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A Predictive Model for the Selective Separation of Aromatic/Non Aromatic Hydrocarbon Mixtures by Pervaporation Using Dense Homogenous Polymer Membranes

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Abstract: Separation of aromatic/non-aromatic mixtures by membrane based pervaportion process is usually analyzed by the solution-diffusion model which assumes that a permeating component is first dissolved in the membrane and then diffuses through the membrane due to its driving force. Therefore, the separate evaluation of sorption equilibria is necessary in order to determine the controlling step in overall mass transport in the membrane. In the present study, the pervaporative separation behavior of theses mixtures through dense homogeneous polymer membranes was modeled by a combination of Flory-Huggins and Maxwell-Stefan model. The systems chosen to validate the model were the separation of benzene/*n*-hexane and benzene/cyclohexane mixtures in dense polyurethane (PU). The sorption of aromatic/aliphatic hydrocarbon mixtures was described by the classical Flory-Huggins thermodynamic model. The binary (polymer-component and component-component) interaction parameters were calculated using pure component uptake data. Using these parameters, the multi-components sorption performance was then predicted by the extended Flory-Huggins model. The results revealed that the aromatic compounds are preferentially adsorbed into polyurethane over the entire range of composition. Diffusion step was modeled by Maxwell-Stefan model with concentration dependent diffusion coefficients. The results showed a close agreement between the experimental data and the predicted values of the component fluxes and selectivity.

Key words: Pervaporation . Flory-Huggins . Maxwell-Stefan

INTRODUCTION

Separation and purification of aromatic/non-aromatic mixtures is one of the great interests in chemical industry [1]. Recently; an increasing trend on membrane technology has been focused for separation processes in chemical industry, since it overcomes several constraints associated with conventional techniques [2]. The main reason for appreciating membrane technology over classical methods of separation and purification like distillation, rectification, extraction and crystallization is that the conventional processes are energy consuming and expensive [3]. Due to the complexity and high costs of the conventional processes, membrane separation technology has been considered in recent years as a viable alternative [4]. In particular, pervaporation is an attractive alternative for separation of azeotropic mixtures and for separation of aqueous and organic mixtures of liquids having close boiling points [5]. The advantage of using membranes is their selective permeation which offers an economical and simple alternative option for traditional processes. Pervaporation is a membrane process for the separation of liquid mixtures that has elements in common with reverse osmosis and membrane gas separation. The separation mechanism in this process is based on the difference in sorption and diffusion properties of the permeating components [6, 7]. The separation of compounds using pervaporation methods can be classified into three major fields, (i) dehydration of aqueous-organic mixtures, (ii) removal of trace volatile organic compounds from aqueous solution and (iii) separation of organic-organic solvent mixtures [8-10]. In pervaporation processes, a liquid mixture is in contact with one side of a dense membrane and the permeate is removed as a vapor from the opposite side of the membrane. Thus, the permeation rate of overall process is a function of solubility and diffusivity, since the desorption step is negligible due to an efficient vacuum. The true driving force for the mass transport across the membrane is chemical potential gradient. The driving force can be created by applying either a vacuum pump or an inert purge (normally an air stream) on the permeate side to maintain the permeate vapor pressure lower than the partial pressure of the

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feed liquid. The mass transport through the membrane, which is generally described by the solution/ diffusion model, involves three steps: sorption, diffusion and desorption [11-13]. A polymeric or zeolite membrane usually serves as the separating barrier for the process. For Pervaporation of aromatic/ aliphatic and aromatic/ alicyclic hydrocarbons such as benzene (Bz)/normal hexane (Hx), benzene (Bz)/cyclohexane (Chx), rubbery polymer membranes such as polyurethane have relatively high performance with high selectivity in compensation for low permeability. In general, rubbery polymers have higher permeability compared with glassy polymers due to higher free volume and more flexible polymer chains. Therefore, in order to achieve both high selectivity and high permeability, rubbery polymers seem to be a better candidate than glassy polymers. The higher affinity to aromatics as well as suppressing excessive swelling of membrane render them as excellent PV membrane materials [14]. The steady-state mass transport flux depends on several parameters, i.e., upstream pressure, downstream pressure, temperature and film thickness. When the downstream pressure is low, the flux is inversely proportional to the film thickness. However, mass transport through a thick dense polymer membrane is a slow process and this generally restricts the usage of pervaporation to breaking the azeotropic barriers alone.

The model proposed in this work follows the classical sorption-diffusion model. On the feed side equilibrium is assumed between the liquid phase and the membrane and the components concentration at the permeate side of the membrane is considered to be zero due. The main objective of this article is to present a predictive model for the selective separation of aromatic-nonaromatic liquid mixtures by pervaporation using only pure component sorption and pervaporation data. The Flory-Huggins (FH) thermodynamic model was used here to describe the sorption step and the Maxwell-Stefan formulation was used to describe the transport steps.

MODEL DESCRIPTION

According to the solution-diffusion model a permeant first dissolve into, then diffuse through a membrane due to a chemical potential gradient. The separation occurs due to the differences in solubility and/or diffusivity of permeants in a membrane. In general, solubility and diffusivity are concentration dependent. A number of mathematical equations for mass transport have been formulated on the basis of Fick's diffusion equation using different empirical correlations for concentration dependence of solubility and/or diffusivity. The transport of mixtures through a

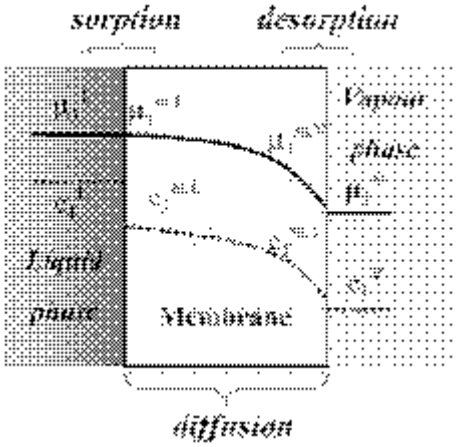

Fig. 1: Schematic representation of solution-diffusion model

polymeric membrane is generally much more complex than a single component, because the systems are often highly interactive. Therefore, two phenomena have to be taken into account in multicomponet permeation in pervaporation; kinetic coupling and thermodynamic interaction leading to preferential sorption and diffusion [15, 16].

