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Effect of Pressure on Proton Jumps in Methanol at 25 °C

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Conductivities of HCl and KCl in methanol containing traces (0.12 to 0.40 mol%) of water have been measured in the concentration range of $\approx$0.4 to $\approx$5 mmol dm^{-3} at 25 °C up to 2000 kg cm^{-2}. The limiting equivalent conductance (Λ°) for HCl and KCl decreased with increasing pressure. The excess proton conductance due to the proton-jump mechanism has been measured by Λ°(HCl)—Λ°(KCl) and found to increase with increasing pressure in nearly and absolutely pure methanol. The acceleration of proton jumps by pressure indicates that the rotation of methanol molecules about the longer molecular axis becomes faster at higher pressure. This anomaly is attributed to distortion with pressure of hydrogen bonds in methanol and to an increase in the repulsive field exerted by the proton on the molecule to rotate.

It is one of the most interesting ionic transport phenomena that protons in hydrogen-bonded solvents have the anomalous (excess) conductance due to proton jumps in addition to the normal hydrodynamic one. Since the rotation of solvent molecules is regarded as the rate-determining step in the proton-jump mechanism,[1,2] the excess proton conductance can be used as a probe for a dynamic study of liquid structure of hydrogen-bonded solvents. Following this line, the effect of pressure on the reorientation of water molecules was investigated at various temperatures in our previous papers;[2,3] the water reorientation was promoted by pressure, and the larger the pressure effect, the lower the temperature. When a hydrogen atom in H_2O is replaced by a methyl group CH_3, the way of hydrogen bonding is simplified; methanol in the solid state contains linear chains of O–H···O hydrogen bonds,[4] while the various types of ice have three-dimensional networks of hydrogen bonds.[5] The present authors attempt here to elucidate the influence of pressure upon proton jumps in methanol hydrogen-bonded in a way simpler than water. Since proton jumps in methanol are markedly influenced by water contained in the solvent, it is to be clarified how the effect of pressure on proton jumps is varied with the content of water. After making it clear whether proton jumps in methanol are accelerated by pressure or not, the effect of pressure on the rotation of methanol molecules is discussed in view of hydrogen bonds in methanol.

Experimental

Methanol of guaranteed reagent grade (Nakarai Chemicals Co., Ltd.) was refluxed over sodium methoxide and silver nitrate and fractionally distilled. The central fraction collected was dried with aluminum amalgam and distilled again. By drying further with molecular sieves (3A, Nakarai) and distilling, methanol for conductivity measurements was prepared. Methanol just after the purification showed a water content of 0.02 mol % in the Karl Fischer test, but easily absorbed moisture from air without special care. The conductivity of methanol was less than $3\times10^{-7}\ \Omega^{-1}$ cm^{-1} in any case. Potassium chloride salt of high purity was obtained from Merck and dried above 150 °C. Methanol solutions of this salt were prepared by use of calibrated pipets and measuring flasks. The stock solution of HCl was obtained by allowing purified methanol absorb dry HCl gas; the HCl gas was generated by the addition of a concentrated aqueous HCl solution to a concentrated H_2SO_4, condensed at −90 °C to remove water, and then slowly evaporated. The concentration was determined by careful titration with carbonate-free NaOH solution standardized against potassium hydrogen phthalate (ultra-pure, Merck) solution.

The density (ρ)[6] and viscosity (η)[7] data of Bridgman for methanol at elevated pressures at various temperatures were interpolated to the required temperature and pressure. The dielectric constant (ε) was cited from Ref. 8. The properties of methanol at high pressure at 25 °C are listed in Table 1.

