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# THE EFFECT OF HIGH PRESSURE ON THE NEAR INFRARED ABSORPTION SPECTRUM OF CERTAIN LIQUIDS*

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## Abstract

Certain absorption bands of liquid water, methyl alcohol, amyl alcohol, and toluene were studied when the liquids were subjected to high pressures. In the case of the first three liquids, pressures up to 5000 kg/cm$^2$ were used, and pressures up to 8000 kg/cm$^2$ were applied to the toluene. No change was found either in the spectral position or in the intensity of the bands studied. The results are of interest since a change in the polymerization of polar liquids is supposed to take place with increase of pressure. The absorption bands are characteristic of the molecules and hence a change in the position and intensity should accompany the change in polymerization. As no such change was observed, it is concluded that there is no change in polymerization in the pressure range studied. The pressure necessary to solidify toluene at 20°C. was found to lie between 8100 kg/cm$^2$ and 8300 kg/cm$^2$.

## Introduction

THE anomalous properties of liquid water have been explained by the hypothesis that it is composed of two or more kinds of molecules. The simplest assumption is that water consists of the molecules $(H_2O)_2$ and $(H_2O)_3$ whose relative proportions depend on the physical conditions such as temperature, pressure, etc. Sutherland[1] has made calculations as to the relative amounts of the two constituents under various conditions of temperature. The author[2] has studied the near infrared absorption spectrum of liquid water from its freezing point to its boiling point and found changes which seem readily explained on Sutherland's assumptions. Redlich[3] has used the author's results to calculate the relative amounts of the two kinds of molecules at various temperatures and finds fair agreement with similar calculations based on the change of magnetic susceptibility of liquid water as the temperature changes.

Sutherland explains the change in the viscosity of water with pressure by assuming that the degree of polymerization changes as the pressure changes. He estimates that a pressure of a few thousand atmospheres should convert all of the triple molecule into the simpler one. Hence, if one may interpret the change in the absorption spectrum as due to a change in the degree of polymerization, the absorption spectrum should show decided

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[1] Sutherland, Phil. Mag. **50**, 460 (1900).

[2] Collins, Phys. Rev. **26**, 771 (1925).

[3] Redlich, Proc. Akad. Wissensch. Wien **53**, 874 (1929).

changes as the pressure on the liquid is increased to several thousand atmospheres. Accordingly, the present experiments were undertaken to find if such changes do occur. Although the principal interest is in the case of water, the experiments were planned to include the study of toluene as a typical nonpolymerizing liquid and as many other liquids that do show polymerization as time would permit. The experiments were performed in the Jefferson Physical Laboratory at Harvard University, and the author is under deep obligation to Professor P. W. Bridgman who kindly designed the pressure chamber which provided plane parallel glass windows through which the radiation could be passed through the specimen.

## Apparatus and Experimental Procedure

The method of measurement was to pass a beam of radiation from an incandescent source through the chamber containing the liquid, to disperse the radiation by means of a spectrometer system and then to measure the intensity of the radiation at the exit slit of the spectrometer by means of a thermopile and galvanometer. On account of the impossibility of moving the absorption chamber, an indirect method of obtaining the fractional absorption of the liquid at the various pressures was used. Figure 1 illustrates diagrammatically the arrangement of apparatus. $L$ is the filament of a street series incandescent lamp, from which two beams of parallel radiation are obtained. One of these beams passes through the absorption chamber $C$ and is then focussed on the entrance slit of the spectrometer system. The other beam, after reflection from suitably placed mirrors, is also focussed on the slit of the spectrometer. By means of the shutter $G_1$ either of these beams may be blocked off and the intensity of the other measured by the thermopile. The beam which does not pass through the specimen serves as a standard of comparison, so that the absorption at any one pressure can be calculated if that at any other pressure is known. The absorption at atmospheric pressure was determined by a separate experiment.

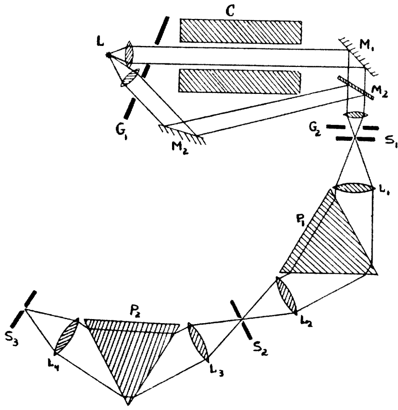

Fig. 1. Diagrammatic arrangement of apparatus.

