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Predicting the structural parameters of integrally skinned porous membranes

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ABSTRACT

The objective of this study is to propose a novel approach for predicting the structural parameters of integrally skinned porous membranes using gas permeation data. It is intended to overcome the limitation of the conventional gas permeation testing (GPT) method, since the latter method seems to suffer from several conceptual drawbacks. In particular, a comparison is made between the theoretical calculation and the experimental data to show the superiority of the newly proposed model. The new model is a modification of Wakao et al.'s model, in which, unlike the conventional GPT method, the contribution of the slip flow is considered. Although Wakao et al.'s model was found superior to the conventional GPT method, the model fitting to the experimental data was not completely satisfactory. It was likely that the slip flow, although its effect cannot be neglected, is not fully developed. Therefore, a factor ψ is introduced to show the extent of the contribution of the slip flow mechanism to the total gas permeation rate. As a result, the new method can overcome the shortcomings of the conventional GPT method by manifesting the following advantages: (i) it can cover the entire range of J versus P diagram, (ii) it can specify the contribution of the individual mechanisms involved in the total gas permeation and (iii) unlike the conventional GPT method, it is not limited by any constraints or conditions of data acquisition. In summary, the model can predict pore size and effective porosity, and also simulate the experimental J versus P trends with sufficient accuracy (within ~2% over the pressure range studied) for all types of membranes, i.e. NF, UF, MF, MD and membrane contactors. In view of this fact, the proposed model is simpler to apply than Rangarajan et al.'s model and more accurate than the conventional GPT method.

1. Introduction

Polymeric membranes with a porous skin layer such as nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), membrane distillation (MD) and, in the recent decade, membrane contactors have been widely utilized in various industries for separation processes. Selection of a satisfactory membrane for a specific purpose requires a deep knowledge of its permeation flux, surface porosity, bubble point, mean pore size as well as pore-size distribution. The pore size and its distribution have been measured using a variety of techniques best exemplified by gas permeation testing [1], permporometry (or gas–liquid displacement) method [2–4], liquid displacement [5–8], solute probe techniques [9,10], atomic force microscopy (AFM) [11–15], and scanning electronic microscopy (SEM) [10,16–19]. Each technique is delimitated by its own unique distinction, by virtue of which it may be suitable for a specific type of membrane, but displays some restrictions for the other types of membranes. For example, pore size detection by AFM directly depends on the tip size of the used cantilever. Thus, the pores which are smaller than it cannot be measured accurately by this method. Also, the degree of roughness can affect the reliable distinction between valleys and actual pores [20]. The measurement of pore size by SEM is limited to the power of SEM magnification (i.e. relatively large pore sizes). For example, the pore size of some membrane contactors or UF membranes possessing small pore sizes cannot be measured by SEM [21,22]. The permporometry technique is not suitable for large pore size membranes [21]. The same problem also can be addressed for liquid–liquid displacement, by which large pore size ($r_p > 20$ nm) cannot be easily detected. Applying mercury porometry, since the surface tension of mercury is very high (485.5 mN/m in comparison to water, 72 mN/m at 25 °C), this method is applicable only for those membranes which are made from very hard materials such as ceramic membranes, which can withstand the compactness of the membrane at high pressure during the porometry test.

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The accuracy of the method in measuring or estimating pore size is an important point which in turn arises from a strong theoretical background.

One of the easiest and the most widely utilized approaches is the well known conventional gas permeation testing (GPT) method. For the first time, this method was introduced by Carman in 1956 for characterization of porous media [23]. The method later became adapted to a constant volume permeation testing set up by Yasuda and Tsai [24] in order to characterize a polymeric membrane made from polysulfone.

Wang et al. [25] modified the technique in an easier way, i.e. by constant pressure gas permeation testing. They developed a mathematical model to relate the gas permeation characteristics to the mean pore size and surface porosity of the asymmetric membrane. The model was applied to characterize the asymmetric flat sheet and hollow fiber membranes prepared from polysulfone in their laboratory. An extensive review was written by Nakao on the determination of pore size and pore size distribution of filtration membranes in 1994 [26]. He investigated almost all of the methods established until then [26,27].

Rangarajan et al. [28] carried out an extensive research to introduce a model to predict the permeance of asymmetric polymeric membranes as well as their structural parameters. Their method was too complicated for practical application. To model the gas permeance, it was required to compute four regression constants, whilst no results were given on the membrane surface porosity. They performed extensive experiments on various kinds of membrane materials and preparation conditions. Five gases including argon, methane, ethylene, hydrogen and helium were employed. They changed the pressure in the interval of 0.25–2.5 MPa. They showed that if $\max r_p > 50\lambda$ (λ is mean free path) all of the mechanisms considered are operative simultaneously with different contributions. As a result, they set the upper limit arbitrarily at $\max r_p = 100$ Å. It was concluded that the pore size predicted by their model would not exceed 100 Å (10 nm).

