V = volume of reaction system [l]
w_i = weight fraction of component i [—]
w_{2e} = weight fraction of polymer when entanglement of polymer begins to affect diffusion of segment [—]
x = conversion of monomer to polymer [—]

β = total volume shrinkage for complete conversion of monomer to polymer [—]
γ = overlap parameter [—]
ε_e = proportion of the number of jumps affected by entanglement points bounded at fixed points to total number of jumps [—]
ξ = ratio of critical volume per mole of solvent [—]
ϕ_I = jump frequency of initiator radical [1/s]
$\phi_{I,react}$ = frequency with which a pair of initiator radicals disappears on recombination [1/s]
ϕ_{I0} = jump frequency of initiator radicals at start of polymerization [1/s]
ϕ_0 = frequency factor of jumps of polymer segments as defined by Eq. (46) [1/s]
ν_e = mass of polymer entangled with other polymers in a unit volume as defined by Eq. (34) [g/ml]
$\mu_P^k, \mu_R^k, \mu_{R^*}^k$ = k-th moment of size distribution of inactive polymer, polymer radical or growing polymer radical [mol/l]
ψ = function defined by Eqs. (31) and (32) [—]

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SEPARATION OF ETHYLENE FROM ETHANE BY SUPPORTED LIQUID MEMBRANES CONTAINING SILVER NITRATE AS A CARRIER

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Key Words: Facilitated Transport, Liquid Membrane, Ethylene, Silver Nitrate, Carrier Transport, Gas Separation

Experimental results for the facilitated transport of ethylene through supported liquid membranes containing silver nitrate as a carrier are presented. The selectivity factor in the separation of ethylene and ethane increases with increasing carrier concentration, reaching about 1000 when silver nitrate concentration is 4 mol/dm^3. An approximation method for calculating the rate of facilitated transport accompanied by an instantaneous reversible reaction is proposed. This method is applicable even to the case where the diffusivities of the carrier and the complex differ from each other. It is found that the effect of experimental condition on the permeation rate of ethylene is satisfactorily explained by assuming that the reaction between ethylene and Ag^+ is instantaneous and reversible.

Introduction

Gas separation technique using carrier-mediated or facilitated transport has been attracting increasing attention because very high selectivity can be easily obtained by incorporating a carrier into a membrane which can selectively and reversibly bind the permeant species to be transported. From this point of view, a number of studies have been presented on the permeation of such gases as carbon monoxide, carbon dioxide, hydrogen sulfide, nitric oxide and oxygen. These works were reviewed and discussed by Kimura *et al.*[2] and Way *et al.*[13]

Concerning the separation of olefinic gases from

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parafins, Steigelman and Hughes[8] have already shown that Milipor® cellulose acetate filters impregnated with aqueous solutions of $AgNO_3$ which functions as a carrier of olefins can selectively transport olefins. This separation is based on the fact that only olefins can react with Ag^+. They reported that the permeability ratio of ethylene to ethane was 310 when carrier concentration was 6 mol/dm^3. LeBlanc *et al.*[3] reported that the use of an ion exchange membrane as the support of a liquid membrane has the advantage that the carrier cannot be forced out or washed out of the membrane as it is bound by strong electrostatic charges. In these works, however, no detailed theoretical analysis of the permeation rate and the selectivity was carried out.

In the present paper, the permeation rates of ethylene and ethane through liquid membranes immobilized in 170 μm-thick cellulose filters are presented, and the effect of experimental conditions on the permeation rates and the selectivity is discussed on the basis of the theory of facilitated transport. Furthermore, an approximation method for predicting the rate of permeation accompanied by an instantaneous reversible reaction between the permeant species and the carrier is presented.

