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FORMATION AND CHARACTERISTICS OF INORGANIC DYNAMIC MEMBRANES FOR ULTRAFILTRATION

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Three kinds of inorganic dynamic membranes for ultrafiltration were formed on ceramic support tubes by filtering colloid solutions of Zr(IV), Al(III) and Fe(III). Permeate fluxes and molecular weight cut-off values were controlled not only by conditions such as pressure, pH and colloid concentration during membrane formation, but also by the membrane formation time. The Zr(IV) dynamic membrane had the best mechanical stability among the three kinds of membranes obtained in this study. This membrane also had good resistance to temperature up to 353 K and to pH in the range of 3–11.

Results of analysis based on the steric-hindrance pore model suggested that the active layer thickness of Zr(IV) membranes, namely the thickness of the deposit layer, was smaller than that of a polymer ultrafiltration membrane, a membrane that had almost the same rejection ability as the Zr(IV) membrane.

Introduction

Dynamic membranes are formed on porous supports such as porous ceramic and stainless steel by filtering membrane-forming materials such as inorganic hydrous oxides, and natural and synthetic organic polyelectrolytes. The principle of dynamic membranes was first reported in 1966 by a research group at the Oak Ridge National Laboratory.⁶⁾ They applied dynamic membranes formed with hydrous oxides to desalination under high pressure. Then, various kinds of polyelectrolytes were tested as membrane-forming materials in addition to hydrous oxides,⁵⁾ and finally it was found that hydrous zirconium oxide–polyacrylic acid [Zr(IV)–PAA] composite membranes had the best performance for reverse

osmosis among the many types of dynamic membranes developed.³⁾ The formation and performance of Zr(IV)–PAA dynamic membranes have been reviewed in detail by D. G. Thomas,^{1,2)} and many applications for waste water treatment have also been reported.^{1,2)}

The principle of solute separation by dynamic membranes is the ion exchange mechanism,⁶⁾ and they have been used as reverse osmosis membranes. It has also been pointed out that Zr(IV)–PAA membranes have the properties of a porous membrane, like an ultrafiltration membrane, because they can reject nonelectrolytes such as glucose, sucrose and polyethylene glycols.^{5,10)} Recently, dynamic membranes which have properties of an ultrafiltration membrane and thus could be used for molecular weight cut-off at low pressure have been developed by filtering only a solution of ovalbumin,¹¹⁾ which formed

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a gel layer rejecting low-molecular weight solutes.⁹⁾

It is well known that the advantages of dynamic membranes are high-temperature stability and high permeate fluxes.⁴⁾ They are therefore suitable for ultrafiltration because high temperature during operation, cleaning or sterilization is required in its applications. It can be supposed that inorganic colloid has a larger resistance to high temperature than polymers such as PAA and ovalbumin.

The objective of this study is to develop inorganic colloid dynamic membranes for ultrafiltration which have mechanical stability and durability at high temperature and under a wide range of pH. Conditions giving different molecular weight cut-off were also studied. Compared with commercial polymer ultrafiltration membranes, structural characteristics of dynamic membranes obtained were studied, based on the steric-hindrance pore model.

1. Experimental

1.1 Apparatus and materials

The experimental apparatus used is schematically shown in Fig. 1 with a detailed illustration of a module. The temperature of the feed solution was controlled by a thermostat, and pH was automatically adjusted to a constant value by adding HCl and NaOH solutions. Permeate was returned to the feed tank to prevent change of feed solution concentration. An alumina ceramic tube having an outer diameter of 1.15 cm, a length of 30 cm and a wall thickness of 0.25 cm was employed as the supporting substrate of the dynamic membrane. The pore size of the tube ranged from 0.5 to 1.0 μm . The ceramic tube was inserted into a cylindrical stainless steel pressure vessel, whose inner diameter was 1.4 cm, and was sealed with two O-rings. The effective membrane area of the module was 93 cm^2 .

Three inorganic colloids of Zr(IV), Al(III) and Fe(III) were used as the materials for the dynamic membranes. Chemical reagents zirconyl chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) and Aluminasol which was manufactured by Nissan Kagaku Kogyo Co. (Japan) were employed as Zr(IV) and Al(III) colloids. Aqueous solution of 0.1 M FeCl_3 was boiled and then Fe(III) colloid was obtained as precipitate.

