DETERMINATION OF MEAN PORE DIAMETER
OF CERAMIC MICROFILTRATION MEMBRANE
USING RETENTION CHARACTERISTICS

Hana ŠEDÁ
Department of Chemical Engineering

Molecular weight cut-off experiments have been done to characterize alumina microporous membrane using PEG and dextran solutions. For the evaluation of the results, the final porous model was applied. The mass transfer coefficient was determined by the velocity variation method. The mean pore radius of the membrane used was estimated to be 60 nm, which corresponds well to the value obtained using the bubble-point technique.

Introduction

The pore size of a membrane is manifested in the permeabilities and separation (retention) characteristics of the membrane. The retention characteristics of a given membrane are usually presented as the retention versus the molecular weight of different macromolecules. The most commonly used model molecules are polyethylene glycol (PEG) polymers which are linear and flexible in nature, and dextrans which are slightly branched.

During the course of a typical permeation and separation process using membranes a variety of phenomena such as concentration polarization, adsorption and internal pore fouling influence the permeate rate. Most of

experimental data are highly affected by these factors, and determination of the membrane transport properties is very uncertain.

A number of methods such as electron microscopy[1,2], thermoporometry[2,3], biliquid permporometry[2], gas permeability method[1,4] and bubble-point technique[1,9] have been considered for evaluation of pore characteristics.

In this paper the determination of the mean pore diameter of tubular ceramic membrane from retention experiments is discussed. A combined viscous flow and frictional model[5] was found to give good correlation with experimental data for ultrafiltration polymeric membranes. The applicability of this finely-porous model for ceramic microfiltration membrane is investigated.

Theoretical

The characteristics of a membrane can be expressed in terms of the permeation flux of the solution and rejection of solute. The observed (apparent) retention R_{obs} can be calculated from the formula

$$R_{obs} = \frac{(C_b - C_p)}{C_b} \tag{1}$$

which utilizes the concentration C_b of the solute in the bulk and C_p in the permeate.

Since separation by a membrane usually gives rise to concentration polarization on the surface of the membrane, the concentration on the surface of the membrane is higher than the concentration in the feed. Therefore, to calculate the true retention R of the membrane, the bulk concentration C_b in Eq. (1) has to be replaced by the concentration C_m on the membrane

$$R = \frac{(C_m - C_p)}{C_m} \tag{2}$$

As C_m cannot usually be measured, it is calculated from the following formula for concentration polarization based on the film theory model

$$\frac{(C_m - C_p)}{(C_b - C_p)} = \exp\left(J_v \frac{d}{D_i}\right) \tag{3}$$

where the quantity D_i/d is defined as the mass transfer coefficient k_i

In turbulent flow, k_i is normally found to be proportional to the flow velocity u according to the relation

$$\frac{k_i d_h}{D_i} = A Re^{0.8} Sc^{0.33} \tag{4}$$

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Thus, the equation for the retention can be derived from Eqs (1) - (4)

$$\ln\frac{1 - R_{obs}}{R_{obs}} = \ln\frac{1 - R}{R} + \frac{J_v}{cu^{0.8}}$$ (5)

By plotting the experimental values of $\ln[(1 - R_{obs})/R_{obs}]$ as a function of $J_v/u^{0.8}$, the true retention and the constant c can be determined graphically. The relation for the mass transfer coefficient as a function of the various experimental variables can now be obtained by fitting the data found in the different experimental circumstances.

According to the final-porous model the true retention is given by the relation[5]

$$\frac{C_m}{C_p} = \frac{1}{1 - R} = \frac{b}{K} + \left(1 - \frac{b}{K}\right)\exp\left[-\frac{t\lambda J_v}{\varepsilon D_i}\right]$$ (6)

The retention data can further be correlated with equations for steric exclusion and frictional interaction with the pore walls given by Ferry and Haberman and Sayre[8]

$$K = 2 (1 - \alpha)^2 - (1 - \alpha)^4$$ (7)

and

$$b = 1 - \frac{0.75857\,\alpha^5}{1 - 2.105\,\alpha - 2.0865\,\alpha^3 - 1.7068\,\alpha^5 + 0.72603\,\alpha^6}$$ (8)

where $\alpha = r_i/r_p$

The different solute radii r_i can be calculated from Stokes-Einstein correlation if data on liquid phase diffusion coefficient and solution viscosity are available

$$D_i = \frac{kT}{6\pi\eta\,r_i}\,.$$ (9)

Experimental

Ceramic alumina tubular membrane manufactured by Terronic, Hradec Kralové, (The Czech Rep.) was used with an inside diameter of 0.6 cm, an outside diameter of 1 cm, a length of 50 cm, and effective membrane area of 94 cm².

