

Separation of Miscible Solvent-water Solutions Using Composite Membranes Employing Hydrocolloids and Natural Rubber Latex

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ABSTRACT

A number of composite membranes have been investigated for the separation of water from miscible organic-water mixtures. Organic solvents studied were ethanol, propanol-2 and acetone. Each composite membrane was formed of at least two fused layers. One layer was prepared from a mixture of natural rubber latex solution and the other layer, from a solution of hydrophilic colloid between 1.25 to 20 per cent by weight on a dry rubber basis. Four hydrophilic colloids with not more than three different molecular masses for each type were used in the preparation of membranes. Each composite membrane was vulcanized before use in an all stainless steel membrane cell. These perm-selectivities have been compared with those obtained from the use of vulcanized natural rubber latex membranes only. The special novel design of this cell along with the entire equipment used, are described and discussed. The method of forming a thin film as well as the techniques for checking its soundness and finally, the proposed mechanism and a model that may be responsible for enhancing the permeation of water through the composite membranes are also discussed. The incorporation of a layer of alginic acid hydrocolloid in the composite membrane did increase the separation factor of water from ethanol-water mixtures by a factor of 24 in comparison with that of a natural rubber membrane alone. Similarly, the separation factors for water with hydrocolloids hydroxypropyl methyl cellulose and methyl cellulose from the solutions containing propanol-2 and acetone were 13.50 and 11, respectively.

Key Words:

composite membranes;
pervaporation;
hydrocolloids;
mechanism of separation.

INTRODUCTION

Polymeric films may be used to separate miscible aqueous organic liquid mixtures where, the separation of constituent components requires expensive technical modification(s) to the process of conventional distillation such as in azeotropic distilla-

tion. The separation of such a mixture may be obtained by applying an enhanced thermodynamic driving force by creating a vacuum on the downstream side of the membrane. This mode of operation is called pervaporation which has been used here.

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Many new membranes have been developed and used for the separation of aqueous organic solutions into their constituents [1-15]. New natural rubber latex based membranes were used for the first time by Bhasi [8]. Bhasi reported that natural rubber latex could be used to separate ethanol water mixtures into their constituents. He also reported that, good water perm-selectivity and reasonable permeation rate could be obtained by using fully cross-linked natural rubber latex membrane(s).

In this study, hydrophilic colloids (in the form of for example polysaccharides) have been selected and layered with natural polymer rubber latex in order to obtain not only a high water selectivity but also achieve other properties such as: strength and formability of thin films, long life spans, etc., to form good composite membrane modules. Natural rubber latex is relatively cheap, easily, and abundantly available for the formation of membrane modules of practically any shape. It has large surface area and is suitable for commercial use. Polysaccharides i.e., the hydrophilic colloids which were used here, did preferentially invert the hydrophobic nature of the rubber membrane. For the selection of a suitable hydrophilic colloid(s), the following attributes have been considered essential.

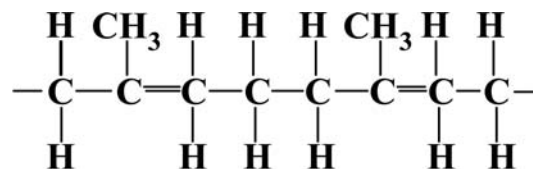
1. The selected compound should be miscible with the water based natural rubber latex solution.
2. The molecular mass should be such that, after drying of the membrane, it cannot be leached back into the aqueous organic-water mixture.
3. It should have the property of forming floc(s) [9] with natural rubber latex particles. This property is essential for inverting the hydrophobic nature of the rubber membrane.
4. The compound should have very good hydration centres [10] i.e., hydrophilic functional groups in its structure(s).

EXPERIMENTAL

Materials

Mixtures of high ammonia compounded natural polymer rubber latex (HA Latex) solution and one of four hydrophilic colloids were used to form thin composite membranes. The HA latex solutions used were obtained, to avoid bias, from three different suppliers

(Hecht, Heyworth & Alcon Ltd, Trylon Ltd, and Revertex) who used the same supplier in Malaysia. The basic building blocks of natural rubber are the isoprene molecules and each molecule is made from 8-hydrogens and 5-carbon atoms:



Natural rubber latex: Isoprene molecule

Typical composition for the latex is reproduced below from Revertex (Malaysia), BERHAD, Yule-Catto Building, Temple Fields, Harlow, Essex, CM20 2BH, UK:

- Total solid content (% by wt.) 60.5 ± 0.5
- pH 10.5 ± 0.5
- Ammonia content (% by wt.) 0.6 to 1
- Viscosity at 30°C (s) 40 ± 5

For the present work four types of hydrophilic colloids namely, sodium salts of alginic acid and carboxymethyl cellulose [CMC], hydroxypropyl methylcellulose [HMC] and methyl cellulose [MC] were used. These four colloids did satisfy all essential properties that have been outlined above. Each selected colloid had either low, medium, high, or very high molecular mass category. The properties of the supplied colloids are given in Table 1.

Preparation of Composite Membrane

A few drops of natural rubber latex (NRL) solution were poured on to a glass plate and were spread out using a glass rod to form a rectangular strip. Next, an applicator with a selected wire depth of 50 micron thickness was placed over this strip and the bar was pulled down the plate slowly and smoothly, until all the solution has been spread out uniformly into a wet film. This cast film was dried at the room temperature of 20°C and then vulcanized for about 10 min at 120°C. The step of vulcanization enhances the physical properties such as: tensile strength, modulus-of-elongation, and percent of elongation-at-break point of a typical thin film. This process of forming membranes has been patented in United Kingdom [15]. The morphology of the membranes has been described elsewhere [13, 14].

Table 1. Molecular masses and viscosity of the hydrophilic colloids.

