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Pressure Effect on Proton Jumps in *t*-Butyl Alcohol–Water Mixtures at 25 °C

Masakatsu Ueno,* Kazuhito Matsukawa, Noriaki Tsuchihashi, and Kiyoshi Shimizu
Department of Applied Chemistry, Faculty of Engineering, Doshisha University,
Karasuma Imadegawa, Kamigyo-ku, Kyoto 602

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The limiting molar conductances, $\Lambda°$, of hydrochloric acid and potassium chloride in 2,3,5,7,10, and 25 mol% *t*-butyl alcohol (TBA)–water mixtures 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 within a dilute concentration range. In each solvent mixture the value of $\Lambda°$(HCl) was about three- to five-times larger than that of $\Lambda°$(KCl). The anomalous excess proton conductance, $\lambda°_E$, as estimated by the equation [$\lambda°_E=\Lambda°(\text{HCl})-\Lambda°(\text{KCl})$], was found to increase with increasing pressure in 2,3,5,and 7 mol% TBA–water mixtures, but to decrease in 10 and 25 mol% TBA–water mixtures. The rate of increase with pressure of the excess proton conductance normalized to the molar concentration of water in the mixture was largest in a 2 mol% TBA mixture, and its magnitude decreased in the order: 2>3>0>5≫7≫10≫25 mol% of TBA. These results are compared with those obtained in ethanol–water mixtures and are discussed in relation to the effect of alcohol molecules on the water structure in the mixtures: the three-dimensional network of water in TBA–water mixtures is more stable at a lower mol% of alcohol, and collapses more rapidly with increasing alcohol content than in ethanol–water mixtures.

The proton is much more useful than any other ion for dynamic studies of the structure of water; this is because the reorientation of water molecules has been considered to be the rate-determining step in the proton-jump mechanism.[1,2] The structure of water is dominated by the directional attractive intermolecular potential and is sensitive to any change in the pressure and/or temperature. An X-ray study on the effect of pressure on the structures of both light and heavy water,[3] as well as molecular dynamic simulation studies on liquid water under high compression,[4–6] shows that the hydrogen bonds in water become distorted at high pressure. The distortion of hydrogen bonds accelerates the rotation of water molecules. In accordance with the pressure effect on the reorientation of water molecules,[7,8] the excess proton conductance, $\lambda°_E$, due to proton jumping increases with increasing pressure; the rate of increasing $\lambda°_E$ with pressure becomes more prominent at lower temperature.[9] That is, the more significant is the water structure at atmospheric pressure, the larger is the pressure effect on $\lambda°_E$.[2] In a previous study,[10] this relation was tested in ethanol–water mixtures; it has been confirmed that a small addition of ethanol to water stabilizes the three-dimensional network of water. In the present work we extend this to *t*-butyl alcohol (TBA)–water mixtures.

The thermodynamic properties of TBA–water mixtures have been studied in order to elucidate the nature of hydrophobic hydration; thermodynamic data indicate that TBA is one of the most powerful structure makers in the water-rich region.[11–14] In addition to the unique effect of TBA molecules on the structure of water, the self-association of TBA molecules in water has been suggested to account for the following phenomena: an excess heat capacity maximum,[15] a large ultrasonic absorption,[16] a remarkable increase in light scattering,[17] and anomalies in the reaction rate[18,19] in TBA–water mixtures in a composition range of 3—5 mol% of TBA. Computer experiments have also shown the promotion of the water structure and the self-association of TBA molecules due to a hydrophobic interaction in a 3 mol% TBA–water mixture.[20] Therefore, it is considered that the water structure in these mixtures changes drastically in the dilute solution region. It was the purpose of the present study to examine whether the pressure dependence of the excess proton conductance sensitively reflects the above-mentioned anomalies or not, and whether excess proton conductance is a good measure of the structure of water.

