

Progress in transport theory and characterization method of Reverse Osmosis (RO) membrane in past fifty years

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ABSTRACT

In this paper an attempt is made to review the progress in membrane characterization and transport theory in historical perspective. Its central theme is the membrane “pore” around which progress has been revolving, irrespective of whether the researcher is “for” or “against” the existence of pores at the top dense layer of the RO membrane.

The article starts from nineteen-fifties when the development of cellulose acetate membrane was launched on the basis of the Preferential Sorption-Capillary Flow (PS-CF) mechanism.

The Sorption-Diffusion (S-D) model, which was presented at almost the same time, regards the top surface layer dense and homogeneous. No heterogeneity is allowed and the presence of pores makes the RO membrane imperfect, causing the leakage of salt. Thus, the PS-CF model came to direct confrontation with the S-D model.

It is shown in this brief historic review how the advanced characterization instrument has revealed the heterogeneous structure of the top surface of the RO membrane and measured its “pore size” and “pore size distribution”.

The advanced transport theory based on Molecular Dynamics (MD) simulation also resulted in the presence of the multi-modal pore size distribution.

1. Introduction

When one of the co-authors (TM) arrived at Dr. Sourirajan's laboratory at the National Research Council of Canada in 1968 October, Dr. Sourirajan gave him a manuscript of the book “Reverse Osmosis”, which was later published in 1970 [1]. He read the book eagerly and was especially fascinated by chapter 1, where Sourirajan wrote how he had launched his reverse osmosis research. According to the book, the invention of the Loeb-Sourirajan RO membrane for seawater desalination was made on the basis of the Preferential Sorption-Capillary Flow (PS-CF) model. As the name of the model implies, pores are required for the transport of water through the RO membrane.

In nineteen-sixties, the Solution-Diffusion model (S-D model) was presented by Lonsdale [2] and it has soon become the mainstream of the RO transport model. Since Lonsdale regarded the pores as the defects of the nonporous semi-permeable membrane, S-D model has been used for a long time to justify the nonexistence of pores in the perfect dense layer of the RO membrane. It should be however pointed out that S-D model is neutral on this issue and does not say anything about the presence or the absence of pores. It might also be noteworthy to

mention that many researchers seemed to believe the presence of pores in the RO membrane deep in their mind. One of the co-authors (TM) remembers the Gordon Conference held in nineteen eighties where many heated discussions were exchanged on the presence or absence of pores in the RO membrane. In one of the conferences W. Pusch of the Max Planck Institute, Germany, asked the conference participants if they were pore-philic and pore-phobic. To my surprise, more than half raised their hands to show that they were pore-philic.

In Sourirajan's laboratory, attempts were continued to interpret the experimental data based on the pore model, which eventually led to the concept of the bimodal pore size distribution comprised of the “network pore” and “aggregate pore” [3,4]. However, when the bimodal distribution was proposed in 1984, it was almost completely ignored by the membrane community, evidenced by very few citations the paper received. Computer did not count the number of citations those days but we could feel how unpopular the theory was.

In the meantime, the membrane characterization techniques were making remarkable progress. In nineteen-sixties and seventies, the only characterization tool was Scanning Electron Microscope (SEM) that did not allow the resolution below 10 nm when the polymeric membrane

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surface was investigated. Needless to say that it was impossible to observe the sub-nanometer pores at the membrane surface and, therefore, the top skin layer was generally thought to be dense and homogeneous.

In 1994, a paper on the characterization of cellulose acetate (CA) RO membranes by Small-Angle Neutron Scattering (SANS) appeared all of sudden. In the paper S. Krause of Rensselaer Polytechnic Institute, Troy, New York, concluded that SANS data could be explained by the bimodal distribution of pores in the dense skin layer of CA RO membrane.

As the industrial membrane fabrication method shifted from the phase inversion technique of cellulose acetate membrane to thin film composite (TFC) polyamide membrane, so did the membranes as the object of membrane characterization. Nowadays most of the characterization methods are applied to TFC polyamide membranes.

Particularly, positron annihilation spectroscopy (PALS) gained popularity in the beginning of the millennium to characterize the synthetic polymeric membranes for various applications. In the PALS papers the term “free volumes” is often used instead of “pores”. But regardless of the chosen term, the measured size is indicative of that of the channel through which the material transport occurs. Kwak's group at Seoul National University characterized the polyamide TFC membrane by PALS and concluded that the bimodal pore size distribution was observed, assigning these distinctive groups of the pores to the “network” and “aggregate” pores.

