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The Ion-Solvent Interactions and Ionic Associations in Solvent Mixtures. 1. The Conductances of Potassium Halides and the Behaviovrns of Ions in n-Propanol-Water Mixtures at 25°C.

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## The Ion-Solvent Interactions and Ionic Associations in Solvent Mixtures. I. The Conductances of Potassium Halides and the Behaviours of Ions in n-Propanol-Water Mixtures at 25°C.

Yosei UEHARA\* and Tsugumasa MORIYAMA\*

### Abstract

The equivalent conductances of KCl, KBr, and KI were measured in n-PrOH-Water mixtures at 25°C. The conductances of these electrolytes increase with the crystalgraphic radii of anions, which are expected from electrostatistical explanation. The concentration effect on the conductance appears to change with the change of composition of the alcohol in solvent mixtures. The association constant  $K$ , the ion-size parameter  $\bar{a}$ , and the limiting equivalent conductance  $\Lambda_0$  were calculated by using the conductance equations. The results have been discussed comparing with the data in water, methanol-water, and ethanol-water.  $\bar{a}$  and  $K$  show the tendency to increase with the size of alcohols in solvent mixtures. The ion-size parameter (solvation radii)  $r_h$  were also calculated by Walden's rule. This gives considerable lower values than  $\bar{a}$ .

### I. INTRODUCTION

The effects of the ions and the solvents on the association constant for the formation of electrostatic ion pairs in nonaqueous solvents or solvent mixtures have been studied by many workers.<sup>1),8)</sup> Especially in the solvents of low dielectric constant, the behaviors of the ionic association of large molecules like tetraalkylammonium salts have been investigated extensively.<sup>4),8)</sup> But a theoretical interpretation of the properties of electrolytic solution in terms of molecular parameters is still in process of development. In the conductance equation derived by Fuoss, et.al.<sup>9)</sup>, however, considerable success has been obtained by using very much oversimplified model, the sphere in continuum, in which ions are represented as rigid charged spheres in a continuous medium which is described electrostatistically by the macroscopic dielectric constant and hydrodynamically by the macroscopic viscosity. With this model, the only interaction which may be considered is that between ions; a continuum, by definition, is without structure and the model therefore excludes ion-solvent interactions.

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Dept. of Chemistry, Sci. & Eng. Div., Univ. of the Ryukyus

The latter includes several distinct types, as well as their combinations. The most extreme interaction between ion-solvent interactions is the formation of complex ions, which, of course, includes solvates. Even if stoichiometric compounds are not formed, there will always be an electrostatic interaction between the fields of solvent dipoles and ions. In the case of hydrogenbonded solvents, the resulting solvent structure can in some cases be reinforced by the presence of ions and in other cases will be destroyed. It should be emphasized that all of these short-range interactions depend on the structure of the solvent and are specifically dependent on shape, size, and charge distribution of the solvent molecules, as well as on the corresponding properties of the ions. It is clear that a continuum model neglects all of these important details and necessarily shows their effect into the ion-size parameter. So, for example, it has been found that the same electrolyte in isodielectric solvents of different chemical composition gives different values for the contact distance and for the association constant.<sup>6), 7)</sup> In a general way, it has been found that the larger the ions are, the better will the simple theory account for the experimental results. This is, of course, about what one would expect; as the ions become larger, the solvent approaches more and more the continuum of the ideal model from the point of view of the ions. That is the reason why most of the works for the ionic association have been published so far have dealt with tetraalkylammonium salts in solvents or solvent mixtures. In the case of electrolytes with small ions, such as the alkali halides in mixtures containing water, specific ion-solvent interactions have been observed. As mentioned above already, the ion-solvent interactions are affected not only by the natures of ions and solvents, but also by the fine structural changes of solvents. Especially in solvent mixtures, various types of solvent can be obtained. Therefore, it is very difficult to generalize the ion-solvent interactions. It is, however, worth to study how the conductance equation derived by Fuoss, et.al.<sup>9)</sup> evaluates the behaviors of ions against the changes of ion-solvent interactions, including the structural changes of solvents. That will be evaluated more in detail by discussing together with the data from photochemical measurements.

