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FTIR, Diffusivity, Selectivity, and Aging Studies of Interactions of Hydrazine, Water, and Hydrazine Hydrate with the Ethylcellulose Membrane†

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ABSTRACT: Specific interaction sites of ethylcellulose with water, hydrazine, and the mixtures of hydrazine hydrate and water have been studied by FTIR spectra. Measurements of diffusion and sorption coefficients of these materials in ethylcellulose were made to determine the overall selectivity. Aging studies of the membrane including an accelerated aging test have also been conducted. The influence of aging on physico-chemical and mechanical properties were assessed by FTIR studies and mechanical tests. These studies showed that the ethylcellulose membrane can be used for prolonged periods in hydrazine hydrate and as such is suitable for the separation of hydrazine−water mixtures.

Introduction

There are several methods to study the specific interaction sites in polymers when they come into contact with liquids,[1−3] or gases.[4,5] The interacting sites in polymers will vary based on the working conditions like nature of the medium in contact, temperature, and duration. Interaction studies will be useful in qualitative and quantitative assessment of the possibility of pereferential separations of one of the components from a mixture using membranes. The study investigates the possibility of using the EC membrane for separation of hydrazine−water mixtures. It is generally observed in pervaporation that the component having a better interaction even at a lesser diffusion rate will be separated selectively from other component(s). However, the degree of interaction, as well as diffusion, and selectivity are strongly dependent upon the composition of the feed mixture. Thus, the separation process is the result of interrelated phenomena of both sorption and diffusion coefficients. The measurements of diffusion of water, and pure hydrazine in the membrane have been conducted in the present studies by the procedures described in the literature.[6−9] The overall selectivities observed during pervaporation studies are reported elsewhere.[10]

Aging, a phenomenon of changes of internal structure with time, is an extremely important factor in polymeric materials. For any polymer there is a minimum requirement with regard to physico-chemical and mechanical properties where the material shows acceptable durability in a range of serivce environments depending on the application. Physical aging of polymers has been followed by measurements of viscoelastic properties,[11,12] tensile testing,[13] FTIR spectroscopy,[14−16] hardness testing,[17−19] and differential scanning calorimetry.[14,20,21] In this study, it was followed by FTIR analysis and tensile testing. The polymer ethylcellulose (EC) was selected for the interaction, diffusion, and aging studies in a hydrazine environment, primarily because EC membranes gave better selectivity and reasonable flux in pervaporation experiments with the hydrazine hydrate mixture than other tested polymers. The reasons for the performance of EC membranes have been explained elsewhere.[10]

Materials and Methods

Materials. Hydrazine is a well-known liquid propellant and an oxygen scavager which forms an azeotrope with water at 71.1 wt % hydrazine, and the azeotrope has a pH > 12. Used as an oxygen-scavenging agent in boilers, hydrazine is a highly reducing as well as a hydrolyzing compound. Pure hydrazine and hydrazine hydrate were supplied by VSSC (ISRO), Trivandrum, India. Ethylcellulose (powder form, ethoxy content: 48−49%) of Loba Chemie, Bombay, India was used as received. Its M_n (63 156) and M_w (89 448) were determined by GPC using polystyrene as the standard. LR grade toluene was also obtained from Loba Chemie.

Methods. Membrane Preparation. An approximately 15% by wt solution of EC in toluene was prepared and cast on a clean glass plate as a dense membrane. The solvent was evaporated to dryness, and the film was vacuum dried for solvent removal. The membrane thickness, measured with a micrometer, was found to be 45 μm.

Interaction Studies. Interactions of water, hydrazine, and hydrazine hydrate 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 M_t/M_α versus $\sqrt{t}/L$, where M_t and M_α are mass uptake at time t and at equilibrium ($t \rightarrow \alpha$ as effectively), respectively, and L is the membrane thickness.[9] The method of determining D is given below.

