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Scope and limitations of the irreversible thermodynamics and the solution diffusion models for the separation of binary and multi-component systems in reverse osmosis process

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Abstract

Reverse osmosis process is used in many industrial applications ranging from solute-solvent to solvent-solvent and gaseous separation. A number of theoretical models have been developed to describe the separation and fluxes of solvent and solute in such processes. This paper looks into the scope and limitations of two main models (the irreversible thermodynamics and the solution diffusion models) used in the past by several researchers for solute-solvent feed separation. Despite the investigation of other complex models, the simple concepts of these models accelerate the feasibility of the implementation of reverse osmosis for different types of systems and variety of industries. Briefly, an extensive review of these mathematical models is conducted by collecting more than 70 examples from literature in this study. In addition, this review has covered the improvement of such models to make them compatible with multi-component systems with consideration of concentration polarization and solvent-solute-membrane interaction.

***Keywords*:** Reverse osmosis, Modelling; The irreversible thermodynamics model;
The solution diffusion model.

1. Introduction

Reverse osmosis is a pressure driven process which can be specifically characterised by the idea of using a semi-permeable membrane (permeable to solvent, impermeable to solute) to separate two mediums of different solute concentration. Generally, in an osmotic process, the solvent spreads through the membrane due to its high osmotic pressure in order to achieve the balance in chemical potential and the equality of solute concentration on both sides of the membrane. The state of osmotic equilibrium can be reached by the gradual increase of concentrated side pressure, which finally inhibits the solvent transfer. However, when applying a higher pressure than the osmotic pressure, the procedure is essentially reversed.

This happens by forcing the solvent to flow from the concentrated side to the diluted side. The theory of solute and solvent flow through semi-permeable membranes can be schematically presented in three events as shown in Fig. 1, which shows two solutions of different concentrations being separated by a semi-permeable membrane. Scenario A represents a natural phenomenon of water diffusion from the low concentration solution into the high concentration solution, which is called osmosis. This process continues until osmotic equilibrium is achieved and which is characterised by the equivalent chemical potential of both solutions. The pressure difference between the two solutions is known as the osmotic pressure difference and from this point onward, no further solvent flow takes place. This state is known as the osmotic equilibrium state, i.e. Scenario B. Lastly, for desalination of the concentrated salt water, the procedure can be reversed by applying higher pressure than the solution osmotic pressure, which forces water to pass over the membrane towards the low concentration solution side accompanied by salt rejection, i.e. Scenario C. Usually, this process can happen under ambient temperature and without any phase change (Jain and Gupta, 2004; Van Gauwbergen and Baeyens, 1998).

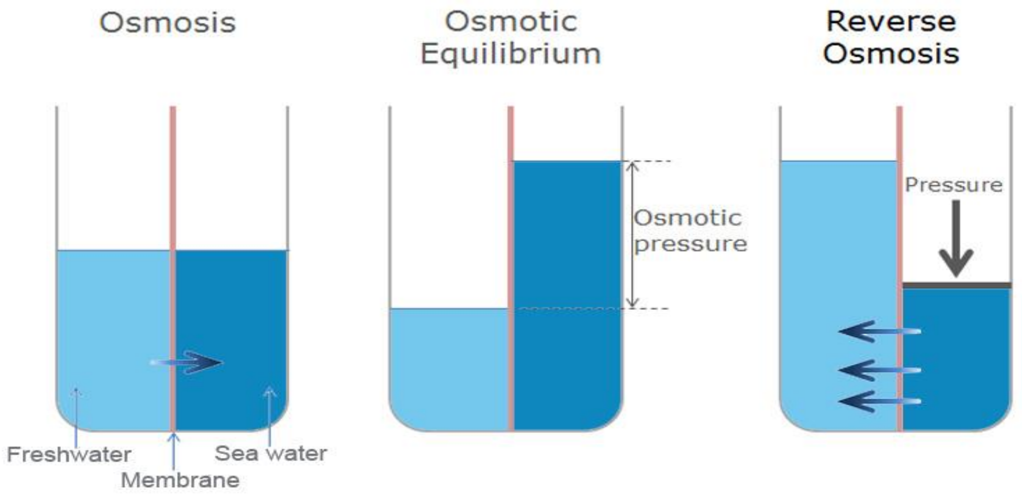

Fig. 1. Scenario A: Osmosis, Scenario B: Osmotic Equilibrium and Scenario C: Reverse Osmosis (UNISCO. int, 2014)

Reverse osmosis can therefore be counted as a prominent separation process in industrial applications due to its power to separate impurities effectively and commensurate with environmental demands. In the past few decades, reverse osmosis has been used for purifying sea and brackish water as well as for treatment of effluents. It has also been extended to different types of industrial applications such as textile, paper, electrochemical and biochemical industries (Bódalo-Santoyo *et al.*, 2003; Nguyen *et al.*, 2009 and Slater *et al.*, 1983). These example applications demonstrate the effective economic process of separation and readily explain the large rise of reverse osmosis markets, which in turn, have motivated further interest in developing and optimising the associated mathematical models. These focus on describing the technique of separation and deducing the performance of the membrane. Investigation and development of such transport models for reverse osmosis operation have attracted the attention of many scientists in recent years researching a specific pattern of reverse osmosis with the perfect conditions for the separation process. These models also enable the evaluation of the performance properties of the membrane with regard to its quality of separation (Sundaramoorthy *et al.*, 2011). It is therefore important to develop rigorous models requiring less experimental and pilot studies and a smaller number of parameters. These include the fluxes of solute and solvent and the efficiency of membrane rejection with regard to the operating conditions such as force per unit area and concentration driving forces, which are important for characterising and evaluating the membrane performance (Jain and Gupta, 2004).

A thorough literature review indicates that there are various models available, and it therefore more appropriate to examine the most popular models, particularly those that accurately relate to the binary and multi-component systems reverse osmosis separation.

Two such main models are identified for estimating the mass transfer across the membrane. They are the irreversible thermodynamics model and the solution diffusion model in this work.

The irreversible thermodynamics model depends on non-equilibrium thermodynamic equations, which consider the membrane as a black box where slow processes are occurring near the equilibrium. Unfortunately, this implies that there is insufficient information for describing flow, transport mechanism and the structure of the membrane. Hence, the applicability of using the irreversible thermodynamics model for accurate speculation of membrane separation is decreased. On the other hand, the solution diffusion model assumes that the transfer of solute and solvent are largely dependent on the physical and chemical properties of both the solution and the membrane. Furthermore, the interaction between the solute, solvent and membrane are included in this model, and the phenomenological relations can explain the reason of fluxes (Van Gauwbergen and Baeyens, 1998; Sapienza *et al.*, 1990 and Jonsson, 1980).

The solution diffusion model can be considered as one of the simplest non-porous or homogeneous models related to transport mechanism criteria. This criterion is characterised by assuming that each solvent and solute are dissolved in the membrane separately on the high-pressure side and they are then diffused in individual fluxes through the membrane under the impact of pressure and concentration differences. The quality of permeate separation occurs due to the mobility of dissolved solute and the rate of its diffusion (Wijmans and Baker, 1995). Thus, the fluxes of solvent and solutes are effectively concerned with the values of solubility and diffusivity of solvent and each solute in the membrane. Nevertheless, there are other types of mathematical models, called the pore models, which include the finely porous, preferential sorption capillary flow and surface force-pore flow models.

Unfortunately, the formula of these models is proposed for a single salt system, which cannot be applied to trace the complicated case of industrial wastewater treatment and organic solutions. This is because of the non-idealist and coupling impact of the interaction between the solutes themselves and with the solvent and the membrane in the case of complicated systems (Rautenbach and Gröschl, 1993). Therefore, the validity of the simple relationships for seawater desalination may fail with the case of organic aqueous diluted solutions (Rautenbach and Gröschl, 1989). There is therefore a need to extend and develop the models used for single solute system in order to explain the complex case of multi-component systems. The complexity of such modelling is due to the demands of different transport properties including osmotic pressure, mass transfer coefficient and diffusivity (Wunnava, 1997).

To sum up, the two main models reviewed have evolved with time in order for them to be suitable for multi-component systems. This is important for the much sought after improved design of reverse osmosis for the separation of feed mixtures (Rangarajan *et al.*, 1985b). Such research has therefore motivated further work for categorising and recording the development of modelling for reverse osmosis units based on these two main models.

2. The Irreversible Thermodynamics Model

The evolution of the irreversible thermodynamics model is highlighted in a tree diagram of Fig. 2, which systematically breaks down and maps out all the investigated theoretical models that have been developed or suggested regarding the home model to form genealogical chart.

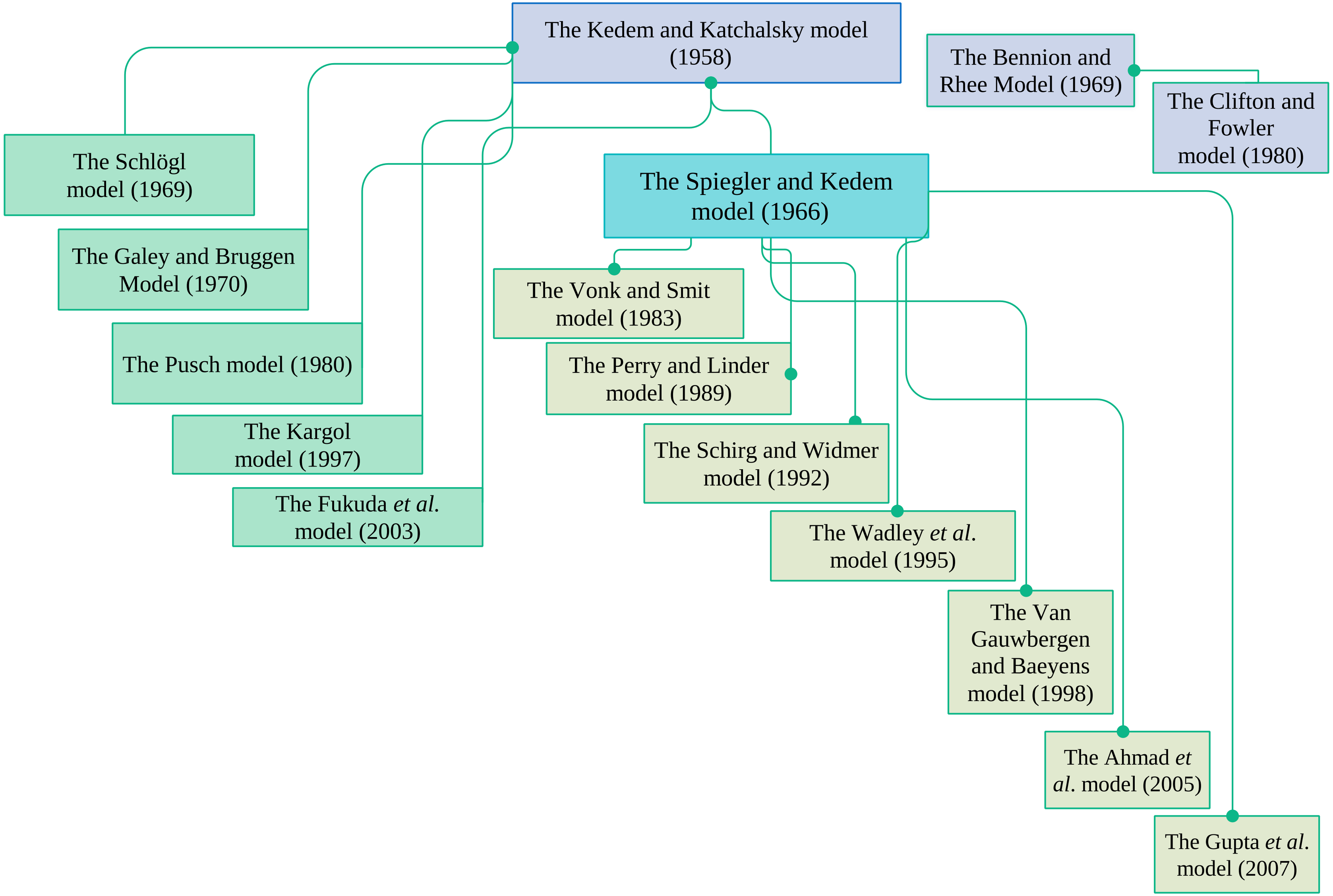

Fig. 2. The evolution of the irreversible thermodynamics model

2.1 The Kedem and Katchalsky Model

The concept behind this model is derived from the principle theory of non-equilibrium thermodynamic systems, which are a type of thermodynamics that simulates most systems found in nature such as the transport processes (Fowler and Guggenheim, 1939). The classical theory of this model was instituted under the assumption of a linear relationship between the fluxes of components with the potential gradients. This assumption eliminates the requirement of knowing the mechanism of transport through the membrane, one that can be accounted for as one of its imperfections. Nevertheless, the membrane performance can be assigned by some phenomenological coefficients, which are investigated experimentally and are somewhat concentration dependent. Kedem and Katchalsky (1958) for a dilute two-component non-electrolyte system of water and solute (binary system) established the starting fundamental formula of the irreversible thermodynamics model as linear equations relating the fluxes of these components. As noted earlier, the irreversible thermodynamics model assumes that the fluxes of solute and solvent are directly relative to the gradient of concentration and pressure alongside the membrane. The primary destination of Kedem and Katchalsky work was to extend and modify the formerly irreversible thermodynamics equations, which have some contradictions in analysing the mechanism of the membrane permeation. They found that these equations have only two permeability coefficients; the solute permeability coefficient and the water permeability coefficient, which were judged unsuitable for the irreversible thermodynamic processes. Hence, they conceived that there should be a combination of three parameters instead of two to estimate the water and solute fluxes. They came up with a third parameter of reflection coefficient σ in order to account for the broad criteria of sensible interaction between solute-solvent-membrane, which enhances the generation of acting force between them. They assumed that the variation of pressure and concentration gradients (the chemical potential) to be linear with low levels of solvent flow rates and the three membrane parameters, specific hydraulic permeability L_p, local solute permeability ω and reflection coefficient σ are constant. Then, they confirmed that for a dilute single solute system, the reflection coefficient σ is approximately equal to one for impermeable solute and less than one for permeable solute. Hence, the transport models have been modified in order to include the reflection coefficient parameter σ, which describes the solute rejection. This is used as a parameter to evaluate the selectivity of solutes by the membrane (Zelman, 1972; Muldowney and Punzi, 1988) and measure the coupling of solute-solvent fluxes through the membrane (Marriott, 2001).

In line with this model, the solvent volume flux J_w is proportional to the divergence between the hydraulic pressure difference ΔP and the osmotic pressure difference $\Delta\pi_s$ across the membrane by the construction:

$$J_w = L_p\,(\Delta P - \sigma\,\Delta\pi_s) \tag{1}$$

Where,

$$\Delta\pi_s = RT\,\Delta C_s = RT\,(C_{s2} - C_{s3})$$

(2)

$\Delta\pi_s,\ R, T$ and ΔC_s are the osmotic pressure difference, the gas constant, the temperature of the brine and solute concentration difference. $C_{s1},\ C_{s2}$ and C_{s3} are solute concentration at feed side, membrane and permeate side respectively.

It can be seen that the osmotic pressure is controlled by the reflection coefficient. While, the solute flux J_s can be calculated from:

$$J_s = \omega\,\Delta\pi_s + C_s^-\,(1-\sigma)\,J_w \tag{3}$$

Where, C_s^- is the average solute concentration that can be defined as:

$$C_s^- = \frac{C_{s1} - C_{s3}}{\ln\left(\frac{C_{s1}}{C_{s3}}\right)} \approx \frac{C_{s1} + C_{s2}}{2} \tag{4}$$

Where,

$$C_{s3} = \frac{J_s}{J_w} \tag{5}$$

In addition, the solute flux can be written in the form of:

$$J_s = \omega\,RT\,(C_{s2} - C_{s3}) + C_s^-\,(1-\sigma)\,J_w \tag{6}$$

The above equations express the solute flux by incorporating of two terms, the first term containing $(\omega\,RT\,(C_{s2} - C_{s3}))$ illustrates the diffusive solute flux, while the second term containing $(C_s^-\,(1-\sigma)\,J_w)$ illustrates the solute transport mechanism by convection, which is caused by the coupling between the solute and solvent through three parameters, σ, C_s^- and J_w. In the case where there is no coupling between the solvent and solute, the term of convection will be zero.

Unfortunately, the expression of average concentration is not exact in the event of high solvent flux or high concentration difference (Mason and Lonsdale, 1990). Furthermore, the three transport parameters of this model, which is known as the hydraulic water permeability constant L_p, the reflection coefficient of the solute σ and the solute permeability coefficient ω are independent of each other and can simply represent the original phenomenological coefficients. They can be expressed as less independent of concentration (Van Gauwbergen and Baeyens, 1998; Jonsson, 1980; Kedem and Katchalsky, 1958; Soltanieh and Gill, 1981).

Moreover, the reflection coefficient can be seen as a scalar of the membrane semi-permeability by varying from zero for non-ideal membrane of non-solute selectivity to one of the ideal membrane, which passes only solvent (Spiegler and Kedem, 1966).

According to Kedem and Katchalsky (1958), the solute retention R_s can be written as:

$$R_s = 1 - \frac{C_{s3}}{C_{s1}} = 1 - \frac{J_s}{J_w\ C_{s1}}$$

(7)

2.2 The Spiegler and Kedem Model

Basically, the prevalent case of a concentration gradient is not linear as mentioned above by Kedem and Katchalsky in Eq. (3). This is more especially so in the case of high concentration gradients and high flow rates, which is characterised by an exact interpret of water flux impact on solute flux by using the first term of this equation. Spiegler and Kedem (1966) have formulated this model by writing the equations in differential form of nonlinear equations, which describe the nonlinearity between the fluxes and potential forces of gradients and then solve these equations by integration around the membrane thickness by assuming constant fluxes and approximate constant values of the three transport parameters. The local developed flux equations can be written as:

$$J_w = -L_p^- \left(\frac{dP}{dx} - \sigma \frac{d\pi_s}{dx}\right) \tag{8}$$

Where, $L_p = \frac{L_p^-}{\Delta x}$ (9)

$$J_s = -\,\omega^- \frac{dC}{dx} + (1-\sigma)\, C_s^-\ J_w \tag{10}$$

Where, $\omega = \frac{\omega^-}{RT\ \Delta x}$ (11)

L_p^- and ω^- are the local water permeability and local solute permeability coefficients. The major difference between Spiegler and Kedem (1966) and Kedem and Katchalsky (1958), is that the model coefficients have no dependence on concentration. Then, the consequence of the integration of Spiegler–Kedem Eq. (10) derived from irreversible thermodynamic processes can give the final expressions of the volumetric water flux.

$$\frac{J_w\,(1-\sigma)\,\Delta x}{\omega^-} = ln \frac{C_{s3}\,\sigma}{(C_{s3}-C_{s1})\,(1-\sigma)} \tag{12}$$

In addition, salt rejection R_s can be described as a function of salt concentration in the feed and permeate sides, while actual salt rejection R_a is related with salt concentration in membrane-feed interface as described below:

$$R_s = \frac{C_{s1}-C_{s3}}{C_{s1}} \tag{13}$$

$$R_a = \frac{C_{s2} - C_{s3}}{C_{s2}} \tag{14}$$

From the above definitions, it is clear that the rejection coefficient R_s strongly depends on the operating conditions, especially those related to pressure difference and the feed concentration. This indicates therefore that the increased the rejection rate when the applied pressure is increased, ultimately results in increased solvent flux.

