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Rectification Effects Using Polyelectrolyte Solutions

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The rectifying properties of liquid junctions of polyelectrolyte solutions are examined and discussed. In the case of liquid junctions between aqueous solutions of poly(styrene-sulfonic acid) and poly(2-vinyl-*N*-*n*-butylpyridinium hydroxide), the rectification effects greatly depend on the concentrations of the polyelectrolytes and on the frequencies of the voltages applied, that is, rectification effects can not be found when the concentrations of polyelectrolytes are lower than 0.68×10^{-3} equivalents per liter and when the frequencies of the alternating voltages are higher than 200 cps. The mechanism of rectification can be explained to some extent by a semiconductor analogy. In the case of liquid junctions between poly(styrene-sulfonic acid) and poly(2-vinyl-*N*-*n*-butylpyridinium bromide), the static current *versus* voltage curves have strong hysteresis loops. The rectification effects can be slightly observed when alternating voltages with frequencies lower than 100 cps are applied. In this case, however, the mechanism of rectification can not be explained by the semiconductor analogy.

Reiss(1) and Fuller(2) have pointed out that the electron excess and the electron defficiency in a semiconductor correspond to the proton excess and the proton defficiency in an aqueous solution

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(1) H. Reiss, *J. Chem. Phys.*, **21**, 1209 (1953).

(2) C. S. Fuller, *Rec. Chem. Progr.*, **17**, 75 (1956).

respectively. An *n*-type semiconductor is strongly analogous to an alkaline solution, containing highly mobile hydroxide ions together with corresponding cations so large as to be entirely immobile, while a *p*-type semiconductor is analogous to an acid solution, containing highly mobile protons together with corresponding anions so large as to be entirely immobile.

In view of these analogies, we may make electrolytic junctions in polyelectrolyte solutions corresponding to *p-n* junctions in semiconductors.

As a matter of fact, Lovreček,3) Läuger,4) Senō5) and others6) found rectification effects using cation-exchange membranes and anion-exchange membranes. In linear polyelectrolyte systems, however, only Lovreček3) has observed rectifying effects, and he has reported only very simple data.

In the present investigations, electrolytic liquid junctions separating the solutions of a polyacid and a polybase by a milipore filter (a cellulose-acetate membrane) were prepared and their rectifying properties were examined. Further, the rectifying properties of liquid junctions between the salt of a polybase and of a polyacid were examined.

Experimental

Materials. *Poly(styrene-sulfonic Acid) (PVSA).* This product was prepared by a method in the literature7); one molecule of this product (molecular weight: 100000) has 420 sulfonic groups.

Poly(2-vinyl-N-n-butylpyridinium Bromide) (NBPB). From 2-vinylpyridine, poly(2-vinyl pyridine) was obtained according to a procedure previously reported.8) NBPB was synthesized from poly(2-vinyl pyridine) by a method in the literature.9) The product was analyzed for Br titmetrically10) and for N by the micro-Dumas method. Found: Br, 21.2%; N, 8.0%. One molecule of NBPB (molecular weight: 15000) has 44 bromide atoms. The conductance of aqueous solutions of this NBPB at 25°C is given in Table 1, where C is the equivalent of bromide per liter and L is the observed specific conductance. The figures in the fourth column would be the equivalent conductance if the effect of the acidity were corrected. The fifth column shows the equivalent conductance, in which the effect of acidity is corrected by R. M. Fuoss' method.9)

TABLE 1. CONDUCTANCE OF NBPB IN WATER AT 25°C

$C\times10^2$	$L\times10^3$	pH	Λ_{uncorr}	Λ
1.36	0.872	3.22	66.8	46.8
0.68	0.503	3.34	81.5	49.7
0.17	0.158	3.80	97.5	54.8
0.085	0.0817	4.09	100.0	57.3
0.021	0.0217	4.72	107.0	66.6

C: equiv/l L: ℧/cm

Poly(2-vinyl-N-n-butylpyridinium Hydroxide) (NBOH). An aqueous solution of NBOH was prepared by treating an NBPB aqueous solution with an anion-exchange resin (OH-form).

Apparatus and Procedure for Measurement. Figure 1 shows a block diagram of the apparatus used for the measurement of the currents *versus* the applied voltages.

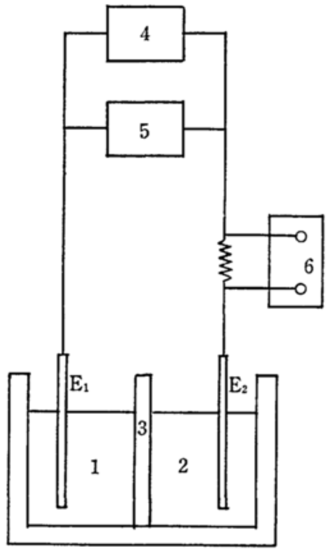

Fig. 1. Apparatus.

