

# Determination of membrane properties for use in the modelling of a membrane distillation module

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## Abstract

Membrane distillation carried out in a counter current flow module, in which latent heat is recovered by heating the incoming cold seawater with the condensing product water flow, is a promising technology for low cost seawater desalination. The membranes used in this module are hydrophobic (polypropylene, polyethylene) and highly permeable fibre membranes. For modelling purposes the Knudsen diffusion and viscous flow membrane characteristics ( $K_0$  and  $B_0$  respectively) of five fibre membranes are determined. This paper presents a new, specially developed method for the determination of  $K_0$  and  $B_0$  values of highly permeable fibre membranes with single gas permeation experiments through a short dead end fibre. In order to be able to make use of a reliable method to determine the values of  $K_0$  and  $B_0$ , it is essential that the pressure inside the permeable part of the membrane is constant. To determine the conditions at which the pressure drop in the permeable part of the membrane fibre is negligible, this part is reduced in length until the values of  $K_0$  and  $B_0$  become constant. For all membranes the gases He, N<sub>2</sub> and CO<sub>2</sub> were used. The gases N<sub>2</sub> and CO<sub>2</sub> lead to consistent values of  $K_0$  and  $B_0$ . Helium gives less accurate results due to its low molecular weight. The three polypropylene membranes have a similar structure and have therefore about the same values for  $K_0$  and  $B_0$ . The same was found for the two polyethylene fibres.

*Keywords:* Membrane distillation; Desalination; Porous fibre membranes; Single gas permeation experiments

## 1. Introduction

An increasing number of areas on our planet suffer from fresh water scarcity because of rapid decrease of ground water levels and depletion of aquifers. One way to address this problem is low

cost seawater desalination. A substantial cost reduction may be possible by carrying out the desalination process at reduced temperatures so that low quality (waste) heat or solar energy can be used as an energy source, provided that the contribution of the investment costs to the total desalination costs become not too large. Membrane distillation carried out in a counter current

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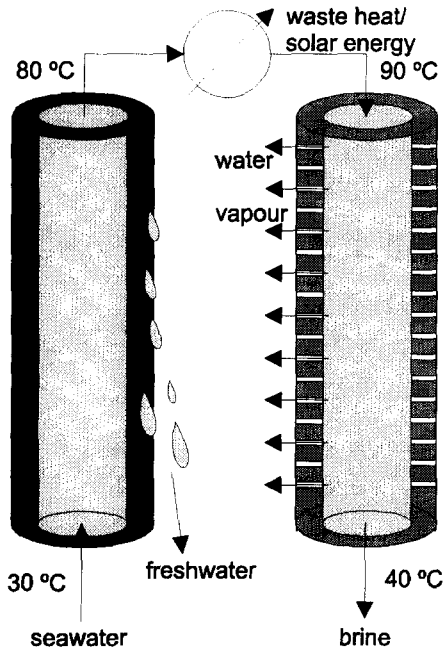


Fig. 1. Schematic presentation of a typical membrane distillation module.

flow module is a very promising technology in this respect. The principle of the counter current flow membrane distillation module is depicted in Fig. 1. Cold seawater feed flows through a condenser tube with non-permeable well-wettable walls via a heater into the membrane evaporator tube in counter current mode. The condenser and evaporator tubes are separated by an air gap. The wall of the evaporator tube consists of a microporous hydrophobic (non-wettable) membrane through which water vapour can diffuse and by which liquid water (with dissolved salts) is retained. The temperature difference between the flows inside the evaporator and condenser tubes generates a vapour pressure difference. This forces the vapour to diffuse through the membrane pores of the evaporator tube and the air gap to the condenser tube, on which the desalinated vapour condenses and latent heat is recovered. The air

gap could alternatively be filled with another inert gas instead of air to enhance mass transfer. At this moment limited knowledge is available about the design and performance of a counter current flow membrane distillation process. Recently we presented a model based on estimated parameters for preliminary calculations [1]. To refine the model, the estimated parameters have to be replaced by measured ones, starting with the membrane mass transfer characteristics. These can be measured independently from all other parameters with single gas permeation and subsequently binary gas diffusion experiments.

