



# International Journal of Engineering Researches and Management Studies

## MATHEMATICAL MODELLING AND PARAMETER ESTIMATION FOR PERVAPORATION PROCESS

Rishabh Verma<sup>\*1</sup> & Prakhar Gupta<sup>2</sup>

### ABSTRACT

Recently, pervaporation as a separation process has been heavily investigated for removal of sulphur containing thiophene and its derivatives from the Fluid Catalytic Cracker (Gasoline) such as Jet Fuel, and a number of membrane materials and modules along with the dependence on varying operation conditions such as temperature and permeate pressure for the separation process have been reported in literature. Scientific papers from most researchers that report experimental data for pervaporation of sulphur impurities from gasoline feeds do not present any mathematical model for the process, which is essential in case of process scale up and commercialization. Hence, the primary objective here is to establish the 'Pore Flow' model of pervaporation as the primary mathematical model for the separation process of sulphur impurities from gasoline via pervaporation, and show that the popular 'Solution Diffusion' model actually fails in many cases with respect to the same process parameters and operating conditions..

**Keywords:** Pervaporation; Mathematical Modelling; Parameter Estimation; Solution Diffusion; Pore Flow.

### 1. INTRODUCTION

Pervaporation currently is one of the many upcoming technologies in the field of membrane separation processes, especially as an efficient liquid-liquid separation process at the molecular scale. This process is considered as an alternative to many conventional processes as it involves two of the most popular technologies on the field of separation – Permeation and Evaporation, and is known to enhance/enrich trace components with great proficiency. Hence, Pervaporation has huge application in areas where product mixtures must fulfil high purity requirements but where one cannot suffer on reduced capacity of continuous production or areas where there is need for new analytical tools to perform advanced level of research, for example the Petrochemical industry, Pharmaceutical Industry or Bio-refineries.

Recently, pervaporation has been heavily investigated for removal of sulphur and its derivatives from the Fluid Catalytic Cracker (Gasoline) such as Jet Fuel, and a number of membrane materials and modules along with the dependence on varying operation conditions such as temperature and permeate pressure for the separation process have been reported in literature. The results obtained have mostly been positive as far as fluxes or enrichment factors in the permeate are concerned, implying that pervaporation as a process has received success on the lab scale. However, from a pilot or commercial scale, there exists a need for establishing a robust and sophisticated mathematical model for the pervaporation of these components, as it is essential for calculating scale-up criteria or commercialization parameters which can then be applied to the wide range of applications this process possesses.

Scientific papers from most researchers that report experimental data for pervaporation of sulphur impurities from gasoline feeds do not present any mathematical model for the process. Some papers do try and fit the popular 'Solution Diffusion' model onto their experimental results, but this model fails for most cases, as will also be demonstrated here. Another model that exists but has been rarely used is the 'Pore Flow' model, but contrary to popular belief, this model actually fits most of the experimental data presented in literature owing to the fundamental concepts used in the construction of the model which seem to suit the process of pervaporation more. Hence, the primary objective here is to establish the 'Pore Flow' model of pervaporation as the primary mathematical model for the separation process of sulphur impurities from gasoline via pervaporation, and show that the popular 'Solution Diffusion' model actually fails in many cases with respect to the same process parameters and operating conditions.

### 2. LITERATURE REVIEW

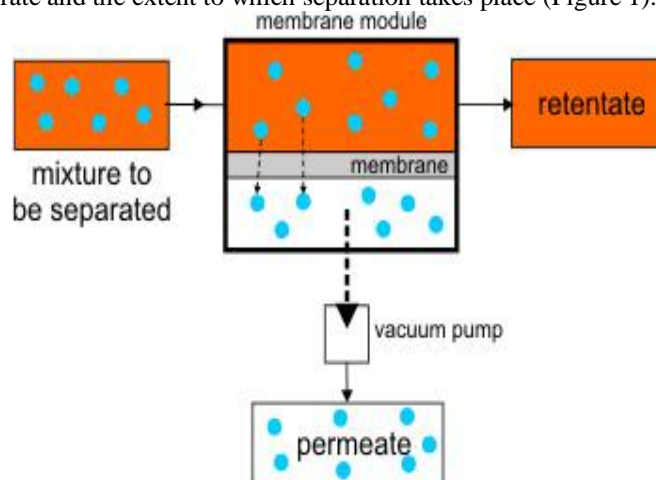
In the following section, an in-depth analysis will be carried out for the process of pervaporation, including basic principles and concepts involved followed by a discussion on the two mathematical models (Solution Diffusion Model and Pore Flow Model), their leading assumptions and propositions, derivations of mathematical equations along with physical interpretations of the proposed model theories.



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### Pervaporation

Pervaporation as a technology is the combination of two of the most popular separation processes present in the industry – Permeation and Evaporation. Accordingly, it is a two-step separation process, the first being permeation of the desired component through a dense non-porous polymeric or inorganic membrane that selectively adsorbs that component from the feed, which is in direct contact with one side of the membrane, and transports it to the permeate, causing enrichment of the component from feed to permeate. The second step of the pervaporation process is the evaporation or partial vaporization and the subsequent removal of the permeate from the opposite side of the membrane into its vapour phase, which is then condensed. This step generally requires an external source of energy such as a vacuum pump, but it is essential for the process as it is responsible for enhancing the driving force (chemical potential difference) for the component being separated, and hence improves the rate and the extent to which separation takes place (Figure 1).



*Figure 1: A schematic diagram for pervaporation process*

Pervaporation is in a sense a very unique process as it uses the liquid-vapour equilibrium to facilitate separation via membranes. The membrane here acts as a selective barrier between the liquid phase feed and the vapour phase permeate, and separation occurs via difference in the rate of permeation of individual components through the pervaporation membrane. Thus, even though evaporation is a critical step in the process of pervaporation, separation results from difference in polarity of individual components and not because of difference in volatility. This feature of pervaporation differentiates it from conventional separation processes such as column distillation.

As far as the origin is concerned, this process was first observed in 1917 by Kober, followed by Binning in 1956 who established the basic concepts, principles and future potential of pervaporation. Later in the 1980's, a breakthrough in the field of pervaporation was achieved by Gesellschaft für Trenntechnik in Germany when he developed a series of PVA-PAN composite membranes for alcohol-water azeotrope separation. This was a revolution and since then over 100 industrial pervaporation units have been installed world-wide, along with a number of patents about pervaporation.