1. PVSA aqueous solution, the concentration of which is C_p.
2. NBOH (or NBPB) aqueous solution, the concentration of which is C_h (or C_{Br}).
3. Milipore filter (pore radius, 10 mμ).
4. Voltage source.
5. Voltmeter.
6. Osciloscope or X-Y recorder.

E_1 and E_2 : Platinum electrodes.

The aqueous solutions of NBOH (or NBPB) and of PVSA were separated by a thin porous membrane (thickness: 0.1 mm, pore radius: 10 mμ), and a platinum electrode was immersed in each of the solutions. A constant voltage was supplied by a battery, and an alternating voltage was supplied by an ultra-low-frequency oscillator (10^{-3}—10^3 cps), Toa-Dempa CR-IE, through a pair of electrodes, E_1 and E_2. The electric current was measured with an X-Y recorder or an osciloscope.

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3) B. Lovreček, A. Despic and J. O'M. Bockris, *J. Phys. Chem.*, **63**, 750 (1959).

4) V. P. Läuger, *Ber. Buns. Phys. Chem.*, **68** (No. 6), 534 (1964).

5) M. Senō and T. Yamabe, This Bulletin, **37**, 668 (1964).

6) T. Teorell, *Z. Physik, Chem., Neue Folge*,**15** , 385 (1958).

7) H. H. Roth, *Ind. Eng. Chem.*, **49**, 1820 (1957).

8) A. Katchalsky, K. Rosenheck and B. Altmann, *J. Polymer Sci.*, **23**, 955 (1957).

9) R. M. Fuoss and U. P. Strauss, *ibid.*, **3**, 246 (1948).

10) S. Hirano, "Kogyo Bunseki Kagaku Zittsuken," Kyoritsu Shuppan, Tokyo (1963), p. 229.

Results

NBOH-PVSA Systems. *Static Voltage-Current Characteristics.* The system in which E_2 is the positive electrode and E_1 is the negative electrode was much more resistant to the direct current than when voltages with the reverse polarity were applied. The curves of the currents *versus* the voltages are shown in Figs. 2 and 3.

The data given in Figs. 2 and 3 were read 30 sec after the voltage was applied. The curves in Fig. 2 were measured while the concentration of NBOH (C_h) was maintained at a constant value (1.36×10^{-2} equivalents per liter), while the concentrations of PVSA (C_p) were varied from 1.36×10^{-2} to 0.68×10^{-3} equivalents per liter. The curves in Fig. 3 were measured while C_p was maintained at a constant value (1.36×10^{-2} equivalents per liter) and the C_h values were varied from 1.36×10^{-2} to 0.68×10^{-3} equivalents per liter.

The curves in Figs. 2 and 3 are well reproduced by the following equation:

$$J = J_s(\exp(\alpha \boldsymbol{e}V/\boldsymbol{k}T) - 1) \qquad (1)$$

where J is the electric current, V is the applied voltage, $\boldsymbol{k}$ is the Boltzmann constant, $\boldsymbol{e}$ is the charge of the electron, α is a parameter that shows the effective portion of an applied voltage, and J_s is an experimental parameter. The experimental

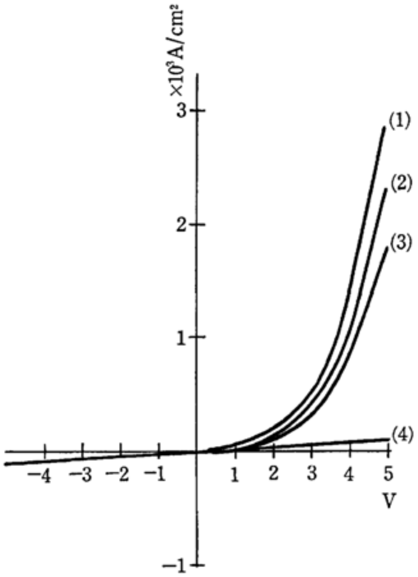

Fig. 2. Current plots *versus* constant voltages in NBOH-PVSA systems.

(1): $C_h=1.36\times10^{-2}$, $C_p=1.36\times10^{-2}$
(2): $C_h=1.36\times10^{-2}$, $C_p=1.02\times10^{-2}$
(3): $C_h=1.36\times10^{-2}$, $C_p=0.68\times10^{-2}$
(4): $C_h=1.36\times10^{-2}$, $C_p=0.068\times10^{-2}$
All values are in equiv/l.

