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A generic transport model for separation of gas mixtures by glassy polymer membranes based on Maxwell-Stefan formulation

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Glassy polymer membranes offer a notable advantage over rubbery membranes for separation of gas mixtures due to better diffusional molecular sieving. However, predicting the separation behaviour of the membrane system is complicated due different coupling effects arising as a result of differences in adsorption and diffusion of permeating components. A true description of multicomponent transport is a basic pace in design and optimization of membrane separation processes. The conventional dual transport model fails to give a correct prediction for glassy polymer systems. Hence, the main purpose of this research was to present a transport model to predict reliably gas mixture separation via glassy polymer membrane. Maxwell-Stefan formulation theory was considered as a basis for development of the model because of its main advantage in which binary diffusivities can be used to describe multicomponent diffusion behaviour. Equilibrium factor was described in terms of dual adsorption model. Two case studies were considered to validate the model prediction behaviour, i.e. CH_4/ CO_2 and also C_3H_6/C_3H_8 separation which are two important processes in natural gas and petrochemical industries. The results obtained revealed very good agreement between experimental and the predicted selectivities by the developed transport model, while it was shown a poor result is obtained by conventional dual transport model. It was also shown neither equilibrium nor kinetic interactions between permeating components can be safely ignored. However, the effect of kinetic coupling is more crucial due to the fact the separation in glassy polymer membranes occurs based on diffusional selectivity rather than adsorption selectivity.

Introduction

Natural gas plays a major rule in energy scene due to its clean and environmental-friendly nature. Therefore, there is a tremendous demand for it in all economic sectors. Although, the main component of natural gas is methane, it contains substantial impurities such as carbon dioxide, water vapor, hydrogen sulphide and etc. Hence, it should be treated before delivering to pipelines or being used for other purposes. Membrane process is an energy efficient technology due to its potential for acid gas capture from gas mixtures. Among available methods for gas treatment such as solvent absorption and pressure swing adsorption, membrane process is favourable due to its high energy efficiency, ease of scale up and environmental friendly characteristic [1]. Membrane-based gas separation contains a wide range of industrial applications such as air separation, natural gas treatment, olefin /paraffin separation, ect. [2]. Another group of membrane-based gas separation likely to develop into a major application area, is olefin /paraffin separation. These compounds are considered as mixtures with close boiling points which are difficult to be separated by conventional distillation process. Theses mixtures are separated on a very large scale in the

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synthesis of ethylene and propylene, the two largest-volume organic chemical feedstock [3].

The major challenge for development of membrane-based gas separation lies in manufacture of membranes with high permeabilities and selectivities for a special species. Polymeric membranes are frequently used for this purpose due to their higher applicability and ease of fabrication. Rubbery polymers offer higher permeability because of enhanced mobility in segments of polymer chains which leads to increase of free volume in polymer matrix; while, higher selectivities are projected for glassy polymers due to their rigid structure which suggest separation of species based on molecular size and diffusional selectivity [4-7]. Therefore, a compromise should be made between these different aspects of a polymer membrane for a special application. It has been observed that commercial glassy polymer membranes suffer plasticization phenomena at high pressure CO_2 separation process which reduces the performance of polymeric membranes. Simons et al [8] have shown that the problem can be significantly overcome by introducing polyetherimide (PEI) polymer film to ODPA-based membrane.

It is assumed that glassy polymers include a mobile section which lies within polymer flexible chains named as Henry's sites and a rigid section with small pores (microvoids) which are called as Langmuir's sites. For glassy membranes, gas permeability is strongly influenced by gas solubility, especially the amount that can be adsorbed onto the Langmuir voids of the polymeric matrix. It is clear that increasing of solubility will lead to increase in gas permeability and this causes enhancement in membrane productivity [9].

Modelling of gas transport via glassy polymers is complicated by different kinds of coupling among permeating species across the membranes [10]. To have a good prediction for separation behaviour of a system employing a glassy polymer, a suitable model must be used which describes properly both the adsorption and diffusion phenomena in polymer matrix. Dual mode sorption model is the most widely used model to describe gas permeation through glassy polymers, since it is easy to apply in a wide variety of polymer/gas systems [11]. However, it is a phenomenological model which is not originated from a robust theory. Moreover, it fails to predict the separation performance of several gas/membrane systems which employ a glassy polymer as separation barrier [12]. To assess the contribution of equilibrium and kinetic couplings to the flux of

permeating components, it is necessary to consider the sorption and diffusion aspects of gas permeation across glassy polymers separately within a mechanistic model. The sorption of gases in glassy polymers is not simply expressed by the Henry's law which is employed for the sorption of gas molecules through the rubbery polymers. Several models have been proposed to describe the sorption of gas molecules in glassy polymers but a model based on the dual-mode sorption theory is more common [13]. It assumes that gas sorption in glassy polymers occurs in two different mods; part of sorption takes places into polymer microvoids (Langmuir sites) which is saturated in low pressure, whereas the remaining sorption occurs in Henry's mode (into free volume available in the segments of polymer chains). Dual sorption models can be easily generalized to the multicomponent sorption system by adding the contribution of other sorbed components in the Langmuir mode. On the other hand, the multicomponent diffusion into glassy polymer can be described by the different ways such generalized Fick's law, irreversible thermodynamics and Maxwell-Stefan (M.S) theory. The two first approaches are phenomenological methods and their transport parameters lack a theoretical interpretation. Besides, there is no relationship between the binary and multicomponent phenomenological transports coefficients. In contrast, the diffusion coefficients in M.S theory have a clear meaning in terms of inverse mutual drag coefficients. In addition, the binary diffusion coefficients in M.S formulation retain their physical significance and can be employed to establish multicomponent diffusivities [14, 15]. The application of M.S theory for description of mass transport across zeolite membrane was well addressed by some researchers [16]. However, modelling of mass transport across the glassy polymer membranes involves more complications due to different modes available within polymer matrix for adsorption and diffusion of penetrating components. Modelling of vapour permeation process using glassy polymer for dehydration of water/organic compound was carried out by Salem and Ghoreyshi [10]. In contrast to vapour permeation process which is carried out at low pressure, gas mixture separation at high pressure by means of glassy polymer is encountered with more complexity because of gas non ideal behaviour and enhanced plasticization effect at higher pressures.

