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Pressure Effect on Transference Numbers for KCl in Ethanol–Water Mixtures at 25 °C

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Cation transference numbers for 0.02 mol dm^{-3} KCl in 0-, 5-, 10-, 15-, 20-, and 30-mol% ethanol–water mixtures were determined by the moving boundary method at 25 °C up to 1500 kg cm^{-2} (1 kg cm^{-2}=0.9807×10^5 Pa). The cation transference number, t_+, initially increases with increasing ethanol content up to 10—15 mol% and then decreases at all the pressures studied. In water and ethanol–water mixtures below 20 mol%, t_+ at the definite solvent decreases with increasing pressure. The decreasing rate becomes smaller as the ethanol content increases, and the tendency is reversed finally at 30 mol%. To account for the variation of t_+ with solvent composition and pressure, specific interactions between the ions and solvent have been taken into consideration.

When we study ionic conductances, transference numbers are required to split electrolyte conductances into the ionic components without any assumptions. There have been several reports on the pressure effect on transference numbers in water,[1–6)] but none in alcohol–water mixtures. Ionic conductances in alcohol–water mixtures are needed to elucidate the ionic transport process, in particular in relation to the liquid structure. Numerous properties of alcohol–water mixtures show a extremum in the water-rich region, which may be a reflection of increased solvent structure.[7)] The solvent structure is also affected by pressure and temperature as well as by solvent composition.

In the previous paper,[8)] conductances of potassium halides in water were measured at high pressure. Here, to provide a basis from which to investigate how the pressure dependence of ionic conductances of K$^+$, Cl$^-$, and other ions varies with the ethanol content in ethanol–water mixtures, we carried out the transference number measurements for KCl in the mixed solvents up to 30 mol% ethanol at 25 °C up to 1500 kg cm^{-2}. The results are compared with the Zwanzig dielectric friction theory,[9)] which gives one important step to a more quantitative theory.

Experimental

Chemicals and Solutions. Ethanol of guaranteed reagent grade (Nakarai Chemical Co., Ltd.) was dried with Molecular Sieves (3A, Nakarai) and purified by distillation under a nitrogen atmosphere. Fractionally distilled ethanol had a density of 0.7853 g cm^{-3}, and showed a water content of 0.05 wt% in the Karl Fischer test. Its conductivity was less than $3\times10^{-7}\,\Omega^{-1}\,\mathrm{cm}^{-1}$. Conductivity water was prepared by passing distilled water through a mono-bed ion-exchange resin. Its conductivity was about $1.2\times10^{-6}\,\Omega^{-1}\,\mathrm{cm}^{-1}$. Potassium chloride salt of high purity was obtained from Merck and dried above 130 °C. Aqueous mixtures up to 30 mol% ethanol were prepared by weighing; the solutions of 0.02 mol dm^{-3} KCl were made by use of measuring flasks. The concentrations of the solutions at high pressure were corrected with the densities of the aqueous mixtures.[10,11)]

Apparatus. Cation transference numbers at high pressure were determined by the moving boundary method with an autogenic-type cell equipped with a cadmium anode and a silver–silver chloride cathode, as shown in Fig. 1. The boundary movement was followed by measuring the change in resistance between platinum probe electrodes separated by 3 cm and sealed into 2 mm i.d. hard glass tube. The resistance was measured by a Yanagimoto MY8 type a.c. bridge. A constant current was supplied by a direct current stabilizer (Metronics 691B type), and measured periodically during electrolysis by potentiometric measurement (a Shimadzu digital potentiometer) of a potential drop across a 100-Ω standard resistor, connected in series with the moving boundary cell. The small current of 0.15 mA was used to minimize the effect of heat developed from electrolysis. A stop-watch was used to measure the time during which the current flowed.

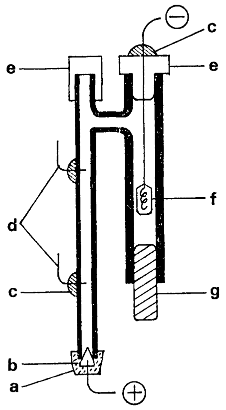

Fig. 1. High pressure autogenic cell for the measurement of the transference number.
a: DeKotinsky, b: cadmium anode, c: Araldite, d: probe electrode, e: Teflon cap, f: silver–silver chloride cathode, g: glass piston.