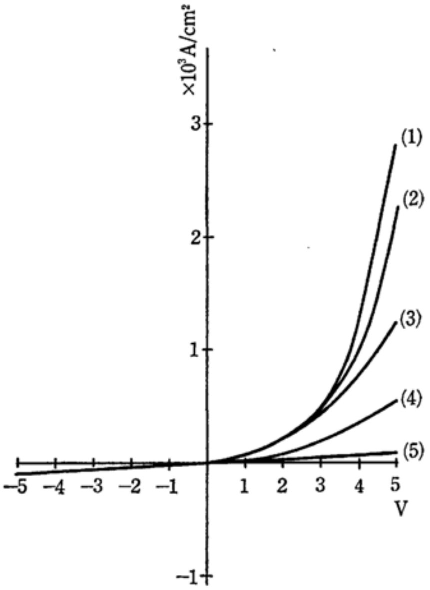

Fig. 3. Current plots *versus* constant voltages in NBOH-PVSA systems.

(1): $C_h=1.36\times10^{-2}$, $C_p=1.36\times10^{-2}$
(2): $C_h=1.02\times10^{-2}$, $C_p=1.36\times10^{-2}$
(3): $C_h=0.68\times10^{-2}$, $C_p=1.36\times10^{-2}$
(4): $C_h=0.272\times10^{-2}$, $C_p=1.36\times10^{-2}$
(5): $C_h=0.068\times10^{-2}$, $C_p=1.36\times10^{-2}$
All values are in equiv/l.

TABLE 2. THE EXPERIMENTAL VALUES OF J_s AND α IN NBOH-PVSA SYSTEMS

$C_h\times10^2$	$C_p\times10^2$	$J_s\times10^5$	$\alpha\times10^2$
1.36	1.36	2.65	2.20
1.36	1.02	3.76	2.00
1.36	0.68	4.90	1.70
1.02	1.36	3.76	1.95
0.68	1.36	5.73	1.05
0.272	1.36	8.63	0.97

C_h, C_p: equiv/l J_s: Coulomb/cm² sec

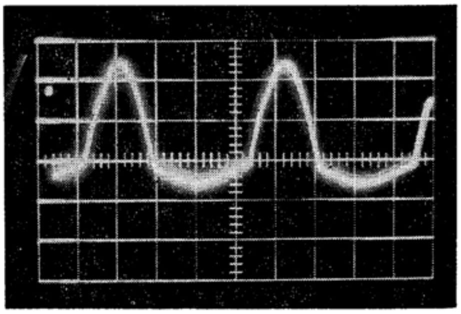

Fig. 4. Rectification of alternating sine-wave current in NBOH-PVSA systems.
$C_h=C_p=1.36\times10^{-2}$ equiv/l
Frequency : 0.1 cps

parameters, J_s and α, can be directly decided from the curves in Figs. 2 and 3; they are shown in Table 2.

Alternating Voltage-Current Characteristics. The rectification phenomena are effective when alternating voltages of ultra low frequencies are applied to the systems. The rectification ratio becomes poorer with an increase in the frequency. An example is shown in Fig. 4. The dependency of the rectification ratio on frequencies is illustrated in Fig. 5.

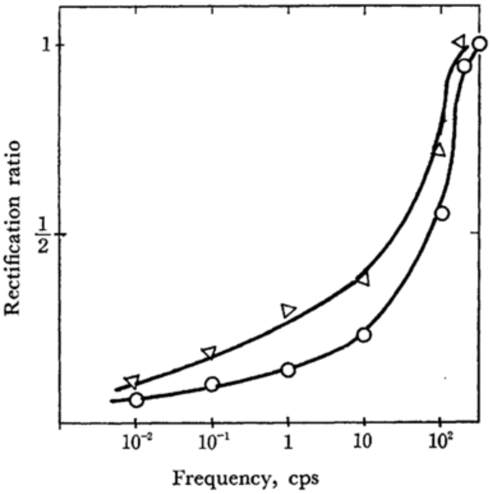

Fig. 5. Dependence of rectification ratio on frequencies in NBOH-PVSA systems. (Rectification ratio stands for the current ratio of the backword against the forward direction.)

○: $C_h=C_p=1.36\times10^{-2}$ equiv/l
△: $C_h=C_p=0.68\times10^{-2}$ equiv/l

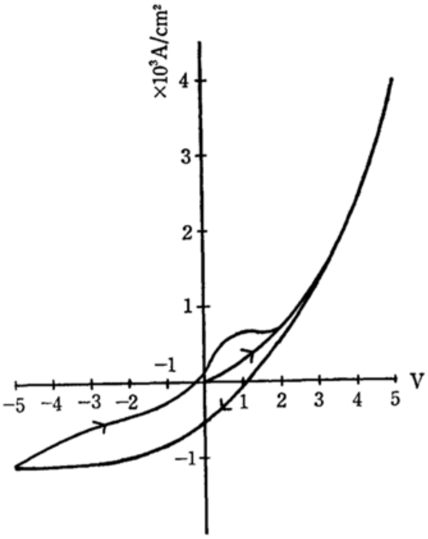

Fig. 6. Current plots *versus* constant voltages in NBPB-PVSA systems.
$C_{Br}=C_p=1.36\times10^{-2}$ equiv/l

From Fig. 4 we can see that the backward current is not very small. As is shown in Fig. 5, when frequencies are higher than 200 cps, the rectification ratio becomes unity, whatever concentrations of NBOH and PVSA are employed.

