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The Pressure Effect on Conductances of KCl in Ethanol–Water Mixtures at 25 °C

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The molar conductances of KCl in 5, 10, 15, 20, and 30 mol% ethanol–water mixtures were measured in the dilute concentration range of $(2-8)\times10^{-4}$ M (1 M=1 mol dm^{-3}) at 25 °C up to 1500 kgf cm^{-2} (1 kgf cm^{-2}=0.9807× 10^5 Pa). The Fuoss-Onsager conductance equation for unassociated electrolytes was used to determine the limiting molar conductance, Λ°, of KCl in 5 and 10 mol% of ethanol. In 15, 20, and 30 mol% of ethanol, where the ionic association takes place, the Shedlovsky equation was employed to obtain Λ° and the association constant K_A of KCl. The limiting ionic molar conductances of the K^+ and Cl^- ions were determined by combining Λ° with the limiting transference number for KCl. The Walden products of both K^+ and Cl^- ions decrease with an increase in the pressure in 5 mol% of ethanol, but in 15 mol% of ethanol and above they increase with an increase in the pressure. These facts indicate that the breaking effect of these ions appears prominently in about 5 mol% of ethanol.

Studies of the electrolytic conductance in binary solvent systems of alcohols and water are of interest because such systems are useful in elucidating not only the effect of a change in the dielectric constant on the association of electrolytes into ion pairs, but also the influence of the solvent structure on the limiting ionic conductances.

In previous papers,[1,2] we reported the pressure and temperature effects on the transference numbers for KCl in ethanol–water mixtures. Here we wish to present data on the electrolytic conductances of KCl in the same solvent systems at high pressures at 25 °C, and to discuss the variation in the ionic Walden products with the ethanol content and the pressure.

Experimental

Chemicals and Solutions. The chemicals used were the same as those described in the previous paper.[1] All the solutions of potassium chloride KCl were prepared by weight. A proper quantity of the stock solution (2×10^{-3} M KCl aqueous solution) was weighed into a dry weighing bottle of about 150 cm^3 and then diluted gravimetrically with conductivity water and ethanol in order to yield the desired composition of the solvent and concentration of the solution. The concentrations of the solutions in M were determined by assuming that the densities of dilute KCl solutions were equal to that of the solvent.

Apparatus. The high-pressure system for the conductance measurement is illustrated in Fig. 1. Pressure generated by means of a hand pump was measured to ±3 kgf cm^{-2} by means of a calibrated Bourdon gauge (Nagano Keiki Seisakusho, Ltd.). The temperature of the oil bath in which a pressure vessel was immersed was kept constant at (25±0.03) °C. The conductance cell installed in the pressure vessel was made by modifying a hypodermic syringe (capacity, 10 cm^3); the oil pressure was transmitted to the solution through a glass piston of the syringe.

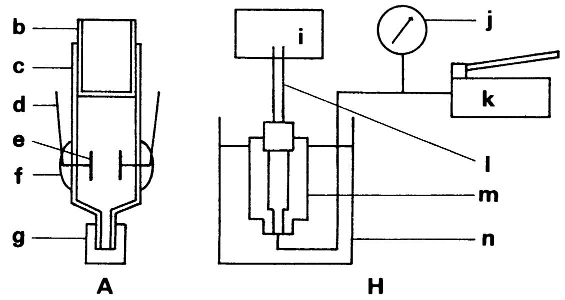

Fig. 1. High-pressure system for the conductance measurement.
A: Conductance cell of a syringe type, b: glass piston, c: glass cylinder, d: platinum lead, e: platinum electrode, f: Araldite, g: Teflon cap; H: pressure-generating system, i: conductance bridge, j: Bourdon-type pressure gauge, k: hand pump, l: leading wire, m: high-pressure vessel, n: oil bath.

Unplatinized electrodes were used for all the measurements, since the resistances of solutions decreased monotonously with the time when lightly platinized electrodes were employed. In order to eliminate electrode polarization errors caused by using unplatinized electrodes, the resistances of solutions were measured at 0.2, 0.5, 1, 2, and 5 kHz by means of a sine wave oscillator (Model 361B), a conductance bridge (Model 362B), and a standard resistor (Model 363B) manufactured by Fuso Seisakusho, Ltd. The measured resistances were found to be linear functions of the reciprocal of the frequency, f, except for 0.2 kHz, and to increase with a decrease in the frequency, as is typical of electrode polarization. The extrapolated value at $1/f=0$ was assumed to be the correct value. The cell constants at atmospheric pressure, as determined by this method from the conductances of 5×10^{-4}, 1×10^{-3}, and 1×10^{-2} M KCl aqueous solutions,[3] agreed within ±0.03%, which indicates that electrode polarization errors are eliminated. The cell constant thus determined was 0.3860 cm^{-1}, and it was assumed to be invariant with the pressure.

