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Molecular sieving effects of disk-shaped molecules on reverse osmosis and nanofiltration separation

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ABSTRACT

The solute separation in reverse osmosis/nanofiltration (RO/NF) membrane processes is mainly controlled by both the diffusivity in a pore and the steric partition factor, and the latter is defined by the geometrical probability at which a solute can be accessible into a pore. The rejection of alcohols has been estimated semi-empirically by using the steric partition factor derived by the approximation of molecular shape as a rectangular parallelepiped. However, the approach was not suitable for crown ethers, and in this work the shape of crown ethers was approximated as a disk: the disk radius and disk thickness were developed as new shape parameters. The calculated rejections of crown ethers by using the disk-shaped model corresponded well to the observed rejections, where the used pore radius was calculated on the basis of the rejections of alcohols. Boric acid in non-dissociated form is also assumed to be a disk-shaped molecule, but the calculated rejection by the disk-shaped model was smaller than the observed one. The results suggest that boric acid transports through membrane pores with hydrated water molecules.

1. Introduction

Antibiotics and pharmaceutical and healthcare chemicals have been recognized as new types of pollutants in drinking water sources in urban areas, where wastewater treatment plants are assumed to be a main pollution source [1,2]. Nanofiltration (NF) and reverse osmosis (RO) membrane processes have been known to be useful and promising technologies for removing hazardous organic micro-pollutants such as pesticides, endocrine disrupting chemicals, pharmaceutical and healthcare chemicals [3–15]. The separation performance of organic compounds is controlled by both molecular sieving effect and attractive interactions between solute and membrane material [5,15]. The attractive interactions have been correlated with the hydrophobic properties of the solute, i.e. *n*-octannol/water partition coefficient (log $K_{o/w}$) [3–5]. The molecular sieving effect has been commonly expressed by a molecular weight cutoff (MWCO), but the molecular shape also influences to molecular sieving and the molecular width parameter has been pointed out as a useful shape parameter [4,16].

For examination of the molecular sieving effect, solutes without interaction with the membrane material are suitable as probe solutes. For this purpose, hydrophilic compounds such as alcohols and saccharides have been used as probe solutes. The molecular sieving effect has been evaluated theoretically on the basis of the pore model [17–22], where the solutes were assumed to be a sphere. In our previous works [23,24], the structures of hydrophilic organic compounds were approximated as rectangular parallelepipeds, and molecular shape parameters (molecular length and molecular width) were employed for calculation of the molecular sieving factor in the pore model. Although the molecular shape parameters were obtained semi-empirically, the calculated rejections corresponded well to the observed rejections. Madsen et al. [25] calculated the rejections of hydrophilic pesticides and pesticide transformation products by the rectangular parallelepiped model and indicated that the calculated rejections corresponded well to the experimental rejections. Madsen et al. [26] reported that the shape model was also useful to calculate the pesticides rejection in forward osmosis system. In addition, in the case of relatively hydrophobic membranes, cylindrical approximation of molecular shape gave better correspondence between the calculated and observed rejections than the rectangular parallelepiped model [25]. Therefore, the rectangular parallelepiped approximation for a molecule may not be always the best approach to evaluate shape parameters. Suitable molecular shape modeling may be different by some group of compound and/or membrane. If so, it is necessary to be prepared for other shape models.

