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DEVELOPMENT OF METHYL CELLULOSE AND CARBOXYMETHYL CELLULOSE COMPOSITE MEMBRANES FOR THE SEPARATION OF MISCIBLE LIQUIDS BY APPLYING PERVAPORATION TECHNIQUE

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Abstract: For the first time pervaporation separation of miscible liquids has been investigated using three and five layered composite membranes. The materials used to construct the different membranes consisted of natural rubber latex (NRL), hydrophilic and/ or hydrophobic polymers, placed sequentially on top of each other. Methyl cellulose (MC) and carboxymethyl cellulose (CMC) were used as hydrophilic polymers to increase the water selectivity of the membrane and in contrast, ultra-high molecular weight polyethylene (UHMWPE) was used to increase the organic component selectivity in the membranes. Two different miscible liquid solutions were used, including ethanol-water and acetone-water. The composition of organic component in the feed was varied within the range of 20 to 90% w/w. The measured mass and concentration of permeate in the cold trap was related to the pervaporation flux and separation factor. Finally, the proposed mechanisms that may be responsible for enhancing the permeation of water or organic components through the membranes have been discussed. It has been demonstrated that the five layered hydrophilic composite membranes containing MC leads to the best pervaporation separation performance for a feed of 90% concentrated ethanol-water, giving a separation factor of 51 and pervaporation separation index of 6167, as opposed to using a blended membrane which would yield a separation factor of 1.5 and pervaporation separation index of 309.

1. Introduction:

Liquid separation by thermal processes has always been highly energy intensive and new separation processes taking advantage of chemical bonding coupled with mass transfer through dense membrane have already shown to be very efficient in energy savings as compared to more classic technologies such as distillation. Amongst these processes, Pervaporation (PV) is very promising (Jonquieres et al. 2002) and in addition to its interesting energetic aspects (Sander and Soukup, 1988), it is becoming a key technology for replacing azeotropic separation and the recovery of (high added value) dilute species (Aptel et al. 1976) from water (Beaumelle et. al 1993). It can also be

considered as so called ‘clean technology’ (Márki, et. al 2001), especially well suited for the treatment and recycling of volatile organic compounds and pollution prevention, (Linke and Kokossis, 2004). Pervaporation is a membrane technique which is used to separate a liquid mixture by vacuum vaporization through a nonporous perm-selective membrane (Neel, 1995). The “feed” mixture is allowed to flow along one side of the membrane and a fraction of it (the “permeate”) is evolved in the vapour state from the opposite side, which is kept under vacuum (Neel, 1991) and (Li et. al. 2006) by continuous pumping or is purged with a stream of carrier gas. The permeate is finally collected in the liquid state after condensation on a cooled wall. It is thus

enriched in the more rapidly permeating (“faster”) component of the feed mixture whereas the retentate is depleted in this component; the “retentate” is the fraction of the feed that does not permeate through the membrane.

In pervaporation the driving force for the transport of matter through the membrane is a gradient in the chemical potential which can be described by a gradient in partial vapour pressure of the components. The separation is governed by the physical-chemical affinity between the membrane material and the species to pass through and thus by sorption and solubility phenomena (Schaezel-1 et al. 2001). The transport through the membrane is affected by diffusion and the differences in the diffusivities of the different components in the membrane are important for the separation efficiency, too (Schaezel-2 et al., 2001). Transport through the membrane can best be described by a so-called “Solution-Diffusion-Mechanism” (Lee, 1975) and (Mulder and Smolders, 1984). In this mechanism it is assumed that a component of the feed having a high affinity to the

membrane is easily and preferentially adsorbed and dissolved in the membrane substance, Figure 1. The better soluble a component is the more matter is dissolved in the membrane and the more the membrane will swell and change its composition.

Following a concentration gradient, $C_{i \text{ Feed}}$ (concentration of component i in the feed) and $C_{i \text{ Permeate}}$ (concentration of component i in the permeate), the components migrates through the membrane by a diffusion process and are desorbed at the downstream side of the membrane into a vapour phase. In pervaporation the components passing through the membrane are absorbed in a liquid phase but desorbed into a vapour phase, as the permeate side partial vapour pressures are maintained below the respective saturation values existing on the feed side. Substances with lower or no solubility in the membrane material can not be dissolved or reach only low concentrations and thus low transport rates. As the diffusion coefficients of small molecules in polymeric matrix do not differ too much, the separation characteristics of the membrane is primarily governed by the different solubilities of the components in the membrane material and to a lesser extend by their diffusion rates. When a smaller molecule is better dissolved in the membrane substance solubility and diffusion enhance each other. This is at least the case in dehydration processes where water is both the better soluble and faster diffusing component.

