*Permeability of Acidic Amino Acid through Anion Exchange Membrane**

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In order to obtain necessary information on the applicability of an ion-exchange membrane to the separation and purification of amino acids, experiments were carried out to study the permeability of an acidic amino acid through an anion exchange membrane comprised of a styrene-butadiene copolymer, and also to find membranes suitable for the separation of amino acids from chloride ions, conditions for electrolysis, and under what conditions acidic amino acids might or might not permeate through the membrane.

It was found that the permselectivity coefficient, T, of an acidic amino acid through an anion exchange membrane varied according to the current density, the total concentration of acidic amino acid and of chloride ions in the mixed solution used, the hydrogen ion concentration of the mixed solution and of the adjacent solution, separated by a membrane, and the character of the ion-exchange membrane used.

The permeability of ions through an ion-exchange membrane is very complicated, for it is affected by many factors. When an ion dialyzes through an ion-exchange membrane, the permeability of the ion is affected by the equilibrium according to the adsorption of ions by the ion-exchange membrane if the size of the ion is sufficiently smaller than that of the pores of the ion-exchange membrane. However, the permeability of an acidic amino acid through an ion-exchange membrane becomes more complicated when the size of the ion is approximately the same as that of the pore. Also, the hydrogen ion concentration in the membrane may have a very marked effect on the mobility of the amino acid in the membrane as acidic amino acid is an amphoteric electrolyte.

An experiment was carried out with a mixed solution of acidic amino acid and of a chloride ion system in order to examine the permeability of an acidic amino acid through an anion exchange membrane; the permselectivity coefficient, T, was also defined.

$$T=\frac{[A]_t}{[Cl]_t}\cdot\frac{[Cl]_s}{[A]_s} \qquad (1)$$

where

$[A]_t$: Moles of acidic amino acid permeated
$[Cl]_t$: Moles of chloride ion permeated
$[A]_s$: Moles of acidic amino acid in the mixed solution
$[Cl]_s$: Moles of chloride ion in the mixed solution

Consequently, the value, T, is a criterion of the permeability of amino acid, with chloride as the standard.

Experimental

Properties of the Anion Exchange Membranes Used.—Membranes A-1 to A-3 were prepared by forming a styrene-butadiene copolymer with a styrene content of 50% into a thin membrane with heating rolls; cross-linkage was carried out by a Friedel-Crafts type catalyst such as the aluminum chloride-ether complex or titanium tetrachloride, followed by chloromethylation and quartenarization[1]. The pore size of the membrane can be changed to any desired size during this process by adjusting the cross-linkage of the resin component of the membrane[2]. The pore size of these membranes is in the decreasing order of A-1, A-2 and A-3

Membranes A-4 to A-6 were prepared by coating the A-3 membrane with a thin layer of such high-molecular substances as styrenesulfonic acid-butadiene copolymer, polyvinylbutyral polymer, and phenolsulfonic acid-formaldehyde condensate to form a porous net. The cation exchange membrane was prepared by sulfonating the above-mentioned thin membrane of styrene-butadiene copolymer with concentrated sulfuric acid[1]. Table I summarizes the properties of these anion and cation exchange membranes. The pore sizes of anion exchange membranes derived from styrene-butadiene copolymer were compared according to the values of water content, W (the amount of water per unit weight of the dry resin), the water penetration ratio[3] (K) of the membrane, and the specific

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1) T. Kuwata and S. Yoshikawa, Japanese Pat. 239596, 239724, 248669; Brit. Pat. 793212, 804176.
2) S. Yoshikawa, Y. Uchida, A. Yamamoto and T. Kuwata, Presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960; T. Kuwata and S. Yoshikawa, Japanese Pat. 248669.
3) Kogyo Butsurikagaku Kenkyu-kai, "Kogyo Butsurikagaku", 2nd Ed., Korona-sha, Tokyo, p. 111.

