WATER-DEUTERIUM OXIDE EXCHANGE IN POLYMERS USED IN SPACECRAFT
Water-Deuterium Oxide Exchange in Polymers Used in Spacecraft Applications

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The replacement of water (H2O) by deuterium oxide (D2O) and the exchange between atmospheric water and adsorbed or absorbed D2O were investigated for the polymeric materials Kapton and Mylar using thermal gravimetric analysis (TGA) and infrared (IR) spectroscopy. Replacement of H2O by D2O is easily accomplished. However, exposure of D2O samples to the ambient atmosphere or gases containing H2O results in rapid proton and deuteron exchange between H2O vapor and adsorbed
D2O. Replacement of H₂O by D₂O would not be a practical solution to alleviate spectral interferences that would result from water outgassing in spacecraft orbital environments. Maintaining the materials of interest in a dehydrated state is a more reasonable approach.
CONTENTS

I. INTRODUCTION ......................................................... 5
II. EXPERIMENTAL .......................................................... 7
III. RESULTS ................................................................. 11
   A. Thermal Gravimetric Analysis .................................. 11
   B. Infrared Analysis .................................................. 11
IV. DISCUSSION ............................................................. 19
V. CONCLUSION .............................................................. 21
REFERENCES ................................................................. 23
FIGURES

1. IR Spectra of 0.003-in. Mylar Film................................. 8
2. IR Spectra of 0.005-in. Kapton Film.............................. 8
3. IR Spectra of 0.005-in. Kapton Film by Difference............... 10
4. 0.005-in. Kapton Water Desorption at 370°K...................... 12
5. 0.005-in Kapton Water Desorption at 370°K, First 
   Order Plot.................................................. 13
6. Exchange of Atmospheric H₂O for D₂O in 0.003-in. 
   Mylar Film.................................................. 15
7. IR Spectra versus Time for Exchange of Atmospheric 
   H₂O for D₂O in 0.005-in. Kapton Film................................ 15
8. IR Spectra versus Time for D₂O Removal from 
   0.005-in. Kapton Film with Dry Nitrogen.......................... 16
9. IR Spectra versus Time for D₂O Uptake by 0.005-in. 
   Kapton Film with Nitrogen Gas Passed Over D₂O.................. 17
10. IR Spectra versus Time for D₂O Uptake by 0.005-in. 
    Kapton Film with Argon Gas Passed Over D₂O.................... 18
11. Optical Density versus Time for Dehydration 
    and Hydration of 0.005-in. Kapton Film.......................... 18
I. INTRODUCTION

Water ice formation on satellite optical surfaces has been suggested as a possible cause of decreased sensitivity of infrared sensing devices. For optimum performance, these devices rely on unattenuated signals in the infrared wavelength region where $\text{H}_2\text{O}$ ice absorption occurs. It has been hypothesized that the $\text{H}_2\text{O}$ collects on the cryocooled optical surfaces after outgassing from materials in close proximity to the surfaces. The most likely sources of $\text{H}_2\text{O}$ are polymeric insulation, such as Kapton, multilayer insulation (MLI), and aluminized Teflon. The suggestion has been made that replacement of associated $\text{H}_2\text{O}$ with $\text{D}_2\text{O}$ in the materials of interest would alleviate the problem by isotopically shifting the infrared ice absorption band out of the wavelength region of interest.

In order for the $\text{H}_2\text{O}$ replacement to be considered a feasible solution to the problem, the following questions should be answered:

1. Is the $\text{H}_2\text{O}$-$\text{D}_2\text{O}$ replacement accomplished easily, and what are the best methods?
2. Once the replacement is accomplished, how difficult is it to maintain the $\text{D}_2\text{O}$ level?
3. How important are exchange processes between associated $\text{D}_2\text{O}$ and ambient atmospheric $\text{H}_2\text{O}$?

