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Saturation Kinetics of Acetic Acid Transport through Perfluorosulfonated Ion-Exchange Membranes

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Abstract

Permeation of acetic acid through perfluorosulfonated polymeric membranes exhibit Michaelis-Menten-type saturation kinetics characterized by a maximum flux for permeating species. It is postulated that the saturation kinetics is probably a result of the solubility of acetic acid reaching a maximum limit in the membrane.

INTRODUCTION

Extensive literature information exists on the applications of perfluorosulfonated ion-exchange membranes, such as Nafion (registered trademark of E. I. du Pont de Nemours & Company), in electrochemical processes (*1–5*). Little is known about the use of these membranes for the potential separation of carboxylic or amino acids. Chum, Hauser, and Sopher (*6*) reported their finding of the transport of some organic acids, such as propionic and levulinic acids, through the acid form of Nafion in aqueous solutions. Recently Sikdar (*7*) demonstrated that formic and acetic acids in aqueous solutions permeate through the acid form of Nafion-117 membrane at rates in the neighborhood of 10^{-7} mol/cm$^2 \cdot$ s. Sikdar (*8*) also showed that amino acids, such as glycine, alanine, lysine, aspartic acid, etc., permeate through these membranes at comparable rates. The fluxes of the amino acids strongly depended on the solution

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pH which, relative to the isoelectric pH of the particular amino acid, determined the composition of its ionic and neutral species in solution.

For the carboxylic acids the following general observations can be made for transport in water-swelled Nafion:

> Smaller molecules permeate faster than larger molecules (e.g., formic vs acetic).
>
> Higher ionization causes reduced fluxes, e.g., trichloroacetic acid permeates extremely slowly compared with acetic acid. Oxalic acid ($pK_a = 1.27$) similarly exhibits very slow permeation.
>
> The flux of acetic acid, for example, is about two times faster for the Na^+-substituted Nafion 117 than for the H^+-Nafion.

Amino acids, being bipolar, exhibit pH-dependent dominant ionic species in aqueous solutions. Below the isoelectric pH the cationic species dominate, and above the isoelectric pH the anionic species dominate. Sikdar's (*8, 9*) work on glycine, alanine, glutamine, lysine, and aspartic acid revealed the following characteristics of amino acid transport in Nafion 117 membranes:

> Transport for the H^+ membrane was favored at pH's lower than the isoelectric pH, i.e., when the aqueous solution contained predominantly cationic species. Since the electrical neutrality of solutions on both sides of the membrane were to be preserved, there could only be a net transfer of neutral species through the membranes. At pH's higher than isoelectric pH's, it was shown that the amino acid permeation rate dropped considerably.
>
> For the Na^+ membrane, however, the permeation was higher at a pH higher than isoelectric compared to that at the isoelectric pH. Though the neutral molecules account for the net transfer, the permeation is augmented by the presence of anionic species in the source solution. Transport of anions presumably was coupled with the free diffusion of Na^+ ions (Donnan effect). Na^+ came from the NaOH used to adjust pH to higher values than the isoelectric pH.
>
> And the flux for H^+ membrane exhibited saturation kinetics. At low amino acid concentration, the flux increased linearly with concentration, but approached zero order as the concentration increased.

The important difference between the permeation characteristics of amino acids and those of carboxylic acids for the H^+-Nafion 117 is that the former exhibited higher fluxes with increasing concentration of positively charged species, whereas the carboxylic acids exhibited increased fluxes at acidic pH's at which these acids cannot be protonated.

The purpose of this paper is to demonstrate that the carboxylic acids exhibit saturation kinetics as well. Also, more light is thrown on the transport characteristics of these acids to facilitate the deduction of mechanisms for the permeation phenomena. Acetic acid was used as an example of a carboxylic acid.

