decreased with temperature to $0.264\times10^{-6}$ mol kg$^{-1}$ at 1 atm and 40°C. The pressure dependence of ionization constant was quantitatively explained by the change of dielectric constant with pressure, and the electrostrictive volume change, and the other volume changes (crystal, void volume change *et al.*) at 1 atm. It was found that both the electrostrictive volume change and the other volume changes play an important role for the pressure effects on the ionization in methanol.

## Introduction

From the measurements of electrical conductivities at high pressures, information about the ion-ion and ion-solvent interactions is obtained without changing the chemical nature of the solvent. Generally the physical properties of solvents, especially organic solvents, show large pressure dependence, and it is interesting to investigate the correlation between such interactions and solvent properties. Although a large number of such investigations have been carried out in aqueous solutions at high pressure, only several investigations have been done systematically in organic solvents in order to compare the results in water. Methanol has been sometimes chosen as the solvent because the dielectric constant is large enough to expect the low degree of association and the data of physical properties are abundant.

Brummer and Hills have measured the temperature and pressure coefficients of conductance in water, methanol, and nitrobenzene over the range 20–60°C and 1–900 atm.1) They discussed the mechanism of ionic migration in liquids in relation to the Walden rule and the theory of transition states. Skinner and Fuoss have reported about the changes of ion-pair association constants and the Walden products in methanol with pressure.2) As for the ionic dissociation, Hamann and Strauss

---

(*Received March 18, 1978*)

* $T/K=273.15+(t/°C)$, 1kg cm$^{-2}$=$0.9805\times10^5$ Pa, 1 kcal=4.184KJ

1) S. B. Brummer and G. J. Hills, *Trans. Faraday Soc.*, **57**, 1816 (1961)

have studied the ionization of piperidine in methanol at high pressures by the conductance method.[3] They have reported the departure of the experimental results in water and methanol at high pressures from the Onsager limiting equation. However, Nakahara *et al.*[4] have reported the validity of the Onsager limiting equation by measuring the electrical conductivity of potassium chloride in aqueous solution. Further, Hamann and Strauss have reported that methylamines are too little ionized in methanol to give "significant" ionization constants by the conductance method. Strauss has measured the anomalous conductivity of hydrogen ion in methanol and reported the ionization constants of picric acid at high pressure.[5] Usually the ionization process from neutral molecules largely depends on pressure, and it is explained mainly by the change of electrostrictive volume. As reviewed and compared by Nakahara[6], several authors have attempted to express the pressure dependence of equilibrium constants in aqueous solutions, but their expressions have never been applied to the organic solvent system. It is important to check the validity of the formula in organic solvent in relation to various kinds of reactions which contain the ionic species and the accurate estimation of the partial molar volume change at each pressure. In this paper not only the results of the electrial conductivities of triethylamine ($N(Et)_3$), potassium chloride (KCl), potassium methoxide (KOMe), and triethylammonium chloride ($HN(Et)_3Cl$), but also the pressure dependence of the ionic dissociation constants of triethylamine in methanol is reported.

## Experimental

The pressure-generating system consisted of two principal components: a hand operated pump, and a pressure bomb immersed in an oil bath. Pressure was measured with a Heise Bourdon Gauge. The cell was a syringe-type cell of glass and the platinum electrodes were coated with platinum black. The cell constant $K_{cell}$ was determined by aqueous potassium chloride solution of $10^{-2}$ mol $dm^{-3}$ at 25°C.[7]

After the distillation of methanol from silver nitrate and sodium methoxide, it was dried by refluxing $3dm^3$ batches over 10g of aluminum powder and 2g of mercuric chloride at least for 10h. The solvent was used after the one more distillation which was done by passing through nitrogen gas; it had a specific conductivity of $(4\text{-}12)\times 10^{-8}$ $ohm^{-1}$ $cm^{-1}$.

Triethylammonium chloride was kindly supplied by Dr. Ueno of our laboratory, potassium chloride was obtained from Merck, and potassium methoxide was synthesized from potassium metal

---

[2] J. F. Skinner and R. M. Fuoss, *J. Phys. Chem.*, **70**, 1426 (1966)

[3] S. D. Hamann and W. Strauss, *Discuss. Faraday Soc.*, **22**, 70 (1966)

[4] M. Nakahara, K. Shimizu, and J. Osugi, *This Journal*, **42**, 12 (1972); **45**, 69 (1975)

[5] W. Strauss, *Aust. J. Chem.*, **10**, 277 (1957)

[6] For example, see (a) M. Nakahara, *This Journal*, **44**, 57 (1974), (b) B. S. El'yanov and S. D. Hamann, *Aust. J. Chem.*, **28**, 945 (1975), (c) N. A. North, *J. Phys. Chem.*, **77**, 931 (1973), (d) D. A. Lown, H. R. Thisk, and L. Wynne-Jones, *Trans. Faraday Soc.*, **64**, 2073 (1968), (e) B. B. Owen and S. R. Brinkley, *Chem. Rev.*, **29**, 461 (1941)

[7] G. C. Benson and A. R. Gordon, *J. Chem. Phys.*, **13**, 473 (1945)

(99.9%). Triethylamine was purified by the way described in the literature.[8] As care is necessary to avoid the influence of the moisture and carbon dioxide, the preparation of the sample was done in a drybox by flowing nitrogen gas.

## Experimental Results and Method of Calculation

The equilibrium constant of the ionic dissociation of triethylamine in methanol,

$$\mathrm{N(Et)_3 + MeOH} \overset{K}{\rightleftharpoons} \mathrm{HN(Et)_3^+ + MeO^-}, \qquad (1)$$

is defined by,

$$K = \frac{a_{HN(Et)_3^+} a_{MeO^-}}{a_{N(Et)_3}}, \qquad (2)$$

where $a$ is the activity of each constituent. The dissociation constant is related to the limiting equivalent conductivity $\Lambda^\circ$ and the equivalent conductivity $\Lambda$ by the following Shedlovsky equation ;[9]

$$\left.\begin{aligned} \frac{1}{\Lambda G(z)} &= \frac{1}{\Lambda^\circ} + \frac{C\Lambda G(z) f^2}{K\Lambda^{\circ 2}} \\ G(z) &= \left[\frac{Z}{2} + \left(1 + \frac{Z^2}{4}\right)^{1/2}\right]^2 \\ Z &= \frac{\alpha\Lambda^\circ + \beta}{\Lambda^{\circ 3/2}} (C\Lambda)^{1/2} \end{aligned}\right\} \qquad (3)$$

where $C$ is the concentration, and $\alpha = 8.203 \times 10^5/(DT)^{3/2}$; $\beta = 82.43/\eta(DT)^{1/2}$ are the Onsager coefficients which involve the dielectric constant ($D$), the viscosity ($\eta$) and temperature ($T$), and the activity coefficient ($f$) is given by the Debye-Hückel equation.

It is impossible to extrapolate to zero concentration for the equivalent conductivity of triethylamine because of their steep increase at high dilution (Fig. 1), where the experimental error is serious. The limiting equivalent conductivity of triethylammonium methoxide is calculated from Kohlrausch's law of the independent migration of ions.

