Constitution of Water in Solutions of Electrolytes as studied by the Raman Effect

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ABSTRACT.

To arrive at a clear conception of the behaviour of water in solutions of electrolytes the results of a more thorough and systematic investigation of the subject than has hitherto been attempted, are described in this paper. The results obtained may be briefly summed up as follows :

(1) The water band obtained in the Raman spectra of solutions of electrolytes is sharper than for pure water.

(2) While with aqueous solutions of nitric acid, sulphuric acid and sodium nitrate the band gets sharper with increasing concentration and shifts as a whole towards greater frequency, the portion of the intensity curve on the smaller frequency side becoming less convex, just the opposite results have been observed with solutions of hydrochloric acid in water.

(3) Whereas there is a progressive shift towards larger frequency in the water band in solutions of electrolytes at the same concentration as we pass from lithium chloride to sodium nitrate and from hydrochloric to sulphuric and nitric acids, these differences tend to vanish when their water content is equalized.

The probable cause of the results observed—hydration of the ions of the dissolved substance or change in the water equilibrium due to variations in the proportions of monohydrol, dihydrol and trihydrol—is discussed in detail and conclusions arrived at.

(4) The cation appears to exert little influence on the behaviour of the solvent, as can be inferred from the similarity of results obtained with acids and salts.

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(5) The intensity curves for sodium nitrate are in general much sharper than those for nitric acid, even when the latter is taken at a much higher concentration. This result is explained as partly due to the formation of more complex hydrates and partly due to the superposition of the NO_2OH band at 3420 cm^{-1} over the band due to water in solutions of nitric acid.

1. *Introduction.*

For a proper understanding of the nature of solution it is necessary to have a clear conception of the behaviour as much of the solvent as of the solute, when one is in combination with the other. And, water being the most important and universal solvent, a detailed study of its nature and constitution in solutions of different characteristic groups of substances, *e.g.*, strong electrolytes, weak electrolytes and non-electrolytes, will lead us a long way in arriving at some clear and definite ideas regarding the nature of solution and the characteristic function that the solvent plays therein. It is therefore proposed to deal in this communication with the author's investigations on the subject with reference to the first characteristic group, *viz.*, the strong electrolytes.

There are several methods of attack of the problem. In general, any physical property of the system, *e.g.*, its specific gravity, electrical conductivity, absorption spectrum or freezing-point determination of the binary system, solvent and solute, at different concentrations, will provide with information on the subject, and these were the methods employed by the earlier workers in the field. But in recent years the Raman effect has been applied with advantage to the investigation of the nature of solution on account of the simpler and at the same time more definite information that is provided by a study of the Raman spectra of solutions. In fact, on account of the very simple relations that exist between the intensity of the Raman lines or bands and the numbers of molecules or ions that give rise to them, the possibility of arriving by this method at very

clear ideas on electrolytic dissociation, particularly in concentrated solutions has been demonstrated by Ramakrishna Rao and others ; [1] and now the author has applied the method to study the other aspect of the problem, namely, that concerning the behaviour of the solvent in solution.

2. *Earlier Work on the Raman Spectra of Solutions.*

Whereas, on the one hand, it is definitely established that electrolytes dissociate into their constituent ions in their aqueous solutions, there is, on the other hand, evidence to show that an entirely different process takes place with respect to the solvent. The water molecules generally combine with the dissociated ions of the solute to form, what are called, hydrates. Mendeleeff[2] was the first to give definite ideas as regards the formation of hydrates in solution. By plotting specific gravities of solutions of sulphuric acid and calcium chloride in water against their respective concentrations he found that the curves exhibited a number of maxima, which he interpreted as being due to the formation of hydrates.

Jones and his collaborators arrived at similar conclusions from their work on the freezing-point measurements with mixtures of acetic acid and sulphuric acid, acetic acid and water, and of acetic acid, water and sulphuric acid. They found that the total lowering of the freezing point of the mixture was less than the sum of the lowerings due to the individual constituents.

[1] I. Ramakrishna Rao : (*i*) Proc. Roy. Acad.. Amsterdam, Vol. 33, No. 6, p. 632 (1930).
        ,,   ,,   (*ii*) Roy. Soc. Proc. A, Vol. 127, p. 279 (1930).
        ,,   ,,   (*iii*) Iudian Journ. Phys., Vol. 8, p. 123 (1933).
        ,,   ,,   (*iv*) Roy. Soc. Proc. A, Vol. 144, p. 159, (1934).
     L. A. Woodward : (*i*) Physikal. Zeits., Vol. 32, p. 212, (1931).
        ,,   (*ii*)   ,,   ,,   Vol. 32, p. 777 (1931).
     L. A. Woodward and R. G. Horrer (*iii*) Roy. Soc. Proc. A., Vol. 144, p. 129 (1984).
     L. Simmons : Soc. Scient. Fenn., Comm. Phys.—Math. VII. 9. (1933).
[2] Ber. d. Ohem. Gessell., Vol. 1, p. 379 (1886).
[3] Publication 210 of the Carnegie Institution of Washington (1915).

This was a phenomenon just opposite to that observed with electrolytes and must therefore be ascribed to an association of the molecules of the solvent with the ions of the solute thus reducing the number of independent molecules which lower the freezing-point.

Later, during the course of their work on water and solutions by a study of their Raman spectra, it was found by the earlier workers that water, unlike other substances which give more or less sharp lines, gives rise to a broad and diffuse band extending over 750 cm^{-1} from about 3000 cm^{-1} to 3750 cm^{-1}, corresponding to the infra-red absorption at $2 \cdot 97 \mu$ and resolvable by an analysis of its intensity curves into three individual components with maxima of intensities at 3610 cm^{-1} ($2 \cdot 77 \mu$), 3413 cm^{-1} ($2 \cdot 93 \mu$) and 3195 cm^{-1} ($3 \cdot 13 \mu$).[4] Notable changes are noticed[5] in the distribution of intensity in the band with change of temperature and with addition of electrolytes to water. Ramakrishna Rao[6] found that the changes observed in the intensity and relative position of the maxima in the band with change of temperature could be best explained on the hypothesis of the presence in water of three types of molecules corresponding to H_2O, $(H_2O)_2$ and $(H_2O)_3$, the relative proportions of which alter with change of temperature. He found that an increase of temperature results in the shift of the maximum of the band to the greater frequency side and is due to a diminution in the proportion of the triple molecules corresponding to the maximum at 3195 cm^{-1} and a proportionate increase in the number of the single molecules corresponding to the maximum at 3610 cm^{-1}. He also noted that the addition of the electrolyte, nitric acid, causes a shift in the position of the intensity maximum of the band towards the larger frequency side similar to the effect of a rise of temperature and interprets it as being due to a change in the proportion of the three types of molecules. He attributes the development of

[4] I. Ramakrishna Rao : Roy. Soc. Proc. A, Vol. 145, p. 489 (1934).
[5]   „   Roy. Soc. Proc. A, Vol. 130, 489 (1931).
[6] loc. cit.

a second maximum in solutions of nitric acid in water at concentrations higher than 76% to the formation of hydrates. A similar observation was recorded by Meyer[7] about the appearance of a second maximum on the short wave-length side in solutions of nitric acid at high concentrations, its intensity exceeding that of the original peak at 14 mols per litre.

Ganesan and Venkateswaran[8] studied the Raman Spectrum of concentrated nitric acid in which they obtained two bands resolved from one another in the position of the usual broad and diffuse band observed with pure water.

