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Separation of Butanol Using Pervaporation: A Review of Mass Transfer Models

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Abstract - Pervaporation is a suitable technique for butanol recovery from aqueous solutions especially ABE fermentation broths. The performance of the membrane, in terms of permeation flux and modelling of the mass transfer through membranes provides a deeper understanding, which may assist to orient the research and the development of pervaporation processes. Modelling of the mass transport through the membrane is based on sorption and diffusion of the components into and across the membrane. In this study, an overview of the different models used for the pervaporation separation of butanol is presented. Up to now, the solutiondiffusion based models were the main methods used and the Maxwell-Stefan theory was very limited. In addition, to our knowledge, the pore-flow model was not applied for the modelling of butanol pervaporation separation. Moreover, the Maxwell-Stefan theory seems to be the most accurate mass transfer model to be used for the pervaporation separation method in comparison to the other models.

Keywords: Pervaporation, Butanol, Mass Transfer, Solution-Diffusion, Maxwell-Stefan, Pore-Flow.

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1. Introduction

The depletion of fossil fuels and world concerns about climate change have motivated researchers to find replacement fuels that would be renewable and near carbon neutral such as biodiesel, bioethanol and biobutanol. Many studies have been performed to propose ways to make the production of biofuels, and specially biobutanol, economically viable [1–6]. Biobutanol, a four-carbon alcohol, has enviable properties in comparison to the other biofuels. Some *Date Received: 2017-10-26 Date Accepted: 2018-04-17 Date Published: 2019-02-11* advantages of using biobutanol as a biofuel are its low volatility, low hydroscopicity and lower corrosiveness. The biological production of n-butanol is achieved via Acetone-Butanol-Ethanol (ABE) fermentation. ABE fermentation using *Clostridium acetobutylicum* yields acetone, butanol and ethanol in a typical ratio of 3:6:1, respectively. However, to make butanol economically viable as a biofuel, the bioconversion efficiency and product purity via the ABE fermentation process should be improved to compensate for the currently very low product yield, product toxicity to microorganisms and multiple end-products [4,7–17].

Many studies have been undertaken in an attempt to increase the efficiency of butanol produced from ABE fermentation [2,3,18–23]. One method to improve the productivity of the ABE fermentation, the in-situ recovery of the solvents, has attracted considerable attention. The main separation methods used for butanol separation from the ABE fermentation process are vacuum fermentation [24] adsorption [25], gasstripping [26], liquid-liquid extraction [27], perstraction [28,29], reverse osmosis [30] and pervaporation [1]. Among these methods, pervaporation is a highly regarded separation technique because of its low energy consumption, high selectivity and absence of harmful effect on microorganisms [1,31,32]. To mitigate the higher cost associated with the incorporation of a pervaporation membrane for the in situ recovery of ABE solvents from fermentation broths, it is necessary to resort to highly efficient membranes.

The performance of a pervaporation membrane is assessed by the permeation flux and selectivity. To improve membrane performance, a judicious synergistic combination of theory and laboratory work is necessary. To explain the migration of species across pervaporation membranes, a few models have been proposed: solution-diffusion model [33], Maxwell-Stefan theory [34], and pore-flow model [35,36]. With these models, it is possible to infer the performance of pervaporation membranes, but pervaporation remains a complex process to be modelled.

Until now, many reviews have considered the pervaporation fundamentals and membranes; however, there are only few studies published in the literature to review the mathematical models for pervaporation processes [37–45]. In this review paper, a brief summary of the mass transfer models used in pervaporation separation is presented followed by the discussion on the models applied for butanol recovery via this process. The main focus of this manuscript was the models applied to pervaporation of butanol separation.

1. 1. Introduction to Pervaporation

Pervaporation is a partial pressure or more generally concentration driven process, which is the combination of two mass transfer mechanisms: permeation and evaporation [46-48]. During pervaporation, a phase change from liquid to vapour occurs. A liquid feed solution to be separated is in contact with one side of the membrane surface and the permeating product leaves at a low vapor pressure from the other side that is kept under vacuum [49] or swept with a purge gas [50]. The permeate is then condensed or released depending on the objective of the separation [51]. Because of the presence of vacuum or the sweeping of an inert purge gas on the permeate side, a driving force across the membrane prevails. The required heat of vaporization comes from the liquid feed such that the temperature of the feed must be set accordingly. In recent years, several studies have been undertaken to better understand the pervaporation process and use it for numerous separation processes including the separation of water and alcohol mixtures hydrophobic membranes [41,46,51-54]. using Generally, pervaporation applications fall under three categories: (i) removal of water from organic solvents, (ii) removal of organic compounds from aqueous solutions, such as the recovery of the aromatic components and biofuels from fermentation broths, and (iii) separation of anhydrous organic mixtures. In this process, the separation depends on the chemical nature of the macromolecules that comprise the membrane, the physical structure of the membrane, the physicochemical properties of the mixtures to be separated, and the permeant-permeant and permeantmembrane interactions. Figure 1 shows the simplified schematic diagram of a typical pervaporation separation experimental system used to test pervaporation membranes.



Figure 1. Simplified schematic diagram for a typical pervaporation separation setup.

1.2. Pervaporation Membranes

Membranes, which have been used for pervaporation separation of butanol, are either zeolite membranes such as silicalite zeolite membranes and ultrathin zeolite X films [55–58] or polymeric membranes. Different kinds of polymers have been reported in the literature for butanol separation such as styrene butadiene rubber (SBR) [59], ethylene (EPDM) propylene diene rubber [60]. polytetrafluoroethylene (PTFE) [61], polypropylene (PP) [62], polyurethane (polyether based) (PUR) [63], polyether block-amide (PEBA) [64], poly (vinylidinedifluoride) (PVDF) [65], poly (methoxy siloxane) (PMS) [66], poly (dimethylsiloxane) (PDMS) [19], poly (1-(trimethylsilyl)-1-propyne) (PTMSP) [67] and polyamide-imide (PAI) containing cyclodextrin (CD) [68]. Polymeric membranes are less expensive and more flexible in comparison to zeolite membranes [46,69]. However, a composite membrane incorporating these two materials have also been used by some researchers [70–73] to benefit from the outstanding characteristics of each medium to enhance membrane performance.

2. Models Used for Mass Transfer in Pervaporation

Description of mass transport through membranes is essential to enhance the design efficiency consequently obtaining better and separation performance. Up to now, different models have been introduced to study the pervaporation separation process by considering the species behaviour, membrane properties and operating conditions. Similar to the proposed models for membrane-based gas separation applications, a resistance-in-series theory can be used to describe the mass transfer of components through membranes in pervaporation separation system. According to this theory, the sorption of species in the liquid feed takes place at the membrane surface and species then diffuse through the membrane prior to desorbing on the other side of the membrane. However, the mass transfer resistance at the permeate side has been reported to be negligible in the overall mass transfer due to considerably lower pressure in the permeate side [45]. Therefore, desorption step can be modelled in a similar way to the sorption step such that it will not be discussed individually in this study. Figure 2 provides an overview of the different mass transfer models, which have been used in pervaporation separation processes.

In addition, Figure 3 shows the chemical potential (μ) , total pressure (p) and concentration (C) profiles of a migrating species across the membrane thickness in the pervaporation separation process assuming a high vacuum on the permeate side and linear concentration profile within the membrane.



Figure 2. Summary of different mass transfer models used for pervaporation separation processes (star refers to models not yet used for butanol mixtures).



Figure 3. Gradient profiles across the membrane and the two boundary layers prevailing for the pervaporation system.

2. 1. Solution-Diffusion Model

The solution-diffusion model is used for membranes under the assumption that the mass transport across the membrane proceeds in three steps: (1) the sorption of the penetrants into the membrane, (2) the diffusion of the sorbed components through the membrane as a result of concentration gradient, and (3) the desorption of the diffused components on the permeate side. Moreover, it is assumed that the total pressure is constant within the membrane and the thermodynamic equilibrium has been reached at the two interfaces.

Considering the Fick's first law of diffusion, the permeation flux of component i can be obtained using Eq. (1) [45].

$$J_i = -D_{M,i} \frac{dC_{M,i}}{dz} \tag{1}$$

where J_i is the permeation flux of component *i* (*kmol.m*-².*s*-¹), $D_{M,i}$ is the diffusion coefficient of component *i* through the membrane ($m^2.s^{-1}$) and $C_{M,i}$ is the concentration of component *i* within the membrane (*kmol.m*-³). This equation can be expressed in terms of the bulk concentration or activity of component on both sides of the membrane [43,45] as the mass transfer driving force (Eq. (2)).

$$J_{i} = \frac{P_{M,i}}{l_{M}} \left(a_{f,i} - a_{p,i} \right)$$
(2a)

$$P_{M,i} = D_{M,i} S_{M,i} \tag{2b}$$

In Eq.(2), $P_{M,i}$ is the permeability of component *i*, which is the product of solubility coefficient $(S_{M,i})$ and diffusion coefficient $(D_{M,i})$ [45]. The solution-diffusion model has been widely used for the development and optimization of membranes. However, for a more accurate prediction of membrane performances, it is necessary to determine the diffusion coefficient and the solubility coefficent or their combined product (permeability). The experimental determination of these parameters comes with a significant level of uncertainties, which makes it difficult to use the solution-diffusion model with confidence. Moreover, the permeability by itself does not provide any information that could be used for membrane development. In addition, the original solution-diffusion theory cannot consider the coupling effect between the migrating species which occurs due to the strong interaction between the penetrant molecules and, consequently, this model is only applicable when the coupling flux is negligible in comparison with individual fluxes of penetrants. However, the influence of the coupling flux may be a significant factor which should be taken into account in modelling the mass transfer in pervaporation separation [74]. The interactions between the dissolved components that have high affinity with each other result in the coupling of the species through the membrane penetration. In other words, the presence of one species in a mixture affects the Gibbs free energy of the other components and consequently results in changing the penetration behaviour through the membrane [75-77]. However, the coupling effect consideration in a model would increase the level of complexity of the model and needs additional experimental parameters.

A semi-empirical approach was proposed [45] for the solution-diffusion model where the driving force in the original solution-diffusion model was replaced by a pressure-based fugacity and the equation was derived from Fick's first law of diffusion for a one-directional mass transfer through the membrane as given in Eq.(3).

$$J_i = -C_i \frac{D_i^T}{f_i^0} \frac{1}{\gamma_i} \frac{df_i}{dz}$$
(3)

where D^T is the thermodynamic diffusion coefficient $(m^2.s^{-1})$, f_i is the fugacity (*bar*) and γ_i is the activity coefficient of component *i*. The coupling effect of the species was considered in this model by introducing coupling coefficients B_{ij} and B_{ji} to establish a relationship between the local activity coefficients and the local fugacity parameters for a binary feed solution as given in Eq. (4).

$$\gamma_i = \exp\left(B_{ii}\left[1 - \left[\frac{f_i}{f_i^0} + B_{ij}\frac{f_i}{f_j^0}\right]\right]\right)$$
(4a)

$$\gamma_{j} = \exp\left(B_{jj}\left[1 - \left[\frac{f_{j}}{f_{j}^{0}} + B_{ji}\frac{f_{i}}{f_{i}^{0}}\right]\right]\right)$$
(4b)

Eq.(4) can be further extended to consider ternary feed solutions as discussed by Lipnizki and Tragardh [45].

