A Qualitative Evaluation of Water and Monomethyl Hydrazine in Ethylcellulose Membrane

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ABSTRACT: Specific interaction sites of ethylcellulose (EC) with water and monomethyl hydrazine (MMH) and its hydrate have been studied by Fourier transform infrared spectra. Measurements of diffusion and sorption coefficients of MMH and water in EC were made from the reduced sorption curves to determine the overall selectivity of the membrane. Flow patterns across the membrane were examined under an optical microscope (OM) equipped with a differential interference contrast (DIC) facility. Correlation of the front velocity and the diffusivity has been used to calculate and compare these values of diffusion coefficient with that obtained from reduced sorption curve. Desorption of MMH hydrate from EC has been attributed to polymer relaxation phenomena. The physical aging process of the membrane has been monitored by FTIR analysis and mechanical strength evaluation. These studies showed that the EC membrane can be used for prolonged periods in MMH and, as such, is suitable for the separation of MMH–water solutions. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 689–700, 1999

Key words: diffusion; desorption; ethylcellulose; momomethylhydrazine; aging

INTRODUCTION

The study of interactions of any liquid when it comes into contact with a polymeric membrane is important for any membrane-based separation process as the separation mechanism is governed by the relative sorption and diffusion of the individual species through the membrane. Several methods are available to study such interactions with liquids¹⁻³ and gases.^{4,5} However, the behavior of interacting sites in polymers will vary based on the working conditions like the nature of the

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medium duration of contact and temperature. The measurements of diffusion of water and pure monomethyl hydrazine (MMH) in the ethylcellulose (EC) have been conducted in present studies by the procedures described in the literature.^{6–9} The overall selectivity calculated from diffusion and sorption values obtained for the separation of a hydrazine–water system¹⁰ closely matches with the separation factor obtained by pervaporation studies.¹¹ The polymer EC was selected for the interaction, diffusion, flow pattern, and aging studies in a MMH hydrazine environment, primarily because EC membranes showed better selectivity and reasonable flux than other tested polymer pervaporation experiments with the MMH hydrate mixture. Similar types of pervaporation results are also obtained for a MMH-water system.¹² The present study investigates the pos-

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sibility of using the EC membrane for the separation of MMH–water mixtures.

The movement of the solvent within a polymer matrix can be observed by various methods. In some studies, techniques such as examination in polarized light or addition of dye^{13,14} to the swelling medium are needed to increase the visibility of those boundaries that are not readily discernible. The diffusion pattern can be observed by using various other methods like nuclear magnetic resonance (NMR) imaging^{15–17} and gravimetric analysis. Electron spin resonance (ESR) techniques provide more direct information but utilize procedures to provide the signal rather than directly examining the solvent.¹⁸ An optical microscope¹⁹ also provides visual information of the solvent distributions; however, it requires doping to enhance the contrast between the polymer and the solvent.

Microscopy is the study of fine structure and morphology of objects with the use of microscope. The size and visibility of the polymer structure to be characterized generally determine which instrument is to be used. In the optical microscope (OM), an image is produced by the interaction of light and an object or a specimen. The image can reveal fine details in or on the specimen at a range of magnification from 4 to $100 \times$. Resolution is limited by the nature of the specimen, the objective lens, and the wavelength of light. The information obtained in the OM normally concerns the length, shape, and relative arrangement of visible features.

Aging, a phenomenon of changes of internal structure with time, is an extremely important factor in polymeric materials. For any polymer, the minimum requirement with regard to physicochemical and mechanical properties is that the material should have acceptable durability in the range of service environments depending on the application. Physical aging of polymers has been followed by measurements of viscoelastic properties,^{20,21} tensile testing,²² Fourier transform infrared (FTIR) spectroscopy,^{23–25} hardness testing,^{26–28} and differential scanning calorimetry.^{23,29,30} In this study, it was followed by FTIR analysis and tensile testing.

MATERIALS AND METHODS

Materials

The polymer used in the study was 48-49% ethoxy content ethylcellulose from Loba Chemie

(Bombay, India). Its M_n (63,156) and M_w (89,448) were determined by gel permeation chromatography (GPC) using polystyrene as the standard. Toluene, a solvent for EC, was also purchased from Loba Chemie, India, and was used as received without any further purification. MMH hydrate was kindly supplied by VSSC (ISRO), Trivandrum, India. Double-distilled deionized water was used in the experiments.