There are numerous advantages of using pervaporation as a technique for separating mixtures. As discussed above, it strikes a contrast between itself and distillation in the basic principle of separation, i.e. separation based on membrane selectivity instead of volatility, although other features remain similar for these processes, such as both methods offer high degrees of separation. Also, the property of separation based on membrane selectivity allows pervaporation to separate azeotropic mixtures where concentrations of desired product is similar in both liquid and vapour phases, something that cannot be achieved by distillation. Moreover, pervaporation experiments need significantly lower energy requirements and capital costs as compared to distillation. It is a very compact technique, can be used flexibly and offers simplicity. Apart from that, the technique of pervaporation is a clean technology as it avoids any sort of cross-contamination. Thus, pervaporation has all characteristics of a distillation column except for its disadvantages, and scientists have made efforts to directly apply pervaporation for a wide range of liquid-liquid separation applications.



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Other advantages of pervaporation include separation of heat sensitive products such as in food industries, as the process can be carried out at low temperatures. One beneficial implication of the property of selective adsorption of the pervaporation membrane is that it can pick up components that are present in trace quantities from the feed stream and provide a significant enrichment to form higher concentration permeate so as to extract that component. This can also be used for detection and elimination of trace impurities and pollutants that are difficult to detect but turn out to be harmful for the respective process involved. Another application of pervaporation is in the essential drying of natural gas that is obtained off-shore.

Another application of pervaporation is the removal/separation of sulphur impurities from petroleum derived fluid mixtures such as FCC/Gasoline. Sulphur compounds, in general, that are present in petroleum products such as transportation fuels have imposed great environmental and health concerns in the recent past. The increased awareness on such matters has led to many governing bodies such as the Environmental Protection Agency (EPA) to enforce stringent laws that reduce the acceptable limits on sulphur content in fuels, so as to reduce the negative effects of sulphur containing pollutants throughout. However, meeting such strict laws, though mandatory for the environment, is a challenge for refineries as there has been a saturation on the performance of conventional techniques, and any changes would not be beneficial from an economical point of view. Scientists have hence looked at alternate methods to tackle such problems, and are working continuously to build a permanent and efficient solution that is cost-effective in the long run.

Gasoline is a mixture of straight run naphtha, reformat naphtha and FCC naphtha based on the method of refining used. Among these, FCC Naphtha contributes about 90% of the total sulphur content. Sulphur is present in the mixture in the form of sulphides, disulphides and Thiophene derivatives, the latter forming the majority proportion. Presently, many processes are used to eliminate these impurities from the gasoline stream, and are based on principles of catalysis and/or chemical adsorption. However, these methods are found to reduce the octave number of the gasoline and hence an alternative is Pervaporation, as it uses non-reactive separation techniques that do not affect the octane number. Hence, the major focus of this paper from now onwards would be to look at one specific application of pervaporation, which is removal of sulphur impurities in the form of "Thiophene" derivatives present in petroleum, or more specifically gasoline.

In the subsequent sections, a study about various mathematical models, also known as membrane transport models, that have been used for the process of pervaporation in the past will be carried out, viz. Solution Diffusion Model and Pore Flow Model, followed by a comparative analysis for the same.

### Solid Diffusion Model

The Solution Diffusion Mechanism is used widely as a membrane transport model for predicting characteristics and parameters for the separation process that occurs, such as fluxes. The solution diffusion model proposes a theory for the mass transfer that takes place during the process of pervaporation, also known as the Solution

Diffusion Mechanism. The mechanism can be broken down into three different steps:

1. Sorption of the permeant (desired component) from feed liquid to the membrane
2. Diffusion of the adsorbed permeant inside the membrane
3. Desorption of the permeant on the other side from the membrane, in vapor phase.

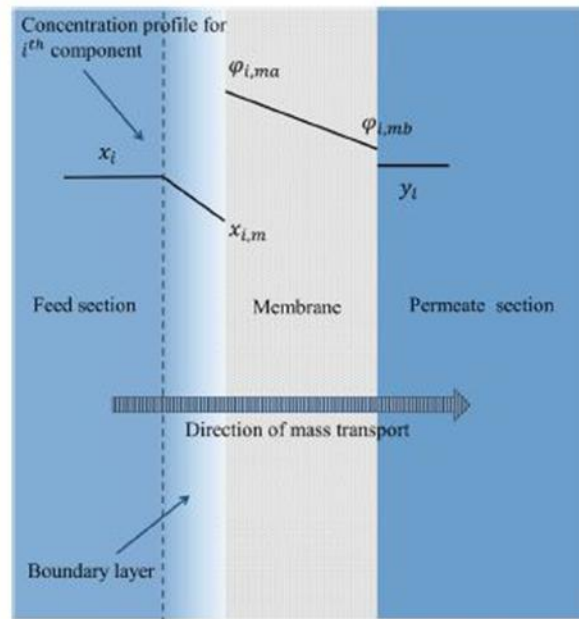


Figure 2: Characteristic Demonstration of the Solution Diffusion Model

The corresponding concentration profiles have also been shown in the figure above (Figure 2). The mathematical aspects of this model are derived from mass transfer equations given by Fick’s laws of diffusion, wherein the driving force for mass transport is equal to the concentration gradient and flux inside the membrane is proportional to this driving force.

Hence, for a component “i” having chemical potential “ $\mu_i$ ” and which is permeating through the membrane along x direction, the flux  $J_i$  is given by:

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

Now some important assumptions are made in order to solve this equation. The first major assumption is that the total pressure is uniform throughout the membrane. This implies that chemical potential depends only on the concentration profile (as change in pressure = 0). Secondly, it is assumed that the potential gradient is exactly equal to the concentration gradient, i.e. the binary mixture is considered to be ideal. Other minor assumptions include parameters such as diffusivity as constant with temperature and uniform concentration polarization. Hence, solving the equation for chemical potential after taking in all assumptions, the following equation is obtained:

$$J_i = K_i (x_i \gamma_i P_i^{sat} - y_i P)$$

Where  $K_i$  is the permeability of component i,  $\gamma_i$  is the activity coefficient of component i,  $P_i^{sat}$  is the saturation pressure of component i and P is the total permeate pressure.