With the above background, the main objective of the present study was to develop a new model for describing the separation behaviour of gas mixture in membrane-based gas separation using a glassy polymer. M.S formulation was used to define multicomponent diffusion; while, extended dual-mode sorption model was employed

to describe the multicomponent sorption behaviour of gas mixture into glassy polymer membrane. Combining the two above mentioned models based on adsorption-diffusion theory established the final model framework. The developed model is a full coupled model which considers contribution of different couplings due to kinetic and equilibrium interactions between penetrating components. The main significance of the model is using only the pure component sorption and permeation data for prediction the multicomponent separation performance. Finally, the model was validated using the experimental data available for two different gas mixtures separated by glassy polymer membranes.

1. Model Description

The starting point for model development is M.S formulation which describes the relationship between the flux of permeating component and concentration gradient. For a single gas (1) permeating through a glassy polymer membrane, m, (a binary system), this relationship is described as [10]:

$$J_1 = -q_t Đ_{1m} \Gamma \nabla x_1$$
(1)

Where J_1 is molar flux of component 1 through the membrane, $Đ_{1m}$ is M.S diffusivity of single gas permeating through the membrane and Γ denotes the thermodynamic factor which approaches to unity for an ideal gas mixture. Selective transport of a binary gas mixture through the membrane e system is considered as a ternary system. For such ternary systems, the flux of two permeating components can be expressed based on the following equations in matrix form [14]:

$$\begin{bmatrix} J_1 \\ J_2 \end{bmatrix} = -q_t \begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix}^{-1} \begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{bmatrix} \begin{bmatrix} \dfrac{\partial x_1}{\partial z} \\ \dfrac{\partial x_2}{\partial z} \end{bmatrix}$$
(2)

Where:

$$B = \begin{bmatrix} \dfrac{x_2}{D_{12}} + \dfrac{x_p}{D_{1p}} & \dfrac{-x_1}{D_{12}} \\ \dfrac{-x_2}{D_{12}} & \dfrac{x_1}{D_{12}} + \dfrac{x_p}{D_{2p}} \end{bmatrix}$$
(3)

$$\Gamma_{ij} = \frac{x_i}{RT} \left(\frac{\partial \mu_i}{\partial x_j} \right)$$
(4)

The $Đ_{1m}$ and $Đ_{2m}$ characterize, in the broadest sense, the component-membrane kinetic interactions. The $Đ_{12}$ is exchange coefficient which quantifies diffusional coupling between the two components. At the molecular level, the $Đ_{12}$ reflects the facility for transport of species 1 through the membrane in the presence of species 2.

In the above equation, $[\Gamma]$ and [B] are diffusivity and equilibrium matrixes which express solution and diffusion significance on the transport process, respectively. The main advantage of M.S theory in multicomponent membrane transport is that it allows separate evaluation of equilibrium and kinetics contributions to the overall transport via the membrane. Proper description of component sorption and diffusion into membrane are the prerequisites for the correct calculation of these two matrixes.

1.1. Sorption

1.1.1. Pure component absorption

To assess the equilibrium term in the transport model, it is required to describe sorption of component into the membrane according to a model isotherm. It is well understood that the sorption of many of gases and vapours into glassy polymer membranes is well expressed by dual sorption model (Langmuir- Henry hybrid model). The idea was first applied for water sorption study [17], then this adsorption mechanism was named in its final form as the dual mode absorption model. In this model, it is assumed that glassy polymer includes matrix continuum (Henry's mode) where the adsorption takes place inside the polymer mobile matrix and fixed small pores among them (Langmuir's mode) where the adsorption occurs on the micro voids surfaces. This assumption has been proved by help of spectrography [18]. This is the best model for adsorption of gaseous components due to proper coincidence with experimental results and also simple expressive description of the process [19].

Dual mode sorption model for single (pure) gas adsorption into glassy polymer membrane is given as [20, 21]:

$$q = k_D f + \frac{q_m b f}{1 + b f}$$
(5)

q is the amount of pure component adsorbed into the membrane which is a function of its fugacity in gas phase, f. k_D is Henry's constant, q_m and b represent Langmuir capacity constant and affinity constant, respectively. In the above equation, fugacity was used instead of pressure due to non-ideal behaviour of gas in high pressure separation.

1.1.2. Mixed components adsorption

Development of Henry- Langmuir's dual model for a gas mixture sorption has been established based on the assumption that competition between penetrating components occurs just on Langmuir's sites and Henry's law constant (k_D) remains independent of presence other components. Furthermore competitive sorption can result in a decrease in sorption of each component [22, 23]. The following equation is mathematical description of the idea:

$$q_i = k_{D_i} f_i + \frac{q_{m_i} b_i f_i}{1 + \sum_{j=1}^{n} b_j f_j} \qquad (6)$$

where q_i is the concentration of component i in adsorbed phase and f_i is the fugacity of component i in gas phase.

1.1.3. Determination of equilibrium matrix

To determine the elements of equilibrium matrix described by equation (3), chemical potential of a component in polymer matrix can be related to its fugacity at constant temperature and pressure based on fundamental thermodynamics [24]:

.

$$d\mu_i = RT d \ln f_i \qquad (7)$$

By combining equations (4) and (7), the following relation can be obtained:

$$\Gamma_{ij} = \frac{x_i}{f_i}\left(\frac{\partial f_i}{\partial x_j}\right) \cong \frac{q_i}{f_i}\left(\frac{\partial f_i}{\partial q_j}\right) \qquad (8)$$

Where $\quad x_i = \dfrac{q_i}{\sum_{i=1}^{n} q_i} \qquad (9)$

Thus, combining (8) and (9), the elements of equilibrium matrix are obtained as follows:

$$[\Gamma] = \begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{bmatrix} = \begin{bmatrix} \dfrac{q_1}{f_1}\dfrac{\partial f_1}{\partial q_1} & \dfrac{q_1}{f_1}\dfrac{\partial f_1}{\partial q_2} \\ \dfrac{q_2}{f_2}\dfrac{\partial f_2}{\partial q_1} & \dfrac{q_2}{f_2}\dfrac{\partial f_2}{\partial q_2} \end{bmatrix} \qquad (10)$$