The high-pressure system for conductivity measurement is illustrated in Fig. 1. Pressure generated by the hand pump (1) was measured to ±1 kg cm^{-2} (1 kg cm^{-2}=0.9807 $\times10^5$ Pa) by a Heise Bourdon gage (3). The temperature of the oil bath (3) was kept constant at 25±0.03 °C. The conductivity cell (8) was put in the vessel (4) and resistances of methanol and solutions in the cell were measured by a commercially available instrument (Yanagimoto MY 7). The cell constant of the conductivity cell was determined at

Table 1. Properties of methanol at 25 °C

P/kg cm^{-2}	ρ/g cm^{-3}	η/10^{-3} Pa s	ε
1	0.7870	0.5445	32.65
500	0.8216	0.6838	34.29
1000	0.8470	0.8134	35.55
1500	0.8702	0.9416	36.58
2000	0.8888	1.072	37.48

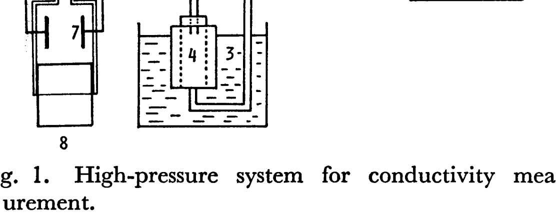

Fig. 1. High-pressure system for conductivity measurement.
1, Hand pump; 2, Heise Bourdon gage; 3, oil bath; 4, high-pressure vessel; 5, leading wire; 6, Teflon cap; 7, platinum electrode; 8, conductivity cell of a syringe type.

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TABLE 2. THE VALUES OF $\Lambda/\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{equiv}^{-1}$ AND $K_A/\mathrm{mol}^{-1}\,\mathrm{dm}^3$ FOR KCl

$10^4\,C$[a] / mol dm^{-3}	P/kg cm^{-2} 1	500	1000	1500	2000
0	104.4	90.6	81.5	74.0	68.0
	(±0.1)	(±0.1)	(±0.1)	(±0.1)	(±0.1)
4.994	98.7	86.3	77.4	70.8	65.3
9.961	96.8	84.6	76.4	69.6	64.1
14.99	95.1	83.5	75.3	68.6	63.4
19.99	93.5	82.2	74.3	67.8	62.4
24.99	92.3	80.9	73.4	67.0	61.9
29.99	91.4	80.4	72.8	66.7	61.6
40.03	89.3	78.8	71.5	65.4	60.5
50.04	87.8	77.8	70.5	64.5	59.7
K_A	6.2	3.4	2.8	1.9	1.5
	(±0.3)	(±0.6)	(±0.1)	(±0.3)	(±0.4)

a) Concentrations at 1 kg cm^{-2}.

atmospheric pressure from the conductivity of 0.01 mol dm^{-3} KCl solution,[9] and assumed invariant with pressure.

Results

The equivalent conductances Λ of KCl and HCl in Tables 2 and 3 were obtained by subtracting the solvenct conductivity and assuming that densities of dilute KCl and HCl solutions were equal to the methanol density at each pressure. The Shedlovsky equation,[10]

$$1/\Lambda S(z) = 1/\Lambda^\circ + K_A C \Lambda S(z) f^2/\Lambda^{\circ\,2},$$

where

$$S(z) = \{z/2+\sqrt{1+(z/2)^2}\}^2, \tag{2}$$

$$Z = 8.204\times10^5\,\Lambda^\circ/(\varepsilon T)^{3/2} + 82.50/\eta(\varepsilon T)^{1/2}\}\sqrt{C\Lambda/\Lambda^{\circ 3}}, \tag{3}$$

and

$$-\ln f^2 = 3.649\times10^6(\varepsilon T)^{3/2}\sqrt{C\Lambda S(z)/\Lambda^\circ}, \tag{4}$$

has been employed to obtain the limiting equivalent conductance Λ° from Λ; here, K_A, C, f^2, η, ε, and T are the association constant, concentration, Debye-Hückel limiting activity coefficient of the solute, the viscosity and dielectric constant of the solvent, and temperature, respectively. The present value of Λ° (KCl)/Ω^{-1} cm^2 equiv^{-1}, 104.4 at atmospheric pressure is comparable with the more accurate ones, 104.78[4] and 104.93[11] in literature.