The permeability can be written as:

$$K_i = \frac{D_{i,m} S_{i,m}}{\delta}$$

Where  $D_{i,m}$  and  $S_{i,m}$  are the diffusion coefficient inside membrane and  $\delta$  is the membrane thickness involved in permeation process.



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Some observations from looking at the final membrane transport equation are that it considers the membrane pores to have no real impact on the transport flux. Also, the model assumes that the liquid-vapour interface occurs at the permeate end of the membrane, an assumption which may not hold true for most cases. Also, the permeability that is obtained does not incorporate well defined details on the membrane geometry or operating conditions, and diffusivity calculations may not be straightforward, resulting in model complexities.

### Pore Flow Model

The Pore Flow Model advocates a preferential-adsorption capillary flow mechanism, wherein a sharp concentration gradient is said to be present at the membrane polymer – fluid interface, and separation of fluids occurs when this interfacial fluid flows through small pores (capillaries) present in the membrane surface. The feed liquid, hence, enters pores present in the membrane from the feed side, and then evaporates into the vapour phase within the pore. Thus, the vapour liquid interface is present inside the membrane (in the pore), unlike the solution diffusion mechanism which says that this interface can only occur at the membrane end. Thereafter, a vapour transport takes place within the pore and a vapour phase permeate comes out from the other side of the membrane (Figure 3).

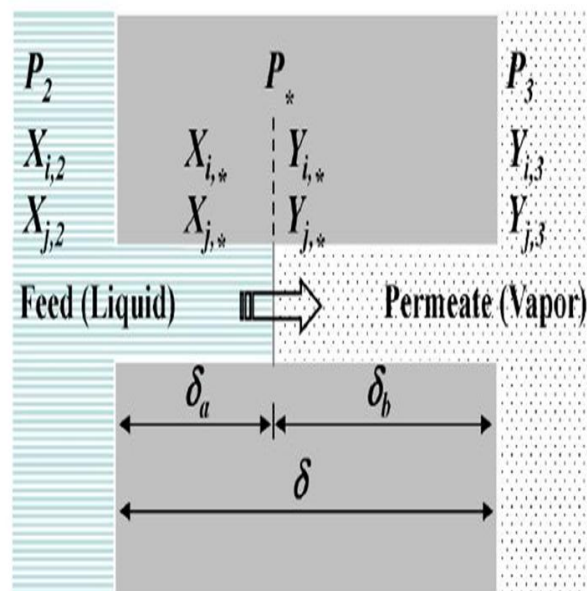


Figure 3: Schematic diagram of a pore according to Pore Flow Mechanism

Within the pore, the following phenomenon takes place, as also evident from the figure:

1. Permeant component from feed transported through the liquid-filled portion of the pore
2. A liquid-to-vapor-phase change takes place inside the pore
3. Permeant transported through the vapor-filled portion of the pore to the permeate

The basic difference between the solution diffusion mechanism and the pore flow mechanism, as discussed above is that no phase change occurs inside the membrane in the former, whereas a clear liquid-vapour boundary must exist in the pore flow model, though this boundary may or may not be present inside the membrane depending on the operating conditions. As there is a boundary present, the transport equations incorporate this accordingly by presenting a change in the phase of the transported substance at the liquid-vapour boundary. A more lucid picture can be obtained from the figure below (Figure 4a,4b).

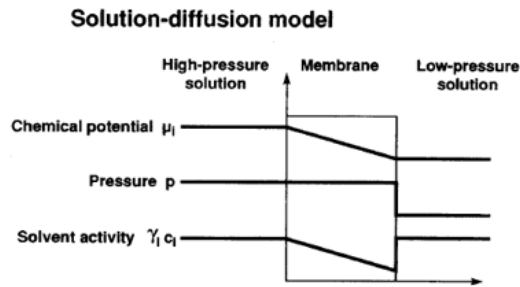


Figure 4a: Diffusion Pore Model

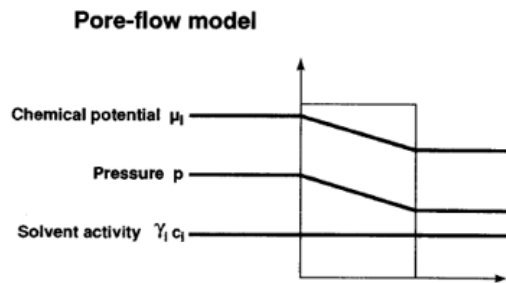


Figure 4b: Pore Diffusion Model

The model development requires some key assumptions. Firstly, it is assumed that the pores in the membrane are cylindrical bundles of uniform length, and penetrate the entire length of the membrane. Secondly, the pore length is present at isothermal conditions. Also, evaporation takes place at the phase boundary, hence the pressure at that location is equal to the saturation pressure. Lastly, the solute and solvent concentrations are uniform throughout the membrane, and hence the driving force for the transport is due to the pressure difference.

Now, the model proposes two different scenarios based on the pressure difference owing to the operating conditions:

**$P_3$  (Permeate Pressure) <  $P_*$  (Saturation Pressure at given temperature)**

In this state, the phenomena described above, i.e. the existence of a clear phase boundary inside the pore, is fulfilled, as the pressure gradient from feed to permeate favours transport in the correct direction.

**$P_3$  (Permeate Pressure)  $\geq P_*$  (Saturation Pressure)**

Whenever this is valid, the phase boundary cannot be observed inside the pore but at the end, and hence the driving force in this case is given by overall pressure drop.

In the first case, the liquid phase transport is given by Darcy's equation:

$$Q_{liq} = \frac{k\rho N_t}{\eta M \delta_a} (P_2 - P_*) = \frac{A}{\delta_a} (P_2 - P_*)$$

For determining the equation for vapour transport, a major assumption is required that flow of vapour is mostly due to the vapour molecules that are adsorbed to the membrane walls, i.e. the pore size is so small that any vapour molecules that are present in the bulk and are not influenced by membrane adsorption can be neglected. Thus, one major drawback of the pore flow model is that it cannot be applied to systems where Knudsen flow has a significant contribution. Thus, if this condition on the pore size is fulfilled, the surface flow model defined by Gilliland can be used without having the need to superimpose any other gas transport mechanisms.



