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The Effect of the Pressure on Proton Jumps in Ethanol–Water Mixtures at 25 °C

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The limiting molar conductances of hydrochloric acid in 0, 5, 10, 20, 30, and 80 mol% ethanol–water mixtures, and those of potassium chloride in 80 mol% of ethanol, were determined at 25 °C as a function of the pressure up to 2000 kgf cm^{-2} (1 kgf cm^{-2}=0.9807×10^5 Pa) from the conductances measured in a dilute concentration range. In each solvent except for 80 mol% of ethanol, the limiting molar conductances of the proton, $\lambda^\circ(\mathrm{H}^+)$, are about four to six times larger than those of the potassium ion, $\lambda^\circ(\mathrm{K}^+)$, at all the pressures studied; in 80 mol% of ethanol, the value of $\lambda^\circ(\mathrm{H}^+)$ is very close to that of $\lambda^\circ(\mathrm{K}^+)$ at atmospheric pressure. The results suggest that the proton-jump mechanism acts in the water-rich region, but not in the ethanol-rich region. The excess proton conductances at an infinite dilution, λ°_E, as estimated by $[\lambda^\circ_\mathrm{E}=\lambda^\circ(\mathrm{H}^+)-\lambda^\circ(\mathrm{K}^+)]$, were found to increase with an increase in the pressure. The pressure dependence of the excess proton conductances normalized to their values at 1 atm, $\lambda^\circ_\mathrm{E}{}^{(P)}/\lambda^\circ_\mathrm{E}{}^{(1)}$, is most prominent in 5 mol% of ethanol; its magnitude decreases in this order; $5>0>10\gg20\gg30$ mol% of ethanol. These results are discussed in relation to the effect of ethanol molecules on the water structure in the mixtures; a small addition of ethanol to water stabilizes the three-dimensional networks of water, while a further addition of ethanol makes it difficult to form them.

The proton is a much better probe than any other usual ion for a study of the solvent structure in hydrogen-bonded solvents, since protons are transferred through the hydrogen-bonded networks in addition to the hydrodynamic migration. In a previous paper,[1] the conductances of HCl and KCl in water were measured at 0 °C as a function of the pressure, and it was found that the excess proton conductance, λ°_E, increases with an increase in the pressure and that the rate of the increase in λ°_E becomes larger with a decrease in the temperature. The lower the temperature, the more significant the water structure. Therefore, the pressure dependence of λ°_E is considered to be closely related to the structural stability of water at atmospheric pressure. The structure of water is dominated by the directional attractive intermolecular potential and is sensitive to any change in pressure or temperature. Another way to change the structure is the introduction of organic molecules into the water. Alcohol–water mixtures have, in particular, attracted many researchers since structural effects appear to be significant in the water-rich region of these mixtures.[2,3] Recently computer experiments on these systems (5 mol% of methanol[4] and 3 mol% of *t*-butyl alcohol[5]) have been carried out, and structural promotion of water has been observed in radial-distribution functions. Accordingly, it seemed that it would be interesting to study the excess proton conductance in compressed alcohol–water mixtures in order to elucidate the influence of alcohol molecules on the water structure. Here, ethanol–water mixtures are used since the physical properties of the mixtures can be used for the analysis of the data on the conductances at high pressures.

Experimental

Chemicals and Solutions. The purification of the water and the ethanol, and the preparation of dilute KCl solutions, were the same as have been described in the previous papers.[6,7] Hydrochloric acid of an ultrapure grade was supplied by Merck. All the dilute solutions of HCl were prepared gravimetrically in a dry box under a nitrogen atmosphere by diluting an aqueous stock solution of HCl [ca. 1×10^{-2} M (1 M=1 mol dm^{-3})] with conductivity water and ethanol. The concentration of the stock solution was determined by measuring the conductance of the solution and by using the empirical equation proposed by Shedlovsky.[8] The concentrations of the dilute HCl solutions at each pressure were calculated by using the density of the stock solution at atmospheric pressure and assuming that the

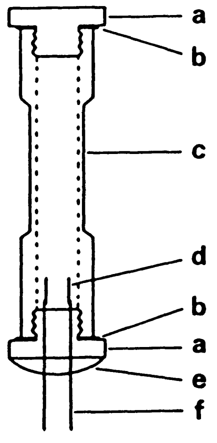

Fig. 1. Conductance cell of Teflon.
a: Teflon plug, b: rubber packing, c: Teflon capsule, d: platinum electrode, e: Araldite, f: platinum lead.

