THE EFFECT OF CERTAIN DISSOLVED SUBSTANCES ON THE INFRA–RED ABSORPTION OF WATER.

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SYNOPSIS.

Infra-red absorption spectra of aqueous solutions of sixteen inorganic compounds from 0.8 to 2.3 μ, have been determined to see how the dissolved substances affect the absorption of the water. Care was taken to eliminate stray light by using two constant deviation glass spectroscopes in series. Readings were taken alternately with a cell containing a solution and with one containing water. Curves were thus obtained for the *alkali hydroxides, five chlorides (Al, Ca, Mg, Na, Sr), five nitrates (Ag, Al, Mg, NH₄, Zn) and three sulphates (Ag, Na, Zn)*. (Figs. 3–16). All solutes decreased the absorption in the water band at 1.44 μ and probably also in the band at 2 μ, whereas all excepting $Al_2(SO_4)_3$, $ZnSO_4$ and the hydroxides increased the absorption in the bands at 0.97 and 1.2 μ. These results do not agree with the solvate theory which ascribes the effect to the formation of hydrates, since some non-hydrating compounds decreased the absorption at 1.44 μ.

Absorption of water, from 0.8 to 2.3 μ, was measured by using cells of different known thicknesses. *The wave-lengths of maximum absorption* were found to be 0.97, 1.20, 1.44, and 2.00 μ, and the corresponding *coefficients* came out 0.448, 1.220, 29.4, and 103, respectively. Such difference as there is between these results and those previously obtained may be due to elimination of stray light. The fact that in the absorption spectrum of water vapor the bands at 1.44 and 2 μ are stronger and the other two bands weaker than for liquid water suggests that the former two bands are associated with a different kind of molecule than the latter two bands. If so, the effect of a dissolved substance on absorption may be due to a change in the relative number of these kinds of molecules produced by the presence of the substance.

INTRODUCTION.

IN their study of infra-red absorption spectra of aqueous solutions, Guy, Schaeffer, and Jones[1] found that, in some cases, the solutions were more transparent than the water present would be if there were no dissolved substance in it. Schaeffer, Paulus, and Jones[2] studied this effect of dissolved substances on the absorption of water further and found that the change in the absorption of the water was generally accompanied by a slight shift in the position of the absorption band toward the longer wave-lengths. Grantham[3] found that the alkaline hydroxides dissolved in water caused a decrease in the absorption of water at one absorption band, the effect due to these substances being greater than that due to the inorganic salts studied by the previous investigators. No conclusion can be drawn as to a shift in the position

[1] Phys. Zeitschr., 14, p. 278 (1913).
[2] Phys. Zeitschr., 15, p. 447 (1914).
[3] PHYS. REV., 18, p. 339 (1921).

of the absorption band caused by the alkaline hydroxides, since the hydroxides have an absorption band which overlaps that of water, thus making it impossible to distinguish the exact form of either absorption band. Further evidence of a shift in the position of an absorption band of water by dissolved substances was obtained by Ångstrom,[1] who measured the reflection of infra-red radiation from the surfaces of solutions. A shift in the positions of maximum and minimum reflection is interpreted as a shift in the position of the absorption band. No information was obtained as to changes in the intensity of absorption of the water.

The most intense absorption bands of water occur at about $3\,\mu$ and $6\,\mu$. Nearer the visible spectrum there are four much less intense bands which differ greatly among themselves in intensity. These bands were located by earlier observers at about $1.0\,\mu$, $1.2\,\mu$, $1.5\,\mu$ and $2.0\,\mu$, this order being also one of increasing intensity. Jones and his co-workers studied the effect of dissolved substances on the absorption of water in the spectral region including the first two of these bands. Grantham's results on the effect of the alkaline hydroxides are confined to the absorption band at $1.5\,\mu$. Ångstrom worked in the near infra-red, but obtained results only for the intense absorption band at $3\,\mu$.

