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The Rectification Effects Using the Ices Doped with Electrolytes

Kuniyoshi SHIMIZU, Yoshiaki YOSHIDA, Manabu SENŌ and Hiroshi NOZAKI

The Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo

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The rectifying properties of the combined systems of two crystals, one being doped with a proton donor (poly(styrene sulfonic acid) or hydrogen fluoride) and the other being doped with a proton acceptor (poly(2-vinyl-*N*-*n*-butylpyridinium bromide), poly(2-vinyl-*N*-*n*-butylpyridinium hydroxide) or lithium hydroxide) are examined and discussed. In the case of the combination of the ices doped with poly(styrene sulfonic acid) and poly(2-vinyl-*N*-*n*-butylpyridinium hydroxide) or poly(2-vinyl-*N*-*n*-butylpyridinium bromide), the current *versus* voltage curves have the hysteresis loops and the rectification ratio defined as the ratio of the forward current to the backward current is low. The dynamic rectification effect is slightly observed. In the case of the combination of the ices doped with lithium hydroxide and hydrogen fluoride, the rectification ratios exceed 100 and the rectification mechanism is presumed to be the same as in the system of the aqueous solutions. The dynamic characteristics depend on the frequencies; the rectification phenomena are not observed when the alternating voltages with frequencies higher than 30 kc are applied.

Reiss and Fuller[1] pointed out that the proton excess and the proton defficiency in an aqueous solution exert a similar function to the electron excess and the electron defficiency in a usual semiconductor, respectively. In the previous paper,[2] the rectification effect on the liquid junction of the aqueous solution of poly(2-vinyl-*N*-*n*-butylpyridinium hydroxide) and the aqueous solution of poly(styrene sulfonic acid) was investigated. The rectification effect was also found by some authors[3] on the composite membrane consisting of cation- and anion-exchange membrane. On the basis of the mobility of the charge carriers, the electron in a semiconductor is more analogous to the proton in ice than the proton in an aqueous solution. As a matter of fact, Eigen and de Maeyer[4] suggested the possibility of rectification effect on the ices doped with LiOH and HF.

In the present investigation, the rectifying properties are examined and discussed on the combined systems of two ices, one being doped with a proton donor (poly(styrene sulfonic acid) or HF) and the other being doped with a proton acceptor (poly(2-vinyl-*N*-*n*-butylpyridinium hydroxide), poly(2-vinyl-*N*-*n*-butylpyridinium bromide) or LiOH).

Experimental

Materials. Poly(styrene sulfonic acid) (PVSA), molecular weight, 100000, was prepared by the same method as in the literature.[5] One molecule of PVSA has 450 sulfonic groups. Poly (2-vinyl-*N*-*n*-butylpyridinium bromide) (NBPB), molecular weight, 15000, was prepared by the method in the literature.[6]

Found: N, 8.0; Br. 21.2%. Calcd for complete quarternarization: N, 5.8; Br, 33.0%.

Poly(2-vinyl-*N*-*n*-butylpyridinium hydroxide) (NBOH) was prepared by the same method as in the previous paper.[2] Lithium hydroxide and hydrogen fluoride of reagent grade were used without further purification. Water used was treated as follows. The deionized water was distilled in a pyrex cell still containing a small amount of $KMnO_4$ and was collected in a polyethylene vessel. Then the distilled water was degassed by using the apparatus reported in the literature.[7] The specific conductivity was of the order, 10^{-7} ohm^{-1} cm^{-1}.

Apparatus and Procedure for Measurements. For measurements of the static conductivity of the ices doped with electrolytes, the electrolyte solutions in the silica tube (Fig. 1) were frozen in a dry-ice - methanol bath while nitrogen gas was flowed through the silica tube. The measurements were started at five hours after the electrolytes solution was poured into the silica tube (diameter: 4.0 cm). For the investigation of the rectification effect using the ices doped with electrolytes, the procedure of solidification of electrolyte solutions was conducted as follows. At first, the solution of NBOH (or NBPB, LiOH) was transferred into the silica tube maintained at $-10°$C in an alcohol bath and was

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[2] K. Shimizu, M. Senō and H. Nozaki, This Bulletin, **41**, 802 (1968).

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[6] R. M. Fuoss and U. P. Strauss, *J. Polymer Sci.*, **3**, 246 (1948).