Experimental

Conductivity water was prepared by passing distilled water through an ion-exchange resin; its conductivity was about 1.0×10^{-6} S cm^{-1} at 25 °C and 1 atm. *t*-Butyl alcohol (TBA) of guaranteed reagent obtained from Nacalai Tesque was used without further purification, and showed a water content of less than 0.2 wt% in the Karl Fischer test (MK-AII type, Kyoto Electronics MFG Co., Ltd.). Hydrochloric acid and potassium chloride of high quality were supplied from Merck. The latter was dried above 130 °C prior to use. Aqueous stock solutions of KCl [2×10^{-2} M (1 M=1 mol dm^{-3})] were made up using measuring flasks; those of HCl (ca. 1×10^{-2} M) were prepared by diluting concentrated HCl with conductivity water. Accurate concentrations of HCl stock solutions were determined by measuring the conductances of the solutions and by using the empirical equation of conductance for a HCl solution proposed by Shedlovsky.[21] All of the dilute solutions of HCl and KCl were prepared gravimetrically by diluting stock solutions of HCl and KCl with conductivity water and TBA. The concentrations of the dilute solutions at each pressure were determined by using the densities of the aqueous stock solutions at atmospheric pressure and those of the dilute solutions at each pressure, as described below. The densities of the stock solutions were calculated for HCl using Eq. 1 in Ref. 10 and for KCl using Eq. 1 with a standard deviation of 5×10^{-6} g cm^{-3}, which can be expressed by

$$\rho(\mathrm{KCl/H_2O}) = 0.9970_5 + 0.046_9 m. \tag{1}$$

Here, ρ is the density in g cm^{-3} and m is the concentration in mol (kg H_2O)$^{-1}$. Equation 1 was obtained from measurements in the range m=0.01—0.1 mol (kg H_2O)$^{-1}$ at 25 °C and 1 atm by means of a digital vibrating densimeter (SS-D-200 twin type, the Shibayama Scientific Co., Ltd.). On the other hand, the densities of the dilute solutions at each pressure were assumed to be equal to those of the solvent mixtures at each pressure because the measured solutions were dilute. All solutions of HCl were treated in a dry box under a nitrogen atmosphere.

Table 1 summarizes the physical properties of the TBA–water mixtures used in this work, such as the density (ρ), viscosity (η), dielectric constant (ε), molar concentration of water in the mixture [$c(H_2O)$], and the observed solvent conductivity (κ).

An acid-proof Teflon cell and a glass cell were employed, respectively, for HCl and KCl solutions. The procedure and apparatus used here for conductance measurements at high pressure were the same as those in previous studies.[10,22] The molar conductances, Λ, obtained by subtrating the solvent conductivity were reproducible within ±0.1%. When ions were not associated, the Fuoss–Onsager equation of conductance[23,24] was used to determine the limiting molar

Table 1. Properties of *t*-Butyl Alcohol–Water Mixtures at 25 °C under High Pressure

P	$\rho^{a)}$	$\eta^{b)}$	$\varepsilon^{c)}$	$c(H_2O)$	$10^6\,\kappa$
kgf cm^{-2}	g cm^{-3}	cP		mol dm^{-3}	S cm^{-1}
		2 mol% of *t*-Butyl Alcohol			
1	0.9849	1.315	73.3	50.44	1.0
500	1.0035	1.336	75.0	51.39	1.3
1000	1.0209	1.362	76.5	52.28	1.5
1500	1.0373	1.393	77.9	53.12	1.8
2000	1.0528	1.423	79.3	53.91	2.1
		3 mol% of *t*-Butyl Alcohol			
1	0.9801	1.575	70.8	48.26	0.9
500	0.9989	1.624	72.6	49.19	1.1
1000	1.0160	1.674	74.2	50.03	1.3
1500	1.0318	1.728	75.7	50.81	1.5
2000	1.0465	1.778	77.1	51.51	1.7
		5 mol% of *t*-Butyl Alcohol			
1	0.9707	2.130	65.8	44.29	0.8
500	0.9892	2.227	67.7	45.14	1.0
1000	1.0059	2.309	69.4	45.90	1.2
1500	1.0211	2.377	70.9	46.59	1.4
2000	1.0351	2.430	72.3	47.23	1.6
		7 mol% of *t*-Butyl Alcohol			
1	0.9593	2.610	60.8	40.66	0.6
500	0.9790	2.848	62.8	41.49	0.6
1000	0.9962	3.080	64.5	42.22	0.7
1500	1.0116	3.307	66.0	42.88	0.8
2000	1.0256	3.529	67.3	43.47	0.9
		10 mol% of *t*-Butyl Alcohol			
1	0.9417	3.219	53.6	35.87	0.4
500	0.9631	3.688	55.8	36.69	0.4
1000	0.9813	4.193	57.7	37.38	0.5
1500	0.9972	4.684	59.3	37.99	0.5
2000	1.0113	5.189	60.7	38.52	0.6
		25 mol% of *t*-Butyl Alcohol			
1	0.8801	4.805	31.0	20.60	0.1
500	0.9059	6.488	33.4	21.20	0.1
1000	0.9268	8.418	35.3	21.69	0.1
1500	0.9443	10.53	36.9	22.10	0.1
2000	0.9596	12.87	38.4	22.46	0.1