The integration of Eq. (3) and taking a geometric average $(\gamma_{M,i})$ between the activity coefficient of the components result in Eq. (5) for the calculation of the permeation flux.

$$J_{i} = \frac{\overline{D}_{i}^{T}}{\gamma_{M,i}} \left[\frac{f_{f,i} - f_{P,i}}{f_{i}^{0}} \right] = \frac{\overline{D}_{i}^{T}}{\gamma_{M,i}} \left(a_{f,i} - a_{P,i} \right)$$
(5a)

$$\overline{D}_i^T = \frac{C_{M,i} D_i^T}{l_M}$$
(5b)

where \overline{D}_i^T is the modified thermodynamic diffusion coefficient. According to Franke [78], this model showed a fairly good agreement with the experimental data for a ternary feed mixture of water, ethanol, and butanol using a PAN/PAV pervaporation membrane.

The modified solution-diffusion model would be very useful when coupling effect impacts the mass transfer through the membrane. However, if coupling effects are negligible, this equation would only add unnecessary complexity to the model. Akin to the main solution-diffusion model, semi-empirical models based on the solution-diffusion model can also be used for process and module design. In the following section, the models which have been used to estimate the sorption peoperties and the diffusivity of the components through membranes are dicussed.

2.1.1. Predictive Models for the Sorption Properties

One of the major mass transfer steps in the pervaporation process is the transfer of a penetrant from the boundary layer to the membrane surface where it can be sorbed. The boundary layer is the thin layer in the vicinity of the membrane interface in which the diffusive mass transfer is the dominating transport mechanism as a result of the decrease of the flow velocity in comparison to the velocity of the bulk liquid [44]. The diffusive flux at the boundary layer of the membrane is a function of the bulk phase velocity, the membrane module geometry, the viscosity of the feed solution and the properties of the penetrants [79]. The diffusion rate of a species in the boundary layer is dictated by the difference of concentration between the bulk liquid and the liquid-membrane interface. The concentration at the interface depends on the solubility of a species in the membrane and the rate of diffusion within the membrane. However, for pervaporation, the rate of diffusion through the membrane in relatively small and the concentration at the surface of the membrane is usually in equilibrium with the liquid bulk concentration. At the interface, there exists a competition for sorption between the different components. The more soluble components with the highest affinity with the membrane material will sorb preferentially into the membrane whereas the other components will sorb less into the polymer and mostly remain in the bulk of the fluid.

Sorption isotherms are used to represent the sorption capacity of a membrane for each species, which is related to the activity or volume fraction of the penetrant in the membrane. Modelling of sorption behaviour is relatively well established and will be briefly reviewed in the following sections.

2.1.1.1. Langmuir and Henry's Law Isotherms

The most common way to represent sorption capacity is through isotherms, which are most often determined experimentally. Henry's law isotherm (Eq. (6)) is typically used for rubbery membrane, while Langmuir isotherm (Eq. (7)) is more accurate in the case of glassy polymers [80].

$$C_{H,i} = k_{D,i} p_i \tag{6}$$

$$C_{H,i} = \frac{C_{H,i}b_{i}p_{i}}{1+b_{i}p_{i}}$$
(7)

Where $C_{H,i}$ is the sorption capacity (*kmol.m*⁻³), $k_{D,i}$ is the Henry's law constant referring to component *i* (*bar*⁻¹), *p*_i is the partial pressure (bar), $C_{{\scriptscriptstyle H},i}^{'}$ is the Langmuir maximum sorption capacity in the polymeric membrane (*kmol.m*⁻³) and b_i is the adsorption or hole affinity constant (bar-1). Langmuir's and Henry's law isotherms are theoretical models to predict the equilibrium sorption of component *i* inside the membrane. Even though the parameters of these isotherms must usually be obtained experimentally, some attempts have been made with molecular dynamic simulations to predict species solubility [81,82]. However, these isotherms are representative for the prediction of sorption capacity of pure feed in the membrane; therefore, these models are only applicable for dilute solutions where the competition among species sorption is negligible. In addition, more complex models such as the extended Langmuir and dual-mode sorption models might be more appropriate to predict the sorption behaviour of multicomponent mixtures which will be discussed in more details in a subsequent section [45,83,84].

2.1.1.2. Solubility Parameter Theory

Solubility parameter theory is a semi-empirical model that has generally been used for the selection of a membrane material to separate a specific component from mixtures. This parameter represents the affinity between the migrating species and the membrane by taking into account the interactions between the solute and the polymer [85]. A high affinity between the penetrating component and the membrane prevails when the solubility parameter for them are similar. However, excessive similarity between them would result in the immobilization of the components in the membrane.

The solubility parameter is defined by Eq. (8) where δ_i is the solubility parameter $(J^{1/2}.m^{-3/2})$, $\Delta E_{vap,i}$ $(J.mol^{-1})$ is the total energy required to remove a molecule from its adjacent molecules, and V_i is the molar volume of component i $(m^3.mol^{-1})$ [86].

$$\delta_i = \sqrt{\frac{\Delta E_{vap,i}}{V_i}} \tag{8}$$

To improve the estimation accuracy of the solubility parameter, Hansen [87] proposed a threedimensional solubility parameter by considering the total energy ($\Delta E_{vap,i}$) as a summation of energies required to overcome dispersion forces ($\Delta E_{df,i}$), dispersion polar interactions ($\Delta E_{di,i}$) and breaking hydrogen bonds ($\Delta E_{hb,i}$), i.e. $\Delta E_{vap,i} = \Delta E_{df,i} + \Delta E_{di,i} + \Delta E_{hb,i}$. Therefore, the threedimensional solubility parameter is defined as follows (Eq. (9)):

$$\delta_i = \sqrt{\delta_{df,i}^2 + \delta_{di,i}^2 + \delta_{hb,i}^2} \tag{9}$$

These parameters are normally used to measure the distance parameter $(\Delta_{p,i})$ defined as the distance between two components, polymer and penetrant. A smaller value of Δ implies a greater affinity between the polymer and the penetrant, which would also increase the membrane swelling during pervaporation.

$$\Delta_{p,i} = \left[\left(\delta_{df,P} - \delta_{df,i} \right)^2 + \left(\delta_{di,P} - \delta_{di,i} \right)^2 + \left(\delta_{hb,P} - \delta_{hb,i} \right)^2 \right]^{1/2}$$
(10)

Zhou et al. studied the affinity of butanol and water for PDMS membranes. Their result revealed that hydrogen bonding and polar interaction parameters are the dominating parameters, which control the affinity of the components. Moreover, Water/PDMS has a greater distance parameter (41.4 MPa^{1/2}) compared to butanol/PDMS (13.0 MPa^{1/2}). The smaller distance for butanol indicates that it has a higher affinity for PDMS compared to water and will be preferentially sorbed into the membrane [88,89].

In another work, the distance parameter for acetone-butanol-ethanol (ABE) solution was reported by Niemisto et al. [90]. A pair of components having a distance value ($\Delta_{PDMS,i}$) closer to zero are more likely to have a higher affinity to each other. According to their study, PDMS has the highest affinity towards acetone ($\Delta_{PDMS,A}$ =10.6), followed by butanol ($\Delta_{PDMS,B}$ =12.4), ethanol ($\Delta_{PDMS,E}$ =17.1) and water ($\Delta_{PDMS,w}$ =40.9).

To increase the estimation accuracy of the threedimensional solubility parameter model presented by Hansen, weight factors could be added to Eq. (10) as shown in Eq. (11). The weight factors (*W*) correspond to the chemical nature of the components [91] and need to be obtained experimentally.

$$\Delta_{p,i} = \left[W_1 \left(\delta_{df,P} - \delta_{df,i} \right)^2 + W_2 \left(\delta_{di,P} - \delta_{di,i} \right)^2 + W_3 \left(\delta_{hb,P} - \delta_{hb,i} \right)^2 \right]^{1/2}$$
(11)

Froehling et al. [92] proposed a modified model to estimate the solubility parameters for a ternary system composed of a binary mixture and the membrane (Eq. (12)). In this equation, ϕ_i accounts for the volume fraction of component *i* in the binary mixture.

$$\delta_{df,ij}^{mix} = \phi_i \delta_{df,i} + \phi_j \delta_{df,j}$$
(12a)

$$\delta_{di,ij}^{mix} = \phi_i \delta_{di,i} + \phi_j \delta_{di,j}$$
(12b)

$$\delta_{hb,ij}^{mix} = \phi_i \delta_{hb,i} + \phi_j \delta_{hb,j} \tag{12c}$$

As mentioned before, the solubility parameter theory has been mostly used for qualitative and not quantitative purposes. In other words, this theory contributes more to material selection whereas it cannot be employed for process and module design or for the simulation of the mass transfer through polymeric membranes.

2.1.1.3. Flory-Huggins Theory

The Flory-Huggins theory, as a semi-empirical model, has been widely used to estimate the sorption properties of pure species and binary solutions in polymeric materials. Regarding the butanol sorption properties on polymeric membranes, the Flory-Huggins model has been successfully applied for the prediction of the sorption capacity of this component in blended poly (dimethylsiloxane)-benzyl-3-butylimidazolium tetrafluoroborate membranes [90].

According to this theory, the solubility of components in membranes will be a function of Gibbs free energy of interacting substances and could be represented by a set of dimensionless parameters, which are called Flory-Huggins interaction parameters (χ_{ij}) . For a ternary system including a binary mixture of components *i* and *j* and the polymeric membrane (non-crosslinked high molecular weight), the Flory-Huggins model is expressed using Eq. (13).

$$\ln a_{i} = \ln \phi_{i} + (1 - \phi_{i}) - \left(\frac{V_{i}}{V_{j}}\right)\phi_{j} - \left(\frac{V_{i}}{V_{p}}\right)\phi_{p} + \left[\left(\chi_{i,j}\phi_{j} + \chi_{i,p}\phi_{p}\right)\left(\phi_{j} + \phi_{p}\right)\right] - \chi_{j,p}\left(\frac{V_{i}}{V_{j}}\right)\phi_{j}\phi_{p}$$

$$(13)$$

In Eq. (13), $\chi_{i,j}$ is the interaction parameter between components *i* and *j*, while $\chi_{i,p}$ and $\chi_{j,p}$ represent the interaction between the components and the polymer. For a binary system consisting of a pure component and a polymeric membrane, Eq. (13) reduces to Eq. (14) by considering that ϕ_j is equal to zero.

$$\ln a_{i} = \ln \phi_{i} + (1 - \phi_{i}) - \left(\frac{V_{i}}{V_{p}}\right) \phi_{p} + \chi_{i,p} \phi_{p}^{2}$$
(14)

Moreover, for a binary system $(a_i = 1 \text{ and } V_i << V_p)$, Eq. (15) could be substituted into Eq. (14) to obtain the Flory-Huggins binary interaction parameter between component *i* and the polymer (Eq. (16)). Furthermore, the activity coefficient (a_i) in the Flory-Huggins equation can be determined using different thermodynamic fluid packages such as NRTL, UNIQUAC, or UNIFAC models.

$$\phi_i + \phi_p = 1 \tag{15}$$

$$\chi_{i,p} = -\left(\frac{\ln(1-\phi_p)+\phi_p}{\phi_p^2}\right)$$
(16)

In Eq. (16), $\chi_{i,p}$ is assumed constant at a fixed temperature and could be obtained experimentally by performing swelling measurement of the polymer in contact with pure components, by sorption measurement of species in polymer or by inverse gas chromatography. However, since the latter method depends on temperature and concentration, it would be difficult to have an accurate estimation of the Flory-Huggins interaction parameter. Therefore, swelling and sorption experiments are the preferred approaches to estimate the Flory-Huggins interaction parameter.