In the equation (10), q_1 and q_2 are concentration of component 1 and 2 at mixed status and because concentration is a function of fugacity, obtaining partial derivatives of fugacity with respect to concentration is mathematically difficult. To derive the final expression for the elements of equilibrium matrix, a special mathematical treatment was considered in this study which is described below. The extended dual sorption model is used to describe the amount of adsorption for each component at mixed status:

$$q_1 = k_{D_1} f_1 + \frac{q_{m_1} b_1 f_1}{1 + b_1 f_1 + b_2 f_2} \qquad (11\text{-}a)$$

$$q_2 = k_{D_2} f_2 + \frac{q_{m_2} b_2 f_2}{1 + b_1 f_1 + b_2 f_2} \qquad (11\text{-}b)$$

Now, differentiation the both sides of equation (11) with respect to q_1 lead to:

$$1 = k_{D_1}\frac{\partial f_1}{\partial q_1} + \frac{q_{m_1} b_1 \dfrac{\partial f_1}{\partial q_1}\left(1 + b_1 f_1 + b_2 f_2\right) - q_{m_1} b_1 f_1\left(b_1 \dfrac{\partial f_1}{\partial q_1} + b_2 \dfrac{\partial f_2}{\partial q_1}\right)}{\left(1 + b_1 f_1 + b_2 f_2\right)^2}$$

(12-a)

$$0 = k_{D_2}\frac{\partial f_2}{\partial q_1} + \frac{q_{m_2} b_2 \dfrac{\partial f_2}{\partial q_1}\left(1 + b_1 f_1 + b_2 f_2\right) - q_{m_2} b_2 f_2\left(b_1 \dfrac{\partial f_1}{\partial q_1} + b_2 \dfrac{\partial f_2}{\partial q_1}\right)}{\left(1 + b_1 f_1 + b_2 f_2\right)^2}$$

(12-b)

Rearranging the above equations results in:

$$\beta^2 = \frac{\partial f_1}{\partial q_1}\left(k_{D_1}\beta^2 + \propto_1 \beta - \propto_1 f_1 b_1\right) - \propto_1 f_1 b_2 \frac{\partial f_2}{\partial q_1}$$

(13-a)

$$0 = \frac{\partial f_2}{\partial q_1}\left(k_{D2}\beta^2 + \propto_2 \beta - \propto_2 f_2 b_2\right) - \propto_2 f_2 b_1 \frac{\partial f_1}{\partial q_1}$$

(13-b)

where $\left(\propto = q_m b\right)$, $\beta = \left(1 + b_1 f_1 + b_2 f_2\right)$.

Looking at the above equations, it is found out that those are two equations with two unknowns $\frac{\partial f_1}{\partial q_1}$ and $\frac{\partial f_2}{\partial q_1}$. By solving them, the unknowns are obtained as:

$$\frac{\partial f_2}{\partial q_1} = \frac{\beta^3 \propto_2 f_2 b_1}{\left[\left(k_{D_2}\beta^2 + \propto_2 \beta - \propto_2 f_2 b_2\right)\left(k_{D_1}\beta^2 + \propto_1 \beta - \propto_1 f_1 b_1\right)\right] - \left(\propto_1 \propto_2 f_1 f_2 b_1 b_2\right)}$$

(14-a)

$$\frac{\partial f_1}{\partial q_1} = \frac{\beta^3 \left(k_{D2}\beta^2 + \propto_2 \beta - \propto_2 f_2 b_2\right)}{\left[\left(k_{D_2}\beta^2 + \propto_2 \beta - \propto_2 f_2 b_2\right)\left(k_{D_1}\beta^2 + \propto_1 \beta - \propto_1 f_1 b_1\right)\right] - \left(\propto_1 \propto_2 f_1 f_2 b_1 b_2\right)}$$

(14-b)

Two other partial derivatives available in the equilibrium matrix are determined in the same style. Differentiating from both sides of equation (11) with respect to q_2, lead to the following expressions:

$$0 = k_{D_1}\frac{\partial f_1}{\partial q_2} + \frac{q_{m_1}b_1 \frac{\partial f_1}{\partial q_2}\left(1 + b_1 f_1 + b_2 f_2\right) - q_{m_1}b_1 f_1\left(b_1 \frac{\partial f_1}{\partial q_2} + b_2 \frac{\partial f_2}{\partial q_2}\right)}{\left(1 + b_1 f_1 + b_2 f_2\right)^2}$$

(15-a)

$$1 = k_{D2}\frac{\partial f_2}{\partial q_2} + \frac{q_{m_2}b_2 \frac{\partial f_2}{\partial q_2}\left(1 + b_1 f_1 + b_2 f_2\right) - q_{m_2}b_2 f_2\left(b_1 \frac{\partial f_1}{\partial q_2} + b_2 \frac{\partial f_2}{\partial q_2}\right)}{\left(1 + b_1 f_1 + b_2 f_2\right)^2}$$

(15-b)

After organizing the above equations, it is obtained:

$$0 = \frac{\partial f_2}{\partial q_2}\left(- \propto_1 f_1 b_2\right) + \left(k_{D_1}B^2 + \propto_1 B - \propto_1 f_1 b_1\right)\frac{\partial f_1}{\partial q_2}$$

(16-a)

$$\beta^2 = \frac{\partial f_1}{\partial q_2}\left(- \propto_2 f_2 b_1\right) + \left(k_{D_2}\beta^2 + \propto_2 \beta - \propto_2 f_2 b_2\right)\frac{\partial f_2}{\partial q_2}$$

(16-b)

Again, the above equations are two equations with two unknowns $\frac{\partial f_1}{\partial q_2}$ and $\frac{\partial f_2}{\partial q_2}$. By solving them the two unknowns are obtained as follows:

$$\frac{\partial f_1}{\partial q_2} = \frac{\beta^3 \propto_1 f_1 b_2}{\left[\left(k_{D_2}\beta^2 + \propto_2 \beta - \propto_2 f_2 b_2\right)\left(k_{D_1}\beta^2 + \propto_1 \beta - \propto_1 f_1 b_1\right)\right] - \left(\propto_1 \propto_2 f_1 f_2 b_1 b_2\right)}$$