EXPERIMENTAL METHODS

The apparatus of this study has been described elsewhere (*7*). In essence, the diffusion cell consisted of two chambers separated by a Nafion-117 membrane (equivalent weight 1100, dry thickness 170 μm, and exposed membrane area 15.5 cm^2). The H^+ membrane for the permeation study was prepared by boiling the membrane, as received (E. I. du Pont de Nemours & Co., Wilmington, Delaware) in water for 1 h. The Na^+ membrane was prepared by boiling H^+ membrane in 5% NaOH for 1 h. A typical experiment consisted of putting a solution on the source side of the membrane and water of pH 5–6 on the receiver side. The receiver samples were analyzed as a function of time for concentrations using an ultraviolet-visible spectrophotometer. The concentration-time data were fitted with a second-degree polynominal of the form

$$Y = bt + ct^2 \tag{1}$$

where Y is the percent transported at time t hours. The initial flux for an experiment was computed from dY/dt at $t = 0$. Provided the membrane thickness, L, is known, the permeability constant for an acid can be calculated using

$$\text{Initial flux} = \frac{P}{L} \Delta C_i \tag{2}$$

where P = permeability, cm^2/s
ΔC_i = initial concentration difference between the source and the receiver, mol/cm^3

Equation (2) is an integrated form of Fick's law of diffusion where $P = DH$ (D is the molecular diffusivity and H is the Henry's law partition coefficient). If Fick's law is obeyed, one would expect a linear relationship between initial flux and concentration difference.

RESULTS AND DISCUSSION

Sikdar (*8*) demonstrated that amino acids, such as glycine and L-alanine, exhibit saturation kinetics of the Michaelis-Menten type while permeating through a H^+-Nafion membrane, i.e., the initial flux (Eq. 2) reached a limiting value at high molar concentrations of the substrates. The flux data satisfied an equation of the form

$$J = \frac{J_{\max}[S]}{K_m + [S]} \tag{3}$$

where J = initial flux, $mol/cm^2 \cdot s$
$J_{\max}$ = limiting flux, $mol/cm^2 \cdot s$
K_m = a Michaelis-Menten constant ($V_{\max}/2$), mol/cm^3
[S] = substrate molar concentration, mol/cm^3

An inspection of the equation shows that in one limiting case, when $[S] \ll K_m$, the initial flux increases linearly with [S], and in the other limiting case, when $K_m \ll [S]$, the initial flux is constant at the limiting value.

Similar saturation kinetics of acetic acid transport were observed for H^+- and Na^+-Nafion membranes. The flux versus acetic acid source concentration behavior for the H^+-Nafion at 23°C is shown in Fig. 1 over a concentration range of 0.67 to 8.6 mol/L. The limiting flux is attained at about 2 mol/L concentration. This can be thought of as a characteristic for the membrane and acetic acid at 23°C. This limiting value will, however, increase with increasing temperature and decreasing membrane thickness. The corresponding flux data for the Na^+-Nafion at 23°C are shown in Fig. 2. What is significant in these observations is that the acetic acid flux for the Na^+-Nafion is 2–3 times higher than that for the H^+-Nafion. The kineitc data of Figs. 1 and 2 are presented in Table 1.

The fact that the flux data satisfy the saturation kinetics can be demonstrated by plotting the inverse of flux versus inverse of concentration (Figs. 3 and 4). A rearrangement of Eq. (3) in the following form also enables one to evaluate values of K_m and $J_{\max}$:

$$\frac{1}{J} = \frac{K_m}{J_{\max}} \frac{1}{[S]} + \frac{1}{J_{\max}} \tag{4}$$

From the least squares lines ($r^2 = 0.97$ and 0.99 for H^+- and Na^+-Nafion, respectively), the limiting fluxes of 1.8×10^{-7} and 5.8×10^{-7} mol/