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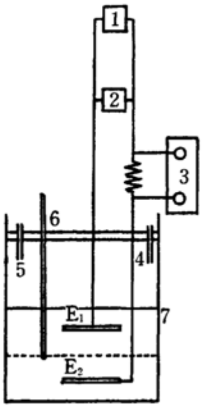

Fig. 1. Apparatus.

1: Voltage source, 2: voltmeter, 3: oscilloscope or X-Y recorder, 4 and 5: inlet and outlet of N_2 gas, 6: thermometer, 7: silica tube, E_1 and E_2: platinum electrodes.

frozen therein. After three hours, the solution of PVSA (or HF) which was supercooled at a few degrees below 0°C was poured above the NBOH (or NBPB, LiOH)-doped ice in the silica tube and was solidified in the alcohol bath for three hours. Then, the electric current was read at 30 sec after the voltage was applied. A constant voltage was supplied by a battery, and an alternating voltage was supplied by an ultra-low frequency oscillator (10^{-3}—10^6 sec).

Results

I. The D. C. Electric Conductivity of Ice Doped with Polyelectrolyte. The d. c. electric conductivities of ices doped with PVSA, NBPB or NBOH were measured by using the apparatus as shown in Fig. 1. In Figs. 2, 3 and 4, the dependence of the electric conductivity (σ) of the ices doped with polyelectrolytes on temperature is shown, where the concentrations of polyelectrolytes are 1.36×10^{-2} and 0.68×10^{-2} equiv/*l*. Although an irregular change was observed near the freezing point, the Arrhenius-type relationship holds in a range of sufficiently low temperatures. From the straight line portions in Figs. 2, 3 and 4, we obtained the following relations.

$$\sigma_p = \sigma_{p,o}\exp(-8.23\times10^3/\boldsymbol{R}T) \qquad (1)$$

$$\sigma_h = \sigma_{h,o}\exp(-13.94\times10^3/\boldsymbol{R}T) \qquad (2)$$

$$\sigma_{h'} = \sigma_{h',o}\exp(-13.94\times10^3/\boldsymbol{R}T) \qquad (3)$$

where the indeces p, h and h' refer to the ices doped with PVSA, NBOH and NBPB, respectively.

The dependence of the electric conductivity of the ices doped with polyelectrolytes on the concentrations of the polyelectrolytes at −10°C is shown in Fig. 5.

II. The Rectification Phenomena Using the Ices Doped with Electrolytes. Making the solid junction of two ices, one doped with a

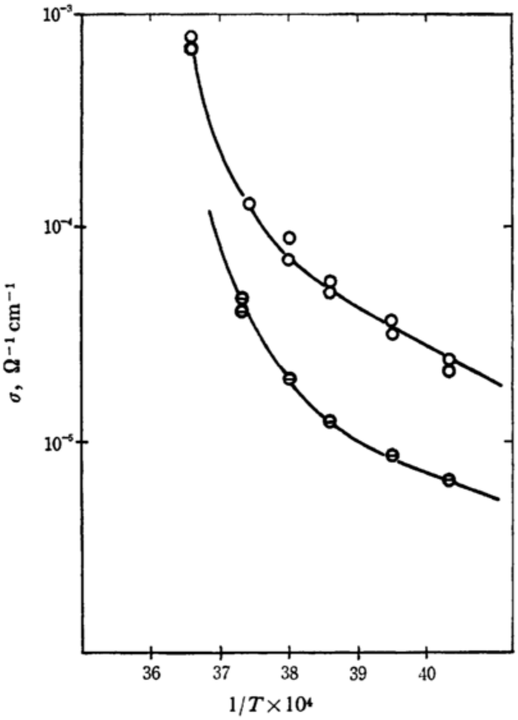

Fig. 2. Dependence of d. c. conductivity of the ice doped with PVSA on temperature.
○: $C_p=1.36\times10^{-2}$ equiv/*l*
⊖: $C_p=0.68\times10^{-2}$ equiv/*l*