The separation and permeation of components, as described in solution-diffusion model, is governed by thermodynamically based sorption and kinetically based diffusion. In solubility modeling, an empirical correlation for activity dependent solubility as well as a molecular theory such as Flory-Huggins thermodynamics has been implemented. On the other hand, empirical correlation for linear or exponential concentration-dependent diffusivity, Fujita's free volume theory and Maxwell-Estefan model have been applied to the diffusion process. The successful interpretation of mutual interaction between permeants and the membrane-permeants makes the solution-diffusion model the most accepted mass transport mechanism for Pervaporation.

The model proposed in this work follows the classical solution-diffusion model. On the feed side equilibrium was assumed between the liquid phase and membrane and the components concentration at the permeate side of the membrane was considered to be zero. The Flory-Huggins (FH) equations were used here to describe the sorption step and the MS equations were used to describe the transport step with an concentration dependent diffusivity.

Sorption step: Figure 1 depicts schematically the individual phenomena occurring during a pervaporation process based on solution-diffusion model.

The sorption step is modeled as liquid-liquid equilibrium (LLE) between the liquid and the polymer phases. The liquid phase is a mixture containing *N* low molecular weight components. The polymer phase contains *N* components and the polymer. The liquid and the polymer phases are considered to be at the same temperature and pressure. The local equilibrium criterion is applied considering the same activity at the polymer/liquid interface. The FH model was used to describe the phase equilibrium, i.e. the sorption step. The general criterion for equilibrium between a liquid mixture and a polymer can be expressed as:

$$\mu_i^{liq}(T,P,x_i) = \mu_i^{mem}(T,P,x_i) \quad (1)$$

To develop a model, the relationship between the Gibbs free energy, enthalpy and entropy of mixture in a polymer solution was considered by the following relationship:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (2)$$

$$\left[\frac{\partial(n\Delta G_m)}{\partial n_i}\right]_{T,P,n_j} = \mu_i = \mu_i^0 + RT\ln a_i \quad (3)$$

The classical flory-huggins model for pure liquids: The lattice model is very useful for describing the treatment of a polymer solution in liquid. This theory is the basis of polymer-solution thermodynamics. Flory considered a lattice with each solute molecule confined to a box and each polymer chain divided into segments with a size comparable to that of the solute molecule, as presented in Fig. 2 [17]. Segments of polymer chain must occupy adjacent sites in the lattice, which restricts the number of possible configurations. Flory demonstrated that the configurational entropy of mixing, ΔS_{cf} for a pure solute-polymer system (binary solution) is given by the following expression:

$$\Delta S_{cf} = -R\left(x_1\ln(\phi_1) + x_M\ln(\phi_M)\right) \quad (4)$$

The entropy of mixing was then assumed to be identical to the configurational entropy:

$$\Delta S_m \cong \Delta S_{cf} \quad (5)$$

The interactions between the solute molecules and the polymer were assumed to contribute only to the enthalpy change of mixing, which was given by an expression analogous to the Van Laar equation [18]:

$$\Delta H_m = RT\,\chi_{1M}x_1\phi_M \quad (6)$$

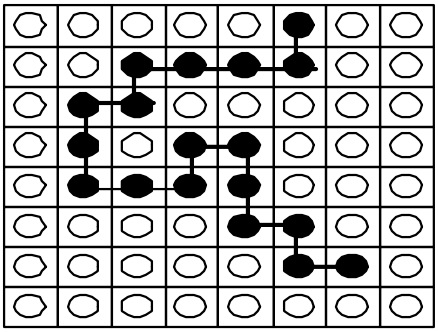

Fig. 2: Segments of a polymer chain located in a liquid lattice

where χ_{1M} is an interaction parameter introduced to account for the interaction between the polymer and the solute molecules. The term $RT\chi_{1M}$ represents the difference between the energy of a solute molecule immersed in pure polymer compared with the one surrounded by molecules of its own type. The binary interaction parameter χ_{1M} is therefore assumed to be constant and independent of composition. Substituting equations (4) and (6) into equation (2) gives:

$$\Delta G_m = RT(x_1\ln\phi_1 + x_M\ln\phi_M + \chi_{1M}x_1\phi_M) \quad (7)$$

The activity of the solute within the polymer can be obtained by differentiating (7) with respect to n_1:

$$\frac{\partial\left(\frac{n\Delta G_m}{RT}\right)}{\partial n_1} = \ln a_1 = \left[\ln\phi_1 + (1-\frac{1}{z})\phi_M + \chi_{1M}\phi_M^2\right] \quad (8)$$

Where

$$z = \left(\frac{\bar{V}_M}{\bar{V}_1}\right)$$

The interaction parameter χ_{1M} can be obtained from a single experiment with a pure liquid. For a pure liquid in equilibrium with a polymer, $a_i^{liq} = a_i^{mem} = 1$ and hence from (8):

$$\chi_{1M} = -\left[\frac{\ln\phi_1 + (1-\phi_1)}{(1-\phi_1)^2}\right] = -\left[\frac{\ln(1-\phi_M) + \phi_M}{\phi_M^2}\right] \quad (9)$$

Note that as ϕ_1 diminishes the numerical value of χ_{1M} decreases, indicating a decreasing affinity between the polymer and the solute.

The classical Flory-Huggins model for liquid mixtures: The transport of mixtures through a

polymeric membrane is generally much more complex than the pure liquid, since the systems are often highly interactive. However, the solubility of component 1 in the membrane is not only determined by component 1 but also by component 2 [19]. The Flory-Huggins model can easily be extended to multicomponent systems. For a binary liquid mixture and a polymer (a ternary system), the free energy of mixing is given by the following expression:

$$\Delta G_m = RT\begin{bmatrix} x_1 \ln\phi_1 + x_2 \ln\phi_2 + x_M \ln\phi_M + \\ \chi_{12}x_1\phi_2 + \chi_{1M}x_1\phi_M + \chi_{2M}x_2\phi_M \end{bmatrix} \quad (10)$$

where subscripts 1 and 2 refer to the sorbed components and subscript M to the polymeric membrane. The solute-polymer interactions are characterized by χ_{1M} and χ_{2M} whilst χ_{12} is a measure of the interaction between the sorbed molecules within the matrix. The activities of the different components are again obtained by differentiating equation (10):

$$\ln a_1 = \ln\phi_1 + (1-\phi_1) - \phi_2\left(\frac{\bar{V}_1}{\bar{V}_2}\right) - \phi_M\left(\frac{\bar{V}_1}{\bar{V}_M}\right) + (\chi_{12}\phi_2 + \chi_{1M}\phi_M)(\phi_2 + \phi_M) - \chi_{2M}\left(\frac{\bar{V}_1}{\bar{V}_2}\right)\phi_2\phi_M \quad (11a)$$

$$\ln a_2 = \ln\phi_2 + (1-\phi_2) - \phi_1\left(\frac{\bar{V}_2}{\bar{V}_1}\right) - \phi_p\left(\frac{\bar{V}_2}{\bar{V}_M}\right) + \left(\chi_{12}\phi_1\left(\frac{\bar{V}_2}{\bar{V}_1}\right) + \chi_{2M}\phi_M\right)(\phi_1 + \phi_M) - \chi_{1M}\left(\frac{\bar{V}_2}{\bar{V}_1}\right)\phi_1\phi_M \quad (11b)$$