Results

The physical properties of the various solvent mixtures, the density, ρ,[4] the viscosity, η,[4,5] and the dielectric constant, ε,[6] at high pressures and at 25 °C used in the data analysis are from the literature; they are summarized in Table 1, where the ρ,[7] η,[8] and ε[9] values of water are also included. Table 2 shows the

TABLE 1. PROPERTIES OF ETHANOL–WATER MIXTURES AT HIGH PRESSURES AT 25 °C

P/kgf cm^{-2}	ρ/g cm^{-3}	ε	η/cP
	Water		
1	0.9970	78.5	0.8937
500	1.0181	80.2	0.8865
1000	1.0372	81.9	0.8897
1500	1.0546	83.5	0.9034
	5 mol% of ethanol		
1	0.9772	71.7	1.426
500	0.9951	73.3	1.396
1000	1.0133	74.9	1.386
1500	1.0300	76.2	1.392
	10 mol% of ethanol		
1	0.9626	66.1	1.973
500	0.9816	67.8	1.996
1000	0.9991	69.3	2.035
1500	1.0142	70.7	2.065
	15 mol% of ethanol		
1	0.9486	60.6	2.310
500	0.9687	62.3	2.460
1000	0.9863	63.8	2.585
1500	1.0025	65.2	2.683
	20 mol% of ethanol		
1	0.9336	55.8	2.453
500	0.9539	57.5	2.663
1000	0.9717	59.1	2.880
1500	0.9877	60.5	3.080
	30 mol% of ethanol		
1	0.9043	47.7	2.467
500	0.9232	49.4	2.800
1000	0.9418	50.8	3.157
1500	0.9590	52.2	3.510

molar conductances, Λ, of KCl in ethanol–water mixtures at 25 °C as a function of the pressure, P. The molar conductances were reproducible within±0.1%.

The limiting molar conductances, Λ°, of KCl in 5 and 10 mol% of ethanol were obtained by analyzing the conductance data with the aid of the Fuoss-Onsager conductance equation for unassociated electrolytes:[10,11]

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

where c is the molar concentration (M) and where S, E, and J are the parameters in Eq. 1; S is the Onsager limiting slope, the form of E is $(E_1\Lambda^\circ - 2E_2)$, in which both E_1 and E_2 depend only upon solvent properties, and J is a function of the ion-size parameter, $\mathring{a}$. However, in 15 mol% of ethanol and above, the data analysis obtained by the use of Eq. 1 gives a very low value of $\mathring{a}$, which means that KCl is slightly associated in these mixtures. Thus, the Shedlovsky equation:[12]

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

where:

$$S(z) = \{z/2 + [1+(z/2)^2]^{1/2}\}^2, \tag{3}$$

$$z = [8.204\times10^5\Lambda^\circ/(\varepsilon T)^{3/2} + 82.50/\eta(\varepsilon T)^{1/2}] \times (c\Lambda/\Lambda^{\circ 3})^{1/2}, \tag{4}$$

TABLE 2. MOLAR CONDUCTANCES Λ/S cm^2 mol^{-1} OF KCl IN COMPRESSED ETHANOL–WATER MIXTURES AT VARIOUS CONCENTRATIONS AT 25 °C