As far as it was mentioned before, selecting the proper thermodynamic fluid package is required to estimate the activity of species and consequently predicting the sorption properties of the components in polymeric membranes via Flory-Huggins theory. Extended Raoult's law could be used to predict the activity of components in equilibrium with the liquid feed composition at different operating conditions (Eq. (17)). In this equation, γ_i and x_i are the activity coefficient and molar fraction in the feed, respectively.

$$a_i = \frac{P_i}{p^{sat}} = \gamma_i x_i \tag{17}$$

The experimental activity coefficient of butanol has been summarized in Table 1 along with the predicted values by different models such as NRTL [93], MOSCED [94], UNIQUAC models [93] for certain specific temperatures. Although the variation between reported experimental activity coefficients is considerable, in general the reported values seem to be different from the ones predicted by theoretical models especially for estimated amounts by the MOSCED method.

2.1.2. Predictive Models for Diffusivity

Diffusion is the second step in pervaporation mass transfer, which is the movement of the molecules based on the chemical potential difference across the membrane. It is also stated that in a highly swollen polymer, the diffusion coefficient of the permeant is related to the degree of swelling, the structure of the polymer, and the permeant size. An increase in the degree of swelling is accompanied by an increase in the free volume inside the polymer which leads to a more permeable pathway for mass transfer of the penetrants and an increase in diffusivity [95–97].

All of the above reports demonstrate that the estimation of the diffusion coefficient is of paramount importance for studying the behaviour of components and the mass transfer through membranes in pervaporation separation processes. Therefore, different models used to calculate the diffusion coefficient are reviewed in the following sections.

2.1.2.1. Empirical Models

Typically, in empirical models, the diffusion coefficient is represented by an exponential function of the solute concentration as shown in Eq. (18).

$$D_i = D_i^0 \exp\left(\varepsilon_i \phi_i\right) \tag{18}$$

where D_i^0 , ε_i , and ϕ_i are, respectively, the diffusion coefficient at infinite dilution of the solute (reference value), the softener [98] (empirical constant), and the volume fraction of the solute, for a single component diffusion in a rubbery polymer [45,99].

In a multicomponent separation, the model would be extended since the interactions of the polymercomponent and component-component need to be taken into consideration. For instance, in a ternary system, including the membrane, Eq. (19) is applicable [99,100].

$$D_i = D_i^0 \exp(\varepsilon_i \phi_i + \varepsilon_j \phi_j)$$
(19a)

$$D_{j} = D_{j}^{0} \exp(\varepsilon_{i} \phi_{i} + \varepsilon_{j} \phi_{j})$$
(19b)

In some studies, a linear relationship between the diffusion coefficient and the solute concentration has been suggested [101,102] for glassy polymers [45].

As it is the case with all the empirical models, the complexity of the suggested model would depend highly on the studied system. In other words, as the number of components increases, the empirical parameters that need to be found experimentally increases, which implies time-consuming laboratory work and calculations. Therefore, these types of models can only be used to design the process and membrane module, while it cannot be used for membrane development.

2.1.2.2. Theory of Free Volume

According to the free volume theory, the molecular movement, a physical phenomenon within the polymer matrix, is the basis of diffusion. The model was fundamentally developed from Fick's first law of diffusion, which is applicable for ideal binary solutions. According to this theory, a penetrant molecule can only be transferred through the polymer if adequate free spaces exist. The free volumes are generated due to the random movement of the polymer segments. In other words, the free volume can be considered as a series of temporary micro-voids that are created in the polymer structure. In addition, in a pervaporation process, the sorption and desorption rates are much higher than that of the diffusion and could be assumed to happen instantly in comparison to the diffusion of species through membrane.

The diffusion coefficient D_i^T for a binary system (component *i* and polymer) can be estimated by Eq. (20) [103,104].

$$D_{i}^{T}\left(\phi_{i},\phi_{C,p},T\right) =$$

$$RTA_{di}\exp\left(-\frac{B_{di}}{f_{p}^{FV}\left(\phi_{i},\phi_{C,p},T\right)}\right)$$
(20)

where *T*, A_{di} and B_{di} are the temperature (should be higher than glass transition temperature of the polymer), a parameter which is a measure of shape and size of the penetrant, and a parameter which is a measure of the size of the sorption area in the polymer, respectively. f_p^{FV} is called the free volume and it depends on the volume fraction of the permeant in the polymer(ϕ_i), the volume fraction of crystalline parts of the polymer (i.e. ϕ_{C_p}) and temperature. In several studies, different equations have been proposed for the determination of f_p^{FV} in glassy and semi-crystalline polymers [105,106].

For a ternary system, Eq. (20) can be extended to Eq. (21) [107].

$$D_{i}^{T}\left(\phi_{i},\phi_{C,p},T\right) = RTA_{di}\exp\left(\frac{-f_{p}^{FV}\left(0,0,T\right)}{B_{i}^{FV}} + \frac{\beta_{i}\left(T\right)B_{j}^{FV}}{B_{i}^{FV}}\phi_{i} + \frac{\beta_{i}\left(T\right)B_{j}^{FV}}{B_{i}^{FV}}\phi_{j}\right)^{-1}$$

$$(21)$$

In eq. (21), the parameter B_i^{FV} is a generalised type of B_{di} to make the equation applicable for both semi-crystalline and glassy polymers, and is evaluated using Eq. (22).

$$B_i^{FV} = \frac{B_{di}}{\left(1 - \phi_{C,P}\right)} \tag{22}$$

The free volume theory has been reported to give a fairly good approximation of the diffusion coefficient and is applicable for membrane development in different pervaporation systems. It can be used to analize the diffusion through different types of membranes [108].

2.1.2.3. Dual-Mode Sorption Model

The dual-mode sorption model, similar to the free volume theory, considers the presence of microvoids within the polymer structure as a transportation and accumulation medium. This model is mainly used for glassy polymers even though it could also be applied for rubbery polymers. It is assumed that the microvoids are uniformly distributed throughout the membrane. The solute molecules may be captured by a neighbouring microvoid if the size of the molecule matches the size of the free space. The solute molecule is able to move through the microvoids if it has a sufficient amount of energy. If another solute molecule occupies the place of the transported molecule, diffusion will take place. Two mechanisms which have been considered for mass transfer in this model: (1) the diffusion of molecules through the microvoids (Henry's sorption sites- $C_{D,i}$) and (2) the immobilised molecules in the free space (C_{Hi}) . The total concentration of species *i* in the membrane is given by the summation of the two populations as expressed in Eq. (23) [45,83].

$$C_{i} = C_{D,i} + C_{H,i} = k_{D,i} p_{i} + \frac{C_{H,i} b_{i} p_{i}}{1 + b_{i} p_{i}}$$
(23)

The first term of Eq. (23) corresponds to the normal dissolution of the permeant and is represented by the Henry's law linear isotherm. The second term, corresponding to the immobilised molecules in the microvoids, is nonlinear and expressed by the Langmuir isotherm. In Eq. (23), b_i is the microvoid affinity constant and represents the ratio of sorption and desorption rate constants of the penetrant through the free space and $C'_{H,i}$ is the Langmuir maximum sorption capacity of component *i* in the polymeric membrane.

The permeability of component *i*, according to the dual-mode sorption model can be calculated using Eq. (24).

$$P_{i} = k_{D,i} D_{D,i} + \frac{C_{H,i} b_{i} D_{H,i}}{1 + b_{i} p_{i}} = k_{D,i} D_{D,i} \left(1 + \frac{F_{i} K_{i}}{1 + b_{i} p_{i}} \right)$$
(24a)

$$F_i = \frac{D_{H,i}}{D_{D,i}} \tag{24b}$$

$$K_i = \frac{C'_{H,i}b_i}{k_{D,i}}$$
 (24c)

where F_i is the ratio of the mobile phase to the immobilized phase diffusion coefficients, i.e. partial immobilization and K_i is the ratio of the nonlinear to the linear sorption parameters. The extended version of the dual-mode sorption model is applicable for multicomponent systems. For a binary mixture, Eq. (25) can be used [84].

$$C_{i} = k_{D,i}p_{i} + \frac{C_{H,i}b_{i}p_{i}}{1 + b_{i}p_{i} + b_{j}p_{j}}$$
(25a)

$$C_{j} = k_{D,j} p_{j} + \frac{C_{H,j} b_{j} p_{j}}{1 + b_{i} p_{i} + b_{j} p_{j}}$$
(25b)

Considering Eq. (24) and Eq. (25), the permeability of component i in a binary mixture can be obtained using Eq. (26) [109].

$$P_{i} = k_{D,i} D_{D,i} \left(1 + \frac{F_{i} K_{i}}{1 + b_{i} p_{i} + b_{j} p_{j}} \right)$$
(26)

The dual-mode sorption model has been typically used for gas separation. However, this model could be a suitable model to predict the permeability in a pervaporation process [83]. Morover, this model could be applied for the purpose of membrane development.

In addition to the models which were discussed in this section, dynamic molecular simulation was also performed for the prediction of the diffusion parameters for the mass transfer through a membrane [110,111]. Although there is no study on butanol diffusion through organic membranes using molecular simulation, it has been mentioned that the molecular simulation would be the model that could be used in the future for analizing the diffusion behaviour [45].

2.1.3. Solution-Diffusion Model for Butanol Pervaporation Separation

Instead of considering the sorption, diffusion and desorption steps separately, the overall mass transfer models take all three steps globally to calculate the permeation flux. The models do not offer a comprehensive understanding of the underlying phenomena but are nevertheless very useful for pervaporation process design and cost estimation. Different empirical models were proposed in the literature and consider the entire mass transfer mechanisms as a whole without considering directly the physico-chemical interactions. These models relies on experimental results to estimate the model parameters and the resulting models are then used for predicting the permeation flux and selectivity. The predictions are obviously valid to specific cases that are similar to the experimental system that was used to generate the data for fitting the model. Therefore, they have very limted use for membrane development.

El-Zanati et al. used the resistance-in-series model based on the solution-diffusion concept to validate the pervaporation process of a binary solution of butanol and water via Pervap 2200 (PVA crosslinked/PAN support) membranes [112]. In this work, to predict the permeation flux, the overall mass transfer resistance was considered including three resistance steps: bulk feed convection, diffusion through the membrane, and the convective removal of permeating species on the permeate side. The flux associated with these three steps can be calculated using Eq. (27).

$$J_{f,i} = k_L C_{tot,L} \left(x_{f,i} - x_i^* \right)$$
 (27a)

$$J_{f,i} = \frac{P_i}{l_M} \left(p_i^{sat} \gamma_i x_i^* - p_i^* \right)$$
(27b)

$$J_{P,i} = k_V \left(p_i^* - p_{P,i} \right)$$
(27c)

where k_L is the mass transfer coefficient at the liquid side, l_M is the thickness of the membrane (*m*) and k_v is the mass transfer coefficient at the vapour side. Under steady state conditions, the molar flux is constant at all positions within the membrane, which can be represented with a simple equation in terms of an overall mass transfer coefficient or overall mass transfer resistance ($1/K_{ov}$) as presented in Eq. (28).

$$J_{i} = K_{ov} \left(p_{i}^{sat} \gamma_{i} x_{i,b} - p_{i,P} \right)$$
(28a)

$$\frac{1}{K_{ov}} = \left(\frac{p_i^{sat}\gamma_i}{k_L C_{tot,L}}\right) + \left(\frac{l}{P_i}\right) + \left(\frac{1}{k_V}\right)$$
(28b)

In the case that the partial pressure on the permeate side approaches zero, the flux in Eq. (28) can be further simplified to Eq. (29).

$$J_{i} = K_{ov} \left(p_{i}^{sat} \gamma_{i} x_{i,b} \right)$$
⁽²⁹⁾

El-Zanati et al. used Eq. (29) to determine the change of butanol concentration as a function of time during the pervaporation process [112]. Performing a mass balance on the feed tank and using Eq. (29), Eq. (30) was obtained to estimate the butanol concentration in the feed tank as a function of time.

$$C_{b} = \left(\frac{C_{tot,L}\left(\frac{J_{b}}{J_{tot}}\right) - C_{b0}}{\left(\frac{J_{tot}A_{m}}{V_{0}^{T}C_{tot,L}}\right)t - 1}\right) + C_{tot,L}\left(\frac{J_{b}}{J_{tot}}\right)$$
(30)

where J_{tot} is the total flux (*kmol.m⁻².s⁻¹*), A_m is the membrane area (m^2), V_0^T is the volume of feed tank (m^3), and C_{b0} is the initial butanol concentration. Based on the results presented by El-Zanati et al., the prediction model provided a good approximation of the flux and butanol concentration as a function of pervaporation time and represented the experimental results very well.