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Nomenclature

A_k	porosity of the membrane (–)
B	solute permeability (m s^{-1})
B^*	calculated solute permeability (m s^{-1})
C	solute concentration in the pore (mol m^{-3})
C_f	feed concentration (mol m^{-3})
C_p	permeate concentration (mol m^{-3})
C_r	retentate concentration (mol m^{-3})
C_i	solute concentration at inlet of the pore (mol m^{-3})
C_o	solute concentration at outlet of the pore (mol m^{-3})
CG_y	y-component of the center of gravity of a disk
D	diffusivity in bulk solution (m^2 s^{-1})
D_p	hindered diffusivity (m^2 s^{-1})
DR	disk radius (m)
DT	disk thickness (m)
G	lag coefficient (–)
J_s	solute flux (mol m^{-2} s^{-1})
J_w	pure water flux (m^3 m^{-2} s^{-1})
J_v	water flux (m^3 m^{-2} s^{-1})
K_d	hindrance factors for diffusion (–)
K_c	hindrance factors for convection (–)
K^{-1}	enhanced drag coefficient (–)
k	Boltzmann constant (J K^{-1})
L	molecular length (m)
MWd	molecular width (m)
ΔP	applied pressure (Pa)
$p(\alpha)$	probability of a solute molecule being oriented at an angle α to the pore surface (–)
Pe	Peclet number (–)
Rc	radius of curvature (nm)
$R_{j(obs)}$	observed rejection (–)
$R_{j(cal)}$	calculated rejection (–)
r_p	effective pore radius (m)
r_s	Stokes radius (m)
S_y	standard deviation of difference between $R_{j(obs)}$ and $R_{j(cal)}$
T	absolute temperature (K)
x	position in a pore from inlet (m)
Δx	pore length (m)
α	angle of the disk plane to the pore surface
η	viscosity of water in a pore (Pa s)
λ	ratio of solute radius to effective pore radius (–)
$\Delta\pi$	osmotic pressure difference (Pa)
Φ	steric partition factor (–)
$\Phi(\alpha)$	steric partition factor at angle α (–)

In our preliminary studies, crown ethers were approximated as rectangular parallelepipeds, but the calculated rejections did not correspond well to the observed rejections: the rectangular parallelepiped approximation led to overestimation of the molecular size. In this work, we examined the development of more suitable shape parameters for crown ethers. Crown ethers are assumed to have disk-shaped structures, and two shape parameters for a disk were developed: disk radius (*DR*) and disk thickness (*DT*). The solute rejections were calculated on the basis of pore model by using disk-shape parameters. In addition, boric acid, which showed low rejection even by RO membrane, is also disk shape molecule, and the disk shaped model was also applied to the rejection estimation of boric acid.

2. Theoretical background

2.1. Shape parameters

In our previous work [23,24], an alcohol was approximated by a rectangular parallelepiped as shown in Fig. 1. A crown ether was also approximated by a rectangular parallelepiped, where the molecular length (*L*) and molecular width (*MWd*) were calculated as the shape parameters. In this work, a crown ether was approximated by a disk as shown in Fig. 1. In this case, *DR* and *DT* were calculated as the shape parameters by the following procedure:

(1) Molecular coordinate of stable conformation was calculated by a semi-empirical molecular orbital method using the MOPAC program in ChemOffice by CambridgeSoft Co. (MA, USA).
(2) Three atoms on the same plane were selected, and the molecular coordinate was rotated so that the three atoms were on the xy-plane.
(3) An atom pair was selected so that the distance between the two atoms on the xy-plane is the longest (taking into account their van der Waals radii). The *DR* was defined as half of the distance.
(4) The maximum distance along the z-axis was calculated and defined as the *DT*, where the van der Waals radius was also taken into account.

2.2. Steric partition factor

The steric partition factor (molecular sieving factor) in the pore model can be defined as the ratio of the solute-accessible area to the total pore area, where a pore is assumed to be a cylinder. For a molecule approximated by a disk, the steric partition factor is expressed by the *DR* and *DT*. When the disk plane faces a pore surface at an angle α, the projection of the disk against the pore surface is an ellipse, and the cross section is a rectangular as shown in Fig. 2(1). The projection ellipse is expressed by Eq. (1):

$$\frac{x^2}{DR^2}+\frac{(y-p)^2}{DR^2\cos^2\alpha}=1. \tag{1}$$

When the ellipse is inscribed in the pore circle (pore radius: r_p), the following two cases are possible: contact at a single point and at two points. For each case, the steric partition factor ($\phi(\alpha)$) is derived as follows:

Case-1: The projection is inscribed at a single point, as shown in Fig. 2(2)

When the projection ellipse contacts only at the point A $(0, r_p)$, the radius of curvature (*Rc*) of the ellipse at point A is smaller than the radius of membrane pore (r_p). Commonly, the radius of curvature (*Rc*) at the point of $x = z$ for the curve expressed by Eq. (2) is defined by Eq. (3).

$$y=f(x), \tag{2}$$

$$Rc^2=\frac{(1+f'(z)^2)^3}{f''(z)^2}. \tag{3}$$

In the case that the ellipse contacts at a single point, the following relation is obtained.

$$0<Rc\,(\text{at } x=0)<r_p, \tag{4}$$

$$\cos\alpha \geqslant \frac{DR}{r_p}. \tag{5}$$