The spectrometer used was a double Van Cittert spectrometer in which the slit $S_2$ is moved across the spectrum focussed in its plane. This movement allows any desired spectral position to be transmitted through the system. The double spectrometer is necessary to obtain the necessary purity of spectrum. The spectrometer was calibrated by means of emission lines from a mercury arc, and by means of the known positions of absorption bands of several liquids. Since the openings at the ends of the absorption chamber were only one quarter of an inch in diameter, the amount of radiation transmitted was very small. It was accordingly necessary to use a thermo-relay to magnify the galvanometer deflections. It was found that a magnification of fifty times was sufficient, and the Moll thermo-relay used was very steady at this magnification. On account of mechanical and electrical disturbances which were present in the daytime, all measurements were made at night.

Figure 2 shows the details of the mounting of the glass windows in the ends of the absorption cell. *A* is the window and was a cylinder of glass seven eighths of an inch in diameter and one and a quarter inches thick. A doubled piece of rubber tubing, *E*, was tightened around this window by means of the tube, *D*, and made a liquid tight seal between the window and holder *C*. This holder was forced in against the shoulder of the cell by means of the screw plug *B*. Packing at *F* was used to make the outside edge of the holder tight. When pressure was applied to the inside of the chamber, the window *A* was forced to a seat against the bottom of the holder. A thin washer of tin was placed between the window and bottom of the holder.

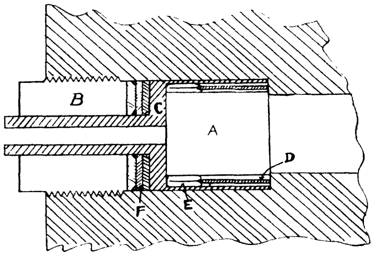

Fig. 2. Detail of mounting the windows in the pressure chamber.

With plate glass as the material of the windows, pressures up to 10000 kg/cm$^2$ could be maintained for long periods of time. Unfortunately, however, plate glass has a strong absorption band in the spectral region being studied, and with the two windows only about one percent of the incident radiation was transmitted. Although several kinds of transparent glasses were tried, none were found which would allow pressures greater than about 5000 kg/cm$^2$ to be maintained for any length of time. Another arrangement which was used in the last part of the experiments was that described by Poulter,[4] which allowed thin windows of plate glass to be used. These windows transmitted sufficient radiation to be measured. The holder, *C*, was

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[4] Poulter, Phys. Rev. **35**, 297 (1930).

made solid and the inner end ground and polished to a plane surface. Then windows five sixteenths of an inch were cemented on to the end of the holder by a very thin layer of Canada balsam.

The original plan was to have the specimen placed in an absorption cell inside the pressure chamber so that the liquid transmitting the pressure would not contaminate the specimen. However, every liquid suitable for the transmission of pressure has strong absorption bands in the spectral region being studied, and so in the final arrangement the specimen filled the whole pressure chamber and as much of the pressure chamber above the absorption chamber as was possible without affecting the manganin coil whose resistance was measured as an indication of the pressure. Kerosene was used to transmit the pressure to the specimen liquid. A capillary tube connected the absorption chamber with the pressure producing apparatus and diffusion of the kerosene through this tube was apparently slow enough to prevent harmful contamination of the specimen. The test of this was to measure the absorption of the specimen after the pressure had been on for some time and then reduced to atmospheric pressure again. No change was noticed which could be ascribed to contamination of the specimen.

The procedure was as follows. The apparatus was assembled and a small pressure applied to find if the packing was liquid tight. Then by means of the shutters $G_1$ and $G_2$ the intensity of the two beams of radiation were obtained for various settings of the spectrometer system through the spectral region desired. Then the pressure was raised to about 1000 $kg/cm^2$ and the process repeated. Pressures higher than 5000 $kg/cm^2$ were not obtained under circumstances which permitted measurements of the absorption except in the case of toluene. This was possibly due to faulty assembly, although the same care was taken in all cases. This pressure is well in excess of that estimated by Sutherland for the complete conversion of the triple molecule of water into the simpler form.

A very interesting method of obtaining the pressure necessary for the solidification of toluene at 20° C. was to observe the interior of the pressure chamber by means of a reading telescope. When the pressure was slowly increased, fine needle like crystals would begin to form, and if the pressure was maintained, the whole of the liquid would become solid. On slowly reducing the pressure, the crystals would begin to melt. As the pressure was successively raised and lowered above and below the solidification point, the pressures at which the solidification and the melting took place came nearer to each other and after a great many trials, the final values obtained were: Freezing pressure 8300 $kg/cm,^2$ melting pressure 8100 $kg/cm.^2$

## Results and Conclusions

The results obtained for five absorption bands of water indicate that there is no change in the spectral position or intensity of the bands. The absorption bands of water which are studied are supposed to be the overtone bands of fundamental bands farther in the infrared. It was expected that these might show even greater changes than the fundamental bands would show. Also they are not so intense as the fundamental bands so that reasonable thicknesses of the liquid could be used. When too thin layers are used, the thickness is increased at the higher pressures on account of the packing becoming compressed and thus allowing the windows to move outward. Only a few of the curves which were obtained are shown as they are all similar in that no change in spectral position is shown and only slight changes in intensity. These changes in intensity are ascribed to the increase in length mentioned above. Account was taken of the increase in density of the liquid as the pressure was increased.