TABLE I. PROPERTIES OF ION-EXCHANGE MEMBRANES USED

Type	Notation	Capacity of ion-exchange radical in membrane meq./g.	Concn. of ion-exchange radical in membrane meq./g.	Water content of membrane W, %	Water penetration ratio[a] K, $\times 10^{-16}$ cm^3	Specific resistance Ω-cm.	Ion permselectivity (0.1 N NaCl)	Thickness mm.
Anion exchange membrane	A-1	1.78	1.84	54.8	0.45	120	0.85	0.45
	A-2	1.69	3.16	47.2	0.23	250	0.91	0.26
	A-3	1.68	3.91	31.2	0.18	—	0.90	0.23
Fabric coated anion exchange membrane[b]	A-4					125		
	A-5					61		
	A-6					—		
Cation exchange membrane	C-1	1.32	2.13	50.1	0.32	100	0.92	0.28

a) Degree of permeation of a diaphragm is a value indicating the size and distribution of pores derived from Poiseville's law on the assumption that the cross-section of pores of diaphragm is round. This is ordinarily indicated by the quantity (cc.) which transfer through 1 cm^2 of diaphragm having a thickness of 1 cm. in one hour under a static pressure of 1 cm. of water column when 0.5 M sucrose solution and water are placed on the opposite sides of the diaphragm.

b) See Table II.

TABLE II. METHOD FOR PRODUCING AN ION-EXCHANGE MEMBRANE COATED WITH HIGH MOLECULAR SUBSTANCES

Notation	Method for producing coated membrane
A-4	A benzene solution of styrene-butadiene copolymer with a styrene content of 50% is coated on one surface of the A-3 membrane and then sulfonated by dipping it in a 96% sulfuric acid solution for 6 hr.
A-5	One surface of the A-3 membrane is coated 3 times with an ethyl acetate solution of a 3% polyvinylbutyral solution with a brush.
A-6	A solution composed of 4 mol. of phenol, 1 mol. of *p*-phenolsulfonic acid, 3 mol. of sodium hydroxide, and 7 mol. of formaldehyde solution is left standing overnight and then heated to 70~80°C, by which means a viscous solution is obtained. The methanol solution of this is coated on one surface of the A-3 membrane, air-dried at 60°C, and cured by heating it at 120°C for 3~4 hr.

resistance (Ω-cm.). Although these values are the products of the size and number of pores of the membranes and do not indicate the size of the pores themselves, these were used as approximate comparative values.

Apparatus and Procedure.—An electrolytic cell*1, separated by 4 sheets of 7.5 cm.×7.5 cm. anion and cation exchange membranes, as illustrated in Fig. 1, was used, with carbon (7 cm.×14 cm.×0.8 cm.) as the anode and nickel plate (7 cm.×7 cm.×0.3 mm.) as the cathode. In the intermediate compartments A and C, a 0.2% sodium sulfate solution was placed, a definite quantity of the mixed solution containing acidic amino acid and chloride ion (a quantity such that the reduction of acidic amino acid and chloride ions before and after the experiment is below 1%) is circulated in the direction of the arrow in compartment B, and a 3% sodium sulfate solution was circulated as the electrode solution in the direction of the arrow at a rate of 0.1~11./hr. in order to neutralyze the hydrogen ions and hydroxide ions produced in the electrode solution at all times and thus to prevent any effect of pH value fluctuation in the intermediate solution. A current of 5000~10000 coulombs was passed through each time. The solution in compartment C was removed after the current had been passed through, a quantitative analysis of the chloride

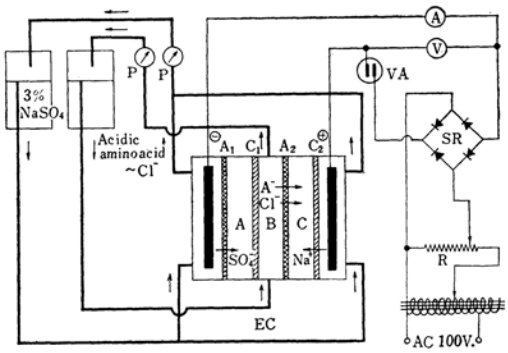

Fig. 1. Apparatus.

A	Ammeter
EC	Electrolytic cell
P	Pump
SR	Selenium rectifier
V	Voltmeter
VA	Copper voltameter

*1 The electrolytic cell was made by assembling the various compartments in the form indicated in Fig. 3 (for intermediate compartments) and in Fig. 4 (for electrode compartments) of a previous paper[4]. The same electrodes as used in this previous work were used.