In addition, Spiegler and Kedem (1966) derived a suitable expression to find salt rejection R_s for a single electrolyte in terms of solvent flux J_w, which is obtained by combining Eq. (1) with C_{s1} and C_{s3} as illustrated below.

$$R_s = 1 - \frac{1-\sigma}{1-\sigma \exp\left|\frac{(\sigma-1)\, J_w}{\omega^-} \Delta x\right|} \tag{15}$$

In simplified form, the above equation, takes the form:

$$R_s = \frac{(1-F)\,\sigma}{1-\sigma\, F} \tag{16}$$

Where, $F = \exp\left(-J_w \frac{1-\sigma}{\omega^-} \Delta x\right)$ or $F = \exp\left(-J_w \frac{1-\sigma}{\omega\, RT}\right)$ or $F = \frac{(C_{s3} - Cs_1)\,(1-\sigma)}{Cs_3 \;\; \sigma}$ (17)

By rearranging the above expression, the water flux can be obtained from:

$$J_w = \frac{\omega^{-}}{\Delta x\, (1-\sigma)}\; ln \left[\frac{\sigma\, (1-R_s)}{(\sigma - R_s)}\right]$$

(18)

Another expression for the observed salt rejection R_s with the pressure gradient can be derived from the combination of Eq. (1) and R_s definition, as:

$$J_w = L_p\, (\Delta P - \Delta\pi_s) + L_p\, (1-\sigma)\, \pi_{s1}\; R_s$$

(19)

Where, π_{s1} is the osmotic pressure of solute at feed side. The final assertion of the Spiegler and Kedem expressions of water flux and salt rejection can show that this modelling mainly depends on three intrinsic parameters, L_p, σ and ω .

Furthermore, it is clearly observed that the final equations of Kedem and Katchalsky (1958), Spiegler and Kedem (1966) models can be distinguished from each other in terms of solute separation, which is induced by the influence of a chemical potential difference on the two sides of the membrane. Hence, Spiegler and Kedem model can be utilized for estimating the fluxes and the reflection coefficient σ, which expresses the solute-membrane interaction. Besides, these equations can be used for a high concentration profile under different volumetric flow rates (Spiegler and Kedem, 1966). Having said this, the Spiegler–Kedem (1966) model has some drawbacks, which can be attributed to the lack of explaining the nature of the membrane structure and mechanism of transport. In addition, the Spiegler–

Kedem model is not capable of describing the performance of the membrane for mixtures of electrolytes unless it is assumed that one of the salts is totally separated by the membrane, or that the salt can be taken for granted as a single species (Perry and Linder, 1989). Consequently, the Spiegler–Kedem model is only suited for a single impermeable solute system without considering of solute-solute interaction. As well as this, this model ignores the impact of the concentration polarization.

Broadly speaking, in a binary system, the performance of solute separation is affected by the impact of solute-solvent, solute-membrane and solvent-membrane interaction, but the scenario is more complicated for a multi-component feed. The important feature of a mixed system is conducted by an additional solute-solute interaction, which affects the rejection quality for each solute (Thiel and Lloyd, 1989). Moreover, the flux of solute in a binary system is affected by the gradient of chemical potential, such as the concentration difference. Nevertheless, for multi-component feed, the dependence on the solutes interaction and sorption and diffusion has to be considered in comparison with the case of the binary system (Ghoreyshi *et al.*, 2002). The concept of this interaction has been argued for the first time by the Spiegler–Kedem theory (Mason and Lonsdale, 1990). Additionally, it is foreseen that the existence of a number of solutes as multi-component feed system, will deviate the separation level of each solute rather than with a binary system. In other words, it appears that the impact of solute-solute interaction is significant for multi-component separation system (electrolyte or non-electrolyte) rather than for the separation of binary system (Mason and Lonsdale, 1990; Soltanieh and Sahebdelfar, 2001).

Using a multi-component electrolyte system, Hodgson (1970) demonstrated that the ion permeability of a particular ion is enhanced by the presence of other similar charged ions of high permeability, while the opposite is true in the presence of ions with low permeability. Besides, it is found that the permeability rate is affected by the concentration difference of the interacted solutes and it can be used to predict the ion permeability of a multi-component system as same as in the binary system. On the other hand, for non-electrolyte systems and electrolyte-non-electrolyte systems, there is an ambiguity about this (Matsuura and Sourirajan, 1971; Perry and Linder, 1989 and Sapienza *et al.*, 1990).

2.3 The Bennion and Rhee Model

To describe the transport phenomenon of water and a single solute in a binary electrolyte system through semi-permeable membranes, Bennion and Rhee (1969) have integrated a set of thermodynamic water and solute flux equations by assuming the water flux is not influenced by coupling the salt flux during reverse osmosis, while the salt flux shows coupling to water flow. The proposed water flux equation as follows:

$$J_w\, V_w = -L_p \left[\bar{a_w} \left([1 + (1-\sigma)\, \bar{a_i}\, V_i] \right) \Delta P + RT \left[\frac{\Delta \bar{a_w}}{V_w} + n_i (1-\sigma)\, \bar{a_w}\, \Delta \bar{a_i} \right] \right]$$

(20)

Where, $V_w, V_i, \bar{a_w}, \bar{a_i}, \Delta\bar{a_w}, \Delta\bar{a_i}$ and n_i are the partial molar volume of water and ion *i*, the main activity of water and ion *i*, the activity difference of water and ion *i* in both two sides of membrane and the number of ions from one molecule of *i* respectively. Likewise, the solute flux of ion i, J_{si} can be shown by the Eq. (21).

$$J_{si} = \bar{a_i} (1-\sigma_i)\, J_w\, V_w - \omega_i \left(\bar{a_i}\, V_i\, \Delta P + n_i\, RT\, \Delta \bar{a_i} \right)$$

(21)

Despite the complexity of this model, it is principally similar to the proposed model of Spiegler and Kedem (1966). The most obvious difference is the interpretation of the transport phenomenon of water and solute and the use of a volumetric flux in place of a water, molar flux, and a different grouping of driving forces. Interestingly, with the intention of extending the single solute mass transport models to compatible multi-component system, a number of researchers have investigated different models under different conditions.

2.4 The Schlögl Model

Schlögl (1969) extended the Kedem and Katchalsky (1958) model and derived two non-linear equations for solute and solvent fluxes for a multi-component dilute solution, as:

$$J_{si} = \bar{C_i}\, (1-\sigma_i)\, J_w + \sum_{j=1}^{n} \omega_{ij}\, \Delta C_j \qquad (j = 1, \ldots\ldots n)$$

(22)

Here, ω_{ij} describes the interaction between the solute-solute and refers to the concentration difference of other solutes in the solution. While the water flux can be illustrated by:

$$J_w = L_p \left(\Delta P - \sum_j \sigma_j\, C_j\, X_j^+ \right)$$

(23)

$$\left(X_j^+ = X_j - \frac{V_j}{V_w} X_w \right)$$

(24)

X_j, V_j, X_w and V_w are the mole fraction and the mean molar volume of ion *j* and water respectively.

The above two equations show the similarity with the Kedem–Katchalsky model of Eqs. (1) and (3) in spite of it is applied to a multi-component dilute solution. Then, Eq. (25) has been composed to describe the solute flux of ion i at position (x) of the membrane, as:

$$J_{si} = C_{i(x)}^{-}\,(1-\sigma_i)\,J_w - \sum_{j=1}^{n} D_{ij}\;K_j\,\frac{dC_{j(x)}}{dx} \qquad (j = 1, \ldots..n) \tag{25}$$

Where, D_{ij} is the membrane diffusion coefficient, which can be defined as: $D_{ij} = \frac{\omega_{ij}\;l}{K_j}$.

Also, K_j is the partition coefficient of species j and ω_{ij} is the permeability coefficient between solutes i and j while l is the membrane length.

The integration of the above equation across the membrane thickness yields the expressions for water and solute fluxes for a multi-component dilute solution.

$$J_{si} = C_i^{-}(1-\sigma_i)\,J_w + \omega_i\;z_i\,\frac{C_i^{-}\;FR}{RT}\,\Delta\vartheta + \omega_i\,\frac{V_i}{\sinh V_i}(C_{i1} - C_{i3}) \tag{26}$$

Where, $C_i^{-} = \frac{C_{i1}+C_{i3}}{2}$ and $C_{i1} = C_i^{-} + 0.5\,\Delta C_i$

FR, z_i and $\Delta\vartheta$ are the Faraday's number, the charge of valency of ion i and electrical potential difference respectively.

$$J_w = L_p\,(\Delta P - \Delta\pi) - L_p\,RT\,\sum_i \sigma_i\,\frac{V_i}{\sinh V_i}(C_{i1} - C_{i3}) \tag{27}$$

These equations are more accurate expressions than alluded to before by containing a new term of $(\frac{V_i}{sinh\;V_i})$ which describes the non-linearity between the driving forces and the particle fluxes. In contrast, these equations may fail in case of higher concentration difference between the two bulk phases. Having said this, one of the drawbacks of this model is the assumption of constant kinetic parameters σ_i and ω_i , which eliminates the consideration of membrane structure.

2.5 The Galey and Bruggen Model

Following similar trend, Galey and Bruggen (1970) extended the model of Kedem and Katchalsky (1958) for a mixture of non-electrolyte dilute solution. They suggested that the flux of each solute affected by other solutes and the solute interaction is mainly dependent on solute permeability in line with Hodgson (1970), and concentration and molecular size.

The flux equation for each solute in a mixture of two solutes i, j in dilute solutions can be given by:

$$J_{si} = C_i^{-}\,(1-\sigma_i)\,J_w + \omega_{ii}\;\Delta C_i + \omega_{ij}\;\Delta C_j \qquad (i \sim j) \tag{28}$$

Where $i \sim j$ indicates that the second equation for J_{sj} can be obtained by rotating the indices. The solute-solute interaction ω_{ij} is expressed by the cross-permeability coefficient between solutes, while the term ω_{ii} represents the self-permeability coefficient of solute i. Also, ΔC_i and ΔC_j are the concentration difference of solutes i, j across the membrane.

Eq. (28) can be modified to express the solute flux in a multi-component mixture as:

$$J_{si} = C_i^- \, (1 - \sigma_i) \, J_w + \omega_{ii} \, \Delta C_i + \sum_{j=0,\ \ j \neq 1}^{n} \omega_{ij} \, \Delta C_j \qquad (29)$$

Here, the reflection coefficient σ_i can be calculated by:

$$\sigma_i = \frac{\pi}{\Delta C \; RT}$$

(30)

Where π is the observed osmotic pressure and $\Delta C \; RT$ is the theoretical Van't Hoff osmotic pressure. For a system of two solutes i and j, the effect of solute flux J_{sj} on solute flux J_{si} can be written as:

$$J_{si} = \left(\frac{\omega_{ij}}{\omega_{jj}}\right) J_{sj}$$

(31)

The above equation describes the impact of solute flux of j on the flux of solute i in terms of self- and cross-permeability coefficient rather than the concentration difference. In addition, Galey and Bruggen (1970) stated that the effective permeability coefficients $(\frac{\omega_{ij}}{\omega_{jj}})$ increase with the decrease of pore size.

2.6 The Clifton and Fowler Model

Clifton and Fowler (1980) have examined the criterion of solute-solute interaction in a solution containing two solutes of organic and inorganic. They found that the impact of solute-solute interaction has an impact of 10% on the total flux of the main solute. They argued that there is no significant solute-solute interaction in multi-component systems. In fact, they based their thinking on the model of Bennion and Rhee (1969), which describes the fluxes of water and solute for a single solute system and modified this model in order to make it compatible for a system with two ionic and non-ionic solutes, which is given by:

$$J_{si} = a_i^- (1 - \sigma_i) \, J_w \, V_w - \omega_i \, (a_i^- \; V_i \;\; \Delta P + n_i \; RT \;\; \Delta a_i^-) - \; \omega_{ij} \; a_i^- \left(a_j^- \;\; V_j \;\; \Delta P + n_j \;\; RT \;\; \Delta a_j\right)$$

(32)

Here, the third term describes the case of two coupling solutes system. Also, the experimental results of Clifton and Fowler (1980) indicates that the concentration polarization has insignificant impact of solute-solute coupling.

2.7 The Pusch Model

Perhaps, Pusch (1980) derived the most specific multi-component thermodynamic model. This was done by improving the underlying equations of the Kedem and Katchalsky (1958) for predicting solvent flux and solute rejection, as given by:

$$J_w = L_p \left[\Delta P - \textstyle\sum_{i=1}^{n} \sigma_i \, \Delta\pi_i\right] \tag{33}$$

$$\frac{1}{R_j} = \frac{1}{R_{aj}} + \sum \frac{\left[\omega_{ji} \;\; \pi_{i1} \left(\frac{R_i}{R_j}\right)\right]}{\left(R_{aj} \;\; J_w\right)} \qquad (i \sim j) \tag{34}$$

Where, Eq. (34) relates the rejection coefficient of solute i with the actual and observed rejection coefficient of solute j (R_{aj} and R_j) respectively. Also, π_{i1} is the osmotic pressure of ion i at the feed side.

Also, Pusch *et al.* (1989) confirmed that the presence of organic compounds has considerably affect the volume flux. Furthermore, for six different types of composite and asymmetric membranes, small solute-solute interaction has been noticed in several binary and ternary systems containing organic compounds. In contrast, the experimental results showed that the solute-membrane interaction has a significant impact on the membrane permeability and the rejection of each solute.

2.8 The Vonk and Smit Model

Vonk and Smit (1983) improved the Spiegler and Kedem (1966) model for the rejection of solutes in a non-electrolyte ternary system (the case of two interacting solutes). They pursued the same approach of Spiegler and Kedem by considering a parameter for solute-solute interactions under the assumption of low values of Pêlect numbers[1] under isothermal condition. From Eq. (25) which is written in a standardized form to indicate the solute flux at position (x) for a homogeneous membrane occupying the region ($0 < x < \ell$) (ℓ is the membrane thickness), they deduced the following equation for two solutes i, j system, as:

$$J_{si} = \bar{C}_{i(x)} \left(1 - \sigma_i\right) J_w - \bar{\omega}_{ii} \frac{dC_{i(x)}}{dx} - \bar{\omega}_{ij} \frac{dC_{j(x)}}{dx} \qquad (i \sim j)$$

(35)

The above equation can be re-written as:

$$\frac{J_{si}}{\bar{\omega}_{ii}} = \frac{\bar{C}_{i(x)} \left(1-\sigma_i\right) \; J_w}{\bar{\omega}_{ii}} - \frac{\bar{\omega}_{ii}}{\bar{\omega}_{ii}} \frac{dC_{i(x)}}{dx} - \frac{\bar{\omega}_{ij}}{\bar{\omega}_{ii}} \frac{dC_{j(x)}}{dx}$$

(36)

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[1] In the context of species or mass transfer, the Péclet number is the product of the Reynolds number and the Schmidt number.

With the assumption of constant permeability and solute rejection coefficients $\omega_i, \omega_j, \sigma_i$ and σ_j and assuming that the cross permeability coefficient $\omega_{\overline{ij}}$ is proportional to concentration $C_{i(x)}$, i.e. $\omega_{ij} = A_{ij}\, C_{i(x)}$, where, A_{ij} is the interaction parameter and introducing the abbreviation of $\emptyset_{ij(x)}$ as:

$$\emptyset_{ij(x)} = \frac{A_{ij}}{\omega_{\overline{ii}}} \left(C_{j(x)} - C_{j(0)}\right) - \frac{(1-\sigma_i)}{\omega_{\overline{ii}}} J_w\, x \tag{37}$$

Then Eq. (36) can be written as:

$$\frac{J_{si}}{\omega_{\overline{ii}}} = -\frac{dC_{i(x)}}{dx} - C_{i(x)} \frac{d\emptyset_{ij(x)}}{dx} \tag{38}$$

The integration of Eq. (38) across the membrane thickness (dx) results:

$$\frac{J_{si}}{\omega_{\overline{ii}}} \int_0^x e^{\emptyset_{ij(x)}}\, dx = C_{i(0)} - C_{i(x)}\, e^{\emptyset_{ij(x)}} \qquad 0 < x < \ell \tag{39}$$

The specific expression for each solute rejection as:

$$R_i = \frac{\left(1-F_{ij}\right)\, \sigma_{ij}}{1-\ \sigma_{ij}\ F_{ij}} \qquad (i \sim j) \tag{40}$$

Where,

$$F_{ij} = exp\left(-J_w\ \frac{1-\sigma_{ij}}{\omega_{\bar{i}}}\ \ell\right) \tag{41}$$

σ_{ij} are the effective reflection coefficient between the two solutes i, j.

Eqs. (39) and (40) are the main expressions used to find the solute retention and express the coupled retentions of two solutes in a multi-component system. However, Eq. (40) is similar to Eq. (16), which was derived by the Spiegler and Kedem (1966) and which was used to calculate the single-solute rejection rate in a binary system.

2.9 The Perry and Linder Model

Likewise, Perry and Linder (1989) stated that the interaction between ions for a mixture of salt and organic ion could have a direct impact on the quality of membrane separation, where the difference in the values of diffusion between these ions can describe the difference of their separation. In addition, they extended the model of the Spiegler and Kedem (1966) for a mixture of salt accompanied by an organic ion. They observed that the interaction between the ions has a big impact on the rates of separation and cannot be calculated from single salt retention only. They subsequently derived the equation of salt rejection R_s in the presence of a retained organic ion. The evolution of their model was under the assumption of no concentration polarization and constant values for both the permeability and reflection coefficient parameters as shown by the following equations:

$$R_s = \frac{(1-\sigma F)-(1-\sigma)\left[1+\frac{\gamma\ C_x^-}{C_{s1}}\right]^{0.5}}{1-\sigma F} \tag{42}$$

Where C_x^- , C_{s1} and γ are the concentration of organic ion in the solution, the salt concentration in the feed side and the number of charged groups carried by the organic ion respectively. This equation can express the impact of organic ion concentration C_x^- and the flow parameter F defined in Eq. (16) with: $\left[1+\frac{\gamma\ Cx^-}{C_1}\right]^{0.5} = \beta$

Eq. (42) can be simplified to:

$$R_s = 1 - \frac{(1-\sigma)\ \beta}{1-\sigma F} \tag{43}$$

The above transforms to Eq. (16) for pure salt, where C_x^- = zero and β = one.

The observations of Perry and Linder's experiments showed that the presence of organic ion (such as, sulfonic or carboxylic group) in an electrolyte solution (such as, sodium salt) could sustain a direct impact on promoting the solute rejection of organic ion in spite of negative salt rejection. The net outcome of this is that it will not only cut down the time and efforts for ultra-purification processes but it also has good economic effects. However, one of the imperfections of the Perry and Linder (1989) model is that this model cannot be applied for a multi-component system and restricted to a single compound of known molar mass and charge.

2.10 The Thiel and Lloyd Model

In order to predict the multi-component effects of dilute non-electrolyte solutions in the pressure driven reverse osmosis, Thiel and Lloyd (1989) studied the rejection of mannitol 1, 6-hexanediol and 1-pentanol from binary and ternary aqueous solutions by using cellulose acetate membrane. The survey of the multi-component effects has been depicted by the phenomenological coefficients of permeates and the membrane. They have combined the correlation of Soltanieh and Gill (1981) of Eq. (44) with the film theory model of Eq. (45) in order to measure the membrane rejection for binary system from Eq. (33) under the approximation of small Pêlect numbers of membrane phase as shown below.

$$(x_{i2} - 1) = (R_i - 1)[1 - exp(-F_i\ J_w)]$$

(44)

$$(x_{i1} - 1) = (x_{i2} - 1)\ exp\left(\frac{-J_w}{c\ k_i}\right)$$

(45)

$$(x_{i1}-1) = (R_i-1)\left[\left(1-exp(-F_i\ J_w)\right)\right] exp\left(\frac{-J_w}{c\,k_i}\right)$$

(46)

Eq. (46) can be re-arranged as:

$$ln\frac{(x_{i1}-1)}{J_w} = ln\left[(R_i-1)\,F_i-\frac{J_w}{c\,k_i}\right]$$

(47)

Where, x_{i1}, x_{i2}, R_i, F_i and k_i are the mole fraction of ion *i* in the feed and the permeate sides, the observed concentration rejection of the solute *i*, the membrane-phase mass transfer resistance of the solute *i* and the liquid phase mass transfer coefficient for solute *i*.