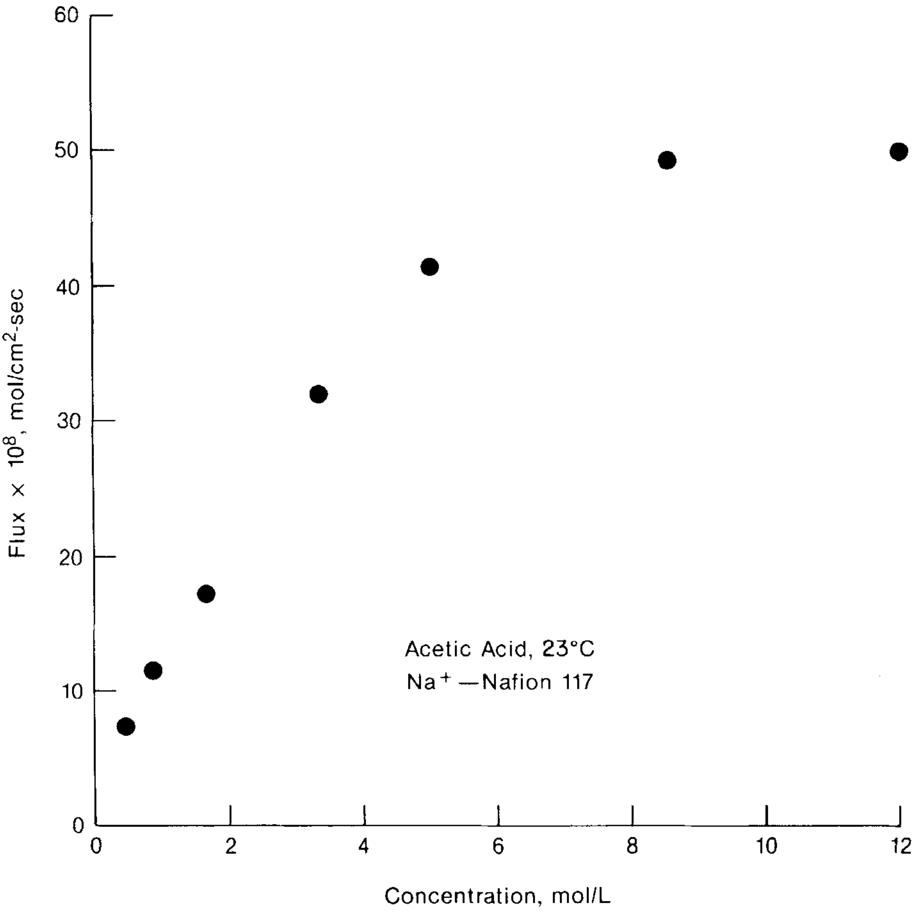

FIG. 1. Concentration saturation of acetic acid fluxes through H$^+$-Nafion 117 at 23°C.

cm^2 · s were obtained. The corresponding K_m values were 1.2 and 3.1 mol/L for H$^+$- and Na$^+$-Nafion, respectively.

We have thus far made two significant observations:

1. The acetic acid flux is higher for the Na$^+$-Nafion
2. The acetic acid transport for both H$^+$- and Na$^+$-Nafion exhibit saturation kinetics