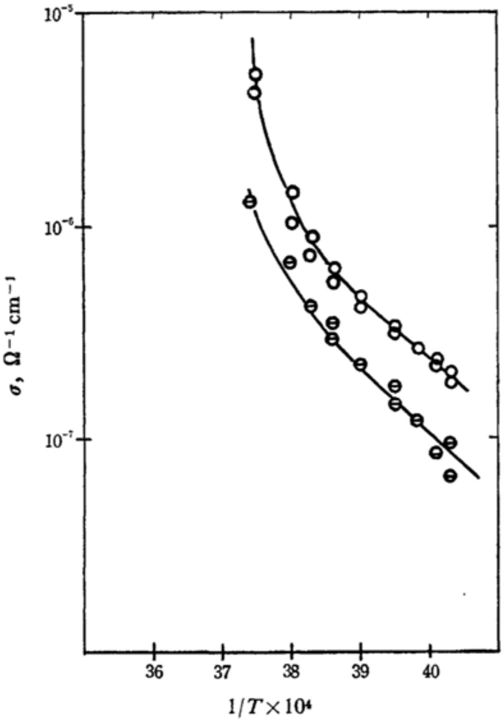

Fig. 3. Dependence of d. c. conductivity of the ice doped with NBPB on temperature.
○: $C_{h'}=1.36\times10^{-2}$ equiv/*l*
⊖: $C_{h'}=0.68\times10^{-2}$ equiv/*l*

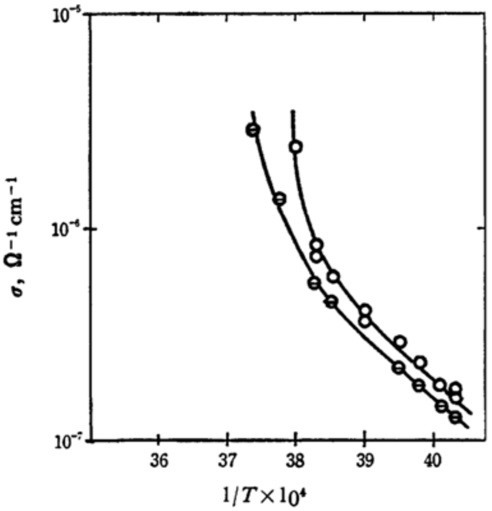

Fig. 4. Dependence of d. c. conductivity of the ice doped with NBOH on temperature.
○: $C_h=1.36\times10^{-2}$ equiv/l
⊖: $C_h=0.68\times10^{-2}$ equiv/l

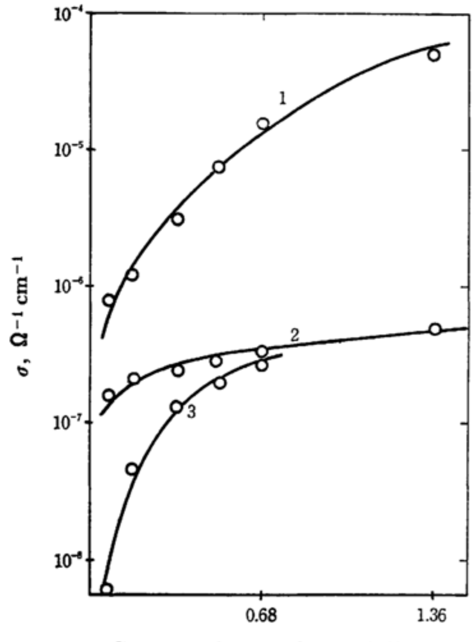

Fig. 5. Dependence of d. c. conductivity of the ice doped with polyelectrolyte on the concentration of charge carrier.
1: PVSA, 2: NBPB, 3: NBOH $T=-10$°C

proton donor (PVSA or HF) and the other doped with a proton acceptor (NBOH, NBPB or LiOH), we investigated the rectification effects, in analogy to the *p-n* junction in an electronic semiconductor.

NBOH-PVSA and NBPB-PVSA Systems. When the positive electrode is placed in the region of ice doped with a proton acceptor and the negative

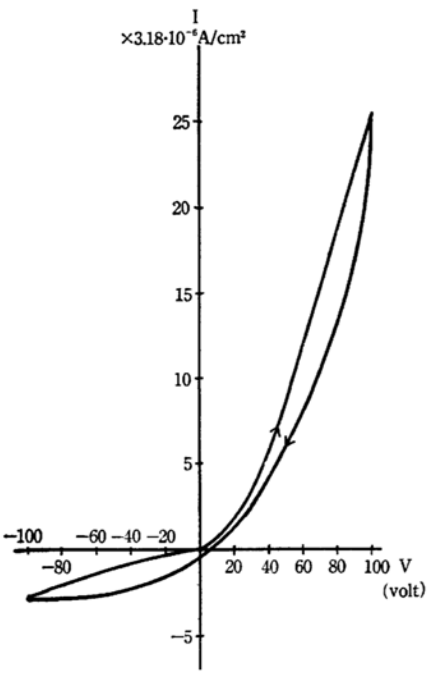

Fig. 6. Current plots *versus* constant voltages of NBPB-PVSA systems.
$C_p=0.34\times10^{-2}$ equiv/l
$C_{h'}=1.36\times10^{-2}$ equiv/l

