EFFECT OF PRESSURE ON IONIZATION OF

TRIETHYLAMINE IN METHANOL

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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 0.502×10^{-6} mol kg^{-1} at 1 atm to 5.78×10^{-6} mol kg^{-1} at 2000kg cm^{-2}, and decreased with temperature to 0.264×10^{-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

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 $(4-12) \times 10^{-8}$ 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)

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(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,

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

is defined by,

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

where a is the activity of each constituent. The dissociation constant is related to the limiting equivalent conductivity Λ° and the equivalent conductivity Λ by the following Shedlovsky equation ;[9]

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

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 (η) 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/cm²	d cm³/g			D			η 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

$$1 - \frac{D^{(1)}}{D^{(p)}} = A\ln\frac{(B+P)}{(B+1)}. \tag{4}$$

where A and B are the empirical constants.[13] Bridgman measured the viscosities of methanol at 30 and 70°C up to 10000kg/cm².[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,

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

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]

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

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 ($C < 4 \times 10^{-4}$ 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)

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would be possible to calculate the limiting equivalent conductivity. Since the equivalent conducti-
vities 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,

$$A(KOMe)_{obs} = (1-x)A(KOMe) + xA(KC),   (7)$$

where KC and x refer to potassium methylcarbonate and the fraction of base converted into car-
bonate.

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

$$A(TC) = A(KC) + A(HN(Et)_3Cl) - A(KCl),   (8)$$

$$A(N(Et)_3)_{obs} = (1-y)A(N(Et)_3) + yA(TC, N(Et)_3),   (9)$$

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 $A-C^{1/2}$ curve and the limiting equivalent conductivity

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

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

| P(kg/cm^2) | C(molarity) at 1 atm | | | | | | |
	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)

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Table 2-2 Λ of $N(Et)_2$ in MeOH at 30°C

$P(kg/cm^2)$	C(molarity) at 1 atm						
	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 Λ of $N(Et)_3$ in MeOH at 40°C

$P(kg/cm^2)$	C(molarity) at 1 atm						
	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 Λ of $HN(Et)_3Cl$ in MeOH at 25°C

$P(kg/cm^2)$	$C \times 10^4$ (molarity) at 1 atm						
	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

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

P(kg/cm²)	$C \times 10^4$ (molarity) at 1 atm							
	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 Λ of HN(Et)$_3$ Cl in MeOH at 40°C

P(kg/cm²)	$C \times 10^4$ (molariry) at 1 atm						
	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 Λ of KOMe in MeOH at 25°C

P(kg/cm²)	$C \times 10^4$ (molarity) at 1 atm						
	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

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Table 2-8 Λ of KOMe in MeOH at 30°C

$P(kg/cm^2)$	$C \times 10^4$ (molarity) at 1 atm						
	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 Λ of KOMe in MeOH at 40°C

$P(kg/cm^2)$	$C \times 10^4$ (molarity) at 1 atm						
	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 Λ of KCl in MeOH at 25°C

$P(kg/cm^2)$	$C \times 10^4$ (molarity) at 1 atm						
	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

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Table 2–11 Λ of KCl in MeOH at 30°C

$P(\mathrm{kg/cm^2})$	$C \times 10^4$ (molarity) at 1 atm						
	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 Λ of KCl at 40°C in MeOH

$P(\mathrm{kg/cm^2})$	$C \times 10^4$ (molarity) at 1 atm						
	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 Λ–$C^{1/2}$ plot, so that they can not give an accurate limiting equivalent conductivity, either. In dilute concentrations, the Λ–$C^{1/2}$ curve becomes a straight line which is known as Kohlrausch's relation,

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

where $S_{\mathrm{obs}}^{(p)}$ is an empirical constant independent of the concentrations. Hamann and Strauss[3] have reported the disagreement in $S_{\mathrm{obs}}^{(p)}$ with $S_{\mathrm{calc}}^{(p)}$ calculated from the Onsager coefficients in Eq. (3) in water and methanol at high pressure. However, Nakahara et al.[4] have reported that $S_{\mathrm{obs}}^{(p)}$ agrees well with $S_{\mathrm{calc}}^{(p)}$ 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 $S_{\mathrm{obs}}^{(p)}$ agrees considerably well with