For ternary systems, Eq. (44) can be written as:

$$(x_{i2}-1) = (R_i-1)[1-exp(-F_i\ J_w)] + \in_{ij}^{m} x_{j3} \qquad (i\#j)$$

(48)

Where, $\in_{ij}^{m}$ is the membrane phase coupling function and demonstrates the coupling effect in a multi-component solution. This term is defined as:

$$\in_{ij}^{m} = \frac{K_j}{K_i}\, V_m\, \ell \left(\varepsilon_{ij}-\varepsilon_{iw}\right) J_w$$

(49)

Where, K_i, K_j, V_m, ℓ are the partition coefficients ($K_i = \frac{x_{i2}}{x_i}$) of the ions *i*, *j* respectively and the molar volume of the membrane phase including the membrane material and all permeates and the membrane thickness. Also, ε_{ij} and ε_{iw} are the apparent membrane phase frictional coefficient between solutes *i* and *j* and between *i* and water respectively. Eq. (48) can be re-written as:

$$(x_{i2}-1) = (R_i-1)[1-exp(-F_i)\, J_w] + \frac{K_j}{K_i}\, V_m\, \ell \left(\varepsilon_{ij}-\varepsilon_{iw}\right) x_{j3}\ J_w \tag{50}$$

The first term of the above equation can be substituted from Eq. (45) of the film theory model to form:

$$\frac{(x_{i1}-1)\, exp\left(\frac{J_w}{c\,k_i}\right)}{J_w} = [(R_i-1)\,F_i] + \left[\frac{K_j}{K_i}\, V_m\, \ell \left(\varepsilon_{ij}-\varepsilon_{iw}\right)x_{j3}\right] \tag{51}$$

Furthermore, by neglecting the coupling effect, the above equation can be written as:

$$\left(x_{ij}-1\right) exp\left(\frac{J_w}{c\,k_i}\right) = [(R_i-1)\,F_i]\ J_w \tag{52}$$

Where x_{ij} is the mole fraction of solute *i* at location *j*. The above approach can make a physical model for prediction of a pressure-driven membrane performance for dilute multi-component solutions of non-electrolytes.

Mason and Lonsdale (1990) reviewed the previously investigated membrane transport models and concluded that the model of the Spiegler and Kedem (1966) can predict the functioning of membrane separation in reverse osmosis units better than the other models investigated. In addition, they concluded that all the old models are differing only by their prediction of transport coefficients.

Concentration polarization can be considered as one of the imperfections of reverse osmosis, which is caused by the accumulation of solutes on the membrane surface by continuous rejection of solutes. Consequently, this phenomenon can decrease the flux of solvent by reducing the potential of pressure difference along the two sides and increasing the value of osmotic pressure (Kimura and Sourirajan, 1967; Sutzkover *et al.*, 2000). Thus, it seems that it is important to consider this phenomenon in reverse osmosis modelling. This phenomenon has been typically described via the film theory model (Brouckaert and Buckley, 1992). This hypothesis assumes that there is a boundary layer of thickness (ℓ) next to the membrane and controlled by the liquid speed and component diffusion parameters.

2.11 The Schirg and Widmer Model

Schirg and Widmer (1992) has merged the model of the Spiegler and Kedem (1966) with the film theory model in order to include the impact of concentration polarization terms of permeate and bulk solute concentration.

The film theory model can be expressed by Eq. (54), which is derived from a simple mass balance over an element of the boundary layer and the membrane shown below in Eq. (53):

$$J_w\, C_s - D_{sw}\, \frac{dC_s}{dx} = J_w\, C_{s3} \tag{53}$$

Where D_{sw} is the diffusion coefficient of the solute in water. The integration of the above equation under conditions:

$C_s = C_{s2}$ at $x = 0,\ C_s = C_{s1}$ at $x = 1$ gives:

$$\frac{(C_{s2} - C_{s3})}{(C_{s1} - C_{s3})} = exp\left(\frac{Jw}{k}\right) \tag{54}$$

Where k is the mass transfer coefficient expressed as, $k = \frac{D_{sw}}{\delta}$, where δ is the boundary layer thickness.

In case of assuming 100% of solute rejection, the above equation can be written as:

$$\frac{(Cs_2)}{(Cs_1)} = exp\left(\frac{Jw}{k}\right) \tag{55}$$

Representing the concentration polarization model in terms of observed rejection R_s and actual rejection R_a, Eq. (54) can be written as:

$$\frac{Cs_3}{C_{s1}-Cs_3} = \frac{1-R_s}{R_s} = \frac{1-R_a}{R_a}\, exp\left(\frac{J_w}{k}\right) \tag{56}$$

In addition, this equation can be re-arranged as a ratio of the observed rejection to the actual rejection, as:

$$\frac{R_s}{R_a} = R_a\,(1 - R_s)\,\mathrm{exp}\left(\frac{-J_w}{\frac{D}{\delta}}\right)$$

(57)

Note, the solute transport equation of the Spiegler–Kedem model of Eq. (12) can be combined with the concentration polarization theory of Eq. (54) and reflection coefficient σ (Schrig and Widmer, 1992) to provide the expression for salt rejection R_s as:

$$ln\left(\frac{1-R_s}{R_s}\right) = ln\left[\left(\frac{1-\sigma}{\sigma}\right)\left(\frac{1}{1-exp\left(-J_w\frac{1-\sigma}{\omega^{-}}\,\Delta x\right)}\right)\right] + \frac{J_w}{k} \tag{58}$$

Alternatively, as:

$$\frac{1-R_s}{R_s} = \frac{1-\sigma}{\sigma}\,\frac{exp\left(\frac{J_w}{k}\right)}{\left[1-exp\left(-J_w\frac{(1-\sigma)}{\omega^{-}}\,\Delta x\right)\right]} \tag{59}$$

This equation can express the dependence of salt rejection on feed concentration and solvent flux for a single salt solution. On the other hand, in case of ignoring concentration polarization, the common equation of the salt rejection can be brought back to Eq. (12). Lastly, Eqs. (1), (6) and (59) can be counted as the combined film–Spiegler–Kedem model. Furthermore, Schrig and Widmer (1992) has introduced an exponential term for the concentration dependence of salt permeability in the Spiegler and Kedem model to estimate the retention of nanofiltration membranes for single salt solution depending on feed concentration and permeate flux.

2.12 The Wadley *et al*. Model

Wadley *et al.* (1995) implemented the solvent and solute fluxes equations of the Spiegler and Kedem (1966) model (Eqs. 8 and 10) to develop a new model in combination with the film theory model for concentration polarization as was done by Schrig and Widmer (1992). Their model simulates a system of sodium chloride and organic compound of different charges. They proposed that each solute has to be handled on an individual basis, meaning that sodium chloride and organic compound have different transport characteristics. Thus, it is possible to apply a linear function for any solute concentration in order to express its osmotic pressure π, i.e.:

$$\pi = \sum_i \emptyset_i \, C_i \tag{60}$$

Where $\emptyset_i$ is the osmotic factor of solute i. In addition, they proposed to use different values of the osmotic factor $\emptyset_i$ of solute on the two sides of the membrane, which led the solvent flux of the Spiegler–Kedem of Eq. (8) to be written as:

$$J_w = L_p \left[\Delta p - \sum_i \sigma_i \left(\emptyset_{i2} \, C_{i2} - \emptyset_{i3} \, C_{i3}\right)\right] \tag{61}$$

Where $\emptyset_{i2}$ and $\emptyset_{i3}$ are osmotic factor of component i at the membrane and permeate side respectively. The above equation demonstrates that the water flux was influenced by the osmotic pressure difference caused by the concentration gradient for each solute in the system.

According to solute flux, the integration of the solute flux of the Spiegler–Kedem model of Eq. (10) over the membrane in the side between C_{i2}, C_{i3} leads to:

$$\frac{C_{i3}}{C_{i2}} = \left[\frac{1-\sigma_i}{1-\sigma_i \, F_i}\right] \tag{62}$$

The combination of Eqs. (62) and (54) will give Eqs. (63) and (64) to calculate the solute concentration in the membrane/feed interface and permeate side respectively.

$$C_{i2} = C_{i1} \left[\frac{exp\left(\frac{Jw}{k}\right) \left(1-\sigma_i \, F_i\right)}{1-\sigma_i \, F_i - (1-\sigma_i)\left(1-exp\left(\frac{Jw}{k}\right)\right)}\right] \tag{63}$$

$$C_{i3} = C_{i1} \left[\frac{exp\left(\frac{Jw}{k}\right)}{1-exp\left(\frac{Jw}{k}\right)}\right] \left[\frac{\left(1-\sigma_i \, F_i\right)}{1-\sigma_i \, F_i - (1-\sigma_i)\left(1-exp\left(\frac{Jw}{k}\right)\right)}\right] \tag{64}$$

The assertion of this model includes only solute-membrane and solute-solvent interactions and does not include the solute-solute interaction, which can lead this model to be an imperfect model (Ahmad *et al*., 2005).

2.13 The Kargol Model

For biological reverse osmosis membranes, Kargol (1997) modified the Kedem and Katchalsky (1958) model to calculate the permeate concentration as a function of transport parameters of the membrane, the pressure difference and the initial concentration, which is given by:

$$C_{i3} = \frac{-L_p \left[\Delta P \, (1+\sigma) - 2 \, \sigma \, RT \, C_{i1}\right] - 2 \, \omega \, RT + \sqrt{\Delta}}{2 \, L_p \, \sigma \, RT (1+\sigma)}$$

(65)

Where

$$\Delta = \llbracket L_p[\Delta P(1+\sigma) - 2\,\sigma\,RT\,C_{i1}] + 2\,\omega\,RT \rrbracket^2 - 4\,L_p\,\sigma\,RT(1+\sigma)\left[L_p\,C_{i1}(1-\sigma)(\sigma\,RT\,C_{i1} - \Delta P) - 2\,\omega\,RT\,C_{i1}\right]$$

(66)

Kargol (1997) emphasised that this equation should be used for σ <0.5. however, for ($\sigma >$ 0.5), the first term of the solute flux Eq. (3) of the Kedem-Katchalsky model will be eliminated. As a result, Eq. (65) will take the form:

$$C_{i3} = \frac{L_p\,(\sigma\,RT\,C_{i1} - \Delta P) - \omega\,RT + \sqrt{\Delta}}{2\,L_p\,\sigma\,RT}$$

(67)

Where

$$\Delta = \left[L_p\,(\Delta P - \sigma\,RT\,C_{i1}) + \omega\,RT\right]^2 + 4\,L_p\,\sigma\,\omega\,C_{i1}\,(RT)^2$$

(68)

However, the impact of feed flow rate on permeate concentration is not considered in this model.

2.14 The Van Gauwbergen and Baeyens Model

Van Gauwbergen and Baeyens (1998) have assessed the validity of the irreversible thermodynamics models of the Kedem and Katchalsky (1958) and the Spiegler and Kedem (1966) by a comparing theoretical and experimental data. They concluded that the Kedem–Katchalsky model can be utilized effectively for high volume flow rates and high concentration gradients and the membrane parameters are less dependent on the pressure difference and concentration.

Furthermore, they stated that the solvent and solute fluxes can be driven under the impact of the cross and straight phenomenological coefficients, L_{ws}, L_{sw} and L_{ww}, L_{ss} respectively. These coefficients can be described by simple phenomenological linear equations of solvent and solute fluxes as follows:

$$J_w = L_{ww}\,\Delta P + L_{ws}\,\Delta\pi \tag{69}$$

$$J_s = L_{sw}\,\Delta P + L_{ss}\,\Delta\pi \tag{70}$$

Where L_{ww}, L_{ws}, L_{sw} and L_{ss} are the straight phenomenological coefficients of water, the cross phenomenological coefficients of water and solute, the cross phenomenological coefficients of solute and water and the straight phenomenological coefficients of the solute respectively.

Under the assumption of no concentration polarization and constant L_{ww}, L_{ws} with respect to concentration, they derived the solvent and solute flux equations as:

$$J_w = \frac{L_{ww}\ V_w^2}{\Delta x}(\Delta P - \Delta\pi) + \frac{L_{ws}\ \tilde{v}\ RT\ V_w}{\Delta x}\ ln\left(\frac{C_{i1}}{C_{i3}}\right) \tag{71}$$

$$J_s = \frac{L_{sw}\ V_w}{\Delta x}(\Delta P - \Delta\pi) + \frac{L_{ss}\ \tilde{v}\ RT}{\Delta x}\ ln\left(\frac{C_{i1}}{C_{i3}}\right) \tag{72}$$

Where $\tilde{v}, \Delta x$ are the stoichiometric coefficient or number of ions produced on complete dissociation of one molecule of electrolyte and the membrane thickness respectively. Then, the evaluation of Kedem and Katchalsky (1958) and the Spiegler and Kedem (1966) is implemented using Eqs. (71) and (72).

2.15 The Fukuda *et al.* Model

For a combination of the electrolyte and non-electrolyte system (KCl–sucrose mixed aqueous solution), the model of the Kedem and Katchalsky (1958), more particularly, Fukuda *et al.* (2003) have modified Eqs. (1) and (3) in order to predict the effect of sucrose on the separation of KCI through a mosaic membrane. The following equations were proposed to calculate the volumetric solvent flux and solute flux in the mixed systems under assuming that the transport rate of impermeable solute (sucrose) was negligible.

$$J_w = L_p\ (\Delta P - \sigma\ \Delta\pi_s - \Delta\pi_{im})$$

(73)

$$J_s = C_s^-\ (1 - \sigma)\ J_w +\ \omega\ \Delta\pi_s$$

(74)

Where $\Delta\pi_s, \Delta\pi i_m$ are the osmotic pressure of the permeable solute and the impermeable solute respectively.

Eq. (73) shows that the flux of solvent depends on the pressure difference (the water flow caused by KCI diffusion), the osmotic pressure difference of the permeable solute (caused by KCI concentration difference) and finally the osmotic pressure difference of impermeable sucrose solute.

2.16 The Ahmad *et al*. Model

The process of building up the irreversible thermodynamics models continued and Ahmad *et al.* (2005) extended the model of the Spiegler and Kedem (1966) considering the solute-solute interactions in a multi-component system. In addition, they proposed a new equation to calculate the solvent and solute fluxes for a multi-component system. They did this by integrating their model over the membrane thickness and considered the effects of concentration polarization in their model.

The expressions of solvent and solute fluxes, which are controlled by the solvent and solute forces for a multi-component system, were represented as shown below:

$$J_w = L_{ww}\, F_w \, \textstyle\sum_{s=1}^{n} L_{ws}\, F_s \tag{75}$$

$$J_s = L_{sw}\, F_w + \textstyle\sum_{i=1}^{n} L_{si}\, F_i \qquad i = 1,2,3,\dots n \tag{76}$$

Where F_s, F_i and F_w are the driving forces exerted by solutes s and i and water respectively. The total volume flux was given as:

$$J_w = -L_{ww}\, V_w^2 \left[\frac{dP}{dx} - \textstyle\sum_{s=1}^{n}\left(1 - \frac{L_{ws}\ C_w}{L_{ww}\ C_s}\right)\frac{d\pi_s}{dx}\right] \tag{77}$$

Where C_w is the molar concentration of water.
The above equation can be simplified to:

$$J_w = L_p^{-}\left[\frac{dP}{dx} - \textstyle\sum_{s=1}^{n} \sigma\ \frac{d\pi_s}{dx}\right] \tag{78}$$

Where $L_p^{-} = -L_{ww}\, V_w^2$ (79)

$$\sigma = \left(1 - \frac{L_{ws}\ C_w}{L_{ww}\ C_s}\right) \tag{80}$$

Also, the total osmotic pressure gradient $d\pi$ for the mixture can be calculated from the summation of the osmotic pressure gradient caused by each solute, $d\pi_s$.

$$\frac{d\pi}{dx} = \textstyle\sum_{s=1}^{n} \frac{d\pi_s}{dx} \tag{81}$$

$$d\pi = \textstyle\sum_{s=1}^{n} RT\left(C_x - C_{(x+dx)}\right) \tag{82}$$

Where C_x, $C_{(x+dx)}$ are solute and solvent concentrations measured on both sides of the membrane. In addition, for a dilute aqueous solution, the osmotic pressure of a system of components can be calculated from the Van't Hoff's equation (Van Gauwbergen *et al.*, 1997), as:

$$\pi = \frac{\sum n_i}{V}\ RT = \textstyle\sum C_i\ RT \tag{83}$$

While the solute flux for each solute is given by:

$$J_s = \textstyle\sum_{i=1}^{n} \omega_{si}^{-}\ \frac{d\pi_i}{dx} + (1-\sigma)\, C_s\ J_w \qquad (i = 1,2,3,4,\dots\dots n) \tag{84}$$

Where ω_{si}^{-} is the local solute permeability constant of solute s with the consideration of the interaction of solute i and can be defined as:

$$\omega_{si}^{-} = \left(\frac{L_{ws}\ L_{wi}}{L_{ww}\ C_i} - \frac{L_{si}}{C_i}\right) \tag{85}$$

This model returns to the Spiegler and Kedem model for a single solute system. The integration of the Eqs. (77) and (84) gives:

$$J_w = L_p\left[\Delta P + \textstyle\sum_{s=1}^{n} \sigma\ RT\ R_a\, C_{s2}\right] \tag{86}$$

$$\frac{C_{s3} - C_{s2}(1-\sigma)}{C_{s3}\ \sigma} = F_s \tag{87}$$

Where C_{s2} and R_a are the concentration of solute at membrane interface and actual solute rejection, ($R_a = 1 - \frac{C_{s3}}{C_{s2}}$) respectively.

Also,
$$F_s = exp\left[\frac{-J_w\,(1-\sigma)}{\omega_{ss}}\left(1 + \textstyle\sum_{i=1}^{n} A_i\right)\right]$$
(88)

Where
$$A_i = \frac{\omega_{si}\,(C_{s3}-C_{s1})\ exp\left(\frac{J_w}{k_i}\right)}{J_w\,[C_{s3}-(1-\sigma)\,C_{s(av)}]}$$
(89)
$$\omega_{ss} = \left(\frac{L_{ws}^2}{L_{ww}\,C_{s(av)}} - \frac{L_{ss}}{C_{s(av)}}\right)\frac{RT}{\ell}$$
(90)

By which ω_{ss}, ω_{si} and ℓ can describe the solute permeability coefficient of solutes with itself interaction and the solute permeability coefficient with solute (i) interaction and membrane thickness respectively. $C_{s(av)}$ is the average solute concentration.

The re-arrangement of Eq. (87) gives the actual rejection as:

$$R_a = \frac{\sigma\,(1-F_s)}{1-\sigma\ \ F_s} \qquad (91)$$

Explicitly, combination of the concentration polarization equation of Eq. (54) with the above expression results in the actual and observed solute rejection as:

$$\frac{1-R_s}{R_s} = \frac{1-\sigma}{\sigma\,(1-F_s)}\ exp\left(\frac{J_w}{k}\right) \qquad (92)$$

Ahmad *et al.* (2007) in another experimental study illustrated the capability of using the above model to predict the solvent and solute fluxes in a system of multiple solutes in complex organic solutions with the determination of concentration of each solute. However, the model has been validated for only multiple solutes nanofiltration membrane.

2.17 The Gupta *et al*. Model

Gupta *et al.* (2007) also considered the coupling of the Spiegler-Kedem (1966) model with the film theory model for dilute binary aqueous salt solutions in order to obtain the boundary layer thickness and the three membrane transport parameters. They assumed a constant boundary-layer thickness across the membrane.

Consequently, the equation of Vant's Hoff has been applied to describe the osmotic pressure difference across the membrane, as:

$$\Delta\pi = \emptyset_m\ \ n\,(C_m - C_p)\ RT$$
(93)

Where $\emptyset_m$ is the osmotic coefficient for non-ideal solutions and n is the number of ions in the salt.