The last question is the most critical. In the condensed phase, proton exchange between $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ occurs just below the diffusion-controlled limit and is, thus, very rapid (Refs. 1 and 2). In addition, the following rapidly established equilibrium is shifted toward the right at room temperature ($K_{eq} = 3.94$ at $20^\circ\text{C}$) (Ref. 3):

$$\text{H}_2\text{O} + \text{D}_2\text{O} \rightleftharpoons 2 \text{HOD}$$

Both $\text{H}_2\text{O}$ and HOD absorb infrared radiation in the wavelength region of interest. Because of the rapidity of proton exchange, the mixing phenomenon is expected to be limited by surface adsorption and bulk diffusion of water.
The $\text{D}_2\text{O}-\text{H}_2\text{O}$ replacement phenomenon was investigated for Kapton, and to a lesser extent Mylar, by TGA and IR spectroscopy. In addition to atmospheric exposure, $\text{N}_2$ and $\text{Ar}$ environments were used to determine if gas adsorption would affect the exchange process significantly.
II. EXPERIMENTAL

The materials in the investigation were 0.005-in. Kapton and 0.003-in. Mylar sheets examined by means of IR and TGA, and aluminized-Mylar MLI, examined by means of TGA.

The TGAs were performed on a Perkin Elmer TGS-1 thermal balance in both the temperature programmed and isothermal modes of operation. Because of the restricted sample size, it was necessary to cut up the MLI into small pieces, which were then piled in the thermal balance weighing pan. The cutting disturbed the layered nature of the MLI and, as a result, the equilibrium $H_2O$ content might be different from that in the layered configuration. The Kapton and Mylar sheets were simply cut to the appropriate size. The sample weights were generally on the order of 1 mg.

Infrared analyses were performed on a Perkin Elmer Model 467 infrared spectrophotometer. The IR spectra of Mylar and Kapton are shown in Figures 1 and 2. The spectral features in the presence and absence of $H_2O$ and $D_2O$ are included. The Mylar spectrum exhibits a rather small absorption due to $H_2O$, and, as a result, only a limited number of experiments were performed. For Kapton, the amount of associated water is larger and, thus, more easily monitored. Despite the larger equilibrium water content, the spectrum of Kapton is complex in the wavelength regions of interest. In order to simplify the spectra, the reference beam of the double-beam spectrophotometer was passed through a sample of "dry" Kapton, which resulted in essentially the spectral features of $H_2O$ and $D_2O$ without interference from the spectral features of Kapton. Two approaches to obtaining these "difference" spectra were employed. In the early stages of the investigation, the "dry" reference sample was stored in an evacuated vacuum dessicator with phosphorous pentoxide as the desiccant. When spectra were obtained, the "dry" sample was placed in the reference beam. In the latter stages of the investigation, a more efficient method was used. A Kapton sample was mounted in a spectrometer gas cell with salt (NaCl) windows. The cell was evacuated to dehydrate the sample and was maintained at low pressure. By means of this approach, the reference sample
Figure 1. IR Spectra of 0.003-in. Mylar Film

Figure 2. IR Spectra of 0.005-in. Kapton Film
could be kept in the "dry" state for long periods of time. Both approaches resulted in comparable spectra. Typical spectra obtained by means of the "difference" method are illustrated in Figure 3.

Two approaches were employed in examining the H₂O and D₂O contents of the polymers. In the early experiments in which pre-equilibrium with D₂O was required, the samples were first submerged in D₂O, then mounted in a "film" sample holder and exposed to the ambient atmosphere (relative humidity = 45 to 58%) for specified lengths of time. At the end of the exposure, IR spectra were obtained. It was found that the heating of the samples by the IR beam caused the samples to dehydrate. The rate of dehydration was measured, and the process was determined to have a half-life of approximately 7 min. As a result of this IR stimulated H₂O loss, it was necessary to adjust the experimental procedures to minimize errors. The length of time that the sample was in the IR beam was limited to approximately 2 min, and each data point followed re-equilibration with D₂O and exposure for specified times. By means of this approach, the spectral intensities were accurate to within 15%.

In later experiments in which other than ambient atmospheric exposure was required, the samples were mounted in a spectrometer cell with KRS-5 windows. Appropriate gases were purged through the cell for measured time intervals. The IR spectra were obtained by closing off the cell and placing it in the spectrometer only long enough to obtain the appropriate spectrum, 2 to 4 min. Minimizing IR exposure time and sealing off the cell minimized errors induced by IR stimulated water loss.