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$$Q_{vap} = \int_{P_3}^{P_*} \frac{x^2}{P} dP$$

Henry's Law is given by:

$$x = k_H P$$

Hence using Henry's equation and assuming a monolayer adsorption, the following equation is obtained:

$$\begin{aligned} Q_{vap} &= \frac{\pi(2rt - t^2)^2 t N_t RT}{4r\delta_b \mu} (k_H'^2) \left(\frac{P_* + P_3}{2}\right) (P_* - P_3) \\ &= \frac{B}{\delta_b} (P_*^2 - P_3^2) \end{aligned}$$

Thus, the flux in the vapour phase here is thus a function of difference of the squares of upstream pressure (saturation pressure) and downstream pressure (permeate pressure). It can be noted here that the adsorption might be a multi-layer one, and other laws such as Langmuir or Freundlich might be more suitable instead of Henry's law, but these are taken so as to keep the mathematics simple.

Now, as  $\delta = \delta_a + \delta_b$

The final equation for flux can be expressed as:

$$Q_{total} = \frac{A}{\delta} (P_2 - P_*) + \frac{B}{\delta} (P_*^2 - P_3^2)$$

For the case where saturation pressure is lesser than the permeate pressure, the flux equation can be directly written as:

$$Q_{total} = \frac{A}{\delta} (P_2 - P_3)$$

As can be seen from the derived equations and model propositions, the pore flow mechanism seems to be more coherent with the principles of pervaporation, especially because it breaks the model into two separate parts based on practical operating conditions, and includes the case where there is a possible vapour transport involved. However, this is just a theoretical intuition and must be proven with the help of experimental data.

### 3. RESULTS AND DISCUSSIONS

To obtain a comparison between the two models, the methodology is to first obtain experimental data on pervaporation of Thiophene derivatives, something that is reported in a number of research or scientific papers. Thereafter, the data would be used to calculate other required parameters present in the model equations. Some of these might be given directly (such as feed and permeate pressures, temperature, concentrations etc.) whereas others need to be calculated (saturation pressure at the specified temperatures).

Calculation of saturation pressure is done via Antoine Equation:

$$\log(p^*) = A - \frac{B}{T + C}$$

So as to keep the mathematics involved simple, only those sets of data are chosen that involve two-component mixture pervaporation, i.e. binary mixtures. The regression is linear and performed on a single parameter, and hence carried out in MS-Excel using "Linest" module.



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### Solution Diffusion Modelling

The solution diffusion model is first chosen for model fitting. The model equation, as described before, is as follows:

$$J_i = K_i (x_i \gamma_i P_i^{\text{sat}} - y_i P)$$

For simplicity, the binary mixture is considered to be an ideal mixture, thus all activity coefficients equal unity. Secondly, the feed temperature is used to determine the saturation pressures, and the feed and permeate pressure are taken to be constant throughout the duration of the experiment. Also, the expression for enrichment factor (used in many papers) is given by:

$$\text{Enrichment (E)} = \frac{y_i}{x_i}$$

Thus, the final model equation so obtained is:

$$J_i = K_i x_i (P_i^{\text{sat}} - E^* P) = K_i * (\text{Driving Force})$$

A plot between  $J_i$  and “Driving Force” should therefore be a straight line with a positive slope that equals the permeability of the membrane system. Following are some experimental data derived from the first scientific paper that have been fitted using the solution diffusion model.

**Table 1: Solution Diffusion Modelling on Paper 1 (6FDA-4MPD 9:1 membrane, batch 1) [7]**

Temp (K)	E	$x_i$	$P^*$ (Pa)	$P_{\text{feed}}$ (Pa)	$P_{\text{permeate}}$ (Pa)	Driving Force
352.8	1.605	0.0025	709.549	101325	2200	-7.054
372.6	2.744	0.0025	1966.27	101325	2200	-10.176
392.4	3.326	0.0025	4761.97	101325	2200	-6.388

**Table 2: Solution Diffusion Modelling on Paper 1 (6FDA-4MPD 9:1 membrane, batch 2) [7]**

Temp (K)	E	$x_i$	$P^*$ (Pa)	$P_{\text{feed}}$ (Pa)	$P_{\text{permeate}}$ (Pa)	Driving Force
352.8	2.128	0.0025	709.549	101325	2200	-9.9301
372.6	2.814	0.0025	1966.271	101325	2200	-10.561
393	3.628	0.0025	4882.441	101325	2200	-7.747

**Table 3: Solution Diffusion Modelling on Paper 1 (6FDA-3MPD 9:1 membrane, batch 1) [7]**

Temp (K)	E	$x_i$	$P^*$ (Pa)	$P_{\text{feed}}$ (Pa)	$P_{\text{permeate}}$ (Pa)	Driving Force
357.2	2.095	0.0025	901.741	101325	2200	-9.268
366	2.41	0.0025	1423.0498	101325	2200	-9.697
375.2	2.915	0.0025	2224.126	101325	2200	-10.472
384.4	3.218	0.0025	3379.554	101325	2200	-9.250
393.6	3.306	0.0025	5005.452	101325	2200	-5.669

**Table 4: Solution Diffusion Modelling on Paper 1 (6FDA-3MPD 9:1 membrane, low pressure) [7]**

Temp (K)	E	$x_i$	$P^*$ (Pa)	$P_{\text{feed}}$ (Pa)	$P_{\text{permeate}}$ (Pa)	Driving Force
372.9	2.909	0.0025	1994.661	101325	2200	-11.0123
383.1	3.187	0.0025	3190.679	101325	2200	-9.552
393	3.305	0.0025	4882.441	101325	2200	-5.971





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**Table 5: Solution Diffusion Modelling on Paper 1 (6FDA-3MPD 9:1 membrane high pressure) [7]**

Temp (K)	E	$x_i$	$P^*$ (Pa)	$P_{feed}$ (Pa)	$P_{permeate}$ (Pa)	Driving Force
372.9	2.503	0.0025	1994.661	101325	2200	-8.779
383.1	2.695	0.0025	3190.679	101325	2200	-6.845
393	2.802	0.0025	4882.441	101325	2200	-3.204

The paper shown above involves pervaporation experiments that separate benzothiophene from n-dodecane feed streams. As evident from all experiments in this paper, the solution diffusion mechanism could not be fitted as the calculations resulted in a negative driving force.