1. Theoretical Analysis of Permeation Rate

Here, the rate of permeation is analyzed for the case where the carrier undergoes an instantaneous reversible reaction with the permeant gas, as shown by Eq. (1).

$$A\,(\text{gas}) + B\,(\text{carrier}) \rightleftharpoons C \tag{1}$$

$$(C_2H_4 + Ag^+ \rightleftharpoons \text{complex})$$

The concentration profiles of the chemical species in the liquid membrane are schematically shown in **Fig. 1**. The steady-state differential mass balances on each component are as follows.

$$D_A(d^2A/dx^2) = kAB - k'C \tag{2}$$

$$D_B(d^2B/dx^2) = kAB - k'C \tag{3}$$

$$D_C(d^2C/dx^2) = -kAB + k'C \tag{4}$$

The boundary conditions are expressed by

$$x=0;\ A=A_F,\ B=B_F,\ C=C_F \tag{5}$$

$$x=L;\ A=A_S,\ B=B_S,\ C=C_S \tag{6}$$

If the reaction rate is so fast that the chemical equilibrium is established throughout the membrane, then Eq. (7) holds.

$$K = k/k' = (C/AB) = (C_F/A_FB_F) = (C_S/A_SB_S) \tag{7}$$

The equation of the conservation of the carrier in the membrane is represented by

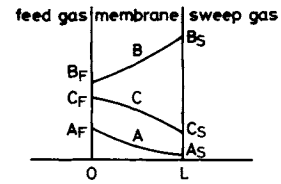

Fig. 1. Concentration profiles of permeant species A, carrier B and complex C in liquid membrane.

$$\int_0^L (B+C)dx = B_0L \tag{8}$$

where B_0 is the total concentration of the carrier. The total flux of A, i.e., the sum of the fluxes of A and C, can be derived from Eqs. (2) and (4).

$$J_A = (D_A\varepsilon/L\tau)(A_F - A_S) + (D_C\varepsilon/L\tau)(C_F - C_S) \tag{9}$$

Here, ε and τ are the porosity and the tortuosity factor of the membrane, respectively.

It has been expediently assumed that D_S is equal to D_C because this assumption leads to an analytical solution for the permeation rate. This assumption is reasonable when the molar volume of the carrier is considerably larger than that of the permeant species. In this case, the following equations are obtained.[12]

$$B_F = B_0/(1+KA_F),\ B_S = B_0/(1+KA_S) \tag{10}$$

$$C_F = KA_FB_0/(1+KA_F),\ C_S = KA_SB_0/(1+KA_S) \tag{11}$$

$$J_A = (D_A\varepsilon/L\tau)(A_F - A_S)\left[1 + \frac{D_C}{D_A}\frac{KB_0}{(1+KA_F)(1+KA_S)}\right] \tag{12}$$

On the other hand, if the diffusivity of the carrier does not differ considerably from that of the permeant species as in the case of the present work, or if ionic species such as H^+ and OH^- which have very high mobility are used as the carrier, the assumption of $D_B = D_C$ is not reasonable. Here, a new approximation method is proposed which can predict the permeation rate regardless of the ratio of diffusivities. The left-hand side of Eq. (8) is evaluated by assuming that the concentration profiles of B and C are linear. Then Eq. (13) is obtained.

$$(B_F + B_S) + (C_F + C_S) = 2B_0 \tag{13}$$

From Eqs. (3) and (4), the following equation is derived without any approximation.

$$(D_B/L)(B_F - B_S) + (D_C/L)(C_F - C_S) = 0 \tag{14}$$

From Eqs. (7), (13) and (14), equations expressing B_F, B_S, C_F and C_S as functions of A_F and A_S are derived as follows:

$$B_F = 2(r_B + KA_Sr_C)B_0/\alpha,\ B_S = 2(r_B + KA_Fr_C)B_0/\alpha \tag{15}$$

$$C_F = 2KA_F(r_B + KA_Sr_C)B_0/\alpha,$$

$$C_S = 2KA_S(r_B + KA_Fr_C)B_0/\alpha \tag{16}$$

where r_B and r_C are D_B/D_A and D_C/D_A, respectively, and α is given by

$$\alpha=(r_B+KA_Fr_C)(1+KA_S)+(r_B+KA_Sr_C)(1+KA_F) \tag{17}$$

The equation for J_A is obtained by substituting Eq. (16) into Eq. (9).

The fluxes of A calculated by this method are compared with the fluxes obtained by the numerical solution of Eqs. (2)–(4) in **Table 1**, where the fluxes calculated by Eq. (12) are also shown. It can be seen that the present approximation method is satisfactory even when D_C is considerably lower than D_B, while Eq. (12) gives lower fluxes.