Table 1. Correction Fractors, $f^{(P)}$, for the Cell Constant of the Teflon Cell

P/kgf cm^{-2}	$f^{(P)}$	$f^{(P)\mathrm{a)}}$
500	0.9926	0.9946
1000	0.9861	0.9893
1500	0.9814	0.9863
2000	0.9775	0.9836

a) These values were estimated from the compression data of Ref. 10.

Table 2. Physical Properties of Ethanol–Water Mixtures at High Pressures and at 25 °C

P/kgf cm^{-2}	ρ/g cm^{-3}	ε	η/cP	P/kgf cm^{-2}	ρ/g cm^{-3}	ε	η/cP
	Water				20 mol% of Ethanol		
1	0.9970	78.5	0.8937	1	0.9336	55.8	2.453
500	1.0181	80.2	0.8865	500	0.9539	57.5	2.663
1000	1.0372	81.9	0.8897	1000	0.9717	59.1	2.880
1500	1.0546	83.5	0.9034	1500	0.9877	60.5	3.080
2000	1.0707	85.0	0.9232	2000	1.0023	61.8	3.280
	5 mol% of Ethanol				30 mol% of Ethanol		
1	0.9772	71.7	1.426	1	0.9043	47.7	2.467
500	0.9951	73.3	1.396	500	0.9232	49.4	2.800
1000	1.0133	74.9	1.386	1000	0.9418	50.8	3.157
1500	1.0300	76.2	1.392	1500	0.9590	52.2	3.510
2000	1.0449	77.5	1.405	2000	0.9739	53.5	3.880
	10 mol% of Ethanol				80 mol% of Ethanol		
1	0.9626	66.1	1.973	1	0.8088	28.0	1.438
500	0.9816	67.8	1.996	500	0.8421	29.5	1.810
1000	0.9991	69.3	2.035	1000	0.8699	30.7	2.164
1500	1.0142	70.7	2.065	1500	0.8902	31.7	2.534
2000	1.0284	71.9	2.098	2000	0.9085	32.6	2.968

densities of the dilute HCl solutions were equal to that of the solvent. To examine the validity of this assumption, the densities of the aqueous HCl solutions, ρ(HCl), were measured as a function of the concentration at 25 °C and at atmospheric pressure by means of a digital vibrating densimeter (SS-D-200 twin-type) manufactured by the Shibayama Scientific Co., Ltd. The following empirical equation was obtained:

$$\rho(\mathrm{HCl}) = 0.9970_6 + 0.018_1 c, \qquad (1)$$

where ρ(HCl) is in g cm^{-3} and where c is the concentration of solution in M. The use of the density of water instead of those of the solutions leads to an increase in the conductances of the dilute HCl solutions of only about 0.02%, indicating that the assumption is not unreasonable.

Apparatus. An acid-proof Teflon cell (capacity, 12 cm^3) with unplatinized electrodes and the glass cell (capacity, 10 cm^3) described in the previous paper[7] were employed, respectively, for the conductance measurements of HCl and KCl aqueous mixtures. As is shown in Fig. 1, the Teflon cell has a membrane thin enough to transmit the oil pressure to the solution in the cell. The cell constants at atmospheric pressure were determined with an accuracy of ±0.03% by using 6×10^{-4}, 1×10^{-3}, 5×10^{-3}, and 1×10^{-2} M aqueous KCl solutions;[9] their values were 0.5592 cm^{-1} for the Teflon cell and 0.3872 cm^{-1} for the glass cell. The cell constant of the glass cell was assumed to be invariant with the pressure. On the other hand, Teflon is compressible, and so the cell constant varies with pressure. Since it is somewhat ambiguous to estimate corrections to the cell constant from the interpolation of the compression data on Teflon,[10] as the phase transition occurs below 2000 kgf cm^{-2} at 25 °C,[11] correction factors as a function of the pressure were determined by comparing the conductances of 2×10^{-3} and 1×10^{-2} M aqueous KCl solutions obtained with the Teflon and glass cells. Table 1 shows the correction factors, $f^{(P)}=K^{(P)}/K^{(1)}$, in which $K^{(P)}$ and $K^{(1)}$ are the cell constant at pressure P and at atmospheric pressure respectively. The values of $f^{(P)}$ determined by this method are smaller than those estimated from the compression data[10] by about 0.5%.