P/kgf cm^{-2}	$c^{a)}$/10^{-4} M					
	2.000	3.000	4.000	5.000	6.000	8.000
			5 mol% of ethanol			
1	102.3_7	102.1_5	101.9_5	101.7_5	101.5_8	101.4_1
500	102.6_5	102.5_5	102.2_5	102.1_3	101.9_0	101.7_3
1000	102.3_8	102.2_5	102.0_5	101.9_0	101.7_3	101.5_1
1500	101.6_3	101.5_5	101.3_5	101.2_0	100.9_7	100.7_3
			10 mol% of ethanol			
1	76.7_7	76.5_8	76.4_2	76.3_1	76.1_7	75.9_7
500	75.3_8	75.1_8	75.0_5	74.8_6	74.7_7	74.6_2
1000	74.1_7	73.9_8	73.8_5	73.7_0	73.5_5	73.4_5
1500	72.9_3	72.7_8	72.7_1	72.5_5	72.3_7	72.2_4
			15 mol% of ethanol			
1	64.4_0	64.1_0	63.8_0	63.6_0	63.4_0	63.1_5
500	61.2_0	60.9_0	60.7_0	60.5_0	60.3_0	60.0_5
1000	58.5_0	58.3_0	58.1_0	57.9_0	57.7_0	57.4_8
1500	56.1_0	55.8_0	55.6_0	55.4_5	55.3_0	55.1_0
			20 mol% of ethanol			
1	57.0_0	56.6_0	56.3_5	56.1_5	55.9_0	55.7_0
500	52.9_0	52.6_0	52.4_0	52.2_0	52.0_0	51.7_5
1000	49.5_0	49.2_0	49.0_0	48.8_0	48.6_5	48.4_5
1500	46.4_0	46.2_0	46.0_0	45.8_5	45.7_0	45.5_0
			30 mol% of ethanol			
1	49.1_0	48.8_0	48.5_5	48.3_0	48.0_5	47.8_0
500	44.7_0	44.4_0	44.2_0	44.0_0	43.8_0	43.5_8
1000	40.7_0	40.4_0	40.2_0	40.0_5	39.9_0	39.7_0
1500	37.0_5	36.8_0	36.6_0	36.5_0	36.3_5	36.2_0

a) Concentrations at atmospheric pressure.

TABLE 3. VALUES OF Λ°/S cm^2 mol^{-1}, t_+°, $\lambda_\pm^\circ$/S cm^2 mol^{-1}, $\mathring{a}$/Å, AND K_A/mol^{-1} dm^3 IN ETHANOL–WATER MIXTURES AS A FUNCTION OF THE PRESSURE AT 25 °C

P/kgf cm^{-2}	Λ°	t_+°	λ_+°	λ_-°	$\mathring{a}$	K_A
Water						
1	149.9_1	0.490_6	73.5_5	76.3_6	$1_{.5}$	
500	151.7_7	0.486_6	73.8_5	77.9_2	$1_{.8}$	
1000	152.2_2	0.481_8	73.3_4	78.8_8	$2_{.6}$	
1500	151.4_2	0.479_5	72.6_1	78.8_1	$5_{.8}$	
5 mol% of ethanol						
1	103.3_2	0.502_4	51.9_1	51.4_1	$1_{.1}$	
500	103.6_5	0.498_4	51.6_6	51.9_9	$1_{.1}$	
1000	103.3_5	0.495_3	51.1_9	52.1_6	$3_{.2}$	
1500	102.6_5	0.492_2	50.5_2	52.1_3	$1_{.1}$	
10 mol% of ethanol						
1	77.5_2	0.505_7	39.2_0	38.3_2	$1_{.2}$	
500	76.1_0	0.503_2	38.2_9	37.8_1	$1_{.2}$	
1000	74.8_7	0.501_9	37.5_8	37.2_9	$1_{.3}$	
1500	73.6_5	0.500_1	36.8_3	36.8_2	$1_{.2}$	
15 mol% of ethanol						
1	65.2_4	0.504_9	32.9_4	32.3_0		$18_{.2}$
500	61.9_8	0.503_2	31.1_9	30.7_9		$16_{.5}$
1000	59.2_6	0.502_2	29.7_6	29.5_0		$15_{.0}$
1500	56.7_5	0.501_3	28.4_5	28.3_0		$13_{.9}$
20 mol% of ethanol						
1	57.8_1	0.500_4	28.9_3	28.8_8		$22_{.4}$
500	53.6_7	0.499_2	26.7_9	26.8_8		$20_{.4}$
1000	50.1_7	0.498_5	25.0_1	25.1_6		$19_{.2}$
1500	47.0_4	0.498_0	23.4_3	23.6_1		$16_{.3}$
30 mol% of ethanol						
1	50.0_4	0.486_6	24.3_5	25.6_9		$26_{.8}$
500	45.4_8	0.487_7	22.1_8	23.3_0		$23_{.1}$
1000	41.3_5	0.488_3	20.1_9	21.1_6		$22_{.2}$
1500	37.6_2	0.489_6	18.4_2	19.2_0		$18_{.4}$