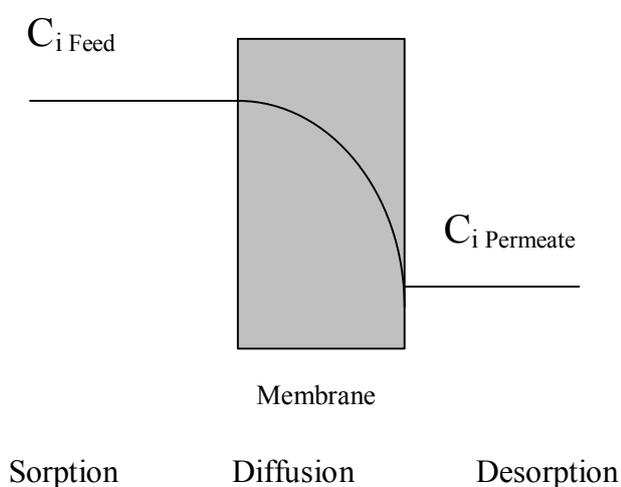


Figure 1: Solution diffusion mechanism

2. Experimental details:

The one layer membrane was made of only natural rubber latex (NRL). To develop the blend membranes and three or five layered composite membranes prevulcanised NRL was used as the base for all the membranes.

NRL solution used in this project was obtained from Revertex and all the hydrophilic and hydrophobic polymers were supplied by Sigma-Aldrich Ltd.

The membranes used were developed in two different possibilities one was a blend of NRL and hydrophilic polymers and the second possibility was composite membranes with three or five layers of polymers (hydrophilic or hydrophobic polymers) and NRL on top of each other. In the three and five layered composite membranes NRL layer was chosen to be the top layer (in direct contact with the miscible mixtures) because of its chemical resistance and stability toward aqueous alcoholic solutions. In the case of using the polymers as the top layer there was this possibility of being washed out by the liquid mixture. NRL was blended or layered in composite membranes with Methyl Cellulose (MC) and Carboxymethyl Cellulose (CMC) to develop hydrophilic membranes.

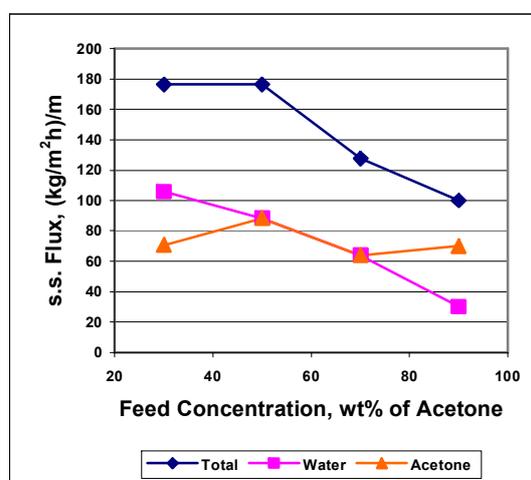
New natural rubber latex (NRL) based membranes were used for the first time by Bhasi (1995). It has been reported that NRL could be used to separate ethanol water mixtures into their constituent parts. It was also reported that good water permselectivity and reasonable permeation rate could be obtained by using fully cross-linked NRL membrane(s). However a novel type of composite membrane with NRL base was developed by Malhotra (2004) to separate water from ethanol-water solutions. The Pulfrich refractometer was used for the analysis of the feed and permeate samples. The refractive indexes of each feed sample and permeate sample were measured.