Equation (11) can be further simplified by noting that the partial molar volume of the polymer is much greater that of the solvent, so that terms including ($\bar{V}_i/\bar{V}_p$) can be dropped.

Given the liquid phase activities and the interaction parameters χ_{1M}, χ_{2M} and χ_{12} the volume fraction in the membrane can be calculated by solving the above equations. The interaction parameter χ_{1M} and χ_{2M} in principle can be obtained from pure liquid/ polymer sorption data using equation (9). The solute-solute interaction within the polymer matrix χ_{12} is independent of the nature of the polymer. It can be determined from liquid/vapor equilibrium data. For a binary liquid mixture, equation (10) is simplified to:

$$\chi_{12} = \frac{1}{x_1\phi_1}\left[-(x_1\ln\phi_1 + x_2\ln\phi_2) + \frac{\Delta G_m}{RT}\right] \quad (12)$$

Experimental data derived from vapor-liquid equilibria is normally expressed in terms of the excess Gibbs free energy, ΔG_E. This can be related to molar Gibbs free energy of mixing by adding the ideal contribution:

$$\frac{\Delta G_m}{RT} = \frac{\Delta G_E}{RT} + [(x_1\ln x_1 + x_2\ln x_2)] \quad (13)$$

Substituting the above equation into equation (12) leads to:

$$\chi_{12} = \frac{1}{x_1\phi_1}\left[(x_1\ln(x_1/\phi_1) + x_2\ln(x_2/\phi_2) + \Delta G_E/RT\right] \quad (14)$$

A similar expression may be resulted in if the molar volumes of the components are equal:

$$\chi_{12} = \frac{1}{x_1\phi_1}\frac{\Delta G_E}{RT} \quad (15)$$

Transport step: In the final transport equation, the mass transfer resistances in the feed and the permeate side were neglected, as well as the component concentrations in the permeate side is assumed to be null. The permeation of the components through the membrane was considered unidirectional and described using the MS equations. However, when polymers are involved, the substitution of the mole fraction, *xi*, by the volume fraction, ϕ_i, proposed by Stephan and Heintz [20], can be used to give a better expression for the population effect on the friction between high weight substances and low weight solvents, stated in equation (16):

$$\frac{d\mu_i}{dz} = \sum_{j=1}^{n}\phi_j(v_j - v_i)\frac{RT}{\mathcal{D}_{ji}} \quad (16)$$

where $d\mu_i/dz$ is the chemical potential gradient across the membrane, v_i the velocity of component *i* and $\mathcal{D}_{ji}$ the MS diffusion coefficient of *i-j* pair and $RT/\mathcal{D}_{ji}$ has the meaning of a friction coefficient accounting for the frictional effect exerted by component *j* on component *i*. where ϕ_j is the volume fraction of component j defined as:

$$\phi_j = \frac{\bar{V}_j x_j}{\sum_i \bar{V}_i x_i} \quad (17)$$

V_i and V_j are partial molar volumes of the corresponding components. Application of equation (17) requires the definition of a frame reference. By

considering polymer frame of reference, $v_M = 0$ and extending equation (16) on the component j, we obtain:

$$\frac{dlna_1}{dz} = \phi_2 \frac{v_2 - v_1}{\mathbf{D}_{12}} - \phi_M \frac{v_1}{\mathbf{D}_{1M}} \quad (18a)$$

$$\frac{dlna_2}{dz} = \phi_1 \frac{v_1 - v_2}{\mathbf{D}_{12}} - \phi_M \frac{v_2}{\mathbf{D}_{2M}} \quad (18b)$$

With solving two above equations, they may be arranged with respect to velocity of components:

$$v_1 = \frac{\mathbf{D}_{1M}}{\phi_M}\left(\frac{\phi_1\mathbf{D}_{2M} + \phi_M\mathbf{D}_{12}}{\phi_1\mathbf{D}_{2M} + \phi_M\mathbf{D}_{12} + \phi_2\mathbf{D}_{1M}}\right)\frac{dlna_1}{dz} + \frac{\mathbf{D}_{1M}}{\phi_M}\left(\frac{\phi_2\mathbf{D}_{2M}}{\phi_1\mathbf{D}_{2M} + \phi_M\mathbf{D}_{12} + \phi_2\mathbf{D}_{1M}}\right)\frac{dlna_2}{dz} \quad (19a)$$

$$v_2 = \frac{\mathbf{D}_{2M}}{\phi_M}\left(\frac{\phi_1\mathbf{D}_{1M}}{\phi_1\mathbf{D}_{2M} + \phi_M\mathbf{D}_{12} + \phi_2\mathbf{D}_{1M}}\right)\frac{dlna_1}{dz} + \frac{\mathbf{D}_{2M}}{\phi_M}\left(\frac{\phi_2\mathbf{D}_{1M} + \phi_M\mathbf{D}_{12}}{\phi_1\mathbf{D}_{2M} + \phi_M\mathbf{D}_{12} + \phi_2\mathbf{D}_{1M}}\right)\frac{dlna_2}{dz} \quad (19b)$$

Based on Flory-Huggins model, the activity of each component in the polymer is a function of both component volume fractions. Therefore, the driving force for each component can be expanded as follows:

$$lna_1 = f(\phi_1, \phi_2) \Rightarrow \frac{dlna_1}{dz} = \frac{dlna_1}{d\phi_1}\nabla\phi_1 + \frac{dlna_1}{d\phi_2}\nabla\phi_2 \quad (20a)$$

$$lna_2 = f(\phi_1, \phi_2) \Rightarrow \frac{dlna_2}{dz} = \frac{dlna_2}{d\phi_1}\nabla\phi_1 + \frac{dlna_2}{d\phi_2}\nabla\phi_2 \quad (20b)$$