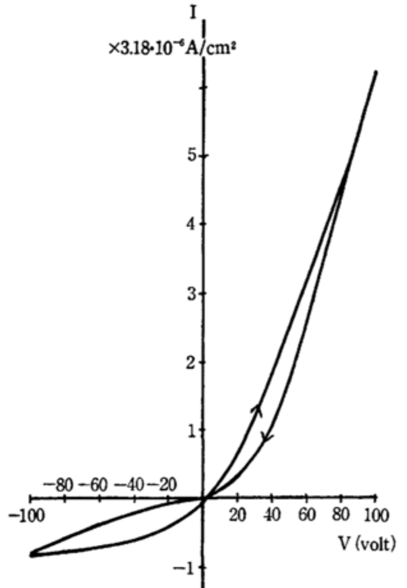

Fig. 7. Current plots *versus* constant voltages of NBOH-PVSA systems.
$C_p=0.34\times10^{-2}$ equiv/l
$C_h=1.36\times10^{-2}$ equiv/l

electrode is placed in the region of ice doped with a proton donor, the system exhibits a greater electric resistance than the case when the voltages with the reverse polarity were applied. The typical curves of the static current *versus* voltage are shown in Figs. 6 and 7. The data given in Figs. 6 and 7 were read at 30 sec after the voltages were applied. From these figures we can see that the curves have the hysteresis loops in both the NBOH-PVSA and the NBPB-PVSA systems.

The dynamic characteristics of rectification phenomena were remarkable when the alternating voltages of ultra-low frequencies were applied to the systems. The rectification effect was slightly observed even when the alternating voltage of 10 kc was applied. An example is shown in Fig. 8.

LiOH-HF System. The static and dynamic rectification phenomena of this system are more remarkable than those of NBOH-PVSA and NBPB-PVSA systems. The static characteristics are shown in Figs. 9 and 10. The curves in Fig. 9 were measured under the condition where the concentration of LiOH was maintained at 0.1 equiv/*l* and the concentration of HF was varied from 0.0097 to 0.0776 equiv/*l*. The curves in

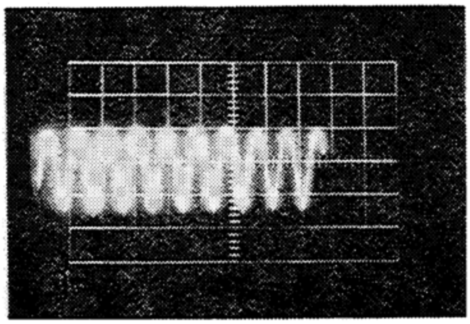

Fig. 8. Rectification of alternating sine-wave current in NBPB-PVSA system.
$C_p=0.34\times10^{-2}$ equiv/*l*
$C_{h'}=1.36\times10^{-2}$ equiv/*l*
Frequency: 5 kc

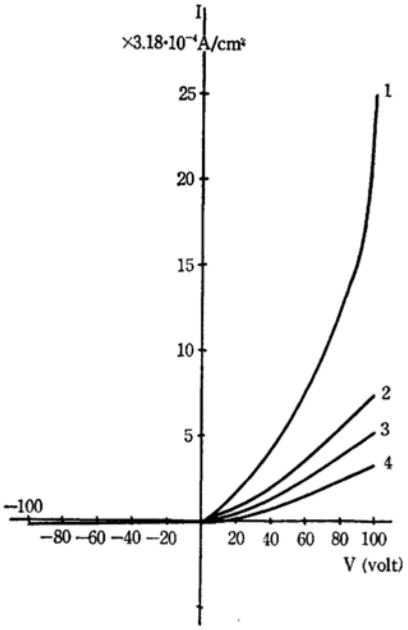

Fig. 9. Current plots *versus* constant voltages of LiOH-HF systems.
1: $C_p=0.0776$, $C_h=0.1$
2: $C_p=0.0388$, $C_h=0.1$
3: $C_p=0.0194$, $C_h=0.1$
4: $C_p=0.0097$, $C_h=0.1$
All values are in equiv/*l*.