(17-a)

$$\frac{\partial f_2}{\partial q_2} = \frac{\beta^3 \left(k_{D_1}\beta^2 + \propto_1 \beta - \propto_1 f_1 b_1\right)}{\left[\left(k_{D_2}\beta^2 + \propto_2 \beta - \propto_2 f_2 b_2\right)\left(k_{D_1}\beta B^2 + \propto_1 \beta - \propto_1 f_1 b_1\right)\right] - \left(\propto_1 \propto_2 f_1 f_2 b_1 b_2\right)}$$

(17-b)

1.2. Determination of kinetics (diffusivity) matrix

The elements of this matrix are described by equation (2). At this equation, x_1, x_2 and x_p are component 1, component 2 and polymer mole fraction, respectively and they are obtained from equation

(8). From this equation it is obvious that to establish the kinetic matrix for ternary system, it is required to have three binary Maxwell Stefan diffusivities, i.e. D_{ij}. Usually the Fick binary diffusivities are extracted from permeability data of single gas through the membrane. According to adsorption-diffusion theory, the permeability coefficient (P) is expressed as the product of diffusivity (D) and solubility (S) coefficients:

$$P = D.S = D.\frac{q}{f} \qquad (18)$$

where P and q are determined from single gas experimental permeation and adsorption data. Also, Fick diffusivity is not usually constant and changes with the amount of gas loading in membrane. In this study, an exponential dependence with q has been considered as follows [25]:

$$D = D_o \exp(\gamma q) \qquad (19)$$

where D_o, is diffusivity at zero concentration and γ is considered as plasticizing factor of diffusing component on the polymer. Therefore, having single gas permeation and adsorption data at different pressures, the Fick's binary diffusivity for each single gas, D_{1p} and D_{2p} are determined from equation (18).

A major shortcoming of phenomenological models such as extended Fickian approach for description of multicomponent diffusion is that the binary Fick diffusivities have no relationship with multicomponent diffusivities [26]. While, the binary M.S diffusivities retain their physical significance and can be directly used to set up the multicomponent diffusivity matrix.

Binary Maxwell Stefan and Fick diffusivities are related together based on the following relationship [16]:

$$\mathcal{D} = D / \Gamma \qquad (20)$$

Appling equation (10) to describe the thermodynamic factor, Γ, for binary system and using equation (20), the following relationship is resulted:

$$\mathcal{D}_{im} = D_{im} \frac{f}{q} \frac{\partial q}{\partial f} \qquad (21)$$

Using dual Henry-Langmuir adsorption model for pure gas adsorption (equation 4) and combining it with equation (21) gives the final expression for M.S diffusivity versus Fickian diffusivity:

$$\mathcal{D}_{im} = D \frac{f}{q} \left(k_D + \frac{q_m b}{(1 + bf)^2} \right) \qquad (22)$$

The component-component mutual diffusivity, $\mathcal{D}_{12}$, required for multicomponent diffusivity matrix assessment is not simply represented by the bulk gas diffusivity. In the polymer matrix, the kinetic interaction between two diffusing components is different from the bulk phase. To obtain component-component diffusion coefficients in the membrane, the relationship proposed by Krishna *et al.* was used [27]:

$$\mathcal{D}_{12} = \mathcal{D}_1^{\left(\frac{q_1}{q_1+q_2}\right)} \mathcal{D}_2^{\left(\frac{q_2}{q_1+q_2}\right)} \qquad (23)$$

1.3. Selectivity

The performance of the model for prediction of multicomponent separation behaviour of a gas mixture is evaluated in terms of selectivity which is defined as:

$$\alpha_{AB} = \frac{\dfrac{Y_A}{Y_B}}{\dfrac{X_A}{X_B}} \qquad (24)$$

where Y_i and X_i are mole fractions of components at permeate and feed sides, respectively. The gas composition at the permeate side can be calculated after calculation of permeating components fluxes:

$$Y_A = \frac{J_A}{J_A + J_B} \qquad (25)$$

Therefore, the elements of equilibrium matrix are described based on pair-equations of (14) and (17).

2. Results and discussion

Examination of the developed model needs only permeation and adsorption data for pure gases which should be separated by a glassy

polymer membrane. Then, the actual selectivity (not ideal selectivity) for any mixture of them at constant temperature and any given pressure can be predicted by the developed model in this study. The experimental selectivity was only employed for comparison. To validate the model, two case studies were considered. First, the data available in the literature for CO_2/CH_4 mixture separation [28] and the second, separation of olefin/paraffin gas mixture, i.e. C_3H_6/C_3H_8 [12] were used for model validation. The predicted and experimental selectivity values are compared. A comparison also is made between the results predicted by the developed model in this study and commonly used dual transport model.

2.1. Case study 1: CO_2/CH_4 separation

Removal of CO_2 from natural gas is an important operation in natural gas processing. In this section, CO_2/CH_4 separation through polyimide membrane was investigated. The mentioned gas mixture included 89.9% of CH_4 and 10.1% of CO_2 at 35C° which diffused through glassy polyamide membrane with thickness of about 20 micron [28].

2.1.1. Sorption of pure components in membrane

Sorption in glassy polymeric membranes follows Henry-Langmuir's dual mode model (equation 4). The sorption model parameters were acquired by nonlinear regression of experimental data pertaining to pure CO_2 and CH_4 sorption into polyimide membrane versus gas fugacity with the aids of MATLAB software (version 7). Since gases are thermodynamically non-ideal at high pressures, therefore pressure values were converted to fugacity by the use of SRK equation of state [29, 30]. The sorption model parameters have been listed in Table 1 and the fitted isotherms for pure CO_2 and CH_4 as well as experimental sorption data were shown in Fig.1.

Figure 1

Table 1

2.1.2. Estimating binary diffusivities

Having the permeation and sorption data in hand for pure components, binary Fick diffusivities, D_{ip}, were calculated from equation (18) and correlated using equation (19). Binary diffusivity

parameters, D_0 and γ were obtained by nonlinear regression and were represented in Table 2. Having the binary Fick diffusivities, the binary M.S diffusivities were found from equation (22). Fig. 2 shows a comparison between binary Fick and M.S diffusivities. The figure indicates that diffusion coefficients increase with feed fugacity and also the values of Fick diffusivity is higher than M.S diffusivity because Fick diffusivity includes kinetic (diffusion) and equilibrium (solubility) effects simultaneously; whereas, M.S diffusivity excludes equilibrium (solubility) effects. The result corresponds with other researchers' studies [31].