NBPB-PVSA Systems. *Static Voltage-Current Characteristics.* The static voltage-current characteristics of the NBPB-PVSA systems are similar to those of the NBOH-PVSA systems, but when the voltage was applied in an inverse direction, the voltage-current curve shows a remarkable hysteresis loops. A typical voltage-current curve is shown in Fig. 6.

The data given in Fig. 6 were read 30 sec after the voltages were applied. Figure 6 was obtained when we started from the application of a forward-bias voltage.

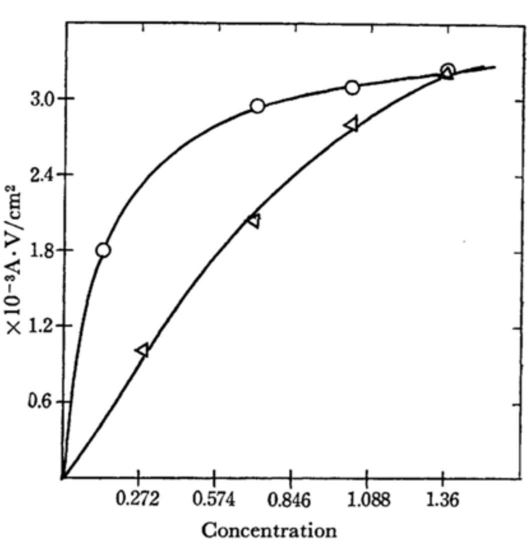

Fig. 7. Dependence of the areas of hysteresis loops on the concentrations of polyelectrolytes.

○: C_{Br} is maintained at the constant value (1.36×10^{-2} equiv/l) and C_p is varied.
△: C_{Br} and C_p are varied under the condition of $C_{Br}=C_p$.

TABLE 3. THE EXPERIMENTAL VALUES OF J_s AND α IN NBPB-PVSA SYSTEMS

$C_{Br}\times10^2$	$C_p\times10^2$	$J_s\times10^4$	$\alpha\times10^2$
1.36	1.36	2.40	1.34
1.36	1.02	2.25	1.23
1.36	0.68	3.70	1.10
1.36	0.136	3.30	0.84
1.02	1.36	2.70	1.25
0.68	1.36	2.30	1.10
0.272	1.36	4.70	1.07
0.136	1.36	3.30	0.68
1.02	1.02	2.50	1.18
0.68	0.68	3.15	0.93
0.272	0.272	7.00	0.34

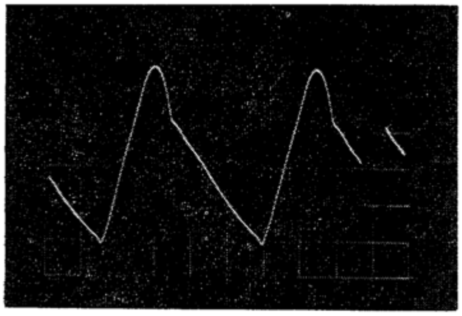

Fig. 8. Rectification of alternating sine-wave current in NBPB-PVSA systems.
$C_{\mathrm{Br}}=C_p=1.36\times10^{-2}$ equiv/l
Frequency: 0.1 cps

The areas of the loops decrease with a decrease in the concentrations of NBPB and PVSA. The dependency of the areas of loops on the concentrations of NBPB and PVSA is shown in Fig. 7.

The experimental values of J_s and α are shown in Table 3.

Alternating Voltage-Current Characteristics. Slight rectification effects were observed when frequencies lower than 100 cps were applied. An example is shown in Fig. 8. The rectification characteristics were not reproducible.

Theoretical

Theoretical considerations of the electrolytic rectification in double-membrane systems have been made by several authors. Katchalsky,[11] Ohki[12] and Läuger[4] developed the theory from the point of view of membrane phenomena. Senō[5] and Oshida[13] treated it as a semiconductor analogy. We also consider the electrolyte-membrane junction as a *p-n* junction in semiconductors.

NBOH-PVSA Systems. The potential profile of protons in the transient region is shown in Fig. 9.