The absorption bands of water at $3\,\mu$ and $6\,\mu$ are so intense that extremely thin layers are necessary for their study, so that a quantitative comparison of the absorption of solutions and water would be very difficult. The other four absorption bands mentioned above are such that measurable thicknesses can be used and an accurate comparison made. It was the purpose of this investigation to study the effect of various dissolved substances on the absorption of water throughout the spectral region containing these four absorption bands.

APPARATUS AND EXPERIMENTAL PROCEDURE.

It was necessary to obtain a spectrometer system free from appreciable stray radiation. Since no single spectrometer was at hand in which the stray radiation was negligible, two spectrometers were used, one serving as a monochromatic illuminator for the slit of the second. As measurements were to be made to $2.3\,\mu$ only, spectrometers with glass lenses and prisms were used. The spectrometers were of the constant deviation type and arranged as illustrated in Fig. 1.

The source of radiation, S', is a series street lighting lamp with a single spiral filament set vertically. It was run on storage batteries to insure constant current. L_1 is a lens so placed as to render the light from S' parallel. Diaphragms D_1 and D_2 were placed in the beam to

[1] PHYS. REV., 3, p. 47 (1914).

limit this beam, so that its cross-section was smaller than that of the cells under investigation. These cells were mounted on a slider P'. This slider could be moved by the observer by means of cords, so that either cell or an opaque screen was placed in the beam. L_2 is a lens which formed an image of the lamp filament on the slit S_1 of the first spec-
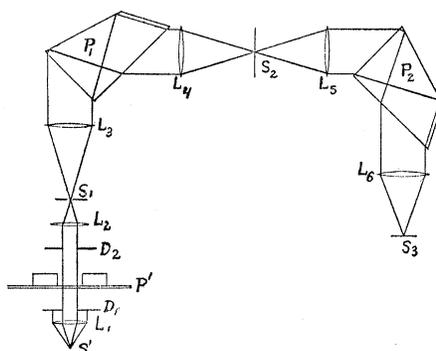
Fig. 1.

trometer. L_3, P_1, and L_4 are the collimator lens, prism, and telescope lens respectively, of this spectrometer, the spectrum being focused in the plane of the slit S_2 of the second spectrometer, of which L_5, P_2, and L_6 are the collimator lens, prism and telescope lens respectively. The spectrum is focused in the plane of the slit S_3, behind which a Coblentz thermopile is mounted. The thermopile is connected to a Coblentz ironclad galvanometer which was read by means of a telescope and scale.

The second spectrometer was used to indicate the wave-length of the radiation incident on the thermopile. The scale on the drum was divided uniformly, the smallest divisions corresponding to a range of about 0.3 $\mu\mu$ in the visible spectrum. This spectrometer was calibrated by observing the drum readings corresponding to the positions of the emission lines of sodium, lithium, potassium and mercury. The lines of the first three metals were obtained by volatilizing their salts in the open arc, and a quartz mercury arc was used for the mercury lines. A considerable number of lines were easy to locate and the location of the lines in the visible region could be checked visually. The wave-lengths of these lines were obtained from Paschen's data.[1]

The cells to contain the liquid under test consisted of two pieces of plane parallel quartz or pyrex glass between which, for the thicker cells, was placed a glass tube with plane parallel ends filled with the liquid. For the thinner cells washers of thin glass or celluloid were used. Since the two spectrometers were used in series it was necessary that the cells

[1] Ann. d. Physik., 27, p. 537 (1908).

have plane parallel ends and that the liquid be of uniform thickness over the entire cell.   Otherwise a change in the direction of the beam of radiation resulted in a change in the amount of radiation reaching the thermopile even with no absorption.   Thus two pieces of transparent quartz, one plane parallel and the other slightly wedge shaped, appeared to have different transmissions when placed alternately in the beam of radiation. This effect was not noticeable if the variations in thickness were not more than 0.001 cm. in a plate of 3 cm. diameter.

The coefficient of absorption of water was determined throughout the spectral region 0.8 μ to 2.3 μ by finding the absorption of known thicknesses.   In order to avoid the error due to reflection at the surfaces of the cells, two cells of different thicknesses were mounted on the slider P' (Fig. 1) and the deflections of the galvanometer observed when the cells were placed in turn in the beam entering the spectrometer system. The ratio of these deflections gives the fractional transmission of a layer of water equal in thickness to the difference of thicknesses of the two cells.