The details of the experimental apparatus and procedure were described in a previous paper.[7]

Results and Discussion

The physical properties of the various solvent mixtures, such as the density, ρ;[12,13] the dielectric constant, ε,[14,15] and the viscosity, η,[16,13,17] used in the present work are collected in Table 2. The molar conductances, Λ, of HCl and KCl in ethanol–water mixtures were determined in the concentration range of $(0.6-6)\times10^{-3}$ M for HCl and $(2-8)\times10^{-4}$ M for KCl after solvent corrections. The conductance data obtained had a maximum deviation of ±0.1%. The data on the Λ of HCl summarized in Table 3 were analyzed by the Fuoss-Onsager conductance equation for unassociated electrolytes,[18,19] which is expressed thus:

$$\Lambda = \Lambda^\circ - Sc^{1/2} + Ec\log c + Jc, \qquad (2)$$

where Λ° is the limiting molar conductance, c is the molar concentration (M), and S, E, and J have the usual meanings. On the other hand, it has been found that KCl is slightly associated in ethanol–water mixtures above 15 mol% of ethanol.[7] Therefore, the Shedlovsky equation:[20]

$$1/\Lambda S(z) = 1/\Lambda^\circ + K_A c\Lambda S(z)f_\pm^2/\Lambda^{\circ 2}, \qquad (3)$$

where:

$$S(z) = \{z/2 + [1+(z/2)^2]^{1/2}\}^2, \qquad (4)$$

$$z = [8.204\times10^5\,\Lambda^\circ/(\varepsilon T)^{3/2} + 82.5/\eta(\varepsilon T)^{1/2}] \times (c\Lambda/\Lambda^{\circ 3})^{1/2}, \qquad (5)$$

Table 3. Molar Conductances (Λ/S cm^2 mol^{-1}) at Various Concentrations, Limiting Molar Conductances ($\Lambda°$/S cm^2 mol^{-1}), Ion-Size Parameters (å/Å), and Standard Deviations of Λ (σ_Λ/S cm^2 mol^{-1}) of HCl in Ethanol–Water Mixtures as a Function of the Pressure at 25 °C