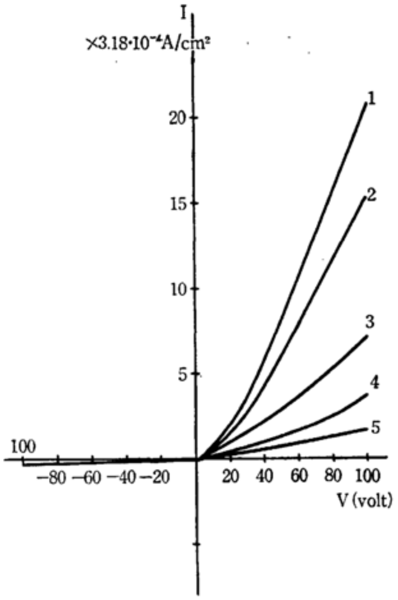

Fig. 10. Current plots *versus* constant voltages of LiOH-HF systems.
1: $C_p=0.0388$, $C_h=0.3$
2: $C_p=0.0388$, $C_h=0.2$
3: $C_p=0.0388$, $C_h=0.1$
4: $C_p=0.0388$, $C_h=0.05$
5: $C_p=0.0388$, $C_h=0.025$
All values are in equiv/*l*.

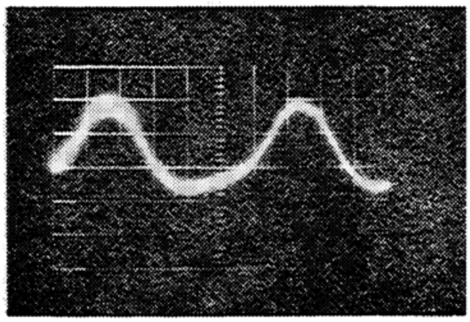

Fig. 11. Dependence of rectification ratio on frequency in LiOH-HF system.
$C_p=0.0388$ equiv/*l* $C_h=0.1$ equiv/*l*

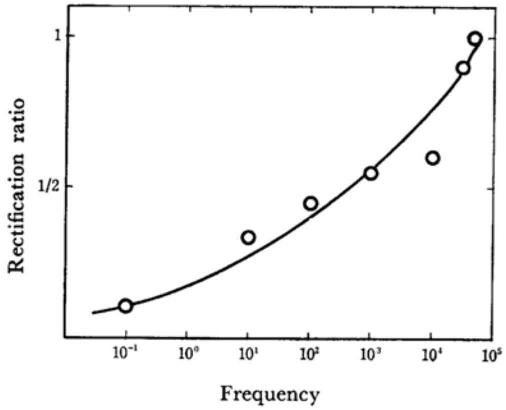

Fig. 12. Rectification of alternating sine-wave current in LiOH-HF system.
$C_p = 0.0388$ equiv/l $C_h = 0.1$ equiv/l
Frequency: 1 kc

Fig. 10 were obtained under the condition where the concentration of HF was maintained at 0.0388 equiv/l and the concentration of LiOH was varied from 0.025 to 0.3 equiv/l. A dynamic characteristic is shown in Fig. 11. The rectification ratio (the ratio of the forward current to the backward one) strongly depends on the frequency of the applied voltage and an example is shown in Fig. 12. The rectification phenomena were slightly observed even when the alternating voltage of 30 kc was applied.

Discussion

The d. c. electrical conductivity of the pure ice measured by Johnstone,[8] Bradley[9] and Granicher[10] was about 10^{-9} ohm^{-1}cm^{-1} at -10°C and the activation energy was 13.8 kcal/mol (by Granicher[10]). In the ice crystal, each oxygen atom is surrounded tetrahedrally by four hydroxyl ions at a distance of 2.76 Å. The pure ice is a good example of a protonic conductor. The mobility of a proton is ten times higher than a hydroxyl ion in ices (the mobilities of hydroxyl ion and proton are $\lesssim 5\times10^{-2}$ cm^{2}V^{-1}sec^{-1} and 0.1 to 0.5 cm^{2}V^{-1}sec^{-1}, respectively). The results in Figs. 2, 3 and 4 may be understood on this basis. Furthermore, the activation energy observed in the pure ice would reflect one for a protonic conduction, and the activation energy for a hydroxyl ion conduction should be greater. The activation energies of the electrical conduction of the ices doped with PVSA, NBPB and NBOH were measured to be 8.23, 13.94 and 13.94 kcal/mol, respectively. From these observations, it can be said that the inclusion of the linear polymers would contribute to the increase in the electrical conduction, owing to an increase in carrier concentrations and a lowering in activation energies caused by the generation of the structural defect in ices. The similarity in the conductivities of ices doped with NBPB and NBOH suggests that the charge carrier in both ices is the same one (OH^-).