Hydrocolloids	Molecular grade	Molecular mass	Viscosities at 25°C
Methyl cellulose (MC)	Very high (VH)	ca. 86,000	4000 cp for 2wt% in water
	High (H)	ca. 63,000	1500 cp for 2wt% in water
	Low (L)	ca. 17,000	25 cp for 2wt% in water
Carboxymethyl cellulose (CMC) (sodium salt)	Very high (VH)	700,000	3400 cp for 1wt% in water
	High (H)	600,000	1500 cp for 1wt% in water
	Medium (M)	ca. 250,000	515 cp for 2wt% in water
	Low (L)	< 90,000	10 to 55 cp for 4 wt% in water
Alginic acid (sodium salt)	High (H)	120,000-190,000	14000 cp for 2 wt% in water
	Medium (M)	8,000-120,000	3500 cp for 2wt% in water
	Low (L)	12,000-80,000	200 to 400 cp for 3 wt% in water
Hydroxypropyl methyl cellulose (HMC)	High (H)	ca. 120,000	100,000 cp for 2wt% in water

Next, another aqueous solution of a colloid with a selected weight percent of the hydrophilic polymer of a known molecular mass was spread over the initial film of natural rubber latex. This solution was prepared in two steps. First, the colloid polymer was dissolved in near boiling distilled water at concentrations, which varied from 0.5 to 3 percent by weight. The choice of a given weight percent was dictated by the solubility in water as well as the viscosity of the final solution. Very high viscous solution tended to trap air, which was difficult to eliminate and also produced imperfect membranes.

A high level of mixing was required and provided by filling a glass tube with known solution and a few steel balls that were held without air and shaken for at least 5 min. This process ensured that no air was present in the mixture in the tube before shaking. Finally, this cooled mixture was poured onto the dried vulcanized NRL film and was spread out in the form of another thin film to yield an overall thickness of 100 microns. For this, the applicator bar containing two stainless steel shims of 100 microns thickness, each one on the either side of the rod, was used until all solution was spread out evenly on the previous vulcanized NRL film. This composite film was allowed to dry at the room temperature of 20°C.

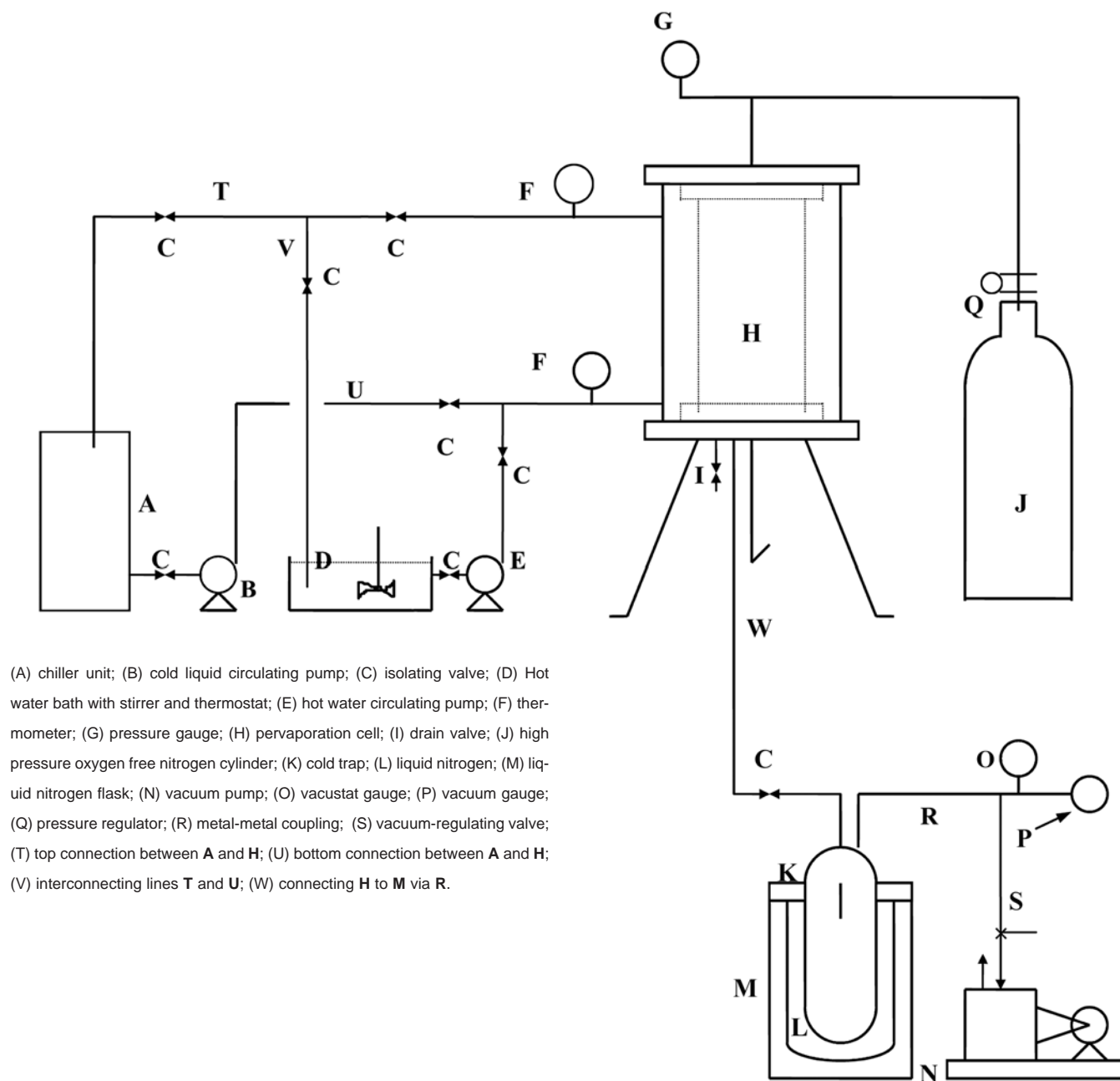
The drying time of the wet layer did vary a lot as it depended on the thickness of the membrane and the

type of the hydrophilic colloid used, as well as, its weight percent present in the blend. During the process of drying the film, its appearance changed from slightly transparent to opaque. Dried membrane layers were vulcanized for another 12 min at a temperature of 120°C using a laboratory oven in order to improve their strengths.

The prepared membranes were extremely thin and therefore were not flat enough to be used on their own in a pervaporation cell. Mounting this thin membrane onto a laboratory filter paper solved this problem. One edge of the film was slowly lifted and a 7 cm diameter filter paper was carefully placed between the membrane and the glass plate. Superglue was used for bonding the membrane on the filter paper. Before lifting the whole film, the superglue was applied to the periphery of the film and the filter paper in order to obtain a permanent joint and yet allow the entire area free for pervaporation. The excess film was trimmed from the edges of the filter paper.