P/kgf cm^{-2}	Λ								$\Lambda°$	å	σ_Λ
	Water										
	0.6656[a]	0.9381[a]	1.514[a]	1.926[a]	2.244[a]	2.781[a]	3.188[a]				
1	422.1	421.4	420.2	419.5	419.0	418.2	417.7		426.2	4.0	0.03
500	434.3	433.6	432.4	431.8	431.4	430.6	430.2		438.3	4.8	0.05
1000	442.7	442.1	441.0	440.4	439.9	439.2	438.8		446.7	5.2	0.05
1500	449.2	448.5	447.4	446.9	446.5	445.8	445.6		453.0	6.0	0.07
2000	453.2	452.4	451.6	451.2	450.8	450.4	450.2		456.7	8.2	0.08
	5 mol% of Ethanol										
	0.6674[a]	0.9049[a]	1.171[a]	1.777[a]	2.556[a]	3.401[a]	4.639[a]	5.923[a]			
1	308.0	307.5	307.1	306.2	305.4	304.8	304.0	303.3	311.0	5.1	0.04
500	316.6	316.4	315.9	315.3	314.4	314.0	313.1	312.3	319.9	5.7	0.17
1000	322.6	322.4	322.1	321.5	320.8	320.4	319.6	318.9	325.9	6.6	0.21
1500	327.5	327.2	327.1	326.5	326.0	325.6	324.9	324.3	330.7	7.5	0.24
2000	331.1	330.9	330.7	330.4	330.0	329.6	329.0	328.6	334.2	8.7	0.28
	10 mol% of Ethanol										
	0.9460[a]	1.262[a]	1.893[a]	2.705[a]	3.311[a]	3.988[a]	4.940[a]	5.973[a]			
1	231.9	231.6	231.1	230.5	230.2	229.9	229.6	229.3	234.8	6.5	0.05
500	235.9	235.6	235.0	234.5	234.1	233.8	233.5	232.9	238.9	5.8	0.11
1000	238.6	238.2	237.9	237.5	237.0	236.8	236.6	235.9	241.5	6.5	0.19
1500	241.3	241.2	240.8	240.4	240.0	239.8	239.6	239.0	244.2	6.9	0.19
2000	243.2	243.0	242.7	242.4	242.1	241.9	241.8	241.3	246.0	7.9	0.18
	20 mol% of Ethanol										
	0.8099[a]	1.256[a]	1.643[a]	2.054[a]	2.620[a]	3.492[a]	4.392[a]	5.651[a]			
1	153.1	152.5	152.2	151.8	151.4	150.9	150.5	150.1	155.5	5.0	0.03
500	150.5	150.0	149.7	149.4	149.1	148.7	148.4	148.1	152.7	5.9	0.01
1000	148.1	147.8	147.4	147.2	146.9	146.6	146.3	146.0	150.2	6.2	0.05
1500	145.9	145.7	145.5	145.4	145.1	144.8	144.5	144.4	148.0	7.1	0.11
2000	144.0	143.8	143.7	143.5	143.3	143.1	142.8	142.6	146.0	7.3	0.12
	30 mol% of Ethanol										
	0.6241[a]	0.9405[a]	1.327[a]	1.844[a]	2.354[a]	2.953[a]	3.538[a]	4.282[a]			
1	115.6	115.1	114.6	114.0	113.6	113.1	112.8	112.4	117.8	4.0	0.04
500	111.4	111.1	110.4	110.0	109.6	109.2	108.9	108.3	113.5	3.7	0.09
1000	107.5	107.2	106.5	106.2	105.8	105.5	105.2	104.7	109.4	3.9	0.10
1500	103.8	103.5	103.0	102.7	102.4	102.1	101.8	101.5	105.5	4.5	0.05
2000	100.5	100.3	99.8	99.5	99.3	98.9	98.7	98.5	102.1	4.7	0.07
	80 mol% of Ethanol										
	0.5938[a]	0.9960[a]	1.494[a]	1.984[a]	2.477[a]	2.975[a]	3.461[a]	4.045[a]			
1	47.82	46.90	46.02	45.29	44.64	44.02	43.49	42.88	51.02	2.5	0.04
500	42.27	41.54	40.93	40.34	39.77	39.28	38.92	38.43	44.86	2.7	0.06
1000	38.20	37.58	37.06	36.56	36.12	35.69	35.39	34.95	40.38	2.7	0.05
1500	35.04	34.48	34.03	33.61	33.26	32.87	32.60	32.23	36.91	2.8	0.04
2000	32.35	31.91	31.50	31.13	30.86	30.51	30.26	29.96	34.00	3.0	0.04

a) Concentrations (10^{-3} M) at atmospheric pressure.

and:

$$-\ln f_\pm^2 = 3.649\times10^6[c\Lambda S(z)/\Lambda°]^{1/2}/(\varepsilon T)^{3/2}, \qquad (6)$$

was employed to obtain $\Lambda°$ and the association constant, K_A, from the data on the Λ of KCl in 80 mol% of ethanol shown in Table 4. Here, $f_\pm$ is the mean activity coefficient as determined by the Debye-Hückel limiting law, and T is the absolute temperature.

The limiting molar conductances, $\Lambda°$(HCl) and $\Lambda°$(KCl), thus obtained are also listed in Tables 3 and 4 respectively, together with their related quantities, the ion-size parameter, å; the association constant, K_A, and the standard deviation of Λ, σ_Λ. The present values of $\Lambda°$(HCl) in various aqueous mixtures at 1 atm (426.2, 311.1, 234.8, 155.5, and 117.8 in 0, 5, 10, 20, and 30 mol% of ethanol respectively) are in good agreement with those obtained from the interpolation of the literature data[21] (426.6, 311, 235, 156, and 118 in 0, 5, 10, 20, and 30 mol% of ethanol respectively). In 80 mol% of ethanol, the value of $\Lambda°$(HCl) at 1 atm is not available in the literature, but the value of $\Lambda°$(KCl), 45.60, is