Substitution of the above equation in the main water flux of Eq. (1) yields:

$$J_w = L_p\,(\Delta P - \sigma\,\emptyset_m\,n\,(C_{s2} - C_{s3})\,RT) \tag{94}$$

Inclusion of concentration polarization in Eq. (54) yields:

$$J_w = L_p\left(\Delta P - \sigma\;\emptyset_m\;n\,(C_{s1} - C_{s3})\,RT\exp\left(\frac{J_w}{\frac{D_{sw}}{\delta}}\right)\right) \tag{95}$$

In addition, they used the correlation of the Kedem-Katchalsky model of Eq. (6) to express the solute flux through the membrane, which expresses the solute flux as a combination of diffusive and convective fluxes. Then, Gupta *et al.* (2007) have derived the contribution rate of the convection flux as the ratio of convective solute flux to the solvent flux $\int$ as:

$$\int = 1 - \frac{\omega\,RT\,(C_{s2} - C_{s3})}{J_w} \tag{96}$$

The above equation can be written in another form to include the solute rejection, as:

$$\int = 1 - \frac{\omega\,RT}{J_w}\left(\frac{R_s}{1 - R_s}\right) \tag{97}$$

The above modelling investigates the ability of taking the account the three transport parameters of the Spiegler-Kedem model with the concentration polarization parameters without taking for granted the mass transfer coefficient in the boundary membrane layer. This can be accomplished by the combination of the two models as mentioned above.

In summary, Table 1 gives an overview the specific characteristics of the irreversible thermodynamics model in respect of its development and applicability in different applications of water desalination and wastewater treatment.

Table 1. Summary literature review of the irreversible thermodynamics model

No.	Author and year	Assumptions	The Specific Features and advantages	Shortcoming
1	Kedem and Katchalsky (1958)	• Assume of a linear relationship between the fluxes of components with the potential gradients. • Assumes the phenomenological coefficients of this model are dependent on salt concentration.	• Includes a model of linear equations for dilute two-component non-electrolyte system of water and solute. • The solvent and solute transport through the membrane is characterised by solvent and solute parameters. • Considers the interaction between solute-solvent-membrane by adding a reflection coefficient.	• Eliminates the describing of the membrane transport mechanism. • The expression of average concentration is not exact in the event of high solvent flux or high concentration difference. • Limited to only sufficiently dilute two component solutions.
2	Spiegler and Kedem (1966)	• Consideration of the assumption of approximate constant values of fluxes and model coefficients of $Lp^{-}, \sigma \; and \; \omega^{-}$. • Relies on the assumption of high flow rate with high concentration gradients.	• Approves the Kedem and Katchalsky (1958) model by deriving the differential nonlinear equations of fluxes and integrated to show the non-linearity between the fluxes and the potential forces of gradients. • The model coefficients have no dependence on salt concentration. • Derived an expression for salt rejection for a single electrolyte in terms of solvent flux.	• Takes into account the fact that the measure of the salt rejection membrane is highlighted without considering the concentration polarization. • Does not consider the solute-solute interaction. • Is not capable to trace the performance of the membrane in the case of a mixture of electrolytes.
3	Bennion and Rhee (1969)	• Assumes the water flux is not mainly inclined by coupling the salt flux, while the reverse is valid.	• Presented a new approach for obtaining the transport phenomenon of water and a single solute in a binary electrolyte system. • Eliminates all possible simplifications and assumptions of linear proposed equations of Kedem and Katchalsky (1958).	• It is essentially a complex model. • The variation in membrane activity was not considered, which affects the salt and water activity.
4	Schlögl (1969)	• Assumes constant kinetic parameters of σ_i and ω_i	• It is essentially a non-linear functions model for solute and solvent fluxes for a multi-component dilute solution. • Involves a new parameter to describe the non-linearity between the driving forces and particle fluxes.	• The mode equations may fail in case of higher concentration difference between the two bulk phases.

Table 1. Summary literature review of the irreversible thermodynamics model (continued)

No.	Author and year	Assumptions	The Specific Features and advantages	Shortcoming
5	Galey and Bruggen (1970)	• The solute-solute interaction is mainly depending on solute permeability, concentration and molecular size.	• Extends the model of the Kedem and Katchalsky (1958) to describe a mixture of non-electrolyte dilute solutions. • Indicates that the flux of each solute is affected by other solutes. • Investigates a new equation for solute flux in a multi-component system by showing of the impact of solute-solute interaction. • Studied the effect of pore size in solute interaction and flux ratios.	• The model doesn't trace the impacts of pore length, tortuosity, surface charge, bound water, molecular shape of the solutes, and hydrogen bonding on solute-pore interaction.
6	Clifton and Fowler (1980)	• No significant solute-solute interaction in multi-component systems.	• Extends the model of the Bennion and Rhee (1969) from the single solute system to a system of two solutes of organic and inorganic solutes. • Includes a third term of solute-solute interaction in a solute flux equation. • Shows that the concentration polarization has a little effect on solute-solute coupling.	• Based on complex thermodynamics equations of Bennion and Rhee (1969).
7	Pusch (1980) and Pusch et al. (1989)	• Based on the same criterion of the Kedem and Katchalsky (1958) model.	• Draws out the equations of the Kedem and Katchalsky (1958) model to be compatible with the shell of a multi-component feed solution. • Confirmed a small solute-solute interaction in several binary and ternary systems containing organic compounds.	
8	Vonk and Smit (1983)	• Low values of Pêlect numbers under isothermal condition.	• Improves the Spiegler and Kedem (1966) model to be compatible with the rejection of a number of solutes in a ternary system.	• The model is only applicable for non-electrolytes systems.

			- Considers a parameter for solute-solute interactions for non-electrolyte solutions. - Holds in the impact of the coupled retention in a multi-element organization of two solutes.	

Table 1. Summary literature review of the irreversible thermodynamics model (continued)

No.	**Author and year**	**Assumptions**	**The Specific Features and advantages**	**Shortcoming**
9	Perry and Linder (1989)	- No concentration polarization and constant values for both the permeability and reflection coefficient parameters.	- Spreads out the model of the Spiegler and Kedem (1966) in order to be satisfied for a mixture of salt accompanied by an organic ion. - Holds in the equation of the salt rejection in the presence of a retained organic ion.	- The lack of overall salt permeability and reflection coefficient dependency upon varying salt concentration in the feed. - The model cannot be applied for a multi-component system and restricted to a single compound of known molar mass and charge.
10	Thiel and Lloyd (1989)	- Approximation of small Pêlect numbers of membrane phase.	- Combines the correlation of the Soltanieh and Gill (1981) with the film theory model. - Uses for performance membrane prediction of binary and ternary non-electrolyte aqueous solutions systems.	- Implemented for dilute non-electrolytes solutions.
11	Schirg and Widmer (1992)	- Assumed that the solute permeability is dependent on feed concentration in an exponential term.	- Combines the Spiegler and Kedem (1966) model with the film theory model. - Traces the impact of concentration polarization in case there is a relation between permeate and bulk solute concentration.	- Implemented for a single salt solution.
12	Wadley *et al.* (1995)	- Assume that each solute has to be handled individually in a system of sodium chloride and organic compound.	- Develops the combination of the Spiegler and Kedem (1966) model with the film theory model. - Holds in the suitable equations to calculate the solute concentration in the	- Neglected the solute-solute interaction.

			membrane/feed interface and permeate side respectively.	

Table 1. Summary literature review of the irreversible thermodynamics model (continued)

No.	Author and year	Assumptions	The Specific Features and advantages	Shortcoming
13	Kargol (1997)	• It is based on the work of Kedem and Katchalsky (1958) equations.	• Calculates the permeate concentration for biological reverse osmosis membranes as a function of transport parameters of the membrane, feed concentration and mechanical pressure.	• Neglected the impact of feed flow rate in the permeate concentration.
14	Van Gauwbergen and Baeyens (1998)	• No concentration polarization and constant cross L_{ws} and straight L_{ww} phenomenological coefficients.	• Contains suitable equations for solute and solvent fluxes under the impact of the cross and straight phenomenological coefficients L_{ws}, L_{sw} and L_{ww}, L_{ss} respectively. • Improved the water and solute fluxes equation, which are used to evaluate the Kedem and Katchalsky (1958) and the Spiegler and Kedem (1966).	• The transport parameters are constants.
15	Fukuda *et al.* (2003)	• Assuming that the transport rate of impermeable solute (sucrose) was negligible.	• Develops the model of the Kedem and Katchalsky (1958) in order to stimulate an aqueous system of electrolyte-non-electrolyte solutes systems of (KCl–sucrose mixed aqueous solution). • Argues that the solvent flux is affected by the presence of the osmotic pressure difference of the impermeable solute.	
16	Ahmad *et al.* (2005) and Ahmad *et al.* (2007)	• Assuming all solutes are semi-permeable to the membrane. • Each solute has constant values of diffusion and mass transfer coefficient in the concentration polarization layer thickness.	• Runs the model of the Spiegler and Kedem (1966) to be suitable for a multi-component system. • Counts on the solvent and solute fluxes for a multi-component system with considering of concentration polarization. • Illustrates the capacity of using their former model to predict the solvent and solute fluxes in a system of multiple solutes in complex organic solutions. • Considers of solute-solute interaction.	• Neglected the charge of solutes. • Neglected the pressure difference along the vertical length of the membrane surface. • The model has been only validated for multiple solutes nanofiltration membrane.

Table 1. Summary literature review of the irreversible thermodynamics model (continued)

No.	Author and year	Assumptions	The Specific Features and advantages	Shortcoming
17	Gupta *et al.* (2007)	• Assuming a constant boundary-layer thickness across the membrane.	• Considers the ability of hitting the three transport parameters of the Spiegler and Kedem (1966) model with the concentration polarization parameters without taking for granted the mass transfer coefficient in the boundary membrane layer. • Counts on the boundary layer thickness. • Derives the contribution rate of the convection flux. • Can be used for both nanofiltration and reverse osmosis membranes.	• Implemented for only dilute aqueous salt solutions.

3. The Solution Diffusion Model

The evolution of the Solution Diffusion model is highlighted in a tree diagram of Fig. 3, which systematically breaks down and maps out all the investigated theoretical models that have been developed or suggested regarding the home model to form genealogical chart.

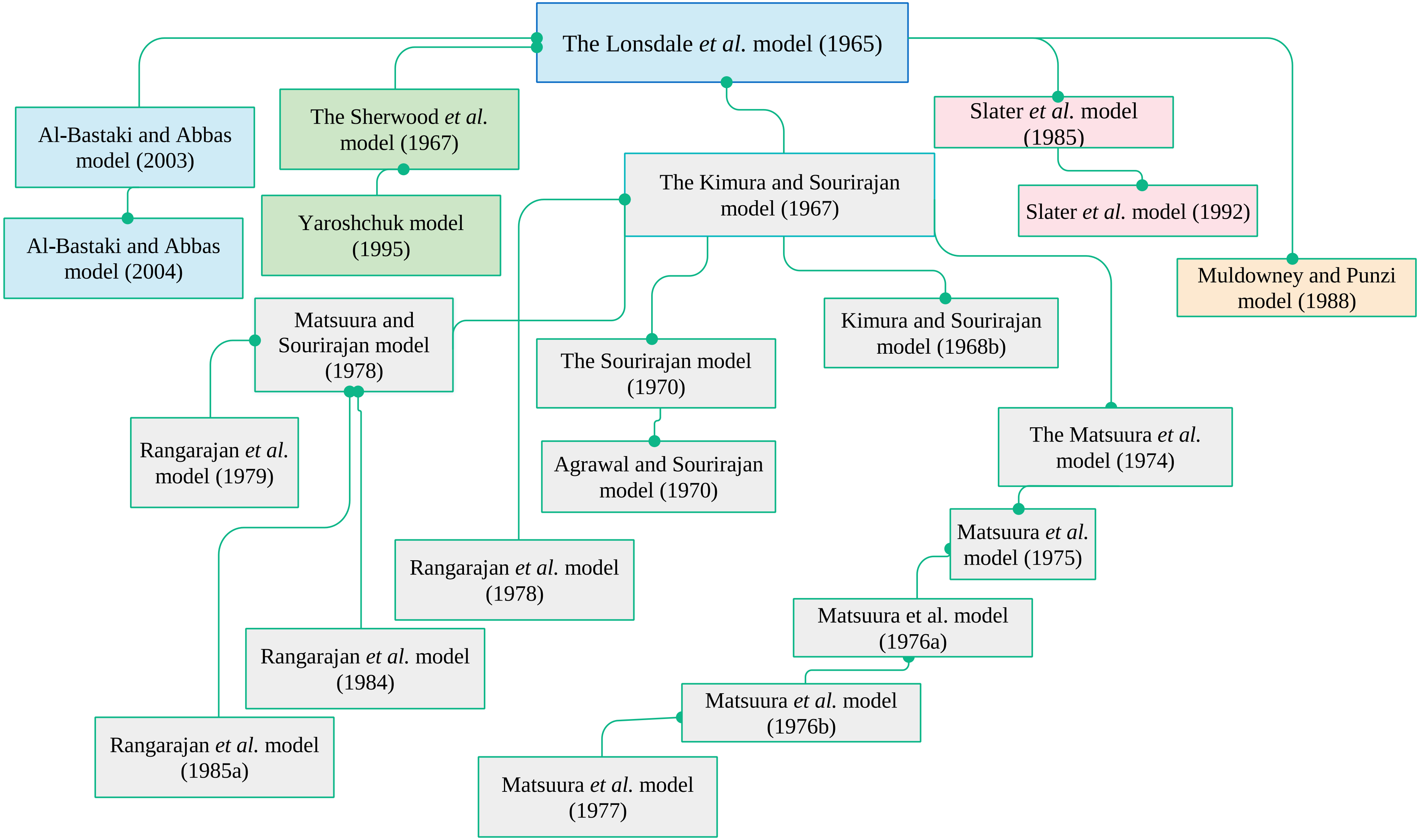

Fig. 3. The evolution of the solution diffusion model

3.1 The Lonsdale *et al.* Model

The beginning stage of the solution diffusion model was proposed by Lonsdale *et al.* (1965) who insists that the separation process can be achieved in reverse osmosis units by both dissolving and diffusing of each species in the solution (salt and solvent) independently through the membrane with dropping of the interaction between salt-solvent-membrane. This model assumes that the process of separation is managed through a homogeneous (non-porous) membrane, which combines three stages – the sorption of components through the membrane followed by diffusion through the membrane and finally desorption on the dilute side. In addition, the rate of diffusion is controlled by the effects of chemical potential gradients, such as the applied pressure and the concentration difference across the membrane for water and salt respectively. Therefore, the fluxes of these species through the membrane are restricted with the rates of its diffusivity for each species in the membrane (Lonsdale *et al.*, 1965; Jonsson, 1980).

The criterion of this model starts from the assumption of the equality between the fluids on either side of the membrane with the membrane interface. It also assumes that the pressure along the membrane is uniform which means that the pressure will hold the same value on the membrane interface in the instance of employing high pressure on the salted solution. Another assumption of this model is characterized by using the concentration gradient across the membrane to show the chemical potential difference of pressure between the two positions.

Wijmans and Baker (1995) have reviewed the process of deriving the first formulations of the solution diffusion model with regard to reverse osmosis units. In line with the starting equation of permeate movement, the flux can be described with regard to the chemical potential by:

$$j_i = -L_i \frac{d\mu_i}{dx}$$

(98)

Where L_i is the coefficient which relates the chemical potential with the flux, while μ_i can extract the chemical potential. The chemical potential parameter of reverse osmosis by which there are pressure and concentration difference forces can be written as:

$$d\mu_i = RT\, d\ln\,(\gamma_i\ C_i) + V_i\ dP$$

(99)

$$\mu_i = \mu_i^{\circ} + RT\ln(\gamma_i\ C_i) + V_i\,(P_i - P_i^{\circ})$$

(100)

Where $P_i^{\circ}, \mu_i^{\circ}, \gamma_i$ and V_i are the reference pressure, the chemical potential of ion *i* at reference pressure, the activity coefficient for the ion *i* and molar volume of ion *i* respectively.

As there is no pressure gradient along the membrane interface and the gradient in chemical potential across the membrane is expressed as a smooth gradient in solvent activity $\gamma_i \; C_i$, the combination of the Eqs. (98) and (99) yields.

$$J_i = \frac{-RT\,L_i}{C_i}\frac{dC_i}{dx} \tag{101}$$

According to Fick's law, $(\frac{RT\,L_i}{C_i})$ is already can be replaced by the diffusion coefficient D_i and the above expression can be written as:

$$J_i = -D_i\,\frac{dC_i}{dx}$$

(102)

Integrating the above equation over the membrane thickness yields.

$$J_i = -D_i\,(C_{i1m} - \; C_{i3m})$$

(103)

Where C_{i1m} and C_{i3m} are the concentration of ion *i* at the membrane interface in both feed side and permeate side respectively.

In case of reverse osmosis where the chemical potentials on both sides of the membrane are the same, this yields two cases:

Case 1: At the feed side ($x = o$), the concentration at the membrane side C_{i1m} is written by:

$$C_{i1m} = K_i^{\circ} \; C_i^{\circ}$$

(104)

Where K_i° and C_i° are the sorption coefficient and represents the activity coefficients $(\frac{\gamma i^{\circ}}{\gamma i_m^{\circ}})$ and the concentration at feed side respectively. Where γi° and γi_m° are the standard chemical potential of ion *i* at both the feed side and at the membrane interface at feed side.

Case 2: At the permeate side ($x = \ell$) where there is a pressure difference and by the equating of chemical potential, $\mu_{i\ell} = \mu_{i\ell m}$ yields.

$$\mu_{i0} + RT\,ln(\gamma_{i\ell} \; C_{i3}) + \; V_i\,(P_\ell - P_i) = \mu_{i0} + RT \; ln(\gamma_{i\ell m}\,C_{i3m}) + \; V_i\,(P_o - P_i)$$

(105)

Where P_o and P_ℓ are the pressure on the feed and permeate phase respectively. Also $\gamma_{i\ell}$ and $\gamma_{i\ell m}$ are the standard chemical potential of ion *i* at both the permeate side and at the membrane interface at permeate side.

By re-arranging the above equations.

$$C_{i3m} = K_i^{\circ}\ C_{i3}\ \ exp\left(\frac{-V_i\,(P_o - P_\ell)}{RT}\right)$$

(106)

This equation can be substituted with the Fick's law to produce.

$$J_i = \frac{D_i\,K_i^{\circ}}{\ell}\left[C_{i1} - C_{i3}\ exp\left(\frac{-V_i\ (P_o - P_\ell)}{RT}\right)\right]$$

(107)

Eq. (107) can introduce the water and salt fluxes in reverse osmosis, as:

1 – For water flux J_w:

In case of osmotic equilibrium and no water flow ($J_i = J_w = 0$), Eq. (107) can be written as:

$$C_{w3} = C_{w1}\ exp\left(\frac{V_w\,(P_o - P_\ell)}{RT}\right) = C_{w1}\ exp\left(\frac{V_w\,\Delta\pi}{RT}\right)$$

(108)

The combination of Eqs. (107) and (108) yields.

$$J_w = \frac{D_w\,K_w^{\circ}\,C_{w1}}{\ell}\left[1 - exp\left(\frac{-V_w\,(\Delta P - \Delta\pi)}{RT}\right)\right]$$

(109)

This equation can be simplified to be:

$$J_w = \frac{D_w\,K_w^{\circ}\,C_{w1}\,V_w\,(\Delta P - \Delta\pi)}{\ell\ RT}$$

(110)

Where K_w° is the sorption coefficient of water phase and membrane phase, ($K_w^{\circ} = \frac{C_{wm}}{C_{w1}}$).

2 – For Solute flux J_s:

The application of Fick's law assumes that the solute flux is not moved by the pressure gradient. Then, Eq. (107) can be simplified below when the term ($\frac{-V_s\,(P_o - P_\ell)}{RT}$) is close to one, as:

$$J_s = \frac{D_{sm}\ K_s^{\circ}}{\ell}\left[C_{s1} - C_{s3}\right]$$

(111)

Where K_s° is the sorption coefficient of solute and membrane, ($K_s^{\circ} = \frac{C_{sm}}{C_{so}}$).

