CHEMISTRY LETTERS, pp. 597-600, 1988.

Active Transport of Formaldehyde through an Anion-Exchange Membrane via the Formation of Bisulfite Adduct

Manabu IGAWA*† and Michael R. HOFFMANN
California Institute of Technology, W. M. Keck Laboratories,
138-78, Pasadena, CA 91125, U.S.A.
†Faculty of Engineering, Kanagawa University,
Rokkakubashi, Kanagawa-ku, Yokohama 221

Formaldehyde reacts with bisulfite to form hydroxymethanesulfonate, which is a conjugate base of a strong acid, and is able to be transported actively by the coupled countertransport of hydroxide ion through an anion-exchange membrane. The permeation rate is controlled by pH and formaldehyde can be separated readily from other types of organic solutes via this method.

There have been many reports on the selective and active transport of electrolytes through membranes under a concentration gradient since macrocyclic compounds, such as monensin1) and dibenzo-18-crown-6,2) were first reported to be effective carriers for the transport of metal ions. A few papers have been reported on the selective transport of organic non-electrolytes, such as the permselectivity of sugars regulated by pH in polyvinyl-polypeptide membranes3) and the concentration of hydrophobic solutes through a hydrophobic membrane under a pressure gradient.4) However, there has been no report on the active transport of organic non-elctrolytes through artificial membranes. We will report on the selective transport of formaldehyde with a coupled countertransport of hydroxide ion through an anion-exchange membrane by the formation of an adduct with bisulfite. The permeation rate depends on pH because the formation and dissociation rate of the sulfonate adduct are strong functions of pH,5) and as a consequence the neutralization dialysis technique6) was applied in this experiment to maintain a constant pH.

The permeation experiment was carried out with a cell composed of two membranes, an anion-exchange membrane and a cation-exchange membrane, and three compartments divided by the two membranes, which were named as a compartment A, B, and D. The ion-exchange membranes used in this study were Selemion AMV and CMV (Asahi Glass Co., Ltd.). Each membrane area was 7.7 cm^2 and the thickness of each compartment was 0.79 mm. In compartment A, compartment B, and compartment D, an acidic solution, an alkaline solution, and a mixed solution of formaldehyde and sodium bisulfite were pumped from each reservoir, respectively. The volume of each solution was 100 cm^3 and pumping rate was 4.2 cm^3 min^{-1}. An aliquot of the solution in each compartment was collected at an interval. The concentration of S(IV) and formaldehyde were analyzed by modified Nash method7) and modified MBTH

(3-methyl-2-benzothiazolinone hydrazone) method,[8] respectively.

Figure 1A shows the concentration change in compartment B in a representative permeation experiment. The solution pH of compartment D was adjusted to about pH 4 by the addition of 10^{-4} mol dm^{-3} HCl because the adduct is most stable in the pH range 3 to 5, where HSO_3^- is the dominant form of S(IV); the solution pH tends to remain constant at about pH 4 in the neutralization dialysis cell.[6] Formaldehyde was transported through an anion-exchange membrane from compartment D to compartment B. Permeation of formaldehyde from compartment D to compartment A through the cation-exchange membrane was not detected. Formaldehyde transport was facilitated by bisulfite because under the same experimental condition other than the absence of bisulfite in compartment D formaldehyde was not permeated to compartment B. Formaldehyde is retained on an anion-exchanger which adsorbs bisulfite ion and eluted with alkaline solution;[9] the active transport of formaldehyde through an anion-exchange membrane occurs on the same basis. Formaldehyde react with bisulfite to form hydroxymethanesulfonate (HMSA) as

$$HCHO + HSO_3^- = HOCH_2SO_3^-. \qquad (1)$$

After permeation through the anion-exchange membrane, HMSA is dissociated in alkaline solution as

$$HOCH_2SO_3^- + OH^- = HCHO + SO_3^{2-} + H_2O, \qquad (2)$$

where the dissociation constant is reported to be $(8.6 \times 10^{-3})[OH^-]\ s^{-1}$.[10] This experiment was carried out in the neutralization dialysis cell and the pH change during the experiment was less than ±0.2 because the concentration of hydroxide ion permeated through the membrane was reduced in compartment D by the reaction with protons permeated through the cation-exchange membrane.[6] When the experiment was carried out without a neutralization dialysis cell, that is, only with an anion-exchange membrane and compartment D and B, the solution pH in compartment D increased from pH 4 to pH 8 during the experiment and the flux of formaldehyde decreased to around a half.