This membrane has an asymmetric structure with the finely porous layer on the inside of the tube. The mean pore radius of the membrane determined by the bubble-point technique[9] was 63 nm.

The polymeric solutes, dextrans T70, T500, T2000 and PEG 35000 obtained from Pharmacia, Uppsala (Sweden) and Merck, Schuchardt (Germany) respectively, were used at the concentration of 0.1 % wt. The molecular characteristics of polymers are listed in Table I.

Table I Molecular characteristics of polymers

Solute	Mw, Dalton	$D_i^{*)}$, cm^{2}s^{-1}	$r_i^{**)}$, Å
PEG 35 000	35,000	4.10×10^{-7}	55
Dextran T70	72,200	3.83×10^{-7}	59
Dextran T500	470,000	1.34×10^{-7}	170
Dextran T2000	2000,000	6.12×10^{-8}	372

*)   The diffusion coefficients taken from literature[7]
**) The pore radii calculated from Eq. (9)

The experiments were carried out in cross-flow configuration, with the feed flowing parallel to the membrane surface and perpendicular to the permeate at the temperature of 293 K. The experimental equipment is depicted in Fig.1.
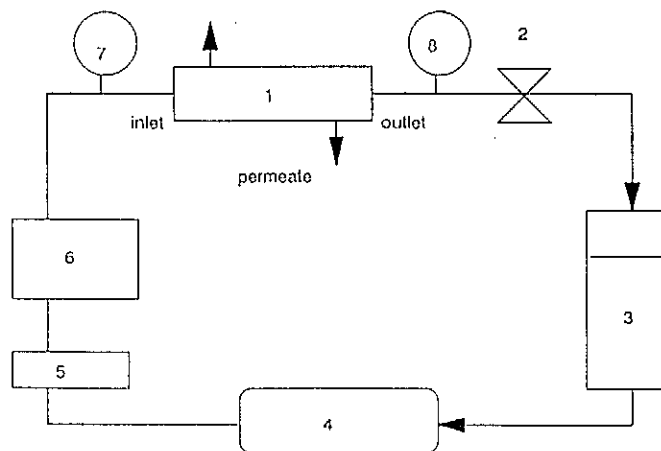

Fig. 1 Schematic representation of the ceramic membrane equipment: 1 modul with tubular ceramic membrane, 2 reduction valve, 3 reservoir, 4 pump, 5 prefilter, 6 thermostat, 7,8 manometer

Two sets of measurements were done:

a) At constant pressure level, the circulation velocity was varied in 5 steps from

1.46 to 3.32 m s^{-1}. It corresponds to Reynolds numbers from 9 220 to 20 970.

b) At constant circulation velocity (1.46 m s^{-1}), the pressure was varied from 0.5 to 4.5 bar.

The circulation velocity was controlled with a pump. Solute concentrations of the feed and permeate were determined refractometrically with a differential refractometer, Waters model R-403.

Results and Discussion

In order to evaluate the mean pore diameter of the membrane used, the mass transfer coefficient and the maximum retention were determined.

As shown in the theoretical section, the experimental data needed for mass transfer coefficient determination are the observed retention R_{obs}, the flux J_v and the cross-flow velocity u. Consequently, a plot of $\ln(1 - R_{obs})/R_{obs}$ versus $J_v/u^{0.8}$ is a straight line intersecting at $\ln(1 - R)/R$ and with a slope equal to $(A D_i^{0.667} d_h^{0.2} v^{0.467})^{-1}$. In Fig. 2 (see also Table II) the example is given for Dextran T2000.
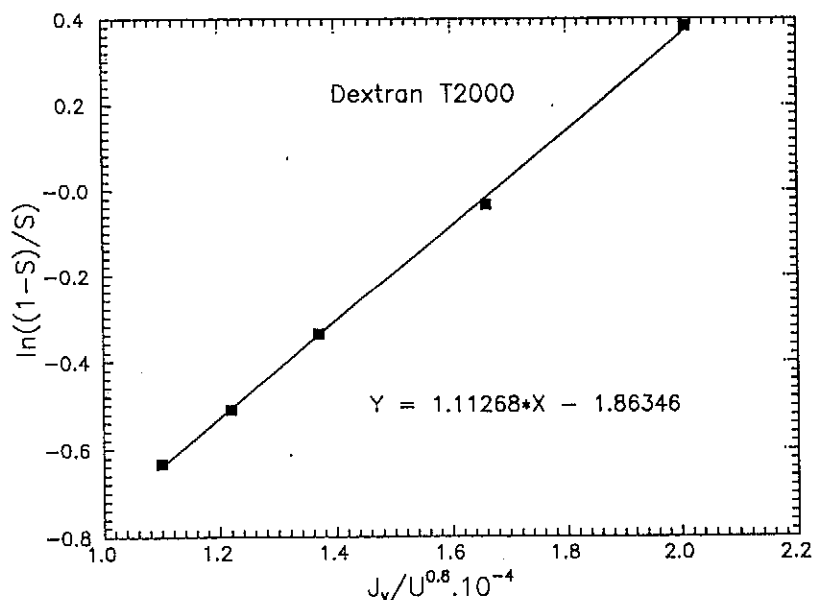