Gerlach[9] worked with water and solutions of dissolved salts and found that water gives rise to a double band ranging over 35 ± 5 Å and that addition of nitrates shifts the short wave band to the violet, while the chlorides tend to blot it out.

Pringsheim and Schlivitch[10] on the one hand, and Brunetti and Ollano[11] on the other, disagree with the observations of the earlier workers as regards the changes in the intensity of the water band with addition of salts. The former, in their work on water and lithium chloride solution, observe that the relative changes in intensity of the water band with change of temperature and with addition of salts noticed by others are spurious. But it has been demonstrated by the recent work of Ramakrishna Rao that the changes observed in the intensity distribution of the water band with rise of temperature are really genuine and are due to changes in the relative proportions of the single $(H_2O)_1$ double $(H_2O)_2$ and triple $(H_2O)_3$ molecules which are supposed to exist in water.

Hatley and Callihan[12] worked with solutions of KCl, NaOH and KOH in water at various concentrations and observed that

[7] Phys. Zeit., Vol. 31, p. 699. (1930).
[8] Ind. Jour. Phys., Vol. 4, p. 236 (1929).
[9] *Phys. Zeits.*, Vol. 31, p. 695 (1930).
[10] Zs. für Phys., Vol. 60, 9-10, p. 581 (1930).
[11] Accad. Lincei, Atti., Vol. 12, p. 522 (1930).
[12] Phys. Rev., Vol. 38, p. 909 (1931).

in all cases the energy appears to shift towards the long wavelength side and that the top of the curve gets sharper with increasing concentration.

Rafalowski[13] working with solutions of hydrochloric acid and nitric acid in water at various concentrations reported that the water band became less sharp with increasing concentration in the case of hydrochloric acid while with nitric acid it became sharper.

Hulubei[14] claimed to have obtained, besides the double band at 3233-3443 cm^{-1}, ten other bands with wave-number shifts lying between 6747-10944 cm^{-1} from the original exciting line. These were found to disappear with addition of salts, which he interpreted as being connected with association in water.

Silveira[15] obtained the Raman spectra of solutions of $MgCl_2$, $Mg(ClO_3)_2$, $Mg(NO_3)_2$, which gave lines with small frequency shifts, 1655 and 376 cm^{-1}, the former being attributed to the Mg ion complex with water and the latter to ClO_3 and NO_3 ion complexes with water. In two later communications[16] his observations with other solutions revealed a large number of lines with small frequency shifts.

Embirikos[17], in continuation of the work of Gerlach referred to above, worked with a number of univalent and divalent chlorides and nitrates and his results, are in agreement with those of Gerlach. Nitrates are, however, noticed to give rise to a second band, the distance between the two components increasing with concentration. The nature of the cation is found to exert no influence on the structure of the Raman band of water. The second band with ammonium nitrate solution, which he wrongly attributed to water, is really due to the NH_4 group, as has been shown in a previous communication. [18]

13 Acad. Polonaise Sci. et Lettres, Bull. 7-10 A, p. 623 (1931).
14 Comptes Rendus, Vol. 194, p. 1474 (1932).
15 Comptes Rendus, Vol. 194, p. 1396 (1932).
16 Comptes Rendus, Vol. 195, p. 416 and p. 521 (1932).
17 Phys. Zeits., vol, 88, p. 946 (1932).
18 Zs. für Physik., Vol, 88, p. 127 (1934).

Cabannes and Riols [19] found that the water band was triple and that the addition of sodium nitrate causes shifts in the intensity of the band to higher frequencies and the disappearance of the component at 3625 cm^{-1} due to the H_2O molecules.

In spite of all this varied amount of work with reference to the behaviour of water in solutions of electrolytes, especially by a shift of its Raman band, there has been so far no attempt at a thorough and systematic investigation of the nature of the changes noticeable in the structure of the water band and to give a satisfactory interpretation thereof.

The present work is, therefore, undertaken with the idea of systematically studying the behaviour and constitution of water in solutions of some of the typical electrolytes, both acids and salts, under conditions easily comparable, and to arrive at a satisfactory understanding of the cause of the variations observed in the structure of the Raman band of water—namely, whether the effect is due to the hydration of the ions of the solute by combination with the molecules of the solvent, water, or whether the effect is similar to that observed with change in temperature, *viz.*, a mere change in the proportions of different types of molecules supposed to exist in water.

3. *Experimental Procedure.*

(a) *Experimental arrangement* : The experimental arrangement employed in these investigations is represented in Fig 1. It consists of the vertical Wood's tube W. T. containing the liquid to be studied, close to which is placed the illuminating mercury lamp H, and the light scattered by the liquid along W. T. through the plane quartz window at the bottom of the tube is reflected on to the slit of the spectrograph through the condensing lens L by means of a plane mirror M held at an inclination of 45° to the vertical. The light from the mercury lamp is concentrated on the Wood's tube containing the liquid by means of an

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[19] Comptes Rendus, Vol. 198, p. 80 (1934).

FIG. 1.
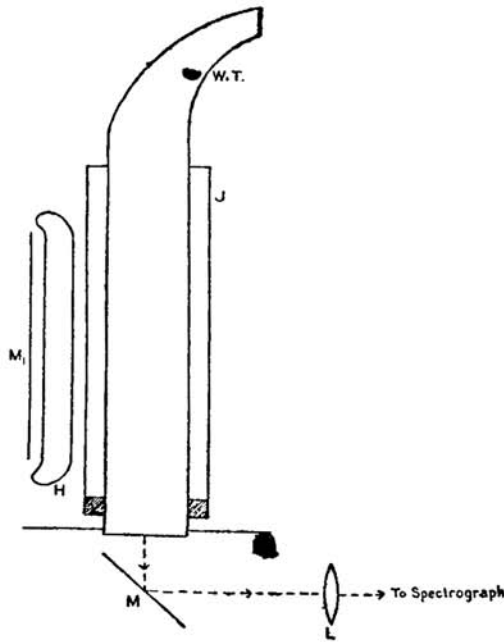
elliptical mirror M_1 made out of a polished sheet of aluminium and held on the side away from the tube. All extraneous light from the lamp is cut off by suitable screens. Further, the light from the lamp is filtered through a solution of cobalt chloride, which transmits the 3650λ group and the 4047λ line of the mercury arc, but effectively cuts off the 4358λ group and the 4916λ line and its accompanying group of faint lines, so that the water bands excited by the former two have been obtained, that due to the 3650λ group being usually the stronger. The filtering solution is contained in the interspace between the Wood's tube and a wider pyrex glass jacket, J, concentric with it and held in position by rubber bands which close the tube water-tight at the bottom. On account of the small depth of the filtering liquid it has to be made somewhat concentrated. Although this arrangement requires rather long exposures, it permits of an easy removal and replacement of the observation tube (W. T.) without disturbing any other arrangement, another advantage

is that a small quantity of filter will suffice and it can be re-filled when necessary from the top during the course of an exposure without disturbing either the tube or the lamp. During the course of exposure the lamp and the tube are cooled by means of a table fan.

Another arrangement, due to Wood,[20] has also been employed in some cases. In this, a cylindrical pyrex glass condenser containing the filtering solution is placed right above the horizontal Wood's tube with the liquid under investigation. In cases where no filter is necessary it is filled with water and placed in position, and a Hewittic mercury lamp of the horizontal type is situated above the cylindrical condenser as close to it as possible. Two elliptical mirrors, one of them placed above the mercury lamp and the other placed below Wood's tube, serve to reflect back the light from the arc on the condenser and the Wood's tube respectively, so that maximum use is made of the light from the arc. This arrangement has been found to be very efficient in practice and permits of comparatively short exposures.