1.2 Procedures

Inorganic dynamic membranes were formed in the following way. Pure water was first circulated at a fixed pressure, flow rate, temperature and pH, and then inorganic colloid was added. After a certain time the circulation of the colloid solution was stopped. Then a dynamic membrane was obtained and kept in pure water. Conditions for dynamic membrane formation were a pressure of 0.8 MPa, a flow rate of 10 l/min (linear velocity of 3.3 m/s at membrane surface) and a temperature of 298 K. The value of pH

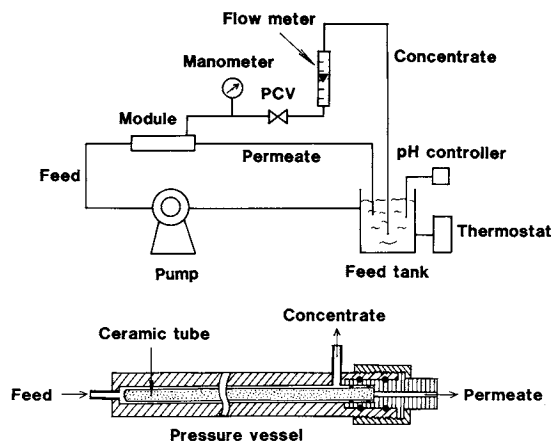


Fig. 1. Schematic flow sheet of experimental apparatus and details of dynamic membrane module.

ranged from 3 to 10 by addition of HCl and NaOH, and the concentration of colloid ranged from about 0.05 to 0.15 kg/m^3 .

To measure the molecular weight cut-off of the dynamic membranes obtained, solutions of polyethylene glycols and dextrans of various molecular weights were ultrafiltered under the standard conditions of pressure 0.2 MPa, flow rate 5 l/min, temperature 298 K and concentration 0.2 kg/m^3 . Gel layer formation on the membrane surface and plugging of membrane pores did not occur under these conditions except for the cases of high flux membranes, for instance the M-2 membrane in Fig. 3. Solute concentration was measured by the total organic carbon analyzer.

2. Results and Discussion

2.1 Formation of inorganic dynamic membranes

Permeate flux through a ceramic tube decreased with time as shown in Fig. 2, because inorganic colloid deposited on the outer surface of the tube and a dynamic membrane was formed. The performance of the membrane obtained depended on the amount of colloid deposited and could be controlled by changing the membrane formation time and conditions. As illustrated in Fig. 2, a longer time and a higher pressure gave a lower-flux membrane. A higher concentration of colloid in the circulation solution also made the flux of the membrane lower.

As illustrated in Fig. 2, two membranes formed under the same conditions (one is marked with circles and the other with triangles) show clearly that reproducibility of the dynamic membrane was very good.

Molecular weight cut-off curves of the Zr(IV) dynamic membranes are shown in Fig. 3 together with permeate fluxes. Solute rejection exhibited on the vertical axis is defined by the following equation.

$$R = 1 - C_p/C_m \quad (1)$$

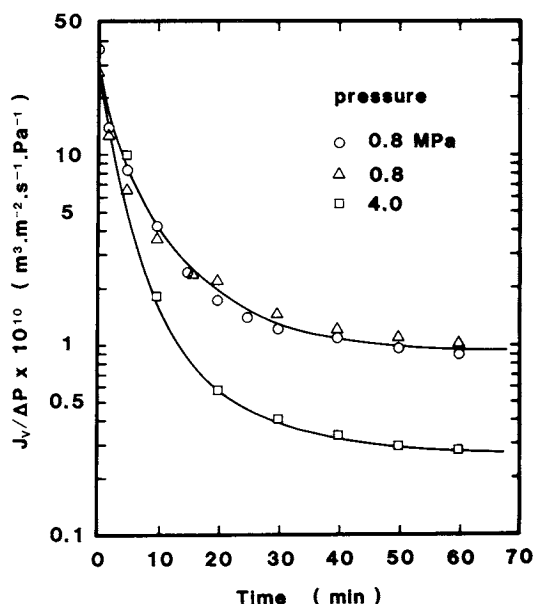


Fig. 2. Flux decline with time during formation of Zr(IV) dynamic membranes at different pressures: Zr(IV) concentration, 0.1 kg/m³.