Fig. 2 Data for Dextran T2000 for estimation of the mass transfer coefficient

Table II Mass transfer coefficient determination for Dextran T2000

R_{obs}	$\ln\!\big((1-R_{obs})/R_{obs}\big)$	$J_v \times 10^{-3}$ $\mathrm{g\,cm^{-2}s^{-1}}$	u $\mathrm{cm\,s^{-1}}$	$J_v/u^{0.8} \times 10^{-5}$ $\mathrm{cm\,s^{-1}}$	$k_i \times 10^{-4}$ $\mathrm{cm\,s^{-1}}$
0.405	0.383	1.083	146	2.01	4.82
0.508	- 0.033	1.125	195	1.66	6.15
0.583	- 0.337	1.111	244	1.37	7.28
0.625	- 0.509	1.139	290	1.22	8.41
0.653	- 0.632	1.139	332	1.10	9.25

Table III Mass transfer coefficients calculated from Eq. (4)

Solute	u, $\mathrm{cm\,s^{-1}}$	A	$K_i \times 10^{-4}$, $\mathrm{cm\,s^{-1}}$
Dextran T70	146	0.0592	16.40
Dextran T500	146	0.0592	8.13

For the other solutes k_i was calculated from Eq. (4) knowing the constant A from the slope in Fig. 2 and results are listed in Table III.

The dependence of the retention on the permeate flux at different cross-flow velocities is shown in Fig. 3.

In Fig. 3, the true retention data were calculated from Eq.(5) using the k_i values from Table II. According to the theory[6], the observed retention increases with increasing cross-flow velocity, while the true retention remains constant.
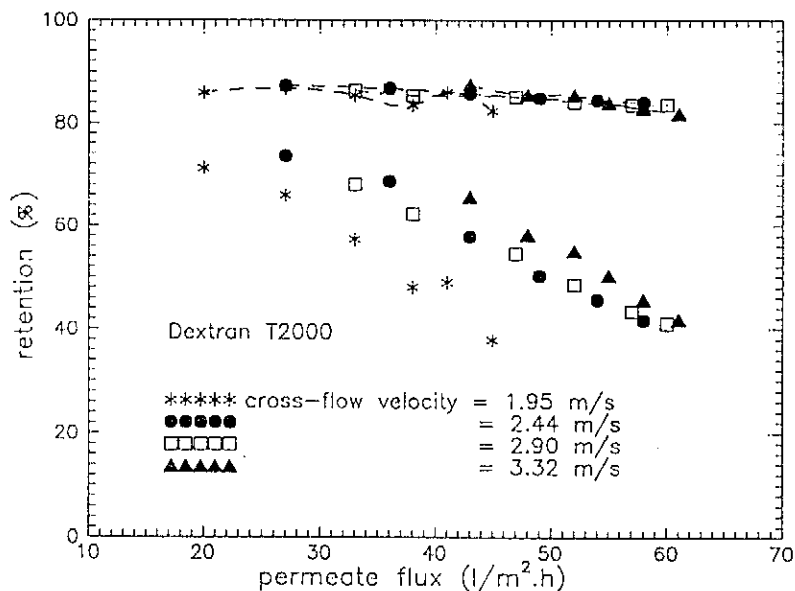

Fig. 3 The effect of the cross-flow velocity on the retention

To find the maximum retention, R_{max}, the parameters b/K and $t\lambda/\varepsilon$ in Eq. (6) were estimated using nonlinear regresion analysis. Due to high correlation between the two parameters, only few of the experimental data-sets give reasonable values of the estimated parameters. However, assuming that $t\lambda/\varepsilon$ is a membrane constant independent on the solutes[8], all the data sets were analyzed together, with b/K being constant for each solute. In this way, $t\lambda/\varepsilon$ was found to be 1.72×10^{-4} cm. The b/K and R_{max}, values for three different dextrans used are listed in Table IV.