The permeation experiments were carried out just after the preparation of the solution and formaldehyde was transported through the membrane as a sulfonate adduct. However, formaldehyde reacts with bisulfite very slowly to form HMSA when the bisulfite concentration was equal to the formaldehyde concentration.

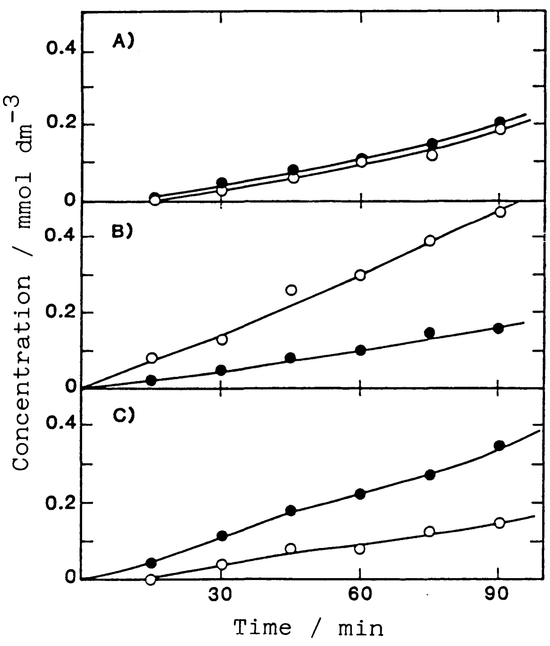

Fig. 1. Formaldehyde and S(IV) transport through anion-exchange membrane. o, HCHO. ●, S(IV).
A)Compartment B, 10^{-3} mol dm^{-3} NaOH. Compartment D, 10^{-3} mol dm^{-3} HCHO and 10^{-3} mol dm^{-3} $NaHSO_3$.
B)Compartment B, 10^{-3} mol dm^{-3} NaOH. Compartment D, 10^{-2} mol dm^{-3} HCHO and 10^{-3} mol dm^{-3} $NaHSO_3$.
C)Compartment B, 10^{-2} mol dm^{-3} NaOH. Compartment D, 10^{-3} mol dm^{-3} HCHO and 10^{-3} mol dm^{-3} $NaHSO_3$.

The half-life of S(IV) is calculated to be about 45 min under these experimental conditions.[5] It can therefore be presumed that bisulfite is adsorbed at the surface of the anion-exchange membrane in a high concentration, where free formaldehydes react with bisulfite ion. The reaction rate depends on the concentration ratio of bisulfite to formaldehyde and it is very fast when one of them was added in large excess.[11] It was ascertained that the flux of formaldehyde did not change when the reagent grade HMSA was used instead of formaldehyde and sodium bisulfite.

Figure 1B is the result when the ratio of formaldehyde to bisulfite was 10 in compartment D. If one bisulfite ion was permeated with one formaldehyde molecule by forming one HMSA ion and formaldehyde was transported as HMSA through the membrane, the flux of S(IV) should not exceed that of formaldehyde. However, the transport rate of formaldehyde was much larger than that of S(IV). Figure 1C shows the result when the sodium hydroxide concentration in compartment B was 0.01 mol dm^{-3}. The permeability of S(IV) increased because of the high concentration gradient of hydroxide ion across the membrane but the flux of formaldehyde decreased and the transport rate of S(IV) was much larger than that of formaldehyde in contrast to Fig. 1B.

The transport mechanism of formaldehyde through an anion-exchange membrane can be explained well as shown in Fig. 2 by the carrier-relay mechanism, which was proposed in the cation transport mediated by a macrocyclic compound under an electric field.[12] Formaldehyde reacts rapidly with bisulfite ion, which is adsorbed on the membrane and permeats with the coupled countertransport of hydroxide ion. Formaldehyde is relayed rapidly from one bisulfite ion to another bisulfite ion under the concentration gradient of formaldehyde. The interaction between bisulfite ion and formaldehyde is weaker than that between the anion-exchange site and bisulfite ion. As a consequence of this pathway, excess formaldehyde is transported relative to bisulfite as shown in Fig. 1B. When NaOH concentration in compartment B was high, the hydroxide concentration in the membrane was also high. Under these conditions HMSA in the membrane was dissociated in the vicinity of compartment D and S(IV) was transported without the associated transport of formaldehyde through the membrane as shown in Fig. 1C.