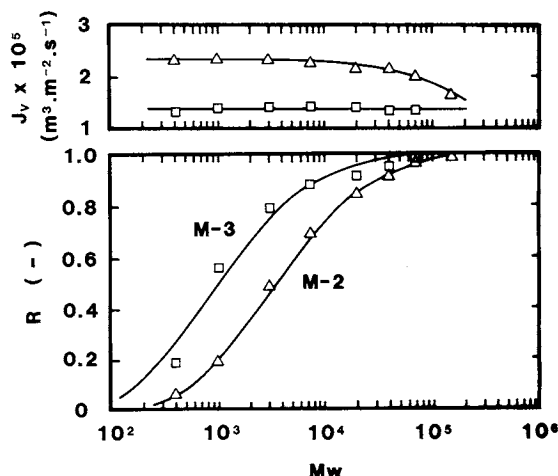


Fig. 3. Effect of membrane formation time on molecular weight cut-off and flux of Zr(IV) dynamic membranes: M-2, 20 min; M-3, 45 min.

where C_m is the concentration at the membrane surface, obtainable by using the so-called concentration polarization equation.⁷⁾

$$(C_m - C_p)/(C_b - C_p) = \exp(J_v/k) \quad (2)$$

The value of k in Eq. (2), which is the mass transfer coefficient in the boundary layer, can be estimated using the Leveque equation.¹¹⁾

$$N_{Sh} = 1.62(N_{Re} \cdot N_{Sc} \cdot d/l)^{1/3} \quad (3)$$

In this study, the rejection is always given by Eq. (1).

The M-2 membrane was obtained after circulation of the colloid solution for 20 minutes and the M-3 was formed by circulation for 45 minutes. A shorter formation time gave a higher flux and a larger molecular weight cut-off.

The concentration at the membrane surface is affected by the concentration polarization phenomenon. As expressed by Eq. (2), larger permeate flux and/or the smaller diffusion coefficient, namely the larger molecular weight, result in a larger value of C_m . Therefore, it is supposed that only in the case of the M-2 membrane with higher molecular weight solutes was the gel layer formed on the membrane surface and the permeate flux decreased as shown in Fig. 3.

Flux decline curves during circulation of Al(III) and Fe(III) colloid solutions are illustrated in Figs. 4 and 5, respectively. Permeate flux decreases with time in a similar way as in Fig. 2 because of colloid deposition on a ceramic tube. It is obvious that both pH and colloid concentration of the circulation solution affect membrane formation. The membrane obtained at the isoelectric point has the smallest porosity and thus the lowest flux, because the cohesion force acting among particles is the strongest at this point. This is shown clearly in Fig. 5.

Molecular weight cut-off curves of Al(III) and Fe(III) membranes are drawn in Fig. 6 together with that of the Zr(IV) membrane, which is the M-3 membrane shown in Fig. 3. The Al(III) membrane was formed by circulation of the colloid solution for 60 minutes, which is marked with circles in Fig. 4. The Fe(III) membrane was formed under the conditions of pH 5 and a membrane formation time of 60 minutes. Pressure was changed from 0.8 to 1.0 MPa during circulation of the colloid solution in order to obtain a membrane having almost the same flux as Al(III) and Zr(IV) membranes.

The difference in rejection property between Al(III) and Fe(III) membranes was not so large, but the difference between these two and the Zr(IV) membrane was rather large. The Zr(IV) colloid particles used in this study were very much smaller than those of the other two colloids. Thus, it is supposed that the Zr(IV) colloid formed a deposit layer which had a lower porosity, namely a membrane having smaller pores. This could be the reason for the difference in molecular weight cut-off among these three membranes.

Not only did the Zr(IV) colloid particles deposit on the surface of the ceramic tube, but they entered into the ceramic as well. Thus, the membrane obtained was a very strong one and it was supposed that this membrane could be washed mechanically, for instance by a sponge. By contrast, Al(III) and Fe(III) colloid particles deposited only on the surface, because they were too large to enter into the ceramic. Thus the membranes obtained did not have durability against mechanical washing, and the deposit layer peeled off when these membranes became dry.

Fine colloid suspended in supernatation of the boiled FeCl₃ solution entered into the ceramic tube

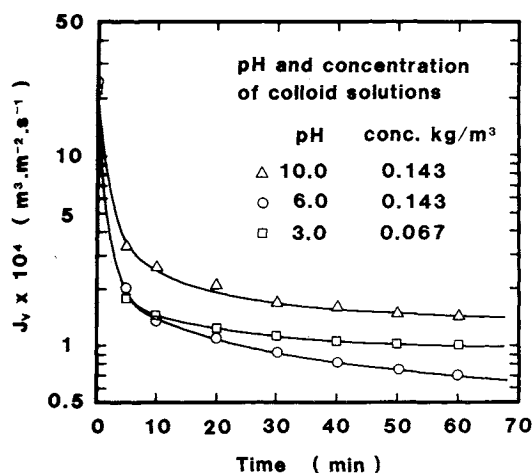


Fig. 4. Flux decline with time during formation of Al(III) dynamic membranes at different colloid concentrations and pH.