a) H. Kubota, Y. Tanaka, and T. Makita, *Int. J. Thermophys.*, **8**, 47 (1987). b) Ref. 28 for 1 atm and Y. Tanaka, Y. Matsuda, H. Fujiwara, H. Kubota, and T. Makita, *Int. J. Thermophys.*, **8**, 147 (1987) for high pressure. c) Ref. 28 for 1 atm and T. Moriyoshi, T. Ishii, Y. Tamai, and M. Tado, *J. Chem. Eng. Data*, **35**, 17 (1990) for high pressure.

conductance Λ°:

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

where c is the molar concentration (M), and S, E, and J have their usual meanings. In the presence of ion pairs, data analysis using Eq. 2 gave a very low value of the ion-size parameter, $\mathring{a}$, involved in J. In this case, the Shedlovsky equation[25] was employed,

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

where

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

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

and

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

Here, $f_\pm$ is the mean activity coefficient, as determined by the Debye–Hückel limiting law, and T is the absolute temperature.

Results and Discussion

The molar conductances, Λ, of HCl and KCl in TBA–water mixtures up to 25 mol% of TBA were measured at five different concentrations in the range $(0.6\text{—}5.0)\times10^{-3}$ M for HCl and $(0.4\text{—}1.6)\times10^{-3}$ M for KCl at 25 °C as a function of the pressure up to 2000 kgf cm^{-2}.[26] The data for Λ were analyzed with Eq. 2 or 3 to obtain the limiting molar conductances, Λ°, at each solvent and pressure. The results are shown in Table 2 together with the related parameters. Although HCl was completely dissociated in all of the

Table 2. Limiting Molar Conductances (Λ°/S cm^2 mol^{-1}), Ion-Size Parameters ($\mathring{a}$/Å), Association Constants (K_A/mol^{-1} dm^3), and Standard Deviation of Λ (σ_Λ/S cm^2 mol^{-1}) of HCl and KCl in t-Butyl Alcohol–Water Mixtures as a Function of the Pressure at 25 °C