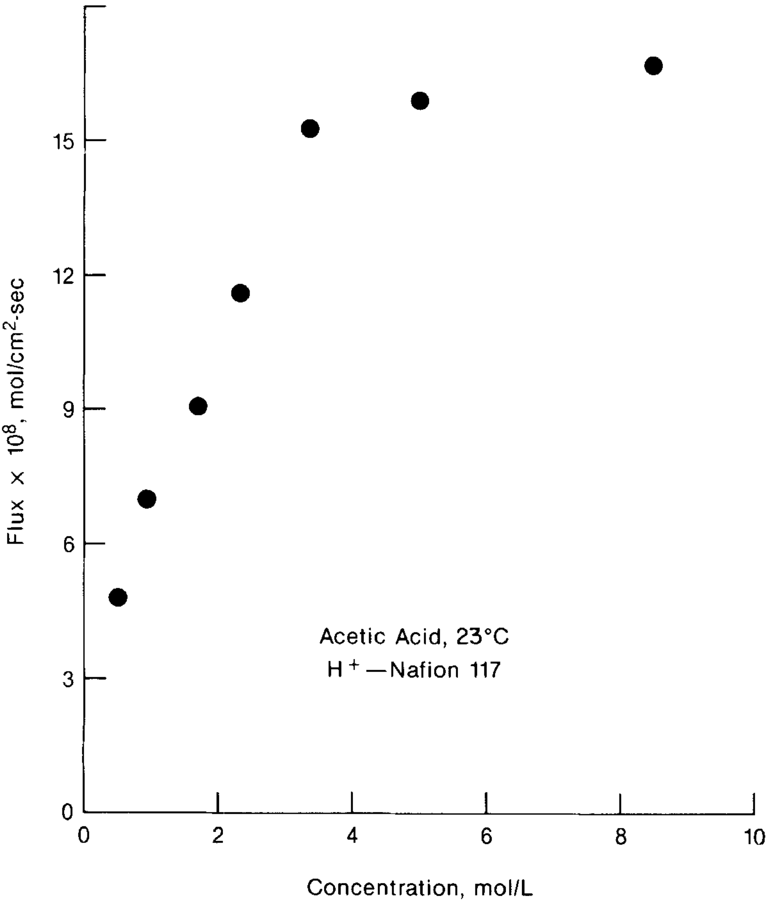

FIG. 2. Concentration saturation of acetic acid fluxes through Na^+-Nafion 117 at 23°C.

It is generally known that swelling of the Nafion membranes controls diffusion of species; the higher the swelling, the higher is the flux. However, extensive experimental evidence (*10–12*) suggests that Na^+-Nafion swells in water to a lesser degree. Recent membrane thickness measurements using precision micrometers (*13*) show that Na^+-Nafion, swelled in boiling water, indeed had a smaller thickness (211 μm). H^+-Nafion in 1.6 mol/L acetic acid solution exhibited an equilibrium thickness of 232 μm, which is not very different from a Na^+-Nafion soaked in the same acid for 2 h (230 μm). It can be argued that the Na^+-

TABLE 1
Flux Data of Acetic Acid for Nafion 117 at 23°C

Initial source concentration (mol/L)	H^+-Nafion initial flux ($mol/cm^2 \cdot s$)	Na^+-Nafion initial flux ($mol/cm^2 \cdot s$)
0.43	3.13×10^{-8}	7.70×10^{-8}
0.86	5.38×10^{-8}	1.15×10^{-7}
1.67	8.61×10^{-8}	1.72×10^{-7}
2.30	1.16×10^{-7}	—
3.35	1.53×10^{-7}	3.20×10^{-7}
5.00	1.59×10^{-7}	4.13×10^{-7}
8.34	1.67×10^{-7}	4.91×10^{-7}
12.00	—	5.00×10^{-7}