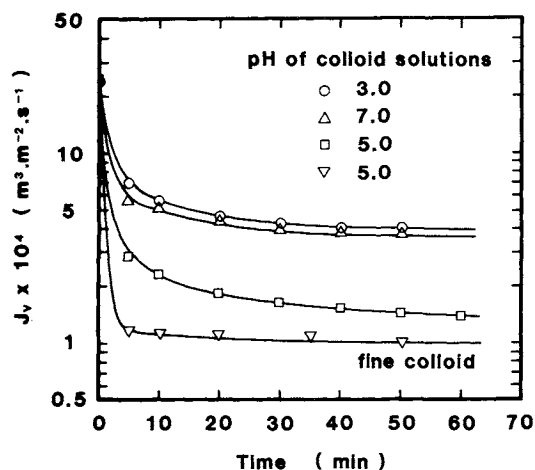


Fig. 5. Flux decline with time during formation of Fe(III) dynamic membranes at different pH: Fe(III) concentration, 0.048 kg/m³.

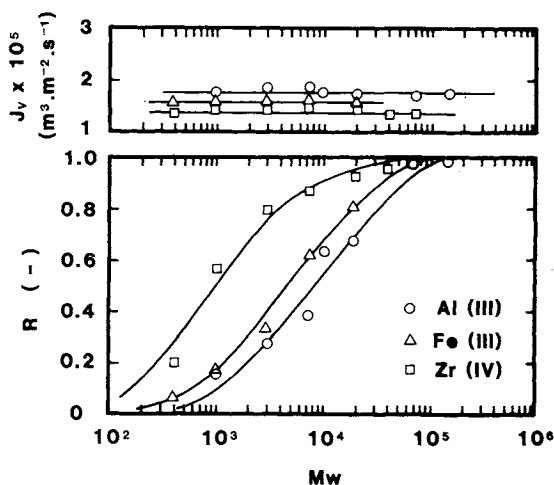


Fig. 6. Molecular weight cut-off curves and fluxes of Zr(IV), Al(III) and Fe(III) dynamic membranes.

and formed a tighter dynamic membrane as shown in Fig. 5.

2.2 Durability of the Zr(IV) membrane

It was concluded from the results mentioned above

that the Zr(IV) dynamic membrane was the best for practical applications among the three membranes. Therefore, the resistance of only this membrane against applied pressure, temperature and pH of a feed solution was measured.

As shown in Fig. 7, the pure water flux was proportional to the applied pressure up to 0.5 MPa. The pure water flux of polymer ultrafiltration membranes bends off at higher pressure in many cases because of the compaction of membranes. The colloid particles used are very rigid compared to the polymer materials of the membrane, and it could be expected that the Zr(IV) membrane is durable against pressures higher than 0.5 MPa.

When neither gel layer formation on membrane surface nor plugging of membrane pores occurs, the permeate flux can be expressed as

$$J_v = \frac{1}{\mu} \frac{\Delta P - \sigma \cdot \Delta \Pi}{R_m} \quad (4)$$

where μ is viscosity of the permeate solution. If no change occurs on the membrane at a higher temperature, pure water flux at any temperature, T K, can be written as the following equation by adopting the temperature of 293 K as standard.

$$J_w = J_w^{293} \frac{\mu^{293}}{\mu^T} \quad (5)$$

In Fig. 8, the fluxes measured agree very well with the solid line drawn by using Eq. (5). It is obvious that the membrane did not become damaged even at 353 K.

The pH resistance of the Zr(IV) dynamic membrane is illustrated in Fig. 9. If the membrane does not have enough durability against low and/or high pH values, the structure of the membrane changes and thus the permeate flux through the deformed membrane also changes. However, fluxes of the Zr(IV) membrane measured were constant within a wide pH range from 3 to 11.