The fractional transmission of the solutions was obtained by mounting on the slider P' two cells of approximately the same thickness, one containing the solution and the other containing pure water.   The galvanometer deflections were observed when these cells were placed in turn in the beam of radiation.   The ratio of their transmissions were thus obtained.   The fractional transmission of the water could be computed from the known coefficients of absorption and then the fractional transmission of the solution calculated from that of water and their ratio.   There are two advantages of comparing the transmission of the solution to that of water instead of determining the fractional transmission of the solution by using two cells of solution.   First, it is the object of the experiments to compare the transmission of the solution with that of water and this method does that with one set of observations instead of two.   Second, a small error in the wave-length setting of the spectrometer on the side of an absorption band will cause a large change in the fractional transmission observed if the fractional transmission of the solution is determined directly; the ratio of the transmission of the solution to that of water does not change so rapidly as we proceed along the spectrum as does the fractional transmission, hence a small error in wave-length setting does not affect the results so much.

Since the four absorption bands of water have different intensities, the cells to contain the liquid were of different thicknesses for each of the four parts of the spectral region studied.   These thicknesses were: about 2 cm. for the range 0.8 μ to 1.1 μ; about 1 cm. for the range 1.1 μ to 1.3 μ; about 0.04 cm. for the range 1.3 μ to 1.7 μ; about 0.025 cm. for the range 1.7 μ to 2.3 μ.

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EXPERIMENTAL RESULTS.

I. *The Absorption Spectrum of Water from 0.8 μ to 2.3 μ.*

The fractional transmission of water for known thicknesses was carefully determined throughout the spectral range studied. The agreement of the values of absorption coefficients calculated from the observed transmission of widely different thicknesses of water indicate that the apparatus was free from appreciable stray radiation. A comparison with the values obtained by Aschkinass[1] and also those calculated from the data of Jones and his co-workers[2] can be made only at the positions of maximum absorption since the wave-length calibration of the prism used by Aschkinass was apparently not correct.[3] Table I. gives the values of the absorption coefficients at these positions.

TABLE I.

Position of Maximum Absorption.	Coefficients of Absorption.		
	Aschkinass.	Jones et al.	Collins.
.97 μ	.416	.446	.448
1.20 μ	1.221	1.297	1.220
1.44 μ	38.4	———	29.4
2.00 μ	123.2	———	103

The agreement at the first two absorption bands at .97 μ and 1.20 μ is remarkably good. At the other two bands, however, the agreement is not good. The thicknesses used by Aschkinass were much smaller than those used in the present investigation and could not be measured so accurately by the method used by him. This may be a possible explanation of the differences shown in Table I.

As may be seen from Table II., the wave-lengths of maximum absorption as determined in the present investigation do not agree with those obtained by some earlier observers. The care taken in eliminating stray radiation in the present investigation may account for some of the differences in the positions of the absorption bands as compared with the results of others.

II. *The Absorption Spectra of Aqueous Solutions.*

In order to compare the absorption spectra of the solutions with that of water the amount of water in each solution was computed from a

[1] Ann. d. Physik, 55, p. 401 (1895).

[2] Loc. cit.

[3] See Coblentz, Carnegie Inst. of Wash. Pub. 65 (1906).

knowledge of the concentration and density of the solution.   Then two curves were plotted on the same axes: (1) the per cent. transmission of

TABLE II.