In this paper which is the first of the series, in order to investigate how a solvent structure affects on the ion-solvent interaction, we used the potassium halides for electrolytes which are the most popular salts and n-propanol-water mixtures for solvents which are well ordering solvents with the hydrogen bond. The use of potassium halides make us possible to compare our results to various data in various kinds of solvents, and the use of alcohol-water mixtures permits us to make the solvent with arbitrary dielectric constant.

In alcohol-water mixtures, it has been reported that some characteristic physical phenomena have been observed at the specific component of alcohols.<sup>2), 8), 10)</sup> Such phenomena will be expected to depend on the structural change of the solvent, i.e., the nature of the hydrogen bond. In the system of propanol-water mixtures, however, available data have not been sufficient to study the ion-solvent interaction or the

ionic association from the point of view of the solvent structure. In this paper, the behaviors of the ions at alcohol-rich region of propanol-water mixtures at 25°C have been discussed by means of the association constant and the ion-size parameter which had been calculated from conductance equations derived by Fuoss, et.al.,<sup>(9)</sup> comparing with the data in methanol-water and in ethanol-water mixtures.

## II. EXPERIMENTAL SECTION

Reagent grade electrolytes were recrystallized from conductance water, put in a dryer for several hours at about 120°C, and cooled in a desiccator. Aqueous stock solutions were prepared for each salt.

The conductance water was prepared by redistilling the distilled water by a pyrex evaporator with NaOH and KMnO<sub>4</sub>. The middle fraction was collected and stored. The redistilled water had the specific conductances of less than 10<sup>-6</sup> mho · cm<sup>-1</sup>. Propanol was prepared by distilling reagent grade 99.5% n-propanol with anhydrous CuSO<sub>4</sub>. The middle fraction was collected and stored.

The solvent mixtures employed in the conductance measurements were individually prepared by mixing purified propanol with the aqueous solution of potassium halides which contain exactly necessary amount of salts to obtain the correct concentration. Prior to the measurements, the mixtures were put in 100ml mess-flasks and placed in the constant-temperature water bath till the temperature equilibrium was obtained. The water bath was maintained within 0.01°C by means of Beckman's thermometer. The room temperature was maintained at 25±1°C during the measurements. All measurements were carried out at 25°C. The instrument used here was TOA Electronics, CM-2A conductometer. The conductance cells which are commercially available from TOA Electronics were used. At low concentration regions CG-2001PL which has cell constant 0.950X 10<sup>-1</sup>cm<sup>-1</sup> was used, otherwise CG-201PL which has cell constant 1.015 cm<sup>-1</sup> was used. The cell constants were checked at 25°C by measuring the conductances of aqueous KCl over the concentration range, 1~10X10<sup>-3</sup>M. The cells were rinsed several times with the solvent before to use, otherwise they were soaked in distilled water.

The viscosity measurements were carried out by Ostwald viscometer. The conductance water was used as standard solution. The densities were measured by using the Weld type pycnometer. The viscosity was calculated by the equation

$$\eta_x = (t_x \rho_x / t_s \rho_s) \eta_s$$

where the symbols  $\eta$ ,  $t$ , and  $\rho$  are viscosity, time, and density respectively. The subscripts x and s designate unknown solution and the standard solution.

The Ion-Solvent Interactions and Ionic Associations in Solvent Mixtures. I. The Conductances of Potassium Halides and the Behaviours of Ions in n-Propanol-Water Mixtures at 25°C.

Table I. The equivalent conductance of KCl in n-PrOH-Water mixture at 25°C.

CX 10 <sup>4</sup> (N)	Equivalent Conductance ( $\Omega^{-1}\text{cm}^2$ )				
	19.46mole%		43.14mole%		49.15mole%
1	61.80	61.95	36.70	37.45	—
4	58.63	58.38	32.63	32.38	28.88
9	54.56	54.44	30.94	30.72	27.78
16	52.39	52.56	29.38	29.31	26.47
25	52.00	52.60	28.92	29.38	25.56
36	50.69	50.56	27.04	—	24.81
49	50.00	50.00	26.43	—	23.88
64	50.16	49.61	25.78	—	23.52
89	—	—	24.71	—	21.97
100	47.70	47.20	23.45	—	21.41

Table II. The equivalent conductance of KBr in n-PrOH-Water mixture at 25°C.