2. Experimental

2.1 Determination of equilibrium constant

The equilibrium constant of the reaction between ethylene and Ag^+ was determined by a volumetric method using an apparatus similar to that described previously.[9] After 50 cm^3 of an aqueous solution of $AgNO_3$ was added to a glass vessel with a volume of 317 cm^3, the vessel was evacuated. Then pure ethylene was introduced until atmospheric pressure was reached, and the vessel was closed. Stirring was started and continued until phase and chemical equilibria were established and no further pressure change was observed. The pressure was measured by a strain gauge. The equilibrium constant was calculated by the following equation.

$$K_{eq}=\{[C_2H_4\cdot Ag^+]/([C_2H_4][Ag^+])\}_{eq}$$
$$=\frac{(p_0-p_e)V_G/RTV_L-(p_e-p_w)/H_A}{\{(p_e-p_w)/H_A\}\{B_0-(p_0-p_e)V_G/RTV_L+(p_e-p_w)/H_A\}} \tag{18}$$

where p_0, p_e and p_w are atmospheric pressure, equilibrium pressure and vapor pressure of water, respectively, V_G and V_L are the volumes of the liquid and gas phases, respectively, and H_A is the Henry constant.

2.2 Supported liquid membrane

Schematic diagrams of the experimental apparatus and the diffusion cell are shown in **Figs. 2** and **3** respectively. The lower and upper compartments, with inner diameter of 76 mm, were made of Teflon and the upper compartment was stirred by a six-bladed turbine agitator 5 cm in diameter and 1 cm in width. The stirring speed was 300 rpm. The cell was placed in an air bath maintained at 298 K. The support of the liquid membrane was 170 μm-thick cellulose filter No. 7 from Toyo Roshi Co., Ltd. After being immersed in an aqueous solution of $AgNO_3$, the filter was sandwiched between two compartments of the cell. The feed gas was supplied to the lower compartment, 1 cm in depth, and the sweep gas, nitrogen, to the upper compartment, 2 cm in depth, at atmospheric pressure.

The purities of ethylene and ethane were 99.5 and 99%, respectively. The sweep gas from the cell was analyzed by a gas chromatograph equipped with a thermal conductivity detector (Shimadzu, GC-8A). The mole fraction of ethylene in the sweep gas was in the range from 0.0003 to 0.022, and that of ethane from 1.13×10^{-5} to 9.1×10^{-5}. The fluxes were calculated from the flow rate and the composition of the gas. The flow rates of both feed and sweep gases were 300 cm^3/min. The membrane area was 50.3 cm^2.

Table 1. Comparison of permeation rates calculated by approximation methods with those obtained by numerical integration of Eqs. (2)–(4). $D_A=1.87\times10^{-9}$ m^2/s, $D_B=1.66\times10^{-9}$ m^2/s, $L=170\,\mu m$, $A_F=4.77$ mol/m^3, $A_S<0.02$ mol/m^3, $B_0=1$ mol/dm^3, $\varepsilon/\tau=0.258$.

K [m^3/mol]	D_C/D_B [—]	J_A (num) [mol/($m^2\cdot s$)]	J_A (this work) [mol/($m^2\cdot s$)]	J_A (Eq. (12)) [mol/($m^2\cdot s$)]
0.110	1	3.390×10^{-3}	3.390×10^{-3}	3.390×10^{-3}
0.110	0.602	2.212×10^{-3}	2.212×10^{-3}	2.064×10^{-3}
0.110	0.301	1.196×10^{-3}	1.197×10^{-3}	1.059×10^{-3}
0.110	0.0602	2.922×10^{-4}	2.923×10^{-4}	2.523×10^{-4}
0.440	0.0602	6.335×10^{-4}	6.343×10^{-4}	4.491×10^{-4}
1.100	0.301	3.505×10^{-3}	3.511×10^{-3}	2.496×10^{-3}

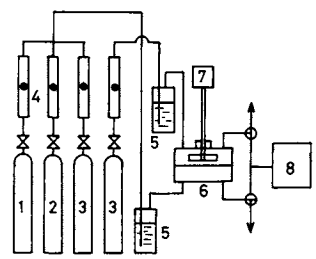

Fig. 2. Schematic diagram of experimental apparatus. 1, C_2H_4 cylinder; 2, C_2H_6 cylinder; 3, N_2 cylinder; 4, rotameter; 5, saturator; 6, permeation cell; 7, motor; 8, gas chromatograph.