Observer.	Date.	Kind of Prism.	Position of Maximum Absorption.			
Paschen.......	1894	Fluorspar	——	——	1.51 μ	2.05 μ
Aschkinass	1895	Flint Glass	1.00 μ	1.24 μ	1.50	1.96
Donath.......	1896	Flint Glass	——	——	1.45	1.96
Coblentz.....	1910	Fluorite	——	——	1.48	1.95
Grantham.....	1921	Rocksalt	——	——	1.48	1.98
Collins........	1921	Flint Glass	.97	1.20	1.44	2.00

the solution as a function of the wave-length and (2) the per cent. transmission of a layer of water equivalent to that present in the solution. Four curves are plotted for each substance as different thicknesses had to be used for different parts of the spectral region studied.   The thicknesses of layers used were in all cases those indicated in Fig. 3.   If the dissolved substance has an effect on the absorption of the water or has an absorption of its own the two curves would not coincide.   If the transmission curve for the solution lies above that for water, the dissolved substance has had an effect on the absorption of the water.   If, however, the curve for the solution lies below that for the water, there are two possible explanations and in general it is impossible to separate them. It seems unlikely that the absorption bands for the dissolved substance would lie exactly at the same position and have the same shape as the water absorption band, so that the transmission curves for the solutions should be distorted from those of water if the dissolved substances have absorption bands in the region studied.   An example of this is shown in Fig. 2.
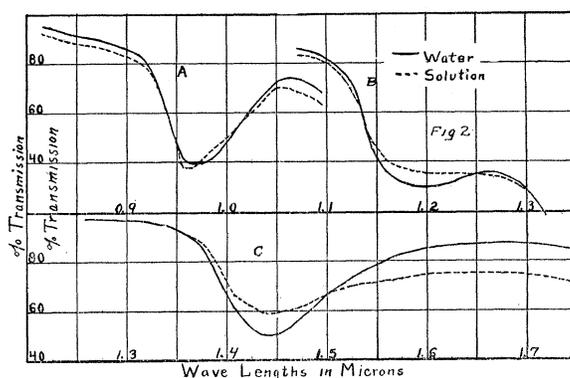
Fig. 2.

5N solution of NaOH.   200 grams per liter.   Density 1.186 gr./c.c.

Solutions of NaOH, KOH and LiOH were studied and curves for NaOH only are shown as they are typical of the results for all three substances. Grantham has already studied solutions of these substances in the region of the absorption at 1.44 μ and showed that all of them rendered the water less absorbing in that band in spite of an absorption band of the substances themselves which overlaps that of water. Curves A and B of Fig. 2 show the effect of NaOH on water in the bands at .97 μ and 1.20 μ. At 1.20 μ there is a decided increase in the transmission but at the other band there is a decrease in transmission on one side of the band. From the distorted shape of the solution curve it was suspected that the hydroxides had absorption bands near .96 μ, 1.1 μ and 1.27 μ. Concentrated solutions were made of KOH in absolute methyl alcohol and absolute ethyl alcohol and the transmission curves determined. Absorption bands were found at the wave-lengths .95 μ and 1.1 μ and 1.26 μ. It seems safe to say then that these three alkaline hydroxides make water more transparent in all three of the absorption bands shown in Fig. 2.

Figures 3 to 15 show the results obtained for several salts, all except the last three being hydrating substances. $Al_2(SO_4)_3$, $ZnSO_4$ and the
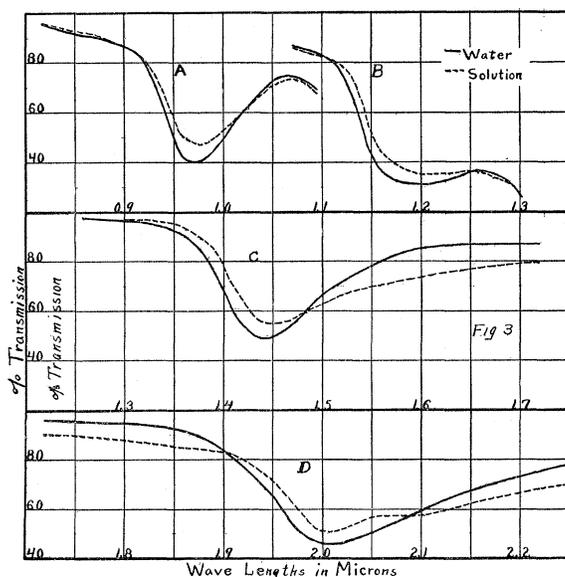
Fig. 3.