P/kgf cm^{-2}	Λ° (HCl)	$\mathring{a}$	σ_Λ	Λ° (KCl)	$\mathring{a}$	K_A	σ_Λ
			2 mol% of t-Butyl Alcohol				
1	339.3	2.8	0.11	110.0	0.7		0.02
500	350.4	4.6	0.25	110.7	0.7		0.09
1000	356.5	3.8	0.26	110.6	2.0		0.07
1500	362.3	4.3	0.10	110.2	5.2		0.10
2000	365.6	5.0	0.24	108.7	1.2		0.11
			3 mol% of t-Butyl Alcohol				
1	304.2	1.0	0.39	96.44	0.9		0.05
500	311.8	1.1	0.40	96.28	2.1		0.08
1000	317.6	1.3	0.44	95.89	2.0		0.01
1500	322.0	2.0	0.46	95.02	3.8		0.02
2000	324.8	2.6	0.44	93.88	7.1		0.02
			5 mol% of t-Butyl Alcohol				
1	245.3	2.8	0.16	76.73		6.3	0.002
500	249.3	2.2	0.36	74.31		5.5	0.07
1000	251.2	3.3	0.38	72.46		5.3	0.08
1500	252.8	4.8	0.54	70.45		3.2	0.05
2000	253.9	5.0	0.44	68.49	1.5		0.06
			7 mol% of t-Butyl Alcohol				
1	211.3	1.7	0.15	65.22		10.1	0.02
500	209.3	1.6	0.14	61.31		10.0	0.07
1000	207.5	1.8	0.13	57.93		9.8	0.07
1500	206.2	1.7	0.06	54.92		9.7	0.08
2000	204.6	3.7	0.26	51.78		2.6	0.05
			10 mol% of t-Butyl Alcohol				
1	170.4	3.5	0.07	53.77		14.1	0.05
500	164.9	5.9	0.14	49.03		9.1	0.12
1000	160.0	7.8	0.22	44.90		7.9	0.08
1500	155.5	8.4	0.11	41.34		7.1	0.07
2000	151.5	7.8	0.37	38.20		5.7	0.06
			25 mol% of t-Butyl Alcohol				
1	76.40	3.9	0.09	26.32		30.5	0.002
500	70.54	4.0	0.06	22.81		27.0	0.04
1000	65.31	3.5	0.10	19.77		21.8	0.04
1500	60.62	4.5	0.14	17.26		19.6	0.05
2000	56.07	3.6	0.16	15.04		16.3	0.04

solutions studied, KCl was slightly associated in TBA–water mixtures containing above 5 mol% of TBA. The obtained values of Λ° at 1 atm were larger on the average by 1.4% for HCl and by 0.4% for KCl than those estimated by interpolation of literature data.[27,28] No high-pressure data are available for a comparison.

As shown in Table 2, the value of Λ°(HCl) is three- to five-times larger than that of Λ°(KCl) in each solvent mixture studied. Furthermore, while Λ°(KCl) in each mixture, except for 2 mol% of TBA, decreases with increasing pressure in accordance with the variation of the solvent fluidity ($1/\eta$) with pressure, Λ°(HCl) increases with increasing pressure in 2,3,and 5 mol% TBA–water mixtures. These results indicate that a special mechanism called "proton jump" plays an important role in TBA–water mixtures.

So far, no exact way to exclusively measure the anomalous excess proton conductance, λ°_E, due to proton jumping has been invented, and an empirical method is often used. The quantity

$$\lambda^\circ_E = \lambda^\circ(H^+) - \lambda^\circ(K^+) = \Lambda^\circ(HCl) - \Lambda^\circ(KCl) \qquad (7)$$

is taken here as being a measure of the anomalous conductance. Although Li^+ and Na^+ ions are chosen elsewhere,[1,29] instead of the K^+ ion, as a measure of the translational mobility of a proton (i.e., the oxonium ion, H_3O^+), the K^+ ion is more appropriate because its ionic size is closer to that of the H_3O^+ ion than are the smaller ions. The values of λ°_E, thus obtained, are listed in Table 3.[30]

The distribution of the protons between water and alcohol molecules for the reaction

$$ROH_2^+ + H_2O \rightleftharpoons ROH + H_3O^+ \qquad (8)$$

has been examined in the alcohol-rich region by the conductivity method.[31] The equilibrium constants for the reaction $K=c(ROH)c(H_3O^+)/c(ROH_2^+)c(H_2O)$, where $c(i)$ is the concentration of the species i in M, are 139 for methanol, 250 for ethanol, 392 for 1-propanol, 765 for 1-butanol, and 1130 for isobutyl alcohol. Assuming that the value of K does not differ so much among isomers, we can estimate the percentage of protons present as $(CH_3)_3COH_2^+$ to be about (0.03—0.04)%, even in a 25 mol% TBA–water mixture. It is therefore reasonable to consider that almost all of the protons were present as H_3O^+ in the TBA–water mixtures studied here, and were transferred from the oxonium ions to adjacent water molecules. Thus, we can regard that the excess proton conductance reflects a variation of the rotational mobility of water molecules in hydrogen-bond networks with the alcohol content and/or pressure.