This paper presents the results of the single gas permeation experiments.

## 2. Theory

The transport of a single gas through a porous membrane can be described by the dusty gas model [2]. Since the mean free path of most gases at ambient conditions is between 40 and 200 nm [3] and the maximum pore size of the membranes used varies from 100–600 nm, both Knudsen diffusion and viscous flow will contribute to the total gas flux through the membrane pores according to Eq. (1).

$$N = -\frac{1}{RT} \left[ K_0 v_M + B_0 \frac{P}{\mu} \right] \nabla P \quad (1)$$

where  $N$  is the molar gas flux,  $R$  the universal gas constant,  $T$  is temperature,  $P$  is the pressure and  $\mu$  the viscosity of the gas.  $\nabla P$  is the derivative from  $P$  in all directions, which in our case can be reduced to the derivative in the radial direction  $dP/dr$ .  $v_M$  is the mean molecular velocity of the gas defined by Eq.(2):

$$v_M = \sqrt{\frac{8RT}{\pi M}} \quad (2)$$

where  $M$  is the molar mass of the gas used.  $K_0$  and  $B_0$  are the Knudsen diffusion and viscous flow morphology parameters of the membrane. For homogeneous membranes  $K_0$  and  $B_0$  are membrane specific constants, that are independent of the permeating gas as long as no other gas-membrane interactions take place than collisions (e.g. no dissolution, adsorption or surface diffusion). For a membrane with ideal cylindrical pores  $K_0$  and  $B_0$  are given by Eq.(3).

$$K_0 = \frac{2\varepsilon r_p}{3\tau}; \quad B_0 = \frac{\varepsilon r_p^2}{8\tau} \quad (3)$$

$$\text{thus, } r_p = \frac{16}{3} \frac{B_0}{K_0}$$

where  $\varepsilon$  is the membrane porosity,  $\tau$  the membrane tortuosity and  $r_p$  the pore radius. Since real membranes have very complex structures,  $K_0$  and  $B_0$  must be determined experimentally. Integrating Eq. (1) over a tubular membrane wall ( $Nr = \text{constant}$ ) gives:

$$N_{out} = \frac{1}{RT} \left[ K_0 v_M + B_0 \frac{P_{av}}{\mu} \right] \frac{\Delta P}{R_{out} \ln \left( \frac{R_{out}}{R_{in}} \right)} \quad (4)$$

where  $N_{out}$  is the molar gas flux with respect to the outer membrane area,  $P_{av}$  is the arithmetic mean of the gas pressure at the inside and at the outside of the membrane fibre,  $\Delta P$  is the pressure

difference between the inside and the outside of the membrane fibre and  $R_{in}$  and  $R_{out}$  are the inner and outer membrane fibre radius respectively.

According to this equation a graph of  $N_{out} R T R_{out} \ln(R_{out}/R_{in}) / (\Delta P v_M)$  versus  $P_{av} / \mu v_M$  will have  $K_0$  as intercept and  $B_0$  as slope for all gases used.

### 3. Method

Due to the high fluxes the standard methods of single gas permeation experiments [4,5] appeared not to be suitable for the determination of  $K_0$  and  $B_0$  of the highly permeable membrane fibres used in our study. See Table 1 for some data on these membranes. Therefore a new method has been developed especially for these fibres. A schematic presentation of the developed experimental set up is depicted in Fig. 2. A dead end construction is chosen so that the entire flow is forced through the membrane. The combination of high transmembrane fluxes and a thin fibre gives considerable pressure drop in the fibre. The pressure drop in the potted part of the membrane fibre is calculated with the Hagen Poiseuille equation applied to a compressible medium [6]. However to be able to use the earlier explained graphical method to determine the values of  $K_0$  and  $B_0$ , it is essential that the pressure inside the permeable part of the membrane is constant. To establish the conditions at which the pressure drop in the