The pressure dependence of the solvent properties (density, dielectric constant, and viscosity) has been calculated from literature data. Values at integral pressures are given in Table 1. From Bridgman's data[10] and the literature value at 25, 30, and 40°C[8] densities were calculated by the Tait equation.[11] The dielectric constants of methanol at high pressures were calculated from the Owen-Brinkley expression :[12]

---

8) J. A. Riddick and W. B. Bunger, "Organic Solvents," Wiley-Interscience, A Division of John Wiley & Sons, Inc., New York (1970)

9) T. Shedlovsky and R. L. Kay, *J. Phys. Chem.*, **60**, 151 (1956).

10) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **49**, 1 (1913)

11) H. S. Harned and B. B. Owen, "Physical Properties of Electrolytic Solution," 3rd ed, Reinhold Publishing Corp., New York (1958)

12) B. B. Owen and S. R. Brinkley, *Phys. Rev.*, **64**, 32 (1943)

Table 1 Solvent properties at 25, 30, and 40°C

| $P$ kg/cm$^2$ | $d$ cm$^3$/g | | | $D$ | | | $\eta$ cP* | | |
|---|---|---|---|---|---|---|---|---|---|
| t/°C | 25 | 30 | 40 | 25 | 30 | 40 | 25 | 30 | 40 |
| 1 | 0.7866 | 0.7818 | 0.773 | 32.65 | 31.75 | 29.86 | 0.5445 | 0.5143 | 0.448 |
| 200 | 0.802 | 0.797 | 0.789 | 33.38 | 32.53 | 30.61 | 0.603 | 0.560 | 0.496 |
| 400 | 0.816 | 0.810 | 0.803 | 34.02 | 33.21 | 31.25 | 0.659 | 0.606 | 0.542 |
| 600 | 0.828 | 0.823 | 0.816 | 34.59 | 33.80 | 31.82 | 0.713 | 0.653 | 0.586 |
| 800 | 0.839 | 0.834 | 0.827 | 35.10 | 34.34 | 32.33 | 0.766 | 0.700 | 0.624 |
| 1000 | 0.849 | 0.844 | 0.837 | 35.58 | 34.83 | 32.80 | 0.817 | 0.747 | 0.661 |
| 1200 | 0.859 | 0.853 | 0.847 | 36.02 | 35.29 | 33.22 | 0.869 | 0.795 | 0.700 |
| 1400 | 0.867 | 0.862 | 0.856 | 36.43 | 35.71 | 33.62 | 0.920 | 0.843 | 0.740 |
| 1600 | 0.875 | 0.870 | 0.864 | 36.81 | 36.10 | 33.99 | 0.973 | 0.892 | 0.778 |
| 1800 | 0.883 | | | 37.18 | | | 1.02 | | |
| 2000 | 0.890 | | | 37.52 | | | 1.07 | | |

* 1cP = $10^{-3}$ Pas

$$1-\frac{D^{(1)}}{D^{(P)}}=A\ln\frac{(B+P)}{(B+1)}, \qquad (4)$$

where $A$ and $B$ are the empirical constants.[13] Bridgman measured the viscosities of methanol at 30 and 70°C up to 10000kg/cm$^2$.[14] From the Arrhenius plot at integral pressures, the viscosities at 25, 30, and 40°C were obtained.

The equivalent conductivity at high pressure, $\Lambda^{(P)}$ is obtained by the following equation,

$$\Lambda^{(P)}=\frac{10^3(\kappa^{(P)}-\kappa^{\circ(P)})}{C^{(P)}}, \qquad (5)$$

where $C^{(P)}$ is the concentration which is corrected for the volume contraction of methanol at high pressure, and $\kappa^{(P)}$ and $\kappa^{\circ(P)}$ are the specific conductivities of a solution and a solvent, respectively. The data were analyzed by the Fuoss-Onsager equation :[15]

$$\Lambda=\Lambda^{\circ}-SC^{1/2}+EC\log C+JC, \qquad (6)$$

where $S$ and $E$ are the functions of the limiting equivalent conductivity, the dielectric constant, the viscosity, and temperature, and $J$ an adjustable parameter.

The plots of the equivalent conductivity of potassium methoxide against $C^{1/2}$ show the concave down curve in very dilute region ($C<4\times10^{-4}$ mol dm$^{-3}$), since carbon dioxide can not be removed completely. However, since the influence of carbon dioxide can be neglected in rather high concentrations ($C>10^{-3}$ mol dm$^{-3}$) from the comparison with the data obtained in the closed system[16], it

---

13) K. R. Srinivasan and R. L. Kay, *J. Solution Chem.*, **4**, 299 (1975)

14) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **77**, 117 (1949)

15) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York (1959)

16) J. Barthel and G. Schwitzgebel, *Z. Phys. Chem. Neue Folge*, **54**, 73 (1967)

would be possible to calculate the limiting equivalent conductivity. Since the equivalent conductivities of potassium methylcarbonate which is produced by the reaction of methoxide ion with carbon dioxide have been measured at 25°C,[17] the concentration of carbon dioxide can be estimated from the difference between the observed equivalent conductivity and the calculated one at high dilution for potassium methoxide and potassium methylcarbonate,

$$\Lambda(\mathrm{KOMe})_{\mathrm{obs}}=(1-x)\Lambda(\mathrm{KOMe})+x\Lambda(\mathrm{KC}), \qquad (7)$$

where KC and $x$ refer to potassium methylcarbonate and the fraction of base converted into carbonate.

A correlation of data of triethylamine can be done by Eqs. (8) and (9),

$$\Lambda(\mathrm{TC})=\Lambda(\mathrm{KC})+\Lambda(\mathrm{HN(Et)_3Cl})-\Lambda(\mathrm{KCl}), \qquad (8)$$

$$\Lambda(\mathrm{N(Et)_3})_{\mathrm{obs}}=(1-y)\Lambda(\mathrm{N(Et)_3})+y\Lambda(\mathrm{TC,\ N(Et)_3}), \qquad (9)$$

where TC refer to triethylammonium methylcarbonate, and $y$ is the fraction of base converted into carbonate. Although Eq. (8) is valid only at infinite dilution or the same degree of association of each salt, it would be applied to the present system of high dilution with a fairly good approximation. The equivalent conductivities are listed in Table 2-1~2-12.