As shown in Table 3, the value of λ°_E, itself, decreases markedly with an increase in the TBA content at each pressure. One of the main factors for the decrease in λ°_E with an increase in the TBA content would be a decrease in the concentration of water in a solvent mixture. That is, the fraction of water molecules adjacent to the H_3O^+ ion decreases with an increase in the TBA content and, consequently, the

Table 3. Excess Proton Conductances (λ°_E/S cm^2 mol^{-1}), Excess Proton Conductances Normalized to the Molar Concentration of Water {[$\lambda^\circ_E/c(H_2O)$]/10^3 S cm^5 mol^{-2}}, and the Ratios of $R=[\lambda^{\circ(P)}/c(H_2O)^{(P)}]/[\lambda^{\circ(1)}/c(H_2O)^{(1)}]$ in *t*-Butyl Alcohol-Water Mixtures as a Function of the Pressure at 25 °C

P/kgf cm^{-2}	λ°_E	$\lambda^\circ_E/c(H_2O)$	R
	Water[a]		
1	276.3	4.993	1.000
500	286.5	5.070	1.015
1000	294.5	5.116	1.025
1500	301.6	5.152	1.032
2000	307.4	5.172	1.036
	2 mol% of *t*-Butyl Alcohol		
1	229.3	4.546	1.000
500	239.7	4.664	1.026
1000	245.9	4.704	1.035
1500	252.1	4.746	1.044
2000	256.9	4.765	1.048
	3 mol% of *t*-Butyl Alcohol		
1	207.8	4.306	1.000
500	215..5	4.381	1.017
1000	221.7	4.431	1.029
1500	227.0	4.468	1.038
2000	230.8	4.479	1.040
	5 mol% of *t*-Butyl Alcohol		
1	168.6	3.807	1.000
500	175.0	3.877	1.018
1000	178.7	3.893	1.023
1500	182.3	3.913	1.028
2000	185.4	3.925	1.031
	7 mol% of *t*-Butyl Alcohol		
1	146.1	3.593	1.000
500	148.0	3.567	0.993
1000	149.6	3.543	0.986
1500	151.3	3.528	0.982
2000	152.8	3.515	0.978
	10 mol% of *t*-Butyl Alcohol		
1	116.6	3.251	1.000
500	115.9	3.159	0.972
1000	115.1	3.079	0.947
1500	114.2	3.006	0.925
2000	113.3	2.941	0.905
	25 mol% of *t*-Butyl Alcohol		
1	50.08	2.431	1.000
500	47.73	2.251	0.926
1000	45.54	2.100	0.864
1500	43.36	1.962	0.807
2000	41.03	1.827	0.752

a) Ref. 10.

frequency of the proton transfer from the H_3O^+ ion to the water molecules diminishes with an increase in the TBA content. Therefore, to evaluate the contribution of water in the mixture to $\lambda^\circ{}_E$, the values of $\lambda^\circ{}_E$ normalized to the molar concentration of water in the mixture, i.e., $\lambda^\circ{}_E/c(H_2O)$, were calculated and are shown in Fig. 1 together with the values for those in ethanol–water mixtures.[32] Figure 1 shows that the value of $\lambda^\circ{}_E/c(H_2O)$ decreases with an increase in the alcohol content, and that the rate of decrease with the alcohol content is larger in TBA–water mixtures than in ethanol–water mixtures. If the contribution of water in the mixture to $\lambda^\circ{}_E$ were the same as that in pure water, $\lambda^\circ{}_E/c(H_2O)$ would not depend on the alcohol content. Thus, to explain the decrease in $\lambda^\circ{}_E$ with an increase in the alcohol content, another factor must be considered in addition to a decrease in the concentration of water in the mixture: the reorientation of water molecules adjacent to the H_3O^+ ion, which is the rate-determining step in the proton-jump mechanism,[1] becomes slower with an increase in the alcohol content, as suggested by the dielectric relaxation time measured in ethanol–water mixtures at 25 °C and 1 atm,[33] and the reorientational correlation time may be longer in TBA–water mixtures than in ethanol–water mixtures because of the higher viscosity of TBA–water mixtures.

