Pervaporation modeling of NaA Zeolite membrane for dehydration of Ethanol-water mixture

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ABSTRACT
Dehydration of solvents using hydrophilic polyvinylalcohol pervaporation membranes is a well-established technology. The recent development of solvent and temperature-resistant, hydrophilic zeolite NaA membranes has made it possible to overcome the above limitations of hydrophilic polymeric membranes. Zeolite membranes have uniform and molecular-sized pores, and they separate molecules based on differences in the molecules’ adsorption and diffusion properties. Strong electrostatic interaction between ionic sites and water molecules (due to its highly polar nature) makes the zeolite NaA membrane very hydrophilic. This work presents a modification simplified model of Estefan Maxwell was used to evaluate the experimental data for water-Ethanol mixtures. Thus water sorption for NaA membrane in different concentrations (0%, 0.1%, 50%, 80%, 90% wt regarding to Ethanol) was tested and then calculated. A comparison between experimental flux and calculated flux using Stefan Maxwell (S.M.) and Modified model correlation was made and a linear trend was found to exist for water flux through the membrane with ethanol concentration. Modified model showed better consistency with experimental data than the model S.M.

Keywords: Pervaporation, ethanol, Zeolite, NaA, Maxwell–Stefan, Model

INTRODUCTION
Zeolites have been conventionally used as catalysts, ion exchangers and adsorbents. Potential of zeolitic materials as membranes for physical separations like pervaporation (PV) and reactive separations like membrane reactors have been realized only in recent years [1-3]. Polymeric PV membranes have been widely studied, major emphasis being on new polymeric materials, modeling of component transport through dense polymers and process design of commercial membrane modules. However, most polymeric membranes fail to give an optimal performance over a broad spectrum of solvents and concentration ranges, in terms of flux and selectivity.

Synthetic zeolites have a highly crystalline ordered structure and hence offer the unique advantage of narrow pore size distribution. Also, due to their inorganic nature, these materials possess higher resistance to a variety of solvents and stability at elevated temperatures. These distinctive properties, which are very critical for many membrane applications, make the use of zeolite membranes more attractive than polymeric membranes. Zeolite membranes can be potentially used in many pharmaceutical applications, which are typically low-volume processes and may contain harsh solvents like dimethylformamide, tetrahydrofuran, etc., and inorganic salts. This paper focuses on separation of Ethanol–water mixtures using hydrophilic zeolite pervaporation membranes. A great deal still remains to be known about the transport mechanisms of various species through zeolite membranes. The transport mechanism of aqueous species through zeolitic materials is more complex than through polymeric membranes, since it can involve movement through both molecularly selective zeolite micro crystals as well as less selective interstitial regions. This produces a complex morphology and transport situation.
This work presents a modification of the simplified model of Estefan Maxwell was used to evaluate the experimental data for water-Ethanol mixtures. A comparison between experimental flux and calculated flux using Stefan Maxwell (S.M.) and Modified model correlation was made and a linear trend was found to exist for water flux through the membrane with ethanol concentration.

2. Zeolite structure, transport mechanisms and Model

The hydrophilic membranes used in this research were composite zeolite NaA membranes. The membranes were basically made of an active NaA layer, deposited on a ceramic porous mullite support. The active NaA layer is responsible for high separation factors achieved in PV of Ethanol mixtures. The structure of zeolite NaA is shown in Figure 1.

As shown in Figure 1, the aluminosilicate framework of zeolite NaA is generated by placing truncated octahedrons (b-cage) at eight corners of a cube and each edge of the cube is formed by joining two b-cages by a D4R linkage. Each b-cage encloses a cavity with a free diameter of 0.66 nm and each unit cell encloses a larger cavity (a-cage) enclosing a free diameter of 1.14 nm. There are two interconnected, three-dimensional channels in zeolite NaA: (i) connected a-cages, 1.14 nm in diameter, separated by 0.42 nm apertures, (ii) b-cages, alternating with a-cages separated by 0.22 nm apertures [4]. Thus, molecules smaller than 0.42 nm in diameter can diffuse easily through the nanopores of the zeolite. Also, position of sodium ions in unit cells is important since these ions act as the sites for water sorption and transport through the membrane. For a typical zeolite, a unit cell having the composition Na12Al12Si12O48.27 H2O, eight (out of 12) sodium ions are located inside an a-cage and four ions are located in b-cages. Transport of solute species (mainly water) through the zeolite matrix comprises of three steps: (i) strong adsorption of the species into a cage from feed side, (ii) surface diffusion of the species from cage to cage and (iii) vaporization of the species to permeate side. Normally, any physical adsorption process includes both van der Waals dispersion-repulsion forces and electrostatic forces comprising of polarization, dipole and quadrupole interactions. However, since the zeolites have an ionic structure, the electrostatic forces become very large in adsorption of polar molecules like H2O. This effect is manifested in the fact that heat of adsorption of water into zeolitic adsorbents is unusually high (25–30 kcal/mole) [5-7]. Researchers have extended the dusty-gas model approach to describe the surface-diffusion of molecules into a zeolite surface. The vacant sites are assumed to be the (n+1) pseudo-species in the system and S.M. Equation is used to correlate surface chemical potential gradient to flux of the various species, as shown in Eq. (1):