Table 1

Data of tested membrane fibres provided by the manufacturer

Material	Name	Inner diameter, $10^{-6}$ m	Wall thickness, $10^{-6}$ m	Pore size, $10^{-6}$ m
Polypropylene	Accurel PP S6/2 <sup>1</sup>	1800 ±200	450±70	0.2
	Accurel PP Q3/2 <sup>1</sup>	600±90	200±45	0.2
	Plasmaphan P1 LX 150/330 <sup>1</sup>	330±20	150±10	0.4–0.6
Polyethylene	EHF 540VA-12 <sup>2</sup>	360	90	0.4
	EHF 270FA-16 <sup>2</sup>	270	55	0.1

Manufacturer: <sup>1</sup>Akzo Nobel, <sup>2</sup>Mitsubishi

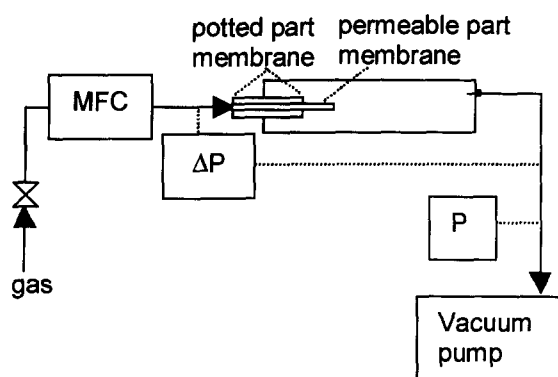


Fig. 2. Schematic presentation of the experimental set up for single gas permeation experiments.

permeable part of the fibre is negligible, this part is reduced in length until the values of  $K_0$  and  $B_0$  become constant. For thin fibres this appeared to be a length of about 7 mm. To obtain sufficient membrane area one to six fibres are potted together.

The gas flow from the gas cylinder is controlled by a Brooks 5850E Series Mass flow controller, which was calibrated for each gas with a Brooks mercury Vol-U-Meter. The pressure difference over the membrane is measured by a Honeywell Smart Transmitter STD624. The absolute pressure at the permeate side of the membrane is measured by a combination of a Honeywell Smart Transmitter STD624 which measures pressure difference with the surroundings and an Ebro vacuum VM 1500 pressure meter which measures the surrounding pressure. The vacuum pump is used for adjustment of the permeate pressure. Each series of measurements (a combination of a membrane fibre and a gas) consists of 21 data points. The permeate pressure is atmospheric (7 points), circa  $6 \cdot 10^4 Pa$  (7 points) or circa  $1 \cdot 10^4 Pa$  (7 points). The transmembrane pressure difference varies from  $2 \cdot 10^4 - 7 \cdot 10^4 Pa$  for a constant permeate pressure. The main reason for

measurements at lower pressures is the fact that  $K_0$  is the intercept of the graph. If only measurements at higher pressures were conducted, most of the data points would be far away from the  $y$ -axis giving a less accurate result. Since the membrane distillation process will be carried out at atmospheric pressure, there is no need for permeation experiments at elevated pressure. For every membrane type the reproducibility is tested by triple experiments using different fibre segments.

Although water vapour is the gas of interest, no single gas permeation experiments are carried out with water vapour. This is because water vapour is a condensable gas at ambient conditions. Single gas permeation with water vapour would complicate the experiments considerably, especially since the membranes used are not stable at temperatures above  $70^\circ C$ . The measurement results would be less accurate using water vapour. Since, according to the theory, the measured values for  $K_0$  and  $B_0$  are independent of the gas used, the gases He,  $N_2$  and  $CO_2$  are used for the single gas permeation experiments.

#### 4. Results

The mean values of all triple experiments are tabulated in Table 2. From the data in Table 2 can be concluded that the values of  $K_0$  and  $B_0$  for  $N_2$  and  $CO_2$  are within each other's error margin. For He all the  $K_0$ 's have a somewhat lower value and all the  $B_0$ 's are a little higher. This gave cause for some additional measurements with Ar and  $CH_4$  for one polyethylene EHF540VA-12 fibre. Fig. 3 shows the results for this fibre.