4) Y. Hara, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), 65, 885 (1962).

ions was made by the Volhard or Mohr method, the acidic amino acid was analyzed by colorimetry[5], and then the T values were determined from these values by using Eq. 1. The transport numbers of the acidic amino acid and of the chloride ions (t_G or t_A*2 and t_{Cl}) were calculated from the following equations from the quantity of electricity Q (coulomb), which had been determined by the use of a copper voltameter:

$$t_G \text{ or } t_A = \frac{Q[A]_t}{96496} \times 100 \quad (2)$$

$$t_{Cl} = \frac{Q[Cl]_t}{96496} \times 100 \quad (3)$$

The experiment was carried out in the temperature range of 15~25°C, but no temperature correction of the T value was made as it was assumed that the relative change in mobility between the acidic amino acid and the chloride ions could be ignored within this temperature range. The electrolytic cell was provided with two pairs of anion and cation exchange membranes, A_1 and C_1, and A_2 and C_2, as is illustrated in Fig. 1, of which, the A_1, C_1 and C_2 membranes were fixed throughout the experiment; only the anion exchange membrane A_2 was changed. Thus, the A-2 membrane was used for the A_1 membrane in Fig. 1, and the C-1 membrane for the C_1 and C_2 membranes.

Results and Discussion

Tables III and IV and Figs. 2—1~2—11 show the experimental conditions and results.

Effect of Current Density.—The permselectivity coefficient, T, should be little affected by varying the current density if the ion-exchange resin pores are sufficiently larger than the size of the acidic amino acid molecules; if this T value changes considerably with the current density, this indicates that the ion-exchange membrane is obstructing the permeation of the ions. Figure 2-1 shows the case of A-2 membrane-glutamic acid (neutral solution). It can be seen that there is a tendency for the ion-exchange membrane to obstruct the

Table III. Experimental conditions

Runs No.	Anion exchange membrane (A_2)	Acidic amino acid*2	Acidic amino acid chrolide ion system		
			pH	$[A]_S$, M	$[Cl]_S$, M
1	A-2	G	6.8	0.10	0.10
2	A-2	G	6.8	0.20	0.20
3	A-2	G	6.8	0.05	0.05
4	A-2	G	6.8	0.09	0.10
5	A-2	G	6.8	0.09	0.08
6	A-2	G	6.8	0.09	0.05
7	A-2	G	6.8	0.09	0.03
8	A-2	G	6.8	0.15	0.05
9	A-2	G	6.8	0.05	0.15
10	A-1	G	6.8	0.10	0.10
11	A-1	G	6.8	0.20	0.20
12	A-2	G	11.6	0.09	0.10
13	A-2	G	3.6	0.09	0.10
14	A-2	G	1.85	0.09	0.10
15	A-1	G	11.6	0.10	0.10
16[a]	A-2	G	6.8	0.10	0.10
17[b]	A-2	G	6.8	0.10	0.10
18[a]	A-1	G	6.8	0.10	0.10
19[b]	A-1	G	6.8	0.10	0.10
20	A-3	G	6.8	0.10	0.10
21	A-4	G	6.8	0.10	0.10
22	A-5	G	6.8	0.10	0.10
23	A-6	G	6.8	0.10	0.10
24	A-2	A	6.8	0.10	0.10
25	A-2	A	6.8	0.20	0.20
26	A-2	A	6.8	0.05	0.05
27	A-1	A	6.8	0.10	0.10
28	A-1	A	11.4	0.10	0.10

Adjacent solution; a) 1 N sulfuric acid solution; b) 0.1 N sulfuric acid solution

5) M. Yamagishi and T. Yoshida, *Yakugaku Zasshi*, 73, 673 (1954).

*2 G stands for glutamic acid and A, for aspartic acid.

TABLE IV. TRANSPORT NUMBER OF ACIDIC AMINO ACID AND CHLORIDE ION

Runs No.	t_G or t_A Currrent density, amp./dm²						t_{Cl} Current density, amp./dm²					
	1.50	1.00	0.75	0.50	0.25	0.10	1.50	1.00	0.75	0.50	0.25	0.10
1	11.3	8.0	8.2	4.6	7.7	2.1	88.8	92.6	100.1	95.9	92.1	94.9
10	24.1	28.1	20.6	15.3	11.9	13.8	65.5	77.6	76.7	84.6	90.4	97.4
11	—	16.0	9.8	10.3	10.1	11.7	—	84.2	84.9	84.2	91.1	103.0
13	—	1.6 (2.7)	—	—	—	—	—	53.5	—	—	—	—
14	1.0 (6.2)	1.1 (4.5)	—	2.9 (8.4)	—	—	50.7	52.0	—	95.9	—	—
16	1.4	0.8	0.3	0.1	—	0.2	71.5	44.3	43.6	37.5	—	31.3
17	1.7	2.0	1.9	1.6	—	1.7	71.4	82.8	81.9	84.1	—	78.7
18	1.3	1.0	1.2	—	—	2.1	26.9	24.2	20.5	—	—	16.2
19	2.7	6.2	9.2	7.3	—	12.1	75.9	76.7	72.1	70.6	—	60.9
20	—	3.4	—	2.3	1.7	2.2	—	100.0	—	100.7	100.4	104.9
21	1.7	—	2.7	—	3.3	—	76.5	—	75.4	—	71.3	—
22	1.9	—	1.1	1.3	2.0	5.5	48.1	—	43.2	40.8	46.1	62.4
23	1.4	1.2	—	2.2	—	5.5	37.8	33.1	—	38.3	—	34.4

