# INTERPRETATION OF STRUCTURE AND ELECTRICAL PROPERTIES OF A POLYAMIDE NANOFILTRATION MEMBRANE

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**Abstract**

Nanofiltration has made tremendous progress during the past decades due to its excellent removal of contaminant from wastewater. These membranes have gained interest recently for the treatment of inorganic effluent to reduce the amount of wastewater produced and in addition improve the quality of effluent. The basic principle of nanofiltation separation is by sieving effect and electrical charge of a membrane. This can be clearly understood by determining the structural (pore radius and membrane porosity ratio) and electrical properties of a membrane. A polyamide thin composite NF membrane (AFC 30) was used to characterize the structural and electrical parameters. The structural values were estimated with permeation experiments of aqueous solution of neutral solutes in conjunction with steric hindrance model (SHP). The fixed charge density on the membrane surface was determined using sodium chloride experiments at different concentrations. The data from sodium chloride experiment were used to evaluate the effective charge density (ΦX) by using the Spiegler-Kedem model together with the charge model called Teorell-Meyer- Sievers (TMS). It was found that the membrane charge depends solely on the salt concentration in the solution, which is because of ion adsorption on the membrane surface.

**Keywords:** Nanofiltration, polyamide membrane, rejection, modelling

## 1. INTRODUCTION

Nanofiltration is a subset of pressure driven process which is intermediate between reverse osmosis (RO) and ultrafiltration (UF) membrane. The main driving force for the separation in NF is the pressure difference between the feed and permeate side of the membrane. NF is a combination of steric, Donnan, dielectric and transport effects. As compared to other pressure driven processes, NF is characterized by a membrane pore size (<1 nm) corresponding to a molecular weight cut off (MWCO) of approximately 300-500 Dalton (Mohammad et al., 2015). Nanofiltration separation has specific advantages over reverse osmosis. These are less energy consumption, lower operating pressure than RO, higher flux in comparison with RO, inexpensive compared to reverse osmosis and monovalent ions partly passes through the membrane whiles multivalent ions are rejected to a certain degree determined by the feed stream (Mikulášek and Cuhorka, 2016). In addition, charged effects can be positive or negative (repulsive) but is result of charge both in the membrane and solute. However, the membrane charge is due to dissociation of ionisable functional group in the membrane surface and pores. This group can be acidic or base in nature or a combination of both based on the material used in manufacturing and fabrication process (Gherasim et al., 2014). Until now, the separation mechanism of nanofiltration is not clearly understood.

For better understanding of the separation mechanism of NF membrane, it is important to determine the structural properties and charge of membrane for practical use. The structural properties refer to the pore ratio and membrane thickness to porosity. Several NF membranes solely depend on the information provided by the manufacturers. But, limited information is given in terms of membrane permeability, solute rejection and neutral solute rejection. Such available information cannot give preliminary values on the structure and electrical properties of the membrane (Bowen and Mohammad, 1998).

Several models have been used to describe and predict flux as well as retention at different operating conditions of both uncharged and charge species by NF membrane. In this present work, experiments were performed using AFC 30 membrane to determine the rejection of different uncharged solutes. By using the permeation of aqueous solution of neutral solutes together with steric hindrance pore model (SHP), the pore radius ($r_p$) and membrane porosity ratio ($\Delta x/A_k$) were estimated. The interpretation of data found from sodium chloride experiment of different concentration was used to predict the charge properties on the surface of the membrane. This was done by using the Spiegler-Kedem and the Teorell-Meyer-Sievers model.

## 2. THEORY

Transport phenomena of single solute and solvent in both NF and RO processes can be described a well-known irreversible thermodynamic (IT) model. Kedem and Katchalsky derived transport equations for the volume flux ($J_v$) and solute flux ($J_s$) as follows (Kedem and Katchalsky, 1985):

$$J_v = L_p(\Delta P - \sigma.\Delta\pi) \tag{1}$$

$$J_s = P\left(c_m - c_p\right) + (1-\sigma).J_v c_s \tag{2}$$

where σ, P and $L_p$ are the reflection coefficient, solute permeability and water permeability respectively. The Spiegler-Kedem model is used when there exist the high difference between the retentate and the permeate (Spiegler and Kedem, 1966). This can be expressed in Eq. 1 in a differential form as follow;

$$J_s = -P\frac{dc_s}{dx} + (1-\sigma)\, c_s J_v \tag{3}$$

Assuming constant fluxes and constant coefficient are integrated through the membrane thickness. The real retention can be calculated by using the following equation;

$$R = 1 - \frac{c_p}{c_m} = \frac{\sigma(1-F)}{1-\sigma F} \qquad \text{with } F = \exp\left(-\frac{1-\sigma}{P}.\ J_v\right) \tag{4}$$

Equation 4 which is the Spiegler-Kedem equation describes the solute retention with solvent volumetric flux and the solute permeability. This model assumes the membrane as a black box and gives no information about the transport mechanism. Several models has been introduces to interpret σ and P to estimate the structural and electrical properties of membrane.