CX 10 <sup>4</sup> (N)	Equivalent Conductance ( $\Omega^{-1}\text{cm}^2$ )							
	19.46mole%		43.14 mole%			49.15 mole%(n-PrOH)		
1			36.55	36.25	36.30	33.95	34.80	34.95
4	68.88	—	32.63	32.63	33.13	31.25	31.50	31.25
9	59.28	—	31.67	31.61	31.89	29.83	29.56	30.17
16	56.44	57.50	30.78	30.41	30.72	28.88	28.66	28.88
25	—	55.20	30.30	30.38	30.18	27.96	28.00	28.00
36	53.89	54.17	28.89	28.89	29.03	26.79	26.92	27.14
49	52.86	52.76	28.37	28.67	28.67	26.32	26.33	26.22
64	51.95	52.50	28.13	27.89	28.13	25.78	25.78	25.55
89	49.38	49.38	26.74	26.58	26.58	24.27	24.61	24.49
100	48.80	49.80	26.00	25.85	26.35	23.60	23.70	23.65

Table III. The equivalent conductance of KI in n-PrOH-Water mixture at 25°C.

CX 10 <sup>4</sup> (N)	Equivalent Conductance ( $\Omega^{-1}\text{cm}^2$ )			
	43.14 mole%		49.15 mole%(n-PrOH)	
1	36.25	36.65	34.50	34.80
4	33.63	34.50	32.50	32.60
9	33.28	33.94	31.61	31.61
16	32.34	32.34	30.44	30.50
25	32.02	32.00	30.40	30.34

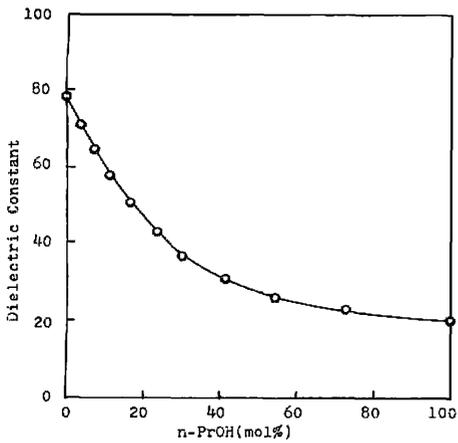


Fig.1. The dielectric constant of n-PrOH-Water at 25°C.

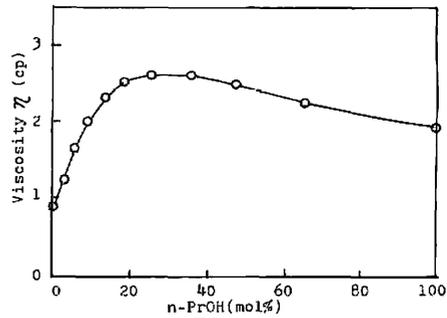


Fig.2. The viscosity of n-PrOH-Water mixture at 25°C.

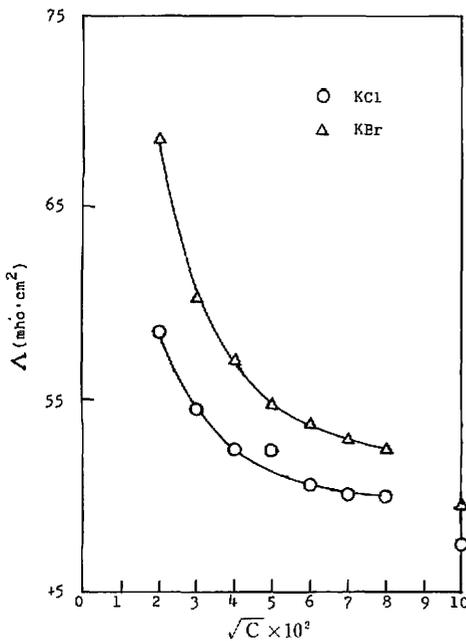


Fig.3. The plots of equivalent conductances of KCl and KBr as the function of  $\sqrt{C}$  in n-PrOH-Water mixture(n-PrOH : 19.46mole%) at 25°C. The experimental data were obtained by averaging the values in Table I,II,and III at each concentration of a salt.