2.3 Structure of inorganic dynamic membranes

Solute transport through a membrane is analyzed by the following transport equations.⁷⁾

$$J_v = L_p(\Delta P - \sigma \cdot \Delta \Pi) \quad (6)$$

$$R = \sigma(1 - F)/(1 - \sigma \cdot F) \quad (7)$$

where

$$F = \exp[-(1 - \sigma)J_v/P] \quad (8)$$

Separation characteristics of a membrane are expressed by the transport parameters, that is, pure water permeability L_p , reflection coefficient σ and solute permeability P , which can be determined from the solute rejection data.⁷⁾

Based on the assumption that a membrane has

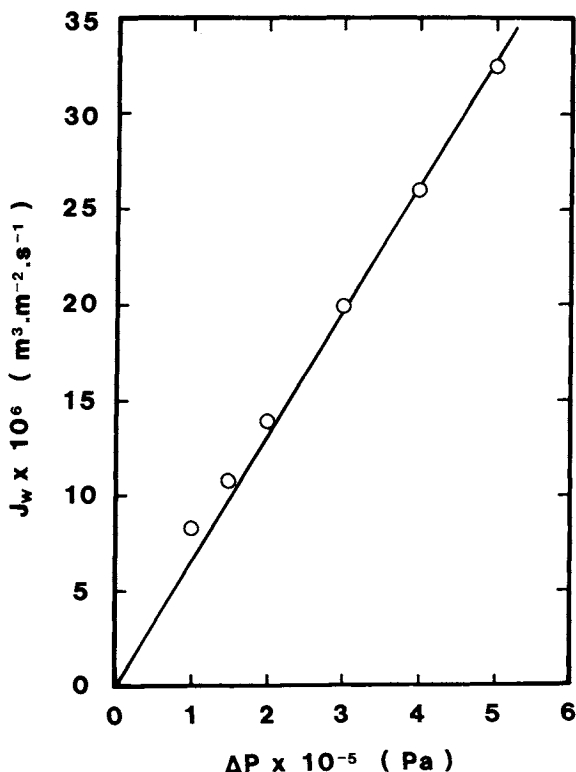


Fig. 7. Relationships between pure water fluxes of Zr(IV) dynamic membrane and applied pressure.

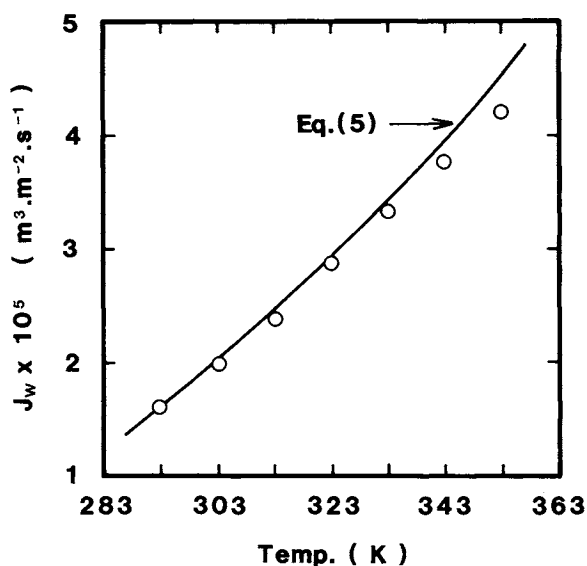


Fig. 8. Effect of temperature of feed solution on pure water flux of Zr(IV) dynamic membrane.

cylindrical pores through which solute permeation takes place, the structural properties of a membrane can be described by radius r_p and length Δx of a membrane pore and pore density A_k . According to the steric-hindrance pore model,⁸⁾ these transport parameters are functions of r_p and $A_k/\Delta x$, expressed as

$$L_p = (r_p^2/8)(A_k/\Delta x) \quad (9)$$

$$\sigma = 1 - (1-q)^2(1+2q-q^2)[1 + (16/9)q^2] \quad (10)$$

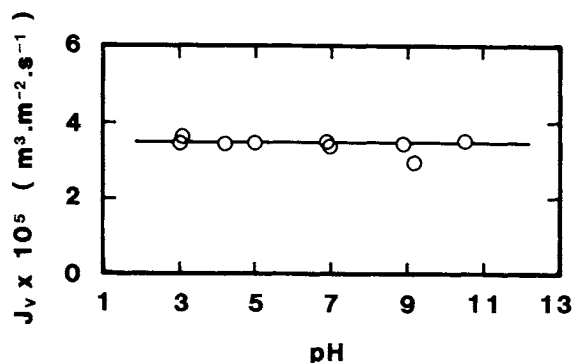


Fig. 9. Effect of pH of feed solution on permeate flux of Zr(IV) dynamic membrane.

$$P = D(1-q)^2 A_k/\Delta x \quad (11)$$

where

$$q = r_s/r_p \quad (12)$$

In the present work, analyzing rejection data of raffinose by using the steric-hindrance pore model, the structure of Zr(IV) and Fe(III) dynamic membranes was estimated.