$$\nabla \mu_i = RT \sum_{k=1}^{n} \theta_k \left( \frac{V_i - V_{sat}}{D_{ik}} \right) + RT \theta_{n+1} \left( \frac{V_i - V_{n+1}}{D_{i,n+1}} \right), \quad i = 1, 2, ..., n \quad (1)
$$

For two components denoted by 1 and 2, diffusing in a zeolite pore where the vacant sites are represented by $v$, individual component equations can be written as shown in Eqs. (2) and (3) (velocity of the sites $v$ is equal to 0). It is also conventional to define surface diffusivity $D_{sv}$ as the ratio of $D_{i,n+1}$ and $\theta_{n+1}$ [8].

$$\begin{align*}
\frac{\nabla \mu_1}{RT} &= \left[ \frac{\theta_1 (V_1 - V_{sat})}{D_{12}} + \frac{\theta_1}{D_{1v}} \right] \\
\frac{\nabla \mu_2}{RT} &= \left[ \frac{\theta_2 (V_2 - V_{sat})}{D_{21}} + \frac{\theta_2}{D_{2v}} \right]
\end{align*} \quad (2)
$$

Surface flux of each species through the zeolite pore is represented by Eqs. (4) and (5), where $\rho$ is density of the zeolite,is site $\theta_i$ into the zeolite, is maximum possible sorption of component i $q_{sat}$ is porosity, $\epsilon$ occupancy of species i and $v_i$ is velocity of component i through the pores.

$$\begin{align*}
J^{s}_1 &= \rho_e q_{sat} \theta_1 v_1 \\
J^{s}_2 &= \rho_e q_{sat} \theta_2 v_2
\end{align*} \quad (4)
$$
Assuming that there is no counter diffusion or coupling between the two species \( \left( [D_{12}]^t \text{ and } [D_{21}]^t \to \infty \right) \) [9], Eqs. (2) and (3) can be further simplified to Eqs. (6) and (7):

\[
-\frac{\nabla \mu_1}{RT} = \frac{J_1^s}{\rho_p eq_{sat} \theta_1 [D_{1v}]} \tag{6}
\]

\[
-\frac{\nabla \mu_2}{RT} = \frac{J_2^s}{\rho_p eq_{sat} \theta_2 [D_{2v}]} \tag{7}
\]

From basic thermodynamics, chemical potential gradients \( \nabla \mu_1 \) and \( \nabla \mu_2 \) can be represented as gradients of the site occupancy of each species by the following equations:

\[
\frac{\theta_1 \nabla \mu_1}{RT} = \theta_1 \frac{\partial \ln a_1}{\partial \theta_1} \frac{d \theta_1}{dz} + \theta_1 \frac{\partial \ln a_1}{\partial \theta_2} \frac{d \theta_2}{dz} \tag{8}
\]

\[
\frac{\theta_2 \nabla \mu_2}{RT} = \theta_2 \frac{\partial \ln a_2}{\partial \theta_2} \frac{d \theta_2}{dz} + \theta_2 \frac{\partial \ln a_2}{\partial \theta_1} \frac{d \theta_1}{dz} \tag{9}
\]

Equating Eqs. (6) and (8) with Eqs. (7) and (9):

\[
J_1^s = -\rho_p eq_{sat} [D_{1v}] \left[ \theta_1 \frac{\partial \ln a_1}{\partial \theta_1} \frac{d \theta_1}{dz} + \theta_1 \frac{\partial \ln a_1}{\partial \theta_2} \frac{d \theta_2}{dz} \right] \tag{10}
\]

\[
J_2^s = -\rho_p eq_{sat} [D_{2v}] \left[ \theta_2 \frac{\partial \ln a_2}{\partial \theta_2} \frac{d \theta_2}{dz} + \theta_2 \frac{\partial \ln a_2}{\partial \theta_1} \frac{d \theta_1}{dz} \right] \tag{11}
\]