$Al_2(SO_4)_3$. 259.3 gr./liter. Density, 1.2200 gr./c.c.
Curve A, 2.090 cm. layer of solution. Curve B, .997 cm. layer of solution.
Curve C, .025 cm. layer of solution. Curve D, .0079 cm. layer of solution.

alkaline hydroxides decrease the absorption of water in all four absorption bands studied. All other substances studied decreased the absorp-

tion in the absorption band at 1.44 μ, increased the absorption in the absorption bands at .97 μ and 1.20 μ. The absorption band at 2.00 μ is not affected in the same way by all substances but in most cases where
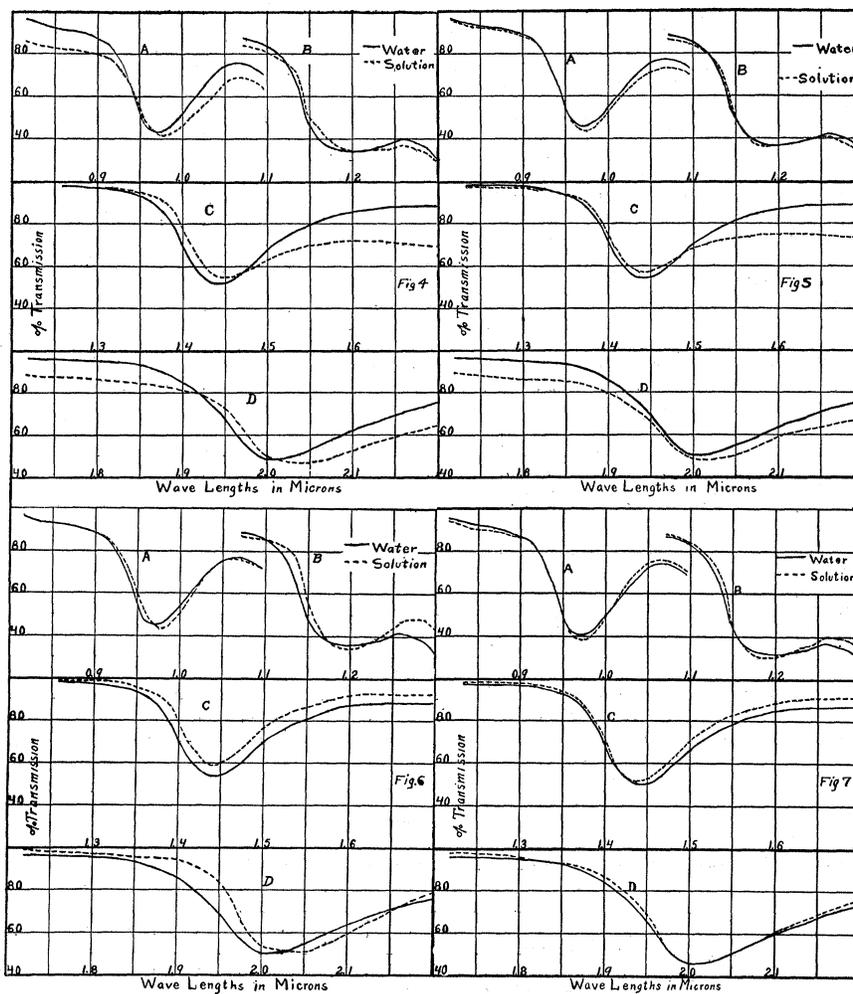
Fig. 4.
AlCl₃.   326.0 gr./liter.   Density, 1.2133 gr./c.c.

Fig. 5.
Al(NO₃)₃.   430 gr./liter.   Density, 1.2517 gr./c.c.

Fig. 6.
CaCl₂.   557.7 gr./liter.   Density, 1.3950 gr./c.c.

Fig. 7.
SrCl₂.   296.0 grams/liter.   Density 1.2445 gr./c.c.