A large number of researchers have applied gas permeation testing for the characterization of membranes with integrated porous skin layer for different purposes, e.g. UF, MF, MD and membrane contactors [27,29–35].

Although the conventional GPT method is relatively easy and fast to be implemented, it suffers from several conceptual drawbacks. First of all, it does not have a strong theoretical background, which is the reason why the model often does not reproduce the trend of the experimental data. Comparing the conventional GPT method with a model based on the work of Wakao et al. [36], it was concluded that the two important parameters to characterize membrane morphology, i.e. pore radius (r_p) and effective porosity (ε/l_p), obtained by the latter model are different from those obtained by the conventional GPT by a factor of $3\pi/16$ and $(16/3\pi)^2$, respectively [37]. Moreover, according to the conventional GPT method, the slope of permeation flux (J) versus mean pressure (P, average of upstream and downstream pressure), a plot is required for the calculation of pore size. However, the slope often depends on the range of P adopted to draw a straight line. In other words, depending on which region of the J versus P plot is selected, different r_p and l_p will be resulted [37]. Finally, in the regions where the slope is negative, the conventional GPT method is not applicable [37]. Hence, the conventional GPT method is believed to be an arbitrary approach to determine the structural parameters. This is the reason why, sometimes with the same membrane fabrication conditions and the same dope formulation, the reported results by the conventional GPT method do not agree with each other.

By a rapid glance through the open literature in the field of membrane science and technology, one can find that, regardless of the advancement in instruments and developing new techniques, researchers are still interested in applying simple and non-expensive techniques such as gas permeation testing or gas–liquid displacement by in house made machines. Therefore, it seems that improving the conventional approaches and removing their drawbacks are still interesting areas of research. This work aims to propose a new method to obtain structural parameters of the porous membrane, i.e. mean pore size (r_p) and effective surface porosity (ε/l_p) from simple gas permeation testing technique. First, the model is tested against the experimental data produced by Rangarajan et al. [28], followed by testing against the data obtained from several membranes prepared by the authors. In addition, the effect of pressure on the J versus P slope is discussed in details. Therefore, a logical feedback between the theory, modeling and experiments is discussed.

2. Theoretical background

The diffusion of gases through porous materials, such as membranes possessing porous skin layers, can be governed by different mechanisms. For porous media having a relatively narrow pore size distribution, several different regimes have been observed, which depend upon the ratio of the mean free path of gas molecules to the mean pore diameter, which is known as the Knudsen number, K_n [38].

Several important issues bonded to gas permeability through the capillary porous membrane should be taken into consideration: first of all, characterization of flow conditions applying the Knudsen number criteria; secondly, describing the mechanism involved and the governing mechanism; next, distinguishing the contribution of every individual mechanism in the overall gas flow; and finally, validity and accuracy of the proposed approach [39]. Depending on the Knudsen number, three distinct regimes in integrally skinned porous membranes can be observed. In this study, the criterion modified by Roy et al. [40,41], which explains the categorization of flow regimes according to the Knudsen number, was utilized [39,42].

If either the pore size or mean pressure is so small that $K_n \geq 10$ then the flow regime occurs in the molecular-free region. In this region, the mean free path is large compared to the pore diameter [37,39] and the flow is governed by Knudsen diffusion [28]. The molecular free region is modeled by the Knudsen diffusion equation as follows:

$$N_K = \frac{2 r_p A_p}{3RT}\left(\frac{8RT}{\pi M}\right)^{0.5}\frac{\Delta P}{l_p} \tag{1}$$

where N_K is the Knudsen flow rate (mol/s), r_p is the pore radius (m), A_p is pore cross-sectional area (m^2), M is the molecular weight, ΔP is the transmembrane pressure difference (Pa), R is a universal gas constant (equal to 8.314 Pa m^3/mol K) and l_p is the pore length (m).

When either the pore size or mean pressure is large enough or $K_n \leq 0.001$ the flow regime is in the continuum region. In the continuum region the mean free path of the gas is small compared with the pore diameter. In a pure gas system a gradient of total pressure results in viscous flow [36,38], which is described by the Hagen–Poiseuille equation:

$$N_V = \frac{r_p^2 A_p P}{8\mu RT}\frac{\Delta P}{l_p} \tag{2}$$

where N_V is the viscous flow rate (mol/s), P is the transmembrane average pressure (Pa), and μ is the gas viscosity (Pa s).

The flow regime is known as transition flow if the mean free path is comparable with the pore diameter or $0.1 \leq K_n \leq 10$. Special care should be taken in this regime, where a combination of various transports mechanisms – Knudsen diffusion, molecular diffusion and viscous flow – is considered according to the dusty gas theorem [38]. In this narrow region, gas molecules collide with