Number in parentheses indicates the transport number of glutamic acid which migrated toward the cathode by passing through cation exchange membrane (C_1).

permeation of acidic amino acid and also that the T value is very low at a low current density but increases with a rise in the current density, irrespective of the concentration. Figure 2–2 shows the relationship between the T value and the current density when the concentration of glutamic acid is fixed and when the molar ratio of chloride ion and glutamic acid is changed variously; almost the same tendency can always be observed despite the changes. This may be assumed as being due to the sieve effect of ions which can be observed when two kinds of ions having different sizes permeate through the ion-exchange membrane. Such a sieve effect is weakened by an increase in the current density, and larger ions will then also begin to permeate. Consequently, the sieve effect of glutamic acid and chloride ions on the ion-exchange membrane increased as the current density becomes lower.

As can be seen in Figs. 2–1 and 2–2, a horizontal movement or a lowering of the T value appears when the current density is increased to a range of 1.0～1.5 amp./dm² in the case of a low-concentration solution. This is due to the participation of hydrogen ions and hydroxide ions arising from the dissociation of water within the membrane as a result of insufficient supplies of glutamic acid and chloride ions resulting from the flow of electric current when the current density is increased more than necessary. Besides this, the relationship between the T value and the current density is affected by the kind and concentration of acidic amino acid, the properties of the membrane, and the hydrogen ion concentration of the mixed solution and of the solution in intermediate compartment C (referred to as the adjacent solution hereafter).

Effect of the Composition of the Mixed Solution.—A change in the composition of the mixed solution should naturally affect the T value due to the change in the ion concentration in the membrane, according to Donnan's membrane equilibrium theory. Figure 2–2 shows the relationship between the current density and the T value with the A-2 membrane when the concentration of glutamic acid is fixed and when the concentration of chloride ions is changed; the increase of the ratio of glutamic acid is accompanied by an increase in the T value when the current density is below 1.5 amp./dm². When the current density is 1.5 amp./dm², dissociation of water takes place above $[G]_s/[G]_s+[Cl]_s=0.65$ and there is a tendency toward a lowering of the T value. On the other hand, if the sum of the concentration of glutamic acid and chloride ions is made constant, the T value does not change very much, even when the solution composition is changed, as is shown in Fig. 2–3. It appears from the above results that the T value has a close relationship with the sum of the concentrations of glutamic acid and chloride ions; and this was also found to be true when comparing the experiments (Runs No. 8 and 9) when the sum of the concentrations of glutamic acid and chloride ions is the same but the concentration of each is reversed, there being almost the same tendencies in the relationship between the T value and the current density of both.

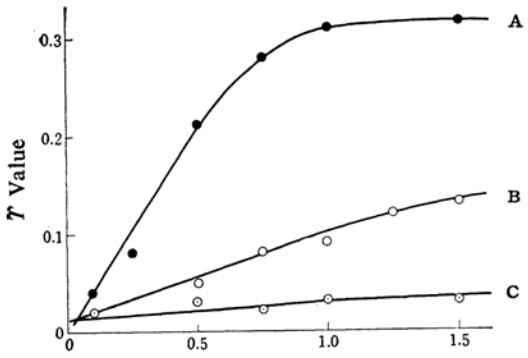

Fig. 2-1. Effect of current density.
Runs No. 3: (A), No. 1: (B), No. 2: (C)

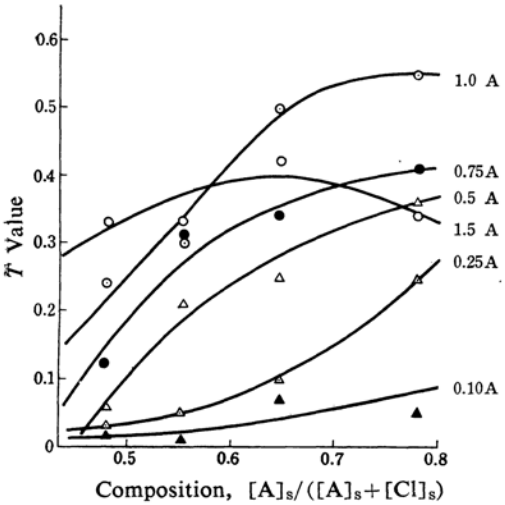

Fig. 2-2. Effect of soltion composition of mixed solution.
Runs No. 4-7, $[A]_s$=const.