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the absorption is increased the irregularity of the curve for the solution indicates that the dissolved substance had absorption bands in this region. No definite conclusions can be drawn as to shifts in the positions of
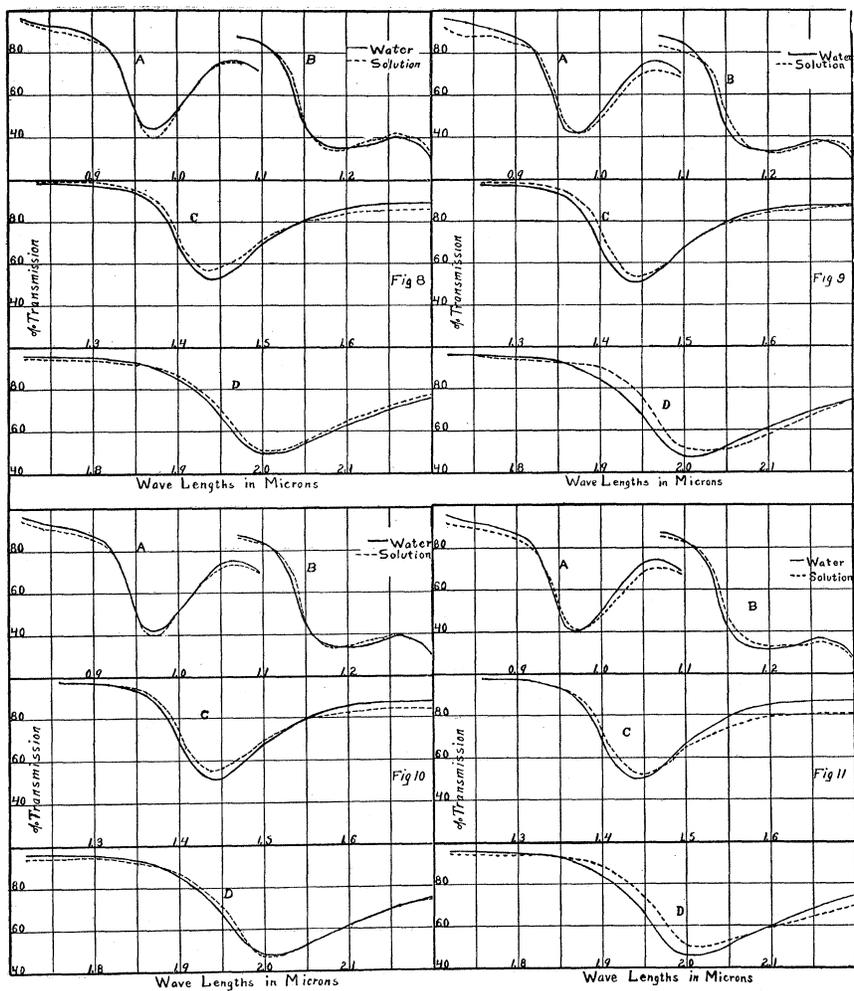
Fig. 8.

Mg(NO₃)₂.   424.5 gr./liter.   Density, 1.2873 gr./c.c.

Fig. 9.

MgCl₂.   319.0 gr./liter.   Density, 1.2360 gr./c.c.

Fig. 10.

Zn(NO₃)₂.   414.5 gr./liter.   Density, 1.3200 gr./c.c.

Fig. 11.

ZnSO₄.   513.0 gr./liter.   Density, 1.466 gr./c.c.