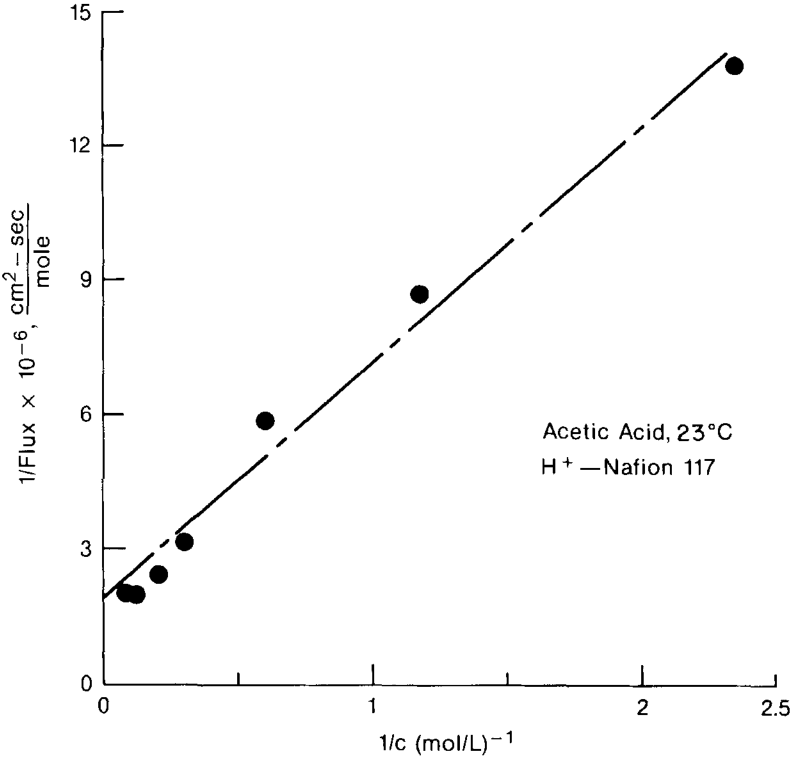

FIG. 3. Verification of Michaelis-Menten kinetics for acetic acid transport for H^+-Nafion at 23°C.

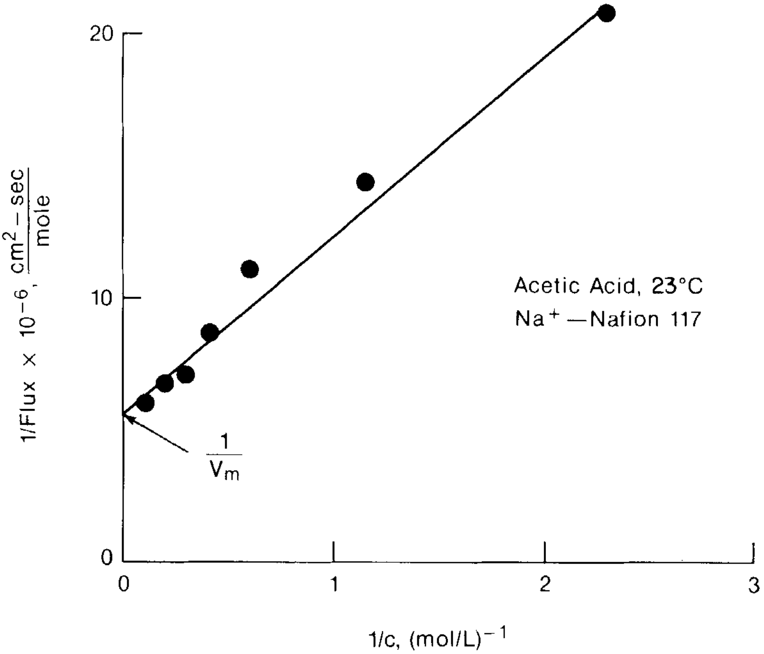

FIG. 4. Verification of Michaelis-Menten kinetics for acetic acid transport for Na$^+$-Nafion at 23°C.

Nafion in contact with the acid changed into the H$^+$ form, at least partially. Even then, the acid fluxes for the Na$^+$ membrane did not degenerate to the lower fluxes for the H$^+$ form, even over a 7-h experimental time. Sikdar (*7*) showed that the flux for the Na$^+$-Nafion decreased more slowly with time than the H$^+$-Nafion flux, although, due to faster transport, the Δc driving force was smaller than for the H$^+$ membrane. In any case, the initial fluxes for the Na$^+$-Nafion membrane did represent fluxes for this form since at zero time the membrane was essentially unconverted.

The mechanism giving rise to the saturation kinetics is not clear. It was argued by Sikdar (*8*) that similar saturation kinetics are expected if the membrane linearly shrinks in thickness with the source substrate concentration. It seems clear from the thickness data presented here that this possibility has to be ruled out.