Pervaporation Experiments

The apparatus shown in Figure 1 was used for the entire experimental work. The pervaporation cell used in this work has been shown separately in Figure 2. Each of the membranes employed was first tested for any inherent defects (e.g., pinholes) and if found satisfactory, it was used for the pervaporation separation of miscible



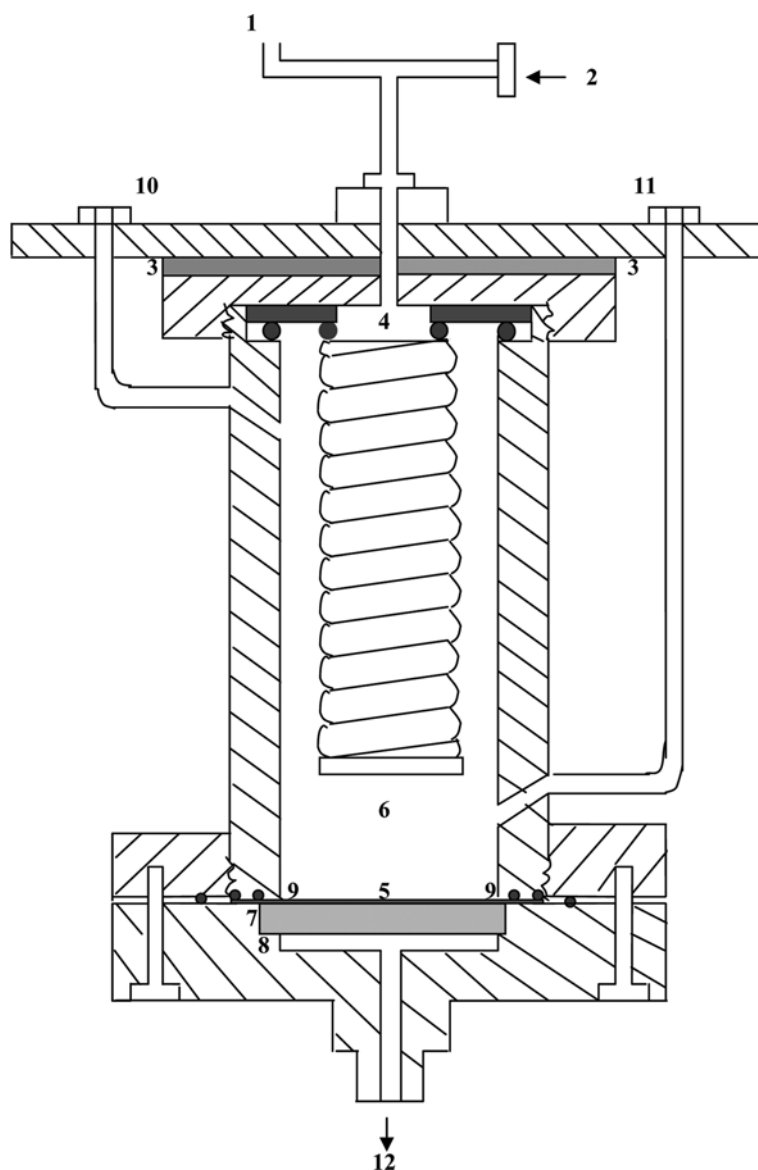
(A) chiller unit; (B) cold liquid circulating pump; (C) isolating valve; (D) Hot water bath with stirrer and thermostat; (E) hot water circulating pump; (F) thermometer; (G) pressure gauge; (H) pervaporation cell; (I) drain valve; (J) high pressure oxygen free nitrogen cylinder; (K) cold trap; (L) liquid nitrogen; (M) liquid nitrogen flask; (N) vacuum pump; (O) vacustat gauge; (P) vacuum gauge; (Q) pressure regulator; (R) metal-metal coupling; (S) vacuum-regulating valve; (T) top connection between A and H; (U) bottom connection between A and H; (V) interconnecting lines T and U; (W) connecting H to M via R.

Figure 1. Schematic flow diagram of the experimental equipment.

organic-water mixtures. This test comprised of subjecting each membrane, while mounted in the cell, to a combination of high pressure at the top of the bellows, (Figure 2), and a full vacuum at the other downstream end. A normal rate of flux was indicative of a sound membrane. Prior to such a test the membrane to be mounted in the cell was placed against an illuminated piece of flat plate of glass. For a sound membrane the intensity of light passing through it, was found to be

uniform and did not show any bright spots that were indicative of pinholes or imperfections.

Referring to the drawings, Figure 1 shows a chiller unit the top of which is connected by line T to the top of a pervaporation cell H, and the bottom of this unit is connected by line U to the bottom of the cell H. In line U the cold liquid was circulated by the pump B. Lines T and U were interconnected by line V which connects T and U to a hot water bath D that was equipped with a



(1) pressure gauge; (2) to oxygen free nitrogen cylinder; (3) gasket; (4) glandless expandable bellows; (5) membrane; (6) feed solution; (7) porous support for the membrane; (8) permeate collection chamber (downstream); (9) three -o- rings seal; (10) inlet port for continuous operation; (11) outlet port for continuous operation; (12) downstream port, i.e., connected to the cold trap for the permeate vapour condensation.

Figure 2. Cross-section of the stainless steel pervaporation cell.

stirrer and thermostatic controller. Line V included a hot water circulating pump E. Isolating valves C provided in lines T, U, and V.

A high-pressure oxygen free nitrogen cylinder J, provided with a pressure regulator Q, was connected to cell H, with a pressure gauge G that was adjacent the cell. Cell H was provided with a drain valve I. Line W connected cell H via a metal metal coupling R to a liquid nitrogen trap K that contained liquid nitrogen L in the flask M. Vacuum pump N evacuated line W, and a vacuum-regulating valve S was provided, which its

downstream is connected to a vacustat gauge O and a vacuum gauge P.

Pervaporation flux measurements were conducted at a constant temperature of 20°C. Before the initiation of the experiment, selected temperature was obtained by continuously circulating either the heating or cooling liquid through the outer jacket of the pervaporation cell for the entire duration of the experimental work. An Edwards vacuum pump was used to evacuate the cold traps by the vacuum line. The vacuum line was connected simultaneously to the downstream compartment and the cold traps

which were immersed in liquid nitrogen. A vacustat was used to accurately measure the vacuum state.

The cold traps were changed approximately once every hour in order to collect the condensed permeate vapour. The inlet and outlet ports of the cold trap were immediately sealed with rubber bellows to eliminate the loss of condensed permeate due to evaporation during the thawing process. The cold traps were weighed to determine the amount of permeate (flux) and then liquid was transferred into a small sample bottle and placed in a refrigerator for chemical analysis by gas liquid column chromatography (GLC). However, in all cases the permeate was analyzed immediately by a refractometer and the results were compared with the analytical data obtained from the GLC analysis.