(b) *Continuous spectrum and colour filters*: As it is the Raman band due to *water* that is the subject of study in these investigations, there is no difficulty as regards its proper assignment to its corresponding exciting line. Thus there is no necessity for using light filters for obtaining perfectly monochromatic light. But a constant source of trouble encountered during the work on the Raman spectra of solutions is the presence in the scattered light of a large amount of continuous spectrum, which gets superposed on the water band, thus rendering difficult any accurate investigation of the distribution of intensity along the band.

This continuous spectrum may be attributed to many causes. Firstly, it is due to the presence of a feeble continuous spectrum in the light from the mercury arc itself, its intensity increasing

[20] Phys. Rev., Vol. 37, p. 1022 (1931).

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with increasing temperature of the arc. Thus it can be reduced to a minimum by running the arc at a low temperature and hence at a low intensity and cooling it, at the same time, by means of a table fan. This, of course, necessarily involves long exposures. A second source of this continuous spectrum is the presence of fluorescent impurities in the substance under investigation. This is eliminated by employing throughout Merck's or Kahlbaum's extra pure chemicals manufactured for analytical purposes and using pure grease-free distilled water for dissolving the chemicals. In some cases, exposure of the substance under study to ultraviolet radiation from the lamp produces photochemical reactions which result in the formation of foreign substances, which may produce a continuous spectrum ; but most of the substances studied in the present investigations do not undergo photochemical decomposition, and so one cause of the trouble does not arise. Yet another cause of this continuous spectrum, which seriously handicaps the work on solutions, is that in the case of a freshly prepared solution the fluctutions in its density and concentration are considerable and since the Rayleigh scattering is dependent on these fluctuations, a freshly prepared solution scatters the continuous spectrum present in the light from the mercury arc much more than does a solution kept for a sufficiently long time, so as to allow it to become perfectly homogeneous and its fluctuations to appreciably vanish. Hence, in all these experiments the solutions are allowed to lie over for some time before their Raman spectra are taken to ensure a perfectly homogeneous distribution of the molecules of the dissolved substances in the solution.

Notwithstanding all these precautions, a faint continuous spectrum still persists in most of the solutions. When it is appreciable, it becomes necessary to suppress it by the use of suitable filters. Generally it extends from 4000A° to 5500A°, and its maximum lies between 4500A° and 5000A°, a region where the water band excited by the 4047, line is

situated. The best filter to eliminate this continuous background is a solution of iodine in carbon tetrachloride, but, on account of its volatility, a solution of cobalt chloride is generally employed in these investigations as it is found to be nearly as good and to be extremely stable towards the ultraviolet radiation from the arc.

There is one advantage in the work on the Raman band of water owing to the fact that it has a very large frequency shift and as such the Raman lines due to the anions present in solution and excited by the same mercury line do not generally get superposed on the band, as they usually have small frequency shifts. But, in same cases, the Raman lines due to the anion, like the NO_3^- and SO_4^{--} ions, excited by strong mercury arc lines other than the line used to excite the band get superposed on the water band and so it becomes imperative in such cases to eliminate such superposition by effectively cutting off such lines by means of suitable filters.

(c) *Choice of substances and exciting lines :* All the previous work on the Raman band of water in solutions was qualitative, no systematic study being made of its changes with special reference either to the amount of solute or solvent contained in the solution. In an investigation of the changes in the structure of the water band under the influence of dissolved substances it is always desirable to take the different substances under the same moral concentration, so that the number of molecules of the solute in a definite volume of the solution remains the same in all cases. Then it is easier to interpret the mutual influence of the solute and the solvent in terms of the number of molecules and the results for different substances become readily comparable with one another. Further the second aspect of the problem, wherein a certain volume of the solution in each case contains the same water content, thereby making the same number of molecules of the solvent influence the solute in the different solutions, is also equally interesting and provides additional valuable

information on the subject.   Both aspects of the problem, outlined above, have been investigated by the author and the results given below.

Again, for observations on the influence of ions on the structure of the Raman water-band, it is necessary to work at as high a concentration as possible, *e.g.* of the order of about 12N, and comparatively few electrolytes dissolve to such a large extent.   Further, the appearance of a large amount of continuous spectrum at high concentrations in some cases renders the work with them rather difficult and uncertain, as has been found, for example, in the case of zinc chloride solution at 12N concentration.   As pointed out before, this is much more so for the band excited by the 4047 λ line of the mercury arc inasmuch as the maximum of the continuous background falls in the same region of the spectrum in which the band due to this line is formed.   Also, most of the electrolytes absorb the ultraviolet thus restricting the work to only a few exciting lines in the visible region or in the near ultraviolet.

Again, a difficulty in using the 4358 λ line as the exciting line is that the band excited by this falls in a region in which most photographic plates are not sufficiently sensitive.   Hence the only band which can be studied in most cases is that excited by the 3650-63 λ group of lines, and this also happens to be more intense than that excited by the 4047 λ line.   Also the dispersion of the Fuess's spectrograph which is about 16 A° per m.m. in this region, is larger in the region of this band thus enabling greater accuracy to be attained in the estimation of frequencies.   But there is one drawback with regard to the use of this band : whereas the band excited by the 4047 λ line is due to a single exciting line, that excited by the 3650-63 λ group is due to a group of three lines, situated close together although of unequal intensity, so that in the latter case there is to some extent a partial superposition of the bands excited by the individual lines of the group.   But from a comparative

study of the intensity curves of the water band excited by the 4047 λ line as well as by the 3650-63 λ group in a number of cases, it has been found that the curves agree with one another to a close approximation if the value for the frequency of the exciting line in the case of the 3650-63 λ group is taken to be 27340 cm^{-1}, a value very nearly the mean for the group. Although the band due to the 4047 λ line is to be preferred on account of its inherent purity, originating as it does in a single exciting line, it had to be given up for the reasons mentioned above and the band excited by the 3650-63 λ group has been studied almost throughou these investigations.
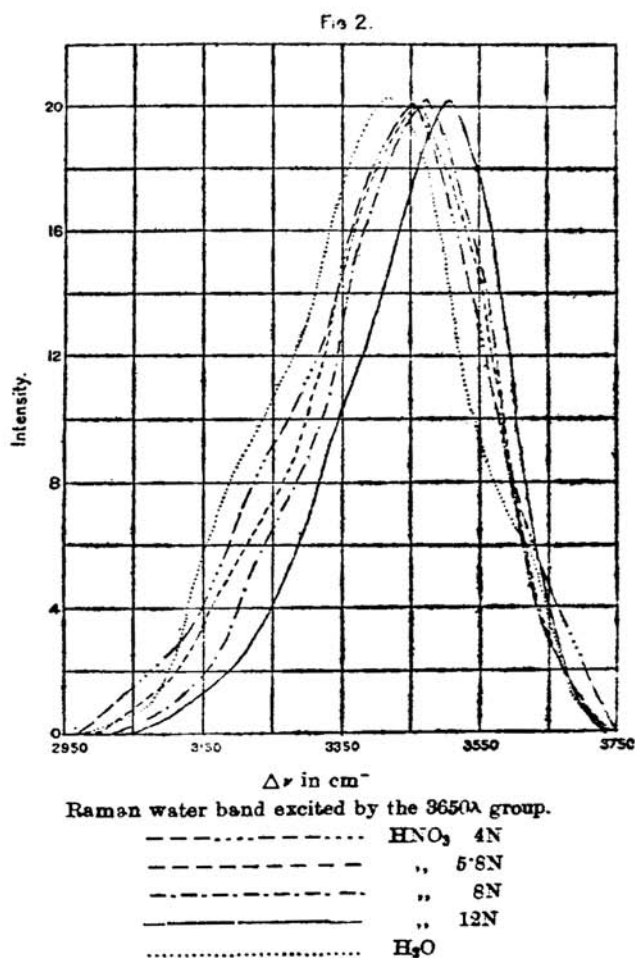
To make a study of the variations that take place in the structure of the water band with addition of other substances it is necessary to examine its intensity curves rather than the band itself, as the latter by itself cannot furnish much useful information. Therefore, the microphotometric curves of the band in each case are taken and by taking on each plate comparison exposures with a calibrated Zeiss step-filter and a straight filament lamp fed under constant voltage, the density-log intensity curve is drawn for each plate in the particular position of the spectrum in which the band is formed, and from this the intensity curve for each band is calculated, density at different points along the band being given by its microphotometric curve. One difficulty experienced in obtaining fairly smooth microphotometric curves of the water band is that on account of the large grain of the plates used owing to their high speed—Ilford golden iso-zenith plates, H and D 1400, being invariably used throughout—the outline of the curve is always very coarse, and this necessarily involves large errors in estimating the actual shape of the curve. The curves were found to improve (1) by making the slit of the thermopile of an optimum width, neither too large nor too narrow, (2) by using a comparatively short deflection between the zero line taken with no light falling on the slit of the thermopile and the blank