## Discussion

### Concentration dependence of $\Lambda$-$C^{1/2}$ curve and the limiting equivalent conductivity

Since the concentration dependence of the equivalent conductivity of a strong electrolyte reflects the ion-ion interaction, the accurate determination of the gradient value of a $\Lambda$-$C^{1/2}$ plot has a great importance. Although a large number of investigations on the pressure dependence of the

Table 2-1 $\Lambda$ of $N(Et)_3$ in MeOH at 25°C

| | $C$(molarity) at 1 atm | | | | | | |
|---|---|---|---|---|---|---|---|
| $P$(kg/cm$^2$) | 0.0180 | 0.0634 | 0.132 | 0.189 | 0.215 | 0.284 | 0.317 |
| 1 | 0.527 | 0.293 | 0.206 | 0.163 | 0.149 | 0.145 | 0.127 |
| 200 | 0.622 | 0.346 | 0.239 | 0.191 | 0.174 | 0.163 | 0.144 |
| 400 | 0.721 | 0.387 | 0.266 | 0.217 | 0.198 | 0.181 | 0.161 |
| 600 | 0.814 | 0.448 | 0.298 | 0.243 | 0.221 | 0.200 | 0.178 |
| 800 | 0.902 | 0.495 | 0.329 | 0.268 | 0.245 | 0.218 | 0.195 |
| 1000 | 0.990 | 0.532 | 0.361 | 0.293 | 0.268 | 0.237 | 0.212 |
| 1200 | 1.08 | 0.581 | 0.392 | 0.319 | 0.291 | 0.253 | 0.230 |
| 1400 | 1.18 | 0.632 | 0.425 | 0.346 | 0.316 | 0.274 | 0.253 |
| 1600 | 1.27 | 0.682 | 0.457 | 0.372 | 0.340 | 0.293 | 0.266 |
| 1800 | 1.37 | 0.732 | 0.489 | 0.399 | 0.362 | 0.313 | 0.284 |
| 2000 | 1.47 | 0.784 | 0.522 | 0.427 | 0.387 | 0.332 | 0.303 |

---

[17] G. E. M. Jones and O. L. Hughes, *J. Chem. Soc.*, 1197 (1934)

Table 2-2 $\Lambda$ of $N(Et)_3$ in MeOH at 30°C

| | C(molarity) at 1 atm | | | | | | |
|---|---|---|---|---|---|---|---|
| P(kg/cm$^2$) | 0.0554 | 0.0652 | 0.101 | 0.158 | 0.284 | 0.331 | 0.427 |
| 1 | 0.279 | 0.252 | 0.210 | 0.175 | 0.122 | 0.108 | 0.0901 |
| 200 | 0.339 | 0.310 | 0.252 | 0.201 | 0.142 | 0.126 | 0.106 |
| 400 | 0.390 | 0.365 | 0.293 | 0.232 | 0.163 | 0.144 | 0.122 |
| 600 | 0.454 | 0.418 | 0.329 | 0.264 | 0.184 | 0.162 | 0.136 |
| 800 | 0.508 | 0.469 | 0.366 | 0.291 | 0.207 | 0.179 | 0.151 |
| 1000 | 0.557 | 0.512 | 0.409 | 0.323 | 0.224 | 0.197 | 0.166 |
| 1200 | 0.610 | 0.563 | 0.452 | 0.357 | 0.246 | 0.215 | 0.180 |
| 1400 | 0.668 | 0.614 | 0.492 | 0.385 | 0.266 | 0.233 | 0.195 |
| 1600 | 0.725 | 0.670 | 0.535 | 0.416 | 0.288 | 0.252 | 0.210 |

Table 2-3 $\Lambda$ of $N(Et)_3$ in MeOH at 40°C

| | C(molarity) at 1 atm | | | | | | |
|---|---|---|---|---|---|---|---|
| P(kg/cm$^2$) | 0.0548 | 0.0619 | 0.0838 | 0.156 | 0.238 | 0.261 | 0.356 |
| 1 | 0.284 | 0.278 | 0.255 | 0.194 | 0.128 | 0.131 | 0.108 |
| 200 | 0.343 | 0.320 | 0.294 | 0.224 | 0.153 | 0.153 | 0.127 |
| 400 | 0.404 | 0.364 | 0.359 | 0.255 | 0.180 | 0.178 | 0.145 |
| 600 | 0.467 | 0.420 | 0.410 | 0.285 | 0.204 | 0.202 | 0.163 |
| 800 | 0.526 | 0.455 | 0.425 | 0.318 | 0.230 | 0.225 | 0.182 |
| 1000 | 0.574 | 0.505 | 0.458 | 0.352 | 0.256 | 0.249 | 0.201 |
| 1200 | 0.634 | 0.537 | 0.485 | 0.384 | 0.282 | 0.273 | 0.220 |
| 1400 | 0.694 | 0.586 | 0.540 | 0.417 | 0.308 | 0.297 | 0.239 |
| 1600 | 0.761 | 0.635 | 0.587 | 0.453 | 0.335 | 0.322 | 0.259 |

Table 2-4 $\Lambda$ of $HN(Et)_3Cl$ in MeOH at 25°C

| | $C\times10^4$ (molarity) at 1 atm | | | | | | |
|---|---|---|---|---|---|---|---|
| P(kg/cm$^2$) | 3.358 | 4.909 | 8.872 | 14.47 | 18.59 | 22.07 | 31.79 |
| 1 | 105.5 | 103.5 | 101.2 | 98.4 | 96.7 | 95.2 | 92.5 |
| 200 | 98.6 | 96.5 | 94.6 | 92.0 | 90.5 | 89.2 | 86.7 |
| 400 | 92.9 | 90.9 | 89.1 | 86.9 | 85.5 | 84.1 | 81.8 |
| 600 | 87.9 | 86.0 | 84.4 | 82.3 | 81.1 | 79.8 | 77.7 |
| 800 | 83.8 | 81.7 | 80.4 | 78.3 | 77.3 | 76.1 | 73.9 |
| 1000 | 80.1 | 79.3 | 76.7 | 74.8 | 73.8 | 72.8 | 70.7 |
| 1200 | 76.7 | 76.0 | 73.5 | 71.7 | 70.7 | 69.7 | 67.6 |
| 1400 | 73.5 | 72.7 | 70.5 | 68.8 | 67.9 | 66.9 | 65.0 |
| 1600 | 70.6 | 70.0 | 67.8 | 66.1 | 65.2 | 64.4 | 62.5 |
| 1800 | 68.1 | 67.3 | 65.2 | 63.6 | 62.8 | 62.0 | 60.1 |
| 2000 | 65.5 | 64.8 | 62.8 | 61.4 | 60.5 | 59.8 | 58.0 |

Table 2-5 $\Lambda$ of HN(Et)$_3$ Cl in MeOH at 30°C

| | $C\times10^4$ (molarity) at 1 atm | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $P$(kg/cm$^2$) | 6.998 | 8.969 | 9.590 | 9.986 | 11.90 | 12.70 | 13.99 | 16.85 |
| 1 | 109.3 | 108.2 | 107.9 | 107.6 | 106.4 | 106.1 | 105.2 | 104.0 |
| 200 | 102.4 | 101.5 | 101.1 | 100.8 | 99.6 | 99.3 | 98.6 | 97.5 |
| 400 | 96.8 | 95.5 | 95.3 | 95.1 | 94.4 | 93.7 | 93.1 | 92.0 |
| 600 | 91.8 | 90.6 | 90.2 | 90.2 | 89.4 | 88.8 | 88.2 | 87.5 |
| 800 | 87.4 | 86.2 | 85.8 | 85.8 | 85.1 | 84.6 | 84.1 | 83.5 |
| 1000 | 83.7 | 82.3 | 81.9 | 81.9 | 81.4 | 80.8 | 80.3 | 79.8 |
| 1200 | 80.4 | 78.9 | 78.4 | 78.5 | 78.0 | 77.4 | 76.9 | 76.5 |
| 1400 | 77.2 | 75.6 | 75.2 | 75.4 | 74.8 | 74.5 | 73.8 | 73.5 |
| 1600 | 74.2 | 72.7 | 72.3 | 72.5 | 72.0 | 71.7 | 71.0 | 70.7 |