Hence, according to Lonsdale *et al.* (1965), the solvent and salt fluxes J_w and J_s can be assessed by using the expressions:

$$J_w = A\ (\Delta P - \Delta\pi) \tag{112}$$

Where $A = \frac{D_w\,K_w^{\circ}\,C_{w1}\ V_w}{\ell\ RT}$ (113)

Where A is the pure water permeability constant in the membrane, which is independent of salt concentration and equivalent in the case of zero concentration polarization and Cw_1 is the concentration of water dissolved in the membrane. In addition, the salt flux is formulated as:

$$J_s = B\ [C_{s1} - C_{s3}] \tag{114}$$

Where $B = \frac{K_s^{\circ}\ D_{sm}}{\ell}$ (115)

Lonsdale *et al.* (1965) stated that the membrane solvent water permeability constant A depends on the structure of the membrane, while the salt permeability constant B depends on salt composition and membrane structure. Likewise, $(\Delta P - \Delta\pi)$ can identify the quantity of force per unit area needed to cope with the osmotic pressure and release pure water from the solution. It is easy to see that this model assumes that the salt flux does not depend on the pressure difference.

Then, the salt rejection rate has been written in the form of:

$$R_s = 1 - \frac{J_s}{\rho_s^1\ J_w} = 1 - \frac{D_{sm}\, K\, RT\ \Delta\rho_s}{D_w\, C_w\, V_w\ \rho_s^1\ (\Delta P - \Delta\pi)} \tag{116}$$

- Where ρ_s^1 is the density of the salt in the high-pressure feed side and K is the distribution coefficient for salt, which is the reciprocal of the sorption coefficient, $\left(K = \frac{C_s\ x_s}{C_{sm}\ x_{sm}}\right)$ and means that the distribution ratio of solute is constant in both the solution and the membrane.

Finally, one of the imperfections of this model that it contains only two parameters need to be estimated experimentally. Also, it neglects the impact of pressure on solute flux, pore flow and the membrane characteristics are not included. Soltanieh and Gill (1981) confirmed that the model is limited to membranes with low water content. However, the solution diffusion model has been widely considered as one of the simplest non-porous or homogeneous models related to transport mechanism through the membrane (Mujtaba, 2012).

3.2 The Sherwood *et al.* Model

The solution diffusion model of Lonsdale *et al.* (1965) has been modified by Sherwood *et al.* (1967) by addressing the shortcomings of the solution diffusion model including; the convection effect (pore flow) and solute-solvent-membrane interactions. Sherwood *et al.* (1967) have assumed the existence of small imperfections or pores over the membrane surface where the solutes are convectively transported without any change of concentration. Therefore, the total transport phenomenon formulated to include pore flow in addition to diffusion of water and solute through the membrane. However, this model is based on the assumption that the concentration at the exit of the pore is the same at the entrance.

The water and solute transport equations are written in the form of:

$$J_w = A_m\,(\Delta P - \Delta\pi) + A_i\,(\Delta P)$$

(117)

$$J_s = B\,[C_{s1} - C_{s3}] + A_i(C_{s1}\,\Delta P)$$

(118)

Where A_m, A_i and B are the equivalent water permeability coefficient, the mechanical permeability of the pores and the solute permeability coefficient respectively. The first and second terms of Eq. (117) are referred to the diffusive flux and pore water flow respectively. While, the solute flux through the pores is described by the second term of Eq. (118).

However, one of the inadequacies of Sherwood *et al.* (1967) model is that it contains three parameters that should be addressed by nonlinear regression. Also, the permeability coefficients are considered as constants, which is actually varied from point to point along the membrane surface due to spatial variation of concentration and pressure. Also, the model claims that the transport coefficients are function of feed concentration and pressure (Soltanieh and Gill, 1981) and finally calculates lower water flux for organic solutes.

3.3 The Kimura and Sourirajan Model

Kimura and Sourirajan (1967) achieved the second advance of the solution diffusion model by developing a specific structure of this model based on binary aqueous solutions (one solute system). The basic equations for their analysis were formulated to quantify the transport of solvent through the porous cellulose acetate membrane. Originally, they pursued the combination of film theory model with pore diffusion model, which can be utilized for whatever type of aqueous solution system that contains a single solute and compatible to cellulose acetate membranes with different porosities. They illustrated that the solvent water transport is strongly driven by the pressure difference and function of feed concentration and flow rate, while the solute transport is proportional to its concentration gradient. Thus,

$$J_w = A\,(\Delta P - \Delta\pi) = A\{P - \pi(x_{s2}) + \pi(x_{s3})\}$$

(119)

Where $A = \frac{PWP}{3600\,M_w\,S\,P}$

(120)

PWP and S are the pure water permeation rate and the effective membrane surface area respectively. While, the transport of solute through the membrane, which is caused by pore diffusion can be estimated from:

$$J_s = \frac{C_{sm}\ D_{sm}}{\delta}(x_{sm2} - x_{sm3}) \tag{121}$$

Where x_{sm2} is the mole fraction of the solute in the membrane phase in equilibrium withx_{s2}. Also, x_{sm3} is the mole fraction of the solute in the membrane phase in equilibrium with x_{s3}. The above equation can be re-arranged to include the distribution coefficient of solute between the membrane and water, ($K = \frac{C_s\ x_s}{C_{sm}\ x_{sm}}$), as:

$$J_s = \frac{D_{sm}}{K\ \delta}\ (c_{s2}\ x_{s2} - c_{s3}\ x_{s3}) \tag{122}$$

Where $B = \frac{D_{sm}}{K\ \delta}$

(123)

B is the solute transport parameter in the membrane, which depends on the type of the solute and independent of the feed flow rate. Also, the mole fraction of solute in the permeate side can be calculated from:

$$\left(x_{s3} = \frac{J_s}{J_s + J_w}\right) \tag{124}$$

$$J_s\ x_{w3} = J_w\ x_{s3} \tag{125}$$

Which means,

$$J_s = \frac{x_{s3}\ J_w}{(1 - x_{s3})} \tag{126}$$

Where x_{w3} is the mole fraction of water in the permeate side. In addition, it is simply to elucidate another equation to calculate the water flux, as:

$$J_w = \frac{D_{sm}}{K\ \delta}\frac{(1 - x_{s3})}{x_{s3}}(C_{s2}\ x_{s2} - C_{s3}\ x_{s3}) \tag{127}$$

In respect of an experimental data of this work, it is investigated that the solute transport parameter B is independent of feed concentration, flow rate and chemical nature of solute. Furthermore, the values of A and B are affected by the operating pressure and related with the type of porous membrane, which interprets its different values (Kimura and Sourirajan, 1968a).

Finally, Kimura and Sourirajan (1967) developed an equation to estimate the mass transfer coefficient k on the high-pressure side of the membrane, which defined implicitly in the formal style of film theory model. Besides, they showed the combination of the film theory model (Eq. 54) with the solvent water flux as indicated below.

The Maxwell-Stefan equation can predict the solute transport through the membrane phase thickness (δ) as follows:

$$J_s = x_s\,(J_s + J_w) - D_{sw}\,C_{s1}\,\frac{d_{xs}}{dx}$$

(128)

The integration of the above equation within the conditions at ($x = 0$, $x_s = x_{s1}$) yields.

$$ln\frac{(x_{s2}-x_{s3})}{(x_{s1}-x_{s3})} = \frac{\delta}{C_{s1}\,D_{sw}}(J_s + J_w) = \frac{J_s+J_w}{k\,C_s}$$

(129)

Where $k = \frac{D_{sw}}{\delta}$

(130)

Eq. (129) can be written for water and solute flux as illustrated below:

$$J_w = k\,C_{s1}\ \ (1 - x_{s3})\ \ ln\left(\frac{x_{s2}-x_{s3}}{x_{s1}-x_{s3}}\right)$$

(131)

$$J_s = k\,C_{s1}\,(x_{s3})\,ln\left(\frac{x_{s2}-x_{s3}}{x_{s1}-x_{s3}}\right) \qquad (132)$$

Agreeing to the above expressions, it is easy to see that this analysis brings into perspective the issue of concentration polarization by comprising the term k, which shows the mass transfer coefficient on the high-pressure side of reverse osmosis membranes.

In the case of assuming constant molar densities of the solution ($C_{s1} = C_{s2} = C_{s3} = C_s$), the above equations can be written as:

$$J_w = k\,C_s\,(1 - x_{s3})\,ln\left(\frac{xs_2-xs_3}{xs_1-xs_3}\right)$$

(133)

$$J_s = \ C_s\,\frac{D_{sm}}{K\,\delta}(x_{s2} - x_{s3}) \qquad (134)$$

In addition, the solute rejection R_s can be calculated from:

$$R_s = 1 - \frac{m_3}{m_1}\ =\ 1 - \frac{xs_3\ \ x_{w1}}{x_{w3}\ \ xs_1}\ =\ \ 1 - \frac{xs_3(1-xs_1)}{xs_1(1-xs_3)} \qquad (135)$$

Where m_1 and m_3 are the molality of solute in the feed and product side respectively. Furthermore, Kimura and Sourirajan (1968a) has incorporated some assumptions;

($J_s << J_w$ and $x_{s3} << 1$), which manipulate the above equations in order to find the mole fraction and the solute concentration in the permeate side, as indicated below.

$$x_{s3} = \frac{J_s}{J_w} \qquad (136)$$

$$J_w = k\,C_s\ \ ln\left(\frac{x_{s2}-x_{s3}}{x_{s1}-x_{s3}}\right) \qquad (137)$$

This finally introduces,

$$x_{s3} = \frac{\frac{D_{sm}}{K\,\delta}}{k\,(1-x_{s3})} \frac{(x_{s2}-x_{s3})}{ln\left[\frac{x_{s2}-x_{s3}}{x_{s1}-x_{s3}}\right]} \quad (138)$$

Kimura and Sourirajan (1968b) and Ohya and Sourirajan (1969) have applied the same previous correlations of Kimura and Sourirajan (1967) into a system of aqueous sucrose and a system of aqueous urea respectively in order to measure the membrane separation performance. They inferred that these correlations are applicable for such systems, and the solute transport parameter ($\frac{D_{sm}}{K\,\delta}$) of sucrose decreases with the increase of the mole fraction of sucrose in the membrane solution x_{s2}. The experimental data confirm that both water permeability constant and solute transport parameter are dependent on the porous structure of the membrane surface, and functions of operating pressure. Also, solute transport parameter is dependent on the chemical nature of the solute.

3.4 The Sourirajan Model

Sourirajan (1970) has extensively advocated the previous statement of the Kimura and Sourirajan (1967) model for the case where water is absorbed at the membrane-solution interface. In general, he exhibited some appropriate modifications for the basic transport equations in order to be suitable for low concentration aqueous multi-component systems in addition to single solute systems. He investigated another approach to obtain the product rate of a mixture of two inorganic salts in aqueous solution containing two solutes with a common ion, such as (s_1 $-$H$_2$O) and (s_2 $-$H$_2$O).

The final equations of this modelling are given for calculating of the mole fraction of each solute in the feed and product sides as follows.

$$x_{s1} = \frac{(m_1)_{s1}}{(m_1)_{s1}+(m_1)_{s2}}$$

(139)

$$x_{s2} = \frac{(m_1)_{s2}}{(m_1)_{s1}+(m_1)_{s2}}$$

(14-

)

Where m_1 is the molality of solute in the feed side. In addition, the production rate of the mixture is given by:

$$[PR]_{mix} = x_{s1}\,[PR]_{s1} + x_{s2}\,[PR]_{s2}$$

(141)

Alternatively, it can be written, as:

$$[PR]_{mix} = x_{s1}\ K_{s1}\ J_{s1} + x_{s2}\ K_{s2}\ J_{s2} + K_w\ (x_{s1}\ J_{w1} + x_{s2}\ J_{w2})$$

(142)

Where K_{s1}, K_{s2} and K_w are the appropriate conversion factors for solutes 1 and 2 and water respectively.

Consequently, the molalities of solutes in the permeate side can be estimated from:

$$(m_3)_{s1} = 1000\ \frac{x_{s1}\ K_{s1}\ J_{s1}}{M_{s1}\ K_w\ (x_{s1}\ J_{w1} + x_{s2}\ J_{w2})} = 55.5\ \frac{x_{s1}\ J_{s1}}{x_{s1}\ J_{w1} + x_{s2}\ J_{w2}}$$

(143)

$$(m_3)_{s2} = 55.5\ \frac{x_{s2}\ J_{s2}}{x_{s1}\ J_{w1} + x_{s2}\ J_{w2}}$$

(144)

Where $\frac{K_{s1}}{K_w} = \frac{M_{s1}}{M_w}$

(145)

M_{s1} is the molecular weight of solutes 1. Ultimately, the solute rejection expressions for both solutes 1 and 2 can be written as:

$$R_{s1} = \frac{(m_1)_{s1} - (m_3)_{s1}}{(m_1)_{s1}}$$

(146)

$$R_{s2} = \frac{(m_1)_{s2} - (m_3)_{s2}}{(m_1)_{s2}}$$

(147)

Furthermore, for low concentration systems containing more than two inorganic solutes with a common ion, the above expressions can be extended to:

$$x_{si} = \frac{(m_1)_{si}}{\sum (m_1)_{si}}$$

(148)

$$[PR]_{mix} = \sum x_{si}\ [PR]_{si}$$

(149)

Finally, the water product rate through a given area of the membrane can be calculated from:

$$PR = \frac{3600\ (J_w\ M_w\ S)}{\left[1 - \left(\frac{1}{1 + \frac{1000}{m_1 (1 - R_S)\ M_S}}\right)\right]} \qquad (150)$$

Where M_s is the mole fraction of the solute.

The above technique of predicting membrane separation can be successfully employed for high concentration mixed inorganic solutes systems with a common ion as shown experimentally by Agrawal and Sourirajan (1970). Indeed, Matsuura and Sourirajan (1971) for aqueous systems of organic solutes using porous cellulose acetate membrane have used the same correlations in single solute systems. They indicated that the solute separation rates and water flux decreases with the increase of feed concentration.

3.5 The Matsuura *et al.* Model

In the field of single and mixed alcohols separation in aqueous solution systems, Matsuura *et al.* (1974) followed the previous expressions of the Kimura and Sourirajan (1967) model and implemented new equations to calculate the values of solute transport parameter and mass transfer coefficient in the cellulose acetate membrane.

For a single solute system, the mass transfer coefficient for alcohol in the high-pressure side of the membrane can be estimated from Eq. (151) in accordance to sodium chloride-water reference solution.

$$k = k_{(ref)} \left[\frac{D_{sw}}{D_{sw(ref)}}\right]^{2/3}$$

(151)

In addition, the alcohol transport parameter can be measured from:

$$\left(\frac{D_{sm}}{K\,\delta}\right) = \frac{[PR]}{3600\,S\,\rho}\,\frac{I - R_S}{R_S}\left[\!\left[\frac{1}{exp\left[\frac{[PR]}{3600\,S\,k\,\rho}\right]}\right]\!\right]$$

(152)

Where ρ is the density of the solution.

Finally, for mixed solute systems of different number of alcohols and under the assumption of a negligible osmotic pressure of alcohol at the feed solution, Matsuura *et al.* (1974) have experimentally concluded that the alcohol separations of mixed solute systems are similar to what was investigated for the single solute system. Likewise, for a system of alcohol in an aqueous sucrose feed solution, they indicated that the alcohol separation rate is decreased for a number of reasons, such as the reduction of mass transfer coefficient of alcohol is reduced due to the high viscosity of sucrose solution. Secondly, the fluid flow is decreased due to an increase of the osmotic pressure of sucrose solution. The above work has expanded the practical implementation of reverse osmosis membrane in concentration of fruit juices.

Interestingly, Matsuura *et al.* (1975) have used another technique to determine the solute transport parameter $(\frac{D_{sm}}{K\,\delta})$ of completely ionized inorganic of mono-valent cations and anion through cellulose acetate membrane with assuming a negligible osmotic pressure of the feed solution as can be shown in Eq. (153). Eq. (153) shows the concept of using the energy parameter for ion $i, (-\frac{\Delta\Delta G}{RT})_i$ and can be obtained in the case of knowing $ln\, C^*_{NaCl}$ as a reference for ($NaCl$ – H_2O) solution. This approach can be effectively used in the modelling equations to determine the membrane separation of different porosities for organic and non-organic solutes corresponding to a single aqueous salt data of $NaCl$.

$$ln\left(\frac{D_{sm}}{K\,\delta}\right)_{salt,solute} = ln\, C^*_{NaCl} + \sum\left(-\frac{\Delta\Delta G}{RT}\right)_i \qquad (153)$$

0r $$ln\left(\frac{D_{sm}}{K\,\delta}\right)_{salt} = ln\, C^*_{NaCl} + \left[n_c\left(-\frac{\Delta\Delta G}{RT}\right)_{cation} + n_a\left(-\frac{\Delta\Delta G}{RT}\right)_{anion}\right] \qquad (154)$$

Where n_c and n_a are the number of moles for the cation and the anion in one mole of the ionized solute respectively. Also $ln\, C^*_{NaCl}$ can be calculated from:

$$ln\, C^*_{NaCl} = ln\left(\frac{D_{sm}}{K\,\delta}\right)_{NaCl} - \left[\left(-\frac{\Delta\Delta G}{RT}\right)_{Na^+} + \left(-\frac{\Delta\Delta G}{RT}\right)_{Cl^-}\right] \qquad (155)$$

The quantity $ln\, C^*_{NaCl}$ in Eq. (155) is a constant and can describe the structure of the membrane surface and the effective average pore size while the quantity $(-\frac{\Delta\Delta G}{RT})$ is a dimensionless polar parameter and a function of the chemical nature of the solute and membrane structure. Also,

$$\Delta\Delta G = \Delta GI - \Delta GB$$

(156)

Where ΔG is the free energy of hydration and I, B indicate the membrane-solution interface and the bulk solution respectively. Simply, the quantity $\Delta\Delta G$ can be defined as the required energy to facilitate the moving of ion from the bulk solution to the membrane interface. Hence, the preferential of water and the solute separation rates will increase by decreasing on this value for involved ion (Rangarajan *et al.*, 1976; Matsuura and Sourirajan, 1978).

In addition, Matsuura *et al.* (1975) have investigated another equation to predict the solute transport parameter for completely non-ionized polar organic solutes (aliphatic and alicyclic) in aqueous solutions as follows.

$$ln\left(\frac{Ds_m}{K\,\delta}\right)_i = ln\, C^*_{NaCl} + ln\,\Delta^* + \left(\frac{-\Delta\Delta G}{RT}\right) + \delta^* \sum Es \qquad (157)$$

The final term of the above equation describes the steric effect of the solute transport parameter. Obviously, the parameter δ^* is a function of the porous structure of the membrane, the solute and solvent materials. In addition, the part $\sum E_s$ expresses the steric parameter of the replaced alcohol molecular group. Furthermore, the above equation has been qualified by the addition of another term $\omega^* \sum s^*$ for the considering of the impact of non-polar character of the solute transport parameter. Therefore, the above equation can be expanded to:

$$ln\left(\frac{Ds_m}{K\,\delta}\right)_i = ln\, C^*_{NaCl} + ln\,\Delta^* + \left(\frac{-\Delta\Delta G}{RT}\right) + \delta^* \sum E_s + \omega^* \sum s^* \qquad (158)$$

Where $\sum E_s$ indicates the Taft's steric parameter for the organic molecule group, while δ^* is the corresponding parameter to $\sum E_s$. Also, $\sum s^*$ can express the nonpolar character impact of the replaced alcohol molecule group and ω^* is the applicable coefficient and as a function of carbon atoms and molecular branching structure which associated with $\sum s^*$.

The most significant point about the above equations is the ability to calculate the value of solute transport parameter for any completely ionized organic or inorganic solutes or completely non-ionized polar organic solutes.

The combination of the above three parameters ($\sum E_s$, δ^* and $\sum s^*$) can interpret the characteristics of solute separation, where the polar parameter can be viewed as a repulsive or attractive force at the membrane surface according to the case of membrane. Indeed, the steric factor can have an impact on the water sorption rate in addition to non-polar parameter, which attracts the solute to the membrane and decrease the water sorption (Matsuura and Sourirajan, 1978).

Rangarajan *et al.* (1976) have applied the same above physicochemical criteria approach to predict the membrane separation rate within inorganic solutions involving polyvalent ions. This work demonstrated that the ion-pair formation can promote the value of $(\frac{D_{sm}}{K\,\delta})$, which finally reduce the quality of membrane separation.