plate line taken with the light passing through the unexposed portion of the plate, and (3) finally by adjusting the spectrum slightly out of focus.

Although it is very necessary that the spectrum should be adjusted in perfect focus for the measurement of intenstities of spectral lines, its adjustment a little out of focus in the present case, where it is a band and not a line that is studied, does not affect the results very much. This is more so, as it is only the relative distribution of the intensities along the band in the several cases that we are concerned with, and not the absolute values. Further to make the results obtained more reliable, all the plates with the different spectra are developed and fixed under identical conditions, as far as practicable, by using the same strength of the developer and always developing for the same interval of time at the same mean temperature, viz., 18°C. Also, the plate is developed sufficiently along (4·5 minutes) to properly bring out the continuous back-ground' of the spectrum without any appreciable fogging of the plate. The intensity values are always corrected for this continuous background.

4. Results.

To begin with, the results for each electrolyte are given. Fig. 2 represents the intensity curves for the water band excited by the 3650-63λ group in the Raman spectra of solutions of nitric acid at four different concentrations, viz., 4·04N, 5·86N, 8N and 12N. The curve for pure water is also given for comparison. The intensity at each point in the band is marked against the corresponding frequency shift. The band being very diffuse, it is not possible to measure wave-lengths by means of a micrometer. Hence to determine the Raman frequencies corresponding to every point in the band, the dispersion curve for the region of the spectrum between 4017 λ and 4358 λ mercury lines

Fig 2.

$\triangle \nu$ in cm⁻

Raman water band excited by the 3650λ group.

— — —....--— — —.... HNO₃ 4N
— — — — — — — — —   ,,   5·8N
—·—·—·—·—·—·—·—·   ,,   8N
————————————   ,,   12N
.... H₂O
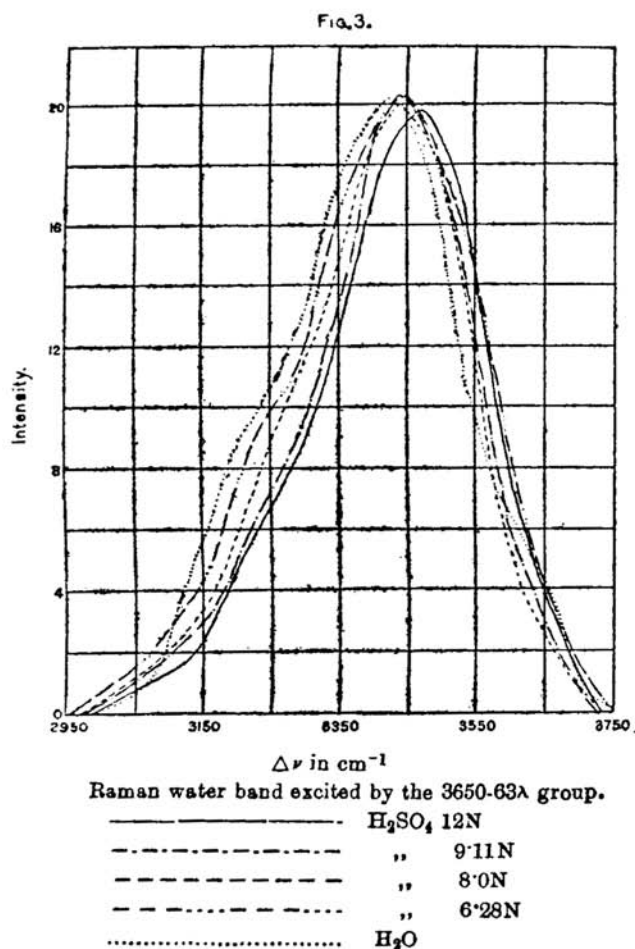
is drawn. The distance of each point on the microphotometric curve of the band from the 4078 λ line is measured and the corresponding wave-length at this point is determined from the above dispersion curve. From an examination of the intensity curves the following results are clear :—

(i) The water band in nitric acid solutions is invariably sharper than for pure water.

From fig. 2 it follows that with increasing concentration of the acid,
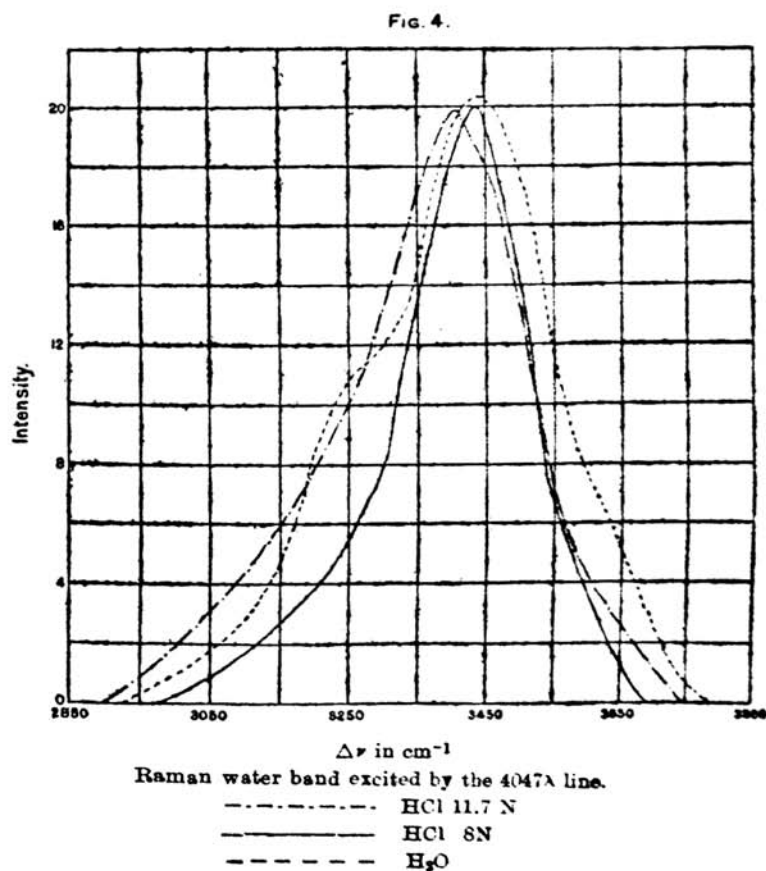
(ii) the band becomes sharper;

Fig. 3.