Figure 4 shows both the experimental and theoretical cut-off curves for dextran, i.e. R_{max} versus Mw. At lower Mw the experimental data are close to the curve for $r_p = 30$ nm, then they cross the curves for $r_p = 40$ nm and $r_p = 60$ nm. At $Mw = 2.000\,000$ they intersect the curve for $r_p = 80$ nm. In spite of that there are no experimental data for $Mw > 2.000\,000$, it can be assumed that the membrane has some pores over this range. The mean pore radius of the membrane used can be estimated as 60 nm, which corresponds well to the value obtained using bubble-point technique.

However, more Mw cut-off values are necessary to confirm these results and to determine pore size distribution of the membrane.

Table IV Estimated values of b/K and R_{max} from Eq. (6)

Solute	b/K	R_{max}, %
Dextran T70	2.09	.52.15
Dextran T500	7.06	85.84
Dextran T2000	9.43	89.40

membrane parametr $t\lambda/\varepsilon = 1.72\,10^{-4}$, cm

Conclusion

Solute rejection measurements provide a simple technique for indicating the performance of a given membrane.

The molecular weight cut-off curves can be used to evaluation of the mean pore diameter of ceramic microfiltration membrane and to give information on the separation properties.

However, membrane characterization cannot be obtained only by such method, since other factors, such as shape and flexibility of the macromolecular solute, its interaction with the membrane material and concentration polarization phenomena influence the permeation rate and membrane selectivity.
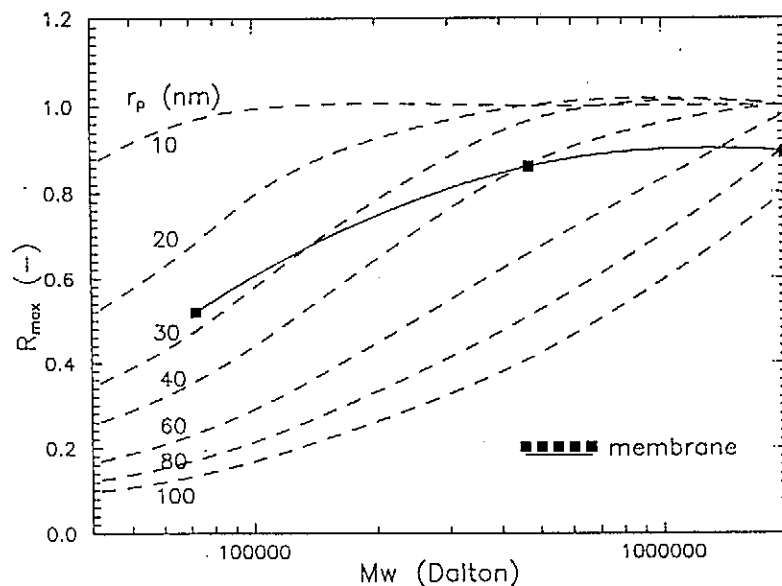
Fig. 4 The maximum retention determined from Eq. (6) versus molecular weight for Dextran
- the dotted curves are calculated from Eqs (7) and (8)

Acknowledgements

Symbols

A coefficient in Eq.(4)

b friction parametr

c constant in Eq. (5)

C_b solute concentration in the bulk, kg m^{-3}

C_m solute concentration at membrane surface, kg m^{-3}

C_p solute concentration in the permeate, kg m^{-3}

d_h equivalent hydraulic diameter, m

D_i diffusion coefficient, m^2s^{-1}

J_v flux, $\text{kg m}^{-2}\text{s}^{-1}$

k Boltzmann constant

k_i mass transfer coeficient, m s^{-1}

K distribution coefficient

r_i solute radius, nm

r_p	pore radius, nm
R	true retention
R_{obs}	observed retention
R_{max}	maximum retention
Re	Reynolds number
Sc	Schmidt number
t	tortuosity factor
T	temperature, K
u	cross-flow velocity, $m\,s^{-1}$
ε	fractional pore area
λ	thiskness of the activ layer, m
ν	kinematic viscosity, $m^2 s^{-1}$
η	dynamic viscosity, $kg\,m^{-1}s^{-1}$

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