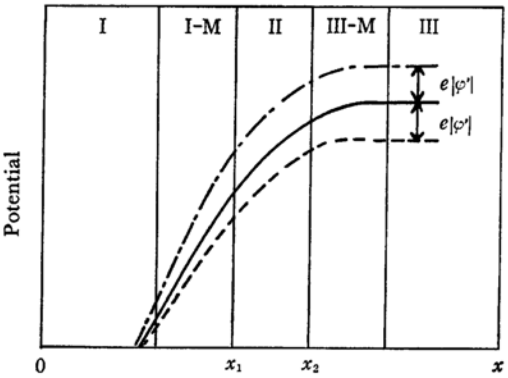

Fig. 9. Potential curve for protons.
I: PVSA aqueous solution. II: Membrane. III: NBOH aqueous solution. I-M, III-M: transition region. Steady line: no applied voltage. Dotted line: forward bias voltage. Chain line: inverse bias voltage.

The electrolytic current of the protons is given by the so-called Nernst-Planck equation:

$$J_p = e\mu_p C_p \mathrm{d}\varphi/\mathrm{d}x + eD_p \mathrm{d}C_p/\mathrm{d}x \tag{2}$$

where μ_p: the mobility of the protons, C_p: the concentration of the protons, D_p: the diffusion coefficient of the protons, and φ: the electrical potential. In the absence of a bias voltage, the electric current equals zero. Then the solution of the above equation is as follows:

$$C_p(x) = C_{p,0}\,\mathrm{epx}(-e\varphi/\boldsymbol{k}T) \tag{3}$$

where $C_{p,0}$ is the concentration of the proton at $\varphi=0$.

When a forward voltage is applied, the potential barrier in the transient region becomes lower, as is shown by the dotted line in Fig. 9. As a result, the diffusional current (the second term of Eq. (2)) surpasses the driving current (the first term of Eq. (2)) and protons diffuse from the membrane region into the III-M region. Then the concentration of protons in the III-M region becomes:

$$C_p = C_{p,3} + \Delta C_p \tag{4}$$

where the subscript 3 refers to the NBOH region.

As soon as the protons enter into the III-M region, the excess protons disappear as a result of the formation of water molecules with hydroxide ions.

The rate of this coupling reaction, R, is:

$$\begin{aligned} R(x) &= \overleftarrow{r}C_pC_{h,3} = \overleftarrow{r}C_{p,3}C_{h,3} + \overleftarrow{r}C_{h,3}\Delta C_p(x) \\ &= g + \overleftarrow{r}C_{h,3}\Delta C_p(x) \end{aligned} \tag{5}$$

where C_h is the concentration of hydroxide ions, $g=\overleftarrow{r}C_{p,3}C_{h,3}$ is the exchange velocity in the dissociation equilibrium of water, and $\overleftarrow{r}$ is the rate constant of the coupling reaction of protons and hydroxide ions. Under such circumstances, the diffusional flow of protons is expressed by Fick's second law:

$$\partial C_p/\partial t = D_p\partial^2 C_p/\partial x^2 \tag{6}$$

The change of C_p in the III-M region is as follows:

$$\partial C_p/\partial t = R(x) - g \tag{7}$$

Then, from Eq. (6) and Eq. (7), we get the following equation:

$$D_p\partial^2 C_p/\partial x^2 = R(x) - g \tag{8}$$

If we accept $x=\infty$; $C_p=C_{p,3}$ as the boundary condition, then the solution of Eq. (8) becomes as follows:

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[11] A. Katchalsky and O. Kedem, *Biophys. J.*, **2**, 53 (1962).

[12] S. Ohki, *J. Phys. Soc. Japan*, **20**, 1674 (1965).

[13] I. Oshida, "Ekitai no Denki Bussei," Maki Shotten, Tokyo (1964), p. 317.

$$C_p(x) = C_{p,3} + C'\exp(-(x-x_2)/L_p) \qquad (9)$$

where $L_p=\sqrt{D_p/\overleftarrow{r}C_{h,3}}$ is the mean distance which protons proceed in the III-M region untill their disappearance and where C' is the integral constant. Therefore, the current carried by the protons is given by:

$$\begin{aligned} J_p(x_2) &= -\boldsymbol{e}D_p(\mathrm{d}C_p/\mathrm{d}x)_{x_2} \\ &= \boldsymbol{e}D_p(C_p(x_2)-C_{p,3}) \end{aligned} \qquad (10)$$

From Boltzmann's distribution law (we suppose that the concentration distribution of protons obeys Boltzmann's law just as in Eq. (3), even if the electric current is not equal to zero.[*1]), we get Eq. (11).