Methods: Membrane Preparation

15 wt % clear polymer solution in toluene was used for casting a membrane of the desired thickness on a clean glass plate. The solvent was evaporated at room temperature for 10 h, then the plate was placed under vacuum at 60°C for complete removal of the solvent. Thickness of the dry membrane was found to be 80 μ m (measured with a micrometer; $\pm 1 \mu$ m accuracy), and pieces of the same membrane were used in the experiments.

Interaction Studies

Interactions of water, hydrazine, MMH, and their hydrates with EC were determined by taking the FTIR spectra of a presoaked membrane. Any excess of the material adhering to the membrane was removed before taking the spectra by gently pressing the membrane with tissue paper.

Diffusion Studies

Diffusion coefficients (D) were determined from

the sorption data by plotting $\left(\frac{M_t}{M_T}\right)$ versus $\left(\frac{\sqrt{t}}{\delta}\right)$, where M_t and M_T are mass uptake at time t and at equilibrium ($t \rightarrow \infty$ as effectively), respectively, and δ is the membrane thickness.⁹ The explanation of the plots corresponding are given in the following section. The method of finding D is as follows.

A circular dry EC membrane having a 3-cm diameter is cut, weighed, and soaked in the solvent (water or MMH or hydrazine as the case may be), and the mass sorbed was determined by weighing the membrane at regular intervals of time (M_t) and finally at the steady state (M_T) . Membrane uptake was plotted against root time divided by its thickness. These experiments were conducted at 30°C. A convenient form for representing this relation is

$$\frac{M_t}{M_T} = I_a \left(\frac{\sqrt{t}}{\delta}\right) + C \tag{1}$$

Fifth-degree polynomials were fitted to the curves, and the initial slope at $t \rightarrow 0$ was determined. The value of *D* is then obtained from

$$D = \left(\frac{\Pi}{16}\right) (I_a)^2 \tag{2}$$

where I_a denotes initial slope of the curve.⁹

Based on eqs. (1) and (2), an equation was developed to find the D from the front velocities observed under the optical microscope. Inserting the I_a from eq. (1) in eq. (2), and neglecting C, which passes through origin, the following equation for D was obtained:

$$D = \frac{\Pi}{16} \left[\left(\frac{M_t}{M_T} \right) \left(\frac{\delta}{\sqrt{t}} \right) \right]^2 \tag{3}$$

Based on the continuity equation, M_t and M_T can be written as

$$M_t = \Gamma A L_t \tag{4}$$

and

$$M_T = \Gamma A L_T \tag{5}$$

where Γ is the density of liquid, A is the total density of polymer matrix, L_t is the length of the front moved during time t seconds, and L_T is the length between two ends of the polymer matrix.

Equation (6) can be derived by inserting the eqs. (4) and (5) in (3) as

$$D = \frac{\Pi}{16} \left[\left(\frac{L_t}{L_T} \right) \left(\frac{\delta}{\sqrt{t}} \right) \right]^2 \tag{6}$$

This was rearranged to get into the linear form as

$$\frac{L_t}{L_T} = \left(\frac{4}{\delta} \sqrt{\frac{t}{\Pi}}\right) \sqrt{D} \tag{7}$$

The square of the slope of the graph drawn between the $\frac{L_t}{L_T}$ and $\left(\frac{4}{\delta}\sqrt{\frac{t}{\Gamma}}\right)$ on Y and X axes, respectively, is the diffusion coefficient the liquid in the polymer matrix.

DIC Microscopic

Typical compound research microscopes are binocular, but the images in the eyepieces are identical. The two images are provided to reduce eye strain. The microscope can be provide equipped for both transmitted and incident light. The objective of the present study is to observe the rate and the manner in which the liquid species, namely, water, pure MMH, and MMH hydrate, are passing through the membrane. A Ziees Axioskop compound microscope is used for the present study. Unless specified, all pictures were drawn at $10 \times$ magnification under a differential interference contrast set up (Normarski Optics). The light source is used a halogen bulb operated at 12 V and 15 W capacity.