A study of the absorption of toluene was made as an example of a non-polarizing liquid and thus, presumably, of a liquid whose molecules do not associate to produce complicated molecules. The two alcohols were studied as other examples of polymerized molecules.

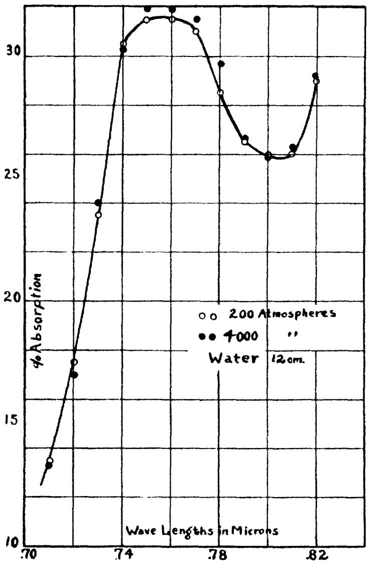

Fig. 3.

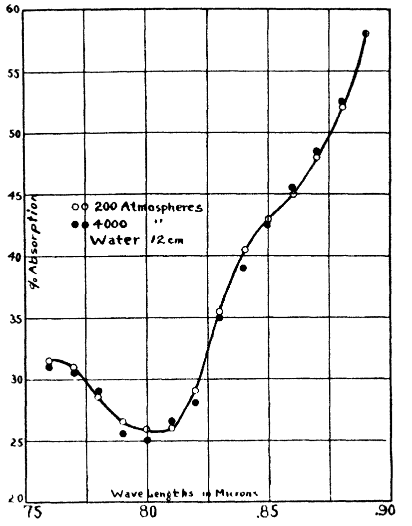

Fig. 4.

Results are plotted for the lowest and highest pressures used as the results for the intermediate pressures lie intermediate between them. In the case of water several runs were taken at each absorption band and the results plotted are from one of the individual runs.

If we are to assume that changes in the absorption bands of a liquid should occur when the degree of polymerization changes, the results of these experiments indicate that no such change in polymerization occur in the pressure range used. It is difficult to imagine a process whereby an increase in pressure would cause a breaking up of the complicated molecules. Bridgman,[5] in discussing the effect of pressure on the thermal expansion of water, concluded that his results do not indicate any breaking up of the complicated

Bridgman, Proc. Am. Acad. Arts, and Sci. **47,** 544 (1912).

molecules. From other considerations, he concludes that the effect of pressure should be one of increasing the complexity of the molecules.

It is interesting in this connection to note that Stewart[6] denies the existence of small molecular groups such as are postulated by Sutherland and others. His results on the x-ray diffraction halos produced by liquid water lead him to postulate the presence of very large groups of molecules with a regular arrangement, these groups having only a temporary existence to be succeeded by other similar groups. The results of the present experiments do not seem incompatible with this view of Stewart, as it seems likely that the absorption of the molecules within these groups would be different than that of the molecules not in the groups, and that there may be some effect of temperature on the number of molecules in the groups or on the time of existence of a given group.

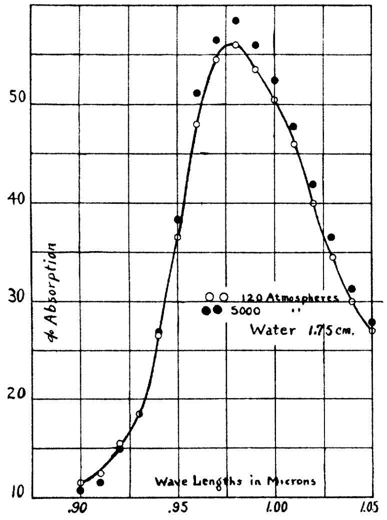

Fig. 5.

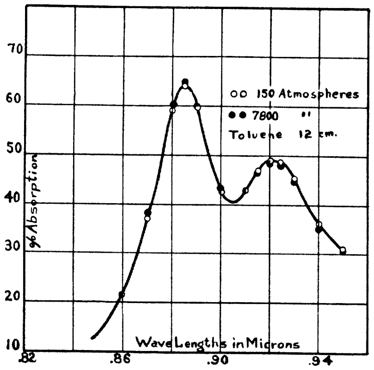

Fig. 6.

The author wishes to make grateful acknowledgment of his indebtedness to Professor Bridgman for placing the pressure apparatus at his disposal. The author also feels under obligation to Mr. Mann, chief mechanician at Jefferson Laboratory, who helped by his skill and advice.

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[6] Stewart, Proc. Am. Phys. Soc. April, 1930.