Table 4. Molar Conductances (Λ/S cm^2 mol^{-1}) at Various Concentrations, Limiting Molar Conductances (Λ°/S cm^2 mol^{-1}), Association Constants (K_A/mol^{-1} dm^3), and Standard Deviations of Λ (σ_Λ/S cm^2 mol^{-1}) of KCl in 80 mol% Ethanol-Water Mixtures as a Function of the Pressure at 25 °C

P/kgf cm^{-2}	Λ						Λ°	K_A	σ_Λ
	2.000[a)]	3.000[a)]	4.000[a)]	5.000[a)]	6.000[a)]	8.000[a)]			
1	43.49	42.91	42.40	41.97	41.56	40.84	45.60	80.8	0.01
500	36.52	36.08	35.74	35.42	35.13	34.58	38.09	57.3	0.01
1000	31.57	31.24	30.91	30.68	30.43	29.98	32.87	50.8	0.02
1500	27.76	27.45	27.21	27.01	26.81	26.45	28.82	42.3	0.02
2000	24.72	24.45	24.25	24.10	23.92	23.60	25.62	38.1	0.02

a) Concentrations (10^{-4} M) at atmospheric pressure.

Table 5. Limiting Ionic Molar Conductances (λ°/S cm^2 mol^{-1}) and Excess Proton Conductances (λ°_E/S cm^2 mol^{-1}) in Compressed Ethanol-Water Mixtures at 25 °C

P/kgf cm^{-2}	λ°			λ°_E	P/kgf cm^{-2}	λ°			λ°_E
	K^+	Cl^-	H^+			K^+	Cl^-	H^+	
	Water					20 mol% of Ethanol			
1	73.6	76.4	349.8	276.2	1	28.9	28.9	126.6	97.7
500	73.9	77.9	360.4	286.5	500	26.8	26.9	125.8	99.0
1000	73.3	78.9	367.8	294.5	1000	25.0	25.2	125.0	100.0
1500	72.6	78.8	374.2	301.6	1500	23.4	23.6	124.4	100.9
2000	71.2	78.0	378.7	307.4	2000	22.1	22.4	123.6	101.5
	5 mol% of Ethanol					30 mol% of Ethanol			
1	51.9	51.4	259.6	207.7	1	24.4	25.7	92.1	67.8
500	51.7	52.0	267.9	216.2	500	22.2	23.3	90.2	68.0
1000	51.2	52.2	273.7	222.5	1000	20.2	21.2	88.2	68.0
1500	50.5	52.1	278.6	228.1	1500	18.4	19.2	86.3	67.9
2000	49.7	51.7	282.5	232.8	2000	16.8	17.5	84.6	67.8
	10 mol% of Ethanol					80 mol% of Ethanol			
1	39.2	38.3	196.5	157.3	1	22.9	22.7	28.3	5.4
500	38.3	37.8	201.1	162.8	500				6.8
1000	37.6	37.3	204.2	166.6	1000				7.5
1500	36.8	36.8	207.4	170.6	1500				8.1
2000	36.2	36.4	209.6	173.4	2000				8.4

somewhat larger than the literature one,[22] 44.6. The pressure dependence of Λ°(HCl) in water agrees well with the literature values[23,24] within ±0.1% up to 1500 kgf cm^{-2}, but at 2000 kgf cm^{-2} our value is smaller by (0.3—0.4)% than theirs. No high-pressure data are available for comparison in ethanol-water mixtures, however. As is shown in Table 3, Λ°(HCl) increases monotonously with an increase in the pressure in 0, 5, and 10 mol% of ethanol, irrespective of the pressure dependence of the solvent viscosity, but in 20 mol% of ethanol and above, Λ°(HCl) diminishes with an increase in the pressure. The variation in Λ°(HCl) in each solvent with the pressure is mainly to be ascribed to the pressure dependence of the limiting molar conductance of the proton, as is shown below.