As known well,[1,12,13] Λ(HCl) in methanol drops very sharply with the increase of the amount of water contained in contrast to Λ(KCl) insensitive to the impurity water, because protons bound to H_2O molecules (H_3O^+) will not tend to jump to neighboring CH_3OH molecules of lower dipole moment and the fraction of protons bound to CH_3OH molecules (CH_3OH^+) decreases on the addition of water to methanol. Hence, three sets of HCl solutions, which are different in the amount of water absorbed, were investigated. The mole fraction x[14] of water contained in methanol has been estimated at atmospheric pressure by means of Strehlow's equation,[13]

TABLE 3. THE VALUES OF $\Lambda/\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{equiv}^{-1}$ AND $K_A/\mathrm{mol}^{-1}\,\mathrm{dm}^3$ FOR HCl

$10^4\,C$[a] / mol dm^{-3}	P/kg cm^{-2} 1	500	1000	1500	2000
			x=0.12 mol %		
0	180.0	169.2	161.0	154.2	148.6
	(±0.3)	(±0.2)	(±0.3)	(±0.3)	(±0.2)
3.958	173.5	163.7	156.3	150.0	144.7
7.923	171.5	162.0	154.6	148.8	143.6
11.88	168.9	159.4	152.4	146.5	141.9
15.85	166.3	157.8	151.4	145.8	140.8
19.80	165.6	157.2	151.3	145.4	140.5
23.17	163.6	155.3	149.7	144.1	139.5
27.73	162.8	154.9	149.1	143.8	139.2
31.70	161.6	153.2	147.4	142.3	137.9
39.62	159.1	151.5	146.1	141.1	136.7
K_A	7.4	6.1	3.2	2.3	1.7
	(±0.7)	(±0.6)	(±0.8)	(±0.7)	(±0.5)
			x=0.31 mol %		
0	168.0	157.9	150.8	144.5	139.3
	(±0.2)	(±0.2)	(±0.2)	(±0.2)	(±0.3)
3.555	161.9	152.8	146.4	140.5	135.6
7.117	159.5	150.5	144.3	138.8	134.1
14.23	155.2	147.4	141.7	136.3	131.8
21.35	152.1	145.2	139.8	134.8	130.7
28.47	149.5	142.6	137.6	133.0	128.8
35.59	147.6	140.7	135.8	131.1	127.0
K_A	11.8	8.7	7.0	5.5	4.9
	(±0.5)	(±0.5)	(±0.5)	(±0.5)	(±0.8)
			x=0.40 mol %		
0	162.6	152.3	145.2	139.0	134.0
	(±0.2)	(±0.3)	(±0.3)	(±0.3)	(±0.2)
8.142	153.9	145.6	139.4	133.8	129.1
12.21	151.9	143.6	137.4	131.9	127.6
16.28	150.3	142.0	136.2	131.0	126.8
20.36	148.4	140.6	135.1	130.1	125.8
24.43	147.5	139.7	133.6	128.8	124.8
28.50	146.1	139.2	133.9	129.1	124.9
32.57	145.2	138.3	132.8	127.8	123.8
36.64	143.8	137.2	132.0	127.1	123.1
K_A	6.9	3.8	3.3	2.7	2.4
	(±0.6)	(±0.8)	(±1.0)	(±0.9)	(±0.7)

a) Concentrations at 1 kg cm^{-2}.

$$\Lambda^\circ_x(\mathrm{HCl}) = \lambda^\circ(\mathrm{CH_3OH_2^+}) + \lambda^\circ(\mathrm{Cl^-}) - \{\lambda^\circ(\mathrm{CH_3OH_2^+}) - \lambda^\circ(\mathrm{H_3O^+})\}Kx/\{1+(K-1)x\}, \tag{5}$$

where

$$K = x_1(1-x)/(1-x_1)x, \tag{6}$$

for the equilibrium,

$$\begin{array}{cccc} 1-x_1 & x & x_1 & 1-x \\ \mathrm{CH_3OH_2^+} + & \mathrm{H_2O} \rightleftharpoons & \mathrm{H_3O^+} + & \mathrm{CH_3OH}, \end{array}$$

and

$$\Lambda^\circ_x(\mathrm{HCl}) = x_1\lambda^\circ(\mathrm{H_3O^+}) + (1-x)\lambda^\circ(\mathrm{CH_3OH_2^+}) + \lambda^\circ(\mathrm{Cl^-}). \tag{8}$$