A circular dry EC membrane having a 3 cm diameter is cut, weighed, and soaked in the solvent (water 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_α). Membrane uptake was plotted against time. These experiments were conducted at 30 °C. Fifth degree polynomials were fitted to the curves and the

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Table 1. Mechanical Properties of Ethylcellulose Membrane Soaked in Hydrazine Hydrate

soaking conditions	nature of membrane	% elongation at break	ultimate tensile strength, kg/cm^2
untreated	dry	6.0	28.25
3 months	wet	7.5	20.6
	dry	6.0	27.5
6 months	wet	7.5	19.9
	dry	6.0	27.0
8 h at 60 °C[a]	wet	6.0	20.0
	dry	5.0	27.5

[a] Accelerated aging test.

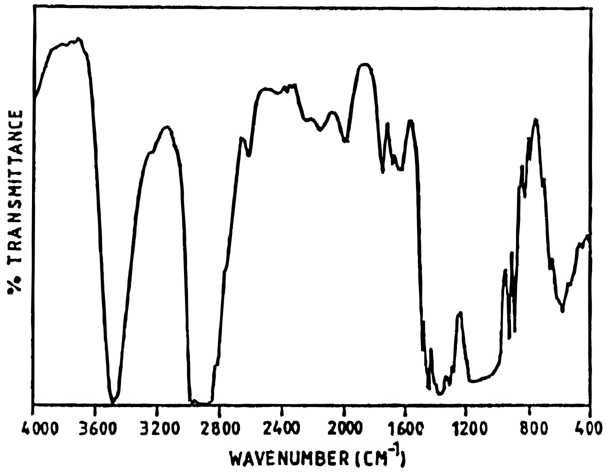

Figure 1. FTIR spectrum of the ethylcellulose membrane.

initial slope at $t \rightarrow 0$ was determined. The value of D is then obtained from

$$D = [\Pi/16](I_a)^2 \quad (1)$$

where I_a denotes the initial slope of the curve.[9]

Aging Experiments. Physical aging of the film was followed by recording the FTIR spectra of the soaked membrane in hydrazine hydrate at intervals of 1 month over a period of 6 months. These were conducted by soaking specimens of the membrane in hydrazine hydrate 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 percent sorption. This membrane was then dried thoroughly to remove the sorbed solvent, initially at room temperature and then at temperatures 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 × 1 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) are given in Table 1, for unsoaked and soaked membranes for a period of 90 and 180 days.

An accelerated aging test was also conducted by soaking the membrane in the solvent at 60−65 °C for 2 days. The film was dried completely, and its condition was assessed by FTIR and mechanical tests, as described above.

Results and Discussion

FTIR Studies. The FTIR spectrum of the pure 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 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 ≈2950 cm^{-1} corresponds to asymmetric structure vibrations of the $-OC_2H_5$ 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.

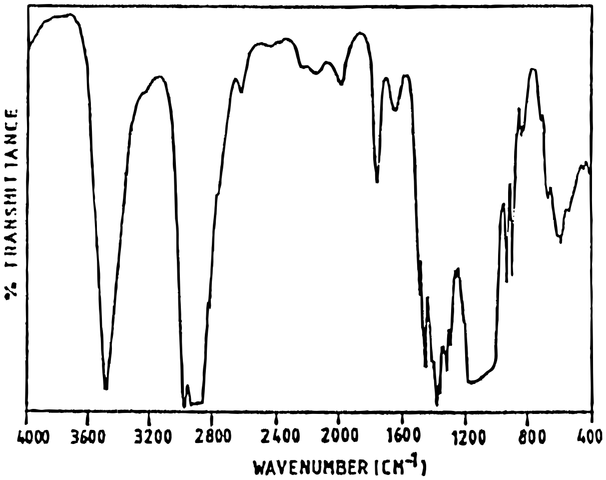

Figure 2. FTIR spectrum of the ethylcellulose membrane soaked in water.

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 EC in Figure 1. As expected, the peak at 3500 cm^{-1} is weakly affected (perhaps because of already adsorbed water molecules), 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 and 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.