3. Results and Discussion:

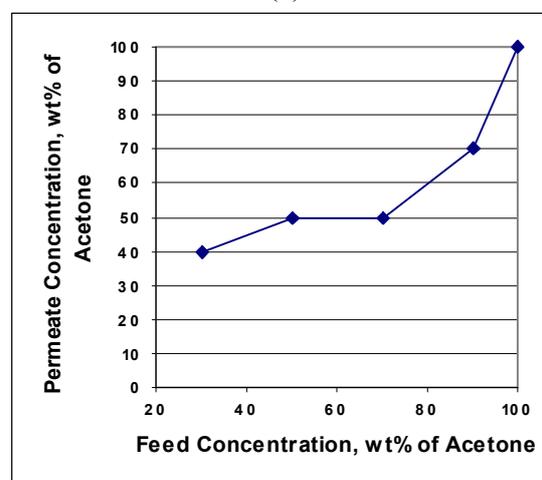
3.1. Performance of NRL membranes:

The influence of feed concentration on steady state flux, permeate concentration, separation factor and pervaporation separation index for NRL membranes are plotted in Figures 2(a) to 2(d).

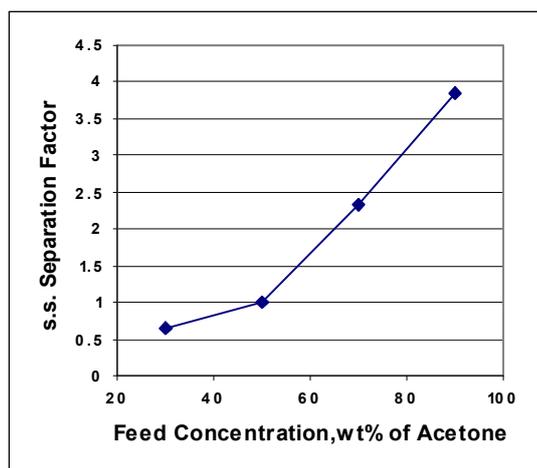
The increase in permeation rate of acetone with an increase in the content of acetone in the feed solution may be attributed to the dominant hydrophobic nature of NRL membrane.



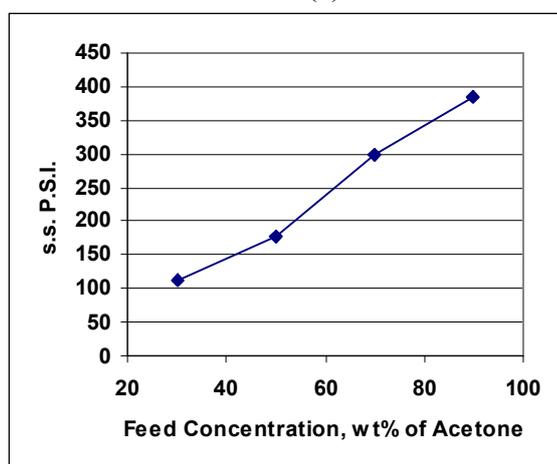
(a)



(b)



(c)



(d)

Figure 2: Influence of feed concentration on steady state flux (a), permeate concentration (b), separation factor (c) and pervaporation separation index (d) for NRL membranes

This hydrophobic nature may lead to an increase in the solubility of acetone in a NRL membrane as acetone content in the feed is increased. Hence, a membrane becomes plasticised with sorbed acetone. Thus, the diffusivity of acetone molecules may be assisted by NRL membrane. The graph in Figure 2 (c) demonstrates that the perm-selectivity of the NRL membrane changed from acetone to water on and above 55% w/w of acetone in the feed solution.

Therefore, a NRL membrane can be used as a water selective membrane at high feed concentration of alcohol. But the water selectivity seems to be too low for any practical commercial use.

3.2. Performance of blend and composite membranes:

Blend membranes and three or five layered composite membranes were used to separate water from ethanol-water solutions. Here the results have been examined to find out which type of membrane showed better pervaporation separation performance. MC and CMC were used in all types of the membranes. Therefore, their results have been investigated individually.

3.2.1. Methyl Cellulose (MC):

The results of pervaporation tests to separate water from ethanol-water solutions by using blend membranes and composite membranes (three or five layers) which contained hydrophilic polymer of MC are presented in Figure 3. Comparison of these results in Figure 3 shows that in 70% w/w of ethanol in the feed the separation factors for blended membrane, composite membranes with three and five layers were 1.556, 5.444 and 31 respectively and their pervaporation separation index were 309.476, 229.372 and 3622.257 respectively. It means composite membranes with five layers showed better pervaporation separation performance in comparison with the blended and composite membrane with three layers. Also it can be said that even composite membranes with three layers showed better selectivity in comparison with the blend membranes and the reason for having less pervaporation separation index is the difference in their thickness, composite membrane with three layers and blend membrane have 0.748 mm

and 0.167 mm thickness respectively, so blend membrane showed higher permeability.