Aging Experiments

Physical aging of the film was followed by recording the FTIR spectra of the soaked membrane in the MMH hydrate at intervals of 15 days over a period of 6 months. These were conducted by soaking specimens of the membrane in liquids for the required amount of time. At the end of the soaking period, the surface is wiped free of adhering liquid and weighed. The difference in the weights per unit weight of the dry membrane gave the sorption percentage. This membrane was then dried thoroughly to remove the sorbed solvent, initially at room temperature and then at temperature around 50-60°C under vacuum for at least 2 days. FTIR spectra (Nicolet-740, Perkin-Elmer-283B FTIR spectrometer) of the dried sample were recorded at a scanning rate of 100 sweeps min and averaged with the averaging procedures supplied with the instrument.

Mechanical Testing

Mechanical strengths of the EC membrane $(5 \times 1 \text{ cm})$ in the wet and dried states were obtained on a bench-scale Instron tester (Instron-1026 Testing Machine in the tensile mode with a chart speed of 1 cm min). The percentage of elongation at break and the ultimate stress (at the break point) of the membrane for a period of 30, 60, and 180 days were obtained.

RESULTS AND DISCUSSIONS

Interaction Studies

The FTIR spectrum of the pure dry EC film is shown in Figure 1. The peak at 3500 cm^{-1} is of —OH groups present on the closed ring structure of the polymer repeating units. It is also likely



Figure 1 FTIR spectrum of the ethylcellulose membrane.

that the polymer may have some sorbed water already due to its hydrophilic nature. The same also represents intra- and intermolecular hydrogen bonding due to the --OH groups. The shoulder peak at 3250 cm⁻¹ corresponds to associated -OH of intermolecular bonding. The small but not sharp peak at $\approx 2950 \text{ cm}^{-1}$ corresponds to asymmetric structure vibrations of the -OC₂H₅ ethoxy groups. There are small peaks between 2850 and 2720 cm⁻¹ corresponding to --CHO stretching, which is sharp at 2650 cm^{-1} . The peaks and valleys between 2000 and 2250 cm^{-1} are of the ---CH stretching (of the saturated ring structure). The peaks at 1730 and 1650 cm^{-1} are for bending of the -OH group structure. The 1350 and 1300 cm⁻¹ responses are due to the $-CH_2$ bending vibrations.

Interactions of EC with Water

The FTIR spectrum of the wet EC film soaked in water shown in Figure 2 can be compared with that of pure dry EC in Figure 1. As expected, the peak at 3500 cm⁻¹ is weakly affected, but the shift of its overtone at ≈ 1625 cm⁻¹ toward the lower regions is clearly due to absorption of water in the membrane. The —CH and —OH bending between 1300–1400 cm⁻¹ are affected to some extent, but the ethoxy group vibrations are brought into focus at 2950 cm⁻¹. Otherwise, the spectrum remains largely unaffected, indicating that the EC film is hydrophilic but has somewhat fewer interactions with water molecules.

Interactions of EC-MMH

The locations or groups with which MMH has the specific interactions are shown in Figure 3. As in

the case of hydrazine,¹⁰ MMH is interacting with the OH groups at 3500 cm⁻¹. This was confirmed by the decrease in the percentage of transmittance at this position. The decrease in wave number of appearance of OH groups clearly indicates the strong interaction of the group with MMH. A new peak at 3330 cm⁻¹ corresponds to the stretching vibration of NH group. Leonard and Owens³¹ proposed an equation for identifying the symmetric and asymmetric —NH₂ stretching in a given compound. This can be written as

$$\gamma_s = 345.53 + 0.876 \ \gamma_{as} \tag{8}$$

where γ is stretching vibrations of symmetric (s) and asymmetric (as) vibrations of ----NH2 groups, respec-tively. Let us suppose that a peak at 3330 cm⁻¹ is due to asymmetric vibrations, then the corresponding symmetric vibrations should appear around 3262 cm^{-1} clearly. A small and broad peak at 3250cm⁻¹ identified in the Figure 3 clearly confirms that the response at 3330 cm^{-1} is due to the asymmetric stretching vibrations of -NH₂ group. In general, the occurrence of this peak is around 3500 cm^{-1} . The decrease in 170 cm⁻¹ peak strongly confirms the hydrogen bonding interactions of MMH and OH functional groups of the EC. The same trend was also observed in symmetric stretching vibrations. The $-OC_2H_5$ ethoxy group at 3000 cm⁻¹ has interactions with MMH as in the case of water and hydrazine hydrate.¹⁰ A small peak appearing at 1622 cm^{-1} is due to the in-plane bending, corresponding to CH₂ scissoring, which is present in \dot{CH}_3 — N_2H_3 (MMH). The small but sharp peak at 1450 cm⁻¹ is due to —NH— bending vibrations. A



Figure 2 FTIR spectrum of the ethylcellulose membrane soaked in water.