The above two equations describe flux of each component through the zeolite pore. Nature of the functions \( \frac{\partial \ln a_1}{\partial \theta_1} \) , \( \frac{\partial \ln a_1}{\partial \theta_2} \) and \( \frac{\partial \ln a_2}{\partial \theta_1} \) and \( \frac{\partial \ln a_2}{\partial \theta_2} \) depends on nature of the sorption isotherm of each compound into the zeolite. Diffusivities \( D_{1v}^s \) and \( D_{2v}^s \) are also dependent on the site occupancies \( \theta_1 \) and \( \theta_2 \). Thus, to be able to model flux of each component through the zeolite cages, knowledge of both diffusion and sorption characteristics is essential. For zeolites with narrow pores (as in the case of zeolite NaA), single file diffusion can be assumed to take place. In the case of single file diffusion, only one molecule can diffuse through the cross-section of the pore at any given time. The S.M. surface diffusivity \( D_{1v}^s \) depends linearly on the vacant sites \( \theta_v \) as shown below:

\[
D_{1v}^s = D_{1v}^s (0) \theta_v \tag{12}
\]

A Langmuirian type of sorption isotherm (for pure water into zeolite sites) to predict activity \( (a_w) \) in the zeolite for a given site occupancy \( (\theta_w) \) can be assumed:

\[
a_w = \frac{A \theta_w}{1 - \theta_w} \tag{13}
\]

For pure water-zeolite system, there is no second component and Eqs. 11-13 can be used to obtain the pure water flux equation as:

\[
J_w^s = \rho eq_{sat} [D_{wv}] (0) \frac{d \theta_w}{dz} \tag{14}
\]

Integrating the above equation between the limits \( z = 0, q_w = q_{w,f} \) and \( z = \delta, \theta_w = \theta_{w,p} \):
The above equation is based on the premise that transport of various species through a dense zeolite membrane follows the solution-diffusion mechanism. It should be mentioned that zeolite membranes obey a sorption–diffusion model like polymeric membranes; however the ionic interactions are stronger in the case of zeolite membranes. The ionic interactions affect both the sorption and the diffusion of water into the membrane. For the zeolite membranes, a solution-diffusion mechanism can be envisioned wherein the water molecules first adsorb preferentially at the cage mouth and then diffuse across the active layer. For solvent molecules, however, the partial molecular sieving effects and permeation through non-zeolitic pores may also need to be considered. So a permeability parameter $K_w$ can also be defined for water permeation through zeolite membranes in a similar manner as for polymeric membranes. The parameter is a lumped parameter comprising of the water diffusivity through the membrane, its sorption onto the membrane material and the membrane thickness. The above equation assumes that the permeability parameter remains constant under various feed concentrations and temperatures. However, this is not always true, especially in the case of polymeric membranes. For example, hydrophilic polymeric membranes tend to swell substantially in the presence of high water concentrations causing substantial changes in the permeability parameter of the polymer. The above model is a comprehensive modeling approach and gives helpful insights into the actual transport process within nanopores of the zeolite [10-13].

MATERIALS AND METHODS

3. Experimental
3.1. Membrane preparation
In ceramic membranes, thin dense layers are usually deposited over porous supports. The porous supports provide mechanical strength for the thin selective layers. Porous supports can be made from alumina, cordierite, mullite, silica, spinel, zirconium, other refractory oxides and various oxide mixtures, carbon, sintered metals and silicon carbide. NaA zeolite membrane was grown hydrothermally on the outer surface of a porous tubular mullite support (14 mm outer diameter, 10 mm inner diameter, 10 cm length) [14]. The hydrothermal synthesis of NaA zeolite membrane was performed as follows. An aluminate solution was prepared by dissolving sodium hydroxide and aluminium hydroxide in distilled water. A silicate solution was prepared by dissolving sodium silicate in distilled water. The aluminate solution was added to the silicate solution and the resulting mixture was stirred vigorously, producing a homogeneous gel. The molar composition of the resulting gel was $\text{SiO}_2/\text{Al}_2\text{O}_3=1.926$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3=3.165$ and $\text{H}_2\text{O}/\text{Al}_2\text{O}_3=128$. The porous support coated with crystal seeds of NaA zeolite was dipped in the gel. After hydrothermal treatment at 100°C for 3 h, the support was taken out, washed by water and dried at reduced pressure. The treated tube was analyzed by X-ray diffraction (XRD) for making sure about the formation of zeolite thin layer on its surface. The surface morphology of the membrane was also observed by scanning electron microscopy (SEM) [15-19].