Furthermore, for non-dissociated (non-ionized) polar organic solutes in dilute aqueous solutions, Matsuura *et al.* (1976a) have used the same previous modelling of predicting the membrane separation for 61 non-ionized organic solutes by estimating the quantity of free energy parameter for each solute using cellulose acetate membrane. It is concluded that the membrane separation for each ion is affected by the combination of three factors; the polar free energy parameter $(\frac{-\Delta\Delta G}{RT})$, steric parameter $(\delta^* \sum E_s)$ and the non-polar parameter $(\omega^* \sum s^*)$.

On the basis of reverse osmosis separation predication for partially dissociated organic acids in dilute aqueous solutions, Matsuura *et al.* (1976b) have achieved a combination of free energy parameter data for both ionized and non-ionized solutes with relying on cellulose acetate membrane data for (NaCl–H2O) solution. This study showed that there is a unique relationship between the dissociated ion and the dissociation constant term $P\,K_a$. Granting to the free energy parameter relation of Matsuura *et al.* (1975), the solute transport parameter for $RCOO^{-}H^{+}$ can be written as:

$$ln\left(\frac{Ds_m}{K\,\delta}\right)_{RCOO^{-}H^{+}} = ln\,C^*_{NaCl} + \left(-\frac{\Delta\Delta G}{RT}\right)_{RCOO^{-}} + \left(-\frac{\Delta\Delta G}{RT}\right)_{H^{+}} \qquad (159)$$

In addition, for un-dissociated acids (such as, mono-carboxylic acids), Eq. (156) has been successfully used.

Matsuura *et al.* (1977) have extensively used the previous criterion for studying the prediction of reverse osmosis solute separation for 33 dilute alcohols aqueous solutions $C_1 - C_9$ using porous cellulose acetate membrane. It is accepted that the high alcohols with high non-polar impact will amend the sorption of water and increase the sorption of solutes in the membrane interface. According to their experiments, which is based on assuming that the numerical value of the free energy parameter $(-\frac{\Delta\Delta G}{RT})$ depends only on the chemical nature of solute, solvent, and membrane material, and it is independent of the porous structure of the membrane surface, they concluded that it is possible to determine the rate of alcohol solute separation for any type of alcohol in the case of knowing both the solute transport parameter and the water transport parameter for only $NaCl$ aqueous solution. As well as this, they ascertained that the rate of solute rejection is restricted with three parameters, polar free energy parameter, steric and non-polar coefficients. Furthermore, Eq. (158) has been reduced by neglecting the term ($\delta^* \sum E_s$), which is quite applicable for the basic relation for estimation the solute transport parameter for alcohols.

However, one of the imperfections of this method that it is only implemented for dilute aqueous organic systems. Also, for aromatic polyamide membrane, the effect of solute concentration on the free energy parameter has not included. Furthermore, the effect of pressure, temperature, feed concentration and the chemical nature of the membrane on the free energy parameter has not investigated. Also, the implementation of the free energy parameter on multiple solute system has not been included.

Recently, the concept of the free energy parameter which is governing non-ionized polar organic solutes in aqueous solution reverse osmosis separation has been used by A'lvarez *et al.* (1998) and Al-Obaidi *et al.* (2017) to predict the solute transport parameters of aroma and sugar compounds.

3.6 The Rangarajan *et al.* Model

Interestingly, Rangarajan *et al.* (1978) have applied the old approach of single solute modelling of the Kimura and Sourirajan (1967) to measure its capability of analyzing mixed solute electrolyte systems containing several ions in aqueous solutions with no common ion for cellulose acetate membranes. This method has been employed to extend the transport equations of the single solute system to be suitable for assessing the performance of separation for a system including several ions in aqueous solutions.

In fact, Rangarajan *et al.* (1978, 1979) have experimentally applied two types of inorganic electrolyte mixtures of uni-univalent electrolyte solutes system containing aqueous solution of two different cations and two different anions and secondly, one uni-univalent and one divalent-univalent electrolyte system respectively. It is suggested that this can predict some difference in the mathematical expressions of these mixtures, which is due to the change of valency. The criterion of free energy parameter has been used to find the solute transport parameter for each ion. As exemplified above, the prediction, technique depends only on the data of the water transport parameter A and the solute transport parameter $(\frac{D_{sm}}{K\,\delta})$ with aqueous sodium chloride feed solution. In addition, these data include the physico-chemical properties of each ion, such as: self-diffusion coefficient in water D_i, osmotic pressure and free-energy parameter for the transport of ions $\left(-\frac{\Delta\Delta G}{RT}\right)$, which shows the contribution of each ion to the solute transport parameter. Primarily, they are based on the transformation of single-solute equations to be suitable for a mixed-solute mixture for different aqueous solutions of two electrolyte solutes. The expanded final equations of water and each ion fluxes for a system of several ions in aqueous solution can be written in the form of:

$$J_w = A\,[P - \pi(\sum x_{i2})_{mix} + \pi(\sum x_{i3})_{mix}] \qquad (160)$$

$$J_i = \left(\frac{D_{im}}{K_{i2}\,\delta}\right) C_{i2}\ x_{i2} - \left(\frac{D_{im}}{K_{i3}\,\delta}\right) C_{i3}\ x_{i3} \qquad (161)$$

$$\text{Where } K_i = \frac{C_i\ x_i}{C_{im}\ x_{im}} \qquad (162)$$

$$\ln\left(\frac{x_{i2}-x_{i3}}{x_{i1}-x_{i3}}\right) = \frac{J_w+\sum J_i}{k\ C_{s1}} \qquad (163)$$

$$\text{Where } x_{i3} = \frac{J_i}{(J_w+\sum J_i)} \qquad (164)$$

The value of K_i is a distinct parameter for a mixture of solutes as the interfacial distribution coefficient for the ion in the solution.

In addition, the overall electro-neutrality equations for each phase are:

$$\sum z_i\ x_{i1} = 0, \qquad \sum z_i\ x_{i2} = 0, \qquad \text{and} \qquad \sum z_i\ x_{i3} = 0$$

It is equally permissible to assume that the molar density of the solution is constant and the flux of water is more outstanding than the flux of ions. In addition, a single average mass transfer coefficient can be used with considering of constant diffusivity of any salt or ion in membrane to water.

$$\frac{D_{sm}}{D_{sw}} = \frac{D_{im}}{D_{iw}}$$

(165)

It is allowable to assume that the osmotic pressure of a solution is proportional to the sum of the mole fraction of all ions and can be written as:

$$\pi(\sum x_i) = B_{av} \sum(x_i)_{mix} \tag{166}$$

Where B_{av} is an average proportionality constant, which can be found from the slop of mole fraction of single solutes $(a, b, c$ and $d)$ versus osmotic pressure. B_{av} could be estimated for a system according to the number of moles of ions that assigned after dissolving one mole of each salt in the mixture. For instance, a system of eight ions of four feed salts, B_{av} should be written in the form of:

$$B_{av} = \frac{B_a+B_b+B_c+B_d}{8} \tag{167}$$

Accordingly, Eqs. (160), (161) and (162) can be moderated and written in the form of:

$$J_w = A - A\, B_{av}[(\sum x_{i1})_{mix} - (\sum x_{i3})_{mix}]\, \alpha \tag{168}$$

Where $\alpha = exp\left(\frac{J_w}{k_{av}\ C}\right)$ (169)

The generalized ionic fluxes J_i can be written in the contour of Eq. (170) and the mole fraction for each ion in the permeate side is:

$$J_i = \left(\frac{D_{im}}{K_{i2}\ \delta}\right) C_i\, x_{i2} - \left(\frac{D_{im}}{K_{i3}\ \delta}\right) C_i\, x_{i3} \tag{170}$$

Where

$$x_{i3} = \frac{J_i}{J_w} \quad , \quad x_{13} = \frac{J_1}{J_w}, \quad x_{23} = \frac{J_2}{J_w} \quad \text{and} \quad x_{33} = \frac{J_3}{J_w} \tag{171}$$

Furthermore, the mole fraction of each ion in the high-pressure membrane side is:

$$x_{i2} = x_{i3} + (x_{i1} - x_{i3})\, \alpha \tag{172}$$

In order to find a solution of the Eq. (170), Rangarajan *et al.* (1978) have derived the basic equations to calculate the solute transport parameter $(\frac{D_{im}}{K_i\ \delta})$ for three different ions (1, 2 and 3) in terms of solute transport parameter $(\frac{D_{sm}}{K\ \delta})$ for different single salts (13, 14 and 23) and phase solution concentration in a system of four ions C_{xi} with their diffusivities D_i by relying on the assumption of Eq. (173).

$$\frac{D_{sm}}{D_{sw}} = \frac{D_{im}}{D_i} = \text{constant} \tag{173}$$

$$\frac{D_{1m}}{K_1\ \delta} = \left[\frac{C_{x3}+\beta_1\, C_{x4}}{C_{x1}+\beta_2\, C_{x2}}\right]^{0.5} \frac{D_1}{D_{13}} \left(\frac{D_{sm}}{K\ \delta}\right)_{13} \tag{174}$$

$$\frac{D_{2m}}{K_2\ \delta} = \left[\frac{C_{x3}+\beta_1\, C_{x4}}{C_{x2}+\frac{1}{\beta_2}C_{x1}}\right]^{0.5} \frac{D_2}{D_{23}} \left(\frac{D_{sm}}{K\ \delta}\right)_{23} \tag{175}$$

$$\frac{D_{3m}}{K_3\ \delta} = \left[\frac{C_{x1}+\beta_2\ C_{x2}}{C_{x3}+\beta_1\ C_{x4}}\right]^{0.5} \frac{D_3}{D_{13}} \left(\frac{D_{sm}}{K\ \delta}\right)_{13} \tag{176}$$

Where,

$$\beta_1 = \left(\frac{K_{13}}{K_{14}}\right)^2 = \frac{\left(\frac{D_{13}}{D_{14}}\right)^2 \left(\frac{D_{sm}}{K\ \delta}\right)^2_{14}}{\left(\frac{D_{sm}}{K\ \delta}\right)^2_{13}} \tag{177}$$

$$\beta_2 = \left(\frac{K_{13}}{K_{14}}\right)^2 = \frac{\left(\frac{D_{13}}{D_{23}}\right)^2 \left(\frac{D_{sm}}{K\ \delta}\right)^2_{23}}{\left(\frac{D_{sm}}{K\ \delta}\right)^2_{13}} \tag{178}$$

The value of the average mass transfer coefficient k_{av} for a mixed solute system of four salts can be keyed out from:

$$k_{av} = \frac{\sum_{i=1}^{4} ki}{4} = \frac{k_1+k_2+k_3+k_4}{4} \tag{179}$$

Likewise, the mass transfer coefficient for each ion in the solution can be calculated from the Eq. (179) with regard to an aqueous solution of $NaCl$ as a reference system.

Sequentially, for the purposes of finding the interfacial equilibrium constant for a single salt K, Rangarajan *et al.* (1978) proposed two equations to calculate this value for a different two cases:

1 – When the concentration of the salt is indicated by itself salt concentration:

$$K = \frac{C_s\ x_{(salt)}}{C_{sm}\ \ x_{(salt)m}} \tag{180}$$

2 – When the concentration of the salt is indicated by ionic concentrations:

$$K^{\wedge} = \frac{C_s\ x^{z-}_{(cation)}\ \ C_s\ x^{z+}_{(anion)}}{\left(C_{sm}\ x_{(cation)m}\right)^{z-}\ \ \left(C_{sm}\ x_{(anion)m}\right)^{z+}} \tag{181}$$

Where $K^{\wedge}$ is the interfacial equilibrium constants for single salts and Z^{+} and Z^{-} are the valencies of both the cation and the anion respectively and:

Since, $Cs\ \ x_{(cation)} = Z^{-}\ C_s\ x_{(salt)}$ and $C_s\ \ x_{(anion)} = Z^{+}\ C_s\ \ x_{(salt)}$ also:

$C_{sm}\ \ x_{(cation)m} = Z^{-}\ C_{sm}\ \ x_{(salt)m}$ and $C_{sm}\ \ x_{(anion)m} = Z^{+}\ C_{sm}\ \ x_{(salt)m}$

These yields:

$$K^{\wedge} = \left[\frac{C_s\ x_{(salt)}}{C_{sm}\ \ x_{(salt)m}}\right]^{(z^{+}+\,z^{-})} \tag{182}$$

Additionally, for the roles of estimating the solute transport parameter, Rangarajan *et al.* (1978) have pursued the concept of free energy parameter of ion similar to Matsuura *et al.* (1975) investigation as mentioned in the Eqs. (153) and (155).

For the aim of predicting the membrane separation for fruit juice and food sugars feed in aqueous solutions, Matsuura and Sourirajan (1978) have applied the same technique of the Kimura and Sourirajan (1967) with the basic equation of free energy parameter. A large number of non-ionized, partially and completely ionized organic solutes have been experimented to speculate the combination of polar free energy parameter, steric parameter and non-polar parameter on the solute transport parameter for each organic solute. In addition, they investigated a new equation to calculate $(\frac{D_{sm}}{K\,\delta})$ based on very low feed solutions on negligible osmotic pressure as:

$$\frac{D_{sm}}{K\,\delta} = \frac{PR}{3600\,S\,\rho}\,\frac{1-R_s}{R_s}\left[exp\,\frac{PR}{3600\,S\,k\,\rho}\right]^{-1}$$

(183)

Then, other authors have applied the same common modelling. For example, Malaiyandi *et al.* (1982) used the same old procedure for modelling of the food industry, including aqueous solutions of food sugar and food-acid mixed solutes from only reference data of sodium chloride aqueous feed solution. In fact, they followed the same approach of Matsuura *et al.* (1976b) for partially dissociated organic acids and un-dissociated organic solutes in a concentrated sugar solution of Matsuura and Sourirajan (1978).

Consequently, the solute flux for each species J_i and its boundary concentration x_{i2} and the permeate concentration x_{i3} respectively will be written in the form of:

$$J_i = \left(\frac{D_{im}}{K\,\delta}\right)(C_{i2}\;x_{i2} - C_{i3}\;\;x_{i3}) \qquad (i \;=\; 1 \text{ to the number of solutes } n)$$

(184)

$$x_{i2} = x_{i3} + (x_{i1} - x_{i3})\,exp(J_w + J_{i1} + J_{i2} + \cdots\, J_{in})$$

(185)

$$x_{i3} = \frac{J_i}{J_w + J_{i1} + J_{i2} + \cdots \ldots J_{in}}$$

(186)

In addition, the dissociation constant for the partially dissociated acid in the feed and the product streams can be calculated from the Eqs. (187) and (188).

$$x_{i1} = \frac{[(0.25\,K_a^2 + 1000\,C_1\,x_{m1}\;\,K_a) - (0.5\;\,K_a)]}{1000\,C_1}$$

(187)

$$x_{i3} = \frac{[(0.25\,K_a^2 + 1000\,C_3\,x_{m3}\,K_a) - (0.5\,K_a)]}{1000\,C_3}$$

(188)

Where x_{m1} and x_{m3} are the mole fraction of the acid on the high-pressure membrane side and low-pressure membrane side respectively. Also, K_a is the dissociation equilibrium constant for the acid at 25 °C.

Then, the fraction solute separation R_i and the total product rate PR can be illustrated by:

$R_i = 1 - \left[\frac{x_{i3}}{1-x_{i3}}\right]\left[\frac{1-x_{i1}}{x_{i1}}\right]$ (i = 1 to the number of solutes n)

(189)

$PR = [(J_w\ M_w) + (J_i\ M_i) + (J_{i2}\ \ M_{i2}) + \cdots (J_n\ \ M_n)]\ [3600\ \ S]$

(190)

Simultaneously, they suggested the same two equations for ionized and non-ionized ions developed by Matsuura *et al.* (1975) for the purposes of estimating values of any polar organic solute transport parameter $(\frac{D_{sm}}{K\delta})$ of each ion corresponding to reference solution $\left(\frac{D_{sm}}{K\delta}\right)_{\text{NaCl}}$ value as mentioned in the Eqs. (153), (155), (157) and (159).

In contrast, they incorporated the correlation of Hsieh *et al.* (1979) of the Eq. (191) to find data of mass transfer coefficient k_i for organic solutes in the mixed solute system.

$$k_i = D_i^{2/3}\left[\left(\frac{k_{NaCl}}{D_{NaCl}^{2/3}}\right) - 1.393x10^7\left(\mu - 8.963\ x\ 10^{-7}\right)\right] \tag{191}$$

Where μ is the kinematic viscosity.

As a consequence of the previous work of an electrolyte aqueous mixture of two uni-univalent solutes (Rangarajan *et al.*, 1978) and a mixture of uni-univalent and di-univalent, Rangarajan *et al.* (1979 and 1984) have investigated another improvement on the old model for the case of three uni-univalent electrolyte mixture, where another improvement has been done for a mixture of nine seawater ions included in eight inorganic electrolytes salts (Rangarajan *et al.*, 1985a). The work of Rangarajan *et al.* (1979 and 1984) has highlighted the implementation of different valencies in a mixture of different ions in the mixed solute system, which results in corresponding changes in the final mathematical expressions needed for prediction of membrane performance in reverse osmosis. Fundamentally, they used the extension of model equations of the single solute system to a mixture of solutes, which has been proposed by Kimura and Sourirajan (1967) and improved by Rangarajan *et al.* (1978) in the system of the Eqs. (160), (161) and (165). As a result, they concluded that this equation system could be used effectively for any number of ions.