At almost the same time progress was also made in the membrane transport theory. Instead of interpreting the experimental data of membrane performance by a set of simple transport equations, it is more fashionable nowadays to use the molecular dynamics (MD), by which the structure of the polymeric membrane and the material transport through the membrane is simulated by using a set of computer softwares. It is particularly interesting to note that many of the MD simulation have resulted in the polymeric membrane structure with bi- or multi-modal pore size distributions.

Both characterization and MD simulation, in which sophisticated instrument or computer software, respectively, is used, describe the membrane structure and the membrane transport very much in detail. However, they have not necessarily offered a clear guideline to improve the membrane performance. In this respect, the paper recently published by Araki et al. is interesting since it shows the disappearance of aggregate pores in the nanocomposite TFC membrane in which single walled carbon nanotubes (SWCNTs) are incorporated.

The objective of this article is to review the progress made in the understanding of the RO membrane structure and the RO membrane transport in historical perspective. Especially, the purpose of the paper is to show that the concept of the membrane pore was always in the centre of the progress.

2. Research before 2000

2.1. Preferential sorption-capillary flow (PS-CF) model

According to Sourirajan's book, the following fundamental equation called the Gibbs Adsorption Isotherm [1] was the basis for the earliest development of reverse osmosis membrane at the University of California Los Angeles (UCLA).

$$\Gamma = -\frac{1}{RT} \frac{\partial \sigma}{\partial \ln a} \quad (1)$$

where Γ is surface excess, R is universal gas constant, T is absolute temperature, σ is surface tension and a is activity.

The equation predicts the presence of a very thin pure water layer at the surface of saline water. Table 1 summarizes the thickness of pure water layer at the air/aqueous sodium chloride interface calculated by Eq. (1), assuming a step function for the salt concentration versus the distance from the interface [5]. The table shows that the thickness ranges from 0.24 to 0.56 nm, depending on the concentration of sodium

Table 1
The thickness of pure water layer at the air/sodium chloride solution interface [5].

NaCl concentration, molality	Pure water layer thickness, nm
0	0.56
0.747	0.38
1.603	0.34
2.435	0.24

(Size of water molecule = ca 0.1 nm).

chloride.

Prof. Yuster challenged for the first time to skim the pure surface water layer mechanically but failed. Believing in the presence of pure water layer at the interface, Sourirajan continued the challenge but by a different approach. Sourirajan tried to collect the pure water layer through a membrane under pressure applied on the saline water. Sourirajan's attempt was rewarded by an immediate success. He was able to collect desalinated water as the permeate of the membrane! After the initial few attempts with cellulose and silicone coated cellulose membranes, a commercial cellulose acetate (CA) membrane from Sartorius was used, which resulted in a high salt rejection, enabling drinking water production from seawater. However, the flux of water was miserably low, with few drops of permeate collected in a day, and the membrane was thought to be practically useless. It is noteworthy that Reid and Breton obtained, quite independently, similar experimental results of seawater desalination by using a CA membrane at the University of Florida [6]. It took another 4 years for Loeb and Sourirajan to develop the CA membranes with fluxes of practical usefulness, which opened up the avenue to the novel membrane desalination process, called Reverse Osmosis (RO).

According to the PS-CF model, desalination by RO membrane occurs in the following way: When salty water, e.g. sodium chloride solution, is in contact with the surface of a membrane, an interfacial pure water layer is formed at the solution/membrane interface. Assuming an analogy between the sodium chloride solution/air interface and the sodium chloride solution/membrane interface, the thickness of the pure water layer, t_i , should be as low as a fraction of nanometer. In the presence of a pore, the diameter of which is smaller than or equal to $2t_i$, the pure water layer will flow through the pore under the pressure applied on the sodium chloride solution and appear on the other side of the membrane as permeate (see Fig. 1). If the pore size is larger than $2t_i$, the sodium chloride solution will flow through the centre of the pore, which leads to the leakage of sodium chloride into the permeate.

On the basis of the above model, an appropriate chemical property of the membrane surface, that allows the formation of the pure water

Preferential Sorption-Capillary Flow Model

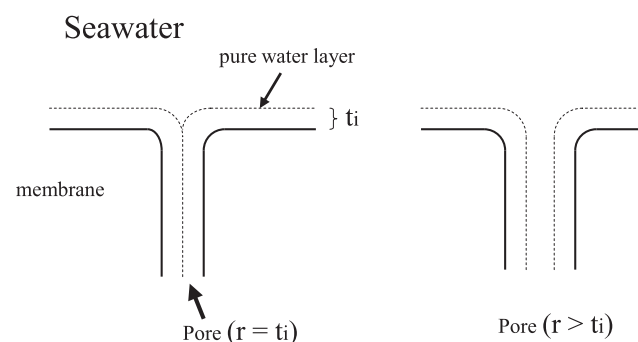


Fig. 1. PS-CF model.

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