3.2. Pervaporation experiments
A PV experimental set up was used to evaluate successful fabrication of NaA zeolite membranes. PV experiments were carried out using a standard PV apparatus. Feed solution, preheated to a constant temperature, was introduced to the outer side of the zeolite membrane in the PV cell. The downstream pressure was maintained at 133 Pa throughout the operation. The zeolite membranes were used for dehydration of aqueous Ethanol mixtures. The Ethanol mixtures (1,5,10,15 and 20 wt%) were used and experiments were carried out at room temperature (25°C) within a period of 30-60 min. Permeate concentrations were measured using GC (TCD detector, Varian 3400, carrier gas: hydrogen, column: polyethylene glycol, sample size: 5 micron, column and detector temperatures: 120-150°C, detector flow rate: 15 ml/min, carrier flow: 5 ml/min, column pressure: 1.6 kPa, GC input pressure: 20 kPa). Performance of PV was evaluated using values of total flux (kg/m².h) and separation factor (dimensionless) [20–25]. Typical and actual experimental setups were employed as presented in Figure 2. The phases Mullite, Cristobalite and SiO$_2$ identification was performed by XRD (Philips PW1710, Philips Co., Netherlands) with CuKα radiation. Morphology of the support and the membrane was examined by SEM (JEM-1200 or JEM-5600LV equipped with an Oxford ISIS-300 X-ray dispersive spectroscopy (EDS)).
3.3. Water sorption experiments

First ethanol-water mixture was prepared in different concentrations (0%, 0.1%, 50%, 80%, 90% wt regarding to Ethanol). After that a little amount of NaA Zeolite powder, about 0.5 gr was added to 5 different plates. The 3g of each mixture added to these plates. Finally the mixtures were homogenized. Let the time to reaches infinity and after 48 hours the concentration of solution in each plate and also the feed was measured by refractometer. Thus water adsorption for NaA membrane was calculated as table 1.

RESULTS AND DISCUSSION

Figure 3 shows XRD patterns of the mullite support and the zeolite NaA membrane. The XRD pattern of NaA zeolite membrane confirms that zeolite NaA crystals were formed. Figure 4 shows SEM photographs of the mullite support and the zeolite NaA membrane. Porous structure of the support and thin layer of the membrane can be easily observed.

The diffusivity of pure water through NaA zeolite at 25 °C was considered 2.97x10^{-11} m^2/s [26] assuming q_{w,p} = 0, z = 1990 kg/m^3, \varepsilon = 0.49 [27], and z = 30 \mu m. According to equation 16, and experimental data [28] and sorption data which are obtained in this research, flux from Estefan Maxwell model was calculated. Figure1 shows that by increasing the concentration deviation from experimental flux increases. And the result shows that the model flux is less than experimental data. Average error is about 10%. For modifying the model an experimental parameter was multiplied in model. The relation for this parameter is explained through equation 17.

$$\alpha = 8 \times 10^{-6} x^2 + 0.0008x + 1$$

In which (x) refers to the concentration (wt%) of ethanol. The results are shown in figure 5. As it is clear from diagram error was reduced to about 2.8%. By increasing the concentration error increases as the model. Therefore modified model can predict the experimental data better, because the effect of concentration was considered in modification of the model. and As seen in Fig. 6, at higher ethanol concentrations error of both model and modified model was increased because in diffusion calculations pure water was considered.

<table>
<thead>
<tr>
<th>Feed concentration</th>
<th>0%</th>
<th>0.1%</th>
<th>50%</th>
<th>80%</th>
<th>90%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorption (gwater/gzeolite)</td>
<td>0.061</td>
<td>0.06</td>
<td>0.052</td>
<td>0.046</td>
<td>0.043</td>
</tr>
</tbody>
</table>

Table1. Sorption of water into NaA Zeolite powder

Figure 1: Repeating unit of zeolite NaA
Figure 2: Experimental PV setup

Figure 3: XRD patterns of the support and membrane

A=NaA
M=Mullite
Figure 4: SEM micrograph of a) the support b) the membrane (surface) c) the membrane (cross section)

Figure 5: The comparison of permeability between experimental data and model (picture 1) modified model (picture 2)
According to the importance of pervaporation in industry it is necessary to extend a model which can predict the behaviour of the process. In this project Estefan Maxwell was used to evaluat the experimentl data related to water- Ethanol feed. A modification has been done by applying the influence of concentration in the model. acording to figure 2 modified model has less deviation from experimental data.therefore it has better performance in describing the process.

REFERENCES