The results for  $CH_4$  are in good agreement with those for  $N_2$  and  $CO_2$ . Ar is slightly divergent. More inconsistent data for different gases in single gas permeation experiments are presented in literature [5,7,8]. In [5] a lower value of  $K_0$  and a higher value of  $B_0$  for He could

Table 2  
 $K_0$  and  $B_0$  values determined with single gas permeation experiments

Polypropylene membranes		PP S6/2	PP Q3/2	P1 LX 150/330
$K_0/10^{-8}$ , m	He	5.60±0.03	5.83±0.07	6.21±0.09
	N <sub>2</sub>	5.93±0.09	6.34±0.05	6.47±0.12
	CO <sub>2</sub>	6.03±0.11	6.43±0.05	6.35±0.07
$B_0/10^{-15}$ , m <sup>2</sup>	He	6.46±0.18	6.90±0.35	7.29±0.35
	N <sub>2</sub>	5.40±0.07	5.15±0.13	5.61±0.13
	CO <sub>2</sub>	5.14±0.05	4.76±0.11	5.37±0.13
Polyethylene membranes		EHF540VA-12 <sup>1</sup>	EHF270FA-16	
$K_0/10^{-8}$ , m	He	3.41±0.14	3.26±0.19	
	N <sub>2</sub>	3.67±0.10	3.63±0.22	
	CO <sub>2</sub>	3.69±0.09	3.64±0.23	
	CH <sub>4</sub>	3.85±0.03		
	Ar	3.96±0.04		
$B_0/10^{-15}$ , m <sup>2</sup>	He	2.16±0.39	2.23±0.55	
	N <sub>2</sub>	1.13±0.06	1.16±0.19	
	CO <sub>2</sub>	1.06±0.07	1.12±0.11	
	CH <sub>4</sub>	1.14±0.03		
	Ar	1.27±0.05		

<sup>1</sup>For EHF540VA-12 four fibres are tested with He, N<sub>2</sub> and CO<sub>2</sub> and only one fibre is tested with CH<sub>4</sub> and Ar.

be satisfactorily explained by the heterogeneous nature of the membrane. A thin dense skin on the membrane could be observed on electron micrographs. Separate  $K_0$  and  $B_0$  values for both layers could cancel the differences for all gases.

The deviations found with different gases for the membranes in Table 1 are rather small. Since He has a low molecular weight and thus a high molecular velocity, the data points for He are spread over a small domain of the  $x$ -axis. The  $K_0$  and  $B_0$  for He are therefore less accurate. The mean values of  $K_0$  and  $B_0$  found with N<sub>2</sub> and CO<sub>2</sub> are therefore considered the final result.

From the results in Table 2 can also be concluded that the differences between the three polypropylene fibres are only marginal ( $K_0 \approx 6.2 \cdot 10^{-8}$  m,  $B_0 \approx 5.2 \cdot 10^{-15}$  m<sup>2</sup>,  $r_p \approx 0.45 \cdot 10^{-6}$  m), this indicates that those membranes have a similar structure. The same was found for the

two polyethylene fibres ( $K_0 \approx 3.6 \cdot 10^{-8}$  m,  $B_0 \approx 1.1 \cdot 10^{-15}$  m<sup>2</sup>,  $r_p \approx 0.16 \cdot 10^{-6}$  m).

## 5. Concluding remarks

A new method has been developed for determination of  $K_0$  and  $B_0$  values of highly permeable fibre membranes with single gas permeation experiments through a short dead end fibre. In order to be able to make use of a reliable method to determine the values of  $K_0$  and  $B_0$  it is essential that the pressure inside the permeable part of the membrane fibre is constant. To determine the conditions at which the pressure drop in the permeable part of the fibre is negligible, this part is reduced in length until the values of  $K_0$  and  $B_0$  become constant.