Some papers use selectivity instead of enrichment factors. Selectivity for a binary mixture is defined as:

$$\text{Selectivity } (\beta) = \frac{y_i (1 - x_i)}{x_i (1 - y_i)}$$

The enrichment factor can be easily calculated from this expression as given in the following equation.

$$E = \frac{y_i}{x_i} = \frac{\beta}{1 + (\beta - 1)x_i}$$

Thus, all information can be determined now so as to perform solution diffusion modelling on the next scientific paper.

**Table 6: Solution Diffusion Modelling on Paper 2 (6FDA-4MPD 49:1 membrane, native) [8]**

Temp (K)	B	$x_i$	$P^*$ (Pa)	$P_{feed}$ (Pa)	$P_{permeate}$ (Pa)	Driving Force
353.17	2.265	0.003	724.222	101325	2200	-12.719
363.23	2.372	0.003	1236.638	101325	2200	-11.881
373.01	2.518	0.003	2005.157	101325	2200	-10.527
383.05	2.204	0.003	3183.597	101325	2200	-4.9432

**Table 7: Solution Diffusion Modelling on Paper 2 (6FDA-4MPD 49:1 membrane, hybrid) [8]**

Temp (K)	B	$x_i$	$P^*$ (Pa)	$P_{feed}$ (Pa)	$P_{permeate}$ (Pa)	Driving Force
353.17	2.372	0.003	724.2223	101325	2200	-13.418
363.23	2.281	0.003	1236.638	101325	2200	-11.287
373.01	2.457	0.003	2005.157	101325	2200	-10.130
383.05	2.457	0.003	3183.597	101325	2200	-6.5948

Once again, it is observed that the driving force for the entire experiment stays negative and hence another benzothiophene experiment cannot be modelled using solution diffusion mechanism.

The third paper chosen involves pervaporation of thiophene and 2-methyl thiophene from an n-octane feed, instead of benzothiophene.



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**Table 8: Solution Diffusion Modelling on Paper 3 (Thiophene separation) [9]**

Temp (K)	B	$x_i$	$P^*$ (Pa)	$P_{feed}$ (Pa)	$P_{permeate}$ (Pa)	Driving Force
303.2	4.952		2466.643	101325	5000	-
		0.0036				79.86971223
313.05	4.425		4125.683	101325	5000	-
		0.0036				64.52584776
323.15	4.233		6713.463	101325	5000	-
		0.0036				51.70751861
333.12	4.118		10474.43	101325	5000	-
		0.0036				35.97958451
343.23	3.916		15920.57	101325	5000	-
		0.0036				12.57179809

**Table 9: Solution Diffusion Modelling on Paper 3 (2-methyl thiophene separation) [9]**

Temp (K)	B	$x_i$	$P^*$ (Pa)	$P_{feed}$ (Pa)	$P_{permeate}$ (Pa)	Driving Force
303.2	2.468	0.00463	2466.643	101325	5000	-
						45.3278
313.05	2.446	0.00463	4125.683	101325	5000	-37.146
323.15	2.368	0.00463	6713.463	101325	5000	-23.391
333.12	2.293	0.00463	10474.43	10325	5000	-4.270
343.23	2.259	0.00463	15920.57	101325	5000	21.719

Barring the last case in the second experiment, it is again observed that the solution diffusion model cannot be fitted, even on experiments that involve pervaporation of thiophene or 2-methyl thiophene. Thus, even though results for pore flow model haven't been shown, the popular 'Solution Diffusion' model has faltered in the specific application chosen for almost all papers.

However, the solution diffusion works well for other applications wherein the permeating component is not a sulphur impurity, such as the experiment given in paper 4.

**Table 10: Solution Diffusion Modelling on Paper 4 (9:1 Naphthalene separation) [6]**

Temp (K)	E	$x_i$	$P^*$ (Pa)	$P_{feed}$ (Pa)	$P_{permeate}$ (Pa)	Driving Force
353.33	1.097	0.05	4098.791	101325	1750	108.952
373.45	2.507	0.05	9676.713	101325	1750	264.473
392.95	2.507	0.05	20031.86	101325	1750	782.230
413.65	2.507	0.05	39528.05	101325	1750	1757.04
423.05	2.46	0.05	52388.31	101325	1750	2404.165

**Table 11: Solution Diffusion Modelling on Paper 4 (19:1 Toluene separation) [6]**

Temp (K)	E	$x_i$	$P^*$ (Pa)	$P_{feed}$ (Pa)	$P_{permeate}$ (Pa)	Driving Force
353.33	2.928	0.05	4098.791	101325	1750	-51.260
373.45	2.053	0.05	9676.713	101325	1750	304.198
392.95	1.241	0.05	20031.86	101325	1750	893.005

Thus, the solution diffusion model can be shown to more or less work well for some other applications, but unfortunately it could not be shown to produce results in the topic of interest here, which is the process of pervaporation of sulphur impurities, especially the components that contain thiophene and its derivatives from the respective gasoline streams.



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## Pore Flow Modelling

For the pore flow model, the model equation that was derived was:

$$Q_{total} = k_A(P_2 - P_*) + k_B(P_*^2 - P_3^2)$$

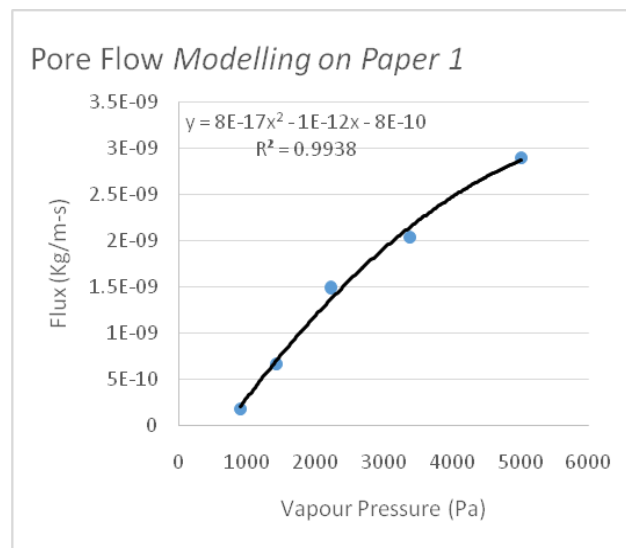
Upon rearranging, the following equation is obtained:

$$Q_{total} = k_B P_*^2 - k_A P_* + (k_A P_2 - k_B P_3^2)$$

Therefore, a plot between the total flux  $Q_{total}$  and Saturation Pressure  $P_*$  should be a quadratic plot. Care must be taken that the saturation pressure is higher than the permeate pressure, otherwise the model equation is not valid.