Table 2

Figure 2

2.1.3. Determination of equilibrium and kinetic couplings

Equation (10) gives the elements of equilibrium matrix in which the partial derivatives is described by the pair equations of (14) and (17). Fig. 3 compares the variation of main terms $\left(\Gamma_{ii}\right)$ and cross terms $\left(\Gamma_{ij}\right)$ in the equilibrium matrix versus feed fugacity for CH_4 and CO_2. As it is perceived from the figure, the values of main term elements are greater than those of cross terms. However, the cross term values are significant and cannot be ignored. For both penetrating components, cross and main term values increase with feed fugacity and then diminish slightly, namely at high fugacities, which indicates the effect of equilibrium coupling on components permeation through the membrane decreases a little at high pressure.

Figure 3

2.1.4. Determination of kinetic coupling

Potential kinetic coupling of fluxes can be evaluated considering the values obtained for inverted elements of a diffusivity matrix (equation (3)). Fig.5 shows main and cross terms ($\left[B_{ii}\right]^{-1}$ and $\left[B_{ij}\right]^{-1}$) of the multicomponent diffusivity matrix as a function of the feed fugacity. For CH_4 permeation through the membrane, both terms increase with fugacity and the cross term is remarkable compared to the main term, which indicates that the permeation of CH_4 through the membrane is strongly affected by the presence of

CO_2 (Fig, 5a). Fig.5b shows that the cross term for CO_2 is negligible compared to the main term. This denotes that the permeation of CO_2 through the membrane is not kinetically affected by the presence of CH4.

Figure 4

2.1.5. Determination of Selectivity

Experimental separation factors of this mixture (CO_2 over CH_4) have been extracted from literature [28] for validation of results, and equation (24) has been used to predict separation factors at different fugacities. Fig.5 represents a comparison between experimental and predicted selectivities. As it is obvious from the figure, the membrane is highly selective toward CO_2. This is due to both higher solubility and diffusivity of CO_2 in the membrane compared to CH_4. As it is observed, there is a good agreement between the experimental and predicted selectivities.

Figure 5

2.2. Case 2: Olefin/paraffin separation

Olefin/paraffin separation is a basic operation in petrochemical industry for production of olefin-based solid polymers. One promising technology for this purpose is membrane based gas permeation. In this part, the separation of propane and propylene mixture containing mole 50% of each component is considered. The separation behaviour of this mixture at the temperature of 323K using 6FDA-TRMPD polyimide membrane was reported in the literature [12].

2.2.1. Adsorption

The measured isotherms of pure components sorption in the 6FDA-TRMPD polyimide membrane have been shown in Fig. 6. The dual mode adsorption parameters were obtained by a nonlinear fit of experimental data with equation (5) and were listed in Table 3.

Table 3

Figure 6

Comparing the maximum adsorption capacity denoted by the constant, q_m, it can be deducted that propylene has higher adsorption capacity owing to its more condensability due to π bond in its molecular structure.

2.2.2. Binary diffusion coefficients

Using pure component sorption and permeation data, the values of binary Fick diffusivities at different sorption uptakes were calculated based on equation (18) and its concentration dependency was correlated by the equation (19). The constants appearing in equation (19) were recovered through a nonlinear fit with binary diffusivities data and are listed in Table 4. Then binary M.S diffusivities were found from equation (22) having the sorption isotherm and binary Fick diffusivities. Fig. 7 shows variation of Fick and M.S diffusivities versus gas fugacity. Similar to CO_2/CH_4 mixture, it is observed that the values of Fick diffusivities are higher than M.S diffusivities and it can be attributed to combining the kinetic and equilibrium effects in Fick diffusivities.

Table 4

Figure 7

2.2.3. Determination of coupling Effects

A full coupled transport model for description of multicomponent gas mixture separation by a membrane is given by equation (2) which considers both equilibrium and kinetic couplings between two permeating components. Separate evaluation of each coupling contribution to overall transport can be carried out by ignoring the other form of coupling in the general transport model. The kinetically and thermodynamically decoupled models is represented by the equation (26) and (27), respectively:

$$\begin{bmatrix} N_1 \\ N_2 \end{bmatrix} = -q_t \begin{bmatrix} B_{11} & 0 \\ 0 & B_{22} \end{bmatrix}^{-1} \begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{bmatrix} \begin{bmatrix} \dfrac{\partial x_1}{\partial z} \\ \dfrac{\partial x_2}{\partial z} \end{bmatrix} \qquad (26)$$

$$\begin{bmatrix} N_1 \\ N_2 \end{bmatrix} = -q_t \begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix}^{-1} \begin{bmatrix} \Gamma_{11} & 0 \\ 0 & \Gamma_{22} \end{bmatrix} \begin{bmatrix} \dfrac{\partial x_1}{\partial z} \\ \dfrac{\partial x_2}{\partial z} \end{bmatrix} \quad (27)$$

The results of flux calculation made based on the two decoupled models is compared with the flux calculated using full coupled model (equation (2)) in Fig. 8 for two permeating components.

Figure 8

It is obvious both couplings have a contribution to the both components fluxes and cannot be ignored. However, the contribution of kinetic coupling is remarkably higher than that of equilibrium couplings. That might be due to the fact that glassy polymer membranes are diffusion selective rather than solubility selective.

2.2.4 Comparison of selectivity between the present model and conventional dual transport model

The calculated selectivity (propylene over propane) based on equation (24) and the experimental values are shown in Fig. 9 as a function of gas fugacity.

As it was mentioned in introduction section, dual transport model is frequently is used to predict the separation behaviour of a gas permeation process which employs a glassy polymer membrane as a selective separation barrier. This model for a multicomponent gas permeation is given as follows:

$$p_i = K_{Di} D_{Di} + \frac{q_{mi} D_{Hi} b_i}{1 + \sum_{j=1}^{n} bf} \quad (28)$$

In this model, part of parameters are recovered from pure component sorption experimental data (q_{mi}, bi and K_{Di}); while, the remaining parameters including the diffusivity parameters in the mobile Henry's mode (D_{Di}) and rigid non-mobile Laugmuir mode (D_{Hi}) are obtained from pure component permeation data.