Here, $\lambda^\circ(\mathrm{H_3O^+})$, $\lambda^\circ(\mathrm{CH_3OH^+})$, and $\lambda^\circ(\mathrm{Cl^-})$ are, respectively, the limiting equivalent conductances of H^+ bound to H_2O with the mole fraction x_1, H^+

TABLE 4. THE VALUES OF $t^\circ(K^+)$, $\lambda^\circ/\Omega^{-1}$ cm^2 equiv^{-1}, AND $\lambda^\circ\eta/\Omega^{-1}$ cm^2 equiv^{-1} mPa s

	P/kg cm^{-2}				
	1	500	1000	1500	2000
$t^\circ(K^+)$	0.500	0.493	0.487	0.481	0.475
$\lambda^\circ(H^+)$[a]	127.8	123.3	119.2	115.8	112.9
$\lambda^\circ(K^+)$	52.2	44.7	39.7	35.6	32.3
$\lambda^\circ(Cl^-)$	52.2	45.9	41.8	38.4	35.7
$\lambda^\circ(H^+)$[a]η	69.6	84.3	97.0	109.0	121.0
$\lambda^\circ(K^+)\eta$	28.4	30.6	32.3	33.5	34.6
$\lambda^\circ(Cl^-)\eta$	28.4	31.4	34.0	36.2	38.3

a) In methanol containing 0.12 mol % water.

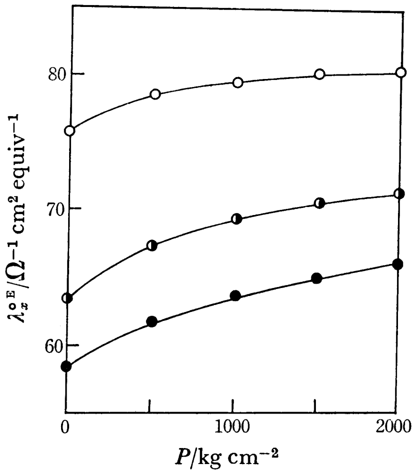

Fig. 2. Pressure dependence of excess proton conductances.
○, x=0.12 mol %; ◑, x=0.31 mol %; ●, x=0.40 mol %.

bound to CH_3OH, and Cl^- in nearly pure methanol. The parameters in Eq. 5 are determined at atmospheric pressure at 25 °C as

$$\Lambda_x^\circ(\mathrm{HCl}) = 198.5 - 1.39\times10^4x/(1+138x). \tag{9}$$

The limiting equivalent conductances of KCl and HCl were divided into their ionic components as in Table 4, using the limiting transference numbers $t^\circ(K^+)$ in KCl solution at atmospheric pressure[15] and those at high pressure which were obtained from Fig. 13 in Ref. 16. The ions decrease their mobilities with the rise in pressure as the methanol viscosity increases with increasing pressure, but initially increase in water qualitatively in parallel with the pressure dependence of the water viscosity.[2] In a quantitative sense, however, the pressure dependence of λ° is not exactly parallel with that of the solvent fluidity η^{-1} because the Walden products of the ions $\lambda^\circ\eta$ are not constant at high pressures as seen in Table 4. The effect of pressure on the Walden products of the ions is in the sequence,

$$H^+ > Cl^- > K^+.$$

Any of these ions has a much larger positive pressure coefficient of the Walden product in methanol than in water.[2,17]

The proton conductance in hydrogen-bonded solvents is due to the parallel series of the proton-jump and hydrodynamic processes.[1,18] However, no exact way to measure exclusively the anomalous conductance due to the proton-jump has been invented, and an empirical method is often used. The quantity,

$$\lambda_x^{\circ\,E} = \Lambda_x^\circ(\mathrm{HCl}) - \Lambda^\circ(\mathrm{KCl}), \tag{10}$$