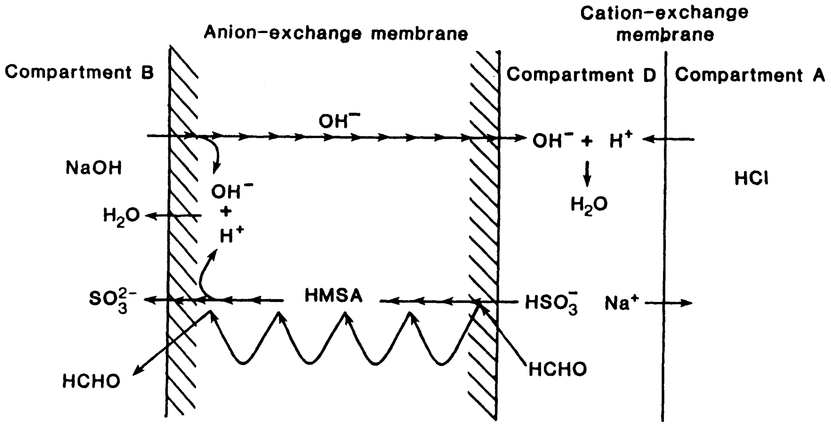

Fig. 2. Transport mechanism.

The details of this transport scheme are now under investigation. None the less, this is the first report of the selective and active transport of an organic non-electrolyte through an artificial membrane. Bisulfite ion reacts selectively with aldehydes[13)] and it will be possible to separate aldehydes from other non-electrolytes. Since some organic non-electrolytes react with ions (e.g. sugar with borate ion),[14)] it will be possible to permeate the organic non-electrolytes actively through ion-exchange membranes. Similar transport mechanism may be important in biomembranes.

References

1) E. M. Choy, D. F. Evans, and E. L. Cussler, J. Am. Chem. Soc., 96, 7085 (1974).

2) C. F. Reusch and E. L. Cussler, AIChE J., 19, 736 (1973).

3) D. Chung, S. Higuchi, M. Maeda, and S. Inoue, J. Am. Chem. Soc., 108, 5823 (1986).

4) M. Igawa, T. Tachibana, K. Yoshida, M. Tanaka, and M. Seno, Chem. Lett., 1984, 1527; M. Igawa, T. Anzai, and M. Seno, Chem. Lett., 1985, 1703.

5) S. Boyce and M. R. Hoffmann, J. Phys. Chem. 88, 4740 (1984); T. M. Olson and M. R. Hoffmann, Atmos. Environ. 20, 2277 (1986).

6) M. Igawa, K. Echizenya, T. Hayashita, and M. Seno, Bull. Chem. Soc. Jpn., 60, 381 (1987); M. Igawa, K. Echizenya, T. Hayashita, and M. Seno, Chem. Lett., 1986, 237.

7) P. K. Dasgupta, K. Decesare, and J. C. Ullrey, Anal. Chem., 52, 1912 (1980).

8) E. Sawicki, T. R. Hauser, T. W. Stanley, and W. Elbert, Anal. Chem., 33, 93 (1961). In this method formaldehyde combined with bisulfite to be HMSA can not be detected and then, NaOH was added to the sample solution to dissociate HMSA. A 1 cm^3 of 0.1% 3-methyl-2-benzothiazolinone hydrazone hydrochloride monohydrate solution was added to the mixed solution of 1 cm^3 of 0.1 mol dm^{-3} NaOH and 0.1 cm^3 of the sample solution. After shaking and standing for 1 hour, 1 cm^3 of 0.1 mol dm^{-3} HNO_3 was added to neutralize the solution and then, 0.15 cm^3 of 1% $FeCl_3 \cdot 6H_2O$ solution was added. After shaking and standing for 1 hour, 2.7 cm^3 acetone was added and the absorbance was measured at 640 nm. In this method total aldehyde can be determined and there is no interference from bisulfite ion.

9) O. Samuelson "Ion Exchangers in Analytical Chemistry," John Wiley & Sons, Inc., New York (1953), p. 190.

10) P. E. Sørensen and V. S. Andersen, Acta Chem. Scand., 24, 1301 (1970).

11) D. L. Duval, M. Rogers, and J. S. Fritz, Anal. Chem. 57, 1583 (1985).

12) H. K. Wipf, W. Pache, P. Jordan, H. Zahner, W. Keller-Schierlein, and W. Simon, Biochem. Biophys. Res. Commun., 36, 387 (1969).

13) E. A. Betterton and M. R. Hoffmann, J. Phys. Chem., 91, 3011 (1987).

14) R. Pasternack, P. P. Regna, R. L. Wagner, A. Bavley, F. A. Hochstein, P. N. Gordon, and K. J. Brunings, J. Am. Chem. Soc., 73, 2399 (1951).

(Received December 23, 1987)