The selectivities calculated based on dual transport model and the transport model developed in the present study are compared with experimental data [28, 12] in Fig. 9. As it is clear from the figure, the

values obtained using dual transport model are too far from the experimental data. On the contrary, there is a good match between experimental data and the present developed model since the dual transport model is an empirical model, whereas, the new developed model has a robust theoretical basis and was obtained from application of M.S theory to the membrane system.

Figure 9

Conclusions

It was well known that the glassy polymers are suitable materials for development of membranes with high selectivity mainly based on diffusional differences between permeating components. However, a major difficulty is correct prediction of the separation behaviour of a gas mixture which is going to be separated using a glassy polymer membrane. The commonly used transport models, such as dual transport model developed, mainly based on empirical basis or use simplified assumption, fail to give a proper description of the transport phenomena occurring within the membrane. The model presented in this study employ the robust theory of Maxwell-Stefan formulation which easily provides the extension of binary diffusing system to the multicomponent system. Assessment of different couplings between permeating components is easily provided within the model. A main advantage of the model is that it uses pure component adsorption and permeation data in the membrane to predict the real mixture selectivity. Two case studies were considered to examine the predictability of the model. These data available for removal of CO_2 from natural gas (methane) and olefin/paraffin separation were used. The results demonstrated that the developed model is capable to give a close prediction to the experimental data, while examination of the dual transport model demonstrated a poor agreement with experimental data. Magnitude of different couplings was assessed by comparing the results obtained using full coupled model and thermodynamically or kinetically decoupled models. It was shown that ignoring the cross terms in equilibrium or kinetic matrix which represent coupling effects can led in different results. The main outcome of this study is that the developed model can be used for a variety of gas permeation processes which employ glassy polymer

membranes. This can be an important step in process design or optimization.

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Symbols

b_i	Pa^{-1}	Langmuir affinity constant of component i
B_{ij}	$s.m^{-2}$	Elements of multi component diffusivity matrix
D_{ij}	$m^2.s^{-1}$	Fick diffusion coefficient for pair i-j
$Ð_{ij}$	$m^2.s^{-1}$	Maxwell Stefan diffusivity for pair i-j
f_i	Pa	Fugacity of component i
J_i	$mol.m^{-2}.s^{-1}$	Molar flux
k_{Di}	$kmol.m^{-3} polymer Pa^{-1}$	Henry's constant of component i
M_i	$g.mol^{-1}$	Molecular weight
N_i	$mol.m^{-2}.s^{-1}$	Molar flux of component I with respect to stationary coordinate
p_i	Pa	Partial pressure
P_i	$Kmol.m.m^{-2}s^{-1} Pa^{-1}$	Permeability constant of component i
q_i	$mol.m^{-3}$	Concentration of component i
q_m	$kmol.g^{-1}$	Langmuir capacity constant of component i
R	$8.314 J.mol^{-1}K^{-1}$	Gas constant
S	$Kmol.m^{-3}.Pa^{-1}$	Solution constant
T	K	Temperature
x_i	-	Mole fraction component i
X_i	-	Mole fraction component i at feed
Y_i	-	Mole fraction component I at the other side of membrane

Greek

ρ_i	$g.cm^{-3}$	Density
μ_i	$J.mol^{-1}$	Molar chemical potential of component i
Γ_{ij}	-	Elements of equilibrium matrix
α	-	Selectivity
γ_i	-	Plasticity of component i

Subscripts

1	Permeating component 1
2	Permeating component 2
p	Polymer

Figure captions:

Fig.1. Pure CO$_2$ and CH$_4$ fitting curve

Fig. 2. Comparison of the Fick and Maxwell-Stefan Diffusivity for (a) pure methane and (b) Carbon dioxide in the 6FDA-HAB polyamide membrane

Fig. 3. Comparison of the main and cross terms in the equilibrium matrix for (a) methane and (b) Carbon dioxide in the 6FDA-HAB polyamide membrane

Fig. 4 Comparison of the main and cross terms in the kinetic matrix for (a) methane and (b) Carbon dioxide in the 6FDA-HAB polyamide membrane

Fig. 5. Comparison of the predicted and experimental selectivity

Fig. 6. Equilibrium sorption isotherms of (a) propane and (b) propylene in the 6FDA-TRMPD polyimide membrane

Fig. 7. Comparison of the Fick and Maxwell-Stefan Diffusivity for (a) propane and (b) propylene in the 6FDA-TRMPD polyimide membrane

Fig. 8 Comparison of calculated flux with coupled and decoupled models (a) propane (b) propylene

Fig. 9 Comparison of experimental [28, 12] and predicted selectivities by conventional dual transport model and the present model

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Table 1. Dual mode sorption parameters for CO_2 and CH_4 on the 6FDA-HAB polyamide membrane

Component	K_D ($\frac{kgmole}{m^3polymer.pa}$)	q_m ($\frac{kgmole}{m^3polymer}$)	b ($\frac{1}{pa}$)
CH_4	0.075 exp(-6)	1.32	1.2 exp(-6)
CO_2	0.086 exp(-5)	1.49	1.06 exp(-5)

Table 2 Parameters of concentration dependent binary Fick diffusivity for 6FDA-HAB polyamide membrane

Component	D_0 $(\dfrac{m^2}{s})$	γ $(\dfrac{m^3 \text{polymer}}{\text{kg mole}})$
CH_4	1.3535 exp(-14)	1.075
CO_2	2.5588 exp(-13)	0.646

Table 3. Dual mode sorption parameters for pure propane and propylene in the 6FDA-TRMPD polyimide membrane

Component	K_D ($\frac{kgmole}{m^3 polymer.pa}$)	q_m ($\frac{kgmole}{m^3 polymer}$)	b ($\frac{1}{pa}$)
C_3H_8	2.62 exp(-6)	0.677	9.212 exp(-5)
C_3H_6	2.366 exp(-6)	0.94	6.289 exp(-5)

Table 4. Parameters of concentration dependent binary Fick diffusivity for 6FDA-TRMPD polyimide membrane