the water absorption bands due to the dissolved substances.   In most
cases where there is an apparent shift in the position of maximum
absorption it is difficult to say that it is a true shift, as the presence of
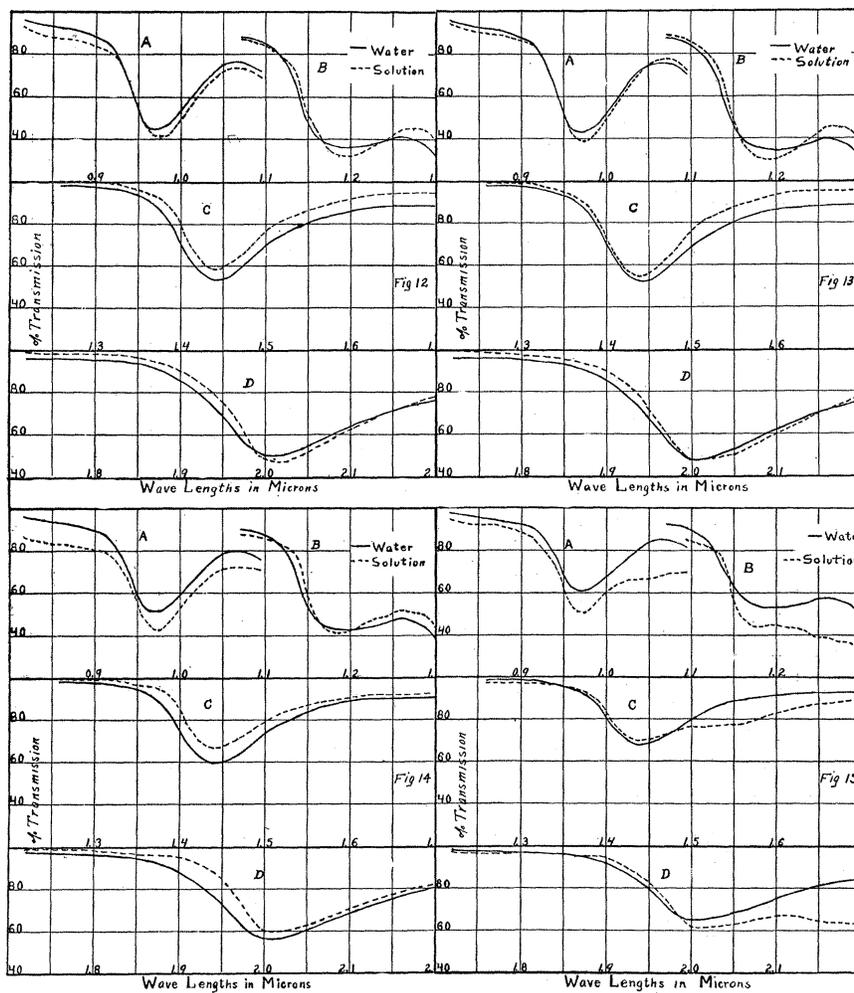
Fig. 12.

Na$_2$S$_2$O$_3$.   524.9 gr./liter.   Density, 1.361 gr./liter.

Fig. 13.

NaCl.   319.8 gr./liter.   Density, 1.2020 gr./c.c.

Fig. 14.

AgNO$_3$.   1413.0 gr./liter.   Density, 2.1180 gr./c.c.

Fig. 15.

NH$_4$NO$_3$.   743.0 gr./liter.   Density, 1.2700 gr./c.c.

an absorption band of the dissolved substance near that of the water
might cause such a change in the shape of the curve.
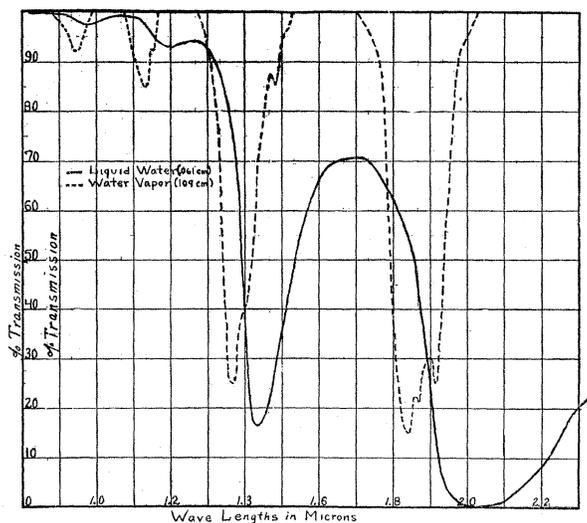
Fig. 16.

DISCUSSION.