Figure 3 FTIR spectrum of the ethylcellulose membrane soaked in monomethyl hydrazine.

rather characteristic out-of-plane bending $-NH_2$ peak corresponding to the $-CH_2$ twisting is seen at 650 cm⁻¹.

The peak at 1800 cm^{-1} has completely disappeared when EC comes into contact with the MMH. Moreover, the peak at 1622 cm^{-1} , which becomes rather sharp again indicates strong interaction of $-NH_2$ with the other groups present in it. The corresponding peaks at 1622, 1360, and 700 cm^{-1} clearly indicate the presence of MMH, and the positional shifts at 3330, 3500, and 1622 cm^{-1} confirm the interaction of the MMH with the EC membrane.

Diffusion, Sorption, and Selectivity

Figure 4(a,b) shows the variation of
$$\left(\frac{M_t}{M_T}\right)$$
 with

 $\left(\frac{\sqrt{t}}{\delta}\right)$ from which values of I_a are obtained. Inserting the values in eq. (2) gives the values of D as 2.57×10^{-8} and 9.51×10^{-9} cm² s for water and MMH, respectively. The equilibrium percentage sorption were 3.4, and 15.66 for water and MMH, respectively. Solubility coefficient values of the penetrant can be calculated by calculating the volume of the penetrant observed per cubic centimeter of dry polymer and dividing it by the vapor pressure of penetrant³² at the temperature at which the experiments were conducted. The values of S were calculated and found to be 1.13 $\times 10^{-3}$ and 3.89×10^{-4} g g⁻¹ mm⁻¹ Hg for water and MMH, respectively. From the solubility and diffusion coefficient values of water and pure MMH with the EC, the relative permeability or the overall selectivity can be calculated by

Overall selectivity =
$$\left(\frac{S_{\text{water}}}{S_{\text{MMH}}}\right) \left(\frac{D_{\text{water}}}{D_{\text{MMH}}}\right) = 7.83$$
 (9)



Figure 4 Reduced sorption curves of ethylcellulose with (a) water and (b) monomethyl hydrazine.

where S is the solubility coefficient. The overall solubility obtained in this manner is an approximate estimate as the above procedure is applicable only to cases where penetrant partial pressures are nearly those in the experiments. Further, prediction of mixture selectivity based on pure component sorption and diffusion serves only as a guideline in cases where penetrants interact intensively with the polymer matrix. However, from this result, it was confirmed that the EC membrane is more selective to water and that water has a higher diffusivity coefficient (and flux) compared to MMH. Under these conditions, diffusion of MMH will require a greater activation energy.

The compatibility of EC with MMH and water is explained on the basis of Hansen's solubility parameter Δ and Flory–Huggins interaction parameter χ . The compatibility between water, MMH, and the polymer is indicated by the following relationship:

$$\Delta = [(\delta_{p,i} - \delta_{p,3})^2 + (\delta_{d,i} - \delta_{d,3})^2 + (\delta_{h,i} - \delta_{h,3})^2]^{1/2}$$
(10)

where δ_p , δ_d , and δ_h are the polar, dispersive, and hydrogen-bonding contributions, and Δ is the magnitude of the vectorial distance in the threedimensional diagram of δ_p , δ_d , and δ_h on x, y, and z axis, respectively.³³ Inserting the values of δ_t of water, MMH, and EC,³⁴ the values of Δ is found to be 9.8 and 30.0 for MMH and water, respectively, with EC. Similarly, the Flory-Huggins interaction parameters³⁵ for MMH and water with the EC membrane were calculated and are found to be equal to 1.39 and 2.54 for EC-MMH, and ECwater systems, respectively. The values of the Δ and χ for MMH with EC are very small compared with that obtained for EC-water system. This could be the reason for the higher solubility of MMH in polymer. Further, water is a smaller molecule compared to MMH. A similar type of behavior was observed in the case of ethanolwater separation³⁶ with hydrophobic PVC, in which PVC had a greater affinity and sorption coefficient for ethanol than water, where water showed a greater overall diffusion selectivity. The selectivity values obtained from diffusion and solubility are of similar order of magnitude as in the pervaporation experiments, which gave an average selectivity value equal to 5.6 for MMH. This confirms the hypothesis that MMH is strongly held by polymer molecules while water is less

strongly held and is thus able to diffuse faster than MMH. Finally, the possibility that the observed effects are in line with the expectations even in the absence of specific interactions of penetrants and polymer matrix cannot be ruled out altogether.