In a different work, Plaza et al. [33] used experimental sweep gas pervaporation data for the separation of butanol from ABE mixtures using a supported PTFE-gelled ionic liquid membrane and a resistance-in-series model to predict the mass transfer and diffusion coefficients. A semi-empirical procedure was used to estimate the diffusion coefficient, where the theoretical flux was assumed equal to the experimental flux and the diffusion coefficient was obtained by minimizing the mean-squared differences between the calculated and experimental values. Results showed a good fit with experimental data. However, as it was mentioned in their paper, a large difference between the calculated diffusion coefficients and values reported in similar works was observed. The values of the diffusion coefficient for butanol in ionic liquid (IL) membranes calculated in their work were approximately twice the values reported by Vopicka et al. [33,113,114].

Li et al. [18] used the solution-diffusion model based on the Fick's first law of diffusion for butanol pervaporation separation from a binary solution of water/butanol, ABE model solutions containing different concentrations of glucose and other main metabolites, and ABE fermentation broths. The authors used a PDMS membrane and were able to quantify the coupling effect through the calculation of the overall mass transfer coefficient for each case. The overall mass transfer coefficient was estimated via the slope of the flux versus the concentration plot. Results showed that the estimated overall mass transfer coefficient for the binary solutions was larger than the estimated coefficient of the ABE model and real fermentation broths by approximately 16 and 28%, respectively. In addition, the coupling effects in ABE model solutions and fermentation broths, the complex interactions among the metabolites, media broth, and biomacromolecules (such as blocking sorption sites and free volume) could also partly explain the difference between the calculated mass transfer coefficients. As the estimation of the overall mass transfer coefficients was strictly based on experimental data, it is not possible to generalize this information to other pervaporation separation systems. However, the insight regarding the effect of coupling and other complex interactions is useful.

Non-equilibrium solution-diffusion was applied by Yang et al. [115] for the pervaporation separation of organic compounds (acetone-butanol-ethanol) from binary aqueous solutions using PDMS membranes. In order to estimate the permeation flux, The concentration polarization and coupling effects have been considered negligible.

The diffusion coefficient of the components and the sorption rate were estimated semi-empirically based on the data from the reciprocal of the flux versus the change in membrane thickness. The model demonstrated a good agreement with the experimental data at low feed concentrations. However, some deviations were observed at high concentrations of the organic compounds in the feed due to the intensified swelling of organics with PDMS polymer chain.

Li et al. [116] used a resistance-in-series model to study the effects of concentration polarization on the pervaporation separation of butanol from an aqueous binary solution by a tri-layer PDMS membrane, where a layer of hydrophobic PE was placed in between a PDMS layer and the metal support. In their work, the overall mass transfer coefficient was estimated using solutiondiffusion model. However, the mass transfer coefficient of butanol in the feed channel was calculated semiempirically using a Sherwood number correlation for rectangular membrane module (Eq. (31)).

$$Sh = \frac{k_b d_H}{D_b} = 1.85 \left(\text{Re} \, Sc \, \frac{d_H}{l_m} \right)^{0.33}$$
 (31)

where d_H and l_m are the characteristic length of the rectangular membrane channel (hydraulic diameter) and the membrane module length, respectively. For this semi-empirical model, the mass transfer coefficient of butanol in the bulk layer is more than three times higher than that of the overall mass transfer coefficient. This clearly indicates that mass transfer is controlled by membrane diffusion, and the concentration polarization has a negligible effect on the transport process even when the system is operating in the laminar flow regime at a Reynolds number of 140.

In another work, Valentínyi et al. [117] improved the basic solution-diffusion model of Rautenbach et al. by considering that the transport coefficient as an exponential function of the permeating compound. In the basic solution-diffusion model, it is assumed that the transport coefficient has negligible concentration dependency and can be considered constant [118]. However, a large deviation between the experimental data and the model predictions was found at higher concentrations. The transport coefficient or permeance

of component i (D_i), defined in Eq. (32), was used by Rautenbach et al. because the concentration dependence of the diffusion coefficient was considered to be negligible.

$$\dot{D}_i = \frac{CD_i}{l_M} \tag{32}$$

In the work of Valentínyi et al., the authors assumed that the transport coefficient varies exponentially with concentration as shown in Eq. (33) since the model suggested by Rautenbach et al. could not be used at high concentrations of the permeating component.

$$\dot{D}_{i,\exp} = \dot{D}_{i} \exp\left(B^{*} x_{f,i}\right)$$
(33)

where B^{*} is a constant. Results obtained by Valentínyi et al. for the dehydration of butanol aqueous solutions by pervaporation using commercial hydrophilic polyvinyl acetate membranes (PVA)/PAN) showed that the estimation of the transport coefficient using Eq. (33) provides better predictions of butanol and water fluxes than the estimations using Eq. (32). The improved solution-diffusion model suggested by Valentínyi et al. could be used for azeotropic solutions with high water content as well as for modelling, design, and optimization of pervaporation processes.

Ashraf et al. used the model proposed by Valentínyi et al. to calculate the size and arrangement of the pervaporation modules [119]. The experimental results for the dehydration of an aqueous solution of butanol using a commercial pervaporation membrane were in good agreement with the proposed model. However, the model is limited to the type of membrane, components and operating conditions used in their experiments [119].

Petrychkovych et al. used the solution-diffusion model for calculating the pervaporation of butanol flux for a binary butanol/water mixture using a PE membrane. The calculated permeation flux was obtained assuming a constant diffusion coefficient, with a good agreement with the experimental permeation flux [120].

To gain a better understanding of the permeation of ABE species through polymeric membranes, it is paramount to investigate the solubility coefficient and diffusion coefficient of these components in various membranes. However, there are not many values reported in the literature for the solubility of ABE components in membranes. Table 2 presents the diffusion coefficients of ABE components reported in several investigations. It is shown that the diffusion coefficients for butanol in PDMS membranes are of the same order of magnitude in the different studies except for the values reported by Yang et al. [115] which are significantly smaller. The same trend was observed for the diffusion coefficients of acetone. For ethanol, the variation of the diffusion coefficients in PDMS membranes was more pronounced.

2.2. Maxwell-Stefan Theory

The generalized Maxwell-Stefan equation is based on the assumption that the migration of species is the result of a driving force that is counteracted by the friction of the migrating species from the other species and the immediate environment. It was formalized by Mason and Viehland for multicomponent systems and later implemented for membrane separation processes separation and such as gas pervaporation [121,121,122]. According to this theory, for multicomponent systems, the sum of the friction forces for a component, balances the driving force as expressed in Eq. (34) [45]. In this equation, D_{ii} represents the inverse draging force between species *i* and *j*, and v_i and v_j are the diffusion velocities for components *i* and *j*.

$$\frac{1}{RT}\frac{d\mu_{i}}{dz} = \sum_{j=1}^{n} \phi_{j} \frac{v_{j} - v_{i}}{\hat{D}_{ji}}$$
(34)

The chemical potential in Eq. (34) is related to the activity of components within the membrane assuming to have an ideal gas mixture. Eq. (35) represents a simplified form of Maxwell-Stefan equation for a ternary system including binary solution and the membrane material [45,123].

$$\frac{d\ln\phi_i}{dz} = \phi_j \frac{v_j - v_i}{\tilde{D}_{ij}} - \phi_M \frac{v_i}{\tilde{D}_{Mi}}$$
(35a)

$$\frac{d \ln \phi_j}{dz} = \phi_j \frac{v_i - v_j}{\tilde{D}_{ji}} - \phi_M \frac{v_{ji}}{\tilde{D}_{Mj}}$$
(35b)

$$\tilde{D}_{ij} = \hat{D}_{ij} \frac{d \ln a_i}{d \ln \phi_i}$$
(35c)

The diffusion coefficients in Eq. (37), i.e. \tilde{D}_{ij} and \tilde{D}_{ji} are the effective diffusion coefficients for component *i* and *j*.

Eq. (35) was rearranged to calculate the permeation flux of each component through the membrane (this model needs to be solved numerically) and it was assumed that the effective diffusion coefficients are equal ($\tilde{D}_{ij} = \tilde{D}_{ji}$) due to symmetrical conditions, which led to Eq. (36) [45].

$$J_{i} = -\frac{\tilde{D}_{Mi}}{\phi_{M}} \left(\frac{\phi_{i}\tilde{D}_{Mj} + \phi_{M}\tilde{D}_{ij}}{\phi_{M}\tilde{D}_{ij} + \phi_{i}\tilde{D}_{Mj} + \phi_{j}\tilde{D}_{Mi}} \right) \frac{dC_{i}}{dz} + \frac{\tilde{D}_{Mi}}{\phi_{M}} \left(\frac{\phi_{i}\tilde{D}_{Mj}}{\phi_{M}\tilde{D}_{ij} + \phi_{i}\tilde{D}_{Mj} + \phi_{j}\tilde{D}_{Mi}} \right) \frac{dC_{j}}{dz}$$
(36a)

$$J_{j} = -\frac{\tilde{D}_{Mj}}{\phi_{M}} \left(\frac{\phi_{j}\tilde{D}_{Mi} + \phi_{M}\tilde{D}_{ij}}{\phi_{M}\tilde{D}_{ij} + \phi_{j}\tilde{D}_{Mi} + \phi_{i}\tilde{D}_{Mj}} \right) \frac{dC_{j}}{dz} + \frac{\tilde{D}_{Mj}}{\phi_{M}} \left(\frac{\phi_{j}\tilde{D}_{Mi}}{\phi_{M}\tilde{D}_{ij} + \phi_{j}\tilde{D}_{Mi} + \phi_{i}\tilde{D}_{Mj}} \right) \frac{dC_{i}}{dz}$$
(36b)

When coupling effects are negligible, \hat{D}_{ij} (and consequently \tilde{D}_{ij}) approaches to infinity and Eq. (36) would be simplified to the Fick's first law of diffusion, where \tilde{D}_{Mi}/ϕ_M and \tilde{D}_{Mj}/ϕ_M are the Fick's diffusion coefficients as shown in Eq. (37) [45,123].

$$J_i = -\frac{D_{Mi}}{\phi_M} \frac{dC_i}{dz}$$
(37a)

$$J_{j} = -\frac{\dot{D}_{Mj}}{\phi_{M}} \frac{dC_{j}}{dz}$$
(37b)

Other researchers have used the same type of equations where the volume fraction was simply replaced by the weight or mole fraction in Eq. (36) [124,125]. Moreover, some modifications have been applied in different studies to obtain analytical solutions from the differential equations (Eq. (36)) using a few assumptions to simplify the integration procedure. The main advantage of Maxwell-Stefan theory could be its ability to predict the flux and selectivity for non-ideal multicomponent systems based on the results of single components, which significantly decreases the number of pervaporation experiments to be performed. Moreover, it has the potential to be used for module and process design together with membrane development.

