Study on Reverse Osmosis. The Permeation Behavior of Amino Acid Solutions through Cellulose Acetate Membranes

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Transport phenomena of some aliphatic amino acids and aminobenzoic acids were investigated with Loeb type membranes annealed at 60—80°C.

The quantitative relation between permeability through the membrane and dissociation of amino acid was examined. The charged species are rich in the solutions of amino acids such as L-leucine, L-alanine, and L-glutamic acid, regardless of the pH of solution, thus making the rejection by membranes large; the rejection of L-leucine which had a rejection of 35% for NaCl, was 63.2% even for the membrane cured at 60°C. On the other hand, for aminobenzoic acids, the number of uncharged species in solution varied with the change in pH, and the rejection varied with pH. The fluxes of aminobenzoic acids were in linear relation to the calculated amount of uncharged species. The results of adsorption experiments indicate that the amounts of adsorbed aminobenzoic acid to cellulose acetate were in logarithmic relation to calculated amounts of undissociated species. The results support the view that dissociated species are more difficult to be distributed in membrane than undissociated ones.

It is known that electrolytes such as NaCl, $MgSO_4$, and CH_3COONa[1] can hardly pass through the Loeb type skinned membranes annealed at or above 80°C, but non-electrolytes such as phenol,[2] acetic acid[3] can do so easily. However, the relation between the ionic dissociation of the molecules in solution and the amount of transport in reverse osmosis processes has not been sufficiently discussed. Aliphatic amino acids and aminobenzoic acids were chosen to clarify the relation, since they are amphoteric and the charged state of molecules can easily be controlled by changing the pH of the solution.[4]

Experimental

The modified cellulose acetate (E-398-3) membranes were prepared by the method reported by Loeb and Manjikian.[5] DDS-880 membranes (Loeb type, De Danske Sukkerfabrikker, Denmark) were also used. Annealing temperatures of the Loeb type membranes were 60, 70, 75, and 80°C. Evaporation temperature was 18±1°C and evaporation time was 1 minute for all Loeb type membranes. The effective membrane area in the desalination cell[3] was 12.6 cm^2. The pressurized (40 atm) solution was circulated along the surface of the membrane at 250 ml/min to reduce concentration polarization. For aminobenzoic acids, a batched type apparatus[6] with 28.3 cm^2 effective membrane area was used in order to obtain more precise values. The impeller was rotated over the membrane at 300 r.p.m. by magnetic induced force. Solutions of 0.1 N NaCl, 0.01 N L-leucine, L-alanine, L-glutamic acid, 0.001 N *p*-aminobenzoic acid, and *m*-aminobenzoic acid were tested. Their pH was controlled by adding 0.1 N HCl to the solution. In all the experiments the permeated water was collected one hour after the beginning of the operation. Analysis of the components was performed by the method of Yemm and Cocking[7] for amino acids and by photo-absorption at 254 mμ and 214 mμ for *p*- and *m*-aminobenzoic acid, respectively, with a spectrophotometer (Simazu MPS 50L). The properties of the membrane were shown by water flux ($g/cm^2 \cdot sec$), salt flux ($mol/cm^2.sec$) and salt rejection. Salt rejection is given by

$$Re = (1 - C_p/C_f) \times 100 \quad (1)$$

where C_p and C_f are solute concentration of product and feed solutions, respectively. The membrane is known to be degradated by hydrolysis[8] in strong alkaline solutions. Thus no base was added to the feed solution, although it was desirable to test the pH effect on transport phenomena.

To avoid marked pH change, experiments were carried out as rapidly as possible.

Results

Rejection of Amino Acids. The rejection of amino acids was larger than that of NaCl as shown in Fig. 1. For instance, the rejection of L-leucine was 63.2% and 99.6% for the membrane annealed at 60°C and 80°C, respectively. There was a difference in the rejection of amino acids, the rejection of L-glutamic acid being somewhat larger than that of L-leucine, especially of the membrane annealed at low temperature (Fig. 1).