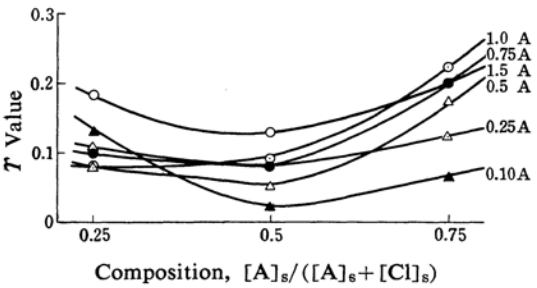

Fig. 2-3. Effect of solution composition of mixed solution.
Runs No. 1, 8 and 9, $[A]_s+[Cl]_s$=const.

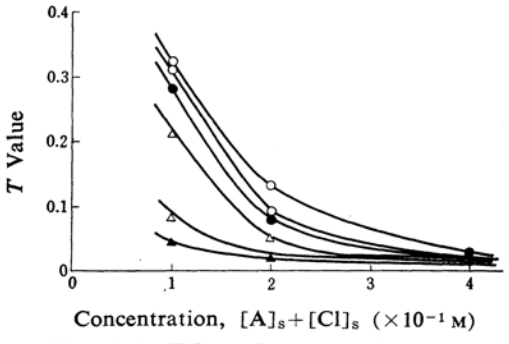

Fig. 2-4. Effect of concentration.
Runs No. 1-3, A-2 membrane, glutamic acid
-○- 1.5 amp. -⊙- 1.0 amp.
-●- 0.75 amp. -△- 0.5 amp.
-◬- 0.25 amp. -▲- 0.10 amp.

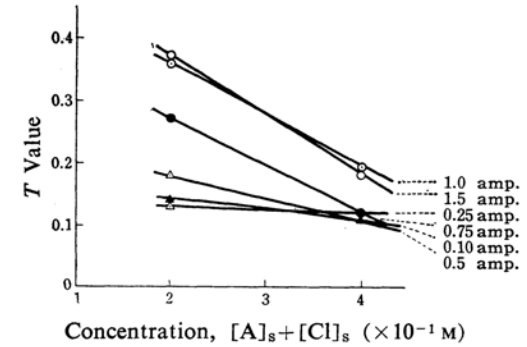

Fig. 2-5. Effect of concentration.
Runs No. 10-11, A-1 membrane, glutamic acid

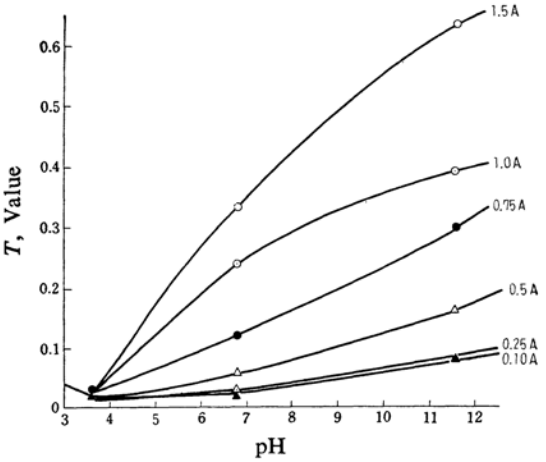

Fig. 2-6. Effect of pH.
Runs No. 4 and 12-14

Effect of Concentration.—The effect of concentration on the permeability of glutamic acid through the A-2 membrane is shown in Fig. 2-4. There is a tendency for the T value to decrease as the concentration increase, and there is almost no permeation of glutamic acid when the concentration of the mixed solution is over 4×10^{-1} M, even if the current density is increased. The permeability of glutamic acid increases in a dilute solution,