In a previous study,[10] the excess proton conductance normalized to its value at 1 atm, $\lambda^\circ{}_E{}^{(p)}/\lambda^\circ{}_E{}^{(1)}$, were examined 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. It is more appropriate, however, to take into consideration the change in the concentration of water at high pressure and to examine the pressure dependence of $R=[\lambda^\circ{}_E{}^{(p)}/c(H_2O)^{(p)}]/[\lambda^\circ{}_E{}^{(1)}/c(H_2O)^{(1)}]$ for the purpose mentioned above, since the concentration of water affects $\lambda^\circ{}_E$ considerably. As shown in Fig. 2, R increases with increasing pressure in (0—5) mol% of TBA, but decreases in above 7 mol% of TBA. These results suggest that the rotation of water molecules adjacent to the H_3O^+ ion is accelerated by pressure in mixtures up to 5 mol% of TBA as well as in pure water, but is retarded in mixtures above 7 mol% of TBA. Figure 2 also shows that the rate of an increase in R with pressure is largest in a 2 mol% TBA–water mixture, and that its magnitude decreases in the order: 2>3>0>5≫7≫10≫25 mol% of TBA.[34] It is shown from studies on $\lambda^\circ{}_E$ in pure water[2,9] that the increase in R with pressure becomes larger with a decrease in temperature. Therefore, the pressure dependence of R is considered to be closely related to the stability of the

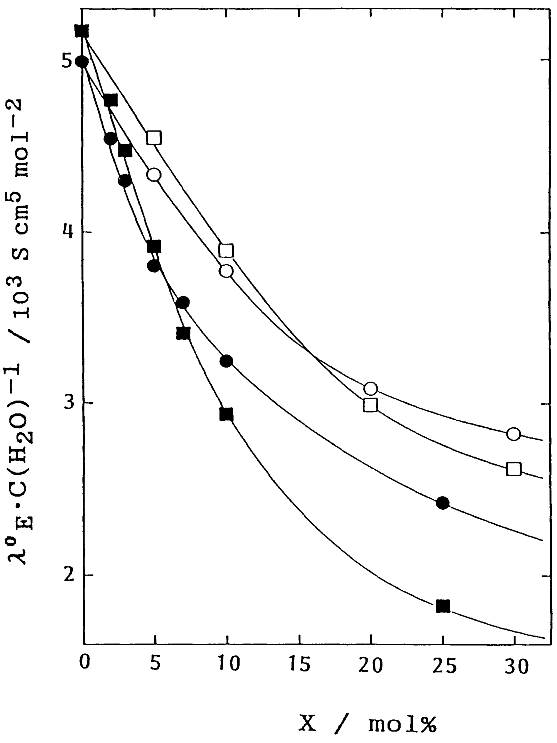

Fig. 1. Variation of the excess proton conductance normalized to the molar concentration of water with *t*-butyl alcohol and ethanol content at 1 and 2000 kgf cm^{-2}. *t*-Butyl alcohol (●: 1, ■: 2000 kgf cm^{-2}); ethanol (○: 1, □: 2000 kgf cm^{-2}).