Effect of pH on the Transport of Amino Acids. To find the relation between the dissociation of the acids and their transport behavior, the permeation of *p*- and *m*-aminobenzoic acids was examined. Since it was required to analyze data more precisely, a DDS-880 membrane reheated at as high a temperature as 85°C was used in order to reduce membrane defects through which the feed solution would permeate at its concentration.

The rejection of NaCl by this membrane was 98.4% at 40 atm. As shown in Fig. 3, the rejection of *p*- and *m*-aminobenzoic acid changed with the pH of feed solution, the rejection of *m*-aminobenzoic acid being 57.0% and 95.7% at pH 3.88 and 1.77, respectively.

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3) C. Kamizawa and S. Ishizaka, *Kogyo Kagaku Zasshi*, **72**, 1227 (1969).
4) J. P. Greenstein and M. Winitz, "Chemistry of the Amino-acids" Vol. 1, Wiley, New York (1961), p. 435.
5) S. Manjikian, S. Loeb, and J. W. McCutchan, First Symposium on Water Desalination Washington, D. C., (1965), SWD/12.
6) T. Nakane and S. Ishizaka, *Bull. Soc. Sea Water Sci. Japan*, **26**, 11 (1972).
7) E. W. Yemm and E. C. Cooking, *Analyst*, **80**, 209 (1955).
8) K. D. Vos, F. Burris, and R. L. Riley, *J. Appl. Polym. Sci.*, **10**, 825 (1966).

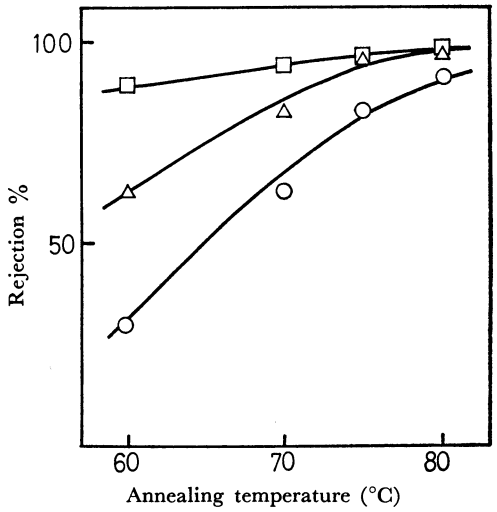


Fig. 1. Rejections of amino acids.
○: NaCl 0.1 M, △: L-leucine 0.01 M (pH 3.60), □: L-glutamic acid 0.01 M (pH 3.80)

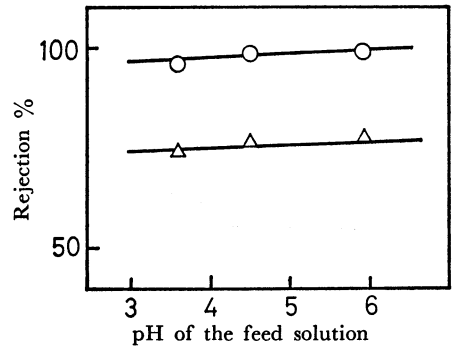


Fig. 2. The effect of pH on the transport of L-leucine.
○: Membrane annealed at 80°C, △: Membrane annealed at 70°C.

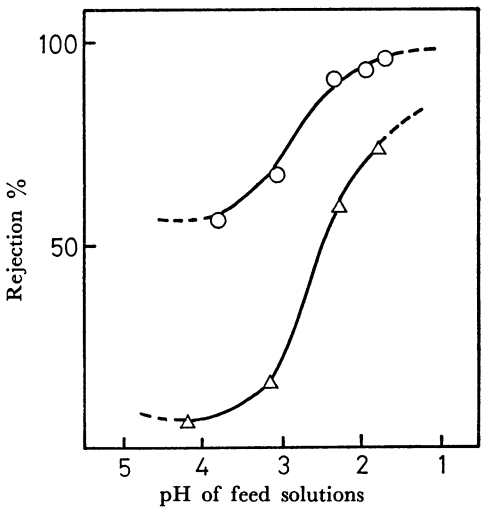
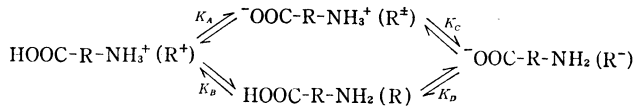


Fig. 3. Rejections of aminobenzoic acids.
○: *m*-Aminobenzoic acid 10^{-3} M, △: *p*-Aminobenzoic acid 10^{-3} M, Membrane: Annealed at 85°C.