Conductivities of solvents and solutions were determined by using a syringe-type cell which is described elsewhere.[12)]

Pressure generated by means of a hand pump was measured to ±3 kg cm^{-2} by a calibrated Bourdon gauge (Nagano Keiki Seisakusho, Ltd.). The oil pressure in the pressure vessel was transmitted to the solution by a glass piston of the syringe. The temperature of the oil bath in which the pressure vessel was immersed was kept constant at 25±0.03 °C.

Determination of the Transference Number. The apparent cation transference number, t_+', can be calculated from the equation:[13)]

$$t_+' = \frac{\Delta V C F}{i\,\Delta t}, \tag{1}$$

where ΔV is the volume (cm^3) swept out by the boundary during time Δt (s) at i (mA) of current, C is the concentration of solution (mol dm^{-3}), and F is the Faraday constant. Considering the change in resistance between probe electrodes $\Delta R(\Omega)$ when the boundary moves upward, Eq. 1 can be transformed to the following equation:[1,5]

$$t_+' = \frac{VCF}{i(R_2-R_1)}\frac{\Delta R}{\Delta t}, \tag{2}$$

where V is the volume (cm^3) between the probe electrodes, and R_1 and R_2 are the resistances (Ω) when the uniform glass tube between the probe electrodes is occupied by KCl solution only and by $CdCl_2$ solution only, respectively. V was determined by calibration runs at 1 atm and 25 °C with 0.02 mol dm^{-3} KCl aqueous solution and by taking Longsworth's value of $t_+=0.4901$.[13] V's at high pressure were corrected with the compressibilities of Pyrex glass.[14] The variation of the resistance between the probe electrodes with time is shown in Fig. 2 for a typical run.

The transference number corrected for the solvent conductivity and volume change at the anode, t_+, is calculated from the following equation:[15]

$$t_+ = (t_+' - C\Delta\overline{V})\left(1+\frac{\kappa^\circ}{\kappa}\right). \tag{3}$$

Here,

$$\Delta\overline{V} = 0.5V^\phi(CdCl_2) - t_+V^\phi(KCl) - 0.5V_m(Cd), \tag{4}$$

and κ° and κ are the solvent and solution conductivities, and V^ϕ and V_m are the apparent molar volume and the molar volume, respectively. The volume correction term is small for dilute solution, so it was neglected.

Estimation of the Experimental Error. From Eq. 2, an estimate can be made of the magnitude of the error. The concentration may be affected through possible contamination with the high pressure system. The volume between probe electrodes, V, was determined within 0.1%. The error for the resistance measurements due to diffusion was about 0.08%. The variation of the current for a given run was within 0.01%. The slope of the resistance *versus* time curve had an error of about 0.05%, when approximately ten points were used for determining the slope. Considering these possible errors in the determined parameters, the transference number given by our measurements should be accurate within 0.3%.

Results and Discussion

Transference numbers obtained are listed in Table 1. The present results at 1 atm are compared with those by other workers.[16–19] As shown in Fig. 3, above 10 mol% our results are higher by 0.8% than those by Erdey-Grúz and Majthényi[16] and lower by 0.8% than those by Fratiello and Kay,[18] and Esteso and Grandoso.[19]

As can be seen in Fig. 4, t_+ has a maximum around 10—15 mol% at all the pressures studied. The solvent composition where t_+ exhibits a maximum slightly shifts to the ethanol-rich region with increasing pressure. In water and aqueous mixtures below 20 mol%, t_+ at the definite solvent decreases with increasing pressure. The decreasing rate becomes smaller as the ethanol content increases, and the tendency is reversed finally at 30 mol%. Since transference numbers for K^+ ion in KCl solutions are close to 0.5, there is very little concentration dependence.[20] In the present discussion, we assume that the variation of t_+ with solvent composition and pressure is equal to that at infinite dilution, t_+°.