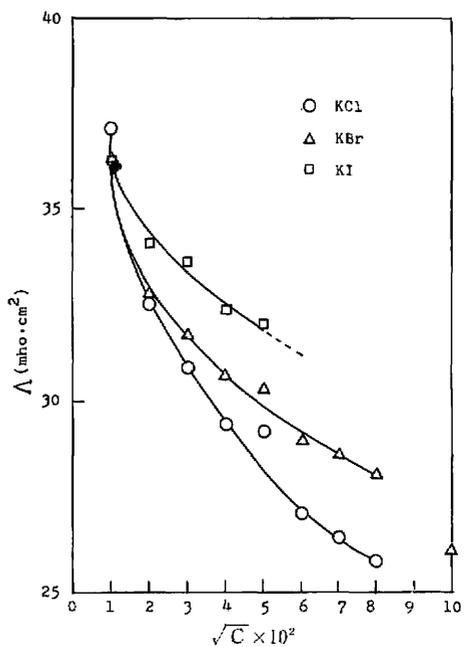


Fig.4. The plots of equivalent conductances of KCl KBr, and KI as the function of  $\sqrt{C}$  in n-PrOH-Water mixture(n-PrOH : 43.14mole%) at 25 °C. The experimental data were obtained by averaging the values in Table I,II,and III at each concentration of a salt.

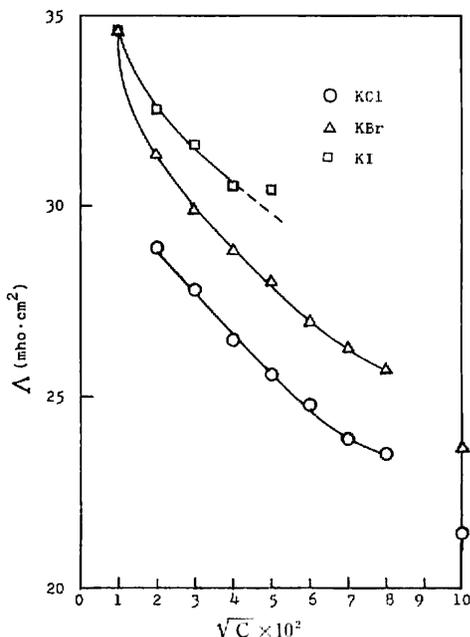
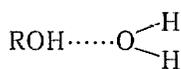


Fig. 5. The plots of equivalent conductances of KCl, KBr, and KI as the function of  $\sqrt{C}$  in n-ProOH-Water mixture (n-ProOH : 49.15mole%) at 25°C. The experimental data were obtained by averaging the values in Table I, II, and III at each concentration of a salt.

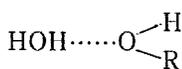
### III. RESULTS AND DISCUSSION

The results of conductance measurements are tabulated in Tables I, II, and III. The Onsager plots are shown in Figs. 3, 4, and 5. From the data, no matter how the mixing ratio of solvents changes, the equivalent conductances in the concentration range investigated here increase with the increase of crystallographic radii of anions. That is expected electrostatically. The concentration effect on conductances appears to be getting smaller as the increase of propanol composition. If a selective solvation occurs, the ionic solvation shell will not change in the solvent mixtures. Consequently the ion-solvent interaction and the concentration effect will not change so much in each of the mixtures. In this case, for each salt, the plots in Figs. 3, 4, and 5 will give the same slope. For lithium chloride in methanol-water mixtures, however, it has been reported that such selective solvation will not occur.<sup>10</sup> In the system of propanol-water mixtures, that might be true also.