Table 2-6 $\Lambda$ of HN(Et)$_3$ Cl in MeOH at 40°C

| | $C\times10^4$ (molariry) at 1 atm | | | | | | |
|---|---|---|---|---|---|---|---|
| $P$(kg/cm$^2$) | 6.022 | 6.750 | 8.356 | 11.78 | 12.08 | 13.88 | 16.70 |
| 1 | 123.0 | 122.4 | 121.3 | 119.0 | 118.9 | 117.9 | 116.7 |
| 200 | 114.7 | 114.3 | 113.4 | 111.3 | 111.3 | 110.1 | 109.2 |
| 400 | 108.4 | 107.7 | 106.9 | 104.9 | 104.9 | 104.1 | 103.2 |
| 600 | 102.6 | 102.0 | 101.3 | 99.5 | 99.6 | 98.7 | 98.0 |
| 800 | 98.5 | 97.1 | 96.5 | 94.8 | 94.9 | 94.2 | 93.4 |
| 1000 | 93.4 | 92.7 | 92.2 | 90.5 | 90.6 | 90.1 | 89.3 |
| 1200 | 89.5 | 88.9 | 88.3 | 86.7 | 86.9 | 86.3 | 85.5 |
| 1400 | 85.9 | 85.4 | 84.9 | 83.2 | 83.6 | 82.9 | 82.3 |
| 1600 | 82.5 | 82.2 | 81.7 | 80.0 | 80.4 | 79.8 | 79.2 |

TOble 2-7 $\Lambda$ of KOMe in MeOH at 25°C

| | $C\times10^4$ (molarity) at 1 atm | | | | | | |
|---|---|---|---|---|---|---|---|
| $P$(kg/cm$^2$) | 7.271 | 10.16 | 11.60 | 13.20 | 14.56 | 17.51 | 19.00 |
| 1 | 99.1 | 98.2 | 97.9 | 97.6 | 96.8 | 96.5 | 96.3 |
| 200 | 93.7 | 92.7 | 92.7 | 92.3 | 92.3 | 91.4 | 91.3 |
| 400 | 89.2 | 88.3 | 88.3 | 88.0 | 87.9 | 87.2 | 87.0 |
| 600 | 85.4 | 84.5 | 84.5 | 84.2 | 84.0 | 83.6 | 83.4 |
| 800 | 82.0 | 81.1 | 81.1 | 80.9 | 80.8 | 80.3 | 80.1 |
| 1000 | 79.0 | 78.1 | 78.1 | 78.0 | 77.8 | 77.5 | 77.3 |
| 1200 | 76.3 | 75.5 | 75.4 | 75.3 | 75.1 | 74.9 | 74.7 |
| 1400 | 73.8 | 73.1 | 73.0 | 73.0 | 72.6 | 72.5 | 72.3 |
| 1600 | 71.5 | 70.7 | 70.7 | 70.7 | 70.4 | 70.4 | 70.2 |
| 1800 | 69.4 | 68.6 | 68.7 | 68.6 | 68.3 | 68.4 | 68.1 |
| 2000 | 67.4 | 66.6 | 66.6 | 66.7 | 66.3 | 66.3 | 66.2 |

Table 2-8 $\Lambda$ of KOMe in MeOH at 30°C

| | $C \times 10^4$ (molarity) at 1 atm | | | | | | |
|---|---|---|---|---|---|---|---|
| $P$(kg/cm$^2$) | 9.610 | 11.43 | 12.06 | 12.43 | 13.75 | 16.08 | 19.02 |
| 1 | 106.3 | 105.8 | 105.6 | 104.5 | 105.0 | 104.1 | 103.6 |
| 200 | 100.1 | 99.6 | 99.3 | 99.4 | 99.0 | 98.3 | 97.9 |
| 400 | 95.1 | 94.7 | 94.6 | 94.5 | 94.3 | 93.7 | 93.1 |
| 600 | 91.1 | 90.7 | 90.7 | 90.6 | 90.4 | 89.7 | 89.5 |
| 800 | 88.0 | 87.6 | 87.6 | 87.2 | 87.3 | 86.5 | 86.2 |
| 1000 | 84.7 | 84.6 | 84.5 | 84.3 | 84.1 | 83.7 | 83.2 |
| 1200 | 81.9 | 81.7 | 81.7 | 81.6 | 81.3 | 80.9 | 80.8 |
| 1400 | 79.3 | 79.2 | 79.3 | 78.9 | 78.7 | 78.5 | 78.4 |
| 1600 | 76.7 | 76.5 | 76.4 | 76.3 | 76.0 | 75.8 | 75.7 |

Table 2-9 $\Lambda$ of KOMe in MeOH at 40°C

| | $C \times 10^4$ (molarity) at 1 atm | | | | | | |
|---|---|---|---|---|---|---|---|
| $P$(kg/cm$^2$) | 9.474 | 11.92 | 12.28 | 13.68 | 13.90 | 14.47 | 15.81 |
| 1 | 119.6 | 118.9 | 118.5 | 117.9 | 118.1 | 117.4 | 117.1 |
| 200 | 113.3 | 112.7 | 112.3 | 111.6 | 112.0 | 111.2 | 111.0 |
| 400 | 107.8 | 107.5 | 107.2 | 106.7 | 106.9 | 106.2 | 105.9 |
| 600 | 103.2 | 102.9 | 102.8 | 102.3 | 102.3 | 101.8 | 101.3 |
| 800 | 99.2 | 99.0 | 98.9 | 98.6 | 98.5 | 97.9 | 97.5 |
| 1000 | 95.7 | 95.5 | 95.4 | 95.1 | 95.0 | 94.6 | 94.0 |
| 1200 | 92.5 | 92.2 | 92.3 | 92.1 | 92.0 | 91.5 | 90.8 |
| 1400 | 89.6 | 89.4 | 89.4 | 89.2 | 89.1 | 88.6 | 88.1 |
| 1600 | 86.9 | 86.7 | 86.7 | 86.6 | 86.5 | 86.0 | 85.3 |

Table 2-10 $\Lambda$ of KCl in MeOH at 25°C

| | $C \times 10^4$ (molarity) at 1 atm | | | | | | |
|---|---|---|---|---|---|---|---|
| $P$(kg/cm$^2$) | 6.293 | 7.207 | 9.399 | 9.801 | 10.79 | 13.37 | 16.81 |
| 1 | 98.3 | 98.2 | 96.7 | 96.9 | 96.3 | 95.5 | 94.5 |
| 200 | 92.5 | 92.5 | 91.2 | 91.3 | 90.7 | 90.3 | 89.1 |
| 400 | 87.9 | 88.1 | 86.5 | 86.7 | 86.1 | 85.7 | 84.4 |
| 600 | 84.0 | 84.0 | 82.7 | 82.6 | 82.4 | 81.8 | 80.9 |
| 800 | 80.5 | 80.4 | 79.2 | 79.1 | 78.9 | 78.3 | 77.7 |
| 1000 | 77.2 | 77.2 | 76.0 | 76.0 | 75.6 | 75.3 | 74.7 |
| 1200 | 74.5 | 74.5 | 73.3 | 73.1 | 72.9 | 72.5 | 71.9 |
| 1400 | 71.9 | 71.8 | 70.6 | 70.5 | 70.3 | 70.0 | 69.2 |
| 1600 | 69.4 | 69.4 | 68.5 | 68.4 | 68.3 | 67.5 | 67.2 |
| 1800 | 67.2 | 67.2 | 66.3 | 66.0 | 65.7 | 65.4 | 65.0 |
| 2000 | 64.7 | 64.6 | 63.8 | 63.8 | 63.6 | 63.2 | 62.7 |