The results are summarized in Table 1 and compared with the results of two commercial polymer ultrafiltration membranes manufactured by Nitto Electric Industrial Co., Ltd. (Japan). The Zr(IV) membrane has almost the same reflection coefficient as that of the NTU-2006 membrane and thus a similar pore radius, but the values of $A_k/\Delta x$ are very different. Large pore density and/or short pore length result in a large value of $A_k/\Delta x$ and thus high flux. The Fe(III) membrane is very similar to the NTU-3508 membrane. Since both dynamic membranes are deposited particle layers, it might be supposed that their pore density is not so different. Therefore, the reason for the larger value of $A_k/\Delta x$ for the Zr(IV) membrane could be the smaller value of Δx , namely the thinner deposit layer. This was also confirmed by inspection of the membrane surface.

Conclusions

Dynamic ultrafiltration membranes were formed on porous ceramic tubes by filtering inorganic colloids of Zr(IV), Al(III) and Fe(III) at a rather low pressure of 0.8 MPa. Performance of the membranes obtained, such as permeate flux and molecular weight cut-off, could be controlled by the filtration time and conditions, for instance pressure, pH and colloid concentration, during membrane formation.

Zr(IV) colloid particles not only deposited on but also penetrated into the ceramic support. Al(III) and Fe(III) colloids, however, deposited only on the surface, and the membranes did not have mechanical durability. The reason for this difference could not be the nature of colloids themselves but was the size of

Table 1. Transport and structural properties of Zr(IV) and Fe(III) dynamic membranes and commercial polymer ultrafiltration membranes

	σ [—]	$P \times 10^6$ [m·s ⁻¹]	r_p [nm]	$L_p \times 10^{11}$ [m·s ⁻¹ ·Pa ⁻¹]	$A_k/\Delta x \times 10^{-4}$ [m ⁻¹]
NTU-2006	0.73	1.70	0.940	2.00	2.53
Zr(IV)	0.72	15.3	0.946	7.78	24.3
NTU-3508	0.32	3.58	1.26	3.90	2.98
Fe(III)	0.33	3.86	1.23	3.90	3.27

colloid particles.

The Zr(IV) dynamic membrane was durable enough to applied pressure up to 0.5 MPa, temperature up to 353 K and pH range from 3 to 11.

The structure of Zr(IV) and Fe(III) dynamic membranes was estimated by the steric-hindrance pore model. Compared with commercial polymer ultrafiltration membranes, it could be supposed that the Zr(IV) membrane had a shorter pore length, namely a thinner deposit layer of colloid particles.

Acknowledgment

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Nomenclature

A_k	= ratio of total cross-sectional pore area to effective membrane area	[—]
C	= concentration	[mol·m ⁻³]
D	= diffusivity	[m ² ·s ⁻¹]
d	= equivalent hydraulic diameter	[m]
J_v	= volume flux	[m ³ ·m ⁻² ·s ⁻¹]
J_w	= pure water flux	[m ³ ·m ⁻² ·s ⁻¹]
k	= mass transfer coefficient	[m·s ⁻¹]
L_p	= pure water permeability	[m ³ ·m ⁻² ·s ⁻¹ ·Pa ⁻¹]
l	= channel length	[m]
N_{Re}	= Reynolds number	[—]
N_{Sc}	= Schmidt number	[—]
N_{Sh}	= Sherwood number	[—]

P	= solute permeability	[m·s ⁻¹]
ΔP	= pressure difference	[Pa]
q	= r_s/r_p	[—]
R	= real rejection	[—]
R_m	= resistance of a membrane	[m ⁻¹]
r_p	= radius of a membrane pore	[m]
r_s	= Stokes radius of solute	[m]
Δx	= pore length	[m]
μ	= viscosity	[Pa·s]
$\Delta \Pi$	= osmotic pressure difference	[Pa]
σ	= reflection coefficient	[—]

<Superscripts>

293	= standard temperature of 293 K
T	= optional temperature of T K

<Subscripts>

b	= bulk
m	= membrane surface
p	= permeate

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