is taken here as a measure of the anomalous conductance. Altough Li^+ and Na^+ are chosen elsewhere[1,19] instead of K^+ as a measure of the hydrodynamic conductance of the protonated species, H_3O^+ and CH_3OH^+, K^+ would be more appropriate because its ionic size is closer to H_3O^+ and CH_3OH^+ than the smaller ions.[20] The values of $\lambda_x^{\circ E}$ are plotted against pressure in Fig. 2. It is to be noted that $\lambda_x^{\circ E}$ increases with increasing pressure in methanol as $\lambda^{\circ E}$ in water.[2] The tendency is observed not only at infinite dilution but also at finite concentrations covered by the present work, while a decrease with pressure in the excess conductance measured at 2.5 mmol kg^{-1} by Λ(HBr)$-$$\Lambda$(NaBr) was reported[19] and later, an increase at infinite dilution was suggested.[21] The reason for the pressure-induced acceleration of proton jumps will be considered in the following section. On the other hand, the overall proton conductance decreases in methanol but increases in water.[2] The difference is explained in view of the facts that the contribution of the anomalous conductance to the overall proton conductance is much larger in the three-dimensionally hydrogen-bonded solvent (water) than in the one-dimensionally hydrogen-bonded solvent (methanol) and that the anomalous proton conductance is increased by pressure in both solvents but the hydrodynamic conductance is not initially promoted by pressure in methanol.

Discussion

It is important, first of all, to prove that the increase with pressure in the excess proton conductance at infinite dilution occurs in absolutely pure methanol as well as in methanol containing water. Using Eqs. 5 and 10 and assuming $\lambda^\circ(H_3O^+)=\lambda^\circ(K^+)$, We can derive the equation,

$$\begin{aligned}\lambda_x^{\circ E} &= \lambda^{\circ E}(1-x)/\{1+(K-1)x\}\\ &\approx \lambda^{\circ E}/\{1+(K-1)x\},\end{aligned} \tag{11}$$

where the limiting excess proton conductance in pure methanol, $\lambda^{\circ E}$ is expressed as

$$\lambda^{\circ\,E} = \lambda^\circ(CH_3OH_2^+) - \lambda^\circ(K^+). \tag{12}$$

The differentiation of Eq. 11 with respect to pressure leads to the equation,

$$\begin{aligned}\partial\lambda^{\circ E}/\partial P = &\{1+(K-1)x\}\partial\lambda_x^{\circ E}/\partial P\\ &+ \lambda^{\circ E}\{1+(K-1)x\}^{-1}x\partial K/\partial P.\end{aligned} \tag{13}$$

Since $\partial\lambda_x^{\circ E}/\partial P$ around 1 kg cm^{-2} is positive as seen in Fig. 2 and K at 1 kg cm^{-2} 139,[13] the first term in the right-hand side of Eq. 13 is positive. The second term is positive more or less because the equilibrium (7) is supposed to be shifted by pressure in some degree toward the right-hand side where the proton is bound to the stronger dipole and would have a smaller volume. Althogh the present data

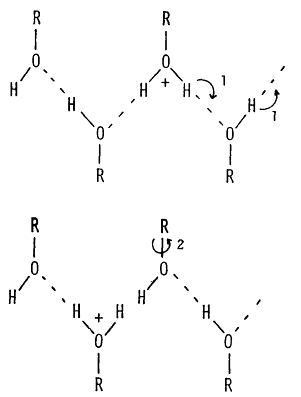

Fig. 3. Model for proton jump in methanol.
1, Proton transfer; 2, molecular rotation; R, methyl group.

are not enough to obtain quantitative information on $\partial\lambda^{\circ E}/\partial P$, they clearly exhibit through Eq. 13 that proton jumps in pure methanol are promoted by pressure to a larger extent than in methanol containing water.