Substitution of equations (20a) and (20b) in (19a) and (19b) gives the final expressions for permeating component velocities. For a compact representation of the equations, it is easier to write them in matrix from as follows:

$$\begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{bmatrix}\begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{bmatrix}\begin{bmatrix} \nabla\phi_1 \\ \nabla\phi_2 \end{bmatrix} \quad (21)$$

kinetic coupling — Equilibrium coupling

The elements of multicomponent diffusivity matrix are given by:

$$A_{11} = \frac{\mathbf{D}_{1M}}{\phi_M}\left(\frac{\phi_1\mathbf{D}_{2M} + \phi_M\mathbf{D}_{12}}{\phi_1\mathbf{D}_{2M} + \phi_M\mathbf{D}_{12} + \phi_2\mathbf{D}_{1M}}\right)$$

$$A_{12} = \frac{\mathbf{D}_{1M}}{\phi_M}\left(\frac{\phi_2\mathbf{D}_{2M}}{\phi_1\mathbf{D}_{2M} + \phi_M\mathbf{D}_{12} + \phi_2\mathbf{D}_{1M}}\right)$$

$$A_{21} = \frac{\mathbf{D}_{2M}}{\phi_M}\left(\frac{\phi_1\mathbf{D}_{1M}}{\phi_1\mathbf{D}_{2M} + \phi_M\mathbf{D}_{12} + \phi_2\mathbf{D}_{1M}}\right)$$

$$A_{22} = \frac{\mathbf{D}_{2M}}{\phi_M}\left(\frac{\phi_2\mathbf{D}_{1M} + \phi_M\mathbf{D}_{12}}{\phi_1\mathbf{D}_{2M} + \phi_M\mathbf{D}_{12} + \phi_2\mathbf{D}_{1M}}\right) \quad (22)$$

and elements of thermodynamic factor, Γ, indicating the thermodynamic coupling is given by:

$$\Gamma = \begin{bmatrix} \frac{dlna_1}{d\phi_1} & \frac{dlna_1}{d\phi_2} \\ \frac{dlna_2}{d\phi_1} & \frac{dlna_2}{d\phi_2} \end{bmatrix} \quad (23)$$

Molar fluxes of components are:

$$N_i = C_i.v_i \quad (24)$$

and

$$C_i = \frac{\phi_i}{V_i} \quad (25)$$

Diffusion coefficients dependence on the penetrant concentration: Based on number of published literature on pervaporation of hydrocarbon mixtures through different polymers, it appears that the composition of the upstream feed has a drastic effect on the selectivity. The order of magnitude of the selectivity is at the same time far lower than the ratio of the fluxes of pure permeants. This behavior is usually interpreted as a plasticizing effect of permeants on the membrane. Although it is well admitted that both kinetic and equilibrium properties of permeants are equally involved in the pervaporation process, diffusivities are most of the time more sensitive to permeants concentrations than solubilities. A linear dependence of permeant diffusivity on concentration is not suitable for taking into account large plasticizing effects. These are more conveniently described in terms of exponentially concentration-dependent diffusivities. One of these models, is Long-model formulation [21]. Long's model has been used to describe the diffusivity dependence on the penetrant concentration. The results are shown as follows:

$$\mathbf{D}_i = \mathbf{D}_i^0 \exp(\alpha_i m_i) \quad (26)$$

where D_i is the diffusion coefficient of penetrant *i* at zero concentration and m_i is uptake of solute

component in the polymer expressed in g/g dry membrane. α_i is the plasticizing constant indicating the plasticizing action of the penetrant on segmental motion. Complications may increase when the diffusion coefficients of each permeating component in the polymer be dependent on both component concentrations. In this case the number of parameters describing the concentration dependence will increase. However, in this study, the form of Long's model was retained, but a pseudo binary volume fraction was used as the representative of concentration as follows:

$$\mathbf{D}_i = \mathbf{D}_i^0 \exp\left(\alpha_i \frac{\phi_i}{\phi_i + \phi_j}\right) \quad (27)$$

RESULTS AND DISCUSSIONS

The model developed in this study was validated against the data available in the literature [4, 22] for the separation of benzene/*n*-hexane and benzene/ cyclohexane mixtures by dense polyurethane (PU). The results for sorption and permeation are discussed separately.

Results of Bz-Hx pervaporation

Sorption: Using the data available in the literature for the sorption of pure benzene and n-hexane in a kind of PU membrane, the component-polymer interaction parameter was calculated using equation (9). The component-component interaction parameter was calculated based on equation (12) using vapor-liquid equilibrium data which was resulted to the values, $\chi_{1M} = 0.807$, $\chi_{2M} = 2.22$ and $\chi_{12} = 0.272$. Using these parameters recovered from only pure component data, it was tried to predict the multicomponent sorption behavior for the system benzene-n-hexane/PU. This needs to solve the two nonlinear equations of (11a) and (11b) simultaneously. These equations were iteratively solved to give the volume fraction of each sorbed component in polymer phase, knowing that at equilibrium $a_i^M = a_i^L$. The Van Laar equation was used for the description of binary liquid phase activities. The results for the sorption of benzene/n-hexane mixture in PU have been presented in Fig. 3 and 4. The results are expressed in terms of total solubility of the components into the polymer matrix (Fig. 3) and as the benzene pseudo-equilibrium curve (Fig. 4). Both results were expressed as a function of the benzene weight fraction in the liquid phase. As expected from sorption experiments of pure organic components in PU, the aromatic compound is preferentially sorbed component. Because swelling of polymer matrix, the solubility of *n*-hexane is higher in presence of benzene in

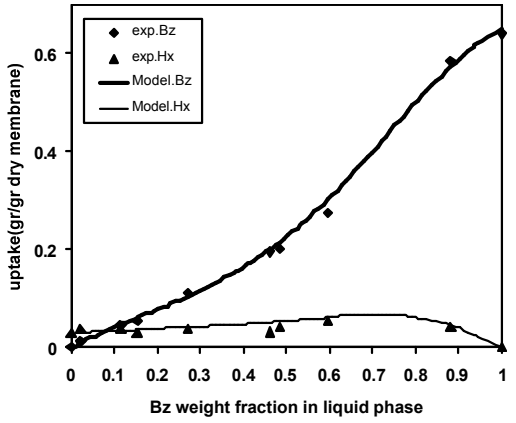

Fig. 3: Individual component solubility of benzene/*n*-hexane mixture in polyurethane versus the benzene weight fraction in liquid phase {experimental data [4]}