Form the above consideration, it should be clear that the charge carriers of the ices doped with electrolytes are protons in the case of addition of PVSA and HF, and hydroxyl ions in the case of addition of NBOH, NBPB and LiOH. Then, by making the solid junction of two ices, one doped with a proton donor and the other with a proton acceptor, the rectification effect could be observed, such as in a *p-n* junction of a semiconductor.

In the case of the liquid junction analogous to a *p-n* junction,[2] the following equations were proposed for the rectification effect; when the forward bias voltages are applied;

$$J = \boldsymbol{e}(D_pC_p/L_p + D_hC_h/L_h)\{\exp(\alpha \boldsymbol{e}V/\boldsymbol{k}T)-1\} \tag{4}$$

when the backward bias voltages are applied;

$$J = \boldsymbol{e}g[\exp(\beta \boldsymbol{e}V/\boldsymbol{k}T) - \exp\{-(1-\beta)\boldsymbol{e}V/\boldsymbol{k}T\}] \tag{5}$$

where J is the electric current, $\boldsymbol{e}$ is the elementary charge, D_p and D_h are the diffusion coefficients of proton and hydroxyl ion, respectively, C_p and C_h are the concentrations of electrolytes in the proton excess region and the proton defficiency region, respectively, L_p and L_h are the mean distances by which proton and hydroxyl ion proceed in the proton defficient and proton excess regions until their disappearance, α is the coefficient showing the effective portion of the applied voltage, β is the transfer number for the neutralization reaction, g is the exchange velocity at the dissociation equilibrium of H_2O, $\boldsymbol{k}$ is the Boltzmann constant and V is the applied voltage. Equation (4) was derived under the assumption that the rate of electrical conduction is controlled by the diffusion of charge carriers in the transition region. On the other hand, Eq. (5) was derived under the assumption that the dissociation reaction of H_2O is the rate-determining step in the electrical conduction mechanism and from this equation the backward currents are shown to be independent of the concentrations of the charge carriers.

In the case of NBPB-PVSA and NBOH-PVSA systems, the recitification effects were observed as expected, but the static characteristics are not explained by Eqs. (4) and (5), and, moreover, the hysteresis is observed in the current *versus* voltage curves even in the forward direction (Figs. 6 and 7). The rectification effects were also slightly

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[10] H. Gränicher, C. Jaccard, P. Scherrer and A. Steinman, *Discussions Faraday Soc.*, **23**, 50 (1957).

observed when the ultra-low frequency a.c. ($\lesssim 10$ kc) was applied. The causes of the hysteresis, which is a principal discrepancy from the theoretical prediction, are considered to be due to the capacitance of the system, the space charge effect or the polarization effect. The capacitance of the system would play a more significant role, as the concentrations of charge carriers becomes lower. The polarization effects are caused by the electrode effects and by the difference in mobilities between the charge carriers in the bulk of ices. The polarization connected with the electrode processes can be neglected at sufficiently high voltages.

In the case of LiOH-HF systems, the rectification curves as shown in Figs. 9 and 10 are well reproduced by Eqs. (4) and (5). The backward currents are almost independent of the concentrations of charge carriers, although the values are higher than in the pure ice. The constancy of the backward currents is well explained by the dissociation controlled mechanism, as derived for the liquid junction. The dynamic characteristics are remarkable when the alternating voltage with frequencies ranged to 30 kc was applied. This could be expected from the higher mobilities of H^+ and OH^- in ice. It is not possible to give detailed discussions here, for the uniform distribution of the doped electrolytes is not confirmed in the present investigation. It may be noticed, however, that the rectification effect observed in the HF-LiOH system is the most excellent of the junction diodes with the ionic conduction mechanism reported up to the present.