Bettens et al. [34] investigated the deviations observed between the experimental results and a theoretical model that combined the extended Langmuir model for sorption and the Maxwell-Stefan diffusion for pervaporation of butanol/water and butanol/methanol. However, in their study, the desired components to be separated were water and methanol. Different types of methylated microporous silica membranes were used for this purpose. In addition, to predict the Maxwell-Stefan diffusion coefficients, three Maxwell-Stefan diffusivities were determined: \tilde{D}_{ij} , \tilde{D}_{iM} and \tilde{D}_{jM} . Moreover, for the counter-exchange Maxwell-Stefan diffusivity the Vignes equation (Eq. 40).

Maxwell–Stefan diffusivity, the Vignes equation (Eq. 40) was used.

$$\left(\tilde{D}_{ij} = \left(\tilde{D}_{iM}\right)^{\frac{C_{H,i}}{C_{H,i}+C_{H,j}}} \left(\tilde{D}_{jM}\right)^{\frac{C_{H,i}}{C_{H,i}+C_{H,j}}}\right)$$
(38)

The single-species Maxwell-Stefan diffusivities were used for the conditions where there were no interactions between different species and the corresponding counter-exchange coefficient was infinite ($\tilde{D}_{ii} \rightarrow \infty$). In this case, species were not able to pass each other in the narrow pores. The single-species Maxwell-Stefan diffusivities could either be independent of the amount adsorbed (Eqs. 39a and 39b) or dependent on the amount adsorbed (Eqs. 39c and 39d).

$$\tilde{D}_{iM} = \tilde{D}_{iM} \left(0 \right) \tag{39a}$$

$$\tilde{D}_{jM} = \tilde{D}_{jM} \left(0 \right) \tag{39b}$$

$$\tilde{D}_{iM} = \tilde{D}_{iM} \left(0 \right) \left(1 - C_{H,i} - C_{H,j} \right)$$
(39c)

$$\tilde{D}_{jM} = \tilde{D}_{jM} \left(0 \right) \left(1 - C_{H,i} - C_{H,j} \right)$$
(39d)

The comparison was made by assuming different case scenarios where the diffusion coefficients between the components and the membrane in the Maxwell-Stefan model were estimated. The pure alcohol Maxwell-Stefan diffusivity at zero coverage $(\tilde{D}_{iM}(0))$ was

derived from the experimental pure alcohol flux and the pure water Maxwell–Stefan micropore diffusivity at zero coverage ($\tilde{D}_{iM}(0)$) was achieved by fitting the experimental water flux data. The four scenarios that were proposed are as follows:

1) There are no interactions between feed species ($\tilde{D}_{ij} \rightarrow \infty$). Moreover, \tilde{D}_{iM} and \tilde{D}_{jM} are independent from the amount adsorbed (Eqs.39a and 39b);

2) There are no interactions between feed species ($\tilde{D}_{ij} \rightarrow \infty$). Moreover \tilde{D}_{iM} and \tilde{D}_{jM} are dependent on the amount adsorbed (Eqs.39c and 39d);

3) There are interactions between feed species and \tilde{D}_{ii} can be obtained by Vignes equation (Eq. 40).

$$\left(\tilde{D}_{ij} = \left(\tilde{D}_{iM}\right)^{\frac{C_{H,i}}{C_{H,i}+C_{H,j}}} \left(\tilde{D}_{jM}\right)^{\frac{C_{H,i}}{C_{H,i}+C_{H,j}}}\right)$$
(40)

Moreover, \tilde{D}_{iM} and \tilde{D}_{jM} are independent from the amount adsorbed (Eqs.39a and 39b);

4) There are interactions between feed species and \tilde{D}_{ij} can be obtained by Eq.40. Moreover, \tilde{D}_{iM} and \tilde{D}_{jM} are dependent on the amount adsorbed (Eqs.39c and 39d).

According to the results, Maxwell-Stefan theory was consistent with experimental pervaporation data for the first case scenario when no interactions took place between the components, and the diffusion coefficients of the components through the membrane were independent from the amount adsorbed. In addition, prediction performed with the second scenario for the calculation of the flux of components demonstrated to be closer to the experimental data compared to the first scenario. However, the last two case scenarios did not have a good fit with experimental data.

In another work, the mass transfer through a PDMS commercial membrane for pervaporation separation of the butanol from aqueous solution has been studied by Ebneyamini et al. [126]. A semiempirical approach on the Maxwell-Stefan model was extended to consider the effect of membrane swelling and the operating temperature on the diffusion coefficient and sorption properties. In order to estimate the effect of the operating temperature on the diffusion coefficients and the sorption of each species, Arrheniustype equations were incorporated into the MaxwellStefan model. Moreover, similar to the free volume theory, an exponential relationship was used to express the diffusion coefficient of each component as a function of the degree of swelling of the membrane at a constant temperature (Eq. 41).

$$D_{M,i} = D_i^0 e^{A_i \psi(C_{f,i}T)}$$
(41a)

$$\psi_{(C_{f,i}T)} = \frac{C_{f,i}k_{D,i}^{*}e^{\frac{-\Delta H_{i}}{RT}} + C_{f,j}k_{D,j}^{*}e^{\frac{-\Delta H_{j}}{RT}}}{\rho_{M}}$$
(41b)

The result of the extended Maxwell-Stefan model showed a better agreement with the experimental data in comparison to the Maxwell-Stefan model. Moreover, the model was able to predict the membrane properties such as solubility and diffusivity at different operating temperatures and feed concentrations.

2.3. Pore-Flow Model

The other proposed model for the overall mass transfer in a pervaporation separation process is the pore-flow model. The difference between this model and the solution-diffusion model is that the solutiondiffusion model considers no phase change in the membrane while, in the pore flow model, there is a phase change inside the membrane at a certain distance from the membrane surface. Considering the phase change inside the membrane, there should be a phase boundary between the liquid and the vapor for the mass transfer equations. In 1991, Okada and Matsuura [34] considered a pore flow model for describing the mass transfer through а cellulose membrane in pervaporation separation of ethyl alcohol/heptane mixtures. In this model, it is assumed that the selective layer of the membrane is formed by a series of straight cylindrical pores distributed within the membrane surface and isothermal conditions are assumed. Furthermore, the length of the pores is equal to the thickness of the active layer.

Three steps have been proposed for this model: (1) liquid transport from the pore inlet to the liquidvapor phase boundary; (2) evaporation at the phase boundary; (3) vapor transport from the phase boundary to the pore outlet [35,36]. Moreover, it was assumed that at the liquid-vapor phase boundary, the components reach to their saturated pressure in equilibrium with the feed solution. According to the above-mentioned assumptions, at steady state for single component permeation, the flux in the liquid and vapor segments can be calculated according to Eq. (42).

$$J_{L} = \frac{A^{Pore}}{l_{L}} \left(p_{L} - p^{sat} \right)$$
(42a)

$$J_{V} = \frac{B^{Pore}}{l_{V}} \left(\left(p^{sat} \right)^{2} - \left(p_{V} \right)^{2} \right)$$
(42b)

$$J = J_V = J_L \tag{42c}$$

where subscripts *L* and *V* represent the liquid and vapor phases, while *l* is the thickness of each phase inside the pore. *A* and *B* constants are obtained using the Darcy's equation and Henry's law (Eq. (43)).

$$A^{pore} = \frac{\pi r_{pore}^4 \rho_i N_i}{8\eta_i M_i}$$
(43a)

$$B^{pore} = \frac{\pi \left(2r_{pore}l_{ad} - l_{ad}^2\right)^2 l_{ad} N_t}{8r_{pore}} \frac{RT}{\mu_i^*} \left(k_{D,i}\right)^2$$
(43b)

where l_{ad} is the thickness of the adsorption monolayer.

Since the constants A and B are determined empirically, the pore-flow model would be limited to assist only in process and module design and it is not applicable for membrane development.

Moreover, there are additional models such as pseudo phase-change solution-diffusion, which combines the specifications of both the solutiondiffusion and the pore-flow models in one single framework. The pseudo phase-change solutiondiffusion takes the coupling effect from the solutiondiffusion model and the pseudo phase-change inside the membrane from the pore-flow model into consideration [127,128]. The pore-flow model has not been used yet for the separation of butanol by pervaporation.

3. Conclusion

Pervaporation is an appropriate process for the separation of butanol from different aqueous solutions especially ABE fermentation broths. However, to be employed at an industrial level using lab-scale experimental data, mathematical models are paramount to predict pervaporation process performances accurately. Such models can assist in the design phase of membrane modules for the purpose of optimization, flow patterns prediction, and vessel design. In addition, the membrane development using modelling could provide valuable information before membrane fabrication.

In this study, mass transfer modelling in a pervaporation separation of butanol from ABE fermentation broth, ABE model solutions and aqueous solutions were reviewed in this study.

Considering the previous works for the pervaporation of butanol, although the number of the diffusion models is very limited, the overall mass transfer was mainly used by researchers to estimate the mass transfer coefficient of the components using sorption models. Among the sorption models, which have been used for pervaporation separation process, Langmuir and Henry's law isotherms are deemed accurate models for the sorption prediction of butanol into membranes. In addition, in comparison to the theory of free volume, the dual-mode sorption model was found to be a simpler and more applicable model for estimating the butanol diffusion coefficient. As shown in Table 3, the solution-diffusion model has been the most frequently used model for the description of the mass transfer in pervaporation separation of butanol. However, the application of the Maxwell-Stefan theory for this purpose has been very limited and, to our knowledge, the pore-flow model has not been reported in the literature for the pervaporation of butanol.

Most of the models used for the pervaporation separation of butanol are semi-empirical models, which fall in between theoretical and empirical models in terms of complexity. Although, in the semi-empirical models, the driving force is well established, the permeability would be experimentally estimated. The complexity of the model increases with the number of components involved in the mass transfer and it further increases by considering the coupling effects. In this case, the Maxwell-Stefan theory seems to be an appropriate option for considering the coupling phenomenon. In addition, it is an accurate model for membrane separation in pervaporation due to its ability to predict the flux and selectivity of the multicomponent systems based on the results of single components, which significantly decreases the number of pervaporation experiments to be performed. In addition, it has the potential to be used for module and process design together with membrane development.

Furthermore, while the information obtained via the overall mass transfer models would be used for fundamental understanding of the process and module design, other information such as concentration polarization, pressure drop, flow pattern, and heat transfer also need to be considered for the purpose of process design. Moreover, molecular simulation could become in the future a very valuable tool for membrane development in the pervaporation of butanol. This study can be helpful in combining different sorption and diffusion models to achieve more rigorous models for the prediction of butanol separation by pervaporation.