EC−Hydrazine Interactions. The locations of groups with which hydrazine has specific or strong interactions are quite obvious from a comparison of the spectrum in Figure 3, for EC−hydrazine with that of pure EC in Figure 1. Hydrazine strongly interacts with OH groups at 3500 cm^{-1}, and transmittance of the wet membrane is sharply reduced. The percent absorbency by OH vibrations becomes rather high, and it increases with a decrease in wave number. A new peak is seen between 3300 and 3500 corresponding to the free and associated forms of $-NH_2$ and −NH−. The former corresponds to that of free hydrazine molecules and the latter to hydrazine bonded with either water already present in the polymer or the −CH of the cellulosic structure. The peak of associated −OH at 3200 cm^{-1}, which was only a shoulder in the dry EC film or in the presence of water, becomes rather sharp in the presence of hydrazine. The ethoxy $-OC_2H_5$ group of 3000 cm^{-1} has similar interactions with hydrazine, as in the case of water. In the range 2250−3000 cm^{-1} corresponding to the −NH structure, the interaction (rather sharp) of

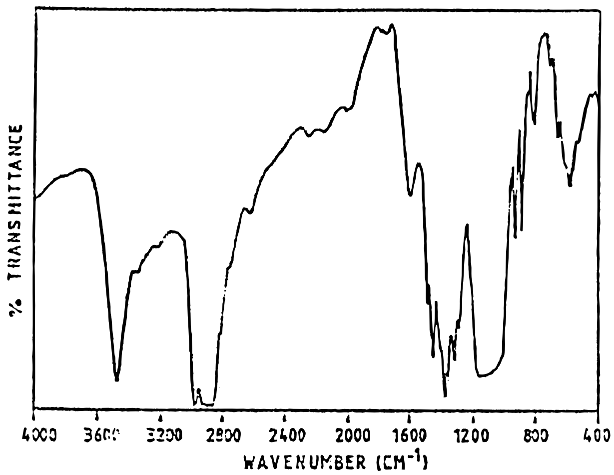

Figure 3. FTIR spectrum of the ethylcellulose membrane soaked in hydrazine.

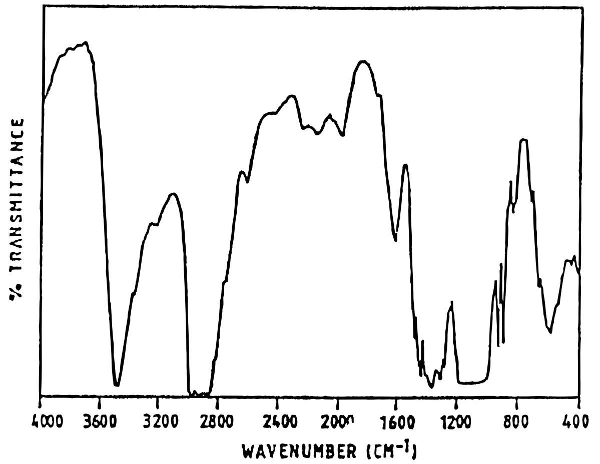

Figure 4. FTIR spectrum of the ethylcellulose membrane soaked in hydrazine hydrate.

EC with hydrazine can be clearly seen. In the same range, water showed hardly any interactions with EC. The peak at 1800 cm^{-1} is not recorded, with the peak at 1600 cm^{-1} becoming rather sharp, again indicating strong in-plane bending interactions of NH_2. The OH peak at 2050 cm^{-1} is also affected by hydrazine. However, both water and hydrazine show somewhat similar interactions and effects in the range 1200−1600 cm^{-1}. The peak at 1800 cm^{-1} is also rather sharp, indicating the possibility of CH···NH type bonding, thereby affecting the −CH bending.

Interactions of EC−Hydrazine Hydrate. When both hydrazine and water molecules are present, it is expected that the locations where water has specific interactions or strong affinity will be slightly or not at all affected by hydrazine and vice versa. Similarly, locations where both show interactions will either be affected by both of them or get nullified or reduced because of stronger interactions between water and hydrazine themselves. The FTIR spectra of the pure EC film and the EC film soaked in hydrazine hydrate are shown in Figures 1 and 4, respectively. For example, the interactions at 3200−3400 cm^{-1} are still present in the hydrazine hydrate mixture, just as in the case of hydrazine alone. The interactions of $-OC_2H_5$ with either of them is suppressed to a major extent. Similarly, the broad shoulder observed in the presence of pure hydrazine between 2200 and 2600 cm^{-1} is somewhat restored to the original shape in the presence of water. The apparent effects of hydrazine at 2000 and 1900 cm^{-1} are suppressed greatly by H_2O, but a new peak at 1730 cm^{-1} of hydrazine hydrate is clearly seen. This could be due to the interactions of −OH (of water) and $-NH_2$ (of hydrazine). Lastly, the second type of behavior expected and explained above is seen in the case of −OH and −CH bending, where the effects of N_2H_4 and water are counterbalanced or nearly nullified, and no effect on EC is present at these wavenumbers (1200−1600 and 400−800 cm^{-1}).