The water flux of Eq. (160) has been moderated by imposing the assumption of osmotic pressure of a mixture of solutes, as: $\sum(x_i)_{mix} = \sum B_i\ (x_i)\ x_i$, then,

$$J_w = A\ P - A[(\sum B_i\ (x_{i2})\ (x_{i2})] + A\ [(\sum B_i\ (x_{i3})\ x_{i3}] \tag{192}$$

Then, the final ion flux equations of a system of three ions (1, 2 and 3) can be written as:

$$J_1 = \frac{D_{1m}}{K_{12}\ \delta}\ C_{x12} - \frac{D_{1m}}{K_{13}\ \ \delta}\ \ C_{x13} \tag{193}$$

$$J_2 = \frac{D_{2m}}{K_{22}\ \delta}\ C_{x22} - \frac{D_{2m}}{K_{23}\ \ \delta}\ \ C_{x23} \tag{194}$$

$$J_3 = \frac{D_{3m}}{K_{32}\ \delta}\ C_{x32} - \frac{D_{3m}}{K_{33}\ \delta}\ C_{x33} \tag{195}$$

Where

$$x_{12} = x_{13} + (x_{11} - x_{13})\ \alpha \tag{196}$$

$$x_{22} = x_{23} + (x_{21} - x_{23})\ \alpha \tag{197}$$

$$x_{32} = x_{33} + (x_{31} - x_{33})\ \alpha \tag{198}$$

$$\alpha = exp\left(\frac{J_w}{k\ C_i}\right) \tag{199}$$

Then, they derived equations relating to the equilibrium distribution coefficient for ion with respect to solution phase concentration and interfacial equilibrium constants for salts (12, 14, 16, 32 and 52) in a mixture of six ions, i.e.

$$\frac{1}{K_1} = \left(\frac{E}{K_{12}}\right)^{\frac{1}{2}}, \qquad \frac{1}{K_3} = \frac{(E\ K_{12})^{\frac{1}{2}}}{K_{32}}, \qquad \frac{1}{K_5} = \frac{(E\ K_{12})^{\frac{1}{2}}}{K_{52}}, \qquad \frac{1}{K_2} = \frac{K^{-0.5}}{K_{12}},$$
$$\frac{1}{K_4} = \left(\frac{K_{12}}{E}\right)^{\frac{1}{2}} \frac{1}{K_{14}} \quad \text{and} \quad \frac{1}{K_6} = \left(\frac{K_{12}}{E}\right)^{\frac{1}{2}} \frac{1}{K_{16}} \tag{200}$$

$$\text{Where } E = \left[\frac{(C_{x2}) + \frac{K_{12}^2}{K_{14}^2}(C_{x4}) + \frac{K_{12}^2}{K^2 16}(C_{x6})}{(C_{x1}) + \frac{K_{12}^2}{K_{32}^2}(C_{x3}) + \frac{K_{12}^2}{K_{52}^2}(C_{x5})}\right] \tag{201}$$

While, the mass transfer coefficient can be calculated from the Eq. (202) for each ion.

$$k_i = k_{NaCl}\left[\frac{D_i}{D_{NaCl}}\right]^{2/3} \tag{202}$$

The simplicity of the above equation can be attributed to the capacity of defining the values of diffusivities for any ion and $NaCl$ in water, which allows predicting the value of mass transfer coefficient of each ion. While, the average mass transfer coefficient k_{av} for a mixture of different four ions can identified from previous expression of the Eq. (202), which has been arrived at form the Eq. (203).

$$k_{av} = \frac{k_{NaCl}}{4\ D_{NaCl}^{2/3}}\left[(D_1^{2/3}) + (D_2^{2/3}) + (D_3^{2/3}) + (D_4^{2/3})\right] \tag{203}$$

3.7 The Slater *et al.* Model

Accordingly, another development of the solution diffusion model has been investigated by Slater *et al.* (1985) who achieved just about moderation and expansion of the solvent and solute flux equations in a reverse osmosis operating in a closed-loop mode. They stated that solvent flux could be combined with solute concentrations by using the Van't Hoff equation, which relates the osmotic pressure and solute concentration, as ($\pi = a_s\ C$), where a_s is the ratio of the osmotic pressure to solute concentration, which is assumed constant. Also, the approach of modelling is based on assuming constant solute concentration along the membrane length with neglecting both the concentration polarization and fouling impacts. Therefore, the concluding statement of their solvent and solute flux equations can be written as:

$$J_w = A\,[\Delta P - a_s\,(C_{s1} - C_{s3})] \tag{204}$$

$$J_s = B\ (C_{s1} - C_{s3}) \tag{205}$$

The permeate concentration can be found from Eq. (206) under the assumption of constant water concentration in both permeate and bulk side ($C_{w3} = C_{w1} = C_w$).

$$C_{s3} = C_{s1}\left[1 + \frac{A\ \Delta P}{B\ C_w} - \frac{A\ a_s\ C_{s1}}{B\ C_w}\right]^{-1} \tag{206}$$

Finally, the solvent flux equation can be written in another form as:

$$J_w = A\left[\Delta P - a_s\,C_{s1} + \frac{C_{s1}}{\left(1+\frac{A\,\Delta P}{B\,C_w} - \frac{A\,a_s\,C_{s1}}{B\,C_w}\right)}\right] \tag{207}$$

In addition, the production rate can be written as:

$$PR = \frac{S\,A}{C_w}\left[\Delta P - a_s\,C_{s1} + \frac{C_{s1}}{\left(1+\frac{A\,\Delta P}{B\,C_w} - \frac{A\,a_s\,C_{s1}}{B\,C_w}\right)}\right] \tag{208}$$

3.8 The Muldowney and Punzi Model

Muldowney and Punzi (1988) have investigated a correlation to calculate the solute rejection factor, which is nominated by $(\frac{C_{s1}}{C_{s3}})$ for the case of the solution diffusion model as indicated in the Eq. (209).

$$\frac{C_{s1}}{C_{s3}} = \frac{D_w}{D_{sm}}\frac{V_w}{RT}(\Delta P - \Delta\pi)\left[\left(\frac{C_{s1}}{C_{sm1} - C_{sm3}}\right)\ K_s\right] \tag{209}$$

Where ($K_s = \frac{C_{sm3}}{C_{s3}}$) is the permeate side distribution coefficient.

Slater *et al.* (1992) for a case of a closed-loop reverse osmosis operating system to deal with a solution of industrial wastewater (Electrochemical industry) have used the same correlations of the solution diffusion model. The growth of this model has been achieved by deriving the material balance equations with the investigation of a new equation for the solute rejection from combining of the main expressions of water, solute fluxes and solute rejection equation as mentioned in the Eq. (210) with considering no concentration polarization and fouling.

$$R_s = \left[1 + \frac{B\,C_{w3}}{A\,(\Delta P - \Delta\pi)}\right]^{-1} \tag{210}$$

The experimental data of this work showed some difference from the model prediction in both the solute rejection and water flux in the case of inorganic solutes. This difference can be ascribed to the impact of concentration polarization, which has been ignored and due to high osmotic pressure to solute concentration ratio in addition to high inorganic solute permeability in comparison with normal salt.

3.9 The Yaroshchuk Model

Yaroshchuk (1995) has modified the solution diffusion imperfection model of Sherwood et al. (1967) by arguing that the solute transport through the pore needs particular correction. This is because that the solute transport is carried out by simultaneous convection and diffusion which illustrates nonlinear solute concentration along the pore. Therefore, the solute flux through the pore of Eq. (118) has been re-written in a differential form of Eq. (211).

$$J_{si} = -P_i^* \frac{dC}{dx} + (C\, J_{wi})$$

(211)

Where J_{wi}, P_i^*, x refers to the water flux through the pore, the partial diffusional permeability of pore and the space variable scaled on the membrane thickness respectively. Here, C should be solved at given feed concentration and permeate concentration due to the existence of both the convection and diffusion flow through the pore.

The solution of Eq. (211) gives:

$$J_{si} = J_{wi} \frac{C_{s1} - C_{s3} \exp(-Pe)}{1 - \exp(-Pe)}$$

(212)

Where Pe is the dimensionless Pêlect number defined as the ratio of convection and diffusion inside the pore.

$$Pe = \frac{P_i^*}{A_i} \Delta P$$

(213)

Where A_i is the mechanical permeability of the pore.

3.10 The Al-Bastaki and Abbas Model

Al-Bastaki and Abbas (2003) and Al-Bastaki (2004) have further developed the use of the solution diffusion mass transport model with the theory of concentration polarization to improve the performance of spiral wound reverse osmosis and for the treatment of colored water effluents respectively. The improvement was enhanced by using of the theory of the Da Costa *et al.* (1994) to calculate the mass transfer coefficients and the pressure drop for flow inside a spacer-filled channel. In addition, they augmented the theory of dynamic membrane, which is formed by using concentrated dye in a solution of colored wastewater. The osmotic coefficient for salt and dye has been calculated by applying the theory of Debye-Hückel (Van Gauwbergen *et al.*, 1997), which shows a good prediction of osmotic pressure rather than using the equation of Van’t Hoff.

3.11 The Wang *et al.* Model

According to molecular advanced characterization techniques, the free volume of dense polymer membrane layer contains interconnected pore-like voids in the size range of 0.2–0.6 nm. This has weaken the assumption of homogeneous (non-porous) skin membrane layer anticipated by the classical form of the solution diffusion model proposed by Lonsdale *et al.* (1965). Therefore, Wang *et al.* (2014) have extended the solution diffusion model for NF/RO membranes by assuming a porous structure. Therefore, the concluding statement of their solvent and solute flux equations for the extended solution diffusion model can be written as:

$$J_w = \frac{k_d\, D_w^{\varphi}\, \varepsilon}{\Delta x}(1-\lambda_w)^2\, exp\left(\frac{-\Delta G_w^*}{k_B\, T}\right)\frac{V_w}{R\, T}(\Delta P - \Delta\pi) = A(\Delta P - \Delta\pi)$$

(214)

$$J_s = \frac{k_d\, D_s^{\varphi}\, \varepsilon}{\Delta x}(1-\lambda_s)^2\, exp\left(\frac{-\Delta G_s^*}{k_B\, T}\right)(\beta^* C_{s1} - C_{s3}) = B(C_{s2} - C_{s3})$$

(215)

Where k_d, $D_w^{\varphi}, D_s^{\varphi}, \lambda_w, \lambda_s$, $\Delta G_w^*, \Delta G_s^*, k_B, \beta^*$ and ε are the diffusive hindrance factor, water and solute diffusion coefficients in the bulk, water and solute membrane sieving factors, water and solute membrane interaction energies, the Boltzmann constant, concentration polarization factor[1] and porosity[2] respectively. The interesting findings of this model is that membrane water permeability is a function of membrane and water physical properties in addition to water chemical affinity. Therefore, this model addresses the impact of feed water chemistry on membrane transport and structural properties of polyamide composite membranes.

Finally, the solute rejection can be written in the form of Eq. (216).

$$R_s = 1 - \frac{\beta^* \frac{k_d\, D_s^{\varphi}\, \varepsilon}{\Delta x}(1-\lambda_s)^2\, exp\left(\frac{-\Delta G_s^*}{k_B\, T}\right)}{J_w + \frac{k_d\, D_s^{\varphi}\, \varepsilon}{\Delta x}(1-\lambda_s)^2\, exp\left(\frac{-\Delta G_s^*}{k_B\, T}\right)}$$

(216)

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[1] : Is defined as a ratio of salt concentration at the membrane surface (Cs_2) to bulk concentration (Cs_1)

[2] : Is defined as the volume of the pores divided by the total volume of the membrane

In a summary, Table 2 gives most features of the solution diffusion models demonstrating its evolution along the last period and its applications in different fields of seawater desalination and industrial wastewater treatment.

Table 2. Summary review of the solution diffusion model

No.	Author and year	Assumptions	The Specific Features and advantages	Shortcomings
1	Lonsdale *et al.* (1965)	• Assumes that the procedure of separation is managed through a homogeneous (non-porous) membrane. • Assumes the effects of chemical potential gradients control the rate of diffusion. • Assumes that the pressure along the membrane is uniform. • The salt flux does not depend on the pressure difference and results from concentration gradient.	• Explains the separation procedure in reverse osmosis units by both dissolving and diffusing of each species in the solution (solute and solvent) independently through the membrane. • Contains only two parameters need to be found experimentally. • Consider as the simplest model that can define the transport phenomenon through the membrane.	• Neglects the interaction between solute-solvent-membrane. • The solute flux is only dependent on solute concentration and the chemical potential due to pressure is neglected. • The pore flow is neglected. • Limited to only membranes with low water content. • Membrane characteristics are not included in the model.
2	Sherwood *et al.* (1967)	• Assumed the existence of small imperfections or pores over the membrane surface. • The concentration at the exit of the pore is the same at the entrance.	• Resolved the imperfections of the solution diffusion model proposed by Lonsdale *et al.* (1965). • Including the pore flow impact on both the solvent and solute fluxes.	• Contains three parameters that should be addressed by nonlinear regression. • The permeability constants are varied from point to point along the membrane surface due to spatial distribution of concentration and pressure and not constant as the model claimed. • The model parameters are function of feed concentration and pressure. • Calculates lower water flux for organic solutes.

Table 2. Summary review of the solution diffusion model (continued)

No.	Author and year	Assumptions	The Specific Features and advantages	Shortcomings
3	Kimura and Sourirajan (1967)	• Assumes the basic equations were written to quantify the transport of solvent through the membrane.	• Develops a specific structure for binary aqueous solutions (one solute system). • Explores the combination of the film theory model with the pore diffusion model. • Illustrated that the solvent water transport is strongly driven by the pressure difference, feed concentration and flow rate, while the solute transport is independent of feed concentration.	• Applicable only for a binary system.
4	Kimura and Sourirajan (1968b)	• Based on the same criterion of the Kimura and Sourirajan (1967) model.	• Uses the same previous correlations of the Kimura and Sourirajan (1967) model into a system of aqueous sucrose to measure the membrane separation performance. • Argues that the solute transport parameter of sucrose decreases with the increase of the mole fraction of sucrose in the membrane solution. • Confirmed both water permeability and solute transport coefficients are dependent on the porous structure of the membrane surface.	
5	Sourirajan (1970)	• Based on the same criterion of the Kimura and Sourirajan (1967) model.	• Investigates some appropriate adjustments for the basic transport equations in order to be suitable for multi-component systems. • Presents another approach to obtain the product rate and solute rejection for a mixture of two inorganic salts in aqueous solution containing two solutes with a common ion.	

Table 2. Summary review of the solution diffusion model (continued)

No.	Author and year	Assumptions	The Specific Features and advantages	Shortcomings
6	Agrawal and Sourirajan (1970)	• Based on the same criterion of the Sourirajan (1970) model.	• Illustrates that the above technique of predicting membrane separation can be successfully employed for high concentration mixed inorganic solutes systems with a common ion.	
7	Matsuura *et al.* (1974)	• Assumes a negligible osmotic pressure of alcohol at the feed solution.	• Predicts single and mixed alcohols separation in aqueous solution systems. • Implements a new equation to estimate the values of solute transport parameter and mass transfer coefficient. • Expanding the investigation of reverse osmosis membrane performance in during concentration of fruit juices.	• The presented model is applied for the case of low alcohol concentrations in aqueous sucrose feed solutions.
8	Matsuura *et al.* (1975)	• Assumes a negligible osmotic pressure of the feed solution. • The rate of solute rejection is restricted with three parameters, polar free energy parameter, steric and non-polar coefficients.	• Uses concept of the energy parameter ($-\frac{\Delta\Delta G}{RT}$) to determine the solute transport parameter of completely ionized inorganic of mono-valent cations and anion through cellulose acetate membrane and can be obtained in the case of knowing ($\ln C^*_{NaCl}$) as a reference for (NaCl – H2O) solution. • The above equations can be used to calculate the solute transport parameter for any completely ionized organic or inorganic solutes or completely non-ionized polar organic solutes.	• The effect of pressure, temperature, feed concentration and the chemical nature of the membrane on the free energy parameter ($-\frac{\Delta\Delta G}{RT}$) has not investigated. • The utility of area of the free energy parameter on multiple solute system has not been studied.

Table 2. Summary review of the solution diffusion model (continued)

No.	Author and year	Assumptions	The Specific Features and advantages	Shortcomings
9	Matsuura *et al.* (1976a)	• Assumes a negligible osmotic pressure of the feed solution.	• Uses the same previous modelling (Matsuura *et al.*, 1975) of predicting the membrane separation for non-dissociated (non-ionized) polar organic solutes in dilute aqueous solutions by estimating the quantity of free energy parameter for each solute using cellulose acetate membrane. • Affirms that the membrane separation for each ion is affected by the combination of three elements; the polar free energy parameter, steric parameter and the non-polar parameter. • Shows that the ion-pair formation can promote the solute transport parameter, which finally reduces the quality of membrane separation.	• The proceed method is only implemented for dilute aqueous organic systems. • For aromatic polyamide membrane, the effect of solute concentration on the free energy parameter has not yet been established.
10	Matsuura *et al.* (1976b)	• Assumes a negligible osmotic pressure of the feed solution compared to the operating pressure.	• Combines the free energy parameters data for both ionized and non-ionized solutes with relying on porous cellulose acetate membrane data for (NaCl–H_2O) solution to assess the separation of partially dissociated organic acids in dilute aqueous solutions. • Argues that there is a unique relation between the dissociated ion and the dissociation constant term (PK_a).	• The proceed method is only implemented for dilute aqueous organic systems.
11	Matsuura *et al.* (1977)	• The numerical value of the free energy parameter ($-\frac{\Delta\Delta G}{RT}$) depends only on the chemical nature of solute, solvent, and membrane material, and it is independent of the porous structure of the membrane surface.	• Examines the prediction of reverse osmosis solute separation for several dilute alcohols aqueous solutions using a cellulose acetate membrane. • Confirms that it is possible to determine the rate of alcohol solute separation for any type of alcohol in case of knowing both the solute transport parameter and the water transport parameter for only (NaCl) aqueous solution.	• The proceed method is only implemented for dilute aqueous organic systems.

			• Reduced the equation used to calculate the solute transport parameter considering dilute alcohol aqueous solutions.	

Table 2. Summary review of the solution diffusion model (continued)

No.	**Author and year**	**Assumptions**	**The Specific Features and advantages**	**Shortcomings**
12	Rangarajan *et al.* (1978)	• Assumes constant diffusivity of any salt or ion in membrane to water. • Assume that the osmotic pressure of a solution is proportional to the sum of the mole fraction of all ions. • A single average is used for mass transfer coefficient on the high-pressure side of the membrane.	• Expands the previous approach of the single solute equation of the Kimura and Sourirajan (1967) model to be compatible with mixed solute electrolyte systems containing several ions in aqueous solutions with no common ion for cellulose acetate membranes. • Measures the performance of separation of a system, including several ions in aqueous solutions. • Ascertains the applicability to inorganic electrolyte mixtures.	• The method has been only applied for cellulose acetate membranes. • The method neglected the implementation of ions have different valencies.
13	Matsuura and Sourirajan (1978)	• Assumes a negligible osmotic pressure of the feed solution compared to the operating pressure. • The water permeability constant is independent of any solute. • Solute permeability constant is independent of feed concentration and flowrate. • The mass transfer coefficient depends on feed concentration.	• Uses the same technique of the Kimura and Sourirajan (1967) model with the basic equation of free energy parameter. • Ascertains the applicability to many non-ionized, partially and completely ionized organic solutes. • Investigates a new equation to calculate solute transport parameter based on very low feed solutions on negligible osmotic pressure.	• Limited to only porous cellulose acetate membranes.
14	Rangarajan *et al.* (1979)	• Assumes a negligible osmotic pressure of the feed solution compared to the operating pressure. • The mass transfer coefficient depends on feed concentration. • Assumes constant diffusivity of any salt or ion in membrane to water.	• Ascertains the applicability to a mixture of uni-univalent and di-univalent aqueous electrolyte solution system. • Highlighted the implementation of different valencies in a mixture of different ions in the mixed solute system.	• Limited to only porous cellulose acetate membranes.
15	Rangarajan *et al.* (1984)	• Assumes a negligible osmotic pressure of the feed solution compared to the operating pressure. • The mass transfer coefficient depends on	• Improves the previous model of Rangarajan *et al.* (1978) for the case of three uni-univalent electrolyte mixture.	• Limited to only porous cellulose acetate membranes.

		feed concentration. - Assumes constant diffusivity of any salt or ion in membrane to water.		

Table 2. Summary review of the solution diffusion model (continued)

No.	**Author and year**	**Assumptions**	**The Specific Features and advantages**	**Shortcomings**
16	Rangarajan *et al.* (1985a)	- Assumes a negligible osmotic pressure of the feed solution compared to the operating pressure. - The mass transfer coefficient depends on feed concentration. - Assumes constant diffusivity of any salt or ion in membrane to water.	- Improves the previous model of Rangarajan *et al.* (1978) for the case of nine seawater ions included in eight inorganic electrolyte salts.	- Limited to only porous cellulose acetate membranes.
17	Slater *et al.* (1985)	- Assumes constant solute concentration coefficient in the osmotic pressure equation. - Constant solute concentration along the membrane length.	- Improves the solvent and solute fluxes equations in a reverse osmosis operating in a closed-loop mode. - States that solvent flux can be combined with solute concentrations by using of the Van't Hoff expression, which relates the osmotic pressure and solute concentration.	- Neglecting both the concentration polarization and fouling impacts.
18	Muldowney and Punzi (1988)	- Based on the same criterion of the solution diffusion model.	- Investigates a correlation to calculate the solute rejection factor which is nominated by $(\frac{Cs_1}{Cs_3})$ for the case of the solution diffusion model.	
19	Slater *et al.* (1992)	- Assumes constant inorganic concentration coefficient in the osmotic pressure equation. - Constant inorganic concentration along the membrane length.	- Applies the same correlations of the solution diffusion model for a case of a closed-loop reverse osmosis operating system to deal with a solution feed of industrial wastewater. - Improves the model by deriving the material balance equations with the investigation of a new equation for the solute rejection from combining of the main expressions of water and solute fluxes and the solute rejection equation.	- Neglecting the impact of fouling and concentration polarization. - The model cannot estimate the solute rejection and water flux in inorganic wastewater accurately.

