On the pH Dependence of Transport Behavior of Weak Acids and Weak Bases across Ion-exchange Membranes

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We have pointed out that the transport behavior of weak acids and bases across ion-exchange membranes depends remarkably on the solution pH[1]. It is noticed that there is a range of pH at which the maximum transport takes place. This behavior is due to the suppression of dissociation of acids in the lower pH range, and to the contribution of the competitive transport of hydroxide ions in the higher pH range, in the case of weak acids for example. In this communication, this problem is treated in general and some useful conclusions are derived.

Let us consider the three-component system consisting of strongly dissociated ions A^-, e.g., chloride ions, weak acid ions B^-, and hydrogen or hydroxide ions. It is assumed that the concentration of each component of the sample solution remains unchanged in course of the electrodialysis experiment and all the electrolytes which are adsorbed in the membrane are in the dissociated state. Then, the permselectivity coefficient $T^{\mathrm{B}}_{\mathrm{A+OH}}$ is defined and written in terms of constant or known quantities as follows:

$$T^{\mathrm{B}}_{\mathrm{A+OH}}=\left(\frac{\bar{t}_{\mathrm{B}}}{\bar{t}_{\mathrm{A}}+\bar{t}_{\mathrm{OH}}}\right)\Bigg/\left(\frac{C_{\mathrm{B}_0}}{C_{\mathrm{A}}+C_{\mathrm{OH}}}\right)$$
$$=T'^{\mathrm{B}}_{\mathrm{A}}\cdot\frac{KC_{\mathrm{OH}}}{1+KC_{\mathrm{OH}}}\cdot\frac{1+(C_{\mathrm{OH}}/C_{\mathrm{A}})}{1+T^{\mathrm{OH}}_{\mathrm{A}}(C_{\mathrm{OH}}/C_{\mathrm{A}})} \quad (1)$$

1) T. Yamabe, M. Senō and N. Takai, This Bulletin, 32, 1383 (1959); *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **64**, 556 (1961); I. Kamii, T. Tanaka and T. Yamabe, *J. Pharm. Soc.* (*Yakugaku Zasshi*), **81**, 931 (1961).

where t transport number, C concentration, $K=K_B/K_W$, K_B and K_W dissociation constants of weak acid BH and water, and

$$T'^{B}_{A}=\left(\frac{\bar{t}_B}{\bar{t}_A}\right)\Big/\left(\frac{C_B}{C_A}\right);\quad T^{OH}_{A}=\left(\frac{\bar{t}_{OH}}{\bar{t}_A}\right)\Big/\left(\frac{C_{OH}}{C_A}\right)$$

are permselectivity coefficients* which are constant independently of experimental conditions, and the absence and presence of bar above symbols refer to the solution and the membrane phase respectively. Subscript B_0 means total acid molecules in dissociated and undissociated states, and B weak acid ions.

The ratio of transport numbers which expresses the relative amount of weak acid transferred across an anion-exchange membrane is

$$\frac{\bar{t}_B}{\bar{t}_A+\bar{t}_B+\bar{t}_{OH}}=\frac{T^{B}_{A+OH}C_{B_0}}{C_A+T^{B}_{A+OH}C_{B_0}+C_{OH}} \qquad (2)$$

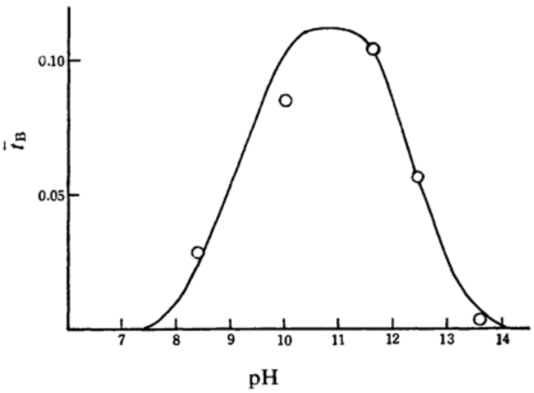

Fig. 1. Transport of boric acid across an anion-exchange membrane.
○ Experimental, —— Theoretical
Experimental conditions; A five-compartment cell, 0.33 mA./cm^2, 1 hr.; Membranes, heterogeneous ones made from Amberlite IR-120 or IRA-400; Stock solution, 0.05 M H_3BO_3, 0.05 M NaCl, NaOH (for adjustment of pH).

The experimental verification of these expressions was obtained in the case of boric acid across an anion-exchange membrane as shown in Fig. 1. The experimental procedure was the same as that in the preceding papers[1]. The transport number $\bar{t}_B$ is the amount (equivalent**) of boric acid transferred across the anion-exchange membrane by passage of the electricity of 1 faraday. The theoretical curve was drawn according to Eqs. 1 and 2, in which quantities were estimated as follows; T^{OH}_{Cl} is 2, T'^{B}_{Cl} is 0.2*, $\bar{t}_{Cl}+\bar{t}_B+\bar{t}_{OH}$, the transport number of anions across the anion-exchange membrane***, is 0.7 and K_B is 7.3×10^{-10}**.

This treatment leads us to the following general conclusion. The minimum pH at which the appreciable transport of a weak acid occurs depends primarily on its dissociation constant and nearly equals to pK_B-1, and the maximum transport takes place in the pH range between pK_B+1 and 12~13. The smaller is T^{OH}_{A} and the larger are C_A and C_B, the higher is the maximum pH. The same treatment can be applied to weak bases. The details will be presented in near future.

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* These are practically dependent on the current densities. T'^{B}_{A} is known from the electrodialysis experiment in the pH range higher than pK_B+1, where

$$T^{B}_{A}=(\bar{t}_B/\bar{t}_A)/(C_{B_0}/C_A)=T'^{B}_{A}.$$

** Only the dissociation of boric acid in the first step was considered. Further dissociations are so weak (dissociation constants 1.8×10^{-13} and 1.6×10^{-14}) that these contributions are neglected in the pH range smaller than 13 and in the larger pH range the contribution of hydroxide ions becomes overwhelming.

*** Strictly, it contains the contribution of the transport number of anions across the adjacent cation-exchange membrane.