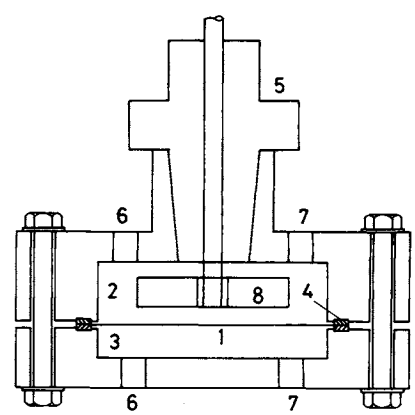

Fig. 3. Schematic diagram of permeation cell. 1, supported liquid membrane; 2, upper compartment; 3, lower compartment; 4, gasket; 5, vacuum seal; 6, inlet; 7, outlet; 8, impeller.

3. Results and Discussion

3.1 Equilibrium constant

The value of H_A, which is necessary to evaluate the equilibrium constant from Eq. (18), was estimated by the following equation.[5)]

$$\log(H_A/H_{AW})=k_S I \tag{19}$$

$$k_S=i_g(C_2H_4)+i_+(Ag^+)+i_-(NO_3^-) \tag{20}$$

Here, $i_g(C_2H_4)$, $i_+(Ag^+)$ and $i_-(NO_3^-)$ are the contributions of solute gas, cation and anion respectively to the salting-out parameter k_S. As the value of $i_+(Ag^+)$ was not reported, $i_+(Ag^+)$ was approximated by $i_+(K^+)$ because the solubility of N_2 in the aqueous $AgNO_3$ solution is approximately equal to that in the aqueous KNO_3 solution.[11)] Here, the values of i reported by Onda *et al.*,[5)] and the value of H_{AW} by Morrison and Billett[4)] were used, i.e.,
$i_g(C_2H_4)=-1.95\times10^{-4}$, $i_+(Ag^+)=-3.62\times10^{-5}$,
$i_-(NO_3^-)=3.23\times10^{-4}\,m^3/mol$,
$H_{AW}=2.12\times10^4\,Pa\cdot m^3/mol$.
The plot of K against the concentration of $AgNO_3$ is shown in **Fig. 4**. While the value of K is almost independent of $[AgNO_3]_0$ in the concentration range below $1\,mol/dm^3$, it becomes large at $[AgNO_3]_0=4\,mol/dm^3$. This is presumably due to the effect of the ionic strength on the activity coefficients of the ionic species. Trueblood and Lucas[10)] reported that the value of K at $[AgNO_3]=1\,mol/dm^3$ is $98\,dm^3/mol$, which agrees approximately with the present result.

3.2 Stability of liquid membrane

Figure 5 shows the time dependency of the permeation rates of ethylene and ethane in their simultaneous permeation when $[AgNO_3]_0$ is $1\,mol/dm^3$. The flux of ethylene increases gradually while the flux of ethane is constant for about 210 min. This may be explained as follows. Although both feed and sweep gases were passed through saturators before being introduced into the cell, it seemed that the gases were not completely saturated with water vapor. Therefore, water in the membrane evaporates, and the evaporation causes a decrease in the thickness and an increase in $AgNO_3$ concentration. Thus, the flux of ethylene increases with time.

On the other hand, the permeation of ethane, which does not react with Ag^+, is expressed by

$$J_{A'}=(D_{A'}\varepsilon/H_{A'}L\tau)(p_{A'F}-p_{A'S}) \tag{21}$$

The values of $D_{A'}\varepsilon/H_{A'}\tau$ determined from the rates of permeation of pure ethane using Eq. (21) are plotted against $[AgNO_3]_0$ in **Fig. 6**, which indicates that the permeability of ethane decreases with an increase in $[AgNO_3]_0$. This is because the solubility of ethane decreases due to the salting-out effect and the diffusivity also decreases due to the increase in viscosity with increasing $[AgNO_3]_0$. The effect of water evaporation on the permeation rate of ethane can be discussed on the basis of the above result. While the decrease in the thickness enhances the permeation rate of ethane, the increase in the carrier concentration lowers both the solubility and the diffusivity of ethane in the membrane. If the former effect is counterbalanced by the latter, the permeation rate of ethane remains constant.

As long as almost all pores of the filter are filled with the membrane solution, ethylene is selectively transported. However, once some part of the membrane dries up, the permeation rates of both gases increase rapidly and no selective permeation is observed because the permeation rate through the pores filled with the gas becomes higher than that through the pores filled with the carrier solution. In this paper, the permeation rates at $t=30$ min are reported hereafter.