Table 2. Summary review of the solution diffusion model (continued)

No.	Author and year	Assumptions	The Specific Features and advantages	Shortcomings
20	Yaroshchuk (1995)	• Assumes that the solute transport is occurred by simultaneous convection and diffusion.	• Modified the solution diffusion imperfection model of Sherwood et al. (1967) by considering the solute flux through the pore is carried out by convection and diffusion.	
20	Al-Bastaki and Abbas (2003)	• Assumes the applicability of Da Costa *et al.* (1994) theory to calculate the mass transfer coefficients and the pressure drop for flow inside a spacer-filled channel.	• Develops the using of the solution diffusion mass transport model with the theory of concentration polarization for the reason of bettering the performance of spiral wound, reverse osmosis and for the treatment of colored water effluents respectively. • Included the estimation of pressure drop inside the feed channel.	• A linear correlation between the osmotic pressure and feed concentration. • Neglected the variation of operating parameters along the membrane length (lumped model).
21	Wang *et al*. (2014)	• The free volume of dense polymer membrane layer contains interconnected pore-like voids.	• Resolving the main shortcoming of the solution diffusion model by considering a homogeneous (non-porous) membrane. • The membrane water permeability is a function of membrane and water physical properties in addition to water chemical affinity. • Addresses the impact of feed water chemistry on membrane transport and structural properties of polyamide composite membranes.	

Conclusions

This paper has reviewed and discussed the main two mathematical models of the irreversible-thermodynamics and the solution diffusion used for measuring the transport mechanism in reverse osmosis systems. The criterion of the research is focused on proving the maturity or otherwise of these models ranging from single solute systems to multi-component systems including the combination of concentration polarization and solute-solvent-membrane interaction. The review has been designed to yield a one stop-shop critical appraisal and evolution of all the underlying models and associated concepts as well as considerations for improvement.

It is therefore concluded that the solution diffusion model has only a few parameters for experimentation to measure the mechanism of transport in comparison with the irreversible thermodynamics model. Having said this, the assumption of mechanical equilibrium but ignoring the diffusive and convective contribution in the irreversible thermodynamics model reduces the quality of elucidation of the transport mechanism. In fact, this model assumes that the solute and solvent fluxes are restricted with the gradient of the driving forces and ignores the structure of the membrane and the diffusive flux. Furthermore, the transport parameters are not linked to the chemical potential gradients, but the interaction between the solute, solvent and membrane are included. In contract, the process of species transport in the solution diffusion model can be characterized by the assumption of uncoupled transport of both solute and solvent (no interaction), which depends on its chemical potential difference. Besides, this model has taken the structure and features of the membrane, which may interpret the primary movement of its simplicity and validity as a widely accepted model for most systems. In particular, the discounting of the pressure difference caused by the solute can accounted for a slight deficiency of this model in spite of the transport parameters being functions of both the pressure and concentration driving forces. Consequently, these models deliver a marked difference in the solute and solvent transport parameters. Further work will explore other characteristics of the models.

Nomenclature

A : The pure water permeability constant in the membrane (*gmol* H_2O/cm^2 *s atm*) or (m/ s atm)
(The solution diffusion model).
A_{ij} : The interaction parameter mentioned in Eq. (37) (m^5/ *s mol*).
a : Parameter defined in Eq. (199).
a_{i}^{-} : The main activity of component *i* (*dimensionless*).

$a_{\bar{w}}$: The main activity of water (*dimensionless*).
A_m, A_i : The equivalent water permeability coefficient and the mechanical permeability of the pores in Sherwood *et al.* (1967) model (*m/ s atm*).
a_s : Osmotic constant (m^3 *Pa/g*) or osmotic pressure to solute concentration ratio (m^2/s^2).
B : The solute permeability coefficient in the membrane (*cm/s*) (*the solution diffusion model*).
B_{av} : Constant defined by Eq. (167) (*atm*).
C_{i1m}, C_{iom} : The concentration of ion *i* at the membrane interface in both feed side and permeate side respectively (*mol/cm*^{3}).
$C_{i3m}, C_{i\ell m}$: The concentration of ion *i* at the membrane interface in the permeate side (*mol/cm*^{3}).
C_i° : The concentration of solute *i* at feed side (*mol/cm*^{3}).
$C_{\bar{i}}, C_{\bar{j}}$: The mean concentration of the solutes *i* and *j* respectively (*mol/cm*^{3}).
$C_{i(x)}$: The concentration of solute *i* at position *x* (*mol/cm*^{3}).
$C,\ C_s$: The concentration of solute in solution (*mol/cm*^{3}).
$C_{s(av)}$: The average solute concentration (*mol/cm*^{3}).
$C_{\bar{s}}$: The logarithmic mean of solute concentration (*dimensionless*).
C_{s1}, C_{i1} : Salt or ion concentration in the feed or bulk side (*mol/cm*^{3}).
C_{s2}, C_{i2} : Salt or ion concentration in the membrane/feed interface (*mol/cm*^{3}).
C_{s3}, C_{i3} : Salt or ion concentrations in the permeate side (*mol/cm*^{3}).
C_{sm} : The molar concentration of solute at membrane interface (*kg/m*^{3}) or (*mol/cm*^{3}).
C_{sm2} : The concentration of solute at the membrane phase in equilibrium with x_{s2}.
C_{sm3} : The concentration of solute at the membrane phase in equilibrium with x_{s3}.
C_w : The molar concentration of water (*kg/m*^{3}) or (*mol/cm*^{3}).
C_{wm} : The molar concentration of water at membrane interface (*kg/m*^{3}) or (*mol/cm*^{3}).
C_{w1}, C_{w3} : The concentration of water in the high-pressure and permeate side respectively (*kg/m*^{3}) or (*mol/cm*^{3}).
D_i : Diffusion coefficient and diffusion coefficient of ion *i* in water (*cm*^{2}*/s*).
D_{ij} : The membrane diffusion coefficient (*cm*^{2}*/s*).
D_{im} : The diffusion coefficient of ion *i* in the membrane phase (*cm*^{2}*/s*).
D_{iw} : The diffusion coefficient of ion *i* in the water (*cm*^{2}*/s*).
D_s : The diffusion coefficient of the salt in water (*cm*^{2}*/s*).
D_{sw} : The diffusion coefficient of the salt in water (*cm*^{2}*/s*).
D_{sm} : The diffusion coefficient of the salt in the membrane phase (*cm*^{2}*/s*).
D_s^{φ} : The solute diffusion coefficient in the bulk (*cm*^{2}*/s*).
D_w : The diffusion coefficient of water in the membrane (*cm*^{2}*/s*).
D_w^{φ} : The water diffusion coefficient in the bulk (*cm*^{2}*/s*).
D_{NaCl} : The diffusion coefficient of *NaCl* in water (*cm*^{2}*/s*).
E : Quantity defined by the Eq. (201).
$E_s, \sum E_s$: Taft's steric parameter.
F : Flow parameter or feed flow rate for single solute system defined in Eq. (17) (*cm*^{3}*/s*).
F_i : The membrane-phase mass transfer resistance for solute *i* (*m*^{2} *s/ mol*).
F_{ij} : The flow parameter for two solutes system defined in Eq. (41).
FR : Faraday's number.
F_s, F_i and F_w : The driving forces exerted by solutes *s* and *i* and water respectively.
J_s : The solute flux through the membrane (*mol/cm*^{2} *s*).
J_{si}, J_{sj}: The solute flux through the membrane for ions i and *j* (*mol/cm*^{2} *s*).
J_w : The total water volume flux (*cm/s*) or (*mol/cm*^{2} *s*).
J_{wi} : The water flux through the pore (*cm/s*) in Yaroshchuk (1995) model.

K : The interfacial equilibrium constant for single salt or the distribution coefficient for salt between the membrane and the water, $K = \frac{c_s \; x_s}{c_{sm} \; x_{sm}}$ (*dimensionless*).

K_i° : The sorption coefficient and represents the activity coefficients.

k, k_i : The mass transfer coefficient and the mass transfer coefficient of the solute *i* (*cm/s*).

K_a : The dissociation equilibrium constant for the acid at 25 °C.

k_B : The Boltzmann constant ($1.38064852 \times 10^{-23}$ $m^2\ kg\ s^{-2}\ K^{-1}$).

k_d: The diffusive hindrance factor in the extended solution diffusion model (cm^2/s).

K_i, K_j: The partition coefficient of the solutes i and *j* respectively ($K_i = \frac{x_{i2}}{x_i}$) (*dimensionless*).

$K^{\wedge}$: The interfacial equilibrium constants for single salts.

K_s : The permeate side distribution coefficient = $\frac{C_{sm3}}{C_{s3}}$.

K_s°, K_i° : The sorption coefficient of solute or ion and membrane ($K_s^{\circ} = \frac{Cs_m}{Cs_1}$).

K_w° : The sorption coefficient of water phase and membrane phase ($K_w^{\circ} = \frac{c_{wm}}{c_{w1}}$).

k_{NaCl} : The mass transfer coefficient of *NaCl* (*cm/s*).

K_1, K_2, K_3 : The mass transfer coefficients for ions (1, 2 and 3) respectively (*cm/s*).

K_{11}, K_{21}, K_{31} : The mass transfer coefficients for ions (1, 2 and 3) respectively in the feed side (*cm/s*).

K_{12}, K_{22}, K_{32} : The mass transfer coefficients for ions (1, 2 and 3) respectively in membrane side (*cm/s*).

K_{31}, K_{32}, K_{33} : The mass transfer coefficients for ions (1, 2 and 3) respectively in the permeate side (*cm/s*).

k_{av} : The average mass transfer coefficient on the feed side (*cm/s*).

$k_{(ref)}$: The mass transfer coefficient for sodium chloride-water reference solution (*cm/s*).

k_{s1}, k_{s2} : The conversion factor for solutes (1 and 2) (cm^2 *s g/gmole*).

k_w : The conversion factor for water (cm^2 *s g/ g mole*).

L_i : The coefficient relates the chemical potential with the flux, Eq. (98).

L_p : The hydraulic water permeability constant (*cm/s kPa*).

$L_{\bar{p}}$: The specific or local water permeability ($cm^2/s\ kPa$) or ($cm^5/\ watt\ s^2$).

L_{ss}, L_{si} : The straight phenomenological coefficients of the solute and solute with ion *i* Respectively.

L_{sw} : The cross-phenomenological coefficients of solute and water.

L_{ws} : The cross-phenomenological coefficients of water and solute.

L_{ww} : The straight phenomenological coefficients of water.

l : The membrane length (*cm*).

M_s, M_{s1}, M_{s2} : The molecular weight of solutes 1 and 2 respectively (*gm/mol*).

m_1, m_3 : The molality of solute in the feed and product side respectively.

M_w : The molecular weight of water =18.0152 (*gm/mol*).

n, n_i, n_j : The number of ions from one molecule of ions *i* and *j* respectively (n_i for non-electrolyte = 1).

n_c, n_a : The number of moles for the cation and the anion in one mole of the ionized solute respectively.

P : Pressure (*bar* or *kPa*).

P_i : Pressure of ion *i* (*bar* or *kPa*).

P_i^* : The partial diffusional permeability of pore in Yaroshchuk (1995) model (cm^2/s).

P_i° : The reference pressure of the ion *i* (*bar* or *kPa*).

P_{ℓ} : The pressure on the permeate side of the membrane (*bar* or *kPa*).

P_o : The pressure on the feed side of the membrane (*bar* or *kPa*).

PR : The water product rate through given area of the membrane (*kg/s*).
$[PR]_{mix}$: The water production rate of a mixture through given area of the membrane (*kg/s*).
PWP: The water permeation per given area of film surface (*gm/hr*).
R : The universal gas constant, (*8.31 watt sec/°K mole*) or (*8.31 Pa* m^3*/°K mol*) or *(0.082 atm* m^3*/ kmol ºK).*
R_a: The actual salt rejection coefficient (*dimensionless*).
R_{aj} : The actual rejection coefficient of solute *j* in a multi-component system (*dimensionless*).
R_i° : The observed salt rejection of component *i* in the binary system (*dimensionless*).
$R_s, R_i, R_j, R_{s1}, R_{s2}$: The observed salt rejection coefficient of solute, solute *i*, solute *j* and solutes 1 and 2 respectively (*dimensionless*).
S : The effective membrane surface area (*cm*^{2}).
$S^*, \sum s^*$: The modified small's number (*non-polar parameter*).
T: The absolute temperature *(°K*).
V_i , V_j : The partial molar volumes of ions *i* and *j* respectively (*cm*^{3}*/mole*).
V_m : The molar volume of the membrane phase including the membrane material and all permeants and the membrane thickness (*cm*^{3}*/mole*).
V_w : The partial molar volume of water (*cm*^{3}*/mole*).
ṽ : Stoichiometric coefficient or number of ions produced on complete dissociation of one molecule of electrolyte.
x : The length coordinate or space coordinates in the transport direction (*cm*).
X_j^+: Parameter defined in Eq. (24).
X_j, X_w : The mole fraction of ion *j* and water respectively.
x_{ij} : The mole fraction of solute *i* at location *j* (*dimensionless*).
x_{im} : The mole fraction of ion *i* in the membrane phase (*dimensionless*).
x_{i1}, x_{i2}, x_{i3} : The mole fraction of ion *i* in the feed side, the membrane side and the permeate side respectively (*dimensionless*).
$\mathrm{x}_{11}, \mathrm{x}_{12}, \mathrm{x}_{13}, \mathrm{x}_{1\mathrm{m}}$: The mole fraction of ion *1* in the feed side, the membrane side and the permeate side respectively (*dimensionless*).
$x_{21}, x_{22}, x_{23}, x_{2m}$: The mole fraction of ion 2 in the feed side, the membrane side and the permeate side respectively (*dimensionless*).
$x_{31}, x_{32}, x_{33}, x_{3m}$: The mole fraction of ion *3* in the feed side, the membrane side and the permeate side respectively (*dimensionless*).
x_s : The mole fraction of the solute in the solution.
x_{s1}, x_{s2}, x_{s3} : The mole fraction of the solute in the feed, membrane and the permeate sides respectively (*dimensionless*).
x_{sm}, x_{sm2}: The mole fraction of the solute in the membrane phase in equilibrium with x_{s2} (*dimensionless*).
x_{sm3}: The mole fraction of the solute in the membrane phase in equilibrium with x_{s3} (*dimensionless*).
x_{m1}, x_{m3} : The mole fraction of solute or ion on the high-pressure membrane side and low pressure membrane side respectively.
x_{w3} : The mole fraction of water in the permeate side (*dimensionless*).
z_i, z_j : The charge of valency of ions *i* and *j* respectively.
Z^+, Z^-*:* The valencies of both the cation and the anion respectively.

Greek symbols

Δ : Parameter defined in Eq. (66).

$\Delta C_i, \Delta C_j$: The concentration difference of ions or solutes *i* and *j* across the membrane.
ΔC_s : The concentration difference of salt across the membrane.
ΔG_s^* : The solute membrane interaction energy (*Joule*).
ΔG_w^* : The water membrane interaction energy (*Joule*).
ΔP : Trans-membrane pressure (*bar* or *kPa*).
$\Delta \pi_s$: The osmotic pressure difference of solute *s* across the membrane (*bar* or *kPa*).
$(\Delta \pi i_m)$: The osmotic pressure of the impermeable solute (*bar* or *kPa*).
Δa_i^{-} : The difference of main activity of ion *i* (*dimensionless*).
Δa_w^{-} : The difference of main activity of water (*dimensionless*).
$\Delta \vartheta$: The electrical potential difference (*volt*).
$\Delta \rho_s$: The salt density difference (*kg/m*^{3}).
ƒ : The ratio of the convective solute flux to the solvent flux.
ℓ : The membrane thickness (*cm*).
γ : The number of charged groups carried by the organic ion.
γ_i, γ_j : The activity coefficient for the ions *i* and *j* respectively.
γi° : The standard chemical potential of ion *i* at the feed side.
γi_m° : The standard chemical potential of ion *i* at the membrane interface at feed side.
$\gamma_{i\ell}$: The standard chemical potential of ion *i* at the permeate side.
$\gamma_{i\ell m}$: The standard chemical potential of ion *i* at the membrane interface at permeate side.
σ : The reflection coefficient of the solute.
σ_i, σ_j : The reflection coefficient of ions *i* and *j* (*dimensionless*).
σ_{ij} : The effective reflection coefficient between the two solutes *i*, *j* defined in Eq. (40) (*dimensionless*).
π, π_i : The osmotic pressure and the osmotic pressure of ion *i* (*kN/m*^{2}) or (*watt s/cm*^{3}).
π_{i1} : The osmotic pressure of ion *i* at feed side (*kN/m*^{2}) or (*watt s/cm*^{3}).
π_{im} : The osmotic pressure of impermeable ion *i* (*kN/m*^{2}) or (*watt s/cm*^{3}).
π_{s1} : The osmotic pressure at feed side (*kN/m*^{2}).
ω, ω_i : The solute or salt permeability coefficient (*mol cm/watt s*^{2}) or (*mol/ kPa cm*^{2} *s*).
ω^* : The coefficient associated with the non-polar parameters, $s^*$and $\sum s^*$
ω^{-}, ω_i^{-} : The local solute permeability coefficient and for ion *i* respectively (*cm*^{2}*/s*).
ω_{ii} : The self-permeability coefficient of solute *i* (*cm*^{2}*/s*).
ω_{ii}^{-} : The local self-solute permeability coefficient for ion *i* (*cm*^{2}*/s*).
ω_{ij}, ω_{ji} : The cross permeability coefficient between solutes *i* and *j* (*cm*^{2}*/s*).
ω_{ij}^{-} : The local permeability coefficient between solutes *i* and *j* (*cm*^{2}*/s*).
ω_{si} : The solute permeability coefficient of solute *s* with the consideration of the interaction of solute *i* (*mol m/watt s*^{2}).
ω_{si}^{-} : The local solute permeability constant of solute *s* with the consideration of the interaction of solute *i* (*cm*^{2}*/s*).
ω_{ss} : The local solute permeability constant of solute *s* with the consideration of the interaction of solute *s* (*mol m/watt s*^{2}).
$\emptyset_i$: The osmotic factor for ion *i* (*Pa m*^{3}*/mol*).
$\emptyset_{i2}, \emptyset_{i3}$: The osmotic factors of ion *i* at membrane and permeate side respectively (*Pa m*^{3}*/mol*).
$\emptyset_m$: The osmotic coefficient based on the solute concentration at the membrane interface for non-ideal solutions.
ϑ : The electrostatic or electrical potential (*volt*).
μ : The kinematic viscosity (*cm*^{2}*/s*).
μ_i, μ_j : The chemical potential of ions *i* and *j* respectively.

$\overset{\circ}{\mu}_i$, $\overset{\circ}{\mu}_j$: The standard state chemical potential of components *i* and *j* at reference pressure respectively.

ρ_s : The salt density (*kg/m*^{3}).

ρ_s^1 : The salt density in the feed side (*kg/m*^{3}).

ρ : The density of solution (*kg/m*^{3}).

$\frac{D_{sm}}{K\delta}$: The solute transport parameter (*treated as a single quantity*) (*cm/s*).

$\left(\frac{D_{sm}}{K\delta}\right)_{14}, \left(\frac{D_{sm}}{K\delta}\right)_{13}, \left(\frac{D_{sm}}{K\delta}\right)_{23}$: The solute transport parameters for the salts (14, 13 and 23).

$ln\ C^*_{NaCl}$: The constants representing the porous structure of the membrane surface.

$\left(-\frac{\Delta\Delta G}{RT}\right)_i$: The free energy parameter of ion *i*.

α : Parameter defined by Eq. (169).

β : Parameter defined in Eq. (43).

$\beta *$: The concentration polarization factor (*dimensionless*).

β_1, β_2 : Two parameters defined by Eqs. (177) and (178).

$ln\Delta^*$: Quantity defined by Eq. (158) when polar, steric and nonpolar effects are each set equal to zero.

δ^* : The coefficient associated with steric parameter E_s or $\sum E_s$.

$\omega^* \sum s^*$: The non-polar parameter defined in Eq. (158).

δ : The mass transfer boundary layer thickness.

$\in^m_{ij}$: The membrane-phase coupling function (*dimensionless*).

ε : The membrane porosity (*dimensionless*).

$\varepsilon_{ij}, \varepsilon_{iw}$: The apparent frictional coefficient between ions *i* and *j*, *i* and *water* respectively (*s/m*^{2}).

λ_w : The water membrane sieving factor (*dimensionless*).

λ_s : The solute membrane sieving factor (*dimensionless*).

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