$\triangle \nu$ in cm^{-1}

Raman water band excited by the 3650-63λ group.

————————————————·   H$_2$SO$_4$ 12N

—·—·—·—·—·—·—·—·—·—   ,,   9·11N

— — — — — — — — —   ,,   8·0N

— — —·····— — —····   ,,   6·28N

······································   H$_2$O

(*iii*) there is a progressive shift in the maximum of the band as well as in the position of the band as whole towards larger frequency ;

(*ic*) the curves become less and less convex on the side of smaller frequency.

In fig. 3 are given the intensity curves for the water band in solutions of sulphuric acid at four different concentrations, *viz.*, 6·28N, 8N, 9·11N and 12N. Results very similar to those observed in the case of nitric acid are found with increasing concentration of sulphuric acid also.

The intensity curves for hydrochloric acid at two different concentrations, 8N and 11·7N, are represented in fig. 4 along with that for water. While the band in solutions of hydrochloric

FIG. 4.

$\Delta \nu$ in cm^{-1}

Raman water band excited by the 4047Å line.

—·—·—·—·—· HCl 11.7 N

—————— HCl 8N

— — — — — — H$_2$O

acid in water is sharper than for the pure solvent, the positions of the maxima almost coinciding, as contrasted with nitric and sulphuric acids, the results obtained with water solutions of hydrochloric acid with increasing concentration of the acid content are as follows :

(i) the band gets broader ;

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(*ii*) there is a relative shift in the maximum of the band as well as in the position of the band as a whole towards the smaller frequency side.

Fig. 5 represents the intensity curves for the water band in solutions of sodium nitrate at two different concentrations, 5·5N and 8N, together with the curve for pure water. While the curves for sodium nitrate are shifted to the side of greater frequency shift relative to that for water, in this case again the

Fig. 5.

$\Delta \nu$ in cm^{-1}

Raman water band

—·—·—·—·—·   NaNO$_3$ 8N

————————   NaNO$_3$ 5.5N

....   H$_2$O
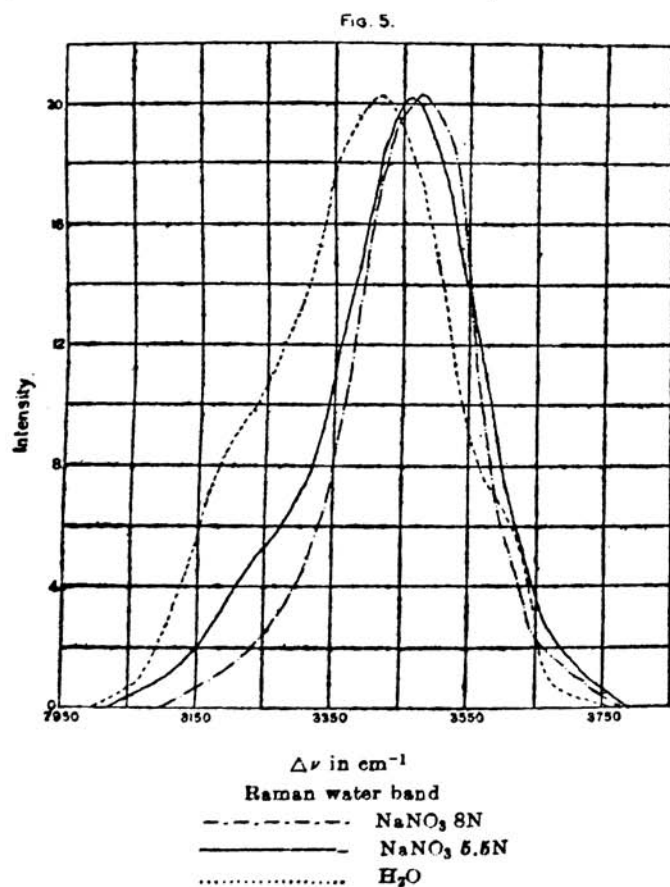
same results are obtained with regard to the relative shift and shape and positions of the bands as are observed in the case of nitric and sulphuric acids under different concentrations.

Table I contains the positions of the maximum of the band at different concentrations of all the above electrolytes.
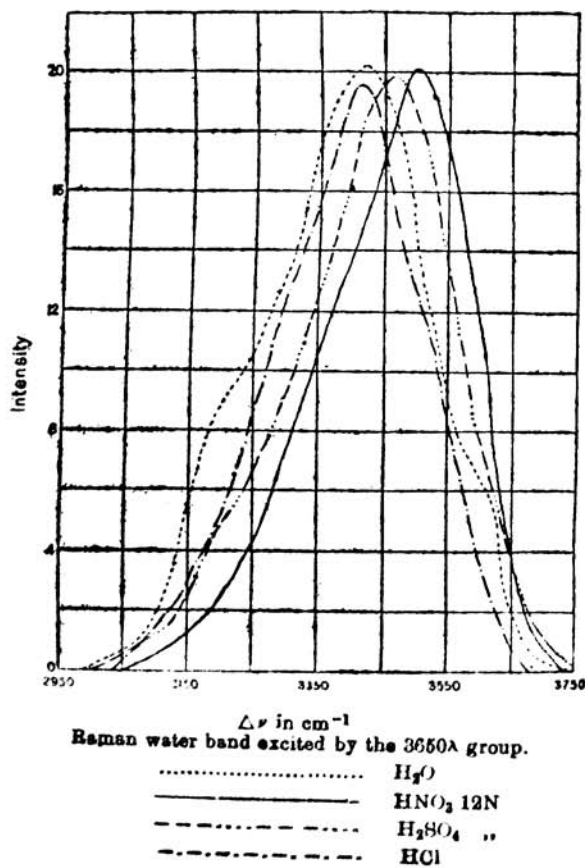
TABLE I

Substance.	Concentration.	Position of the maximum.
1. H_2O	—	3424 cm^{-1}
2. HNO_3	4·04N	3450 ,,
,	5·86N	3460 ..
,,	8·0 N	3474 ..
,,	12·0 N	3504 ,.
3. H_2SO_4	6·28N	3433 ,.
,.	8·0 N	3436 ,,
,,	9·11N	3440 ..
,,	12·0 N	3468 ,,
4. HCl	8·0 N	3435 ,, (4047λ excit)
,,	11·7 N	3415 .,
5. $NaNO_3$	5·5 N	3463 .,
,,	8·0 N	3480 ..