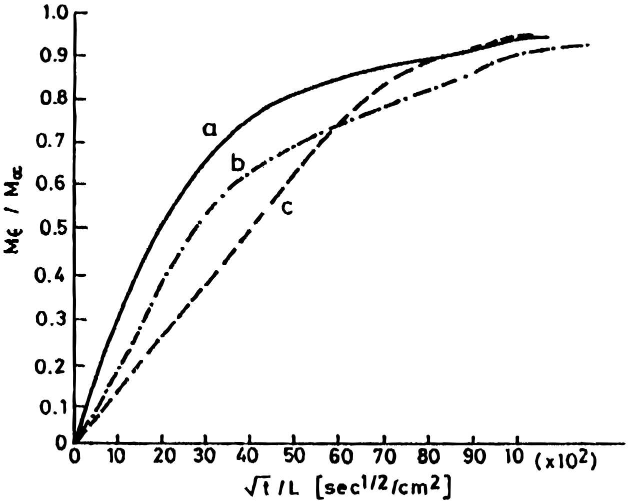

Figure 5. Reduced sorption curves of ethylcellulose with (a) water, (b) hydrazine, and (c) hydrazine hydrate.

Diffusion, Sorption, and Selectivity. Inserting the values of T_a obtained from Figure 5a−c in eq 1 gives the values of D as 2.57×10^{-8}, 0.28×10^{-8}, and 0.19×10^{-4} cm^2/s for water, hydrazine, and hydrazine hydrate, respectively. The equilibrium percentage sorptions were 3.4, 7.96, and 4.86 for water, hydrazine, and hydrazine hydrate, respectively. Solubility coefficient values of the penetrant can be calculated by calculating the volume of penetrant observed per cubic centimeter of dry polymer and dividing it by the vapor pressure of the penetrant[22] at the temperature at which the experiments were conducted. The values of S were calculated and found to be 1.13×10^{-3}, 4.71×10^{-3}, and 4.28×10^{-3} (g/g)/mmHg for water, hydrazine, and hydrazine hydrate, respectively. From the solubility and diffusion coefficient values of water and pure hydrazine with the EC, the relative permeability or the overall selectivity can be calculated by

$$\text{overall selectivity} = \frac{S_{\text{water}}}{S_{\text{hydrazine}}}\frac{D_{\text{water}}}{D_{\text{hydrazine}}} = 2.1657 \quad (2)$$

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 is only 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 hyrazine. This is consistent with the fact that hydrazine is strongly held by the membrane (as shown by sorption and IR studies) and less of it exists in the bulk free liquid form due to its strong interaction with water. Under these conditions, diffusion of hydrazine will require a greater activation energy.

The compatibility of EC with hydrazine and water is explained on the basis of Hansen's solubility parameter Δ and Flory–Huggins interaction parameter χ. The compatibility among water (1), hydrazine (2), and the polymer (3) is indicated by the relationship

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

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 3-dimensional diagram of δ_p, δ_d, and δ_h on the x, y, z axis, respectively.[23] Inserting the values of δ_l of water, hydrazine, and EC,[24] the values of Δ are found to be 16.0 and 30.0 for hydrazine and water, respectively, with EC. Similarly, the Flory–Huggins interaction parameter[25] for hydrazine and water with the EC membrane were calculated and are found to be equal to 1.84 and 2.54 for the EC–hydrazine and EC–water systems, respectively. The values of the Δ and χ for hydrazine with EC are very small compared with that obtained for the EC–water system. This could be the reason for the higher solubility of hydrazine in the polymer. Further, water is a smaller molecule (d = 3.106 Å) compared to hydrazine (d = 3.7565 Å) or hydrazine hydrate (d = 4.31 Å).[26]

A similar type of behavior was observed in the case of ethanol–water separation[27] 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 obtained from diffusion has yielded results which are of similar order of magnitude (under static feed conditions) as in the pervaporation experiments, which gave an average selectivity value equal to 3.74. This confirms the hypothesis that hydrazine is strongly held by polymer molecules while water is less strongly held and is thus able to diffuse faster than hydrazine. 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.