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

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

P(kg/cm²)	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 Λ° of the strong electrolytes in MeOH at 25°C

P(kg/cm²)	KOMe	HN(Et)₃Cl	KCl	HN(Et)₃OMe
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 Λ° of the strong electrolytes in MeOH at 30°C

P(kg/cm²)	KOMe	HN(Et)₃Cl	KCl	HN(Et)₃OMe
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

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Table 4-3 Λ° of the strong electrolytes in MeOH at 40°C

P(kg/cm²)	KOMe	HN(Et)₃Cl	KCl	HN(Et)₃OMe
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
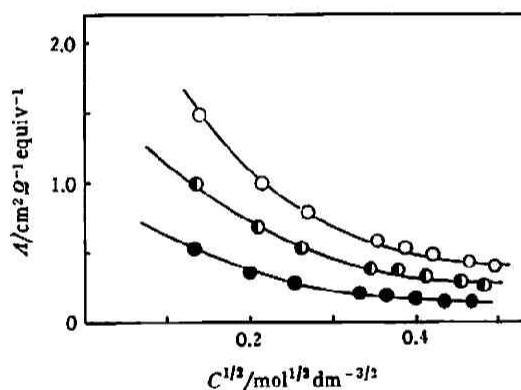
Fig. 1   Equivalent conductivities of N(Et)₃ in MeOH vs. $C^{1/2}$ (mol$^{1/2}$ dm$^{-3/2}$) at 25°C and given pressures
●: 1 atm,   ◐: 1000kg cm⁻²,
○: 2000kg cm⁻²

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.

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
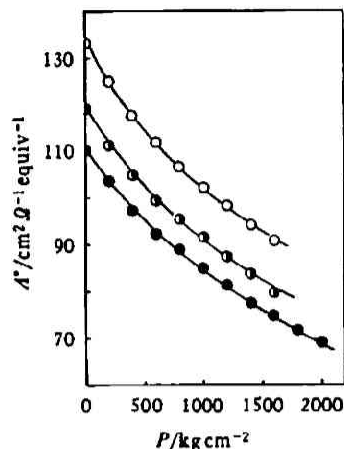
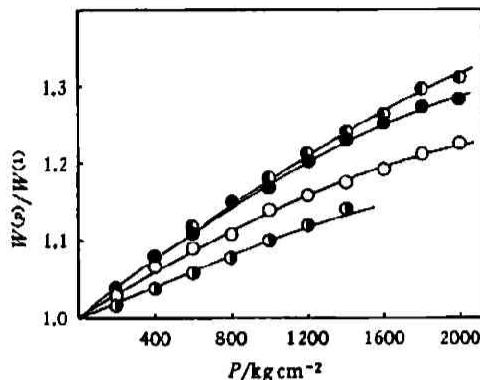Fig. 2 Pressure dependence of Λ° (HN(Et)$_3$OMe) in MeOH at 25, 30, and 40°C

●: 25°C, ◗: 30°C, ○: 40°C

Fig. 3 Pressure dependence of the Walden product of KCl, KOMe, HN(Et)$_3$Cl in MeOH

◖: KOMe at 25°C,   ●: KCl at 25°C

○: HN(Et)$_3$Cl at25°C, ◑: HN(Et)$_3$Cl 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$\sim$2.4 kcal mol^{-1}, HN(Et)$_3$Cl$\sim$2.2 kcal mol^{-1}, KOMe$\sim$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)

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pressure and Nakahara's derivation[6], in which Eq. (13) was integrated with the assumption of the invariance of the ionic radii, give Eq. (14),

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

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

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

$P(\text{kg/cm}^2)$	$T/°C$	$K \times 10^6 (\text{mol/kg})$		
		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		

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.