The limiting ionic molar conductances, λ°, of the proton under the various conditions were determined by using Λ°(HCl), Λ°(KCl),[7] and the limiting cation-transference number for KCl, $t^\circ(K^+)$,[6,7] as follows:

$$\lambda^\circ(K^+) = \Lambda^\circ(KCl)t^\circ(K^+), \tag{7}$$

$$\lambda^\circ(Cl^-) = \Lambda^\circ(KCl) - \lambda^\circ(K^+), \tag{8}$$

and:

$$\lambda^\circ(H^+) = \Lambda^\circ(HCl) - \lambda^\circ(Cl^-). \tag{9}$$

The values of $\lambda^\circ(H^+)$ thus obtained are listed in Table 5, together with those of $\lambda^\circ(K^+)$ and $\lambda^\circ(Cl^-)$, in which the values of $\lambda^\circ(K^+)$ and $\lambda^\circ(Cl^-)$ at 2000 kgf cm^{-2} in the mixtures below 30 mol% of ethanol were obtained by expressing the data on Λ°(KCl) and $t^\circ(K^+)$ up to 1500 kgf cm^{-2} [7] as quadratic equations of pressure. The standard deviations of the empirical equations were (0.01—0.06) conductance units for Λ°(KCl) and (1—7)$\times10^{-4}$ for $t^\circ(K^+)$. No data are available for $t^\circ(K^+)$ in 80 mol% of ethanol except at atmospheric pressure.[25] As is shown in Table 5, the values of $\lambda^\circ(H^+)$ are about four to six times larger than those of $\lambda^\circ(K^+)$ in 5, 10, 20, and 30 mol% of ethanol as well as in water, indicating that the proton-jump mechanism works well in these mixtures and that it dominates the conductance of the proton. However, the value of $\lambda^\circ(H^+)$ is very close to that of $\lambda^\circ(K^+)$ in 80 mol% of ethanol.

The excess proton conductance due to the proton jump, λ°_E, was estimated thus:

$$\lambda^\circ_E = \lambda^\circ(H^+) - \lambda^\circ(K^+) = \Lambda^\circ(HCl) - \Lambda^\circ(KCl), \quad (10)$$

where the translational mobility of the proton, i.e., the oxonium ion, H_3O^+, is approximated by that of the K^+ ion because of their similarity in size. The values of λ°_E are also shown in Table 5. Here, one problem is whether the protons are present as the oxonium ions in ethanol–water mixtures. The distribution of the protons between water and ethanol molecules for this reaction:

$$C_2H_5OH + H_3O^+ \rightleftharpoons C_2H_5OH_2^+ + H_2O, \quad (11)$$

has been investigated in the ethanol-rich region by the conductivity method[26,27] and by the use of an acid-base indicator[28] at 25 °C and at atmospheric pressure. The equilibrium constant for the reaction, $K=c(EtOH_2^+)c(H_2O)/c(H_3O^+)$, in which c(i) is the concentration of the species i in M, is in the range of (0.052—0.059) M, which indicates that the protons are present almost entirely as H_3O^+ under the experimental conditions studied here; even in 80 mol% of ethanol, the percentage of protons present as $C_2H_5OH_2^+$ is estimated to be below 1.5%. Therefore, it seems reasonable to consider that almost all the protons are transferred from the H_3O^+ ions to water molecules, and that the excess proton conductances reflect the variation in the hydrogen bonds between water molecules with the ethanol content and/or the pressure.

It has been proved that the rotation of hydrogen-bonded water molecules near the H_3O^+ ion is the rate-determining step in the proton-jump mechanism.[29] This mechanism of the proton jump has been confirmed[23] by comparing the pressure dependence of the excess proton conductance with that of the reorientational relaxation time of water molecules derived approximately from the NMR spin-lattice relaxation time;[30] the increase in the excess proton conductance with the pressure has been ascribed to the distortion and weakness of the hydrogen bonds between water molecules caused by the pressure.[1] As is shown in Table 5, λ°_E increases with an increase in the pressure, especially in the water-rich region. Therefore, it can be said that the reorientation of water molecules is promoted by the pressure in the ethanol–water mixtures as well as in water until it becomes retarded by an increase in the number of nearest neighbors.