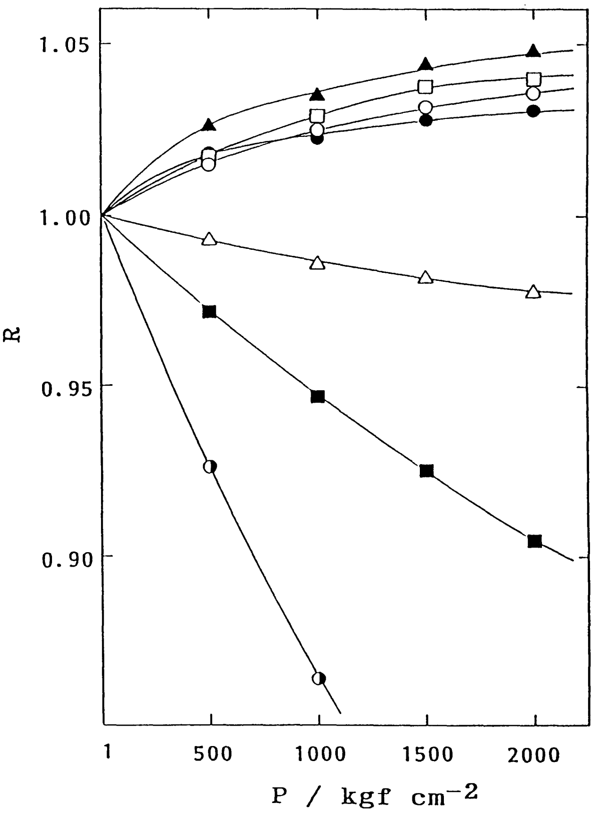

Fig. 2. Ratios of $\lambda^0{}_E/c(H_2O)$ at pressure P to that at 1 atm as a function of the pressure. ○: Water, ▲: 2 mol%, □: 3 mol%, ●: 5 mol%, △: 7 mol%, ■: 10 mol%, ◑: 25 mol% of *t*-butyl alcohol.

water structure: the more stable are the hydrogen bonds between water molecules at atmospheric pressure, the more prominent is the pressure effect on R. If this finding is applied to the results found for TBA–water mixtures, we can draw a conclusion that below 3 mol% of TBA the three-dimensional network of water is stabilized by the addition of TBA to water due to hydrophobic hydration around the *t*-butyl group. However, a large increase in the TBA content begins to make it difficult to form stable hydrogen bonds between water molecules, as can be seen in 7, 10, and 25 mol% TBA–water mixtures: R decreases with increasing pressure. Computer simulations[20,35] have shown the stabilization and promotion of the water structure by TBA molecules in a 3 mol% TBA–water mixture as well as an infinitely dilute aqueous solution, and at the same time the association of TBA molecules due to the hydrophobic interaction in a 3 mol% TBA–water mixture. This kind of association is promoted with an increase in the TBA content; the structural stabilization of water due to hydrophobic hydration rapidly decreases because TBA–water interactions are replaced by TBA–TBA interactions.

According to a previous study on proton jumping in ethanol–water mixtures at high pressure,[10] it was disclosed that the rate of increase in R with pressure is most prominent in a 5 mol% ethanol–water mixture.[32] Apparently, the rate of increase in R with pressure becomes maximum at a lower mol% of alcohol, and decreases more rapidly with an increase in the alcohol content in TBA–water mixtures than in ethanol–water mixtures. These trends are consistent with those observed regarding such properties of alcohol–water mixtures as the partial molar volumes of alcohols,[12] the temperature of maximum density,[13] and the velocity of sound.[36] The present results therefore indicate that the three-dimensional network of water in TBA–water mixtures is more stable at a lower mol% of alcohol and begins to collapse more rapidly with increasing alcohol content than in ethanol–water mixtures, since the association of alcohol molecules due to the hydrophobic interaction occurs at a lower mol% of alcohol with an increase in the surface area of the alkyl group.

Conclusions

The present experimental study has disclosed that the pressure effect on the excess proton conductance normalized to the molar concentration of water, $\lambda^{\circ}{}_{\mathrm{E}}/c(\mathrm{H_2O})$, drastically changes with the alcohol content in TBA–water mixtures in comparison with ethanol–water mixtures. $\lambda^{\circ}{}_{\mathrm{E}}/c(\mathrm{H_2O})$ in 2 and 3 mol% TBA–water mixtures increases with increasing pressure at a larger rate than that in pure water. However, the rate of increase in $\lambda^{\circ}{}_{\mathrm{E}}/c(\mathrm{H_2O})$ with pressure decreases with an increase in the alcohol content, and in mixtures above 7 mol% TBA–water $\lambda^{\circ}{}_{\mathrm{E}}/c(\mathrm{H_2O})$ decreases with increasing pressure, in contrast to the finding that $\lambda^{\circ}{}_{\mathrm{E}}/c(\mathrm{H_2O})$ increases with pressure in ethanol–water mixtures up to at least 10 mol% of ethanol. In conclusion, these results reflect a difference in the stability of hydrogen bonds between water molecules in these mixtures at atmospheric pressure; the variation of $\lambda^{\circ}{}_{\mathrm{E}}/c(\mathrm{H_2O})$ with pressure becomes a good measure of the stability of the water structure at atmospheric pressure.

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