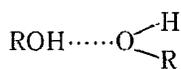
In alcohol-water mixtures, some characteristic physical phenomena have been observed.<sup>21, 81, 100</sup> Bobtelsky<sup>11</sup> suggested four types of hydrogen bond in alcohol-water mixtures as follows :



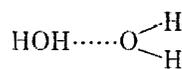
(a)



(b)



(c)



(d)

which type of hydrogen bond is significant depends on their relative amounts in the mixtures. In order to investigate those hydrogen bonds, the help of photochemical measurements is required. In the systems investigated here, however, we have not been able to observe any specific behaviors of ions so far.

The dielectric constant is one of the main factors which affect on the conductance. The dielectric constants measured by Akerlof<sup>12)</sup> in propanol-water mixtures at 25°C is shown in Fig.1 as the function of propanol mole%. From Tables I,II,III, and Fig.1, it is clear that the equivalent conductance decreases as the dielectric constant decreases. According to the Bjerrum theory,<sup>13)</sup> the ionic association increases as the dielectric constant decreases, hence decreases the concentration of ions per mole. Bjerrum proposed that the ionic distance in which ions can form ion pairs is defined by the equation

$$q = Z_+ Z_- e^2 / (8 \pi \epsilon_0 \epsilon k T) \tag{1}$$

where  $\epsilon_0$  and  $\epsilon$  are the dielectric constants in a vacuum and in a solution respectively.  $q$  is called the Bjerrum's critical distance. From equation (1), as the dielectric constant decreases,  $q$  increases and therefore the possibility of the occurrence of ionic association increases. By using Bjerrum theory, the ionic association constant,  $K$  is derived as

$$K = (4 \pi N / 1000) \bar{a}^3 b^3 Q(b) \tag{2}$$

where

$$b = Z_i Z_j e^2 / (4 \pi \epsilon_0 \epsilon k T \bar{a}) = \frac{2}{\bar{a}} q \tag{3}$$

$$Q(b) = \int_2^b x^4 e^x dx \tag{4}$$

$$x = -Z_i Z_j e^2 / (4 \pi \epsilon_0 \epsilon k T r) \tag{5}$$

$N$  is the Avogadro's number,  $\bar{a}$  the nearest distance between  $i$  and  $j$  ions. Relationg to the Bjerrum's equation, Fuoss derived the following equation

$$K = 4 \pi N \bar{a}^3 e^b / 3000 \tag{6}$$

The equation (6) shows that the plot of  $\ln K$  v.s.  $1/\epsilon$  gives stright line at constant temperature in the system where  $\bar{a}$  will change little.

The data reported in this paper were calculated by using the conductance equations

$$A = A_0 - S(c\gamma)^{\frac{1}{2}} + Ec\gamma(\log c\gamma) + Jc\gamma - Kf^2 c\gamma A \tag{7}$$

which was derived by Fuoss-Onsager-Skinner<sup>9)</sup> and

$$A/F(Z) = A_0 - (cA^2 f^2 K / (A_0 F(Z)^2)) \tag{8}$$

which was derived by Fuoss<sup>15)</sup> by linearizing the Onsager's equation

$$A = A_0 - S(c\gamma)^{\frac{1}{2}} \quad (9)$$

using

$$K = c(1 - \gamma)/(c\gamma)^2 f^2 \quad (10)$$

and

$$\gamma = A/(A_0 F(Z)) \quad (11)$$

$$F(Z) = 1 - Z(1 - Z(1 - Z(\dots)^{-\frac{1}{2}})^{-\frac{1}{2}})^{-\frac{1}{2}} \quad (12)$$