and:

$$-\ln f_\pm^2 = 3.649\times10^6[c\Lambda S(z)/\Lambda^\circ]^{1/2}/(\varepsilon T)^{3/2} \tag{5}$$

was employed to obtain Λ° and the association constant, K_A, from Λ in 15 mol% of ethanol and above; here, $f_\pm$ and T are the mean activity coefficient by the Debye-Hückel limiting law and the absolute temperature respectively. The values of Λ°, $\mathring{a}$, and K_A thus obtained are listed in Table 3, together with those of Λ° and $\mathring{a}$ in water, which were obtained by recalculating the data in Ref. 13 with the aid of Eq. 1. The present values of Λ° at atmospheric pressure are in good agreement with the more accurate ones[14] within ±0.2%. No high-pressure data are available for comparison in these systems, however. As is shown in Table 3, Λ° decreases with an increase in the ethanol content at each pressure and with an increase in the pressure in each solvent except for 5 mol% of ethanol, where the Λ°-*vs.*-pressure curve has a slight maximum, as in the case of water.

The limiting ionic molar conductances, λ_i°, of the K^+ and Cl^- ions listed in Table 3 were determined by combining Λ° with the limiting cation-transference number, t_+°, for KCl as follows:

$$\lambda_+^\circ = \Lambda^\circ t_+^\circ, \tag{6}$$

$$\lambda_-^\circ = \Lambda^\circ - \lambda_+^\circ. \tag{7}$$

The limiting cation-transference numbers shown in Table 3 were obtained using the Kay-Dye equation:[15]

$$t_+^\circ = t_+ + [(0.5-t_+)/\Lambda^\circ]\Delta\Lambda_e, \tag{8}$$

where t_+ is the cation-transference number at the molar concentration c and where $\Delta\Lambda_e$ is the electrophoretic contribution to conductance, expressed by the Fuoss-Onsager conductance equation:[10]

$$\Delta\Lambda_e = \beta c^{1/2}/(1+\kappa'\mathring{a}), \tag{9}$$

$$\beta = 82.50/\eta(\varepsilon T)^{1/2}, \tag{10}$$

$$\kappa' = 50.3c^{1/2}/(\varepsilon T)^{1/2}, \tag{11}$$

where $\mathring{a}$ is the ion-size parameter in Å. The values of η and ε are given in Table 1, Λ° is determined in this work, and the value of t_+ in 0.02 M KCl solution is taken from Ref. 1; the value of $\mathring{a}$ taken from Ref. 16, *i.e.*, 3.08 Å, is assumed to be independent of the solvent composition and the pressure. It should be noted that the ionic association has no direct effect on the transference number, since it is the ratio of the conductance of the ion to that of the salt, and that the value of t_+° is little affected by the use of a nominal

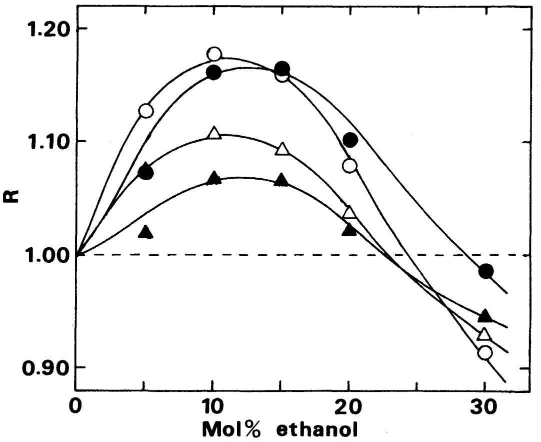

Fig. 2. Ionic Walden products normalized to their values in water as a function of mol% of ethanol. ○: 1 atm, ●: 1500 kgf cm^{-2} for the K$^+$ ion, and △: 1 atm, ▲: 1500 kgf cm^{-2} for the Cl$^-$ ion.