By using a single neutral solute and a NF membrane, σ and P can be determined by the SHP model. Nakao and Kimura proposed the steric hindrance pore (SHP) model which was modified from the pore model (Nakao and Kimura, 1982).

$$\sigma_s = 1 - (1 + \frac{16}{9}\lambda^2)(1-\lambda)^2\,[2 - (1-\lambda)^2] \tag{5}$$

$$P_s = (1-\lambda)^2 D_s (A_k/\Delta_x) \tag{6}$$

where λ is defined as the ratio of the solute radius ($r_s$) to pore radius ($r_p$).

To a salt solution of 1-1 type electrolyte and negative charged NF membrane, the Teorell-Meyer-Sievers (TSM) model equation is used (Wang et al., 1995; Hoffer and Kedem, 1967). The equations which involve reflection coefficient (σ) and solute permeability (*P*) are given as follow;

$$\sigma_s = 1 - \frac{2}{(2\alpha-1)\xi + (\xi^2+4)^{1/2}} \tag{7}$$

$$P_s = D_s(1-\sigma)\,(A_k/\Delta_x) \tag{8}$$

where ξ is the parameter which expresses the electrostatic effects and is defined as the ratio of the fixed charge density of the membrane (*X*) to the concentration of the 1-1 electrolyte *(c).*

## 3. MATERIALS AND METHODS

### 3.1. Material

The membrane used in this experiment is NF tubular membrane labelled, AFC 30 (PCI membrane systems). It is a thin film composite membrane consisting of an aromatic polyamide skin-layer on a polysulfone substrate. The membrane is capable of withstanding pressure up to 60 bars, temperature below 70º C and pH in 1.5 - 10.5 range.

All the reagents used were of analytical reagent grade. The aqueous solution was prepared by dissolving the reagents which are sodium chloride, glucose, glycerol, triethylene glycol (TEG), and lactose. It was supplied by Penta Co., the Czech Republic. The solutions were prepared by dissolving the reagents in highly demineralised water (conductivity< 1 µS/cm, pH 6.0± 0.2).

### 3.2. Experimental set-up and procedure

The cross flow separation unit used can be seen in previous published article by Gherasim et al., 2014. The experiment temperature of the feed solution was at a constant value of 25 º C by using the heat exchanger and transmembrane pressure which varies in a range of 5-30 bars. The pure water flux was measured at various transmembrane pressures at the same range and the membrane pure water permeability was estimated. The value obtained for pure water permeability is $Lp$ = 5.84 $m^{-2}$ $h^{-1}$ $bar^{-1}$ at 25 º C. The NF experiments were performed in total recycle mode, for both permeate and retentate returned to the feed tank to maintain a constant concentration in feed. The permeate flux was determined by weighing using an electronic balanced connected to a personal computer, and samples of permeate and feed were collected at each transmembrane pressure. The structural parameters of the membrane that are the effective pore radius ($r_p$) and membrane thickness to porosity ratio ($\Delta x/Ak$) can be obtained from the uncharged solutes rejection values. The experiment was performed using 500 mg $l^{-1}$ solutions of glycerol, triethylene glycol, glucose and lactose at the natural pH demineralized water (6.0 ± 0.2). The uncharged solutes concentration in feed and permeate was determined by the total organic carbon (TOC) technique. The membrane surface charge is another parameter which is necessary for characterization of membrane. Permeation experiments of NaCl solution at different concentrations from 100-1000 mg/L at pH 6.0 was used to estimate the surface charge of the membrane. Conductivity was measured by using a WTW Cond 340i conductometer equipped with a WTW TetraCon 325 electrode.

## 4. RESULTS AND DISCUSSION

### 4.1. Estimation of structural properties

The rejections for 500 mg $l^{-1}$ solution of neutral solutes are plotted against the flux by AFC 30 membrane. The experiments values of the neutral solutes (symbol) were fitted with Spiegler-Kedem model (dash) which was in good agreement as presented in **Figure 1**. It can be observed that the bigger the molecular weight of solute, the higher the rejection. By using these fittings, the values of the parameters model (coefficient of reflection and solute permeability) were estimated. From equations 5 (SHP model), the pore radius ($r_p$) were determined by fitting with the reflection coefficient from the Spiegler-Kedem model. The values of $r_p$ were in good agreement excluding lactose, with average value of 0.374 nm. Likewise, the solute permeability (P) was used to determine the membrane porosity ratio ($\Delta x/A_k$) from equation 6 (SHP model) and the results were found in **Table 1**. The average value of ($\Delta x/A_k$) was calculated from **Table 1** which is 0.327x $10^{-7}$ m without lactose. This is because reflection coefficient (σ) of lactose is close to unity and produce value which is not in good agreement with the other neutral solutes. This depicts, that the SHP model cannot be applied to for solute with very high retention. In addition, the membrane porosity ratio increases with increase in both molecular weight and stroke radius for neutral solutes being considered. Similar results were obtained from previous studies (Nakao and Kimura, 1981).