Table 2-11 $\Lambda$ of KCl in MeOH at 30°C

| | $C\times10^4$ (molarity) at 1 atm | | | | | | |
|---|---|---|---|---|---|---|---|
| $P$(kg/cm$^2$) | 6.903 | 10.85 | 13.85 | 14.83 | 19.01 | 21.33 | 25.73 |
| 1 | 105.8 | 103.8 | 102.4 | 102.3 | 100.7 | 99.9 | 99.0 |
| 200 | 99.8 | 97.8 | 96.8 | 96.7 | 95.3 | 94.5 | 93.0 |
| 400 | 94.8 | 93.0 | 91.9 | 91.9 | 90.6 | 89.8 | 89.1 |
| 600 | 90.4 | 88.7 | 87.7 | 87.9 | 86.7 | 85.7 | 85.2 |
| 800 | 86.6 | 85.0 | 84.2 | 84.2 | 82.9 | 82.3 | 81.7 |
| 1000 | 83.1 | 81.6 | 80.9 | 80.9 | 79.7 | 79.2 | 78.7 |
| 1200 | 80.1 | 78.6 | 77.9 | 78.0 | 76.9 | 76.3 | 75.9 |
| 1400 | 77.2 | 75.9 | 75.2 | 75.4 | 74.2 | 73.7 | 73.4 |
| 1600 | 74.7 | 73.3 | 72.7 | 72.8 | 71.6 | 71.2 | 71.0 |

Table 2-12 $\Lambda$ of KCl at 40°C in MeOH

| | $C\times10^4$ (molarity) at 1 atm | | | | | | |
|---|---|---|---|---|---|---|---|
| $P$(kg/cm$^2$) | 7.879 | 9.605 | 12.37 | 12.90 | 14.04 | 15.47 | 18.49 |
| 1 | 118.7 | 117.7 | 116.8 | 116.3 | 115.4 | 115.3 | 114.0 |
| 200 | 112.2 | 110.8 | 110.0 | 109.8 | 109.1 | 108.8 | 107.7 |
| 400 | 106.6 | 105.3 | 104.8 | 104.5 | 103.7 | 103.5 | 102.6 |
| 600 | 101.6 | 100.4 | 100.1 | 99.6 | 99.0 | 99.0 | 97.9 |
| 800 | 97.5 | 96.2 | 96.1 | 95.6 | 95.1 | 94.9 | 94.0 |
| 1000 | 93.7 | 92.4 | 92.3 | 92.0 | 91.5 | 91.3 | 90.5 |
| 1200 | 90.3 | 88.9 | 89.1 | 88.8 | 88.2 | 88.1 | 87.3 |
| 1400 | 87.3 | 85.9 | 86.1 | 85.8 | 85.2 | 85.1 | 84.4 |
| 1600 | 84.5 | 82.9 | 83.3 | 83.0 | 82.4 | 82.4 | 81.6 |

conductance have been carried out, there are not enough data in dilute region to calculate the gradient of $\Lambda$-$C^{1/2}$ plot, so that they can not give an accurate limiting equivalent conductivity, either. In dilute concentrations, the $\Lambda$-$C^{1/2}$ curve becomes a straight line which is known as Kohlrausch's relation,

$$\Lambda=\Lambda^{\circ}-S_{\rm obs}^{(p)}C^{1/2}, \tag{10}$$

where $S_{\rm obs}^{(p)}$ is an empirical constant independent of the concentrations. Hamann and Strauss[3] have reported the disagreement in $S_{\rm obs}^{(p)}$ with $S_{\rm calc}^{(p)}$ calculated from the Onsager coefficients in Eq. (3) in water and methanol at high pressure. However, Nakahara *et al.*[4] have reported that $S_{\rm obs}^{(p)}$ agrees well with $S_{\rm calc}^{(p)}$ for potassium chloride in water, and pointed out the validity of the Debye-Hückel-Onsager theory at high pressures.

In a methanolic solution the concentration dependence of the conductivity of potassium chloride obeys fairly well the Onsager equation, and the mean activity coefficients in dilute solutions fit well to the Debye-Hückel limiting law at 1 atm.[18] Since $S_{\rm obs}^{(p)}$ agrees considerably well with

---

[18] A. K. Covington and T. Dickinson, "Physical Chemistry of Organic Solvent Systems," Plenum Press, London and New York (1973)

Table 3 Comparison of $S_{calc}^{(p)}$ and $S_{obs}^{(p)}$

| $P$(kg/cm$^2$) | $T$/°C 25 | | 30 | | 40 | |
|---|---|---|---|---|---|---|
| | $S_{calc}^{(p)}$ | $S_{obs}^{(p)}$ | $S_{calc}^{(p)}$ | $S_{obs}^{(p)}$ | $S_{calc}^{(p)}$ | $S_{obs}^{(p)}$ |
| 1 | 243 | 257± 3 | 283 | 262± 8 | 306 | 314± 4 |
| 400 | 201 | 223± 3 | 218 | 232± 2 | 250 | 255± 3 |
| 800 | 171 | 198± 3 | 187 | 178±10 | 215 | 216± 4 |
| 1200 | 150 | 161± 3 | 163 | 165± 3 | 189 | 169± 7 |
| 1600 | 143 | 144± 1 | 145 | 148± 8 | 169 | 160± 8 |

$S_{calc}^{(p)}$ as listed in Table 3, the use of the Fuoss-Onsager equation and Shedlovsky's method which contains the Debye-Hückel limiting law is justified at high pressure.