The values of λ°_E themselves decrease markedly with an increase in the ethanol content at each pressure. Factors responsible for that would be: (i) the reorientation of water molecules becomes slower with an increase in the ethanol content, as is suggested by the dielectric relaxation time measured at atmospheric pressure,[31] and (ii) the fraction of water molecules adjacent to the H_3O^+ ion decreases with an increase in the ethanol content, and consequently the frequency of the proton transfer from the H_3O^+ ion to the water molecules diminishes with an increase in the ethanol content. Thus, the excess proton conductances, normalized to their values at 1 atm, $\lambda^\circ_{E}{}^{(P)}/\lambda^\circ_{E}{}^{(1)}$, were calculated in each solvent; they are shown in Fig. 2 as a function of the pressure as a step toward determining the pressure effect on the excess proton conductance for one rotator, i.e., one water molecule adjacent to the H_3O^+ ion. Figure 2 shows that the pressure dependence of $\lambda^\circ_{E}{}^{(P)}/\lambda^\circ_{E}{}^{(1)}$ is most prominent in 5 mol% of ethanol and that its magnitude decreases in this order; 5>0>10 ≫20 ≫30 mol% of ethanol. It has been found in pure water that the pressure dependence of $\lambda^\circ_{E}{}^{(P)}/\lambda^\circ_{E}{}^{(1)}$ becomes larger with a decrease in the temperature.[1,23] Since the hydrogen bonds between water molecules become more stable and are strengthened at lower temperatures because of the weaker thermal motion of water molecules, the water structure is more stabilized and enhanced at lower temperatures. Therefore, it is reasonable to consider that the pressure effect on $\lambda^\circ_{E}{}^{(P)}/\lambda^\circ_{E}{}^{(1)}$ is closely related to the structural stability of water: The more stable the hydrogen bonds between water molecules at atmospheric pressure, the more prominent the pressure effect on $\lambda^\circ_{E}{}^{(P)}/\lambda^\circ_{E}{}^{(1)}$. If this finding is applied to the results in ethanol–water mixtures, the fact that the pressure dependence of $\lambda^\circ_{E}{}^{(P)}/\lambda^\circ_{E}{}^{(1)}$ is larger in 5 mol% of ethanol than in water will confirm the viewpoint that a small addition of ethanol to water stabilizes the three-dimensional networks of water, mainly because of the hydrophobic hydration around the ethyl group.

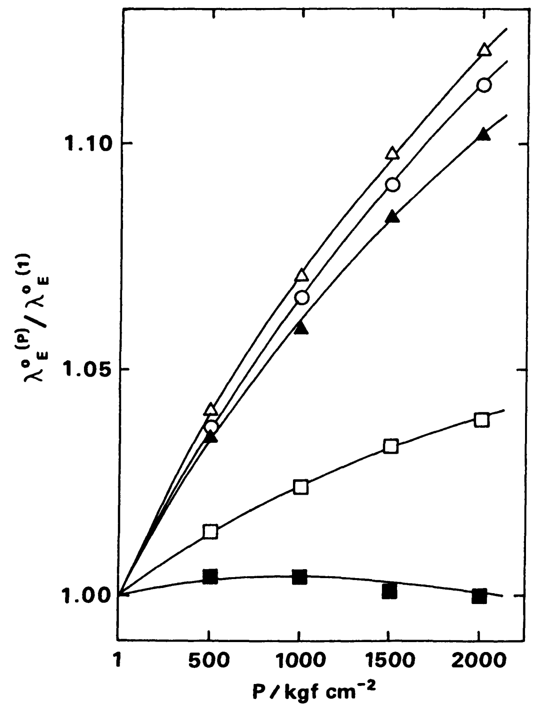

Fig. 2. Excess proton conductances normalized to their values at 1 atm as a function of the pressure. ○: Water, △: 5 mol%, ▲: 10 mol%, □: 20 mol%, ■: 30 mol% of ethanol.

With an increase in the ethanol content, it seems to become difficult to form stable bonds, as may be seen in 30 mol% of ethanol in Fig. 2. Furthermore, in 80 mol% of ethanol the value of $\lambda^\circ(H^+)$ is close to that of $\lambda^\circ(K^+)$, as has been mentioned above. In this case, the contribution of the proton jump may be very small, and that of the hydrodynamic migration may be dominant. Thus, the increase in the Walden product, $\Lambda^\circ\eta$, of HCl and KCl with the pressure may be explained qualitatively in terms of the dielectric friction theory,32) described in a previous paper.7)

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