The mechanism of proton jumps in alcohols has been proposed by Conway *et al.*[1] on the basis of the comparison between the excess proton conductance and the dielectric relaxation time in water and a few alcohols; there are two elementary processes, the proton transfer and the rotation of solvent molecules, the latter being the rate-determining step as in water. The same mechanism is assumed here and the molecular model is illustrated in Fig. 3. According to this mechanism, the increase with pressure in the excess proton conductance in methanol indicates that the rotation of methanol molecules about the longer molecular axis is promoted by pressure in spite of the increase in the density and the number of the hydrogen bonds.[22] When methanol is subjected to high pressure, the system is compressed to a denser state, irrespective of gain or loss in energy. For compression of the chain shown in the second row of Fig. 3, the following two factors are to be considered: (1) pushing the molecules above and below the plane of the chain so that the methyl groups may get closer, pressure distorts or bends the hydrogen bonds and weakens the strength; (2) keeping the molecules in the chain on the same plane, pressure decreases the intermolecular distance between the molecule to rotate and the hydrogen-bonded molecule (on the right side) and that between the molecule to rotate and the protonated molecule (on the left side). In the latter case, pressure gives more repulsive field to the molecule to rotate in favor of the rotation and at the same time, the strengthened hydrogen bond increases in some degree the potential barrier to the rotation. Although any conclusion on the relative importance of these factors must meet more straightforward studies, such as dielectric relaxation, NMR relaxation, and spectroscopic measurements at high pressure, at least, the factor (1) could not be neglected. As a matter of fact, the static dielectric constant of methanol increases and the Kirkwood correlation factor *g* decreases as methanol is compressed.[8] The increase in the dielectric constant is dominated by the density increase due to compression, but the decrease in the correlation factor suggests that such kind of distortion of the hydrogen bonds occurs that reduces the sum[23] of the average cosines of the angles between the dipoles of the correlated molecules in the hydrogen-bond chain.

References

1) B. E. Conway, J. O'M. Bockris, and H. Linton, *J. Chem. Phys.*, **24**, 834 (1956).

2) M. Nakahara and J. Osugi, *Rev. Phys. Chem. Jpn.*, **47**, 1 (1977).

3) M. Ueno, M. Nakahara, and J. Osugi, *J. Solution Chem.*, **8**, 881 (1979).

4) K. J. Tauer and W. N. Lipscomb, *Acta Crystallogr.*, **5**, 606 (1952).

5) D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water," Oxford Universirty Press, London (1969).

6) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **49**, 3 (1913).

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

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

9) J. P. Butler, H. I. Schiff, and A. R. Gordon, *J. Chem. Phys.*, **19**, 752 (1951).

10) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938); R. M. Fuoss and T. Shedlovsky, *J. Am. Chem. Soc.*, **71**, 1496 (1949).

11) E. C. Evers and A. G. Knox, *J. Am. Chem. Soc.*, **73**, 1739 (1951).

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

13) H. Strehlow, *Z. Phys. Chem.*, *N. F.*, **24**, 240 (1960).

14) Water in HCl solution exists in the forms H_2O and H_3O^+, as expressed in Fig. 7. However, the contribution of the latter form to the total concentration is negligible at infinite dilution where proton conductances are considered.

15) J. A. Davies, R. L. Kay, and A. R. Gordon, *J. Chem. Phys.*, **19**, 749 (1951).

16) B. Watson and R. L. Kay, cited by Kay in "Water," ed by F. Franks, Plenum, New York (1973), Vol. 3, Chap. 4.

17) M. Nakahara, K. Shimizu, and J. Osugi, *Rev. Phys. Chem. Jpn.*, **42**, 12 (1972).

18) T. Erdey-Grúz and S. Lengyel, "Modern Aspects of Electrochemistry," ed by J. O'M. Bockris and B. E. Conway Plenum, New York (1977), Chap. 1.

19) W. Strauss, *Aust. J. Chem.*, **10**, 277 (1957).

20) According to Ref. 16, the smaller ions Li^+ and Na^+ and the larger ion Me_4N^+ decrease their mobilities to a larger extent than K^+ as pressure increases. Therefore, to replace K^+ in Eq. 10 by Li^+, Na^+, or Me_4N^+ makes more positive the pressure coefficient of $\lambda_x^{\circ E}$.

21) J. F. Cukurins and W. Strauss, *Aust. J. Chem.*, **29**, 249 (1976).

22) E. Fishman and H. G. Drickamer, *J. Chem. Phys.*, **24**, 548 (1956); S. D. Hamann, "High Pressure Physics and Chemistry," ed by R. S. Bradley, Academic press, London (1963), Vol. 2, P. 144.

23) G. Oster and J. G. Kirkwood, *J. Chem. Phys.*, **11**, 175 (1943).