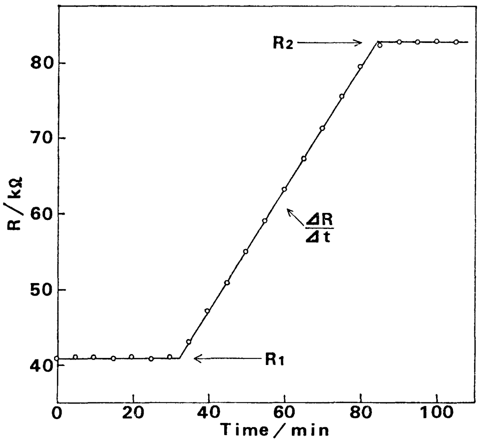

Fig. 2. A typical plot of resistance against time. 5 mol%, 25 °C, 500 kg cm^{-2}.

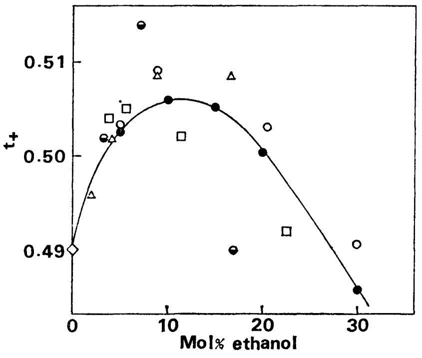

Fig. 3. Variation of the transference number for K^+ ion with mol% of ethanol at 1 atm and 25 °C. ●: Present work, □: Ref. 16, ◓: Ref. 17, ○: Ref. 18, △: Ref. 19, ◇: Ref. 13.

Table 1. Cation transference numbers for 0.02 mol dm^{-3} KCl in ethanol-water mixtures at 25 °C under pressure

p	Mol% of ethanol					
kg cm^{-2}	0	5	10	15	20	30
1	0.4901[a]	0.5025(4)[b]	0.5060(7)	0.5052(6)	0.5004(5)	0.4856(5)
500	0.4859(5)	0.4983(8)	0.5034(4)	0.5034(5)	0.4992(8)	0.4869(7)
1000	0.4809(5)	0.4951(7)	0.5020(5)	0.5023(6)	0.4984(6)	0.4875(6)
1500	0.4785(5)	0.4918(5)	0.5001(6)	0.5014(7)	0.4979(7)	0.4889(7)

a) Ref. 13. b) The numbers in parentheses are 10^4 times the standard deviation of repeated runs.

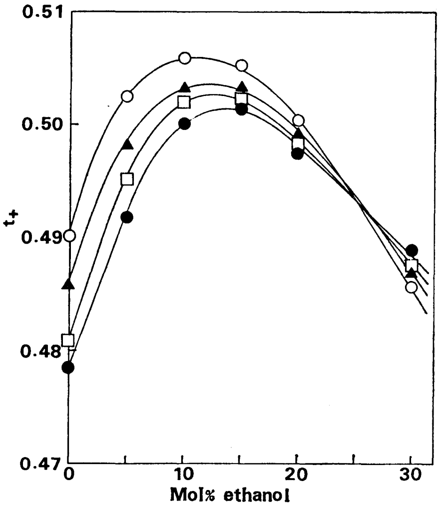

Fig. 4. Variation of the transference number for K$^+$ ion with mol% of ethanol at various pressures. ○: 1 atm, ▲: 500 kg cm^{-2}, □: 1000 kg cm^{-2}, ●: 1500 kg cm^{-2}.