Flow Pattern of Liquid in Membrane

Under the OM, in general, the following two distinct boundaries are evident in a swelling glassy polymer: the penetrant front (inner boundary) and the swelling front (outer boundary). In some polymer solvent systems, these advancing boundaries are so sharp that they are clearly visible. This was true for glassy gelatine beads swollen with water. This highly contrasted boundary between dry and swollen regions of a polymer has enabled direct measurements with optical microscopy.^{37,38} Fickian and non-Fickian transport of solvent in the glassy membrane can be demonstrated by observing a sharp distinct boundary between the inner glass core and the outer swollen rubbery phase. In particular, non-Fickian transport behavior has been directed towards application in controlled drug delivery.³⁹ Controlled drug delivery is possible when the solvent front velocities are lower than drug diffusion through the swollen phase so that the front is the ratecontrolling entity. Klech and Simonelli⁴⁰ observed the effect of solution pH on moving the boundary in a controlled drug delivery system through a membrane by using OM. Water penetration into the glassy gelatine matrix is one of the combinations that allows direct measurement of the inner penetrant boundary. On account of this situation, OM becomes an effective measuring techniques for the study of these variables that may offer the velocity of either moving front in glassy gelatine beads.

Liquid sorbed by the membrane causes some structural relaxation in the membrane. But, the relaxation, unlike diffusion, is not a fast process. Front movement caused by the diffusion of liquid results in physical changes in the membrane. On the other hand, the chemical changes, like the structural modifications and/or relaxation caused by the sorbed liquid in a polymer matrix, should cause definite and detectable dimensional changes in the membrane. This is true only when the polymer sorbs higher amount of liquid. In such cases, dimensional changes in the polymer structure can be recorded by weighing methods or by scanning under an ordinary microscope. When a polymer sorbs, as in the present case, a lesser amount of solvent, no detectable structural changes will result. In such cases, after an elapse of sufficient time, that is, after attaining the steady state, the sorbed liquid starts binding or interacting or destabilising the polymer matrix, causing a chemical change. Such relaxation, caused by the chemical changes, will result in minute changes in the matrix at microscopic level. Then the behavior of the matrix before and after relaxation will be different. Relaxation effects the transmission of optical beam passing through the material. When a white light passes though the relaxed polymer, the inhomogeneity caused by the relaxation will scatter the light, producing several combinations of colors. Hence, the transmitted light will exhibit a difference in color. A good example for this is the observation of spherulites under OM; here, the spherulite, because of a difference in the orientation with the other parts of the membrane, produces its own color. Even an injection-molded thermoplastic polymer sample, when viewed under OM, reveals various colors due to the difference in orientation at the skin and the core regions.⁴¹ By observing the change in the color and the difference in intensity of the transmitted light, structural relaxation within the polymer caused by the sorbed liquid can be examined.

Water in EC

The movement of water across an EC membrane of 100 μ m thickness was observed with the optical microscope. A small strip of dry EC membrane was placed on the platform just above the light source. One end of the membrane was placed in contact with a good quality filter paper, which was previously soaked in distilled water. Proper care was taken to avoid any possibility of contact of the filter paper to any surface of the membrane, which might result in water droplets on it. Edges of the membranes were very thin, and, hence, use of filter paper to place minimum amount water on it was essential. The filter paper acts as a solvent reservoir. Experiments were carried out without using dyes as the dye may interfere in the movement of mixture of solvents like the MMH hydrate.

As soon as the filter paper and membrane are placed end to end in contact, water starts diffusing into the membrane. Membranes as well as water are transparent, and, hence, the water diffusion is clearly visible through the eyepieces.



Figure 5 OM flow pattern studies of water in EC membrane: (a) dry EC; (b) after 20 and (c) 45 min; (d) saturated with water.