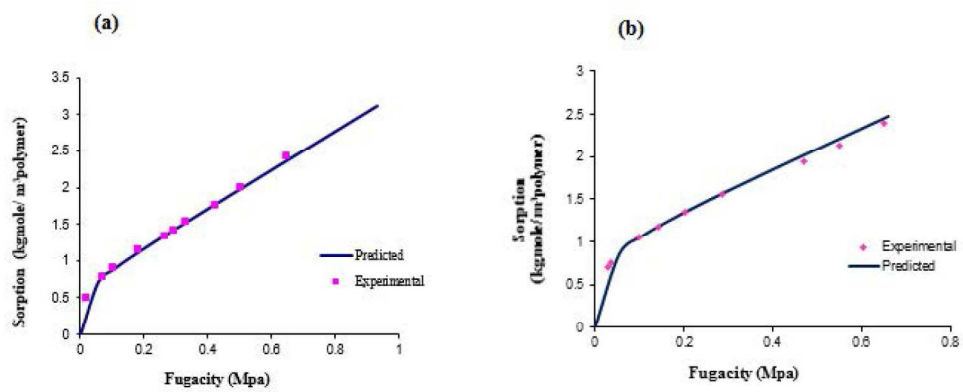| Component	D_0 ($\frac{m^2}{s}$)	γ ($\frac{m^3 \text{polymer}}{\text{kg mole}}$)
C_3H_8	3.79 exp(-14)	0.675
C_3H_6	5.942 exp(-13)	0.546
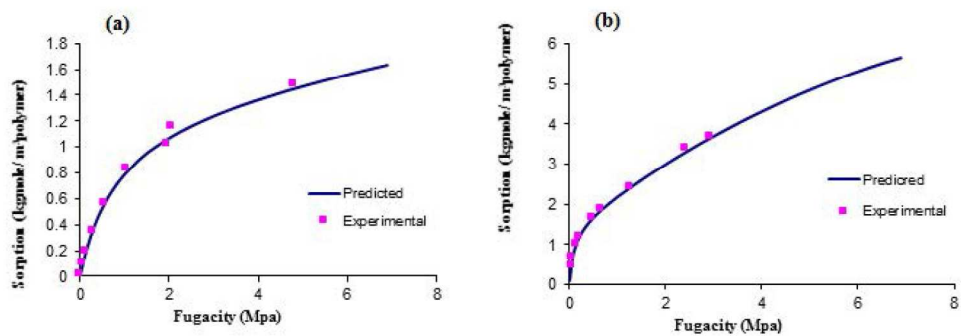
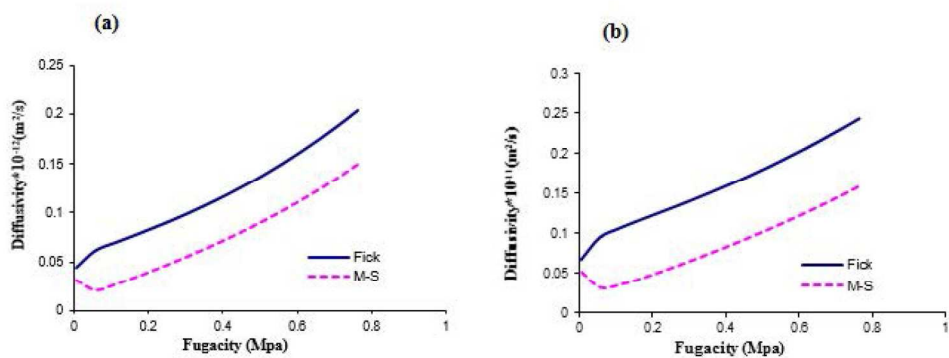Fig. 1
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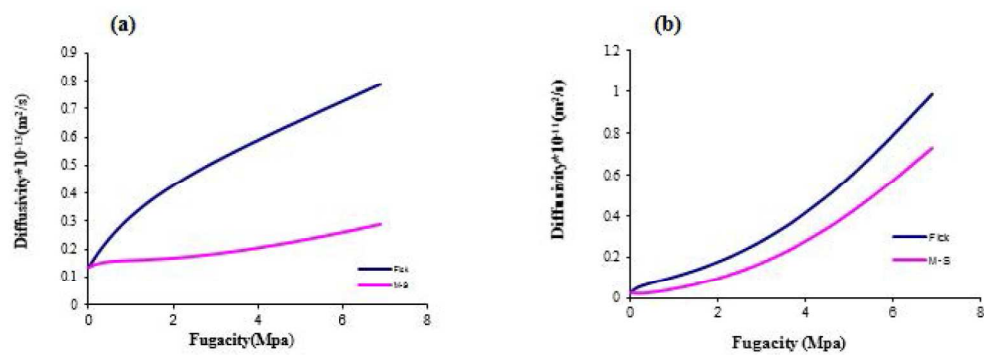
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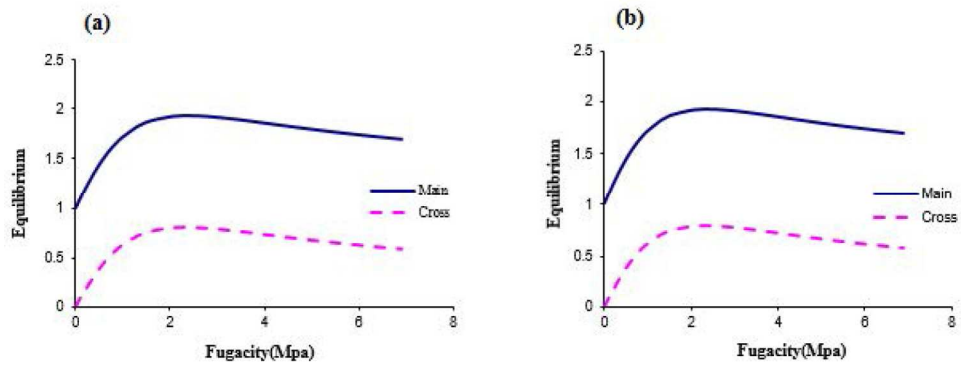