$$Z = (S/A_0)(cA)^{\frac{1}{2}} \quad (13)$$

where  $\gamma$  is the degree of dissociation,  $f$  the mean activity coefficient, and  $S$  the Onsager slope.  $S$ ,  $E$ , and  $J$  were calculated by machine calculations. From equation (7), the limiting equivalent conductance  $A_0$ , the ion-size parameter  $\bar{a}$ , and the association constant  $K$  were computed by the least square method. The results are shown in Tables IV and V with other parameters. From equation (8), the plot of  $A/F(Z)$  v.s.  $cA^2 f^2 / F(Z)^2$  gives  $A_0$  as the intercept and  $K/A_0$  as the slope. The results are tabulated in Table VI. The computing procedures are described elsewhere.<sup>1)</sup> All calculations had been done by using FACOM 235 computer. From Tables IV, V, and VI, for KI and KBr, the association constant seems to have the tendency of the increase as the dielectric constant decreases. But for KCl, that is not clear so much. Comparing the data in Tables IV and V with those in Table VI, the association constants calculated from equation (8) mostly give lower values than those from equation (7). The association constants for alkali halides had been reported to be less than 1 in aqueous solution, up to 40 or less in methanol-water mixtures, and up to 100 or less in ethanol-water mixtures.<sup>1)-2)</sup> Therefore in propanol-water mixtures, they will be up to several hundreds or less. The increase of the association constant as the increase of the size of the alkyl group of alcohol, which is obviously accompanied by the decrease of dielectric constant, had already been expected from the equation (6). But in solvent mixtures, equation (6) does not always hold.<sup>7)</sup> It is considered that a solvent structure affects on the association constant complicatedly.

In general, the association constant increases with the ion-size parameter.<sup>1), 8)</sup> The ion-size parameters are tabulated in Tables IV, V, and VI.  $r_h$  in Table VI was calculated by using Walden's equation

$$\eta_0 A_0 = Z_i e^2 F / (6 \pi r_h) \quad (14)$$

which is obtained by applying the Stock's law to an ionic solution.  $r_h$  is considered the solvation radius. From the Tables IV, V, and VI,  $\bar{a}$  and  $r_h$  are quite different each other in the magnitude of their numerical values. The crystallographic radii of

Table IV. The conductance parameters for potassium halides calculated from Fuoss-Onsager equation in n-PrOH-Water mixture at 25°C. Where symbols,  $\Lambda_0$ ,  $\dot{a}$ , and  $K$  are the limiting equivalent conductance, the ion size parameter, and the association constant respectively.

		n-PrOH composition					
		43.14 mole%			49.15 mole%		
		A <sup>a</sup>	B	C	A	B	C
KCl	$\Lambda_0$	35.32	33.90	32.50	31.26	30.32	30.22
	$\dot{a}$	20.90	6.59	*	20.93	7.74	7.27
	K	196.48	75.18	* <sup>b</sup>	170.00	57.84	51.90
KBr	$\Lambda_0$	34.66	34.37	32.80	33.22	33.58	32.42
	$\dot{a}$	6.14	8.59	* <sup>b</sup>	12.30	13.72	7.21
	K	49.86	52.81	* <sup>b</sup>	97.86	119.40	44.16
KI	$\Lambda_0$	35.62	—	—	34.50	—	—
	$\dot{a}$	4.14	—	—	12.15	—	—
	K	6.76	—	—	67.45	—	—

a The concentration range of salts; A:  $4 \times 10^{-4} \sim 16 \times 10^{-3} \text{M}$ ,  
 B:  $16 \times 10^{-3} \sim 36 \times 10^{-3} \text{M}$ , C:  $36 \times 10^{-3} \sim 64 \times 10^{-3} \text{M}$ .

b The calculation gives the negative value of  $K$ .

Table V. The conductance parameters which will be considered the most reasonable values among those in Table IV are tabulated for each salt.

n-PrOH mole% : 43.14

	$\Lambda_0$ (mho·cm <sup>2</sup> )	$\dot{a}$ (Å)	K	S	E	J
KCl	$33.90 \pm 0.01$	$6.59 \pm 0.07$	$75.18 \pm 0.31$	67.54	118.09	533.74
KBr	$34.66 \pm 0.00$	$6.14 \pm 0.06$	$49.86 \pm 0.25$	68.27	121.19	496.68
KI	$35.62 \pm 0.00$	$4.14 \pm 0.01$	$6.78 \pm 0.03$	69.20	125.14	278.41

n-PrOH mole% : 49.15

	$\Lambda_0$ (mho·cm <sup>2</sup> )	$\dot{a}$ (Å)	K	S	E	J
KCl	$30.22 \pm 0.01$	$7.27 \pm 0.04$	$51.90 \pm 0.13$	69.50	128.13	663.75
BBr	$32.42 \pm 0.01$	$7.21 \pm 0.09$	$44.16 \pm 0.25$	71.78	138.81	626.58
KI	$34.50 \pm 0.01$	$12.1 \pm 0.04$	$67.45 \pm 0.13$	74.00	149.29	1196.0