Each pervaporation experiment was carried out for a steady state period of approximately 7 h every day. In some cases, the test was continued the following day or for the rest of the following week. Hence, the pervaporation flux measurement was carried out for a maximum 120 h. Pervaporation experiments were also conducted with membranes, which had already been used. The results (i.e., separation, flux) were found to be the same as the freshly prepared membranes.

The feed was also analyzed by gas chromatography as well as by refractive index measurement. Concentration of organic compound, in the mixtures of organic compound and water varied between distilled water to pure organic compound. Some experiments were conducted within the range of 5-97.5 percent by weight of ethanol. Other experimental work was carried out with 30-90 weight percent of propanol-2 or acetone.

RESULTS AND DISCUSSION

Experimental Results

First, pervaporation results have been given for vulcanized natural polymer rubber latex membranes alone in Figure 3. It can be seen, that the rubber membranes are more hydrophobic up to 50% organic compound in the aqueous feed, but for 70 to 96% by weight, they are water selective. This change seems to occur between 60 to 70 wt% of organic compound in the feed solution.

Second, pervaporation results for composite membranes which have been prepared with 3 to 20 wt%, on a dry rubber basis, of low or medium or high molecular mass of CMC (sodium salt) or MC or alginic acid (sodi-

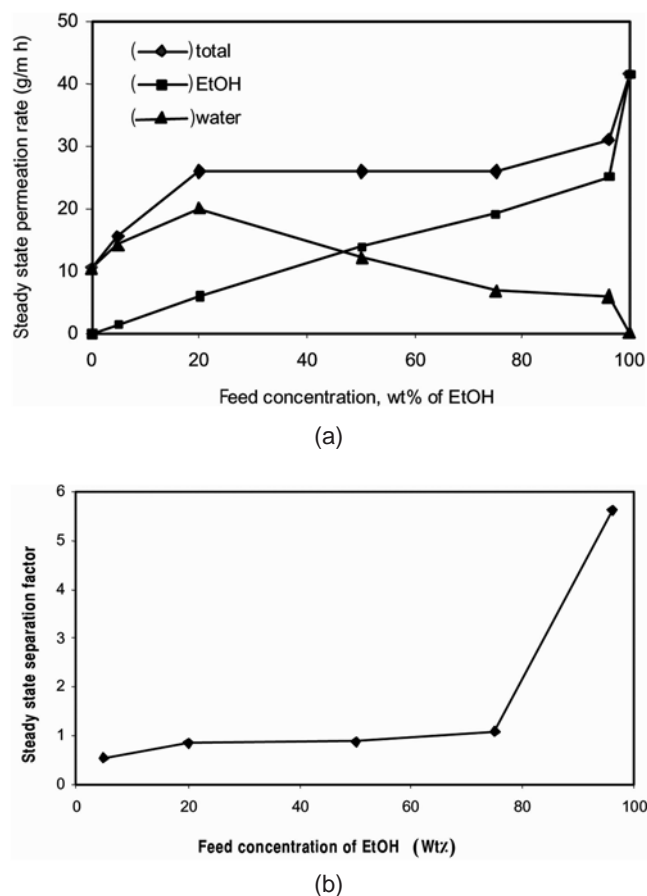


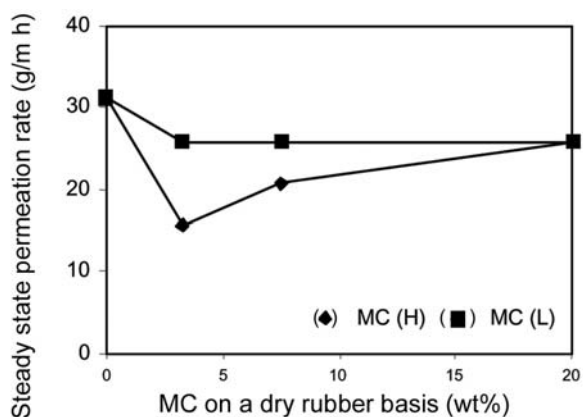
Figure 3. Influence of feed concentration on steady state permeation rate (a) and separation factor (b) for vulcanized natural rubber latex membranes at the operating temperature of 20°C.

um salt), are given in Figures 4-6. In these experiments an azeotropic composition of ethanol was used throughout.

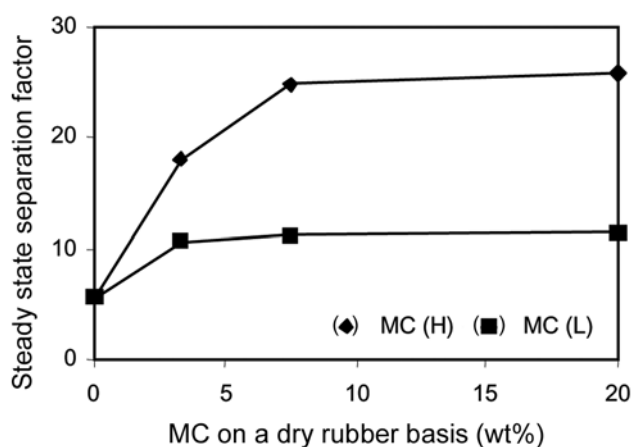
Third, pervaporation results for composite membranes which have been prepared with 3 wt%, on a dry rubber basis, of very high molecular mass of HMC, MC and CMC (sodium salt), are given in Tables 2-6. In these experiments propanol-2 and acetone were used as organic components. In each experiment a different membrane has been used and none of them has been used twice.

The separation factor S which is used here may be defined as the ratio of concentrations of components A and B in the permeate divided by their concentration ratio in the feed. It may be represented and calculated by the following formula:

$$S = (C_A/C_B)_{\text{permeate}} / (C_A/C_B)_{\text{feed}}$$



(a)



(b)

Figure 4. Effect of wt% and molecular mass of methyl cellulose (H and L) in the top layer of composite membranes on steady state permeation rate (a) and separation factor (b) for 96 wt% of ethanol in water at the operating temperature of 20°C.

C_A and C_B are the wt% concentrations of the compo-

Table 2. The pervaporation result for HMC (the organic component is propanol-2).

Hydroxypropyl methyl cellulose was used as hydrophilic polymer in the membrane		
The wt% of propanol-2 in the feed	The wt% of propanol-2 in the permeate	Water/propanol-2 separation factor
50	35	1.71
70	50	2.33
90	40	13.50

Table 3. The pervaporation result for MC (the organic component is propanol-2).