To investigate the variation of the transference number with solvent composition, the experimental results are compared with the Zwanzig dielectric friction theory,[9] which is based on a continuum model for solvent. It is expressed by Eq. 5 for the slipping case:

$$\lambda_i^\circ = \frac{eF}{\eta(4\pi r_i + \phi r_i^{-3})}, \tag{5}$$

where,

$$\phi = \frac{3}{4}\left(\frac{e^2\tau}{\eta}\right)\frac{(\varepsilon_0 - \varepsilon_\infty)}{\varepsilon_0(2\varepsilon_0 + 1)}. \tag{6}$$

Here, λ_i°, r_i, e, η, τ, ε_0, and ε_∞ are the molar conductance of the monovalent ion at infinite dilution, the radius of the ion, the protonic charge, the solvent viscosity, the solvent dielectric relaxation time, the low and the infinite frequency dielectric constants, respectively. From the definition,

$$t_+^\circ = \frac{\lambda^\circ(K^+)}{\lambda^\circ(K^+) + \lambda^\circ(Cl^-)}. \tag{7}$$

Examination of Eqs. 5 and 7 shows that t_+° decreases with increasing ϕ, if r_i is taken to be the crystallographic radius of the ion.[21] By using the values of τ,[22] ε_0,[23] and η[24] at 0-, 20-, and 30-mol% at 1 atm, and with the assumption that ε_∞ is equal to that of water,[25] the calculated value of ϕ in Eq. 6 is shown to increase with increasing ethanol content. That is, t_+° should decrease with increasing ethanol content, which does not agree with the experimental results seen in Fig. 4. Kay *et al.*[26] also pointed out that the initial increase in ionic Walden products with ethanol content can not be explained qualitatively by the Zwanzig theory. Therefore, it is necessary to consider specific interactions between the ions and solvent.

As is reviewed by Franks and Ives,[7] the addition of ethanol to water initially increases the degree of structure of the solvent and then decreases it. From a wide variety of thermodynamic and transport data, both K$^+$ and Cl$^-$ ions are classified as structure breakers in hydrogen-bonded solvents. If the structure-breaking effect of K$^+$ ion is larger than that of Cl$^-$ ion, the structural excess mobility of K$^+$ ion is greater than that of Cl$^-$ ion.[27] The effect is more pronounced in more highly structured solvents. Since the degree of structure of the aqueous mixtures is enhanced in the water-rich region containing up to about 10 mol%, the mobility of K$^+$ ion becomes progressively faster with respect to Cl$^-$ ion. The initial increase in t_+ obtained with increasing ethanol content would be primarily ascribed to the relative structure-breaking properties of these two ions.

Zwanzig theory can not also account for the pressure dependence of the transference number in water. With the values of ε_0[28] and η,[29] and with the assumption that the pressure dependence of τ at 20 °C[30] is equal to that at 25 °C and ε_∞ is invariant under compression, ϕ in Eq. 6 is shown to decrease with increasing pressure. That is, t_+° in Eq. 7 should increase with increasing pressure, which is in contradiction to the experimental results.

To interpret the pressure dependence of the transference number in water, the effect of pressure to break the water structure may be taken into consideration.[4] As pressure weakens the hydrogen bonds and decreases the degree of structure of water, the structural excess mobility of K$^+$ ions may decrease relatively more than that of Cl$^-$ ions with increasing pressure. Consequently, the cation transference number may decrease with increasing pressure. In the mixed solvents containing a small amount of ethanol, the decreasing rate of the cation transference number is expected to be larger than in pure water. However, this is not in conformity with the experimental results. Other specific interactions between the ions and solvent must be considered.

The orientation of solvent molecules around the negative ion, Cl$^-$, may be different from that around the positive ion, K$^+$. The ion-solvent interaction of K$^+$ ion is mostly dominated by the ion-dipole interaction, while that of Cl$^-$ ion involves the additional contribution of hydrogen bonds.[31] The hydrogen bonds between water molecules and Cl$^-$ ions may be broken down by pressure, and the degree of the hydration of Cl$^-$ ion may decrease slightly with increasing pressure. The decrease of the cation transference number in water with increasing pressure was ascribed to this pressure effect.[5] Water molecules in alcohol–water mixtures are more basic than in pure water.[32] The contribution of hydrogen bonds between water molecules and Cl$^-$ ion would be smaller in ethanol–water mixtures than in pure water. Therefore, the decreasing tendency of the cation transference number with pressure would become weaker with an increase in ethanol content. At 30 mol%, the specific interaction between water molecules and Cl$^-$ ions would be insignificant.

Further conductivity measurements for KCl and various electrolytes at high pressure will reveal the ion-solvent interactions more thoroughly.

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