**Table 1** Calculation of $\sigma$ and $P$ of neutral solutes and structural parameters of NF membrane using SHP model

| Solute | Molecular weight | Diffusivity | $r_s$ | σ | $P$ | $r_p$ | $\Delta x/A_k$ |
|---|---|---|---|---|---|---|---|
| | $gmol^{-1}$ | $10^{-10}$ $m^2.s^{-1}$ | nm | [-] | [$10^{-6}$ m.s$^{-1}$] | [nm] | [$10^{-7}$ m] |
| Glycerol | 92.1 | 9.5 | 0.258 | 0.764 | 19.5 | 0.342 | 0.294 |
| TEG | 150 | 7.31 | 0.336 | 0.915 | 4.20 | 0.389 | 0.321 |
| Glucose | 189 | 6.7 | 0.355 | 0.950 | 1.64 | 0.392 | 0.365 |
| Lactose | 340 | 4.9 | 0.501 | 0.992 | 0.20 | 0.522* | 0.432* |
| Average | | | | | | **0.374** | **0.327** |

*Average of $r_p$ and $\Delta x/A_k$ calculated excluding lactose

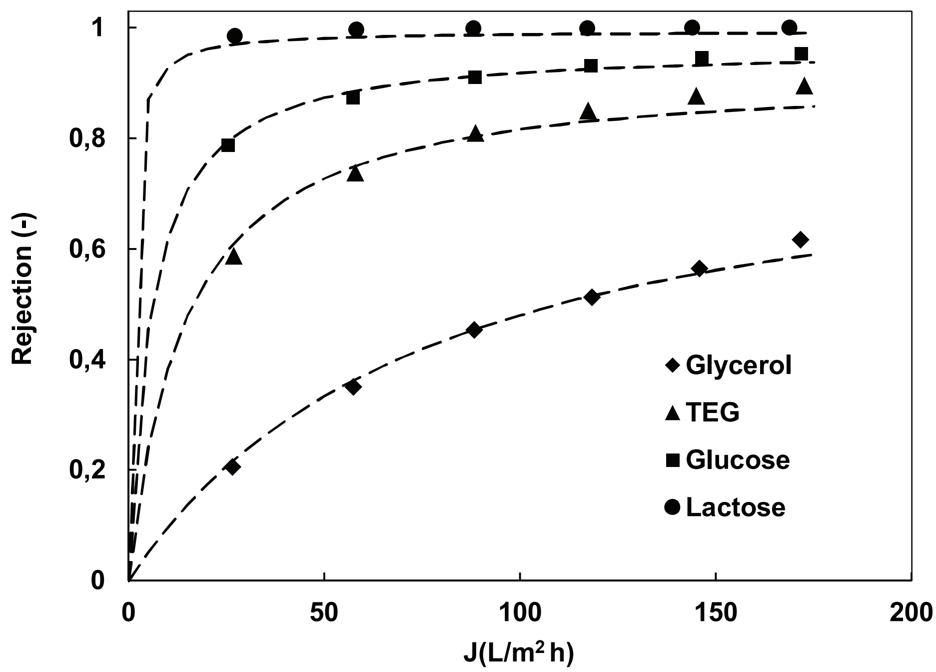


**Figure 1** Rejection of neutral solutes against flux (AFC 30 membrane). Experimental data (points) were fitted by the Spiegler- Kedem model (dashed lines)

### 4.2. Estimation of electrical properties

To determine the membrane charged, different experiment were performed with NaCl at various feed concentration ranges from 100-1000 mg/L. The real rejection against the permeate flux of AFC 30 was dependent on NaCl concentration as represented in **Figure 2**. It can be observed that the solute rejections become low at higher NaCl concentration in feed solution. At the same time, increase in transmembrane pressure increases the solute removal for all NaCl concentrations. The reflection coefficient and solute permeability can be estimated by a best fit method using the Spiegler-Kedem in Eq. 4 from the real rejection of NaCl against the flux for feed solutions. The values of the membrane parameters can be found in **Table 2**.