The conductance of strong electrolytes shows a common pattern against pressure at all concentrations: the conductance decreases with increasing pressure. Triethylamine exhibits an increase in

Table 4-1 $\Lambda^{\circ}$ of the strong electrolytes in MeOH at 25°C

| $P$(kg/cm$^2$) | KOMe | HN(Et)$_3$Cl | KCl | HN(Et)$_3$OMe |
|---|---|---|---|---|
| 1 | 105.5 | 109.8 | 104.7 | 110.6 |
| 200 | 99.2 | 102.6 | 98.3 | 103.5 |
| 400 | 94.2 | 96.6 | 93.7 | 97.1 |
| 600 | 89.9 | 91.3 | 89.0 | 92.2 |
| 800 | 86.2 | 86.8 | 85.0 | 88.0 |
| 1000 | 82.8 | 83.4 | 81.5 | 84.7 |
| 1200 | 79.9 | 79.9 | 78.6 | 81.2 |
| 1400 | 77.2 | 76.3 | 76.0 | 77.5 |
| 1600 | 74.6 | 73.4 | 73.2 | 74.8 |
| 1800 | 72.4 | 70.6 | 70.8 | 72.2 |
| 2000 | 70.2 | 68.0 | 68.7 | 69.5 |

Table 4-2 $\Lambda^{\circ}$ of the strong electrolytes in MeOH at 30°C

| $P$(kg/cm$^2$) | KOMe | HN(Et)$_3$Cl | KCl | HN(Et)$_3$OMe |
|---|---|---|---|---|
| 1 | 114.1 | 117.9 | 113.1 | 118.9 |
| 200 | 107.2 | 110.4 | 106.8 | 110.8 |
| 400 | 101.6 | 104.0 | 100.9 | 104.7 |
| 600 | 96.9 | 98.4 | 96.1 | 99.2 |
| 800 | 93.7 | 93.4 | 91.9 | 95.2 |
| 1000 | 90.1 | 89.0 | 88.0 | 91.1 |
| 1200 | 86.6 | 85.5 | 84.7 | 87.4 |
| 1400 | 83.7 | 81.6 | 81.5 | 83.8 |
| 1600 | 80.7 | 78.5 | 79.4 | 79.8 |

Table 4-3 $\Lambda^\circ$ of the strong electrolytes in MeOH at 40°C

| $P$(kg/cm$^2$) | KOMe | HN(Et)$_3$Cl | KCl | HN(Et)$_3$OMe |
|---|---|---|---|---|
| 1 | 129.3 | 131.6 | 127.9 | 133.0 |
| 200 | 122.3 | 122.5 | 120.3 | 124.5 |
| 400 | 115.8 | 115.4 | 113.9 | 117.3 |
| 600 | 110.9 | 109.0 | 108.4 | 111.5 |
| 800 | 106.3 | 104.3 | 103.8 | 106.8 |
| 1000 | 102.5 | 98.9 | 99.4 | 102.0 |
| 1200 | 98.8 | 94.8 | 95.5 | 98.1 |
| 1400 | 95.5 | 90.9 | 92.3 | 94.1 |
| 1600 | 92.8 | 87.3 | 89.2 | 90.9 |

conductance with pressure in contrast to strong electrolytes (Fig. 1). This fact is easily understood by taking into account that the increase of the number of ionized species with pressure overcomes the decrease of the mobility of free ions due to the enhancement of the viscosity of the medium.

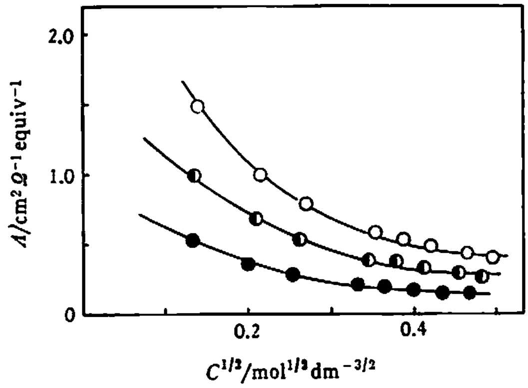

Fig. 1 Equivalent conductivities of N(Et)$_3$ in MeOH *vs.* $C^{1/2}$ (mol$^{1/2}$ dm$^{-3/2}$) at 25°C and given pressures
●: 1 atm, ◐: 1000kg cm$^{-2}$,
○: 2000kg cm$^{-2}$

The limiting equivalent conductivities of triethylammonium methoxide decrease with pressure and increase with temperature as shown in Fig. 2. The limiting equivalent conductivities of each salt do not decrease so rapidly as the macroscopic viscosity increases ; that is, the Walden products of the salts increase with pressure as shown in Fig. 3. Since the Walden product is considered to be one of the quantities which reflect the ion-solvent interaction in the vicinity of an ion, it is necessary to separate the Walden products of the salts into two terms of single ions. However, it is difficult at present to discuss the term of single ion because of the lack of the numerical value of the transference number at each condition. The Walden products of potassium methoxide and potassium chloride increase with pressure nearly in the same proportion. The Walden product of triethylammonium chloride shows a rather small increase in comparison with those of other salts, which would be attributed to the term of the triethylammonium ion. From these results it seems to suggest that in methanol pressure does not affect the properties of the solvents in the vicinity of an ion so much as

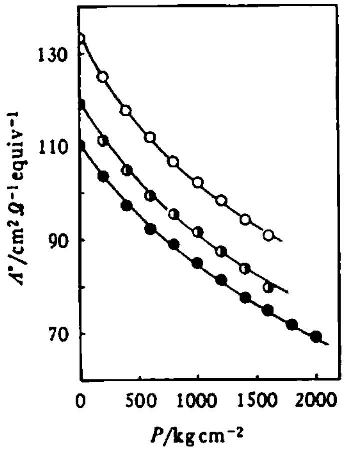

Fig. 2 Pressure dependence of $\Lambda^\circ$ ($HN(Et)_3OMe$) in MeOH at 25, 30, and 40°C
●: 25°C, ◑: 30°C, ○: 40°C

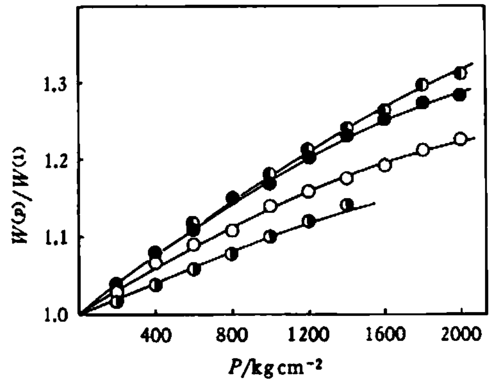

Fig. 3 Pressure dependence of the Walden product of KCl, KOMe, $HN(Et)_3Cl$ in MeOH
◐: KOMe at 25°C, ●: KCl at 25°C
○: $HN(Et)_3Cl$ at25°C, ◑: $HN(Et)_3Cl$ at 30°C

to do the properties of the pure solvent. The activation energies of strong electrolytes in methanol are invariant with pressure within experimental error (±0.1 kcal mol$^{-1}$); KCl~2.4 kcal mol$^{-1}$, $HN(Et)_3Cl$~2.2 kcal mol$^{-1}$, KOMe~2.5 kcal mol$^{-1}$. The activation energy of potassium chloride in methanol at high pressure is always smaller than that in water at 25°C.[4]

### Ionic dissociation constnat of triethylamine

If the difference in the partial molar volumes of the product and reactant can be integrated with pressure, the pressure dependence of equilibrium constant can be calculated from the thermodynamic relationship,

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

And it is assumed that

$$\Delta\bar{V}^\circ = \Delta\bar{V}_1^\circ + \Delta\bar{V}_2^\circ, \tag{12}$$

where the subscripts 1 and 2 refer to the electrostrictive volume and the others (which can be attributed to the change of the following components; crystal volume, disordered volume[19], caged volume, and so on), respectively.