The gases used in the investigation were N₂ and Ar. They were both dried by passage through a drying cartridge containing molecular sieves. After drying, the gases were either admitted to the sample cell in the "dry" state or passed over H₂O or D₂O liquid prior to passage through the sample cell. The gas flow rates were approximately 30 ml/min for N₂ and approximately 40 ml/min for Ar. The D₂O was from Merck and Co. and had a deuterium content of 99.7 at% D.
Figure 3. IR Spectra of 0.005-in. Kapton Film by Difference
III. RESULTS

A. THERMAL GRAVIMETRIC ANALYSIS

Mylar, MLI, and Kapton were analyzed in both temperature-programmed and isothermal modes of operation. The three materials exhibited two weight-loss processes, the first occurring in the temperature range 300 to 400°C, and the second at approximately 600°C. The first process is attributed to H₂O loss, whereas the second is consistent with sample thermal decomposition. The weight losses resulting from H₂O desorption were determined to be 0.93, 0.37, and 0.24% for Kapton, Mylar, and MLI, respectively.

Isothermal analysis was useful for the Kapton sample but not for Mylar and MLI. For the latter two, instrumental limitations on sample size coupled with low H₂O content resulted in isothermal-weight-loss profiles that did not permit detailed analysis, i.e., the signal-to-noise ratio was very low. For Kapton, isothermal desorption of water at 370°C resulted in a weight versus time profile (Figure 4) that could be analyzed. The curve is exponential with a half-life of 112 sec. The first-order behavior is illustrated in Figure 5. The observation of first-order kinetics is consistent with both bulk diffusion limited and surface desorption limited processes (Ref. 4). In addition, exponential behavior is consistent with just water loss; additional concurrent processes, such as polymer decomposition and outgassing, would result in non-exponential behavior unless the processes had identical relaxation times.

B. INFRARED ANALYSIS

The IR absorption maxima for H₂O associated with Kapton and Mylar occur at 3550 to 3620 cm⁻¹ (2.76 to 2.82 μm) (Ref. 5). The shift to higher energy for the polymer samples implies that the H₂O is absorbed into the polymer matrix rather than being primarily present as physisorbed layers on the surface. Deuterium oxide exhibits a maximum absorption at 2600 to 2700 cm⁻¹ (3.70 to 3.85 μm) in Kapton.

The analysis of the H₂O-D₂O exchange for Mylar was limited by the low-equilibrium H₂O content and, thus, small IR signal levels. However, some data
Figure 4. 0.005-in. Kapton Water Desorption at 370°K
Figure 5. 0.005-in. Kapton Water Desorption at 330°K.
First order plot with \(\frac{1}{\tau} = 6.21 \times 10^{-3} \text{sec}^{-1}\)
were obtained for atmospheric H$_2$O exchange in a sample that was equilibrated with D$_2$O. These data are given in Figure 6. The IR absorption that results from the O-H stretching of H$_2$O and HOD increases with time and reaches approximately 95% of the maximum absorption in 60 min of exposure to the ambient atmosphere.

For Kapton, the larger equilibrium H$_2$O content permitted more extensive analysis. The change in the O-H and O-D vibration absorption amplitudes as a function of time for a sample that was equilibrated in D$_2$O and then exposed to the ambient atmosphere is shown in Figure 7. The shape of the O-H vibration absorption band appears to change with time. In addition, there appears to be a time-dependent shift in the wavelength of maximum absorption. These changes can be attributed to differing relative amounts of H$_2$O and HOD as the D$_2$O is undergoing exchange. The O-H absorption reaches 75 to 80% of its maximum value in approximately 50 min and 90% of the maximum in approximately 90 min, which is nearly the same as that for Mylar.

The elimination of D$_2$O from a Kapton sample by "dry" N$_2$ gas was investigated. The spectral changes are shown in Figure 8. By purging the sample gas cell with N$_2$ gas, the D$_2$O is eliminated by means of an exponential process with a half-life of approximately 97 min.

Equilibration of a sample with "dry" gas followed by purging with the same gas passed over D$_2$O was investigated. The O-D absorption spectral changes are shown in Figures 9 and 10 for N$_2$ and Ar, respectively. The D$_2$O band grows in faster in the N$_2$ case, implying that Ar is more difficult to displace by D$_2$O than is N$_2$. The changes in optical density versus time for the data in Figures 8 through 10 are illustrated in Figure 11.