Thus, while with increasing concentration of the electrolyte in water in the case of nitric acid, sulphuric acid and sodium nitrate there is a sharpening of the band and a progressive shift to the larger frequency side, just the contrary results of a broadening of the band with a relative shift to the smaller frequency side have been obtained with increasing concentration in the case of hydrochloric acid. Again, the appearance of convexity, though slight, observed in the shape of the intensity curves at higher dilutions in the case of sulphuric acid, nitric acid and sodium nitrate does not seem to be present in the case of hydrochloric acid. On the contrary, it even appears that there is a slightly greater concavity on the smaller frequency side at the smaller concentration in the case of hydrochloric acid.
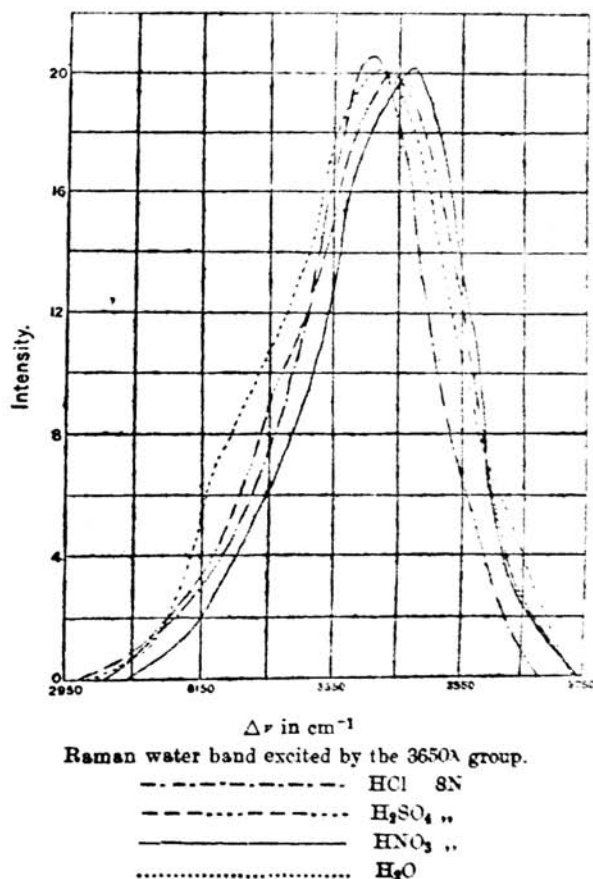
Thus far a study has been made of the changes in the structre of the water band at different concentrations only of each electrolyte separately. To determine if there is any relationship between the bands obtained with the same concentration of different electrolytes, their Raman spectra are taken as far as possible under identical conditions of illumination from the mercury lamp, etc. The work is undertaken to examine the nature of the dependence of the constitution of water on the electrolyte dissolved in it.

Fig. 6 gives the intensity curves for the three acids, nitric, sulphuric and hydrochloric, at the same concentration, *viz.*, 12N, and for pure water. One very striking feature that is at once

Fig. 6.

$\Delta \nu$ in cm^{-1}

Raman water band excited by the 3650λ group.

.... H$_2$O

———————— HNO$_3$ 12N

— — — .... — —.... H$_2$SO$_4$,,

—.—.—.—.—.—.—. HCl

noticeable in the curves is the relative shift in the positions of
the maxima to the larger frequency side as we pass from hydro-

$\Delta\nu$ in cm^{-1}

Raman water band excited by the 3650Å group.

—·—·—·—·—·—·—·—· HCl 8N
— — —·····— — —···· H$_2$SO$_4$,,
————————— HNO$_3$,,
························· H$_2$O

chloric acid to sulphuric and nitric acids, the shift in the case
of nitric acid being the greatest. The same relative shift in
the band as a whole is also very conspicuous from the intensity
curves, the shift of the band gradually increasing from hydro-
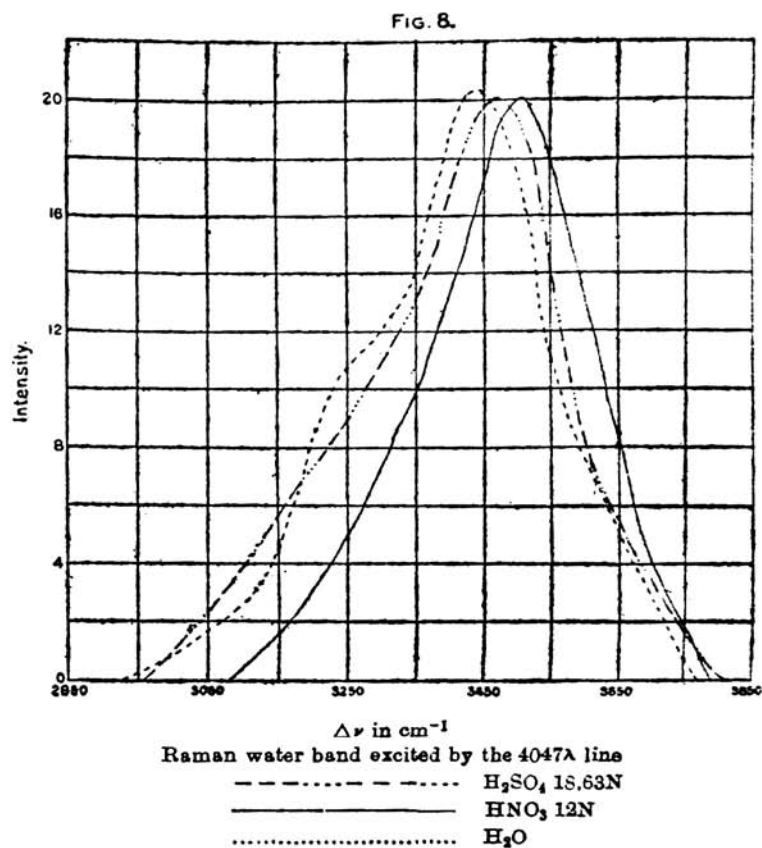chloric to sulphuric and nitric acids, being a maximum for
the last.

Fig. 7 gives the intensity curves for the same three acids at
another concentration, viz., 8N. The same results noticed
above with 12N concentration of the acids are observed in the

present case also, although to a less conspicuous degree. Also, at the smaller concentration the bands are in general less sharp (except in the case of hydrochloric acid where the opposite result has been observed) than at the higher concentration, a result one might naturally expect by reason of the increased proportion of water.

Having investigated the water band for different electrolytes at the same concentration and each of them under different concentrations, further work was found necessary in order to arrive at a more satisfactory conclusion as to the observed effect of the dissolved substances on the constitution of water, namely, whether it is due to an association of the molecules of water with the ions of the dissolved electrolyte in the form of water of hydration, or whether it is simply due to a change in the water equilibrium due to a change in the proportion of the single, double and triple molecules, an effect similar to that observed with change of temperature. If the cause of the observed results is mainly the second, then it is to be expected, when the amount of water content in the different electrolytes is equalized, that there would be a close similarity in the intensity curves of the water band in the different substances. This will also lead us to infer that the nature of the electrolyte has little to do with the observed phenomenon. Therefore, the above acids were next studied with the same water content, the same number of molecules of the solvent being influenced by those of the solute in each case.