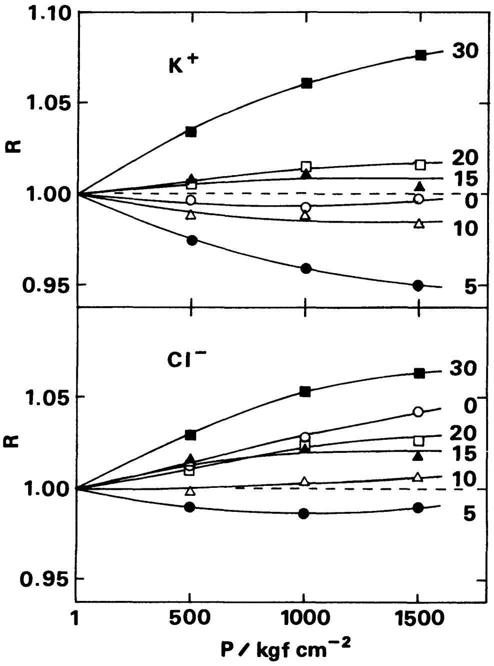

Fig. 3. Ionic Walden products normalized to their values at 1 atm as a function of the pressure. Mol% of ethanol is shown in the plot.

concentration (0.02 M) instead of a real concentration in Eqs. 9 and 11, since the ionic association is slight, the concentration of the solution is low enough, and the value of t_+ is close to 0.5 in our case.

The pressure dependence of λ_i° in the various solvent mixtures agrees qualitatively with that of the fluidity of the solvent mixtures, $1/\eta$, except in the case of 5 mol% of ethanol, where λ_+° decreases monotonously with an increase in the pressure, though $1/\eta$ has a maximum at about 900 kgf cm^{-2}.

Figures 2 and 3 show the variation in the ionic Walden products, $\lambda_i^\circ\eta$, with the ethanol content and the pressure respectively. The ionic Walden products initially increase with the ethanol content up to about 10 mol% of ethanol and then decrease at each pressure studied. As is shown in Fig. 3, the pressure coefficient of the Walden product of the K$^+$ ion at atmospheric pressure is negative for water, 5, and 10 mol% of ethanol, is most negative for 5 mol% of ethanol, and becomes positive for 15 mol% of ethanol and above, while that of the Cl$^-$ ion is negative for only 5 mol% of ethanol.

The association constant, K_A, increases with the ethanol content and decreases with the pressure, as is shown in Table 3. This trend coincides with the change in the dielectric constant of the solvent. The volume change on the ionic association, $\Delta\bar{V}^\circ$, was estimated by means of the equation:[17)]

$$\Delta\bar{V}^\circ = -RT(\partial \ln K_A/\partial P)_T - RT\beta_s, \qquad (12)$$

where β_s is the compressibility of the solvent and R is the gas constant. The values obtained at atmospheric pressure are 3.5, 4.0, and 4.8 cm^3 mol^{-1} for 15, 20, and 30 mol% of ethanol respectively.

Discussion

It is convenient to express the ionic Walden product as a sum of terms:[18)]

$$\lambda_i^\circ\eta = (\lambda_i^\circ\eta)_{CS} + (\lambda_i^\circ\eta)_{CE}, \qquad (13)$$

where the charged-sphere contribution, $(\lambda_i^\circ\eta)_{CS}$, is written as:

$$(1/\lambda_i^\circ\eta)_{CS} = (1/\lambda_i^\circ\eta)_{IS} + (1/\lambda_i^\circ\eta)_{DR}. \qquad (14)$$

Here, the term IS gives the contribution to the conductance to be expected from inert spheres, while the term subscripted DR gives the contribution to the conductance resulting from charging the spheres and is identified as a solvent dipole relaxation effect. The last term, subscripted CE, is a term that contains the effects resulting from changes in the solvent in the vicinity of an ion.

If we use, as the charged-sphere contribution, the Zwanzig dielectric friction theory,[19)] which is based on a continuum model for the solvent, the ionic Walden product is expressed as:

$$\lambda_i^\circ\eta = eF/[A_s\pi r_i + A_z\phi r_i^{-3}], \qquad (15)$$

where ϕ is given by:

$$\phi = e^2(\tau/\eta)[(\varepsilon-\varepsilon_\infty)/\varepsilon(2\varepsilon+1)], \qquad (16)$$

with A_s=6 and A_z=3/8 for complete sticking, and A_s=4 and A_z=3/4 for complete slipping. Here, e, F, r_i, τ, and ε_∞ are the protonic charge, the Faraday constant, the radius of an ion, the solvent dielectric relaxation time, and the infinite-frequency dielectric constant respectively. Equation 15 predicts that the increase in ϕ will lead to a decrease in the ionic Walden product if r_i is taken to be the crystallographic radius of the ion and does not change with the solvent composition and the pressure. At atmospheric pressure, ϕ is shown to increase with the ethanol content by using the values of τ,[20] η, and ε of water, 20 and 30 mol% of ethanol, and on the assumption that ε_∞ is equal to that of water.[21] Therefore, the Zwanzig equation cannot explain the initial increase in the ionic Walden products with the ethanol content, as was pointed out by Kay *et al.*[22] However, the decrease in the ionic Walden products with the ethanol content in the range of (20—30) mol% of ethanol is qualitatively in agreement with the experimental results shown in Fig. 2.