Discussion

Rejection of Amino Acids. An evidence for the zwitter-ion structure of amino acids has been presented.[4] Amino acids dissociate as follows.



The equilibrium can be represented by the equations

$$K_1 = \frac{(H^+)[(R^\pm)+(R)]}{(R^+)} = K_A + K_B \qquad (2)$$

$$K_2 = \frac{(H^+)(R^-)}{(R^\pm)+(R)} \quad ; \quad \frac{1}{K_2} = \frac{1}{K_C} + \frac{1}{K_D} \qquad (3)$$

where K_A, K_B, K_C, and K_D are equilibrium constants for R^+ and $R^\pm$, R^+ and R, $R^\pm$ and R^-, and R and R^-, respectively. We obtain the relation

$$K_Z = \frac{(R^\pm)}{(R)} = \frac{K_A}{K_B} = \frac{K_D}{K_C} = \frac{K_1}{K_E} - 1 \qquad (4)$$

where K_E, the dissociation constant of the amino acid ester, was assumed to be almost equal to K_B and is used in place of K_B. As K_1 is much larger than K_E, for aliphatic amino acids[9] Eq. (4) is reduced to

$$K_Z = \frac{K_1}{K_E} \quad ; \quad -\log K_Z = pK_Z \qquad (5)$$

K_Z is of the order of 10^5 for most amino acids, and the quantity of uncharged species normally present in their solutions is insignificant. If the pH of the solution is changed, the composed ratio of R^+, $R^\pm$, R, and R^- changes, but the quantity of uncharged species remains insignificant. This seems to be the cause of the large rejection of amino acids regardless of the change of pH in the solution. The $R^\pm$; NH_3^+–R–COO^- species of the amino acid are of a dissociated form, but the apparent effective charge is zero. Thus in electrophoresis, ions do not move as if they had no charge but seem to act as charged species in reverse osmosis experiments.

Rejections of Aminobenzoic Acids. Only in the case of aminobenzoic acids, where $-pK_Z$ are −0.70, +0.36, and −0.87, for *o*-, *m*-, and *p*-compounds, respectively, the uncharged species assumes comparable concentration (Fig. 4). The behaviors of *m*- and *p*-compounds whose values of $R^\pm/R$ are 2.29 and 0.135, respecitively, were examined with values of K_A, K_B, K_C, K_D, K_1, and K_2 taken from a table.[10] The quantities of $R^\pm$, R^+, R, and R^-, were calculated from Eqs. (2), (3), (4), and (5). The calculated values of R in the *m*- and *p*-aminobenzoic solutions at various pHs are shown in Fig. 4. The relation between the concentration of R, uncharged species in equilibrium at pH of the feed and the permeated fluxes of *m*-aminobenzoic acid is shown in Fig. 5. The solute fluxes of *m*-aminobenzoic acid are proportional to the amounts of the uncharged species in the feed solutions. In the same manner, the relation holds for *p*-aminobenzoic acid. It can thus be said that the dissociation of the molecule plays an important role in the transport phenomena through the Loeb type membrane. Some differences were seen between the pH of feed and permeated solu-

9) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptide as Ions and Dipolar Ions" (1943), p. 99.
10) Greenstein and Winiz, "Chemistry of the Aminoacids" Vol. 1 (1952), p. 447.