Higher quantity of MC in the composite membranes with five layers was the reason for higher presence of hydration centres and hydrophilic channels in the membrane and this causes higher water selectivity in comparison with the blend and three layered composite membranes. Also in composite membranes because of the existence of the polymers in a layer form there are more chances for water molecules to be absorbed to the polymer layer than when there is a blend mixture of polymer and NRL.

In 90% w/w of ethanol in the feed the separation factors for composite membranes

with three and five layers were the same 51, but their pervaporation separation index were 4274.769 and 6167.838 respectively. It means composite membrane with five layers showed better pervaporation separation index the reason was the difference in their thickness, composite membrane with three layers and five layers have 0.376 mm and 0.259 mm thickness respectively, so composite membrane with five layers showed higher permeability. It means by increasing the number of layers and reducing the thickness of the composite membrane, it is possible to increase the pervaporation flux and also keep the water selectivity almost constant.

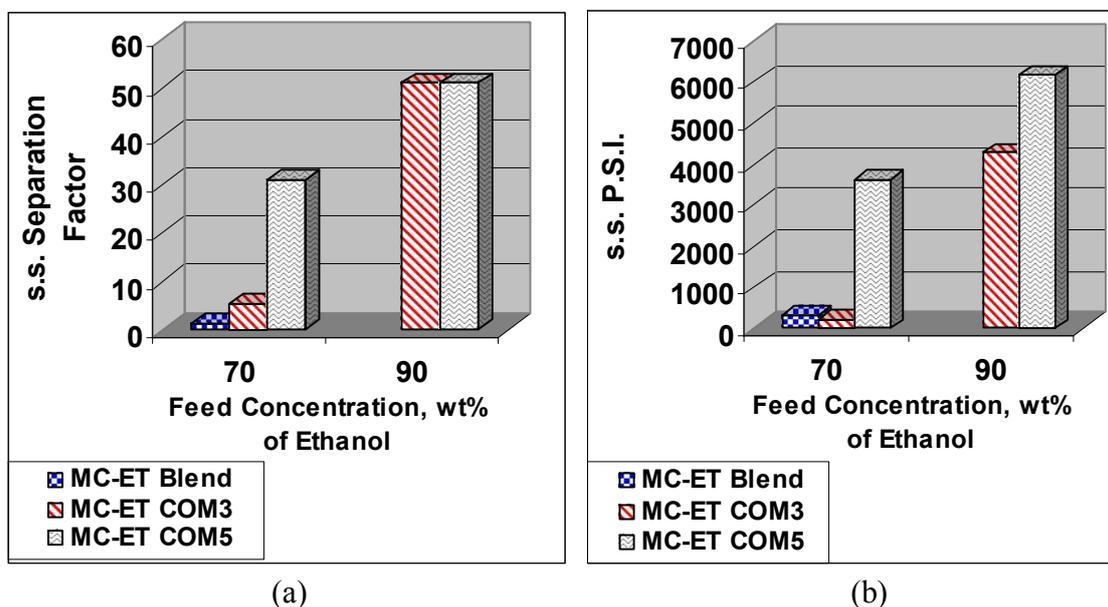


Figure 3: Comparison of membrane pervaporation performance, steady state separation factor (a) and pervaporation separation index (b) in separation of water from ethanol-water solutions by using blend membranes and composite membranes (three or five layered) which containing hydrophilic polymer of MC