Fig. 8 represents the intensity curves for pure water, sulphuric acid at 18·63 N concentration, and nitric acid at 12 N concentration, the last two containing the same water content. Hydrochloric acid could not be studied with this water content, as the highest concentration of the acid available, about 12 N, contains more water than nitric acid of 12 N concentration. The above curves are for the Raman water band excited by the 4047λ line, as, on account of the very high concentration of sulphuric acid necessary in this case, some of the Raman lines due
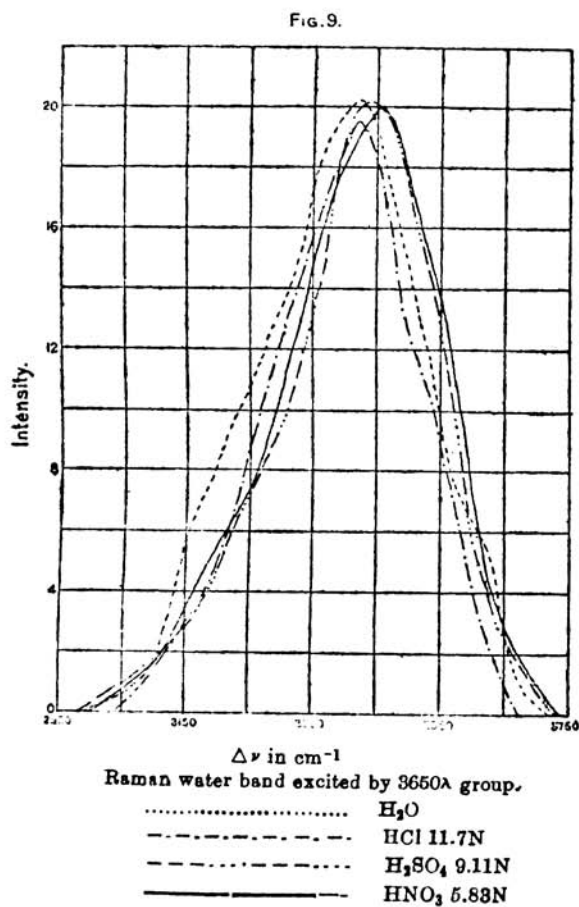
FIG. 8.

$\triangle \nu$ in cm^{-1}

Raman water band excited by the 4047λ line

— — —·····— — —····   H$_2$SO$_4$ 18.63N

——————————   HNO$_3$ 12N

···························   H$_2$O

to the SO$_4$ ion and excited by the 4047 λ line got superposed over the band excited by the 3650-63λ group and so this band could not be used. The shift between the curves for H$_2$SO$_4$ and HNO$_3$ noticed before at the same concentration still remains considerable and the increased similarity between the curves observed with the same water content at smaller concentrations is not so obvious in the present case.
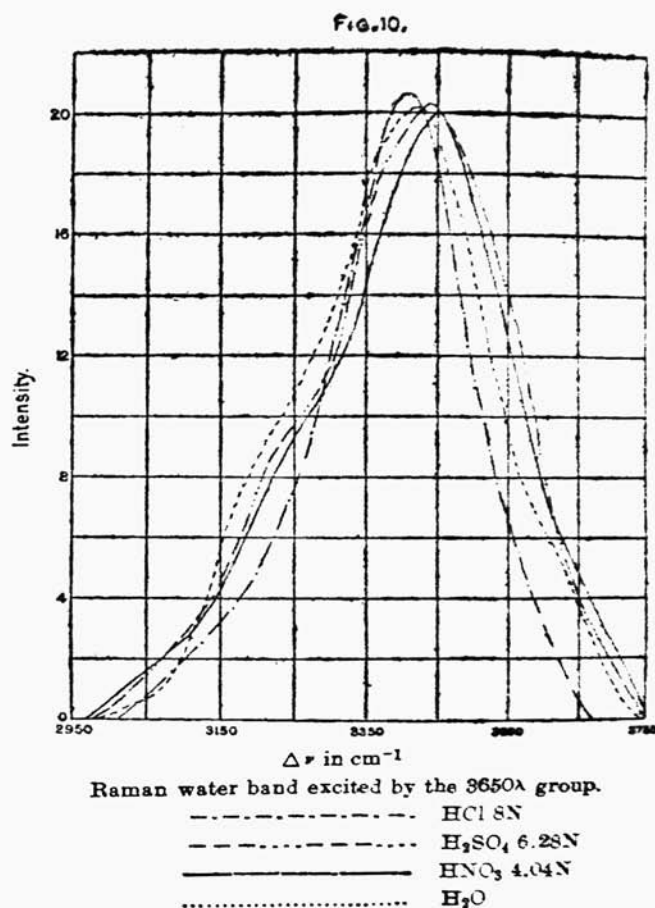
In fig. 9 are given the intensity curves for pure water, and for nitric, sulphuric and hydrochloric acids, all of them with the same water content as 12 N concentration of hydrochloric acid. When the proportion of water content is equalised in the three

acids a remarkable change is noticed in the relative positions of their intensity curves. The relative shifts between the curves tend to vanish, the curves get closer to each other and they become more and more similar, except for some m inor differences which still persist.

FIG. 9.

$\triangle \nu$ in cm^{-1}

Raman water band excited by 3650λ group.

.... H_2O
— · — · — · — · — · — · HCl 11.7N
— — — · · · · — — — · · · · H_2SO_4 9.11N
———————————— HNO_3 5.88N

The same result is also noticed from the intensity curves given in fig. 10 for the same three acids and pure water, the former being taken with the same water content as 8 N solution of hydrochloric acid.

Thus, while the three acids, when studied at the same concentration, exhibit marked differences in the shape and position

FIG. 10.

Intensity.

Δ ν in cm⁻¹

Raman water band excited by the 3650Å group.

—·—·—·—·—·—·—·— ·—.   HCl 8N
— — —·····— — —····   H₂SO₄ 6.28N
———————————   HNO₃ 4.04N
·······························   H₂O

of the water band in their solutions, when studied with the same water content these differences tend to disappear and the intensity curves and hence the bands themselves become increasingly similar.

Fig. 11 gives the intensity curves for pure water and the two salts, sodium nitrate and lithium chloride, both of them being of the same concentration, viz., 8N. Not many salts dissolve even to such high concentrations as 8 N and above, and of the few that do so, ammonium salts had to be rejected on account of the partial overlapping of the NH₄⁻ band[21] at about
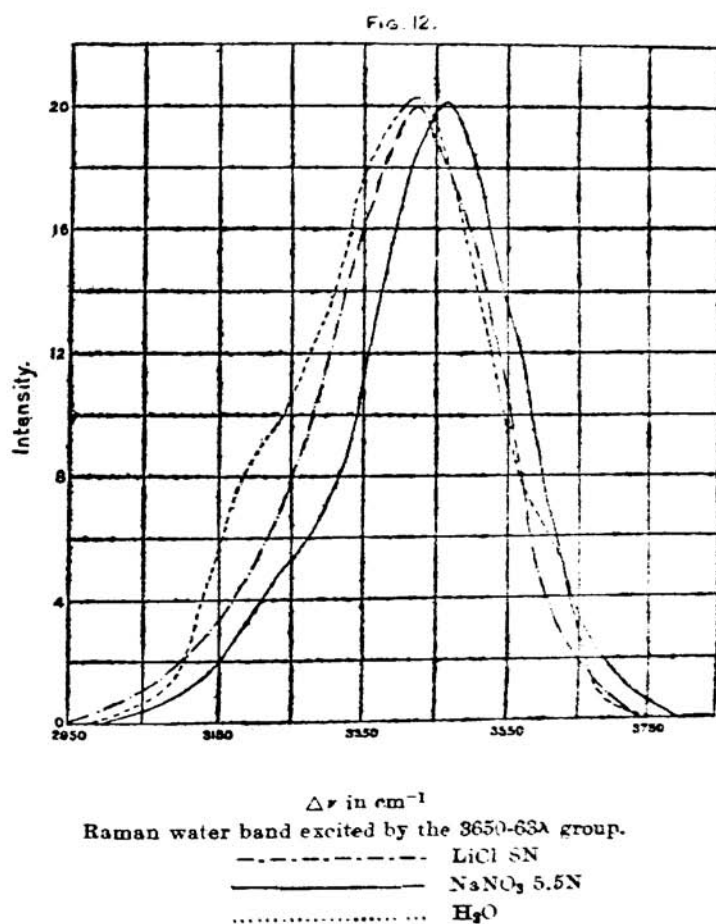
[21]   Zs. für Physik, Vol. 88, 1-2, p. 127 (1934).