Methyl cellulose was used as hydrophilic polymer in the membrane		
The wt% of propanol-2 in the feed	The wt% of propanol-2 in the permeate	Water/propanol-2 separation factor
30	10	3.86
50	15	5.67
90	40	13.50

nents A and B, respectively.

Pervaporation Separation Performance of Vulcanized NRL Membrane

Permeation of the molecules through a non-porous polymer membrane may be explained by a solution diffusion mechanism. In this mechanism it is assumed that a component of the feed with a high affinity to the membrane, is easily and preferentially absorbed and therefore dissolved in the membrane substance. The membrane may swell with a more soluble component and change its composition.

In Figures 3a and 3b by following a concentration gradient, the components migrate through the membrane by diffusion process and are desorbed at the downstream side of the membrane into a vapour phase. Substances with low or no solubility in the membrane material cannot be dissolved or ultimately reach only low concentrations and thus low transportation rates.

Table 4. The pervaporation result for CMC (the organic component is propanol-2).

Carboxymethyl cellulose was used as hydrophilic polymer in the membrane		
The wt% of propanol-2 in the feed	The wt% of propanol-2 in the permeate	Water/propanol-2 separation factor
30	15	1.91
50	30	2.33
70	55	2.43
90	60	6.00

Table 5. The pervaporation result for HMC (the organic compound is acetone).

Hydroxypropyl methyl cellulose was used as hydrophilic polymer in the membrane		
The wt% of acetone in the feed	The wt% of acetone in the permeate	Water/acetone separation factor
50	20	4.00
90	45	11.00

As the diffusion coefficients of small molecules in a polymeric matrix do not differ too much, the separation characteristics of the membranes may also be assisted by different rates of absorptions, which is dependent on concentration gradient of the components in the membrane material. This may explain the dehydration process through the membrane. Hence, the overall process may be described as a sequence of three steps namely, sorption, diffusion and evaporation [10,11]. According to this model, the solubility and diffusivity of the components permeating through the membrane determine the perm-selective properties of each membranes in pervaporation.

Increase in permeation rate of the organic component, with an increase in the concentration of organic component in the feed solution, may be attributed to the dominant hydrophobic nature of NRL membrane. This hydrophobic nature may lead to an increase in the solubility of organic component in a vulcanized NRL membrane, as the organic component concentration in the feed is increased. Hence, a membrane becomes plasticized with sorbed organic component. Thus, the diffusivity of organic component molecules may be

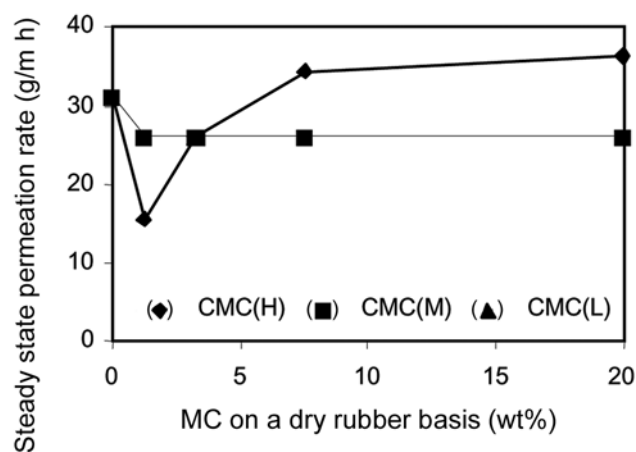
Table 6. The pervaporation result for MC (the organic compound is acetone).

Methyl cellulose was used as hydrophilic polymer in the membrane		
The wt% of acetone in the feed	The wt% of acetone in the permeate	Water/acetone separation factor
50	30	2.33
90	65	4.85

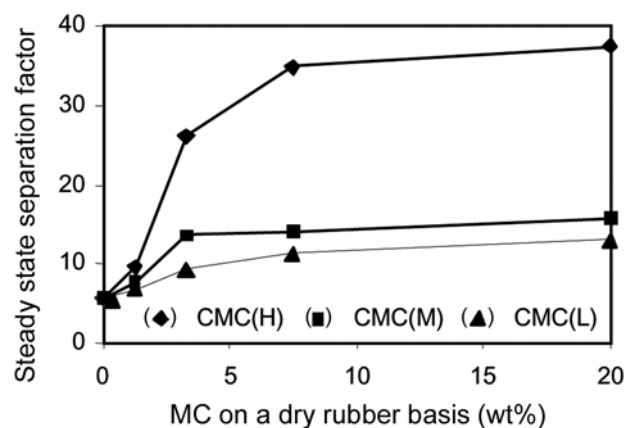
assisted by the vulcanized NRL membrane.

It was found that the perm-selectivity of the vulcanized NRL membrane was changed from organic component to water, for 60-70 weight percent of organic component concentration, in the feed. A possible explanation for this transition may be offered as follows.

Sorption of organic component molecules S_o on the top surface of the vulcanized NRL membrane was high which, might be mainly due to the hydrophobic interaction between organic component and molecules of polyisoprene. On the other hand, sorption of water molecules S_w on the top surface of the vulcanized NRL membrane was low and might mainly be due to



(a)



(b)

Figure 5. Effect of wt% and molecular mass of carboxy methyl-cellulose (H, M and L) in the top layer of composite membranes on steady state permeation rate (a) and separation factor (b) for 96 wt% of ethanol in water at the operating temperature of 20°C.

the hydrophilic and ionic interaction between water molecules and proteins. But the sorption of water molecules S_w in vulcanized NRL membranes was low because the non-rubber constituent is small compared to polyisoprene. Hence, experimental data suggest that S_w might have been smaller than S_o .