$$C_p(x_2) = C_{p,3}\ \exp(\boldsymbol{e}\varphi'/\boldsymbol{k}T) \qquad (11)$$

These relations lead to the following expression:

$$\begin{aligned} J_p(x) &= (\boldsymbol{e}D_pC_{p,3}/L_p)\{\exp(\boldsymbol{e}\varphi'/\boldsymbol{k}T)-1\} \\ &= (\boldsymbol{e}D_pC_{p,3}/L_p)\{\exp(\alpha\boldsymbol{e}V/\boldsymbol{k}T)-1\} \end{aligned} \qquad (12)$$

where α is a parameter which shows the effective portion of applied voltage,

$$\varphi' = \alpha V \qquad (13)$$

Exactly the same procedure is used for hydroxide ions. Therefore, the total current is expressed by:

$$\begin{aligned} J = \boldsymbol{e}(&D_pC_{p,3}/L_p \\ &+D_hC_{h,1}/L_h)\{\exp(\alpha\boldsymbol{e}V/\boldsymbol{k}T)-1\} \end{aligned} \qquad (14)$$

where the subscript h refers to hydroxide ions, the subscript p refers to protons, and the subscript 1 refers to the PVSA region.

When a reverse bias voltage is applied, the density of protons at $x=x_2$ decreases by a ratio of $\exp(-\boldsymbol{e}\alpha|V|/\boldsymbol{k}T)$. As a result, protons diffuse out from the region III. However, this current is small and soon attains saturation because of the low density of protons in this region.

NBPB-PVSA Systems. Here also we adopt the above procedure, in which the role of hydroxide ions is to be displaced by bromide ions. Then the relation of the electric current *versus* the voltage is expressed by:

$$\begin{aligned} J = \boldsymbol{e}(&D_pC_{p,3}/L_p \\ &+ D_{\mathrm{Br}}C_{\mathrm{Br}}/L_{\mathrm{Br}})\{\exp(\alpha\boldsymbol{e}V/\boldsymbol{k}T)-1\} \end{aligned} \qquad (16)$$

where the subscript Br represents bromide ions.

Discussion

NBOH-PVSA Systems. Currents *versus* voltages curves are expressed by Eq. (14). Comparing Eq. (1) and Eq. (14), we get the following relation:

$$J_s = \boldsymbol{e}(D_pC_{p,3}/L_p+D_hC_{h,1}/L_h) \qquad (17)$$

Considering the dissociation equilibrium of water, we get the following equation:

$$C_{p,1}C_{h,1} = C_{p,3}C_{h,3} = K_w \qquad (18)$$

where K_w is the ionic product of water.

Then Eq. (17) and Eq. (18) lead to:

$$J_s = \boldsymbol{e}K_w\sqrt{\overleftarrow{r}}\ \left(\sqrt{D_h/C_{p,1}}+\sqrt{D_pC_{h,3}}\right) \qquad (19)$$

From Eq. (19) we can calculate the values of J_s. Then the calculated values of $J_s/(J_s)_{1,1}$, where $(J_s)_{1,1}$ is the value of J_s at $C_{p,1}=C_{h,3}=1.36\times10^{-2}$ equivalents per liter, and the experimental values of $J_s/(J_s)_{1,1}$ are compared in Table 4.

TABLE 4. COMPARISON OF $\{J_s/(J_s)_{1,1}\}_{\mathrm{calc}}$ WITH $\{J_s/(J_s)_{1,1}\}_{\mathrm{exp}}$ IN NBOH-PVSA SYSTEMS

$C_h\times10^2$	$C_p\times10^2$	$\{J_s/(J_s)_{1,1}\}_{\mathrm{calc}}$	$\{J_s/(J_s)_{1,1}\}_{\mathrm{exp}}$
1.36	1.36	1.00	1.00
1.36	1.02	1.07	1.35
1.36	0.68	1.18	1.85
1.02	1.36	1.09	1.42
0.68	1.36	1.23	1.54
0.272	1.36	1.68	3.26

We can see from Table 4 that the calculated values show characteristics similar to the experimental values, although no quantitative coincidence is found.

When a backward-bias voltage is applied, the electric current is independent of the concentrations of NBOH and PVSA (as is clear from Figs. 2 and 3). On the other hand, Eq. (14) shows that it must depend on the concentrations of NBOH and PVSA. Therefore, when a backward-bias voltage is applied, the diffusional mechanism can not be adopted as the conduction mechanism.

