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SUBJECT: Measurements of Small Amounts of H₂O in D₂O
by Near-Infrared Absorption Spectroscopy
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The literature on the near-infrared and infra-red absorption spectra of liquid H₂O and D₂O, and other literature related to the determination of small amounts of one in the presence of the other was reviewed. Near-infrared absorption techniques appear to be very convenient, rapid, and almost ideally suited for the determination of H₂O in the concentration range from 0 to 10% in D₂O. The absorption spectra of H₂O, D₂O, (HDO), and of mixtures of H₂O in D₂O were obtained using a Cary Model 14 PM Recording Spectrophotometer.

As expected, the H₂O has been found to undergo very rapid and almost complete exchange to HDO, especially at relatively low H₂O concentrations. In agreement with some previously reported French and Japanese work, a relatively intense and very useful absorption band for HDO has been found at 1.668 μ , and is used for the determination. By the use of the procedure described, 0.5, 2, 4, and 7 wt. % H₂O in D₂O can be determined with respective approximate relative standard deviations of 7, 2, 1 and 0.7% when 1 cm absorption cells are used, in conjunction with a pure D₂O reference liquid.

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MEASUREMENT OF SMALL AMOUNTS OF H₂O IN D₂O BY NEAR-INFRARED
ABSORPTION SPECTROSCOPY

R. E. Biggers

In preference to infrared absorption techniques,⁽¹⁻⁶⁾ a near-infrared absorption technique has been used to determine H₂O in the concentration range from 0 to 10% in D₂O. Water (less than 5 vol %) in D₂O can be determined by infrared absorption spectroscopy;^(7,8) however, near-infrared absorption spectroscopy has the following advantages. The absorption resulting from overtone and combination frequencies of H₂O and D₂O in the near-infrared region are much less intense than the fundamental frequencies in the infrared region. Therefore in the near-infrared region much longer cells (i.e., of the order of centimeters) can be used; cells as long as 10 cm can be used for very low H₂O concentrations. Larger quantities of samples can be used since the absorption-cell lengths for use in the infrared are of the order of a few hundredths of a centimeter. The construction of the cells is simpler and the filling and cleaning is easier when the near-infrared is used. In addition, the path lengths of near-infrared cells can be measured with much greater accuracy than those of infrared cells. Furthermore there are no complications from window deterioration and dissolution when glass or quartz near-infrared cells are used, and the cells and windows are not so fragile.

The near-infrared spectrum of water has been obtained by previous workers^(9,10) and by the present author; previous work is adequately

summarized by Curcio and Petty.⁽¹¹⁾ Near-infrared absorption spectra of D₂O have been measured,^(12,13,14) and the analytical applications of the near infrared have been discussed.⁽¹⁵⁾

When small amounts of H₂O are added to D₂O, the exchange reaction that leads to HDO is instantaneous and practically complete; only when the concentration of H₂O is greater than about 8 vol % does unexchanged H₂O exist. It has been found⁽¹⁵⁾ and confirmed by the present work that the near-infrared spectral character of H₂O is not observed as H₂O is added to D₂O. Instead a completely new absorption band, which is characteristic of HDO, is observed at 1.668 μ .

The experimental approach of the present work has been similar to that previously proposed.⁽¹⁵⁾ All absorption spectra have been obtained with a Cary model 14 PM automatic recording spectrophotometer. Cylindrical, ground-glass-stoppered quartz absorption cells (1- to 10-cm length) were used.

The near-infrared spectra of H₂O and of D₂O (99.7 atom % D) were obtained, as well as absolute cell balances using D₂O for cells of different lengths. (The balance control knob on the Cary should be replaced with a 10-turn, duo-dial indicator so that it is possible to return to the same balance conditions when running a sample as was used for the cell beam balance). All transfers of D₂O and H₂O used in the preparation of standards and in the filling of absorption cells were carried out in a glove box in a nitrogen atmosphere saturated with D₂O vapor. D₂O and water were kept in small bottles that were sealed with rubber serum caps. All transfers were made with clean, dry (dried for 24 hr)

hypodermic syringes.

Standards (5 or 10 ml containing about 0.3, 0.5, 1.0, 2.0 ... 9.0 vol % H_2O) were prepared as follows: The calculated volumes of D_2O were transferred using the syringe technique into accurately tared serum-capped vials. After the vials were weighed, the appropriate volume of H_2O was similarly added. The vials were then reweighed. The weight per cent H_2O was then calculated and, by means of accurate density data, was converted to volume per cent. The samples were mixed well and then individually and successively transferred into a clean dry sample absorption cell that had previously been balanced with a similar reference cell with the pure D_2O used. The stoppered absorption cells filling necks were then covered and tightly sealed with thin plastic covers. Near-infrared absorption spectra were then obtained from 0.7 to 1.87 μ . The absorbancy at 1.668 μ (HDO peak) was then plotted vs both the weight and volume per cent H_2O . Samples were run in a similar manner.

If the D_2O used for a reference medium is less than 100% isotopically pure the per cent H_2O content of the reference D_2O must be added to that measured in the sample. Fortunately D_2O does not absorb very strongly at 1.668 μ ; however, the effective D_2O path length decrease in the sample cell due to the replacement of the D_2O by H_2O (and formation of HDO) occurs both in the samples and standards. This decrease amounts to approximately 0.0015 absorbancy units per volume per cent H_2O . At approximately 8 vol % H_2O , the calibration curve departs (negatively) from strict linearity because of incomplete exchange to form HDO . This

occurs because the unexchanged H_2O remaining absorbs less than the HDO at 1.668μ . However, for a given cell length both the above errors are eliminated since an empirical, but accurate calibration curve is used.

By use of the previously described procedure,⁽¹⁵⁾ 0.5, 2, 4, and 7 wt % H_2O in D_2O can be determined with respective approximate relative standard deviations of 7, 2, 1, and 0.7% when 1-cm absorption cells are used. For this length of cells, the lower limit of quantitative measurement is ~ 0.2 wt % H_2O in D_2O . For less than 1 wt % H_2O , the use of longer absorption cells (up to 10 cm) results in a corresponding decrease in the lower limit of quantitative measurement; however, the relative standard deviations for correspondingly smaller weight percentages of H_2O are about the same.

No additional work is planned at the present time.

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