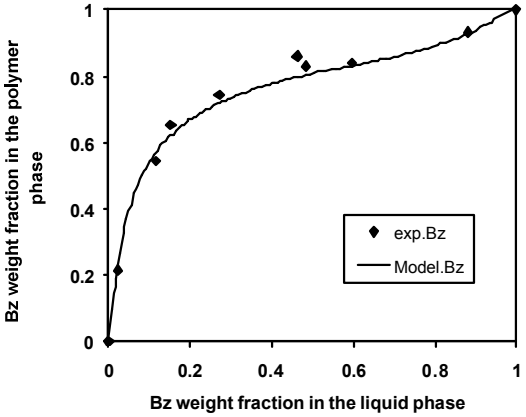

Fig. 4: Benzene pseudo-equilibrium curve {experimental data [4]}

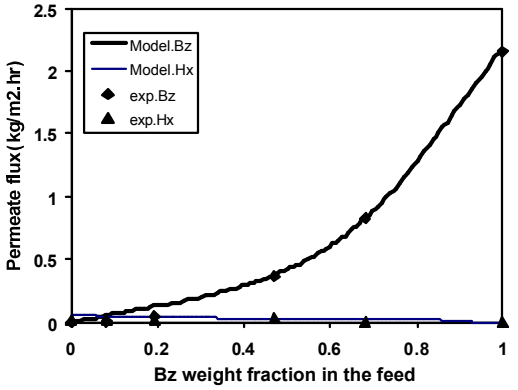

Fig. 5: Pervaporation result of the benzene/*n*-hexane mixture using PU membrane in terms of individual component flux as a function of the benzene weight fraction in the feed {experimental data [4]}

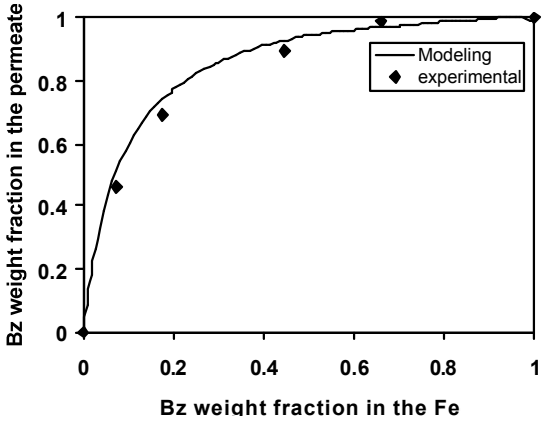

Fig. 6: Pervaporation result of the benzene/*n*-hexane mixture using PU membrane in terms of the permeate composition as a function of t the feed composition {experimental data [4]}

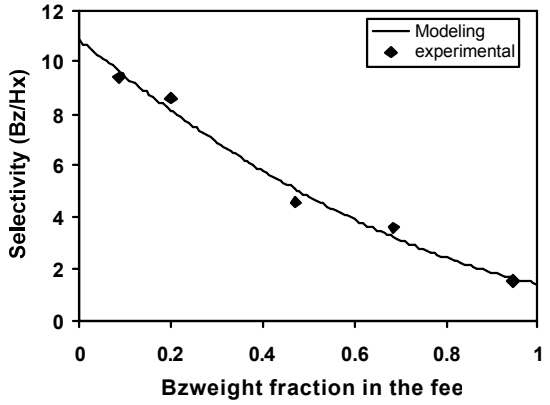

Fig. 7: Bz/Hx separation factor, as a function of the Bz weight fraction the feed {experimental data [4]}

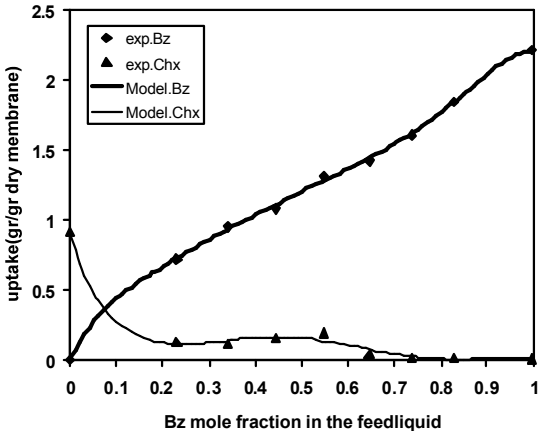

Fig. 8: Individual sorption values of benzene/ cyclohexane mixture in polyurethane {experimental data [24]}

comparison to pure n-hexane solubility, but it is remarkable to notice that it remains almost constant in the whole range of liquid composition. The pseudo-equilibrium curve for benzene (Fig. 4) shows clearly the effect of its higher interaction with the polymer on the sorption selectivity. For instance, a benzene weight fraction of 0.2 in the liquid phase, results in a benzene weight fraction of 0.6 in the polymer phase. The both model predicted values and experimental data were plotted in this figure for comparison.

It is important to emphasize that predictions were based on only pure components sorption data and a good agreement between the models predicted values and experimental data is observed in the whole composition range. The preferential sorption of aromatic compound indicates that PU has a strong potential as membrane material for aromatics removal from aromatic/aliphatic mixtures using pervaporation process.

Pervaporation: Using the transport model developed in this study, equations (21) to (24), the pervaportive separation performance of benzene/n-hexane mixture through the PU membrane were predicted. The partial derivatives in the thermodynamic factor, equation (23), were obtained by differentiating equations (11a) and (11b) and were calculated for the system under study. The flux coupling effect was also taken into account using the coupled equations of the proposed model. The elements of multicomponent diffusivity factor, equation (22), were calculated using binary diffusivities which were found from pure component pervaporation data. Figure 5 and 6 show the pervaporation results of the benzene/*n*-hexane mixture. For this mixture the pervaporation flux of individual component and the aromatic weight fraction in the permeate were presented as a function of the aromatic weight fraction in the feed. In each figure, the results predicted by the proposed transport model were also plotted for comparison.