Therefore, it may be supposed that, while a backward-bias voltage is being applied, the electric currents are controlled not by the rate of diffusion, but by the rate of the dissociation of water in the transient region.

$$H_2O \underset{\overleftarrow{r}}{\overset{\overrightarrow{r}}{\rightleftarrows}} H^+ + OH^-$$

[*1] When the electric current is not equal to zero, we get the following solution from Eq. (2):

$$\begin{aligned} C_p(x) = \exp\!\left(-\boldsymbol{e}\int_0^x \mathrm{d}\varphi\right)&\left\{\int_0^x (-J/\boldsymbol{e}D_p)\right. \\ &\left.\times\exp\!\left(\boldsymbol{e}/\boldsymbol{k}T\int_0^{x'}(\partial\varphi/\partial x'')\mathrm{d}x''\right)\mathrm{d}x' + C_{p,1}\right\} \end{aligned} \qquad (15)$$

Then we must use Eq. (15) as the concentration distribution function. However, when a bias voltage is not applied, the potential difference in the transient region, $\Delta\varphi=(\boldsymbol{k}T/\boldsymbol{e})\,x\ln(C_{p,1}/C_{p,3})$, is about 0.6 V at $C_{p,1}=C_{h,3}=1.36\times10^{-2}$ equivalents per liter, and when a bias voltage ($V\leq5$ V) is applied, the effective portion of the applied voltage in the transient region is found from Table 2 to be of the order of 10^{-2}. Then the potential difference does change not so much that we must not adopt Boltzmann's law instead of Eq. (15) as the concentration distribution function.

where $\overrightarrow{r}$ and $\overleftarrow{r}$ are the rate constants in each direction. In the absence of a bias voltage, the rate of dissociation equals that of the recombination reaction:

$$\overrightarrow{v} = \overrightarrow{r}_0[\mathrm{H_2O}] = \overleftarrow{v} = \overleftarrow{r}_0[\mathrm{H^+}][\mathrm{OH^-}] = g \qquad (20)$$

where g is the exchange velocity, and $\overrightarrow{r}_0$ and $\overleftarrow{r}_0$ are the rate constants in each direction in the absence of a bias voltage. In the presence of a bias voltage $(-V)$, the potential of the reactants (H_2O) increases by $\delta G_1^{\neq}$, and that of the products ($H^+ + OH^-$) decreases by $\delta G_2^{\neq}$, while the potential at the transition state remains constant ($\Delta G^{\neq}$), then

$$\delta G_1^{\neq} + \delta G_2^{\neq} = \boldsymbol{N}eV \qquad (21)$$

where $\boldsymbol{N}$ is the Avogadro number.

The rates of the reactions in the forward and backward directions becomes as follows:

$$\begin{aligned}\overrightarrow{v} = \overrightarrow{r}[\mathrm{H_2O}] &= \\ &\boldsymbol{k}T/\boldsymbol{h}\exp\{-(\Delta G^{\neq}-\delta G_1^{\neq})/\boldsymbol{R}T\}[\mathrm{H_2O}] \\ &= g\exp(\delta G_1^{\neq}/\boldsymbol{R}T) \qquad (22)\end{aligned}$$

$$\begin{aligned}\overleftarrow{v} = \overleftarrow{r}[\mathrm{H^+}][\mathrm{OH^-}] &= \\ &\boldsymbol{k}T/\boldsymbol{h}\exp\{-(\Delta G^{\neq}+\delta G_2^{\neq})/\boldsymbol{R}T\}[\mathrm{H^+}][\mathrm{OH^-}] \\ &= \overleftarrow{r}_0[\mathrm{H^+}][\mathrm{OH^-}]\exp(-\delta G_2^{\neq}/\boldsymbol{R}T) \qquad (23)\end{aligned}$$

The H^+ and OH^- produced by the electric field are quickly caused to migrate by the electric field. Therefore, the concentrations of H^+ and OH^- would not be influenced by the electric field.

Then the total rate of the reaction is:

$$\begin{aligned}v &= \overrightarrow{v} - \overleftarrow{v} \\ &= g[\exp(\delta G_1^{\neq}/\boldsymbol{R}T) - \exp(-\delta G_2^{\neq}/\boldsymbol{R}T)] \\ &= g[\exp(\beta eV/\boldsymbol{k}T) - \exp\{-(1-\beta)eV/\boldsymbol{k}T\}] \qquad (24)\end{aligned}$$

where β is the so-called transfer coefficient.

$$\delta G_1^{\neq} = \boldsymbol{N}\beta eV, \quad \delta G_2^{\neq} = \boldsymbol{N}(1-\beta)eV \qquad (25)$$

Therefore, the electric current is as follows:

$$\begin{aligned}J = eg[&\exp(\beta eV/\boldsymbol{k}T) \\ &- \exp\{-(1-\beta)eV/\boldsymbol{k}T\}] \qquad (26)\end{aligned}$$

The J derived from Eq. (26) does not depend on the concentrations of NBOH and PVSA.

Therefore, it can be considered that when a forward-bias voltage is applied, the current *versus* voltage curves are decided by Eq. (14), while when a backward-bias voltage is applied, the current *versus* voltage curves are decided by Eq. (26).