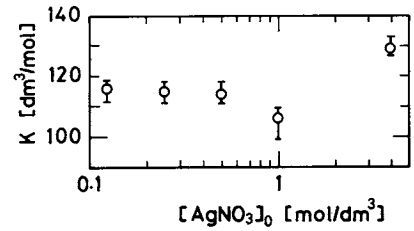

Fig. 4. Effect of $[AgNO_3]_0$ on chemical equilibrium constant.

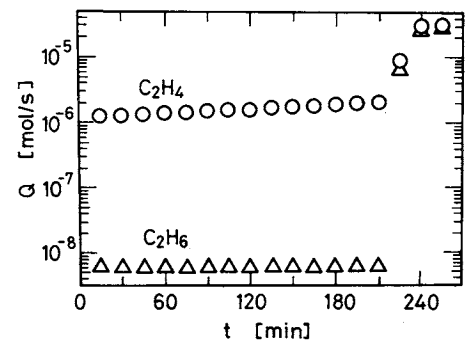

Fig. 5. Time-courses of permeation rates of ethylene and ethane. $[AgNO_3]=1\,mol/dm^3$; $p_{AF}=p_{A'F}=49.1\,kPa$.

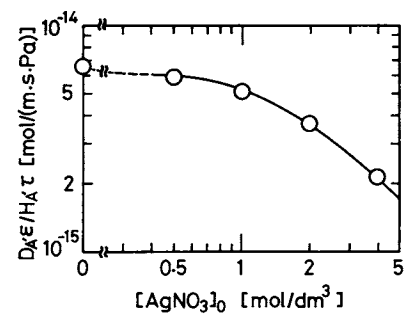

Fig. 6. Effect of $[AgNO_3]_0$ on $D_{A'}\varepsilon/H_{A'}\tau$. Single permeation of ethane.

3.3 Permeation rates of ethylene and ethane

The effect of the partial pressure of ethylene on the permeation rate is shown in **Fig. 7**. Nitrogen was used to dilute ethylene. It can be seen that the flux is approximately proportional to the partial pressure, and also that the flux increases with the carrier concentration. The permeability of ethylene, which is defined by Eq. (22), is about 1.57×10^{-12} mol·m/(m^2·Pa), or 4.7×10^{-7} Ncm^3·cm/(cm^2·cmHg) when p_{AF} is 0.1 MPa and $[AgNO_3]_0$ is 4 mol/dm^3.

$$P_j = J_j L/(p_{jF} - p_{jS}),\ (j = A,\ A') \qquad (22)$$

The facilitation factor of ethylene, defined as the ratio of the permeability of the facilitated transport to that of physical transport, is about 70 when $[AgNO_3]_0$ is 4 mol/dm^3. **Figure 8** shows the effect of carrier concentration in the simultaneous transport of ethylene and ethane. As $[AgNO_3]_0$ increases, the permeation rate of ethylene increases while that of ethane decreases. Therefore, the selectivity factor, which is defined by the permeability ratio of ethylene to ethane, also increases. The selectivity factor is 1000 at $[AgNO_3]_0 = 4$ mol/dm^3. This value is considerably higher than the 310 reported by Steigelman and Hughes.[8] This is probably because they carried out the experiment at higher pressure where J_A does not increase linearly with p_{AF} due to the saturation behavior caused by the limited amount of the carrier in the membrane while $J_{A'}$ increases linearly with $p_{A'F}$.

3.4 Comparison of experimental data with computed results

To calculate the permeation rate corresponding to each experimental condition by the proposed approximation method, it is necessary to estimate the diffusivity of each species. D_A was estimated from the value in water reported by Duda and Ventras[1] (1.87×10^{-9} m^2/s) using the Stokes-Einstein equation, i.e., $D_A\mu/T$=constant. The viscosities of aqueous solutions were measured by an Ostwald viscometer. The diffusivities of ionic species were estimated from those at infinite dilution by the method of Sherwood and Wei.[7] The diffusivity of Ag^+ at infinite dilution was calculated as 1.66×10^{-9} m^2/s from its mobility.[6] The diffusivity of the complex at infinite dilution was determined so that the best fit between the computed and observed fluxes might be obtained. The value thus determined was 1.1×10^{-9} m^2/s. The value of ε/τ was calculated as 0.258 from the physical permeation rate of ethylene. Gas-phase mass transfer resistance was neglected because the stirring speed did not influence the permeation rate. The computed results are shown by the solid lines in Figs. 7 and 8. The dotted line in Fig. 8 is the flux of ethane calculated from Eq. (21) using the data shown in Fig. 6. It can be seen that the agreement between computed and observed rates is satisfactory.