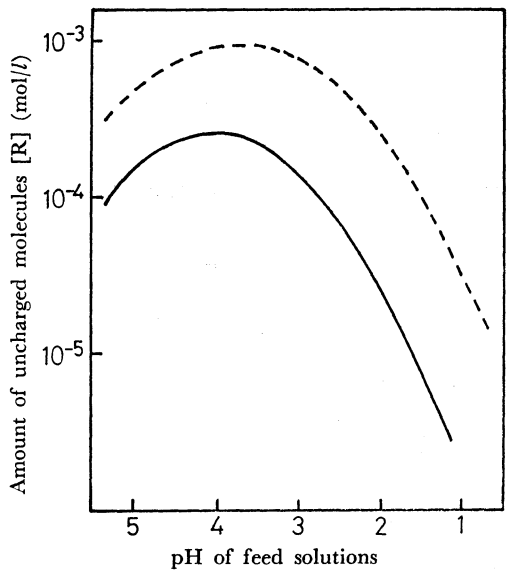


Fig. 4. Calculated amount foruncharged molecules.
——: *m*-Aminobenzoic acid 10^{-3} M, ----: *p*-Aminobenzoic acid 10^{-3} M.

tions, as 3.86 and 4.19, respectively, in the case of *m*-aminobenzoic acid. Thus a gradient of pH exists in the membrane.

However, in spite of the pH gradient, the interface between the membrane and the feed solution seems to be more effective for the transport of the solute than the charged molecules in the membrane, as is indicated by the result shown in Fig. 5.

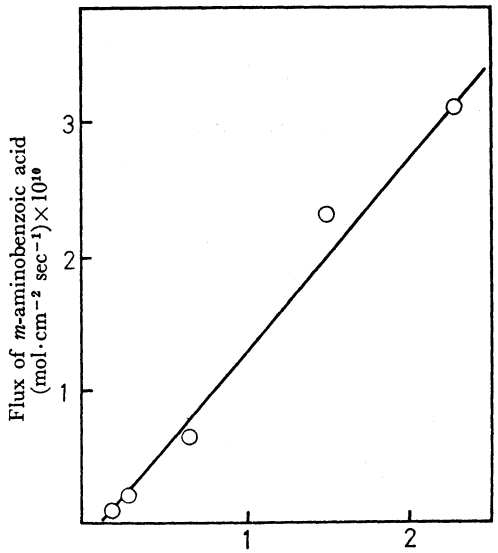


Fig. 5. The relation between the quantity of uncharged molecules and the flux.

Adsorption of m-*Aminobenzoic Acid to Cellulose Acetate Powder.* To understand the relation between the permeation and the dissociation of the solute more precisely, the adsorption of *m*-aminobenzoic acid to cellulose acetate powder was measured.

A definite amount of each of the *m*-aminobenzoic solutions (0.001 N) containing various amounts of HCl, was mixed with 3 g of dry cellulose acetate powder in a 200 m*l* conical flask. It was left at ambient temperature and shaken vigorously from time to time, The apparent adsorbed amount was determined from the difference between the solute concentrations before and after the adsorption. Adsorption of water to cellulose acetate was not taken into consideration.

The adsorbed amounts of *m*-aminobenzoic acid were proportional to the logarithm of calculated amounts of uncharged species (R) in the form of Freundlich type adsorption isotherm (Fig. 6).

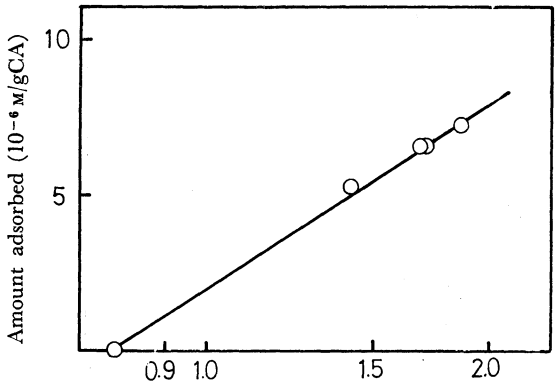


Fig. 6. Amounts adsorbed of *m*-aminobenzoic acid to cellulose acetate powder.

This seems to indicate that undissociated species have greater affinity to cellulose acetate. If affinity of solute to cellulose acetate is considered to be an important factor for determining the distribution coefficient, our result would support the fact that the dissociated species are more difficult to be distributed in the membrane than the undissociated ones. On the rejection of electrolytes, Glueckauf described[11] the potential wall by dielectric constant of cellulose acetate, but this is not satisfactory for explaining the behavior of most electrolytes.[12]

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12) T. S. Govindan and S. Sourirajan, *Ind. Eng. Chem. Proc. Des. Develop.* **5**, 422 (1966).