The dynamic characteristics are shown in Fig. 5. From Fig. 5 we can see that the rectification effect becomes poorer as the frequencies become higher. The primary cause is probably the contribution of the capacitance of the systems.5) The contribution of the relaxation effect of the ionic atmosphere can be neglected, because the Wien effect and the Falkenhagen effect will appear at the frequencies higher than 10^7 cps.14)

NBPB-PVSA Systems. Just as in the NBOH-PVSA systems we can get the following equation instead of Eq. (19):

$$J_s = eK\sqrt{r'}\left(\sqrt{D_{\mathrm{Br}}/C_{p,1}} + \sqrt{D_p/C_{\mathrm{Br}}}\right) \qquad (27)$$

where $K = K_{\mathrm{HBr}}[\mathrm{HBr}]$, where K_{HBr} is the dissociation constant of HBr, and where r' is the rate constant of the dissociation equilibrium of HBr. In Table 5 the values of $J_s/(J_s)_{1,1}$ calculated using Eq. (27) are compared with the experimental values.

TABLE 5. COMPARISON OF $\{J_s/(J_s)_{1,1}\}_{\mathrm{calc}}$ WITH $\{J_s/(J_s)_{1,1}\}_{\mathrm{exp}}$ IN NBPB-PVSA SYSTEMS

$C_{\mathrm{Br}}\times 10^2$	$C_p\times 10^2$	$\{J_s/(J_s)_{1,1}\}_{\mathrm{calc}}$	$\{J_s/(J_s)_{1,1}\}_{\mathrm{exp}}$
1.36	1.36	1.00	1.00
1.36	1.02	1.05	0.98
1.36	0.68	1.13	1.61
1.36	0.136	1.69	1.43
1.02	1.36	1.11	1.17
0.68	1.36	1.27	1.00
0.272	1.36	1.82	2.05
0.136	1.36	2.47	1.43
1.02	1.02	1.16	1.09
0.68	0.68	1.40	1.35
0.272	0.272	1.88	3.05

From Table 5 it is clear not only that the values of $[J_s/(J_s)_{1,1}]_{\mathrm{calc}}$ do not agree quantitatively with those of $[J_s/(J_s)_{1,1}]_{\mathrm{exp}}$, but also that the qualitative tendency of the calculated values does not agree with that of the experimental values.

This disagreement and the hysteresis of the current *versus* voltage curves (Fig. 6) may be caused by the high degrees of the dissociation of hydrogen bromide and by the acidity of NBPB.

Another experiment was then carried out. At first a backward-bias voltage $(-V)$ was applied for 60 sec (while a backward-bias voltage is being applied, only the dissociation reaction of water occurs in the membrane region); the current after 60 sec was denoted I_{60}. Then suddenly we applied the forward-bias voltage (V) for 30 sec, after which we again applied $-V$ until the current became equal to I_{60} (in the transient region, at first the HBr accumulated by the forward current would begin to flow out). We then again applied the forward-bias voltage (V) for 60 sec, followed by the backward-bias voltage until the current equaled to

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14) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions, " Reinhold Pub. Corp., New York (1950), p. 211.

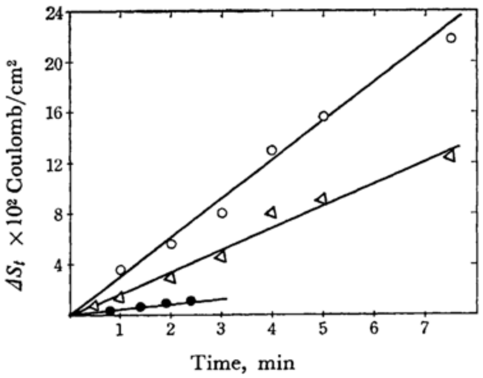

Fig. 10. The change of the backward electric quantities by the forward electric quantities. $C_{\mathrm{Br}}=C_p=1.36\times10^{-2}$ equiv/l

I_{60}. Then we applied the forward-bias voltage for 120 sec, and so on.

In Fig. 10 the $\Delta S_t(=S_t-S_0)$-t curves are shown, where S_t are the electric quantities carried by the backward currents, which flowed after the forward-bias voltage was applied for t sec, until the currents became equal to I_{60}. S_0 is the electric quantities which flowed while we first applied the backward voltage. ΔS_t indicates the extra electric quantities caused by applying the forward voltage and corresponds to the quantities of HBr accumulated in the transient region.

Figure 10 shows that the relation between ΔS_t and t is linear. This means that hysteresis is caused by the HBr accumulated in the membrane region.

While a forward-bias voltage is applied, HBr is accumulated in the transient region. When a backward-bias voltage is applied thereafter, the electric current is at first carried by H^+ and Br^-, and then, when the accumulated HBr has disappeared, the H_2O may begin to dissociate into H^+ and OH^-. Thus, the greater the quantity of HBr in the transient region, the larger the areas of the hysteresis loops.