According to the Born theory, $\Delta\bar{V}_1^\circ$ is expressed as follows;

$$\Delta\bar{V}_1^\circ = -\frac{Nz^2e^2}{2}\left(\frac{1}{r^+}+\frac{1}{r^-}\right)\frac{1}{D^2}\left(\frac{\partial D}{\partial P}\right)_T, \tag{13}$$

where $N$, $e$, $z$, and $r$ are Avogadro's number, the electronic charge, the valence number, and the ionic radius, respectively. The integration of $\Delta\bar{V}_2^\circ$ with the assumption that $\Delta\bar{V}_2^\circ$ is independent of

---

[19] F. J. Millero, *J. Phys. Chem.*, 73, 2417 (1969)

pressure and Nakahara's derivation⁶⁾, in which Eq. (13) was integrated with the assumption of the invariance of the ionic radii, give Eq. (14),

$$\frac{-RT}{(P-1)}\ln\frac{K^{(P)}}{K^{(1)}}=\Delta\bar{V}_2^{\circ(1)}+\Delta\bar{V}_1^{\circ(1)}\frac{(B+1)}{(P-1)}\ln\frac{(B+P)}{(B+1)}, \tag{14}$$

where $B$ is the empirical constant in Eq. (4), and $\Delta\bar{V}_1^{\circ(1)}$ and $\Delta\bar{V}_2^{\circ(1)}$ stand for each volume change at 1 atm.

The validity of Eq. (14) was tested for the ionization of triethylamine in methanol by plotting the left-hand side (Table 5) against $[(B+1)/(P-1)]\ln[(B+P)/(B+1)]$ as shown in Fig. 4, where the experimental points lie well on the calculated straight line.[20] And further, Eq. (14) holds well for the experimental results of any other ionization of bases and acids as shown in Fig. 5. Since the experimental results of the ionization of piperidine in methanol at 45C° exhibit the apparent curvature, $\Delta\bar{V}_1^{\circ(1)}$ and $\Delta\bar{V}_2^{\circ(1)}$ of piperidine at 45°C could not be estimated. The values of $\Delta\bar{V}_1^{\circ(1)}$ and $\Delta\bar{V}_2^{\circ(1)}$ estimated from Eq. (14) are listed in Table 6.

Table 5 Ionic dissociation constant of $N(Et)_3$ in MeOH

| $P$(kg/cm$^2$) $T$/°C | $K\times10^6$(mol/kg) | | |
|---|---|---|---|
| | 25 | 30 | 40 |
| 1 | 0.502 | 0.280 | 0.264 |
| 200 | 0.718 | 0.406 | 0.397 |
| 400 | 0.953 | 0.568 | 0.585 |
| 600 | 1.28 | 0.772 | 0.781 |
| 800 | 1.67 | 1.02 | 1.12 |
| 1000 | 2.11 | 1.31 | 1.49 |
| 1200 | 2.61 | 1.66 | 2.00 |
| 1400 | 3.31 | 2.06 | 2.50 |
| 1600 | 4.01 | 2.60 | 3.03 |
| 1800 | 4.83 | | |
| 2000 | 5.79 | | |

Although $\Delta\bar{V}_1^{\circ(1)}$ and $\Delta\bar{V}_2^{\circ(1)}$ of methylamine in water seem to be curious*, the electrostrictive volume changes of weak bases in methanol are more negative than those of bases and acids in water, and the electrostrictive volume change of triethylamine in methanol becomes largely negative with increasing temperature. Generally weak acids in methanol and water are more positive $\Delta\bar{V}_1^{\circ(1)}$ than those of weak bases in the corresponding medium. Rather small negative value of $\Delta\bar{V}_1^{\circ(1)}$ of acids would be attributed to the delocalization effect of anion. And the tendency of the electrostrictive volume changes of carboxylic acids has been explained by the effects of the alkyl group on the

---

[20] H. Inoue, K. Hara, and J. Osugi, *Chem. Lett.*, 377 (1978)

* It would be necessary to accumulate the data in order to confirm these values.

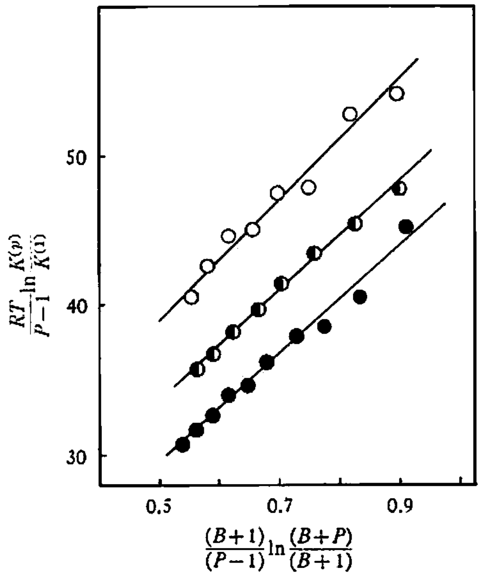

Fig. 4 Pressure dependence of the ionic dissociation constant of $N(Et)_3$ in MeOH at 25, 30, and 40°C
●: 25°C
◐: 30°C
○: 40°C

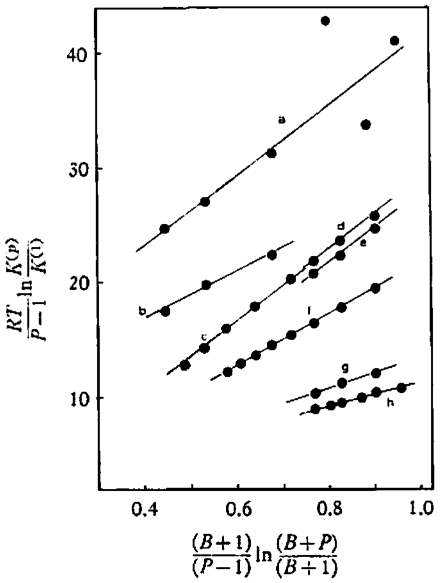

Fig. 5 Pressure dependence of the ionization constant of various electrolytes in methanol and water at 25°C
a ) ionization of piperidine in methanol[3]
b ) ionization of picric acid in methanol[5]
c ) ionization of ammonium in water[21]
d ) ionization of trimethylamine in water[21]
e ) ionization of dimethylamine in water[22]
f ) self ionization of water[23]
g ) ionization of propionic acid in water[24]
h ) ionization of acetic acid in water[25]

structure of water.[26] Temperature and solvent effects on the electrostrictive volume changes can be explained qualitatively by $D^{-2}(\partial D/\partial P)$ in Eq. (13), which is expressed by the differential of Eq. (4) as follows ;

$$\frac{1}{D^2}\left(\frac{\partial D}{\partial P}\right)_T=\frac{A}{(B+P)D_1}\cdot \qquad (15)$$

The tendency of the experimental results in Table 7 is consistent with the calculated results.