Figure 5(a) is an optical micrograph of pure EC strip. The front developed by the water moving in was snapped at time intervals of 20 and 45 min, as shown in Figure 5(b,c), respectively. At the end, a sample of EC membrane previously soaked in water to attain steady state was also examined by optical microscope. This is shown in Figure 5(d). The filter paper is kept in a wet condition with water throughout the experiment. From the above optical micrographs, it was clear that the water movement in the membrane is steady and constant. The movement clearly creating a definite boundary (front), which is visible through OM. The front movement is sufficiently sharp. The last photograph, that is, the water-saturated EC membrane, was brighter than the pure EC membrane [Fig. 5(a)]. The brightness is especially due to the relaxation of the polymer matrix caused by water. The brightness was not observed when the water was diffusing in the membrane because it will not have sufficient time



Figure 6 OM flow pattern studies of MMH in EC membrane: (a) after 10 and (b) 20 min; (c) just before saturation; (d) saturated with MMH.

to relax in the matrix. On the contrary, in the last snap, where the membrane was in contact with water for longer period, allowing sufficient time for relaxation, some relaxation is caused, resulting in enhanced brightness of the film.

MMH Movement in EC

Experiments were repeated with EC membrane and MMH. MMH is hygroscopic in nature and produces lot of fumes as it comes into contact with air. The passage of pure MMH in the EC membrane is shown in Figure 6(a-d) at different times of the experiment. Compared to the case with pure water, here it is not possible to observe the exact front movement. Instead of the liquid movement, the movement of the vapors generated by MMH is clearly visible. First the vapors activate the membrane layer through which the liquid diffuses. White cloudlike front in the photomicrographs is the movement of the liquid diffusing into the membrane. Figure 6(c) is taken at a lower magnification just before the liquid reached the other end; wherein the white cloud is almost covering the entire area. Figure 6(d) is a picture of the membrane saturated with the MMH. Even this photograph, similar to the one of water-saturated EC, produces brightness in the membrane.

By measuring and following the distance travelled by the liquid at different times (L_t) from the photomicrographs and the total time required (T)to reach the other end of distance (L_T) , a plot of the straight line passing through the origin was obtained (Fig. 7) when the graph was drawn between $\frac{L_t}{L_T}$ and $\left(\frac{4}{\delta}\sqrt{\frac{t}{\Pi}}\right)$ on the Y and X axis, respectively. The square of the slope of the graph gives D for MMH equal to 2.05×10^{-9} cm² s. This value is nearly matching the D calculated from the reduced sorption curves explained earlier.

MMH in EC

It is already stated that the relaxation is a slow process. Strips of EC membranes are allowed to relax by soaking them in MMH and MMH hydrate solutions for sufficient time (until they reach the steady state). After removing excess solution, one such membrane was examined. The optical micrograph of the film saturated with MMH is shown in Figure 8(a), where the membrane is of a bright yellow color. As such, EC membrane and pure MMH or even MMH hydrate



Figure 7 Graphical representation of MMH front movement in the EC membrane.



Figure 8 OM flow pattern studies of MMH in EC membrane: (a) saturated with pure MMH; (b) MMH hydrate; after (c) 15, (d) 45, (e) 60, (f) 90, and (g) 120 min desorption.

are colorless substances. Optical observation also confirmed the same. Clearly, structural changes due to the relaxation are responsible for imparting color. A change in the color of the membrane was not seen at the time of front development (within that time, there is no possibility of any relaxation). Moreover, the membrane saturated with MMH hydrate also generated a yellow color of lesser intensity. One point already stated is that the membrane saturated with water is bright white. All three experimental results confirm that the development of bright yellow color is due to relaxation caused by the MMH liquid component. With hydrated MMH, where the concentration of MMH is comparatively less, the membrane gave a yellow color of lesser intensity [Fig. 8(b)]. The decreased intensity is due to the reduction in MMH concentration.

MMH Desorption Studies

The desorption study was carried out by evaporating MMH hydrate present in the membrane and observing the change in the color of the membrane. Figure 8(c) is an optical micrograph snapped after 15 min of evaporation. Experimental data proved that the evaporation rate of MMH is faster than water due to its low boiling points. This implies that for the period of desorption, the membrane is loosing a greater amount of MMH than water. Poor brightness of the yellow color in the membrane, snapped after 15 min of solvent evaporation, is due to a major loss of MMH from the membrane. The micrographs taken at evaporation timings of 45, 60, 90, and 120 min are shown in Figure 8(c-g), respectively, which confirm that during desorption, the concentration of MMH in the membrane is steadily decreasing. Simultaneously, water also evaporates from the membrane, but the losses are low compared with that of MMH. After a certain period of desorption, a state is reached where all MMH is almost completely evaporated so that the membrane contains only water but in lesser quantity. The last snap compared with the one of the EC membrane saturated with water indicate that both were similar with reference to brightness.