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

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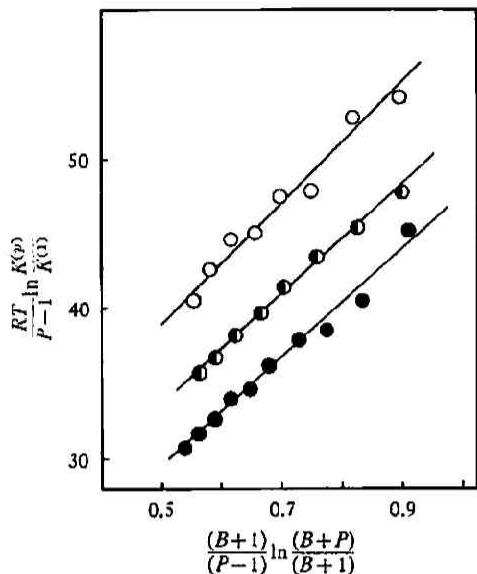
Fig. 4 Pressure dependence of the ionic dissociation constant of N(Et)$_3$ in MeOH at 25, 30, and 40°C
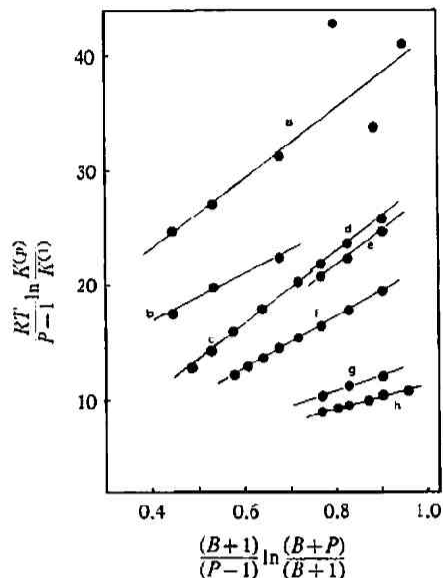
●: 25°C
◐: 30°C
○: 40°C

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 ;

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

(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)

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Table 6   Comparison of $\Delta \bar{V}^{*}{}_{1}{}^{(1)}$ and $\Delta \bar{V}^{*}{}_{2}{}^{(1)}$ (cm³ mol⁻¹) of various electrolytes in methanol and water

Electrolyte	$T/°C$	Solvent	This work			Literature values
			$\Delta\bar{V}^{*}{}_{1}{}^{(1)}$	$\Delta\bar{V}^{*}{}_{2}{}^{(1)}$	$\Delta\bar{V}^{*(1)}$	$\Delta\bar{V}^{*(1)}$
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[9]
Picric acid	25	MeOH	−20.3	− 9.3	−29.6	−25.0[6]
NH₃	25	H₂O	−29.0	+ 0.3	−28.7	−28.9[21]
NH₃	45	H₂O	−29.9	− 2.0	−31.9	−28.5[22]
NH₂Me	25	H₂O	−42.4	+13.0	−29.4	−26.4[21]
NH(Me)₂	25	H₂O	−29.0	+ 1.5	−27.5	−27.2[22]
N(Me)₃	25	H₂O	−28.8	+ 0.3	−28.5	−28.1[22]
H₂O	25	H₂O	−22.2	+ 0.6	−21.6	−21.1[23]
HCO₂H	25	H₂O	− 7.6	− 1.3	− 8.9	− 8.8[24]
CH₃CO₂H	25	H₂O	−10.4	− 1.0	−11.4	−11.7[25]
CH₃CH₂CO₂H	25	H₂O	−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 $\Delta\bar{V}_{1}{}^{*(1)}$ (cm³ 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	3.76×10^{-6}	−23.7
30	MeOH	4.22×10^{-6}	−26.6
40	MeOH	4.59×10^{-6}	−28.9
25	H₂O*	6.00×10^{-7}	− 3.8
40	H₂O*	6.79×10^{-7}	− 4.3

* from ref. 28), $r^{+}=3 \times 10^{-8}$cm ;   ** $r^{-}=1.8 \times 10^{-8}$cm

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

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 $\Delta \bar{V}_2^{\circ(1)}$ may be explained by the crystal volume change from neutral molecule to ion. However, in methanol $\Delta \bar{V}_2^{\circ(1)}$ 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 $\Delta \bar{V}_2^{\circ(1)}$. 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 $\bar{V}_2^{\circ(1)}$ of each constituent including the ionization process.

Acknowledgement

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