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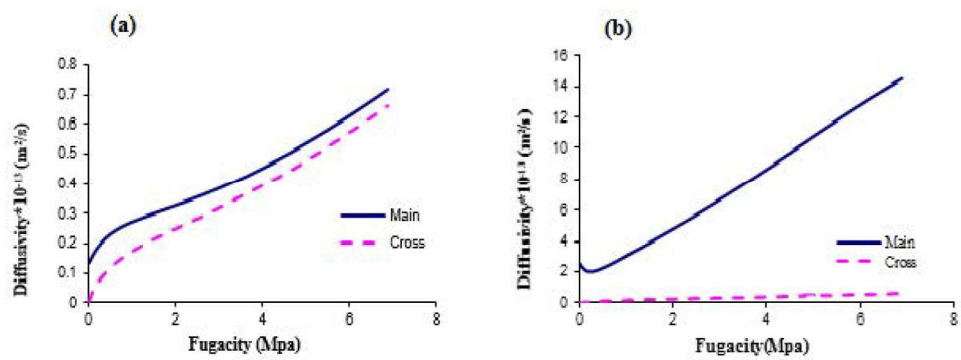
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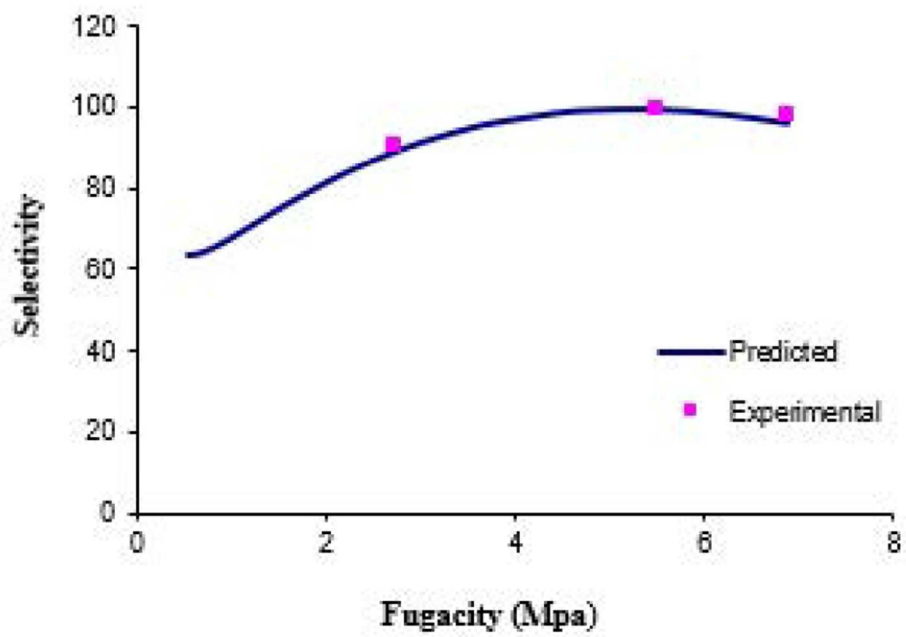
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Fig. 6
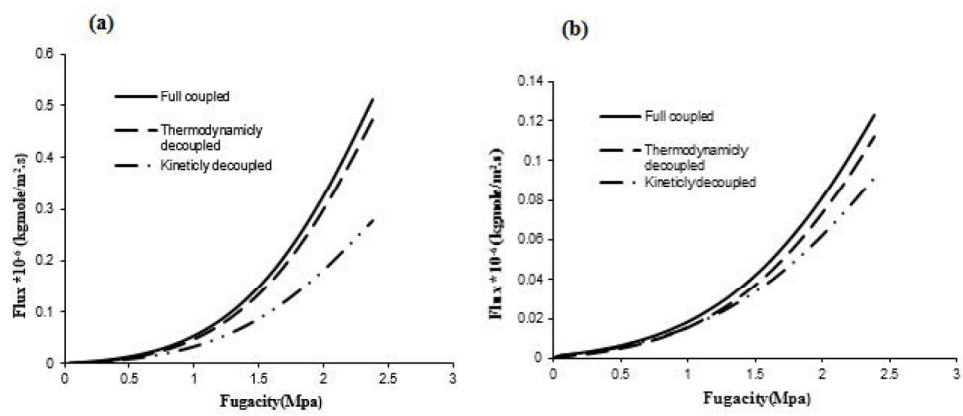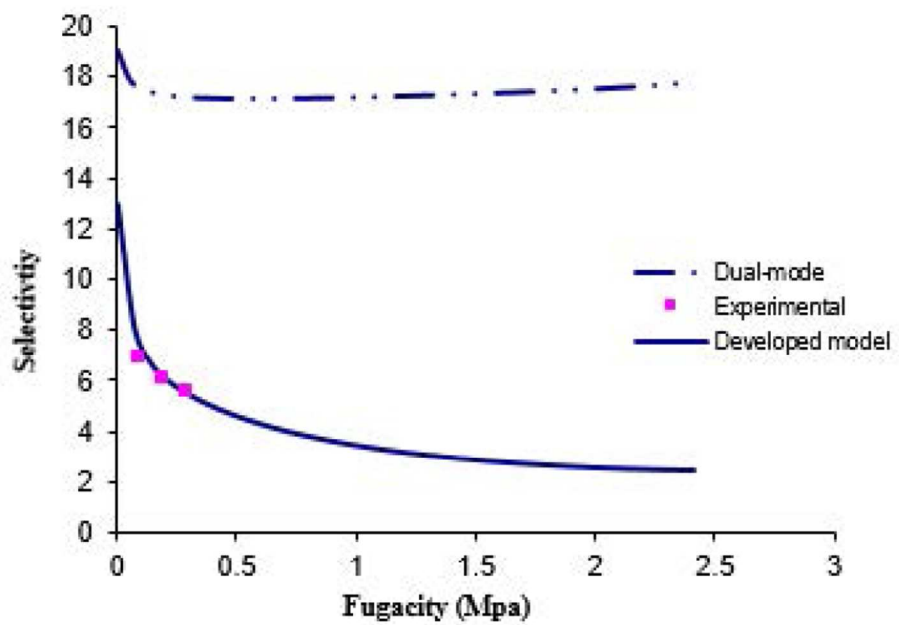178x76mm (300 x 300 DPI)

Fig. 7
178x71mm (300 x 300 DPI)

Fig. 8
175x86mm (300 x 300 DPI)

Fig.9
100x72mm (300 x 300 DPI)