Here, let us consider the pressure dependence of the ionic Walden products in each solvent. The pressure dependence of ϕ is expressed as follows:

$$\frac{1}{\phi}\left(\frac{\partial\phi}{\partial P}\right)_T = \left[\frac{-2\varepsilon(\varepsilon-2\varepsilon_\infty)+\varepsilon_\infty}{\varepsilon(\varepsilon-\varepsilon_\infty)(2\varepsilon+1)}\right]\left(\frac{\partial\varepsilon}{\partial P}\right)_T + \frac{1}{\tau}\left(\frac{\partial\tau}{\partial P}\right)_T - \frac{1}{\eta}\left(\frac{\partial\eta}{\partial P}\right)_T. \tag{17}$$

The first term on the right-hand side of Eq. 17 is negative for all the solvent mixtures studied, because ε increases with an increase in the pressure, as is shown in Table 1, and ε_∞ can be expected to be very small compared with ε. Although there is no available data on τ at high pressures in ethanol–water mixtures, τ is anticipated to decrease with an increase in the pressure, by analogy with the case of water.[23] The decrease in the τ of water with the pressure is attributed to the bending of hydrogen bonds between water molecules caused by pressure. Therefore, the second term can also be expected to be negative. The third term, except in the cases of water and 5 mol% of ethanol, is negative, since η increases with an increase in the pressure, as is shown in Table 1. Thus, ϕ decreases with an increase in the pressure in 10 mol% of ethanol and above. In the cases of water and 5 mol% of ethanol, η initially decreases with an increase in the pressure. However, this contribution to $(1/\phi)(\partial\phi/\partial P)_T$ is comparable with that of the first term, and the two contributions cancel each other out; in the case of water, the contribution of the second term is about twice as large as those of the first and third terms. Therefore, ϕ decreases with the pressure even in water and 5 mol% of ethanol. The Zwanzig equation predicts that the ionic Walden product will increase with the pressure. This prediction agrees with the experimental results in 15 mol% of ethanol and above, as is shown in Fig. 3. However, the pressure coefficients of the Walden product of the K^+ ion in water, 5, and 10 mol% of ethanol and that of the Cl^- ion in 5 mol% of ethanol, *i.e.*, in the water-rich region, do not agree with the predictions of the theory.

In the water-rich region, the water structure is more strengthened than that in water by the addition of a small amount of ethanol.[24] Thus, in this region the second term on the right-hand side of Eq. 13, $(\lambda_i{}^\circ\eta)_{CE}$, must be taken into consideration. If the effective viscosity in the vicinity of an ion is less than the bulk viscosity of a solvent, the ion obtains excess mobility. An increase in the pressure will cause the water structure to weaken by bending the hydrogen bonds between water molecules. Thus, the excess mobility will decrease with an increase in the pressure. This effect brings about the decrease in the ionic Walden product with an increase in the pressure. For the K^+ ion, this can be seen in water, 5, and 10 mol% of ethanol; it is most prominent in 5 mol% of ethanol. The Cl^- ion is also classified as a breaking ion. However, the Walden product in water increases with an increase in the pressure. The assumption that this is based on the contribution of the dielectric friction is curious, because the contribution of the dielectric friction to the conductance may be expected to be less for the Cl^- ion than for the K^+ ion, since the crystallographic radius of a Cl^- ion is larger than that of a K^+ ion.[25] Therefore, the specific interaction between the Cl^- ion and water molecules must be considered. The interaction between the Cl^- ion and water molecules includes the contribution of hydrogen bonds.[26] If the pressure weakens the hydrogen bonds, the Cl^- ion will obtain excess mobility. This effect may be gradually reduced by adding ethanol to water, thus enhancing the basicity of the solvent mixtures,[27] and the decrease in the Walden product of the Cl^- ion in 5 mol% of ethanol with the pressure may be attributed to the structure-breaking effect of the Cl^- ion, since the water structure is most strengthened in this region.

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