**Table 12: Pore Flow Modelling on Paper 1 (6FDA-3MPD 9:1 membrane, batch 1) [7]**

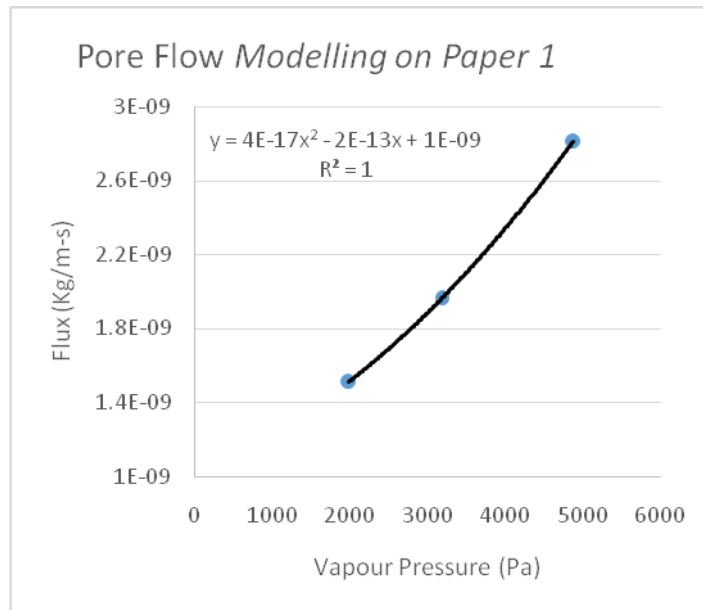
Temp (K)	Flux (Kg/m-s)	P* (Pa)	P <sub>feed</sub> (Pa)	P <sub>permeate</sub> (Pa)
357.2	1.82861E-10	901.741	101325	2200
366	6.70556E-10	1423.049	101325	2200
375.2	1.49333E-09	2224.126	101325	2200
384.4	2.04194E-09	3379.554	101325	2200
393.6	2.89444E-09	5005.452	101325	2200



**Figure 5: Pore Flow Modelling on Paper 1 (6FDA-3MPD 9:1 membrane, batch 1) [7]**

**Table 13: Pore Flow Modelling on Paper 1 (6FDA-3MPD 9:1 membrane, low pressure) [7]**

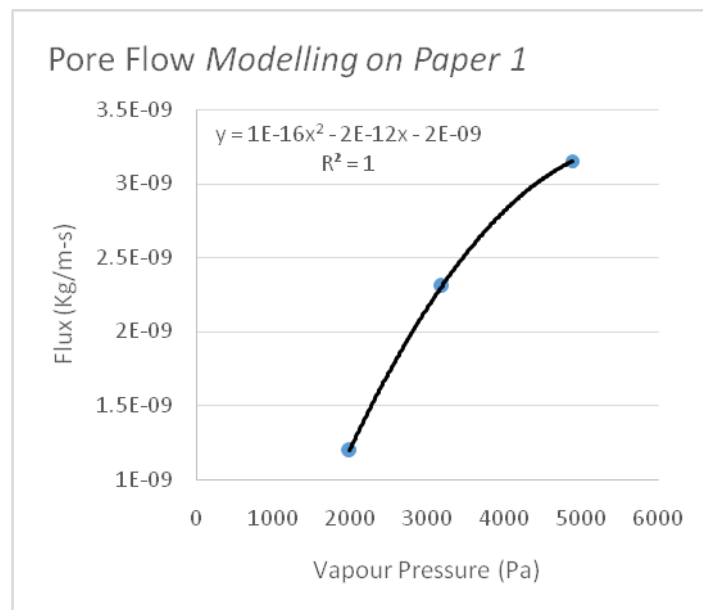
Temp (K)	Flux (Kg/m-s)	P* (Pa)	P <sub>feed</sub> (Pa)	P <sub>permeate</sub> (Pa)
372.9	1.51E-09	1994.661	101325	2200
383.1	1.96028E-09	3190.679	101325	2200
393	2.80833E-09	4882.441	101325	2200



**Figure 6:** Pore Flow Modelling on Paper 1 (6FDA-3MPD 9:1 membrane, low pressure) [7]

**Table 14:** Pore Flow Modelling on Paper 1 (6FDA-3MPD 9:1 membrane, high pressure) [7]

Temp (K)	Flux (Kg/m-s)	P* (Pa)	P <sub>feed</sub> (Pa)	P <sub>permeate</sub> (Pa)
372.9	1.19222E-09	1994.661	101325	4200
383.1	2.30472E-09	3190.679	101325	4200
393	3.15278E-09	4882.441	101325	4200



**Figure 7:** Pore Flow Modelling on Paper 1 (6FDA-3MPD 9:1 membrane, high pressure) [7]



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As can be seen from all regression plots of flux v/s vapour pressure in paper 1, the pore flow model fits very well in a quadratic fit.

The parameters obtained from each of these based on the model equations are:

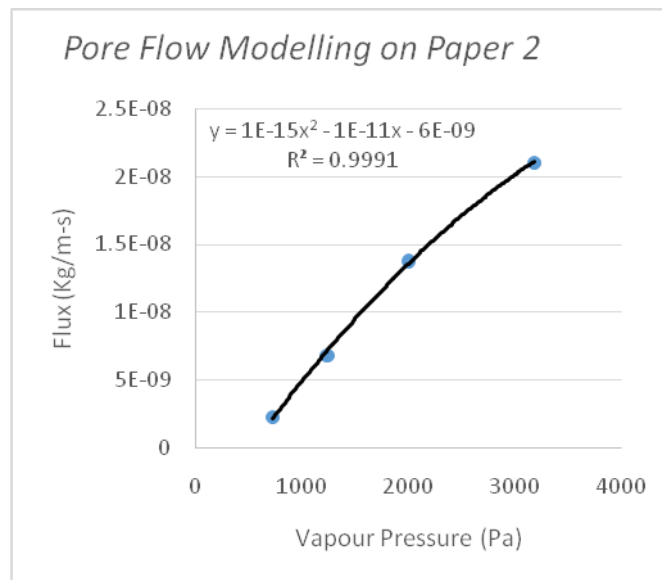
**Table 15: Pore Flow Modelling – Parameters in Paper 1 [7]**

Regression Figure	$K_A$ (Kg/m-s-Pa)	$K_B$ (Kg/m-s-Pa <sup>2</sup> )
5	1.13599E-12	8.23819E-17
6	1.52379E-13	4.32182E-17
7	1.70028E-12	1.48517E-16

The analysis is now done for paper 2 to check for results.