The temperature dependence of the initial fluxes was examined to find clues to the mechanism. Figure 5 shows the Arrhenius plot for an experiment conducted with 1.63 mol/L acetic acid concentration, which

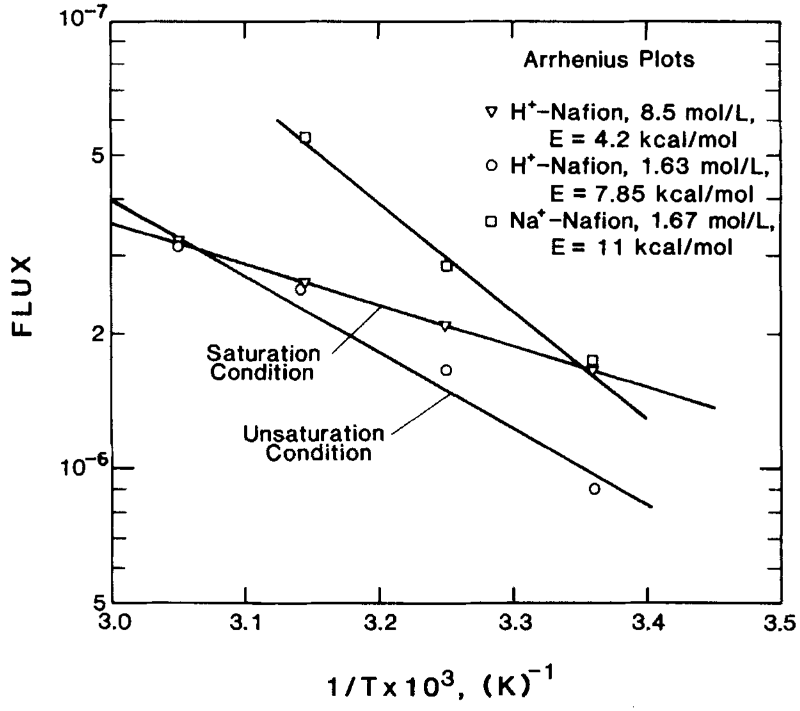

FIG. 5. Arrhenius plots of acetic acid for Nafion 117.

falls on the subsaturation part of Fig. 1. The activation energy over a temperature range of 298 to 328 K is 7.85 kcal/mol. The magnitude of this activation energy falls at the lower end of that expected for a chemical reaction. On the other hand, Arrhenius data of an experiment for a concentration at saturation, viz., 8.5 mol/L, yielded a much lower activation energy, viz., 4.2 kcal/mol, which is typical of diffusion processes. The activation energy of transport for the Na^+-Nafion at 1.67 mol/L concentration was found to be 11 kcal/mol, somewhat higher than the corresponding transport through the H^+-Nafion. Based on this information, it is tempting to postulate a mechanism which involves a reversible reaction of acetic acid with the membrane, much like the biochemical active transport which also exhibits Michaelis-Menten-type kinetics. According to this postulate, the forward reaction rate increases linearly with concentration until the diffusion of species inside the membrane becomes the slower step causing the saturation phenomenon.

However, a chemical reaction with the membrane, either in H^+ or Na^+ form, is hard to imagine.

It is likely that the saturation kinetics is the result of a linearly decreasing partition coefficient (hence the permeability) between the membrane and the source solution. If the solubility of acetic acid in the H^+ membrane, whose environment is different from the source solution, reaches saturation, then the partition coefficient ($H = C_m/C_s$, where C_m is the concentration inside the membrane and C_s is that in the source) will decrease linearly with C_s for higher concentrations. As a result, the flux will remain constant. The difference between the initial fluxes for the H^+- and Na^+-Nafion would then be the result of the different values of diffusivity (D) and partition coefficient (H). Direct measurement of partition coefficients for these membranes is hard and was not tried.

CONCLUDING REMARKS

Data presented in this paper demonstrate that Michaelis-Menten-type saturation kinetics is obeyed by permeating acetic acid through both H^+- and Ma^+-Nafion. The activation energy data obtained at subsaturation and at saturation conditions do not conclusively reveal mechanistic information. On physical grounds, it appears possible that the mechanism is based on the membranes reaching solubility limits of the diffusing species.

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