As anticipated from sorption experiments, the results in Fig. 5 and 6 show that the PU membrane is selective to the aromatic component in the liquid permeation through the membrane. For instance, in benzene/*n*-hexane/ PU system, a permeate flux of about 0.5 Kg/m^2 h is obtained at weight fraction of 0.5 for benzene in the feed, corresponding to a benzene weight fraction of 0.8 in the permeate, i.e. a selectivity of about 4 where the mixture selectivity defined as:

$$\alpha = \left(\frac{y_i / y_j}{x_i / x_j} \right)$$

where y_i and x_i indicate the mole fraction of component i in permeate and feed respectively. Figure 7 shows the

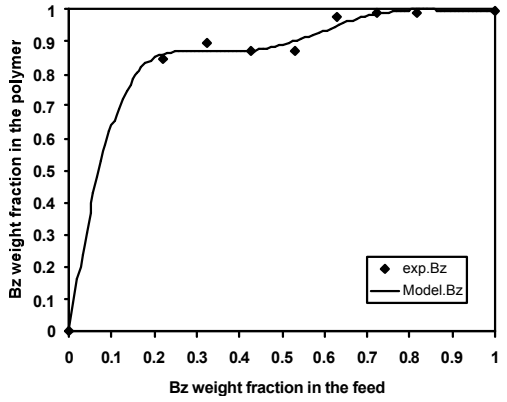

Fig. 9: Benzene pseudo-equilibrium curve in Bz-Chx/PU system{experimental data [24]}

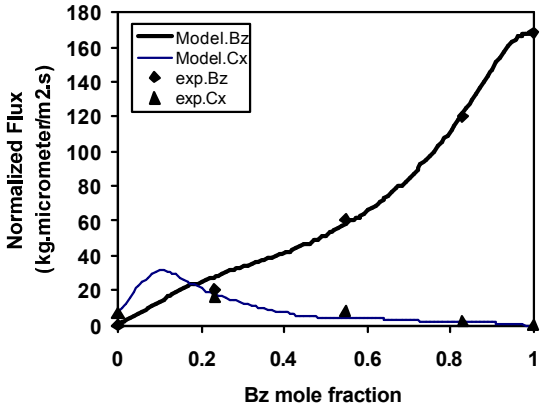

Fig. 10: Pervaporation results of benzene/cyclo hexane mixture using PU membrane in terms of permeate flux as a function of the benzene weight fraction in the feed {experimental data [24]}

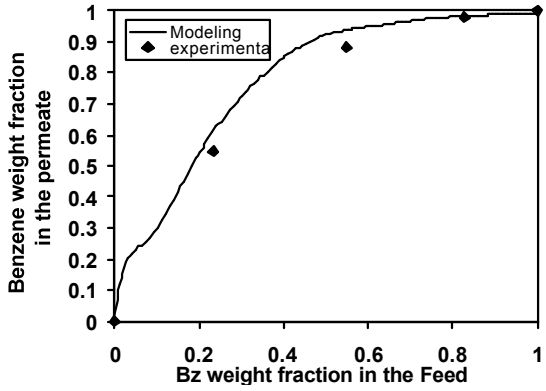

Fig. 11: Pervaporation results of benzene/cyclo hexane mixture using PU membrane in terms of permeate pseudo binary composition as a function of the benzene weight fraction in the feed {experimental data [24]}

variation of the selectivity values with the benzene composition in the feed. Decreasing trend can be attributed to coupling effect which indicates that at the presence of benzene the transport of slower component is facilitated, therefore reducing the selectivity.

Results of Bz-Chx pervaporation Sorption: The sorption behavior of Bz and Chx in the PU membrane were examined by extended Flory Huggins model. Through a number publications in the literature, it is understood that the PU membrane had strong affinity for aromatic organic solvents and favors Bz. Experimental results shows that the pure Bz uptake was 2.4 times greater than pure Chx in the PU membrane (2.22 versus 0.91 g/g dry membrane) [22]. This preference can be attributed to the polarity of the aromatic ring due to the presence of π electrons in Bz. Benzene molecule exhibits stronger dispersion, polar and hydrogen-bonding capability. Therefore a polar structure membrane will induce interaction with the π electrons and favor Bz sorption. The component-polymer and component-component interaction solubility parameters in Flory-Huggins model was calculated using pure component sorption data which resulted to values, χ_{1M} =0.588, χ_{2M} = 0.767 and χ_{12} = 0.115. Using these parameters the multicomponent sorption behavior was carried out. Figure 8 and 9 show the experimental and the predicted values of individual component and the pseudo equilibrium curve for benzene which indicated a proper match between the experimental data and the model predicted values. This reveals that the mixing effect is well covered by the Flory-Huggins model.

Pervaporation: Again the pervaporative separation behavior for the system benzene-cyclohexane/PU was predicted using the proposed transport model. Figure 10 and 11 show the normalized permeation flux for individual component and the pseudo binary permeate composition in the PU membrane, as a function of the feed composition. The Bz flux increased as Bz content increased in the feed solution as expected. The Chx flux increased at 0-10% Bz feed and decreased with a further increase in Bz content. This is due to plasticization effect of Bz (Fig. 8). Bz molecules are preferentially sorbed and can diffuse at an appreciable rate into the unrelaxed polymer state, resulting in a soft and mobile structure. Thus, the diffusion of Chx molecules into the polymer matrix is facilitated at low Bz composition. However, once Chx has been sorbed, its further mobility into the membranes is retained at the higher bz concentration due to the sorption competition effect. Figure 12 also indicates that the selectivity increases in favor of aromatic component with an increase in its composition in the feed.

SEPARATE EVALUATION OF EQUILIBRIUM AND KINETIC COUPLING

Equilibrium coupling effect: It is constructive at this point to consider the equilibrium coupling effect on the flux of permeating components through the membrane. This was carried out by calculating the elements of equilibrium based thermodynamic factor represented by $[\phi_i \partial \ln a_i/\partial\phi_j]$ for the system benzene/n-hexane/PU. Figure 13 shows the diagonal (main) and off-diagonal equilibrium terms calculated from the classical Flory-Huggins model as a function of benzene volume fraction in the membrane. From the Fig. 13, as the benzene volume fraction is diminished the cross term $[\phi_1 \partial \ln a_1/\partial\phi_2]$ tends to zero while the main term $[\phi_1 \partial \ln a_1/\partial\phi_1]$ approaches unity. This implies that at low benzene concentration the flux of benzene is not largely affected by the flux of n-hexane. In contrast, the cross term $[\phi_2 \partial \ln a_2/\partial\phi_1]$ does not approaches to zero and takes a finite value comparable to the main term $[\phi_2 \partial \ln a_2/\partial\phi_2]$. This indicates that the flux of n-hexane is strongly coupled to that of benzene at a large benzene concentration on a thermodynamic basis. The coupling effect diminishes as the benzene concentration of benzene increases. It should be note that the extent of the coupling of fluxes observed will of course depend on the magnitude of the concentration gradient through the membrane and therefore may differ for each specific system.