Schaeffer, Paulus, and Jones explained their results on the basis of the
solvate theory.   The dissolved substances which form loose combinations
with some of the water in which they are dissolved render this part of the
water less absorbing.   Non-hydrating substances should have no effect
on the absorption of the water.   Their explanation did not fit all the
data which they published and does not agree with all the results shown
here. $Al_2(SO_4)_3$, $ZnSO_4$, and the alkaline hydroxides make the water
less absorbing at all the absorption bands, but all the remaining hydrating
salts studied cause a greater absorption at some of the absorption bands.
Also the three non-hydrating salts, NaCl, NH_4NO_3, and $AgNO_3$ all
caused a decrease in absorption by water at one absorption band.

Livens[1] has deduced an explanation of an effect of a dissolved substance
on the absorption of the solvent on the basis of the Lorentz electron
theory.   If the solute has absorption bands at wave-lengths much longer
than that of the solvent, the solvent should absorb less than it would if
the solute were absent and the position of maximum absorption should
be shifted toward the shorter wave-lengths.   If the solute has absorption
bands at wave-lengths shorter than that of the solvent, the solvent
should be more absorbing in the presence of the solute and the position

[1] Phys. Zeitschr., 14, p. 660 (1913).

of maximum absorption should be shifted toward the longer wave-
lengths. This explanation would seem to lead to the conclusion that all
the absorption bands of water here studied should be affected alike, as
they lie close together and thus have the same relation to the absorption
bands of the dissolved substance.

Neither of these explanations fits the experimentally determined facts
completely. With the exceptions of $Al_2(SO_4)_3$, $ZnSO_4$ and the alkaline
hydroxides, the solutes used caused an increase in the absorption of the
water at the absorption bands located at .97 μ and 1.20 μ, and a decrease
in the absorption of the water at the band located at 1.44 μ. From an
examination of the curves it seems likely that the dissolved substances
decrease the absorption of the water in the band at 2.00 μ, although in
many cases this effect is apparently masked by the presence of absorption
bands of the dissolved substance.

With the above exceptions then it may be said that the effect of dis-
solved substances is to increase the absorption of the water at two absorp-
tion bands (.97 μ and 1.20 μ) and to decrease the absorption of the water
at the other two bands (1.44 μ and 2.00 μ). A parallel to this is found
by comparing the absorption of water vapor and liquid water for layers
having equal number of molecules. Fig. 16 shows the absorption spectra
of equivalent thicknesses of water vapor and liquid water. The water-
vapor curve is taken from the results of Hettner.[1] There is an absorption
band in the vapor curve for each band in the liquid curve, but displaced
toward the shorter wave-lengths. The absorption bands of water at
.97 μ and 1.20 μ are less intense than the corresponding bands for the
vapor, while the bands at 1.44 μ and 2.00 μ are more intense than the
corresponding vapor bands. This fact suggests that there may be some
connection between the effect of dissolved substances on the absorption
of water and the effect of changing from vapor to liquid.

The fact that all the absorption bands of liquid water are present when
the water is converted into vapor indicate that these absorption bands
are due to the molecules and not to aggregations of molecules. Hence it
seems that the only way in which the absorption could be changed to a
great extent would be by a change in the number of absorbing molecules
present. If there are different kinds of water molecules there is a possi-
bility of their relative number being changed by the presence of a dis-
solved substance, by polymerization of the water, by change of tempera-
ture, etc. According to Langmuir's[2] model of the water molecule there
may be four kinds of water molecules as the hydrogen nuclei may be

[1] Ann. d. Physik., 55, p. 476 (1919).
[2] Jour. Amer. Chem. Soc., 41, p. 893 (1919).

arranged in four different relative positions about the oxygen nucleus. These different molecules would probably have different modes of vibration which would give rise to absorption bands of different frequencies. The relative intensities of these absorption bands would depend in part on the relative number of each kind of molecule present in the water. Some such explanation together with the fact that some dissolved substances form loose combinations with the water in which they are dissolved may be able to fit the experimental results when more data are available. At present no simple explanation fits all the known results.

The writer wishes to thank Professor R. C. Gibbs, under whose direction the investigation was carried out, for his encouragement and helpful advice during its progress.

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