Equilibration of a Kapton sample in air followed by exposure to D$_2$O in N$_2$ gas resulted in isotopic exchange that occurred at essentially the same rate as equilibration in D$_2$O followed by air exposure.
Figure 6. Exchange of Atmospheric H\textsubscript{2}O for D\textsubscript{2}O in 0.003-in. Mylar Film. 
\(\Delta\%T\) transmittance versus time for 3620-cm\(^{-1}\) absorption.

Figure 7. IR Spectra versus Time for Exchange of Atmospheric H\textsubscript{2}O for D\textsubscript{2}O in 0.005-in. Kapton Film.
Figure 8. IR Spectra versus Time for $\text{D}_2\text{O}$ Removal from 0.005-in. Kapton Film with Dry Nitrogen. Nitrogen flow rate = 30 ml/min.
Figure 9. IR Spectra versus Time for D$_2$O Uptake by 0.005-in. Kapton Film. Nitrogen gas passed over D$_2$O at 30 ml/min flow rate.
Figure 10. IR Spectra versus Time for $\text{D}_2\text{O}$ Uptake by 0.005-in. Kapton Film. Argon gas passed over $\text{D}_2\text{O}$ at 40 ml/min flow rate.

Figure 11. Optical Density versus Time for Dehydration and Hydration of 0.005-in Kapton Film
IV. DISCUSSION

The TGA and IR data indicate that \( \text{H}_2\text{O} \) is easily removed from the materials of interest. In addition, once the material is dehydrated, \( \text{D}_2\text{O} \) can be readily introduced. The major problem that must be overcome is exchange between adsorbed \( \text{D}_2\text{O} \) and \( \text{H}_2\text{O} \) from the ambient atmosphere.

The exchange data indicate that exposure of \( \text{D}_2\text{O} \) equilibrated material to \( \text{H}_2\text{O} \)-containing atmospheres must be strictly avoided. The reaction between \( \text{D}_2\text{O} \) and \( \text{H}_2\text{O} \) to yield HOD occurs rapidly and results in a mixture of \( \text{H}_2\text{O} \), \( \text{D}_2\text{O} \), and HOD. There should not be a significant isotope effect on diffusion and desorption. As a result, these three species would be expected to outgas from polymers with essentially the same rate. Oxygen-hydrogen bonds in \( \text{H}_2\text{O} \) and HOD contribute to the interferences in the infrared region of interest. Thus, ice formation with significant amounts of HOD on optical surfaces would cause IR signal attenuation.

It would be necessary to keep a constant \( \text{D}_2\text{O} \)-saturated atmosphere to maintain the \( \text{D}_2\text{O} \) levels in the materials in the prelaunch environment. A more reasonable approach would be to purge the materials with "dry" air or some inert gas. Our data on the thin sheet polymer samples indicate that purging of the materials with dry gas will result in dehydration in a relatively short time, i.e., on the order of several hours. Extrapolation of these data to bulk materials cannot be readily achieved. However, purging bulk materials with dry gas over a 24-to 48-hour period should result in significant removal of \( \text{H}_2\text{O} \). The materials could be maintained in the dehydrated state, or at the latest possible time, the system could be flushed with \( \text{D}_2\text{O} \)-containing gas to equilibrate the materials with \( \text{D}_2\text{O} \). Maintaining the materials at elevated temperatures, i.e., 50°C, during prelaunch would also dehydrate the materials. As in the "dry" air purging, equilibration with \( \text{D}_2\text{O} \) prior to launch or maintenance of the dehydrated condition would be required.
V. CONCLUSION

Because of the rapidity of proton exchange reactions between H$_2$O and D$_2$O, it would be very difficult to maintain equilibrium D$_2$O levels in Kapton and Mylar without employing very stringent controls pertaining to the exclusion of H$_2$O from the materials. The alternative methods of maintaining the materials in a "dehydrated" state by mild heating or purging the system with "dry" air would appear to be more feasible than maintaining D$_2$O equilibrium levels. These latter choices require either launching the system in a dehydrated state or equilibrating the material with D$_2$O immediately prior to launch. Water exclusion measures would also be important for these methods. Although these methods appear to be reasonable a priori, the rigorous exclusion of water from critical spacecraft surfaces would be extremely difficult, if not impossible.
REFERENCES


LABORATORY OPERATIONS

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