Kinetic coupling effect: The influence of kinetic coupling is the most easily brought out by considering the elements of multicomponent diffusivity matrix, A_{ij}. Figure 14 shows the variation of the diagonal (main) and off-diagonal (cross tem) elements of diffusivity matrix with the benzene volume fraction in the membrane. As is evident from figures, the flux of benzene is kinetically unaffected by the presence of n-hexane, while the flux of n-hexane is coupled to the flux of benzene at only low concentration of n-hexane. This can be attributed to the high magnitude of binary liquid-liquid diffusivity compared to binary liquid-polymer diffusivity which causes the main terms in diffusivity matrix become nil.

CONCLUSIONS

The sorption and pervaporation behavior of aromatic/non aromatic (aliphatic) mixtures were well predicted by the proposed transport model in present study based on a combination of Flory-Huggins model and Maxwell-Stefan formulation. The main objective of the developed model was to make a sound design basis

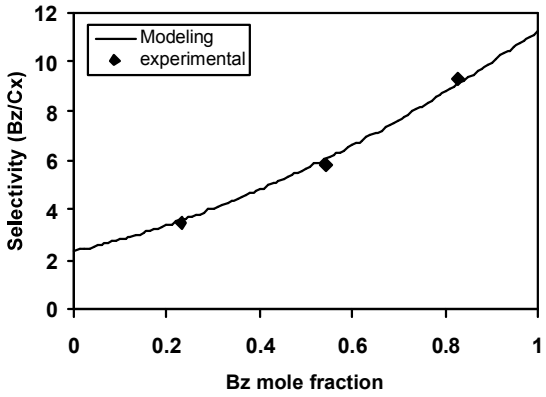

Fig. 12: Benzene/ cyclohehane selectivity as a function of the benzene weight fraction in the feed{experimental data [24]}

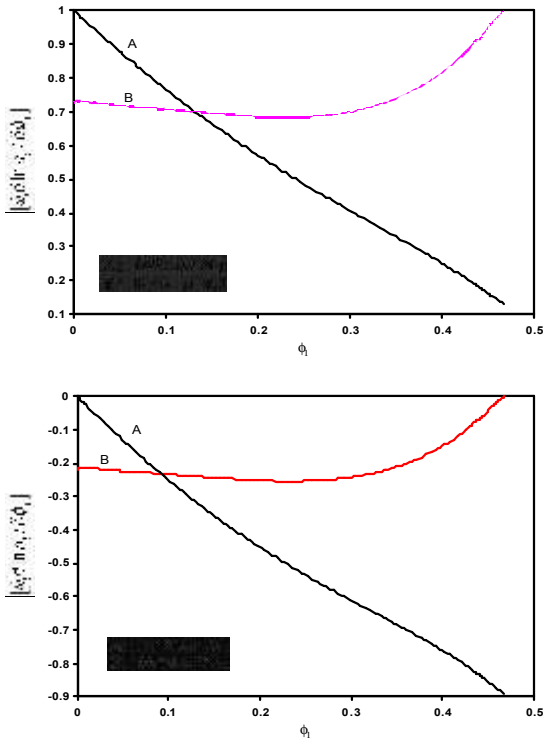

Fig. 13: Equilibrium coupling effect in the benzene/n-hexane/PU system

of prevaporation process for the separation of aromatic/non aromatic mixtures using dense polymeric membranes. The model parameters were recovered from simple pure component sorption and pervaportion experimentations and used for the prediction of multicomponent separation behavior employing a sophisticated extension of sorption and diffusion theories. The results obtained in present study, render the PU membranes as useful material for the selective

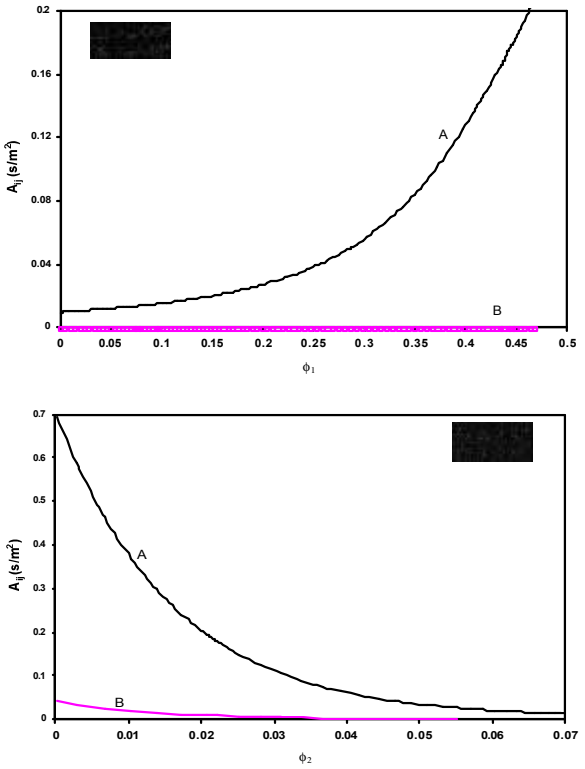

Fig. 14: Magnitude of kinetic coupling effect in the benzene/n-hexane/PU system

separation of aromatic/non aromatic hydrocarbons from their mixtures. The aromatic compounds exhibited preferential sorption and permeation in all composition range, leading to permeate enriched in these components. The extended Flory-Huggins model was used to predict the sorption selectivity for a pair of aromatic/non aromatic mixtures using the solubility parameter recovered from single component sorption data. A good agreement between the experimental data and the model predicted values indicated that the mixing effect on sorption is well covered by the Flory-Huggins model. The main advantage of the Maxwell-Stefan theory used in present study for the description of multicomponent diffusion is that the binary diffusion coefficients recovered from pure component pervaporation experiments retain their physical significance and can be used for the multicomponent systems. These diffusivity parameters along with a suitable solubility model incorporated into the proposed transport model provided a good prediction of separation behavior for the systems under investigation. In both investigated mixtures, the total permeate flux was controlled by the aromatic component and the coupling effect was observed to have an impact on the transport of the aliphatic compounds.