3.2.2. Carboxymethyl Cellulose (CMC):

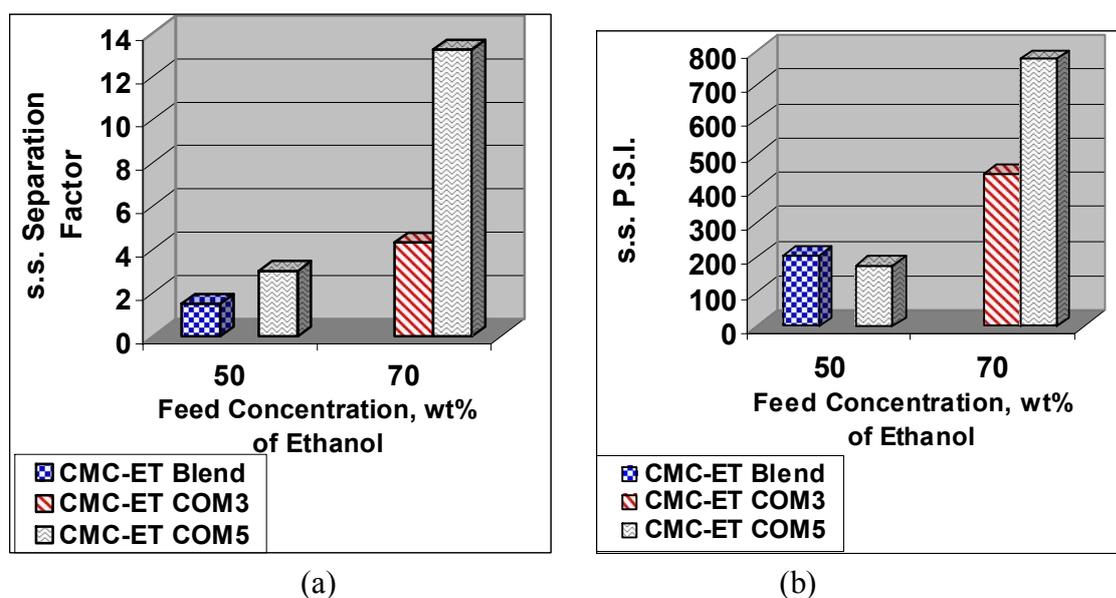


Figure 4: Comparison of membrane pervaporation performance, steady state separation factor (a) and pervaporation separation index (b) in separation of water from ethanol-water solutions by using blend membranes and composite membranes (three or five layered) which containing hydrophilic polymer of CMC

The results of pervaporation tests to separate water from ethanol-water solutions by using blend membranes and composite membranes (three and five layered) which contained hydrophilic polymer of CMC are presented in Figure 4. Comparison of these results shows that in 50% w/w of ethanol in the feed the separation factors for blended membrane and composite membranes with five layers were 1.500 and 3 respectively and their pervaporation separation index were 207.735 and 176.271 respectively. It means composite membranes with five layers showed better water selectivity in comparison with blend membrane. But the pervaporation separation index is lower and the reason is their difference in the thickness. Blend membrane and composite membrane with five layers have 0.255 mm and 0.572 mm thickness respectively, so

blend membrane showed higher permeability.

In 70% w/w of ethanol in the feed the separation factors for composite membranes with three and five layers were 4.333 and 13.222 respectively and their pervaporation separation index were 445.237 and 776.885 respectively. It means composite membrane with five layers showed better pervaporation separation performance. Higher quantity of CMC in the composite membranes with five layers was the reason for higher presence of hydration centres and hydrophilic channels in the membrane and consequently higher water selectivity in comparison with the three layered composite membranes.