The diffusivity of a component through the membrane, at constant temperature, may be considered as the sum of molecular diffusivity D_m (concentration dependent) and pore diffusivity D_p (dependent on both the size of molecules, as well as, the pores). Next, the rate of permeation may be considered directly proportional to:

(Solubility of water or organic component) = $(D_m + D_p)$

At a concentration about 30 % by weight of an organic component, the values of D_m and D_p may be considered low due to low concentration gradient across the membrane and large molecular size of organic component, respectively. The values of D_m and D_p for water may be considered high due to the high concentration gradient across the membrane and the low molecular size of water, respectively. Hence, even when S_o was considered larger than S_w , the rate of permeation for water was high because:

$$S_w (D_{m, \text{water}} + D_{p, \text{water}}) > S_o (D_{m,o} + D_{p,o})$$

Suggested Process for the Distribution of Hydrophilic Ingredients in the Top Layer of the Composite Membrane

At the interface of the composite membrane hydrophilic ingredients become blended with NRL surface in order to increase the water permeation properties. Pervaporation separation results for the composite membranes have been discussed with reference to this schematic model that is summarized in Figures 7(a)-7(d):

First Stage

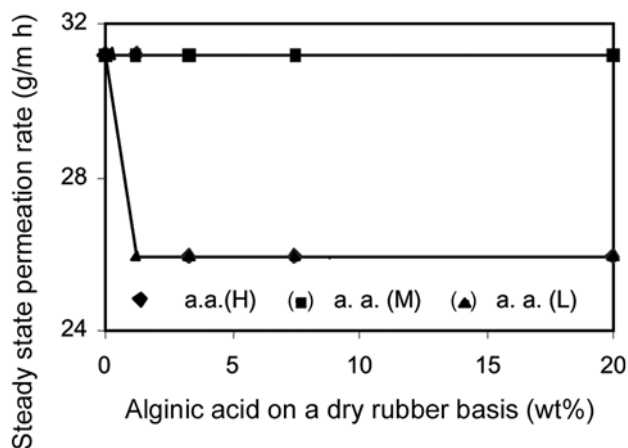
At the interface the process initiates with the distribution at a high shear, created by the application, of polymer ingredient on the compounded NRL film which has been shown in Figure 7(a). Also, due to high shear the hydrocolloid polymer solution is highly likely to penetrate into the NRL film at its interface that may cause bridging to occur within the pores leaving the hydrated pore surface for action.

Second Stage

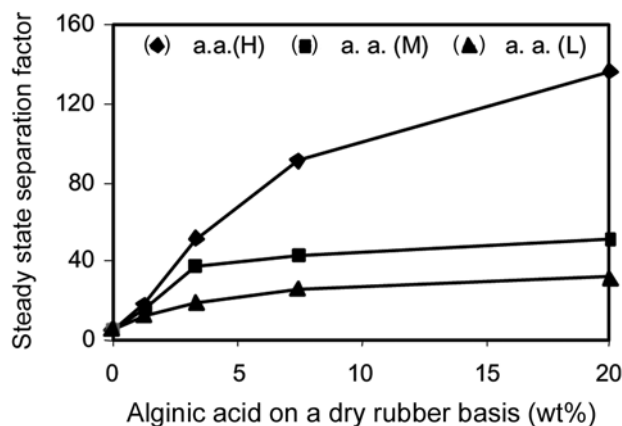
Depending on the functional group(s) of the polymer ingredient employed, its active chain may or may not anchor to the surface of the rubber particles as shown in Figure 7(b).

Third Stage

These active chains may join with the rubber particles and may be named clusters that are shown in Figure 7(c). The chain length of blend ingredient would determine the ultimate size of a cluster. The outer surface of clus-



(a)



(b)

Figure 6. Effect of wt% and molecular mass of alginic acid (H, M, and L) in the top layer of composite membranes on steady state permeation rate (a) and separation factor (b) for 96 wt% of ethanol in water at the operating temperature of 20°C.