Nomenclatures

a_i Activity of component i in mixture (-)
A_{ij} Elements of multicomponent diffusivity matrix (mole.m^2/J.s)
C_i Concentration of component i in mixture (mole/m^3)
D_0 Diffusion coefficient in trance concentration (m^2/s)
$\mathbb{D}_{ij}$ Binary Maxwell-Stefan diffusivity (m^2/s)
G_m Gibbs free energy of mixing (J/mole)
G_E Excess Gibbs free energy of mixing (J/mole)
H_m Enthalpy of mixing (J/mole)
m_i Mass of component i sorbed in membrane (Kg/Kg fry mem.)
N_i Molar flux of component i (moles/m^2.s)
P Pressure (Pa)
R Universal gas constant ((J.mole.K)
S_m Entropy of mixing ((J.mole.K)
S_{sc} Configurational entropy of mixing (J.mole.K)
T Temperature (K)
v_i Velocity of component i in mixture (m/s)
$\bar{V}_i$ Partial molar volume of component i in mixture (m^3/mole)
x_i mole fraction of component i in mixture (-)
z distance in membrane (-)

Greek symbols

α Membrane selectivity (-)
α_I Plasticization factor of component i on polymer(-)
Γ_{ij} Elements of multicomponent thermodynamic matrix (-)
μ_I Chemical potential of component I in mixture (J/mole)
ϕ_i Volume fraction of component i in mixture (-)
χ_{ij} Binary interaction parameter in Flory-Huggins Thermodynamic model (-)

Subscripts

1 Component 1
2 Component 2
M Membrane

Superscripts

liq Liquid phase
mem Membrane phase

Abbreviation

PU Polyurethane
Bz Benzene
Hx Normal hexane
Chx Cyclohexane

Mathematical symbols

Δ Difference operator

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REFERENCES

1. Ren, J, C. Staudt-Bickel, R.N. Lichtenthaler, 2001. Separation of aromatics: Aliphatics with crosslinked 6FDA-based copolyimides. Sep. Pur. Tech., pp: 22-23, 31-34.
2. Razdan, U, S.V. Joshi and V.J. Shah, 2003. Novel membrane processes for separation of organics: Review, Current Sci., 85: 761-771.
3. Katarzynski, D. and C. Staudt-Bickel, 2006. Separation of multi component aromatic/aliphatic mixtures by Pervaporation with copolyimide membranes, Desalination, 189: 81-86.
4. Cunha, S, M.L.L. Paredes, C.P. Borges, A.C. Habert and R. Nobrega, 2002. Removal of aromatics from multicomponent organic mixtures by pervaporation using polyurethane membranes: Experimental and modeling. J. Mem. Sci., 206: 277-290.
5. Khaye, M., M.M. Nasef and J.I. Mengual, 2005. Radiation grafted poly (ethylene terephthalate)-*graft*-polystyrene Pervaporation membranes for organic/organic separation. J. Mem. Sci., 263: 77-95.
6. Feng, X. and R.Y.M. Huang, 1997. Liquid separation by membrane pervaporation: A review, Ind. Eng. Chem. Res., 36: 1048-1066.
7. Shao, P. and R.Y.M. Huang, 2007. Polymeric membrane pervaporation, J. Mem. Sci., 287: 162-179.
8. Smitha, B., D. Suhanya and S. Sridhar, 2004. Ramakrishna M, Separation of organic-organic mixture by pervaporation-a Review. J. Mem. Sci., 241: 1-21.
9. Peng, F., F. Pan, D. Li and Z. Jiang, 2005. Pervaporation properties of PDMS membranes for removal of benzene from aqueous solution: Experimental and modeling, Chem. Eng. J., 114: 123-129.
10. Villaluenga. J.P.G., P. Godino, M. Khayet, B. Seoane and J.I. Mengual, 2004. Pervaporation of Alcohols and Methyl tert-Butyl Ether through a Dense Poly (2,6-dimethyl-1,4-phenylene oxide) Membrane. Ind. Eng. Chem., 43: 2548-2555.
11. Gonza´ lez, B. and I. Ortiz Uribe, 2001. Mathematical Modeling of the Pervaporative Separation of Methanol-Methylterbutyl Ether Mixtures. Ind. Eng. Chem., 40: 1720-1731.
12. Wolin´ska-Grabczyk, A., 2004. Relationships between permeation properties of the polyurethane-based pervaporation membranes and their structure studied by a spin probe method, Polymer, 45: 4391-4402.
13. Izák, P., L. Bartovská, K. Friess, M. Š´ipek and P. Uchytil, 2003. Description of binary liquid mixtures transport through non-porous membrane by modified Maxwell-Stefan equations. J. Mem. Sci., 214: 293-309.
14. Wang, Y., S. Hirakawa, H. Wang, K. Tanaka, H. Kita and K. Okamoto, 2002. Pervaporation properties to aromatic/non-aromatic hydrocarbon mixtures of cross-linked membranes of copoly (methacrylates) with pendant phosphate and carbamoylphosphonate groups. J. Mem. Sci., 199: 13-25.
15. Ghoreyshi, A.A., F.A. Farhadpour and M. Soltanieh, 2002. Multicomponent Transport across nonporous polymeric membranes, Desalination, 144: 93-101.
16. Jeng, J.Y.H. and J.Y.H. Huang, 1998. A Pseudophase-change solution-Diffusion model for pervaporation. I. single component permeation. Sep. Sci. Tech., 33: 767-785.
17. Flory, P.J., 1953. Principles of polymer chemistry. Cornell University Press, Ithaca, New York.
18. Reid, R.C., J.M. Prausits and B. Poling, 1987. The properties of gases and liquids, 4th Ed., Mc Graw Hill, New York.
19. Huang, R.Y.M., 1991. Pervaporation membrane separation processes, Elsevier, Amsterdam.
20. Heintz, A. and W. Stephan, 1994. A generalized solution-Diffusion model of Pervaporation process through composite membranes, Part II. Concentration polarization, coupled diffusion and the influence of the porous support layer, J. Mem. Sci., 89: 153-169.
21. Brun, J.P., C. Larchet, R. Melet and G. Bulvestre, 1985. Modeling of the pervaporation of binary mixtures through moderately swelling, non-reacting membranes, J. Mem. Sci., pp: 257-283.
22. Lue, S.J. and S.H. Peng, 2003. Polyurethane (PU) membrane preparation with and without hydroxypropyl-β-cyclodextrin and their pervaporation characteristics. J. Mem. Sci., 222: 203-217.