**Table 16: Pore Flow Modelling on Paper 2 (6FDA-4MPD 49:1 membrane, native) [8]**

Temp (K)	Flux (Kg/m-s)	$P^*$ (Pa)	$P_{feed}$ (Pa)	$P_{permeate}$ (Pa)
353.17	2.29583E-09	724.222	101325	2450
363.23	6.80278E-09	1236.638	101325	2450
373.01	1.3775E-08	2005.157	101325	2450
383.05	2.10028E-08	3183.596	101325	2450



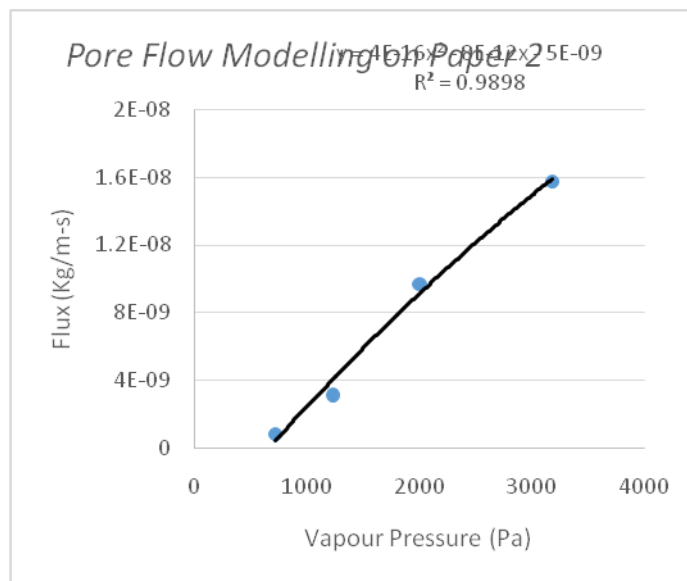
**Figure 8: Pore Flow Modelling on Paper 2 (6FDA-4MPD 49:1 membrane, native) [8]**



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**Table 17: Pore Flow Modelling on Paper 2(6FDA-4MPD 49:1 membrane, hybrid) [8]**

Temp (K)	Flux (Kg/m-s)	P* (Pa)	P <sub>feed</sub> (Pa)	P <sub>permeate</sub> (Pa)
353.17	8.50278E-10	724.2223469	101325	2450
363.23	3.14722E-09	1236.637801	101325	2450
373.01	9.69444E-09	2005.1574	101325	2450
383.05	1.57306E-08	3183.596937	101325	2450



**Figure 9: Pore Flow Modelling on Paper 2(6FDA-4MPD 49:1 membrane, native) [8]**

Hence, a positive result has been achieved again from the second paper. The parameter values are given below:

**Table 18: Pore Flow Modelling – Parameters in Paper 2 [8]**

Regression Figure	K <sub>A</sub> (Kg/m-s-Pa)	K <sub>B</sub> (Kg/m-s-Pa <sup>2</sup> )
8	1.17621E-11	1.04309E-15
9	7.92E-12	4.2145E-16

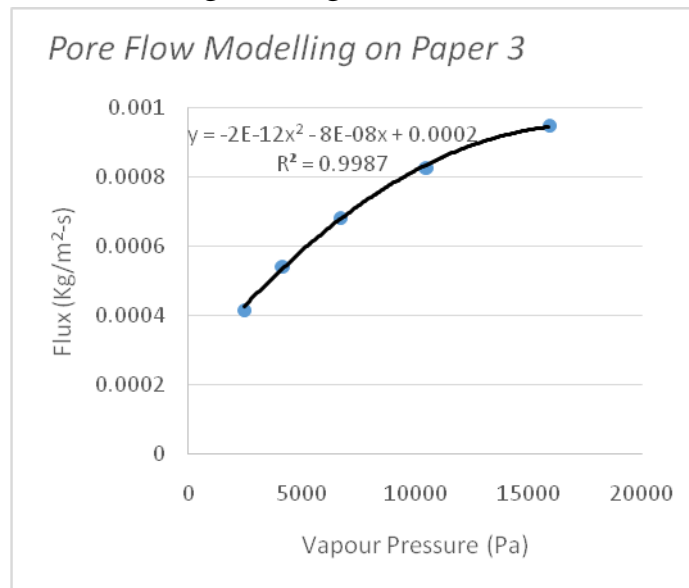
The third paper will now be considered for analysis.

**Table 19: Pore Flow Modelling on Paper 3 (Thiophene separation) [9]**

Temp (K)	Flux (Kg/m <sup>2</sup> -s)	P* (Pa)	P <sub>feed</sub> (Pa)	P <sub>permeate</sub> (Pa)
303.2	0.000416	2466.643	101325	5000
313.05	0.000541	4125.683	101325	5000
323.15	0.000682	6713.462	101325	5000
333.12	0.000825	10474.434	101325	5000
343.23	0.000947	15920.565	101325	5000