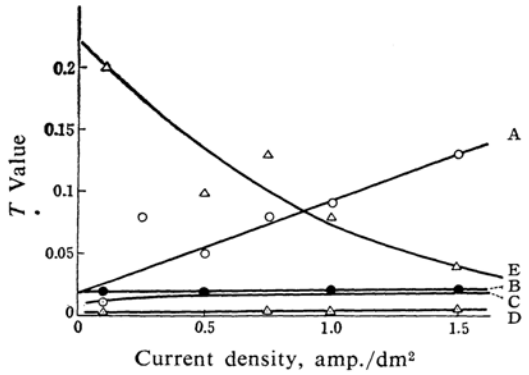

Fig. 2-7. Effect of adjacent solution.
Runs No. 1: (A), No. 16: (B), No. 17: (C), No. 18: (E), No. 19: (D)

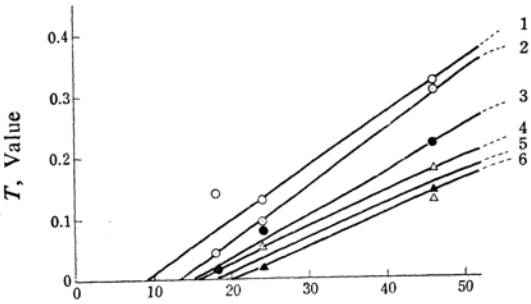

Fig. 2-8. Relation between water penetration ratio (K) of membrane and T value.
Runs No. 1, 10 and 20
1 1.5 amp. 2 1.0 amp. 3 0.75 amp.
4 0.5 amp. 5 0.25 amp. 6 0.10 amp.

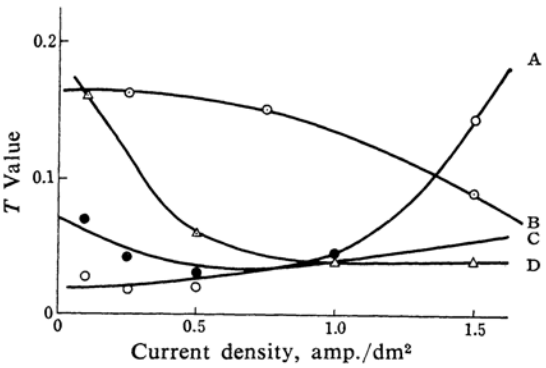

Fig. 2-9. Permeability of glutamic acid through coated membrane.
Runs No. 20: (A), No. 21: (B), No. 22: (C), No. 23: (D)

but water dissociation starts at a high-current density. It was observed from these results that the conditions which make the permeation of glutamic acid through A-2 membrane easiest are the concentration of the mixed solution at 1×10^{-1} M and a current density in the neighborhood of 1.0 amp./dm², and that

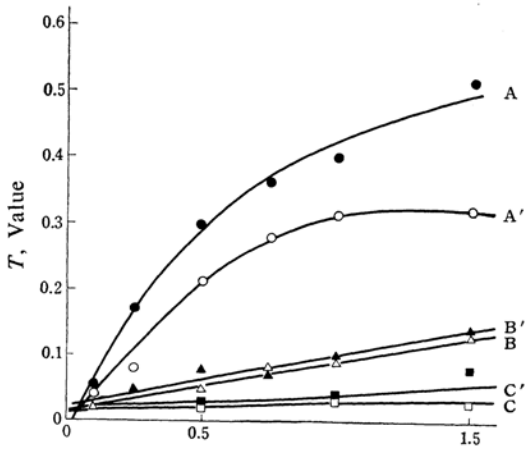

Fig. 2-10. Comparison of permeability of glutamic acid and aspartic acid (through A-2 membrane).
Runs No. 3: (A), No. 26: (A′), No. 1: (B), No. 24: (B′), No. 2: (C), No. 25: (C′)
A, B and C: Glutamic acid system
A′, B′ and C′: Aspartic acid system

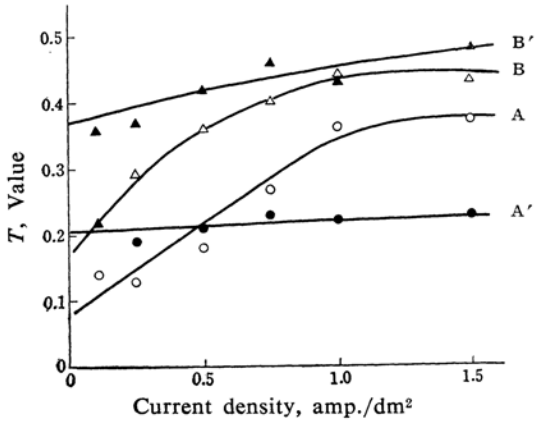

Fig. 2-11. Comparison of permeability of glutamic acid and aspartic acid (through A-1 membrane).
Runs No. 10: (A), No. 27: (A′), No. 15: (B), No. 28: (B′)
A and B: Glutamic acid system
A′ and B′: Aspartic acid system