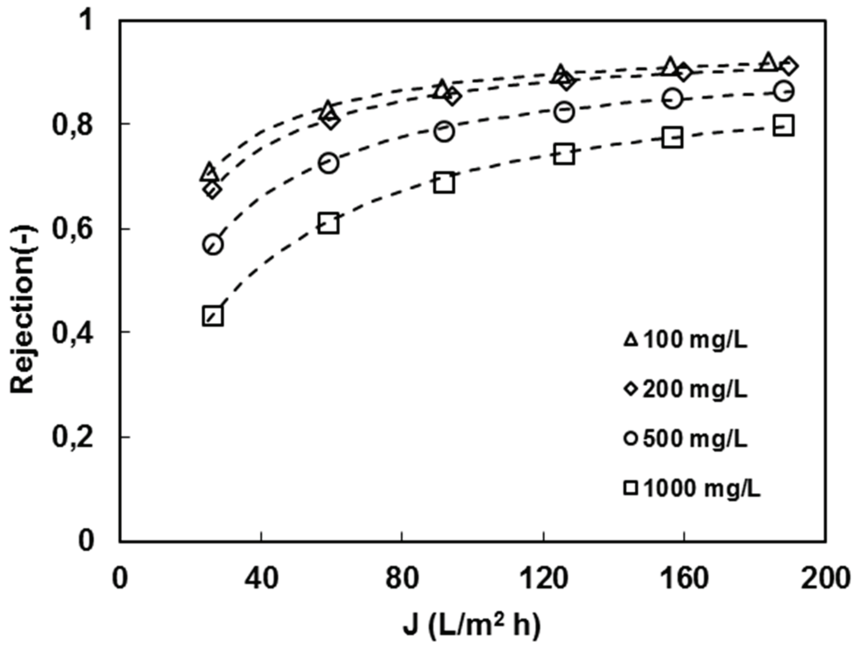


**Figure 2** Rejection of NaCl against flux (AFC 30 membrane). Experimental data (points) were fitted by Spiegler-Kedem model (dashed lines)

The TMS model in eq. (7) can be simplified when the transport number of cation in the free solution (α) was calculated with constant value of 0.3954. When this value is inserted in the TMS model, it can be further simplified into a quadratic equation. This equation is valid specifically for sodium chloride and is as follows:

$$\mathbf{0.956202}\xi^2 + \frac{\mathbf{0.83712}\xi}{(\sigma-\mathbf{1})} + \mathbf{4} - \left(\frac{\mathbf{2}}{\sigma-\mathbf{1}}\right)^2 = \mathbf{0} \qquad (9)$$

The value of the effective fixed charge density was calculated from Eq. (9) based on the reflection coefficient for each NaCl concentration. Both positive and negative values were found for membrane charge using Eq. (9). The negative values were used because it has physical meaning since the membrane is negatively charged.

**Table 2** Reflection coefficients (σ) and solute permeabilities (ω) determined by fitting experimental data of NaCl rejection with Spiegler-Kedem model

| NaCl Concentration | Spiegler-Kedem model parameters | | Effective fixed charge density | Quality of fitting |
|---|---|---|---|---|
| mg/L | σ (-) | ω ($m^{-2}$ $h^{-1}$) | -Φx (mV) | $x^2$ |
| 100 | 0.940 | 9.071 | 48.8 | $1.230x\ 10^{-4}$ |
| 200 | 0.936 | 10.967 | 87.9 | $9.247x\ 10^{-5}$ |
| 500 | 0.903 | 16.585 | 144.0 | $1.081x\ 10^{-4}$ |
| 1000 | 0.873 | 28.366 | 211.2 | $1.303x\ 10^{-4}$ |

The values of the non-linear parameter $x^2$ in **Table 2** shows that the Spiegler-Kedem model describes a very well the experimental rejection data for all NaCl concentrations considered. As can be observed in **Figure 2** and **Table 2**, the reflection coefficient (σ) decreases and the solute permeability (ω) increases by increasing the salt concentration in the feed solution. The Spiegler-Kedem model can estimate a good description of the experimental results of NaCl rejection.

## 5. CONCLUSION

The membrane was characterized by using modelling of rejection experiment of different neutral solutes and NaCl concentration. The membrane parameters (pore radius and membrane porosity ratio) were found by using Spiegler Kedem model together with steric hindrance pore model for neutral solutes. The average pore radius was 0.374 nm calculated from SHP model using reflection coefficient of different neutral solutes. The SHP model is very useful for determining the structural parameter of a membrane. However, it should be noted that this model could not be applied to solute of high retention and coefficient of reflection almost close to unity. The electrical properties were estimated from the rejections experiments values of NaCl solutions of various concentrations by using Spiegler-Kedem and Teorell-Meyer-Sievers model. It was found that the charge density increment depends on the NaCl concentration. This could be explained that the ions from the solution are absorbed on the surface of membrane, which in turn increases the negative charge.

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