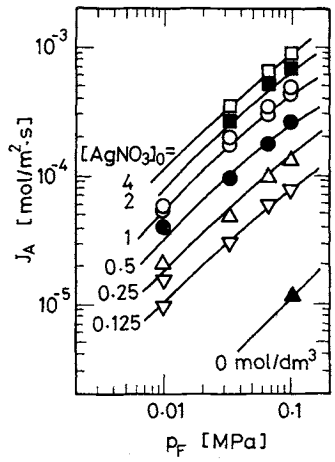

Fig. 7. Effect of partial pressure of ethylene on permeation rate. Single permeation.

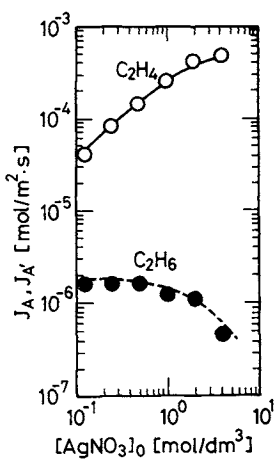

Fig. 8. Effect of carrier concentration on permeation rates of ethylene and ethane. Simultaneous permeation. $p_{AF} = p_{A'F} = 49.1$ kPa.

In the present study, both the feed and receiving phases were atmospheric. To concentrate ethylene in the receiving phase, this phase must be held at pressure lower than the feed phase. However, the results obtained here are considered to be useful in estimating the gas concentrations in each side of the membrane when the receiving side is kept at lower pressure. The method of stabilizing the membrane without decreasing the permeation rate will be reported elsewhere.

Conclusion

A series of experiments was carried out on the permeation of ethylene and ethane through supported liquid membranes containing aqueous solutions of $AgNO_3$. It was found that the facilitation factor of ethylene and the permeability ratio of ethylene to ethane were 70 and 1000, respectively, when $AgNO_3$ concentration was 4 mol/dm^3. The permeation rate of ethylene was satisfactorily predicted by the proposed approximation method, which is generally applicable

to facilitated transport accompanied by an instantaneous reversible reaction. The behavior of the change in the permeation rate due to the evaporation of water was also discussed.

Acknowledgment

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Nomenclature

A	= concentration of permeant species (ethylene)	[mol/m^3]
B	= concentration of carrier (Ag^+)	[mol/m^3]
C	= concentration of complex ($C_2H_4 \cdot Ag^+$)	[mol/m^3]
D	= diffusivity	[m^2/s]
H	= Henry constant	[Pa·m^3/mol]
I	= ionic strength	[mol/m^3]
i_g, i_+, i_-	= contributions of gas, cation and anion respectively to k_s	[m^3/mol]
J	= flux	[mol/(m^2·s)]
K	= chemical equilibrium constant	[m^3/mol]
k	= forward reaction rate constant	[m^3/(mol·s)]
k'	= reverse reaction rate constant	[s^{-1}]
k_s	= salting-out parameter	[m^3/mol]
L	= thickness of membrane	[m]
P	= permeability	[mol·m/(m^2·s·Pa)]
p	= partial pressure or pressure	[Pa]
Q	= total permeation rate	[mol/s]
T	= temperature	[K]
V_G, V_L	= volumes of gas and liquid phases, respectively	[m^3]
x	= distance	[m]
α	= quantity defined by Eq. (17)	[—]
ε	= porosity of filter	[—]
τ	= tortuosity factor of filter	[—]
μ	= viscosity	[Pa·s]

⟨Subscripts⟩

A	= ethylene
A'	= ethane
B	= carrier (Ag^+)
C	= complex ($C_2H_4 \cdot Ag^+$)
e	= equilibrium
F	= feed gas or feed gas-membrane interface
S	= sweep gas or sweep gas-membrane interface
w	= water
0	= initial

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