Abbreviations

ABE	Acetone, Butanol, Ethanol
CIRC	Circulation equilibrium still
COSMO-RS	Conductor like screening model
	for real solvents
DDST	Differential distillation
EBUL	Ebuliometry
EPDM	Ethylene propylene diene rubber
GEM-RS	Generalized regular solution model
GLC	Gas-liquid chromatography
HSA	Headspace analysis
IGS	Inert gas stripping
LLE	Liquid-liquid extraction
LSG	Local surface Guggenheim equation
MBEA	Molecular beams
MMM	Mixed matrix membrane
MOSCED	Modified separation of cohesive energy
	density model
NRTL	Non-random two-liquid model
NSGLC	Non-steady state gas-liquid
	chromatography
PAI	Polyamide-imide
PAN	Polyacrylonitrile
PAV	Polyarylene vinylene
PDMS	Polydimethylsiloxane
PE	Polyethylene
PET	Polyethylene terephthalate
PEBA	Polyether block-amide
PRV	Phase ratio variation method
PV	Pervaporation
PVA	Poly(vinyl acetate)
PI	Polyimide
POMS	Poly(octhylmethyl siloxane)
PMS	Poly (methoxy siloxane)

PP	Polypropylene
PTFE	Polytetrafluoroethylene
PTMSP	Poly (1-(trimethylsilyl)-1-propyne)
RDIST	Rayleigh distillation
RO	Reverses osmosis
TENS	Tensimetry
UNIQUAC	Universal quasichemical
VPC	Vapour phase calibration
WWC	Wetted wall column

Nomenclature

а	activity [-]
A 1:	free volume parameter of component <i>i</i> for
n _{al}	the glassy region in polymer [-]
A_i	dimensionless constant in Eq. (40)
A_M	membrane area [m ²]
Anore	constant defined for a pure component
Aporto	system in the pore flow model [-]
b	adsorption or hole affinity constant [bar-1]
	coupling coefficients in semi-empirical
В	model after Meyer-Blumenroth
	[kmol.m ⁻¹ .s ⁻¹ .bar ²]
B^*	Constant parameter in Eq. (35) [-]
Dnore	constant for a pure component system in
DPore	the pore flow model [-]
D	free volume parameter of component <i>i</i> for
Ddi	the glassy region in polymer [-]
B^{FV}	generalised free volume parameter [-]
С	concentration [kmol.m ⁻³ , kg.m ⁻³]
C	concentration of diffusing in membrane
CD	[kmol.m ⁻³ , kg.m ⁻³]
C.,	concentration in microvoids [kmol.m ⁻³ ,
c_H	kg.m ⁻³]
	Langmuir maximum sorption capacity in
C_{H}	the polymeric membrane
	[kmol.m ⁻³ , kg.m ⁻³]
D	diffusion coefficient [m ² .s ⁻¹]
D0	diffusion coefficient in infinite dilution
D°	[m ² .s ⁻¹]
Da	diffusion coefficient in the Henry's Law
D_D	mode [m ² .s ⁻¹]
D.,	diffusion coefficient in the Langmuir mode
D_H	$[m^2.s^{-1}]$
\mathbf{D}^T	thermodynamic diffusion coefficient
D	[m ² .s ⁻¹]
$\overline{\mathbf{D}}^T$	modified thermodynamic diffusion
D	coefficient [m ² .s ⁻¹]
ñ	effective concentration-dependent
D	diffusion coefficient [m ² .s ⁻¹]

\hat{D}	Maxwell-Stefan interaction parameter [m ² .s ⁻¹]	Vo ^T	the volume in feeding tank [m ³] weight factors for three dimensional
'n	permeance [kg.m ⁻² .s ⁻¹]	W ₁ , W ₂ , W ₃	solubility parameters [-]
D	energy required to overcome dispersion	X	mole fraction [-]
$\Delta E_{di,}$	nolar interactions [I mol-1]	X _{i,b}	the bulk mole fraction [-]
	energy required to overcome hydrogen	<i>X</i> *	the interface mole fraction [-]
ΔE_{hb}	[I mol-1]	Ζ	z-co-ordinate [m]
ΛF	energy of vanorisation [I mol·1]	0	proportional constant in free volume
ΔL_{vap}	fugacity [bar]	þ	theory [-]
J fFV	free volume [-]	V	activity coefficient [-]
J F	as defined in Eq. (24) [-]	7 i	
лн	heat of adsorption [I mol-1]	Y	average activity coefficient of component i
I	flux [kmol m ⁻² s ⁻¹]	/ M ,i	in membrane [-]
J	Henry's law constant referring to	δ_{i}	solubility parameter [J ^{1/2} .m ^{-3/2}]
$k_{D,i}$	component <i>i</i> [bar-1]		solubility parameter due to hydrogen
- *	dimensionless Henry's law constant	δ_{ii}	bonds with reference to component <i>i</i>
$k_{D,i}$	[a m-3/a m-3]	- <i>nD</i> , <i>i</i>	[[1/2.m ^{-3/2}]
_ ,-	[g.m ~ / g.m ~] houndary layer mass transfer coefficient		solubility parameter due to dispersion
k		δ_{rr} .	forces with reference to component <i>i</i>
	L J (unit weight of polymer per volume of	aj "i	[[1/2.m ^{-3/2}]
k'	adsorbed gas molecule $i \} \times k_{2}$		solubility parameter due to dispersion
$\kappa_{D,i}$	[mol m-3 har-1]	δ_{zz}	polar interactions with reference to
K.	$2 \operatorname{Grinod} \operatorname{in} \operatorname{Fa} (24) [-]$	<i>a</i> 1,1	component <i>i</i> [$I^{1/2}$.m ^{-3/2}]
N i	as defined in Eq. (24) [-]	E	empirical constant or 'softener' [-]
Kov	membrane [-]	n	liquid viscosity [Pa.s]
1.	thickness of the adsorption monolayer [m]	U	chemical potential [I.mol ⁻¹]
	thickness of membrane M [m]	, - ,	Surface viscosity of adsorptive layer of
I M	length of the liquid-filled proportion of the	μ	vapour [Pa.s]
l_L	nore in the nore flow model [m]	ρ	density [kg.m ⁻³]
	length of the vanour-filled proportion of	, Фс	crystallinity of polymer P [-]
l_V	the pore in the pore flow model [m]	ø	volume fraction [-]
М	molar weight [kg kmol-1]	Υ 	as defined in Equation (40), (degree of
1.1	total number of nores per effective	ψ	swelling) [g.g ⁻¹]
N_t	membrane area [-]		Flory-Huggins binary interaction
n	nartial pressure [bar Pa]	X	parameter [-]
Ρ	Pressure in boundary layer in Eq. (27)	_	distance between polymer <i>P</i> and
p^*	[har]	$\Delta_{p,i}$	component <i>i</i> in -space $[I^{1/2}.m^{-3/2}]$
	permeability with reference to an activity	Subscripts	
Р	driving force [kmol.m ⁻¹ .s ⁻¹ .bar ⁻¹]	b	butanol concentration
rnora	pore radius [m]	b_{a}	initial butanol concentration
R	gas constant [Lmo] ⁻¹ .K ⁻¹]	exp	experimental
Re	Revnolds number [-]	f	feed
S	Solubility coefficient [kmol.m ⁻³]	i,i	component <i>i</i> and <i>j</i>
Sc	Schmidt number [-]	Ĺ	liquid phase
Sh	Sherwood number [-]	т	module
t	time [s]	М	membrane
T	temperature [K]	p	polymer
v	diffusion velocity [m ² .s]	P	permeate
V	molar volume [m ³ .mol ⁻¹]	sat	saturated
	L 3		

tot	Total
V	vapour phase
Suparaminta	

Superscripts

0	reference
FV	free volume
L	liquid phase
mix	Mixture

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Tables

Table 1. Summary of the updated data in the literature for infinite dilution activity coefficients of butanol in water.