Usually the partial molar volume of an ion at infinite dilution is expressed by using the semi-empirical equation.[27]

---

21) J. Buchanan and S. D. Hamann, *Trans. Faraday Soc.*, **51**, 1684 (1955)
22) S. D. Hamann and W. Strauss, *Trans. Faraday Soc.*, **51**, 1984 (1955)
23) E. D. Linov and P. A. Kryukov, *Izu. Sib. Dtd. Akad. Nauk SSSR, Ser. Khim. Nauk*, **4**, 10 (1972)
24) S. D. Hamann, "Physico-Chemical Effects of Pressure," Butterworth, London (1957)
25) D. A. Lown, H. R. Thisk, and L. Wynne-Jones, *Trans. Faraday Soc.*, **66**, 51 (1970)
26) E. J. King, *J. Phys. Chem.*, **73**, 1220 (1969)
27) L. G. Hepler, *J. Phys. Chem.*, **61**, 1426 (1957)

Table 6 Comparison of $\Delta\bar{V}^*_1{}^{(1)}$ and $\Delta\bar{V}^*_2{}^{(1)}$ ($cm^3\ mol^{-1}$) of various electrolytes in methanol and water

| Electrolyte | $T$/°C | Solvent | This work<br>$\Delta\bar{V}^*_1{}^{(1)}$ | <br>$\Delta\bar{V}^*_2{}^{(1)}$ | <br>$\Delta\bar{V}^{*(1)}$ | Literature values<br>$\Delta\bar{V}^{*(1)}$ |
|---|---|---|---|---|---|---|
| $N(Et)_3$* | 25 | MeOH | −36.2 | −11.5 | −47.7 | |
| $N(Et)_3$ | 30 | MeOH | −36.7 | −15.3 | −52.0 | |
| $N(Et)_3$ | 40 | MeOH | −39.0 | −20.0 | −59.0 | |
| Piperidine | 25 | MeOH | −31.1 | −11.2 | −42.3 | $-45.0^{3)}$ |
| Picric acid | 25 | MeOH | −20.3 | − 9.3 | −29.6 | $-25.0^{6)}$ |
| $NH_3$ | 25 | $H_2O$ | −29.0 | + 0.3 | −28.7 | $-28.9^{21)}$ |
| $NH_3$ | 45 | $H_2O$ | −29.9 | − 2.0 | −31.9 | $-28.5^{22)}$ |
| $NH_2Me$ | 25 | $H_2O$ | −42.4 | +13.0 | −29.4 | $-26.4^{21)}$ |
| $NH(Me)_2$ | 25 | $H_2O$ | −29.0 | + 1.5 | −27.5 | $-27.2^{22)}$ |
| $N(Me)_3$ | 25 | $H_2O$ | −28.8 | + 0.3 | −28.5 | $-28.1^{22)}$ |
| $H_2O$ | 25 | $H_2O$ | −22.2 | + 0.6 | −21.6 | $-21.1^{23)}$ |
| $HCO_2H$ | 25 | $H_2O$ | − 7.6 | − 1.3 | − 8.9 | $-8.8^{24)}$ |
| $CH_3CO_2H$ | 25 | $H_2O$ | −10.4 | − 1.0 | −11.4 | $-11.7^{25)}$ |
| $CH_3CH_2CO_2H$ | 25 | $H_2O$ | −12.4 | − 0.9 | −13.3 | $-12.9^{24)}$ |

* from ref. 20)

Table 7 The value of $D^{-2}(\partial D/\partial P)_{T,P=1}$ ($P$/kg $cm^{-2}$) and the estimation of $\Delta\bar{V}_1{}^{*(1)}$ ($cm^3\ mol^{-1}$) by Eq. (13) at the assumed ionic radii**

| $T$/°C | Solvent | $D^{-2}(\partial D/\partial P)_{T,P=1}$ | $\Delta\bar{V}_1{}^{*(1)}$ |
|---|---|---|---|
| 25 | MeOH | $3.76\times10^{-6}$ | −23.7 |
| 30 | MeOH | $4.22\times10^{-6}$ | −26.6 |
| 40 | MeOH | $4.59\times10^{-6}$ | −28.9 |
| 25 | $H_2O$* | $6.00\times10^{-7}$ | − 3.8 |
| 40 | $H_2O$* | $6.79\times10^{-7}$ | − 4.3 |

* from ref. 28), $r^+=3\times10^{-8}$cm ; ** $r^-=1.8\times10^{-8}$cm

$$\bar{V}^c=A'r^3-B'z^2/r, \tag{16}$$

where $A'$ and $B'$ are the parameters concerning with the geometric contribution which includes the crystal volume and the void space around the ion *et al.*, and the electrostrictive volume, respectively. $B'$ of tetraalkylammonium ions in methanol is much larger than that of the theoretical value calculated from the equation similar to Eq. (13), and alkali and halide ions show the reverse tendency.$^{29)}$ So the electrostrictive volume of triethylammonium ion would be more negative than that of methoxide ion. In water $B'$ of ions is about 2.6 times as large as that of the theoretical value. Although the causes of these differences have been considered to be the dielectric saturation effects, it seems to be difficult at present to explain quantitatively because of the ambiguity of solvation.$^{30)}$

---

28) K. R. Srinivasan and R. L. Kay, *J. Chem. Phys.*, **60**, 3645 (1974)

29) F. Kawaizumi and R. Zana, *J. Phys. Chem.*, **78**, 1099 (1974)

30) F. J. Millero, *Chem. Rev.*, **71**, 147 (1971)

The numerical value of $B'$ is different from the calculated results, but the pressure dependence of the ionic dissociation constant can be sufficiently explained only by the change of the dielectric constant of the medium judging from the experimental results.

In water the values of $\Delta\bar{V}_2^{\circ(\mathrm{I})}$ may be explained by the crystal volume change from neutral molecule to ion. However, in methanol $\Delta\bar{V}_2^{\circ(\mathrm{I})}$ would be too large to explain only by the crystal volume change, and it is necessary to consider other factors. The geometric contribution of each ion and the solvation of un-ionized solute would be important to interpret the value of $\Delta\bar{V}_2^{\circ(\mathrm{I})}$. It has been reported that the magnitude and order of the constant, $A'$, do not show a simple correlation to the physical properties of the medium, but correlate the void space caused by the solvated ion.19) In methanol, the value of $A'$ for tetraalkylammonium ion exhibits the case of a hard sphere immersed in a continuous solvent, and the value of $A'$ for halide and alkali metal ions is much smaller than in water ;29) that is, it would expect the small void volume for an ion in methanol.

The geometry of solute-solvent interaction has been proposed, considering the values of $A'$ and $B'$,29,30) or the molecular orbital treatments,31) but it is difficult to estimate the numerical value of $\bar{V}_2^{\circ(\mathrm{I})}$ of each constituent including the ionization process.

## Acknowledgement

The authors wish to thank Dr. M. Ueno and Dr. M. Sasaki for their helpful suggestions, and are indebted to Dr. M. Nakahara and Y. Kumooka for their preliminary measurements of electrical conductivity in methanol.

*Laboratory of Physical Chemistry*
*Department of Chemistry*
*Faculty of Science*
*Kyoto University*
*Kyoto 606 Japan*

---

31) For example, P. Russegger, H. Lischka, and P. Schuster, *Theoret. Chim. Acta.*, **24**, 191 (1972)