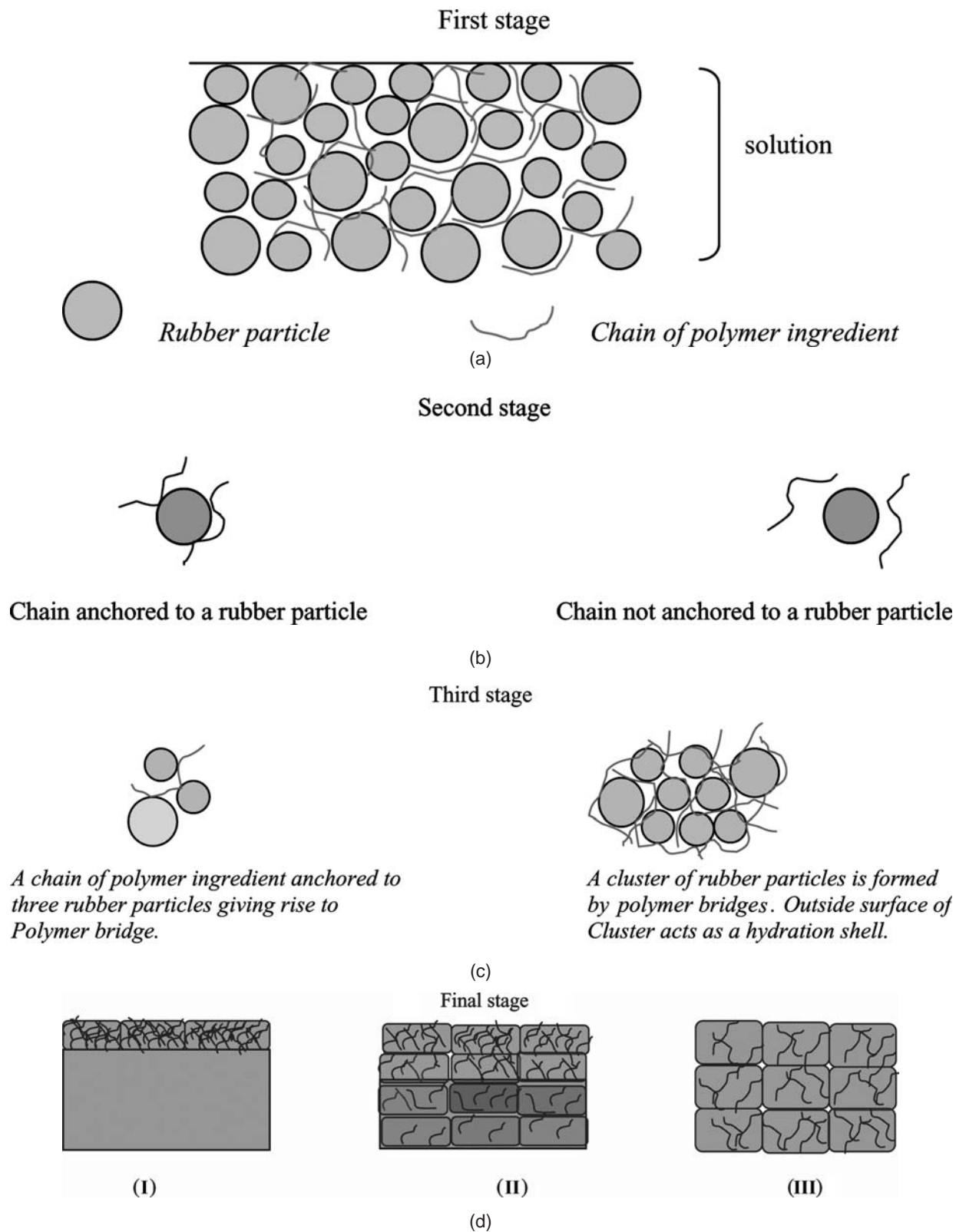


Figure 7. (a) Distribution of the chains of polymer ingredients on a compounded interface; (b) Adsorption (anchoring) of the chain(s) of polymer ingredients on to the surface of a rubber particle(s); (c) Formation of clusters of rubber particle in the vicinity of the interface and (d): Distribution of cluster(s) in a: low viscous (I), medium viscous (II) and high viscous (III) air free solution of a hydrocolloid and NRL solution inside the interfacial cross section a membrane.

ters acts as a hydration shell which according to experimental data does appear to affect water selectivity.

Final Stage

Finally, during the process of drying as well as further heat treatment of the composite membrane some rearrangements of clusters, as shown in Figure 7(d), may take place.

Formation of Clusters of Rubber Particles

According to the current thinking [12], water soluble macromolecules such as MC, CMC when present in a lyphobic solution (i.e., NRL solution) are expected to be adsorbed at the surface of the rubber particles. Use of the word macromolecules inherently implies the presence of clumps of molecules that suggests the efficiency of mixing at the interface of two adjacent layers of the composite membrane might not have been ideal, that is 100 % at molecular level. Hence, some interparticle bridging is expected to occur by the polymer s macromolecules if its molecular mass is sufficiently high [12]. MC, CMC, HMC and alginic acid are polymers which belong to water-soluble macromolecules and natural rubber particles in the latex solution are called lyphobic solution. This bridging mechanism may be the reason for the formation of clusters of rubber particles with the hydrocolloids. The mechanism of bridging remains obscure [12] although, the phenomenon has been known to occur.

Influence of Molecular Mass of Hydrocolloid(s) in the Blended Layer on Pervaporation Separation Performance

The water selectivity i.e., the separation factor of composite membranes increases with an increase in the molecular mass of layered i.e., composite hydrophilic colloid(s). This increase in the water selectivity may be linked to the high viscosity of the mixture which creates conditions of a good distribution of hydrophilic colloids within the blended interfacial layer of the composite membranes.

CMC (M) and CMC (L) have the same permeation rate (cf. Figure 5a) and a.a. (H) and a.a. (L) have the same permeation rate (cf. Figure 6a)

High Molecular Hydrocolloid(s)

The outer surface of a cluster of rubber particles may

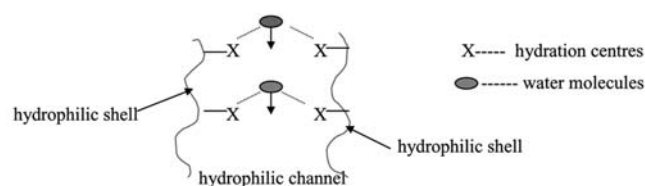


Figure 8. An illustration of a conceptual channel / pathway.

act as a hydration shell which may be created by the hydration centres of the specific hydrophilic functional groups at the surface of the cluster, as shown in Figure 7(c). Consequently, a hydrophilic channel i.e., a pathway for the preferential permeation of a water molecule(s) may be formed between these clusters. A graphical illustration of one of these channels has been shown in Figure 8.

Next, polymer bridging inside each cluster might create similar hydrophilic channel(s) which, would form interconnecting, hydrophilic channels throughout the entire cross section of the blended layer as shown in Figure 9. The existence of such channels would increase the permeation of water in preference of organic component. It is this phenomenon that may be responsible for the increase of water selectivity of the composite membrane.

The phenomenon of permeation of water molecules through the channels may be explained by a chain reaction which is cascading down the thickness of the membrane. First, hydrogen bonds may be formed between a water molecule and the hydration centres on either side of the hydration shell, as shown in Figure 10. 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 leads to the passage of water molecules along the

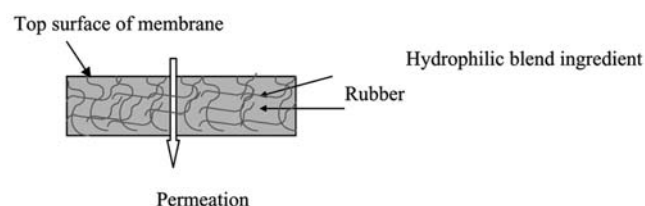


Figure 9. Cross-section of an interfacial layer of a composite membrane.

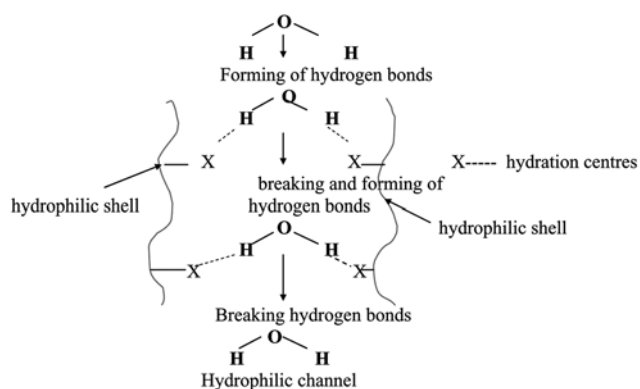


Figure 10. An illustration of a conceptual channel / pathway at the interface.

hydration centres of the hydrophilic channel. These exchange reactions may explain the transport of water molecules via the hydrophilic channel(s) within the blended layer of composite membrane.

Medium Molecular Mass Hydrocolloid (s)

The distribution within the interface of a compound membrane, of a medium molecular mass hydrocolloid(s) is not as dense as a high molecular mass hydrocolloid(s). At or near the top surface of the membrane, the population density of polymer bridged clusters of rubber particles is high which progressively decreases with depth towards the base of the membrane. Consequently, hydrophilic channels are not likely to be uniformly distributed throughout the whole cross-section of layers of the composite membranes. These non-uniform hydrophilic channels across the thickness of the blend at the interface lead to gradual thinning of the pathways to water permeation. This factor coupled with hydrophobicity of the remaining part of the rubber membrane leads to an overall reduction in water selectivity.