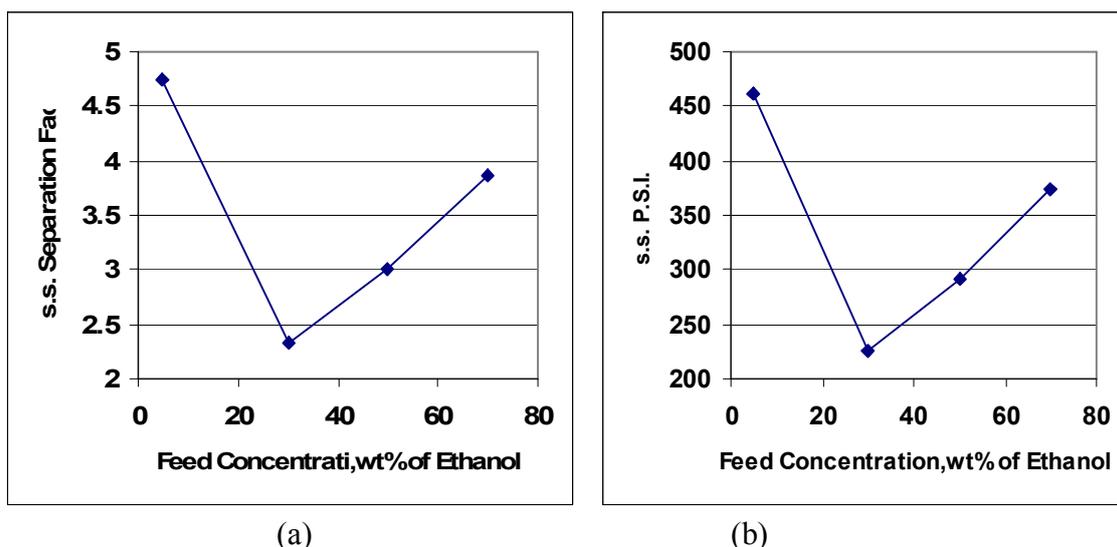


Figure 5: Influence of feed concentration on separation factor (a) and pervaporation separation index (b) in separation of ethanol from ethanol-water solution by using three layered composite membranes which contained hydrophobic polymer UHMWPE

Hydrophobic membranes

Influence of feed concentration on permeate concentration, separation factor and pervaporation separation index for composite membranes with three layers, two layers of NRL and one layer of a hydrophobic polymer (UHMWPE) in the middle has been plotted in Figure 5. The total average flux has been 97.075 (kg/m²h)/m. By observing, examining and analysing the results in Figure 5, it can be said that in 5% w/w of ethanol in the feed the separation factor was 4.750 and after that the separation factor decreased and again increased but the reason for high amount of separation factor in low concentration is that both NRL layer and the UHMWPE layer show hydrophobic behaviour but in average or high concentration of ethanol in the feed NRL layer showed hydrophilic behaviour, therefore, the ethanol selectivity increased only because of increase in weight percent of ethanol in the feed (ethanol diffusivity is

higher because of the high concentration) and hydrophobicity of the membrane. Hence hydrophobic polymers are more useful in low concentration of alcohol in the feed.

3.3. Proposed models for the performance the membranes:

3.3.1. Membranes containing hydrophilic polymers:

The hydrophilic channels at the outer surface of a cluster of rubber particles can act as a hydration shell which was created by the hydration centres of the specific hydrophilic functional groups at the surface of the cluster. Consequently, a hydrophilic channel i.e. a pathway for the preferential permeation of a water molecule(s) can be formed in between these clusters. Next, polymer bridging inside each cluster might create similar hydrophilic channel(s) which would form interconnecting hydrophilic

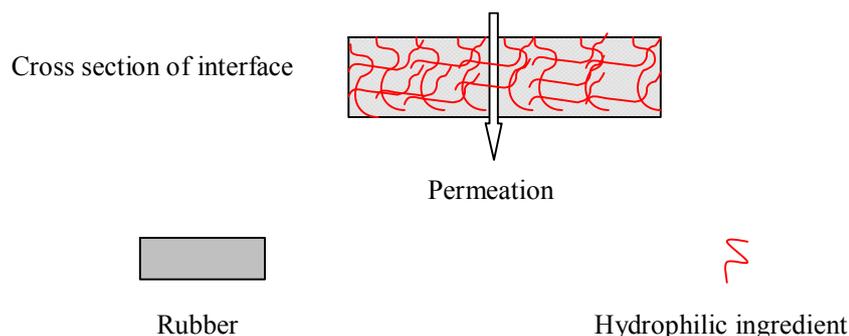


Figure 6: Cross section of an interfacial layer of a composite membrane.

channels throughout the entire cross section of the interface as shown in Figure 6.

The presence of such channels would increase the permeation of water in preference to organic compound. It is this phenomenon that can be responsible for an increase of the water selectivity of the composite membrane. Then, these bonds may break under the influence of vacuum and form other hydrogen bonds between water molecules and the next set of hydration centres present towards the base of the membrane. This formation and breaking of hydrogen bonds lead to the passage of water molecules along the hydration centres of the hydrophilic channel. This exchange reaction can explain the transport of water molecules via the hydrophilic channel(s) within the interface layer and because of the hydrophilic polymer layer is very thin water molecules passes to the next layer and this process continues through all cross section of composite membrane. Semenov (1997) used hydrogen bonds as a reason for passing water molecules through the membrane and named it as push-pull mechanism. According to his theory when one water molecule in the feed is incorporated into the second water layer by the hydrogen-bonding interaction, one water molecule is released

from the opposite side of the membrane. Cabasso et al. (1986) and Cabasso and Zhong-Zhou Liu (1985) made the supposition of the existence of two different channels (hydrophilic and hydrophobic) for permeation of water and organics.