The case of membrane saturated with azeotropic liquid is worth considering. At this composition at any time, the membrane should contain the same compositions of the mixtures as it is in the beginning. Photomicrographs don't confirm this hypothesis, as expected. The membrane is highly selective to one of the components of the feed, and that particular component competes with the other component and diffuses well inside the membrane material. Now the membrane sublayers are enriched selectivity with one of the components. Hence, the membrane is not saturated with liquid of azeotropic composition. This is how the separation takes place in pervaporation. The photomicrographs shown above confirm that the yellow color produced by the membrane is due to the presence of MMH.

Mechanical Strength

The FTIR spectra of the EC membrane after soaking periods of 30, 90, and 180 in MMH hydrate are shown in Figure 9(a-c), respectively. It can be seen by comparing the spectra with that of the unsoaked membrane in Figure 1 that no physical

Figure 9 FTIR spectra of aged EC membrane soaked in MMH hydrate: (a) after 30 and (b) 180 days; (c) accelerated aged.

or chemical changes had taken place during the above soaking periods. As expected, the wet membranes had a comparatively reduced mechanical strength compared to the dry ones. Soaked membrane got some brittleness that always reduces the strength and percentage of elongation; but the soaked and dried membrane did not show any loss in its original strength, which was almost fully regained, and similarly, the percent elongation at break also remained the same. One interesting observation about the membranes soaked in MMH hydrate is that the membranes are brittle when soaked; but as the liquid evaporates during drying, the membrane regains its flexibility and the mechanical strength. The membranes soaked in water do not show such behavior. The results shown in Table I combined with the FTIR studies point to the fact that no degradation had taken place, even after 6 months of soaking time.

CONCLUSIONS

From the results obtained by FTIR analysis, it can be concluded that both MMH and water are influencing the free —OH group in the polymer matrix. A shift of this peak towards the lower wave number is an indication of the strong hydrogen bonding interaction between MMH and EC. Moreover, MMH interacts more with the ethoxy groups of EC than that of water. MMH interactions with EC are more effective and stronger than with water, and, hence, its equilibrium sorption is greater than that of water.

Diffusion coefficients of the solvents in EC determined by the reduced sorption curves are found to be 2.57×10^{-8} and 9.5×10^{-9} cm² s for water and MMH, respectively. Linearity of the curves were observed only below 0.5 of $\frac{M_t}{M_T}$, indicating that the diffusion coefficients were independent of the concentrations of water and MMH

Table IMechanical Properties of Ethylcellulose Membrane Soakedin MMH Hydrate

Soaking Condition	Nature of Membrane	Elongation at Break (%)	Ultimate Tensile Strength (kg cm ²)
Untreated	Dry	6.0	28.25
1 Month	Wet	5	16.34
	Dry	5.67	28.0
2 Months	Wet	4.68	16.66
	Dry	5.6	27.76
6 Months	Wet	4.6	16.84
	Dry	5.87	27.54

in EC.⁴² The solubility coefficients of water and MMH with EC are found to be 1.13×10^{-3} and 3.89×10^{-4} g g⁻¹ mm⁻¹ Hg, respectively. The overall selectivity of EC for water is 7.83. The greater interaction and sorption coupled with the slower diffusion of the other component MMH has made EC less selective for MMH.

During the diffusion studies with OM, it was observed that the rapid development of a liquid front does not cause any structural changes in the membrane. Desorption of MMH hydrate from EC has been monitored under OM and by taking the photographs at regular intervals of time, which clearly provide evidence that desorption of MMH from the membrane has been faster than water. An equation correlating the velocities of moving front and D has been derived. From this equation, the D was found to be 2.03×10^{-9} . The validity of this equation was checked by comparing D calculated from other methods. Significant reorientation of the polymer matrix was observed from the desorption experiments.

Physical aging of the film was followed by recording the FTIR spectra of the soaked membrane in MMH hydrate at intervals of 15 days over a period of 6 months. Mechanical strength and the percentage of elongation of the membranes soaked in MMH hydrate were similarly assessed. The FTIR and mechanical tests confirm that the membrane is neither degraded nor lost its mechanical properties even after 180 days of exposure.

Based on the above observation, it was concluded that ethylcellulose membranes can be used for the dehydration of MMH, with the membrane being permselective to water.

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