The Ion-Solvent Interactions and Ionic Associations in Solvent Mixtures. I. The Conductances of Potassium Halides and the Behaviours of Ions in n-Propanol-Water Mixtures at 25°C.

Table VI. The conductance parameters for potassium halides calculated from Fuoss method in the n-PrOH-Water mixtures at 25°C.

	n-PrOH 43.14 mole%			n-PrOH 49.15 mole%		
	$\Lambda_0$ (mho·cm <sup>2</sup> )K	$r_h$ (Å) <sup>a</sup>		$\Lambda_0$ (mho·cm <sup>2</sup> )K	$r_h$ (Å) <sup>a</sup>	
KCl	35.35	48.48	1.93	31.34	23.23	2.13
KBr	34.57	10.82	1.87	33.29	17.92	2.01
KI	35.49	-0.23	1.83	34.48	10.10	1.94

a.  $r_h$  was calculated by using the Walden's rule.

Table VII. The densities and viscosities Of n-PrOH-Water mixtures at 25°C.

n-PrOH (mole%)	Density (g/cm)	Viscosity (cp)	n-PrOH (mole%)	Density (g/cm)	Viscosity (cp)
0	0.9975	0.8903	25.6	0.8983	2.6216
	0.9975	0.8903		0.8989	2.6261
2.7	0.9850	1.2408	35.9	0.8765	2.5898
	0.9852	1.2391		0.8770	2.6059
5.5	0.9732	1.6538	47.4	0.8546	2.4705
	0.9736	1.6611		0.8548	2.4847
9.2	0.9575	2.0176	65.5	0.8309	2.2223
	0.9575	2.0168		0.8304	2.2343
13.7	0.9386	2.3101	100	0.8005	1.9075
	0.9388	2.3189		0.8008	1.9207
18.6	0.9189	2.5177			
	0.9189	2.5288			

KCl, KBr, and KI have been given by Pauling as 3.14Å, 3.28Å, and 3.49Å respectively.<sup>17</sup> The values from Walden's equation gives considerable low estimate for  $r_h$ . It has been reported by other workers that  $\bar{a}$  of KCl is 3.11 in water, 3.28 in methanol, and 4.6 in ethanol.<sup>11</sup> For KI, however,  $\bar{a}$  is 3.67 in water, 3.78 in methanol, and 3.6 in propanol.<sup>11</sup> For tetraalkylammonium halides,  $\bar{a}$  is 3 to 4 in methanol, 4 to 5 in ethanol, and 5 to 6 in propanol.<sup>51, 6), 16</sup> The values from Fuoss equation give somewhat high estimation for  $\bar{a}$ . As mentioned above, in alcohols, the ion-size parameter appears to increase as the increase of the size of alkylic groups of alcohols.

The ion-size parameter is intimately related to the ion-solvent interaction. In the solvent mixtures, solvation numbers, that is, the solvation sheath often changes as the mixing ratio changes.<sup>10)</sup> Consequently the ion-size parameter which is considered effective ionic radius or solvation radius, will change with the change of a mixing ratio.<sup>2), 7)</sup> The data in Table IV are insufficient to evaluate that.

In propanol-water mixtures, what we are most interested in is the behaviours of ions in vicinity of the azeotropic mixture from the point of view of solvent structure. In our lab., the conductance measurements in the azeotropic mixture and in the vicinity of it are being undertaken. We are going to report the results in next paper.

The data reported here will contain some errors which can not be overlooked, because we can not sufficiently prevent the solutions from the contamination of atmosphere, especially of CO<sub>2</sub> in the air. Now we are improving the procedure of the measurements.

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