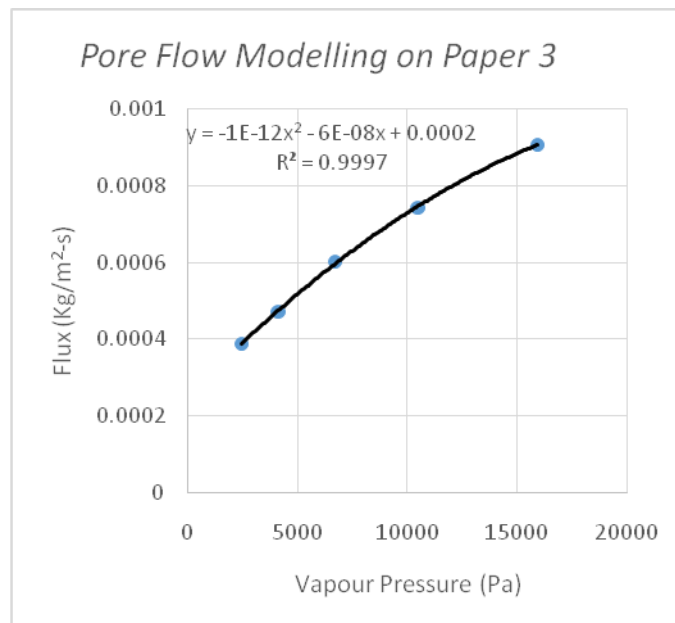
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**Figure 10:** Pore Flow Modelling on Paper 3 (Thiophene separation) [9]

**Table 20:** Pore Flow Modelling on Paper 3 (2-methyl thiophene separation) [9]

Temp (K)	Flux (Kg/m <sup>2</sup> -s)	P* (Pa)	P <sub>feed</sub> (Pa)	P <sub>permeate</sub> (Pa)
303.2	0.000389	2466.643	101325	5000
313.05	0.000472	4125.683	101325	5000
323.15	0.000601	6713.462	101325	5000
333.12	0.000742	10474.434	101325	5000
343.23	0.00091	15920.565	101325	5000



**Figure 11:** Pore Flow Modelling on Paper 3 (2-methyl thiophene separation) [9]

As observed in this case, the model fits a quadratic equation, but with a negative coefficient, implying that one of the permeability's in this case is negative.



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**Table 21: Pore Flow Modelling – Parameters in Paper 3 [9]**

Regression Figure	$K_A$ (Kg/m <sup>2</sup> -s- Pa)	$K_B$ (Kg/m <sup>2</sup> -s- Pa <sup>2</sup> )
10	8.07027E-08	-2.28454E-12
11	5.9155E-08	-1.13331E-12

Also, as the reported fluxes are higher in this particular paper, the permeability orders are higher than those observed previously.

### 4. CONCLUSION

The major objective of this paper was to analyse the mathematical models that are currently present in the literature for pervaporation process, viz. Solution Diffusion and Pore Flow, specifically with respect to the use of pervaporation to separate sulphur containing impurities such as thiophene and its derivatives from their respective feed stream consisting of FCC/ Gasoline.

As far as the solution diffusion model is concerned, the model could not even predict a positive driving force for the application specific process, even though good amounts of fluxes have been reported experimentally. This implies that the use of Solution Diffusion model should be avoided when engineering the process of pervaporation, especially when the process involves removal of sulphur impurities.

On the other hand, the pore flow model has shown much better results in terms of model fitting and parameter estimation. The parameters obtained have been observed to be consistent, and regression coefficients are also suitable for concluding that the model equations fit well, barring one paper wherein one of the parameters came out to be negative. One disadvantage in this method was the lack of data within a single experiment, something that could have allowed for better result predictability, especially when quadratic equation fitting is carried out.

Nevertheless, it can be concluded that with the given data analysis that the pore flow model seems to be a more accurate and robust mathematical model as compared to the solution diffusion model as far as model assumptions, predictions, model equations, parameter estimations and results are concerned.

### 5. FUTURE SCOPE

The next step in this project would be provide theoretical proof for all model parameters determined after fitting the model equations on experimental data. This step, if successful, would allow for ultimate establishment of the Pore Flow Model with respect to the given application of separating thiophene and its derivatives from gasoline feed streams.

Also, another future strategy is to actually carry out a sensitivity analysis for the obtained parameters, i.e. the dependence of permeabilities obtained on various operational parameters such as temperature and pressure, along with the effect of change in membrane characteristics such as geometric measures of the membrane, type of module used, loading fraction of additives or cross-linking agents etc.

### REFERENCES

1. Manish Jain, Dinesh Attarde, Sharad Kumar Gupta, *Journal of Membrane Science* 490 (2015) 328–345 – Removal of thiophene from n-heptane/thiophene mixtures by spiral wound pervaporation module: Modelling, validation and influence of operating conditions.
2. J.G. Wijmans, R.W. Baker, *Journal of Membrane Science* 107 (1995) 1-21 – The solution-diffusion model: a review.
3. Lan Ying Jiang, Yan Wang, Tai-Shung Chung, Xiang Yi Qiao, Jun-Yih Lai, *Progress in Polymer Science* 34 (2009) 1135–1160 – Polyimides membranes for pervaporation and biofuels separation.
4. Tomoyuki Okada and Takeshi Matsuura, *Journal of Membrane Science*, 59 (1991) 133-150 – A new transport model for pervaporation.
5. PanuSukitpaneenit, Tai-Shung Chung, Lan Ying Jiang *Journal of Membrane Science* 362 (2010) 393–406 – Modified pore-flow model for pervaporation mass transport in PVDF hollow fiber membranes for ethanol–water separation.





## International Journal of Engineering Researches and Management Studies

6. D. Katarzynski, C. Staudt, *Journal of Membrane Science* 348 (2010) 84–90 – Temperature-dependent separation of naphthalene/n-decane mixtures using 6FDA–DABA-copolyimide membranes.
7. I. Bettermann, C. Staudt, *Journal of Membrane Science* 343 (2009) 119–127 – Desulphurization of kerosene: Pervaporation of benzothiophene/n-dodecane mixtures.
8. Roman Konietzny, ToenjesKoschine, Klaus Rätzke, Claudia Staudt, *Separation and Purification Technology* 123 (2014) 175–182 – POSS-hybrid membranes for the removal of sulphur aromatics by pervaporation.
9. Rongbin Qi, Changwei Zhao, Jiding Li, Yujun Wang, Shenlin Zhu, *Journal of Membrane Science* 269 (2006) 94–100 – Removal of thiophenes from n-octane/thiophene mixtures by pervaporation.
10. Rongbin Qi, Yujun Wang, Jiding Li, Changwei Zhao, Shenlin Zhu, *Journal of Membrane Science* 280 (2006) 545–552 – Pervaporation separation of alkane/thiophene mixtures with PDMS membrane