Low Molecular Mass Hydrocolloid(s)

The entire low molecular mass of the hydrocolloid(s) e.g., MC or CMC appears at or near the top surface of the compounded interface of the membrane. Hence, hydrophilic channels may only be formed close to the top surface of the layers of the composite membranes. Hence, the bulk of the cross section would predominantly remain hydrophobic in nature. Consequently, the water selectivity (separation factor) of such composite membranes has been found to be significantly lower

than that for the composite membranes which contain either high or medium molecular mass hydrocolloids. Low molecular mass alginic acid i.e., alginic acid (L) has proved an exception. This alginic acid (L) forms a more viscous mixture in comparison to that of MC (L) or CMC (L).

Effect of Weight Percent of Hydrocolloids in the Blended Interfacial Layer of the Composite Membrane on Pervaporation Separation Performance

Water selectivity that is the separation factor, has been found to increase steadily and appears to reach an almost constant value with an increase in the level of hydrocolloids used in the blended interfacial layer of the composite membranes, (Figures 4b, 5b and 6b). The reasons for this behaviour are given below:

High Molecular Mass Hydrocolloids

This increase in water selectivity may be attributed to and explained by the following three main factors.

1. the viscosity of the blended interface increases as the weight percent of the hydrocolloid added is enhanced.
2. The population density of the polymer bridged clusters of rubber particle also increases as the amount in weight percent of the hydrocolloid added is increased.
3. The functional group(s) of hydrocolloids do have an influence on the effective diffusivity and hence selectivity of water molecules through the composite membrane.

An increase in viscosity in regard to increase in weight percent is highly likely, to retain more bridged clusters of rubber particles and pathways for the permeation of water inside the rubber base composite membrane, correspondingly. This factor explains the increase in permeation selectivity with respect to water.

When an increasing weight percentage of hydrocolloid is present in the blended interface, any further rate of increase in the number of new water pathways tends to take the appearance of approaching a constant value. This is because some of the water molecular diffusivity plus its enhancement due to the existence of slowly increasing water pathways becomes nearly constant. This explains the flattening of the curve of water selectivity versus weight of the hydrocolloid used in the

composite membrane.

Finally, the number of pathways and effective water diffusivity also depend on functional groupings of the high molecular mass hydrocolloid employed. This last point gives rise to different constant values of water selectivity as a function of the molecular structure which is used to form a composite membrane.

Low Molecular Mass Hydrocolloids

Pervaporation separation experimental results with membranes containing different amounts of low molecular mass hydrocolloids have shown that, the increase in water selectivity is not as high as that of high molecular mass hydrocolloids. This may be explained as follows.

Stratification of hydrocolloids takes place during the period of drying and is mainly due to the low viscosity of the mixture used to form the membrane. Hence, the water pathways i.e., hydrophilic channels are only close enough to the interface of a composite membrane. Hydrophilicity of the remaining cross-section of the blended layer of membrane may not change much, which explains the reasons of the low value of water selectivity (separation factor) in comparison with membranes containing high or medium molecular mass hydrocolloids.

Effect of Weight Percent of Hydrocolloids in the Blended Interfacial Layer, of the Composite Membrane, on the Rate of Permeation during Pervaporation Separation Performance.

The dip in curves of permeation rate versus weight percent of hydrocolloids, as shown in Figures 4(a) and 5(a), may be explained by an increase in the population density of hydrophilic channels that are dependent proportionally on the mass percent of the hydrocolloid used as well as its molecular mass and chemical structure.

The use of a layer of hydrocolloid on top of the layer of natural rubber as composite at the beginning would have low concentration of hydrophilic channels, and hence more resistance to flow. This increase in resistance of the composite membrane may explain the existence of the dips in the permeation rate curves, as shown in Figures 4(a) and 5(a). Next, as the mass percent of the hydrocolloid at the interface of the membrane increases, the resistance to the flow of water mol-

ecules reduced. This reduction flow is proportional to additional weight percent of the hydrocolloid used that is followed by the preferential assisted flow of water molecules over the flow of ethanol, which is helped by special property of hydrophilic channels and their population density that support an increase in the amount of permeated liquid, as, e.g. in Figures 4(a) and 5(a).

Equally, enhanced permeation of water molecules over ethanol also supports increase in the values of the separation factors, as the weight percent of hydrocolloid is progressively increased, as are shown in Figures 4(b) and 5(b). In some instances that very high molecular mass hydrocolloid, CMC(H), has been used the enhanced flow of water molecules through hydrophilic channels suggests a further reduction to the overall resistance of the composite membrane that it increases the permeation rate over that of the natural rubber membrane, as is shown in Figure 5(a).

CONCLUSION

1. For a feed concentration up to 60 percent by weight of organic component in an aqueous organic water solution, the vulcanized natural rubber latex (NRL) membrane acts as a hydrophobic membrane. The separation factor for water varies between 0.53 to 1.
2. For the feed concentration above 60 wt% of organic component in water, the vulcanized NRL membrane acts as a hydrophilic membrane. The separation factor for water varies between 1 to 5.6.
3. All hydrocolloids used here via, MC (VH, H; or L), CMC (VH, H, M, or L), HMC(H), and alginic acid(H, M, or L) produced higher water selectivity than that of a vulcanized NRL membrane. This increase in separation factor for water varies from 6.8 to 136.
4. A composite membrane which contained 20 wt% of alginic acid (H) on a dry rubber basis has produced the maximum water selectivity, i.e., 136; which is 24 times higher than that of a vulcanized NRL membrane used for the separation of azeotropic mixture of aqueous ethanol.
5. The rate of permeation initially decreases at very low weight percent of hydrocolloid present at the interface of the composite membrane. As this weight percent is increased, both the rates of permeation, as well as, the separation factors are gradually increased.

6. The elastic and tear strengths of the cast and dried membranes were not good to yield a workable membrane beyond 20 wt% of any high molecular mass hydrocolloid.

7. Considering operational handling factors such as the tear strength and the elastic properties etc., the composite membrane which contained 7.5 wt% of alginic acid(H) was the best membrane for maximum separation of water from aqueous organic compound mixtures at or near the azeotropic concentration.

Nomenclature

CMC	Carboxymethyl cellulose
D_m	Molecular diffusivity
D_p	Pore volume diffusivity
HMC	Hydroxypropyl methyl cellulose
MC	Methyl cellulose
S_o	Sorption of organic compound molecules
S_w	Sorption of water molecules

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