The separation of ethanol-water and water-isopropanol mixtures by pervaporation by using sulfonated polyethylene ion-exchange membranes was carried out by Li et al. (1988) and established that activation energy of permeation for isopropanol was much higher than for water. Therefore, the author assumed that alcohol and water permeated through different channels in the polymer. A similar conclusion was made by Kujawski et al. (1988). The self-diffusions of water, ethanol and ethanol-water mixtures were investigated by Volkov et al. (1998) using the NMR technique. It was found that activation energy of self-diffusion of ethanol was much higher than that of water. It was demonstrated by the NMR-method that water and ethanol were situated in different parts of the polymer matrix and diffused through different channels. The hydrophobic channel consists of the free volume which was created by hydrophobic parts of the polymer matrix. Therefore, the similar channels or pathways which were explained for water can exist for the other components

like ethanol, propanol 2 and acetone. In hydrophobic membranes the organic component pass through the channel easier than water and consequently the organic component will be separated from water and the membrane shows better selectivity towards the organic component not water.

3.3.2. Membranes containing hydrophobic polymers:

Sourirajan (1963) proposed the model of Preferential Sorption Capillary Flow (PSCF) in order to explain the mechanism of desalination of seawater by the reverse osmosis membrane. According to the model, water molecules are attracted by the hydrogen bonds within the hydrophilic membrane (cellulose acetate membrane) and permeate through the membrane. In contrast, salt molecules in the seawater are expelled by capillary action in the hydrophilic membrane. Ghofar and Kokugan (2004) proposed the Hydrophobic Sorption Distillation (HSD) model in order to explain the mechanism of pervaporation of ethanol solution by hydrophobic porous membranes. In his hydrophobic sorption distillation (HSD) model, the membrane, permeate and retentate are hydrophobic, alcohol, and water, respectively, while in the PSCF model, they are hydrophilic, water, and salt, respectively. Moreover, the region of effective separation is located within the membrane for PSCF, but on the membrane surface for the HSD model. These membranes attract ethanol molecules and repel water molecules within the effective region under chemical interaction from the membrane surface. The local ethanol concentration of the solution in the effective region gradually becomes higher than the concentration of the feed solution, and the separation factor increases proportionally

with the residence time of the solution in the effective region.

In our hydrophobic sorption process, the composite membrane with three layers (two layers of NRL and one layer of hydrophobic polymer in the middle), permeate and retentate are alcohol and water, respectively. At low concentration of alcohol in the feed, the region of effective separation is on and within the membrane, because NRL layer shows hydrophobic behaviour, therefore, it attracts alcohol molecules (Van der waals force) and repels water molecules. But at high concentration of alcohol in the feed NRL layer shows hydrophilic behaviour. Therefore, the region of effective separation is located within the membrane. Both high concentration of alcohol in the feed and having the large space of free volume in NRL causing alcohol molecules go through the membrane and in the next step they will be attracted by hydrophobic groups in the membrane (Van der waals force). Therefore, they pass through the channels and they will leave the membrane from the other end.

4. Conclusions

- Five layered hydrophilic composite membranes which contained MC showed the best pervaporation separation performance in comparison to the blend and three layered composite membranes. The performance for five layered composite membrane gives a separation factor of 51 and pervaporation separation index of 6167, in the case of ethanol-water with 90% ethanol concentration in the feed. However in the case of blended membrane the separation factor was 1.5 and pervaporation separation index of 309.

- For a feed concentration of up to 55% w/w acetone in the feed, the NRL membrane acted as a hydrophobic membrane. The separation factor for water varied from 0.643 to 1. Above this concentration it behaved as a hydrophilic membrane. The separation factor for water varied 1 to 3.8.
- By using the hydrophilic polymers in the blended membrane with NRL the hydrophobic nature of NRL membrane changed to hydrophilic behaviour for all concentrations of alcohol in the feed.
- In the hydrophilic membranes the separation factor and pervaporation separation index increased by raising the feed concentration of the organic component. Any increase in the concentration of organic component in the feed results in a decrease in the swelling of membrane by water decrease which leads to more water molecules passing through (increase of water selectivity).
- For the first time ever three layered composite membranes have been developed using a sandwich structure of NRL-polymer-NRL, with a hydrophobic polymer. The test results show that the organic component selectivity is higher at its low concentration in the feed, because NRL shows hydrophobic behaviour resulting in increased solubility of the organic component.

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