chloride ions permeate selectively when dialyzed at a high concentration and in a low current density. Figure 2-5 shows the permeability of glutamic acid the A-1 membrane, which has larger pores than the A-2 membrane and in which quite a large T value was found even at a high concentration of over 4×10^{-1} M and in which quite a large penetration of glutamic acid was found through the A-1 membrane. The permeability of aspartic acid through the A-2 membrane was investigated in Run No.

24—26, in which it was observed that the effect of the change in concentration on the T value was more sensitive in the case of aspartic acid than in glutamic acid, since permeability with a dilute solution of below 1×10^{-1} M was good, and also, that it was dialyzed slightly even with a concentrated solution of over 4×10^{-1} M (Fig. 2–10).

Effect of the pH Value.—Amino acids are amphoteric electrolytes, with both anion and cation radicals in the molecule, and naturally their mobilities change according to the pH value when the dissociation condition of these radicals changes. In the present experiment, the permeability of glutamic and aspartic acids was examined under the conditions of hydrogen ion concentration at which the amino radical of acidic amino acid dissociates (near a pH value of 1.8), near the isoelectric point (pH value 3), near the neutral point when the first carboxyl dissociates, and at a pH value of 11.4~11.6 when the second carboxyl dissociates. As a general rule, it can be said that the permeability of an acidic amino acid through an anion exchange membrane is proportional to the degree of the dissociation of its carboxylic radical, which increases as the pH value rises. Consequently, it is advantageous to effect the migration of acidic amino acids in a bivalent state. In looking at the permeability of glutamic acid through the A-2 membrane indicated in Fig. 2–6, it can be observed that the T value increases with a rise in the pH value and that it is advantageous to dialyze glutamic acid in the bivalent rather than in the univalent form. A comparison of Runs No. 10 and 15 indicates that the T value does not increase so much on the weak alkaline side with the A-1 membrane, which has larger pores than the A-2 membrane, and that, consequently, it is not necessarily disadvantageous to dialyze glutamic acid in the univalent state. The same tendency can be observed in the case of aspartic acid (compare Runs No. 27 and 28). Besides the migration of acidic amino acid toward the anode by permeation through the anion exchange membrane (A_2), approximately the same amount migrates toward the cathode by passing through the cation exchange membrane (C_1) within the pH value range near the isoelectric point (Run No. 13). This is proof that amino acid is not in an electrical uncharged state at the isoelectric point but is present as zwitterion, having both negative and positive charges, and is neutral in appearance. It is also of interest to note that in an acid solution (pH value: 1.85) in which the amino radical of acidic amino acid dissociates sufficiently, glutamic acid migrates toward the anode by permeation through the anion exchange membrane (A_2), in addition to its movement toward the cathode through the cation exchange membrane (C_1). (Run No. 14). These results are in accord with those of the report by Yamabe et al.[6], in which they used a heterogeneous ion-exchange membrane, and indicate that amino acid in an aqueous solution is in an equilibrium relations as in the following equation (4);

$$\begin{array}{ccc} NH_3^+\text{-}CH\text{-}COOH & \rightleftharpoons & NH_3^+\text{-}CH\text{-}COO^- \\ \quad\vert R & & \quad\vert R \\ \quad + & & \quad + \\ \quad OH^- & & \quad H_2O \end{array}$$