Mechanical Strength Evaluations. The FTIR spectra of the EC membrane after soaking periods of 30 and 180 days in hydrazine hydrate are shown in Figure 6a,b, respectively. It can be seen by comparing the spectra with that of the unsoaked membrane in Figure 1 that no physical or chemical changes had taken place during the above soaking periods. As expected, the wet membranes had a somewhat reduced mechanical strength compared to the dry ones, but it is not unduly low. Perhaps small sorption capacity and low membrane swelling are responsible for this marginal change. More importantly, 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. These results combined with the FTIR studies point to the fact that no degradation had taken place even after 180 days (6 months) of soaking time of the membrane.

The corresponding FTIR spectrum after accelerated aging is shown in Figure 6c, and the Instron results are presented in Table 1, which again indicate no major changes in the integrity of the membrane.

Conclusions

From the results obtained by FTIR analysis it can be concluded that both hydrazine and water are interacting with free –OH and ethoxy groups of EC. Hydrazine interactions with EC are more effective and stronger than with water, and hence its equilibrium sorption is greater than that of water. However, in hydrazine hydrate EC showed less interaction than water or hydrazine alone, possibly because of the stronger interactions between water and hydrazine than between water or hydrazine with the EC polymer matrix.

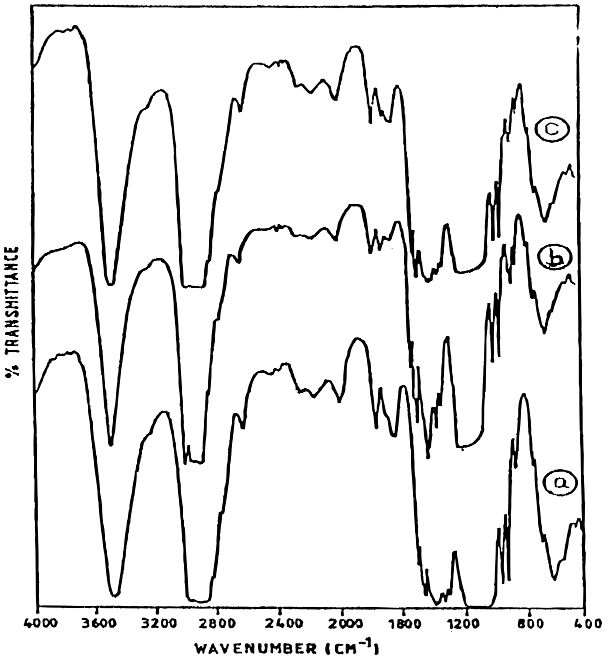

Figure 6. FTIR spectra of the ethylcellulose membrane (a) after 30 days, (b) after 180 days, and (c) accelerated aged.

Diffusion coefficients of the solvents determined by the reduced sorption curves (M_t/M_α vs $\sqrt{t}/L$) are found to be 2.57×10^{-8} and $0.28 \times 10^{-}18$ cm^2/s for water and hydrazine, respectively, in EC. But, for the EC–hydrazine hydrate system the graph is even linear beyond values of $M_t/M_\alpha > 0.5$, indicating that the diffusion coefficient is a function of concentration.[28] In this case the mean value of the diffusion coefficient is found to be 0.19×10^8. The solubility coefficient of water, hydrazine, and hydrazine hydrate with EC are found to be 1.13×10^{-3}, 4.71×10^{-3}, and 4.28×10^{-3}. The greater interaction and sorption coupled with slower diffusion of hydrazine has made it less selective with EC, and hence the membrane is selective toward water.

The aging performance of EC with hydrazine hydrate has been studied by FTIR and mechanical strength evaluations. The results showed that the membrane had neither degraded nor lost the mechanical properties even after 6 months of soaking. Accelerated aging tests also showed a similar performance.

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