273.15 40.21 HSA [129] 273.15 32.59 HSA [130] 283.15 40.41 HSA [130] 288.15 49.01 IGS [131] 290 20.72 MOSCED [94] 293.15 46.48 IGS [131] 293.15 41.39 HSA [132] 293.15 48.38 HSA [130] 298.15 46.48 IGS [133] 298.15 46.48 IGS [134] 298.15 44.48 IGS [136] 298.15 54.98 HSA [137] 298.15 54.98 HSA [137] 298.15 53.68 NSGLC [138] 298.15 53.68 NSGLC [139] 298.15 53.62 WWC [143] 298.15 53.62 WWC [144] 298.15 56.90 UNIQUAC [93] 298.15 55.80	T (K)	γ	Method	Ref
273.15 32.59 HSA [130] 283.15 40.41 HSA [130] 288.15 49.01 IGS [131] 290 20.72 MOSCED [94] 293.15 46.48 IGS [131] 293.15 44.38 HSA [132] 293.15 46.48 IGS [133] 298.15 46.48 IGS [133] 298.15 46.48 IGS [134] 298.15 52.88 DDST [134] 298.15 54.98 HSA [137] 298.15 54.98 HSA [137] 298.15 54.98 HSA [137] 298.15 53.30 HSA [149] 298.15 53.68 NSCLC [139] 298.15 53.62 WWC [143] 298.15 53.62 WWC [144] 298.15 54.60 UNIQUAC [93] 298.15 55.80	273.15	40.21	HSA	[129]
283.15 40.41 HSA [130] 288.15 49.01 IGS [131] 290 20.72 MOSCED [94] 293.15 46.48 IGS [131] 293.15 41.39 HSA [132] 293.15 46.48 IGS [133] 298.15 52.88 DDST [134] 298.15 52.88 DDST [135] 298.15 54.98 HSA [137] 298.15 54.98 HSA [137] 298.15 54.98 HSA [138] 298.15 54.98 HSA [137] 298.15 54.98 HSA [138] 298.15 54.98 HSA [139] 298.15 53.68 NGLC [139] 298.15 53.68 HSA [140] 298.15 56.90 UNIQUAC [93] 298.15 51.37 GLC [93] 298.15 51.37	273.15	32.59	HSA	[130]
288.15 49.01 IGS [131] 290 20.72 MOSCED [94] 293.15 46.48 IGS [131] 293.15 41.39 HSA [132] 293.15 48.38 HSA [130] 298.15 46.48 IGS [133] 298.15 52.88 DDST [134] 298.15 44.48 IGS [135] 298.15 54.98 HSA [137] 298.15 54.98 HSA [138] 298.15 54.98 HSA [138] 298.15 52.83 HSA [138] 298.15 53.68 NSGLC [139] 298.15 53.68 NSGLC [139] 298.15 53.68 NSGLC [140] 298.15 53.62 WWC [143] 298.15 56.20 GEM-RS [93] 298.15 56.20 GEM-RS [93] 298.15 51.37 <td>283.15</td> <td>40.41</td> <td>HSA</td> <td>[130]</td>	283.15	40.41	HSA	[130]
290 20.72 MOSCED [94] 293.15 46.48 IGS [131] 293.15 41.39 HSA [132] 293.15 48.38 HSA [130] 298.15 46.48 IGS [133] 298.15 52.88 DDST [134] 298.15 52.88 DDST [135] 298.15 54.98 HSA [137] 298.15 54.98 HSA [137] 298.15 54.98 HSA [138] 298.15 54.98 HSA [137] 298.15 53.68 NSGLC [139] 298.15 53.68 NSGLC [139] 298.15 53.68 NSGLC [140] 298.15 53.62 WWC [143] 298.15 53.62 WWC [143] 298.15 56.20 GEM-RS [93] 298.15 55.80 NRTL [93] 298.15 55.80	288.15	49.01	IGS	[131]
293.15 46.48 IGS [131] 293.15 41.39 HSA [132] 293.15 48.38 HSA [130] 298.15 46.48 IGS [133] 298.15 52.88 DDST [134] 298.15 48.18 TENS [135] 298.15 44.48 IGS [137] 298.15 54.98 HSA [137] 298.15 54.98 HSA [138] 298.15 52.83 HSA [138] 298.15 52.83 HSA [139] 298.15 53.68 NSGLC [139] 298.15 53.68 NSGLC [139] 298.15 53.62 WWC [141] 298.15 53.62 WWC [143] 298.15 53.62 WWC [143] 298.15 56.90 UNIQUAC [93] 298.15 51.37 GLC [93] 298.15 51.37	290	20.72	MOSCED	[94]
293.15 41.39 HSA [132] 293.15 48.38 HSA [130] 298.15 46.48 IGS [133] 298.15 52.88 DDST [134] 298.15 48.18 TENS [135] 298.15 44.48 IGS [136] 298.15 54.98 HSA [137] 298.15 54.98 HSA [137] 298.15 52.83 HSA [138] 298.15 52.83 HSA [138] 298.15 52.83 HSA [139] 298.15 53.68 NSGLC [139] 298.15 53.68 NSGLC [139] 298.15 53.68 NSGLC [141] 298.15 53.62 WWC [143] 298.15 53.62 WWC [143] 298.15 55.40 UNIQUAC [93] 298.15 56.20 GEM-RS [93] 298.15 51.37 GLC [93] 298.15 51.37 GLC [93	293.15	46.48	IGS	[131]
293.15 48.38 HSA [130] 298.15 46.48 IGS [133] 298.15 52.88 DDST [134] 298.15 48.18 TENS [135] 298.15 44.48 IGS [136] 298.15 54.98 HSA [137] 298.15 52.83 HSA [138] 298.15 52.83 HSA [139] 298.15 47.09 IGS [131] 298.15 53.68 NSGLC [139] 298.15 53.68 NSGLC [139] 298.15 53.68 NSGLC [141] 298.15 53.62 WWC [143] 298.15 53.62 WWC [143] 298.15 57.40 IGS [144] 298.15 58.10 LSG [93] 298.15 58.10 LSG [93] 298.15 58.20 GEM-RS [93] 298.15 51.37	293.15	41.39	HSA	[132]
298.15 46.48 IGS [133] 298.15 52.88 DDST [134] 298.15 48.18 TENS [135] 298.15 44.48 IGS [136] 298.15 54.98 HSA [137] 298.15 52.83 HSA [138] 298.15 52.83 HSA [139] 298.15 47.09 IGS [131] 298.15 49.45 HSA [129] 298.15 53.68 NSGLC [139] 298.15 53.68 NSGLC [139] 298.15 53.68 HSA [141] 298.15 58.85 HSA [141] 298.15 53.62 WWC [143] 298.15 57.40 IGS [144] 298.15 56.90 UNIQUAC [93] 298.15 58.10 LSG [93] 298.15 51.37 GLC [93] 298.15 51.37	293.15	48.38	HSA	[130]
298.15 52.88 DDST [134] 298.15 48.18 TENS [135] 298.15 44.48 IGS [136] 298.15 54.98 HSA [137] 298.15 52.83 HSA [138] 298.15 52.83 HSA [131] 298.15 47.09 IGS [131] 298.15 49.45 HSA [129] 298.15 53.68 NSGLC [139] 298.15 53.68 NSGLC [141] 298.15 53.62 WWC [141] 298.15 53.62 WWC [143] 298.15 53.62 WWC [143] 298.15 53.62 WWC [143] 298.15 56.90 UNIQUAC [93] 298.15 58.10 LSG [93] 298.15 51.37 GLC [93] 298.15 51.37 GLC [93] 298.2 55.20	298.15	46.48	IGS	[133]
298.15 48.18 TENS [135] 298.15 44.48 IGS [136] 298.15 54.98 HSA [137] 298.15 52.83 HSA [138] 298.15 52.83 HSA [131] 298.15 47.09 IGS [131] 298.15 49.45 HSA [129] 298.15 53.68 NSGLC [139] 298.15 53.68 NSGLC [139] 298.15 53.68 HSA [141] 298.15 53.62 WWC [143] 298.15 53.62 WWC [143] 298.15 53.62 WWC [143] 298.15 57.40 IGS [144] 298.15 56.90 UNIQUAC [93] 298.15 58.10 LSG [93] 298.15 51.37 GLC [93] 298.15 51.37 GLC [93] 298.2 55.20	298.15	52.88	DDST	[134]
298.15 44.48 IGS [136] 298.15 54.98 HSA [137] 298.15 52.83 HSA [138] 298.15 47.09 IGS [131] 298.15 49.45 HSA [129] 298.15 53.68 NSGLC [139] 298.15 53.30 HSA [140] 298.15 58.85 HSA [141] 298.15 58.85 HSA [141] 298.15 53.62 WWC [143] 298.15 53.62 WWC [143] 298.15 57.40 IGS [144] 298.15 56.90 UNIQUAC [93] 298.15 56.20 GEM-RS [93] 298.15 51.37 GLC [93] 298.15 51.37 GLC [93] 298.2 55.20 GLC [144] 303.15 81.61 HSA [142] 303.15 51.68	298.15	48.18	TENS	[135]
298.15 54.98 HSA [137] 298.15 52.83 HSA [138] 298.15 47.09 IGS [131] 298.15 49.45 HSA [129] 298.15 53.68 NSGLC [139] 298.15 53.68 NSGLC [140] 298.15 53.68 HSA [141] 298.15 58.85 HSA [141] 298.15 53.62 WWC [143] 298.15 53.62 WWC [143] 298.15 57.40 IGS [144] 298.15 56.90 UNIQUAC [93] 298.15 56.20 GEM-RS [93] 298.15 51.37 GLC [93] 298.15 51.37 GLC [93] 298.2 55.20 GLC [145] 298.45 51.11 HSA [146] 300 18.89 MOSCED [94] 303.15 51.68	298.15	44.48	IGS	[136]
298.1552.83HSA[138]298.1547.09IGS[131]298.1549.45HSA[129]298.1553.68NSGLC[139]298.1553.30HSA[140]298.1553.30HSA[141]298.1558.85HSA[141]298.1553.62WWC[143]298.1553.62WWC[143]298.1557.40IGS[144]298.1556.90UNIQUAC[93]298.1556.90UNIQUAC[93]298.1556.20GEM-RS[93]298.1555.80NRTL[93]298.1551.37GLC[145]298.1551.11HSA[146]30018.89MOSCED[94]303.1551.68HSA[142]303.1553.41TENS[130]308.1557.23TENS[130]31017.16MOSCED(94)313.1589.57VPC[149]	298.15	54.98	HSA	[137]
298.1547.09IGS[131]298.1549.45HSA[129]298.1553.68NSGLC[139]298.1553.30HSA[140]298.1558.85HSA[141]298.1558.85HSA[141]298.1553.62WWC[143]298.1553.62WWC[143]298.1557.40IGS[144]298.1556.90UNIQUAC[93]298.1556.90UNIQUAC[93]298.1556.20GEM-RS[93]298.1555.80NRTL[93]298.1551.37GLC[145]298.1551.11HSA[146]30018.89MOSCED[94]303.1551.68HSA[142]303.1553.41TENS[130]308.1539.49HSA[142]303.1557.23TENS[130]31017.16MOSCED(94)313.1589.57VPC[149]	298.15	52.83	HSA	[138]
298.1549.45HSA[129]298.1553.68NSGLC[139]298.1553.30HSA[140]298.1558.85HSA[141]298.1558.85HSA[141]298.1553.62WWC[143]298.1553.62WWC[143]298.1557.40IGS[144]298.1556.90UNIQUAC[93]298.1558.10LSG[93]298.1556.20GEM-RS[93]298.1551.37GLC[93]298.1551.37GLC[145]298.255.20GLC[145]298.351.11HSA[146]30018.89MOSCED[94]303.1551.68HSA[142]303.1553.41TENS[130]308.1539.49HSA[142]308.1557.23TENS[130]31017.16MOSCED(94)313.1589.57VPC[149]	298.15	47.09	IGS	[131]
298.1553.68NSGLC[139]298.1553.30HSA[140]298.1558.85HSA[141]298.1558.85HSA[141]298.1553.62WWC[143]298.1557.40IGS[144]298.1556.90UNIQUAC[93]298.1556.90UNIQUAC[93]298.1556.20GEM-RS[93]298.1556.20GEM-RS[93]298.1551.37GLC[93]298.1551.37GLC[145]298.255.20GLC[145]298.351.11HSA[146]30018.89MOSCED[94]303.1551.68HSA[142]303.1553.41TENS[130]308.1539.49HSA[142]308.1557.23TENS[130]31017.16MOSCED(94)313.1589.57VPC[149]	298.15	49.45	HSA	[129]
298.1553.30HSA[140]298.1558.85HSA[141]298.1548.18HSA[142]298.1553.62WWC[143]298.1557.40IGS[144]298.1556.90UNIQUAC[93]298.1556.90UNIQUAC[93]298.1556.20GEM-RS[93]298.1555.80NRTL[93]298.1551.37GLC[93]298.1551.37GLC[93]298.1551.11HSA[146]30018.89MOSCED[94]303.1551.68HSA[142]303.1553.41TENS[130]308.1539.49HSA[142]308.1557.23TENS[130]31017.16MOSCED(94)313.1589.57VPC[149]	298.15	53.68	NSGLC	[139]
298.1558.85HSA[141]298.1548.18HSA[142]298.1553.62WWC[143]298.1557.40IGS[144]298.1556.90UNIQUAC[93]298.1558.10LSG[93]298.1556.20GEM-RS[93]298.1555.80NRTL[93]298.1551.37GLC[93]298.1551.37GLC[93]298.255.20GLC[145]298.4551.11HSA[146]30018.89MOSCED[94]303.1551.68HSA[142]303.1553.41TENS[130]308.1557.23TENS[130]31017.16MOSCED(94)313.1589.57VPC[149]	298.15	53.30	HSA	[140]
298.1548.18HSA[142]298.1553.62WWC[143]298.1557.40IGS[144]298.1556.90UNIQUAC[93]298.1558.10LSG[93]298.1556.20GEM-RS[93]298.1555.80NRTL[93]298.1551.37GLC[93]298.255.20GLC[145]298.4551.11HSA[146]30018.89MOSCED[94]303.1551.68HSA[142]303.1553.41TENS[130]308.1557.23TENS[130]31017.16MOSCED(94)313.1549.50GLC[148]313.1589.57VPC[149]	298.15	58.85	HSA	[141]
298.1553.62WWC[143]298.1557.40IGS[144]298.1556.90UNIQUAC[93]298.1558.10LSG[93]298.1556.20GEM-RS[93]298.1555.80NRTL[93]298.1551.37GLC[93]298.255.20GLC[145]298.4551.11HSA[146]30018.89MOSCED[94]303.1551.68HSA[142]303.1553.41TENS[130]308.1557.23TENS[130]31017.16MOSCED(94)313.1589.57VPC[149]	298.15	48.18	HSA	[142]
298.1557.40IGS[144]298.1556.90UNIQUAC[93]298.1558.10LSG[93]298.1556.20GEM-RS[93]298.1555.80NRTL[93]298.1551.37GLC[93]298.255.20GLC[145]298.4551.11HSA[146]30018.89MOSCED[94]303.1581.61HSA[147]303.1551.68HSA[142]308.1557.23TENS[130]31017.16MOSCED(94)313.1589.57VPC[149]	298.15	53.62	WWC	[143]
298.1556.90UNIQUAC[93]298.1558.10LSG[93]298.1556.20GEM-RS[93]298.1555.80NRTL[93]298.1551.37GLC[93]298.255.20GLC[145]298.4551.11HSA[146]30018.89MOSCED[94]303.1581.61HSA[147]303.1551.68HSA[142]303.1553.41TENS[130]308.1557.23TENS[130]31017.16MOSCED(94)313.1589.57VPC[149]	298.15	57.40	IGS	[144]
298.1558.10LSG[93]298.1556.20GEM-RS[93]298.1555.80NRTL[93]298.1551.37GLC[93]298.255.20GLC[145]298.4551.11HSA[146]30018.89MOSCED[94]303.1581.61HSA[147]303.1551.68HSA[142]303.1553.41TENS[130]308.1539.49HSA[142]308.1557.23TENS[130]31017.16MOSCED(94)313.1589.57VPC[149]	298.15	56.90	UNIQUAC	[93]
298.1556.20GEM-RS[93]298.1555.80NRTL[93]298.1551.37GLC[93]298.255.20GLC[145]298.4551.11HSA[146]30018.89MOSCED[94]303.1581.61HSA[147]303.1551.68HSA[142]303.1553.41TENS[130]308.1557.23TENS[130]31017.16MOSCED(94)313.1589.57VPC[149]	298.15	58.10	LSG	[93]
298.1555.80NRTL[93]298.1551.37GLC[93]298.255.20GLC[145]298.4551.11HSA[146]30018.89MOSCED[94]303.1581.61HSA[147]303.1551.68HSA[142]303.1553.41TENS[130]308.1539.49HSA[142]308.1557.23TENS[130]31017.16MOSCED(94)313.1589.57VPC[149]	298.15	56.20	GEM-RS	[93]
298.1551.37GLC[93]298.255.20GLC[145]298.4551.11HSA[146]30018.89MOSCED[94]303.1581.61HSA[147]303.1551.68HSA[142]303.1553.41TENS[130]308.1539.49HSA[142]308.1557.23TENS[130]31017.16MOSCED(94)313.1589.57VPC[149]	298.15	55.80	NRTL	[93]
298.255.20GLC[145]298.4551.11HSA[146]30018.89MOSCED[94]303.1581.61HSA[147]303.1551.68HSA[142]303.1553.41TENS[130]308.1539.49HSA[142]308.1557.23TENS[130]31017.16MOSCED(94)313.1589.57VPC[149]	298.15	51.37	GLC	[93]
298.4551.11HSA[146]30018.89MOSCED[94]303.1581.61HSA[147]303.1551.68HSA[142]303.1553.41TENS[130]308.1539.49HSA[142]308.1557.23TENS[130]31017.16MOSCED(94)313.1589.57VPC[149]	298.2	55.20	GLC	[145]
30018.89MOSCED[94]303.1581.61HSA[147]303.1551.68HSA[142]303.1553.41TENS[130]308.1539.49HSA[142]308.1557.23TENS[130]31017.16MOSCED(94)313.1549.50GLC[148]313.1589.57VPC[149]	298.45	51.11	HSA	[146]
303.1581.61HSA[147]303.1551.68HSA[142]303.1553.41TENS[130]308.1539.49HSA[142]308.1557.23TENS[130]31017.16MOSCED(94)313.1549.50GLC[148]313.1589.57VPC[149]	300	18.89	MOSCED	[94]
303.1551.68HSA[142]303.1553.41TENS[130]308.1539.49HSA[142]308.1557.23TENS[130]31017.16MOSCED(94)313.1549.50GLC[148]313.1589.57VPC[149]	303.15	81.61	HSA	[147]
303.15 53.41 TENS [130] 308.15 39.49 HSA [142] 308.15 57.23 TENS [130] 310 17.16 MOSCED (94) 313.15 49.50 GLC [148] 313.15 89.57 VPC [149]	303.15	51.68	HSA	[142]
308.15 39.49 HSA [142] 308.15 57.23 TENS [130] 310 17.16 MOSCED (94) 313.15 49.50 GLC [148] 313.15 89.57 VPC [149]	303.15	53.41	TENS	[130]
308.15 57.23 TENS [130] 310 17.16 MOSCED (94) 313.15 49.50 GLC [148] 313.15 89.57 VPC [149]	308.15	39.49	HSA	[142]
310 17.16 MOSCED (94) 313.15 49.50 GLC [148] 313.15 89.57 VPC [149]	308.15	57.23	TENS	[130]
313.15 49.50 GLC [148] 313.15 89.57 VPC [149]	310	17.16	MOSCED	(94)
313.15 89.57 VPC [149]	313.15	49.50	GLC	[148]
	313.15	89.57	VPC	[149]