$$\rightleftharpoons NH_2\text{-}CH\text{-}COO^- \quad (4)$$

$$\quad\vert R$$

$$\quad +$$

$$\quad H_3O^+$$

Effect of the Adjacent Solution.—When the anion in the intermediate compartment **B** solution permeates toward the anode through the anion exchange membrane (A_2), the hydrogen ion migrates toward the cathode through A_2 membrane since it can pass through the anion exchange membrane easily from the opposite direction if the hydrogen ion concentration in the adjacent solution (the intermediate compartment C solution) is high; as a result, the transport number of anions (acidic amino acid and chloride ions) in the anion exchange membrane becomes lower. Furthermore, dissociation of the carboxyl radical of acidic amino acid is suppressed and the transport number of acidic amino acid is lowered considerably if the hydrogen ion concentration in the membrane becomes high. Figure 2–7 shows the permeability of glutamic acid through the A-2 membrane when solutions with varying hydrogen ion concentrations (dilute sulfuric acid) were used as the adjacent solution. There was almost no dialysis of glutamic acid when a 0.1 N sulfuric acid solution was used as the adjacent solution, even when the current density was increased. Inhibition of the same degree against glutamic acid was observed when an 1N sulfuric acid solution was used as the adjacent solution with a A-1 membrane, which has a larger pore size. Furthermore, as a general tendency, the transport number (t_G) of glutamic acid becomes higher at a low current density if such an acidic solution is placed as the adjacent solution. It was made clear from these results that the hydrogen ion concentration of the adjacent solution has a great effect on the permeability of acidic amino acid; a hydrogen ion concentration of even about 0.1 N obstructs

6) T. Yamabe, M. Seno and N. Takai, This Bulletin, **32**, 1383 (1959); *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **64**, 556 (1961).

the dialysis of acidic amino acid considerably, and this becomes more marked as the pores of the anion exchange membrane become smaller.

Effect of the Properties of the Anion Exchange Membrane.—Figure 2-8 shows the relationship between the pore size of the membrane and the permeability of glutamic acid. It can be seen from Runs No. 1, 10 and 20 that the permeation of glutamic acid is obstructed considerably with membranes A-2 and A-3, which have small pores, while permeation is not obstructed to such an extent by membrane A-1; a horizontal movement of the T value is observed with a current density of over 1.0 amp./dm^2, and the permselectivity of anions as a whole becomes lower at a high current density. It can, therefore, be seen that A-1 is an appropriate membrane for the permeation of glutamic acid and that A-3 is the most unsuitable membrane of the three for the dialysis of glutamic acid.

Membranes coated with high-molecular substances (A-4 to A-6 membranes) were prepared in order to extend the characteristics of the A-3 membrane to retain the acidic amino acid, pass chloride ions selectively, and increase the mutual-sieving capacity of anions. The permeability of glutamic acid through these coated membranes and the basic A-3 membrane are compared in Fig. 2-9 and Runs No. 21-23, from which it can be seen that, as a common tendency, the permeation of glutamic acid is obstructed over a wide range of current densiy in coated membranes and that there is only a slight dialysis of glutamic acid. However, not only glutamic acid but also the permeation of chloride ions is obstructed by such a coated membrane; a very marked water dissociation takes place over a wide range of current densities in the coated membrane, as is observed from the sum of the transport numbers ($t_G + t_{Cl}$) of glutamic acid and chloride ions. The obstruction of glutamic acid dialysis by membranes coated with high molecular substances is in the decreasing order of A-6, > A-5 and > A-4 membranes; this is assumed to be correlated to the pore size intrinsic to the high molecular substances coated on the membrane. The membrane coated with phenolsulfonic acid-formaldehyde condensate (the A-6 membrane) obstructs the permeation of glutamic acid the most, and this tendency becomes weaker in the order of membranes coated with polyvinylbutyral (the A-5 membrane) and the product of styrenesulfonic acid - butadiene copolymer (the A-4 membrane). An inverse increase in T value is observed in the current density region in all of these coated membranes, but this is due to the fact that the transport number (t_G) of glutamic acid does not lower relative to that (t_{Cl}) of chloride ions.

Comparison of the Permeability of Glutamic Acid and Aspartic Acid.—A comparative study was made of glutamic acid and aspartic acid as representatives of acidic amino acids having a different number of methylene carbons. The permeability of glutamic acid and aspartic acid through the A-2 membrane is shown in Fig. 2-10, from which it can be seen that the permeability of aspartic acid is generally better than that of glutamic acid. The change in T value due to the change in current density with a concentrated solution in the case of aspartic acid is very slight, but the change is more violent with a dilute solution than in the case of glutamic acid. However, in the case of glutamic acid, the dissociation of water takes place with a dilute solution as the current density is increased; this results in a lowering of the T value. It is believed that glutamic acid encounters considerable resistance when permeating through the A-2 membrane. Figure 2-11 compares the permeability of these two acids through the A-1 membrane; it can be seen that the T value of aspartic acid is almost unaffected by the current density in the neutral or weakly alkaline states. In other words, the A-1 membrane does not obstruct the permeation of aspartic acid, but it does obstruct that of glutamic acid slightly. It is clear from this that ions which can permeate perfectly through the A-1 membrane have fewer than four carbon atoms.

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