Single gas permeation experiments with He, N<sub>2</sub> and CO<sub>2</sub> for five fibre membranes have been

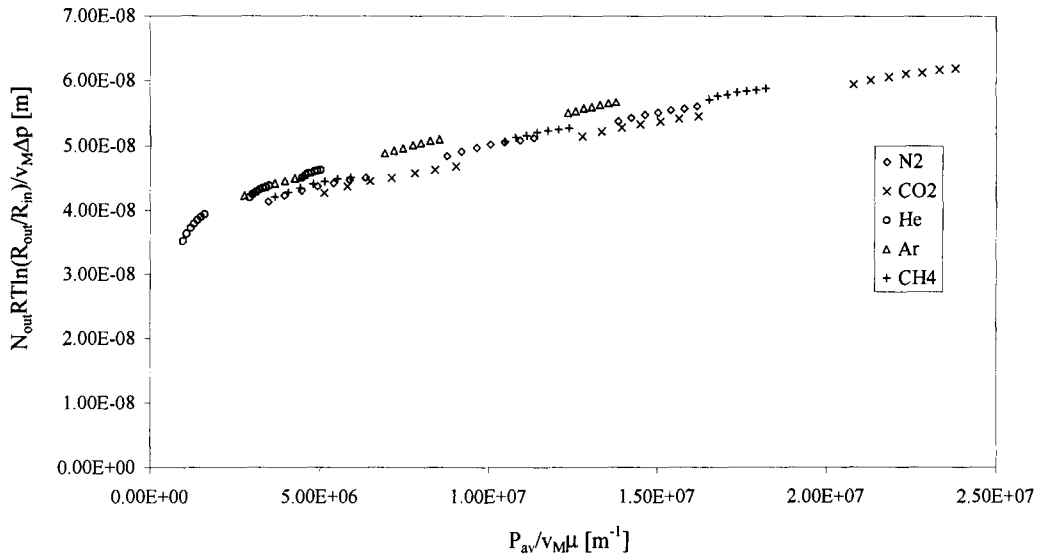


Fig. 3. Results for one polyethylene EHF540VA-12 membrane with five different gases.

carried out. The gases N<sub>2</sub> and CO<sub>2</sub> lead to consistent values of *K*<sub>0</sub> and *B*<sub>0</sub>. Helium gives less accurate results due to its low molecular weight. The three polypropylene fibres have a similar structure and therefore about the same values for *K*<sub>0</sub> and *B*<sub>0</sub>. The same was found for the two polyethylene fibres.

The decision as to which membrane is most suitable for membrane distillation cannot be based on *K*<sub>0</sub> and *B*<sub>0</sub> values alone. First of all, the membrane thickness should be taken into account [see Eq. (4)]. Secondly in the membrane distillation process, especially at lower temperatures, air will be present in the membrane pores and diffusion of water vapour through air will take place. Binary diffusion experiments for the determination of the membrane morphology parameter for molecular diffusion will be done in the near future to complete the membrane characterization necessary for membrane distillation modelling and comparison of the membranes.

**6. Symbols**

- B*<sub>0</sub> — viscous flow morphology parameter, meter, m<sup>2</sup>
- K*<sub>0</sub> — Knudsen diffusion morphology parameter, m
- M* — molecular mass, kg/kmol
- N* — molar gas flux through the membrane, kmol/m<sup>2</sup>s
- N*<sub>out</sub> — molar gas flux through the membrane with respect to the outer membrane area, kmol/m<sup>2</sup>s
- P* — pressure, Pa
- P*<sub>av</sub> — arithmetic mean of pressure inside and outside membrane fibre, Pa
- R* — universal gas constant, 8314 J/kmol·K
- R*<sub>in</sub> — inner membrane radius, m
- r*<sub>p</sub> — membrane pore radius, m
- R*<sub>out</sub> — outer membrane radius, m
- T* — temperature, K
- v*<sub>M</sub> — mean molecular velocity, m/s

### Greek

- $\varepsilon$  — membrane porosity  
 $\mu$  — viscosity, Pa·s  
 $\tau$  — membrane tortuosity

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