313.15	73.19	PRV	[150]
313.15	54.60	COSMO-RS	[151]
318.15	60.22	TENS	[130]
320	15.55	MOSCED	[94]
323.15	73.11	PRV	[150]
323.15	61.37	RDIST	[152]
323.15	62.30	RDIST	[152]
323.15	61.50	TENS	[130]
323.15	58.67	HSA	[130]
323.15	59.38	HSA	[130]
323.2	58.67	GLC	[145]
323.23	78.73	TENS	[153]
328.15	61.62	NSGLC	[154]
328.15	62.80	TENS	[130]
330	14.09	MOSCED	[94]
333.15	47.80	TENS	[135]
333.15	59.32	GLC	[148]
333.15	79.28	VPC	[149]
333.15	73.70	PRV	[150]
333.15	66.69	RDIST	[152]
333.15	64.39	RDIST	[152]
333.15	65.10	RDIST	[152]
333.15	63.37	TENS	[130]
333.2	61.13	GLC	[145]
340	12.76	MOSCED	[94]
343.15	59.32	EBUL	[155]
343.15	67.83	EBUL	[156]
343.15	79.68	VPC	[149]
343.15	75.04	PRV	[150]
343.15	63.82	RDIST	[152]
353.15	57.23	EBUL	[155]
353.15	46.48	EBUL	[156]
353.15	73.19	VPC	[149]
353.15	76.55	PRV	[150]
353.15	62.80	RDIST	[152]
363.15	55.48	EBUL	[155]
363.15	79.52	PRV	[150]
372.15	27.11	EBUL	[156]
372.15	56.09	CIRC	[130]
373.15	54.00	EBUL	[155]
373.15	88.23	EBUL	[157]

Polymer/Solution	Component	Temperature (K)	Diffusivity (m ² /s)	Ref	
	Acetone	308	0.85x10 ⁻¹⁰		
DDMC /Dune component	n-Butanol	308	0.3x10 ⁻¹⁰	[150]	
PDMS/Pure component	Ethanol	308	0.60x10 ⁻¹⁰	[158]	
	Water	308	0.55x10 ⁻¹⁰		
	Ethanol	298.15	0.6x10 ⁻⁹		
PDMS/Ethanol-Water mixture	Water	298.15	4.4x10 ⁻⁹	[159]	
	Ethanol- water	298.15	0.37x10 ⁻⁹	[103]	
	n-Butanol	303.15	3.11x10 ^{-10*}		
DDMS / Pure component	t-Butanol	303.15	2.66x10 ^{-10*}	[160]	
r DM3/ r ure component	s-Butanol	303.15	2.25x10 ^{-10*}	[100]	
	Water	303.15	129.05x10 ^{-10*}		
PDMS (GE615)/Pure water	Water	298.15	1.7x10 ^{-9 (a)}		
PDMS (PS342.5)/Pure water	Water	298.15	2x10 ^{-9 (a)}	[161]	
PDMS/Pure water	Water	298.15	7.8x10 ^{-10 (a)}		
	n-Butanol	303.15	0.65x10 ⁻¹⁰		
	Ethanol	353.15	7.1x10 ^{-10*}		
PDMS/Alcohols aqueous binary	n-Butanol	353.15	5.5x10 ⁻¹⁰	[162]	
solutions	Ethanol	353.15	12x10 ⁻¹⁰	[102]	
	Water	353.15	12x10 ⁻¹⁰		
	Water	298.15	3x10 ⁻¹⁰		
PDMS/Aqueous solutions	n-Butanol	299.15	1.6x10 ^{-10 (b)}	[163]	
	n-Butanol	398.15	0.563x10 ^{-10*}		
	Ethanol	398.15	0.793x10 ^{-10*}		
Creasingly A Dilute solutions	Ethanol	393.15	0.787x10 ^{-10*}	[1 (4]	
Crossinked PVA/Dilute solutions	Ethanol	383.15	0.92x10 ⁻¹⁰ *	[164]	
	Water	393.15	39.08x10 ⁻¹⁰ *		
	Water	383.15	8.89x10 ^{-10*}		
	Ethanol	300	0.45x10 ⁻⁹		
PDMS/Pure component	Water	300	1.45x10 ⁻⁹	[110]	
DE /Dure	Ethanol	300	0.07x10-9	[110]	
PE/Pure	Water	300	0.78x10 ⁻⁹		
	Acetone	313.2	6.106x10 ⁻¹²		
DDMC (A success bis served by the served by	n-Butanol	313.2	2.589x10 ⁻¹²	[11]]	
PDMS/Aqueous binary solutions	Ethanol	313.2	2.05x10 ⁻¹²	[115]	
	Water	313.2	1.867x10 ⁻¹²		
PERVAP [®] 4060/Aqueous binary	Ethanol	303.15	9.55x10 ⁻⁹		
solutions	Water	303.15	6.52x10 ⁻¹⁰	[102]	
Ciliarlita 1 marlita (Durana annua annu	n-Butanol	293	4.5x10 ⁻¹⁵		
Sincante-1 zeonte/Pure component	Ethanol	293	13.2x10 ⁻¹⁶	[166]	

Table 2. Diffusion coefficients of ABE components reported in the literature for different pervaporation membranes.

Silicalite-1 zeolite/Pure component	Water	298	1.7x10 ⁻⁹	[57]	
	Acetone	303.15	4.6x10 ⁻¹⁰ _4.9x10 ⁻¹⁰		
IL gel layer/ABE solutions	n-Butanol	303.15	4.2x10 ⁻¹¹ _3.9x10 ⁻¹⁰	[33]	
	Ethanol	303.15	5.6x10 ⁻¹² _5.2x10 ⁻¹⁰		
Methylated silica/ Aqueous binary solutions	n-Butanol	333.15	4.7x10 ^{-14(c)}		
	Ethanol	333.15	1.1x10 ^{-13(c)}	[34]	
	Water	333.15	$3.7 x 10^{-12} _{7.1 x 10^{-12} (c)}$		
* infinite dilute diffusion coefficient					
(a) determined on the transient slope					
(b) determined at half saturation of transient					
(c) Maxwell–Stefan single-file diffusivities					

Table 3. Mathematical models which have been used for the pervaporation separation of butanol.

Membrane	Feed	Modelling method	Ref
Supported gelled ionic liquid	ABE mixtures	Solution diffusion	[33]
Composite PVA membrane on PAN support	butanol/water	Solution diffusion	[112]
Composite PDMS	ABE fermentation	Solution diffusion	[18]
Tri-layer PDMS	butanol/water	Solution diffusion	[116]
PVA/PAN	water/butanol	Solution diffusion	[117]
PERVAP 2510	water/butanol	Solution diffusion	[119]
PE	butanol/water	Solution diffusion	[120]
PDMS	ABE water binary	Non-equilibrium solution diffusion	[115]
PDMS	butanol/water	Maxwell–Stefan	[126]
Methylated microporous silica	butanol/water, butanol/methanol	Maxwell–Stefan	[34]