29

Fig. II.
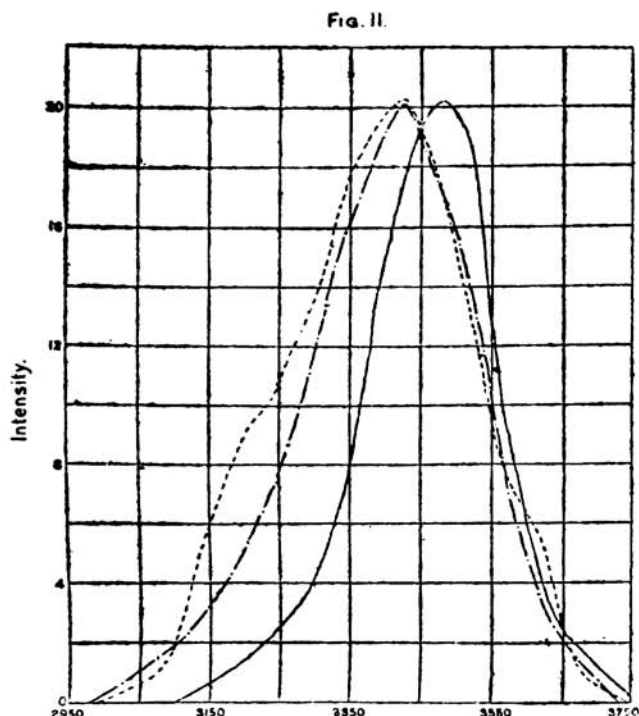
$\triangle\nu$ in cm^{-1}

Raman water band excited by the 3650-68λ group.

——————— NaNO$_3$ 8N
— · — · — · — · — · LiCl 3N
························ H$_2$O

3220 cm^{-1} over that of water, thus rendering very difficult any correct estimation of the intensity distribution in the latter : and in the case of salts like zinc chloride and lithium nitrate the presence of the continuous spectrum, in spite of the filter, was so great that here again no correct estimation of the intensity distribution in the band could be made. Hence, only these two salts, NaNO$_3$ and LiCl, have been studied. In the case of the salts also the same relative shifts are observed in the positions of the bands as in the case of hydrochloric and nitric acids in fig. 6. When the quantity of water content in the two salts

Fig. 12.

$\triangle \nu$ in cm^{-1}

Raman water band excited by the 3650-63λ group.

—·—··—·—··—·—   LiCl 5N
————————   NaNO$_3$ 5.5N
··················· ···   H$_2$O

is equalized it is found, as can be seen from fig. 12, that the curves tend to get closer and become more similar, although the effect does not seem to be so great as with the acids.

Table 2 gives the positions of the maximum of the water band in acids and salts at the same concentration and same water content.
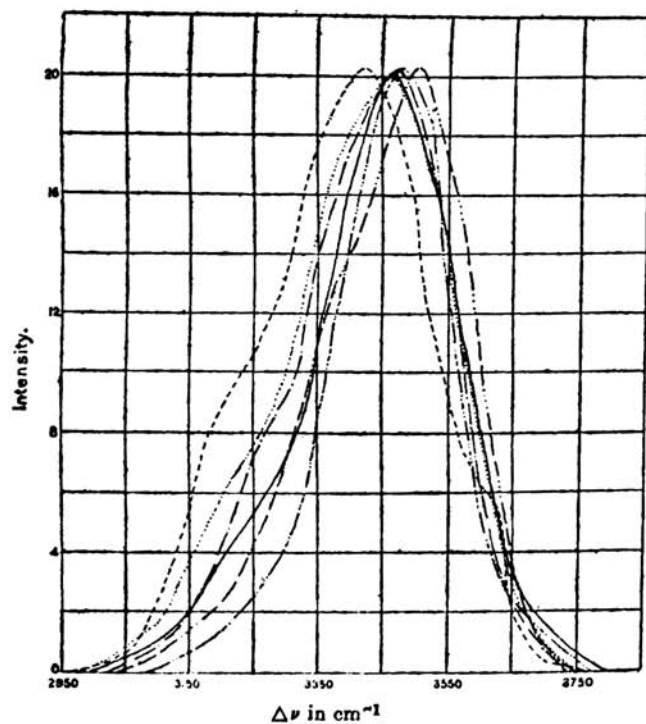
Finally, in fig. 13 are given, for purposes of mutual comparison, the intensity curves for water and for nitric acid and sodium nitrate at different concentrations. It is at once apparent that the curves for sodium nitrate are, in general, much sharper than

TABLE II.

Position of maximum.

Substance.	at 12 N concentration.	at 8N concentration.	At the same water conten	
			as 11·7N HCl	as 8NHCl (or LiCl)
1. H_2O	3424 cm^{-1}	3424 cm^{-1}	3424 cm^{-1}	3424 cm^{-1}
2. HCl	3418 ,,	3425 ,,	3418 ,,	3425 ,,
3. HNO_3	3504 ,,	3474 ,,	3460 ,,	3450 ,,
4. H_2SO_4	3468 ,,	3436 ,,	3440 ,,	3433 ,,
5. LiCl	—	3427 ,,	—	3427 ,,
6. $NaNo_3$	—	3480 ,,	—	3463 ,,

Fig. 13.

$\triangle \nu$ in cm^{-1}

Raman water band excited by the 3650-63λ group

    — — —....— — —.... HNO_3 12N

    —.—.—.—.—.—.—.—. HNO_3 8N

    .... HNO_3 5.86N

    —..... —..... —.....— $NaNO_3$ 8N

    ——————— $NaNO_3$ 5.5N

    —————————— H_2O

CONSTITUTION OF WATER IN SOLUTIONS

those for nitric acid.   In fact, the curves for the 8N nitrate solu-
tion, the maximum concentration under which it has been
studied, are sharper than even the curve for nitric acid at a much
higher concentration, namely 12 N.

5. *Summary of the Results.*

The following is a generalized summary of the results ob-
tanied from a study of the intensity curves of the different electro-
lytes under different conditions which permit of an easy compari-
son of the results.

(1)   The water band in solutions of electrolytes is invariably
sharper than for pure water.

In the case of nitric and sulphuric acids and sodium
nitrate,

(2)   the band gets sharper with increasing concentra-
tion ;

(3)   there is a clear shift in position of the maximum as
also of the band as a whole towards the side of greater frequency
with increasing concentration.

(4)   there is the appearance of a certain amount of conca-
vity, though slight, in the shape of the curve on the side of
smaller frequency at higher concentrations.

In the case of hydrochloric acid, **however,**

(5) the band is sharper with 8N acid than at 11·7 N,
although in both cases the band is sharper than for pure
water ;

(6) there is a shift in the band towards the smaller fre-
quency side as the concentration is increased; and

(7) the shorter frequency side of the intensity curve appears
to be less concave at the higher concentration.

(8) In the case of acids, as well as salts, at the same
concentration, there is a progressive relative shift in the posi-
tions of the maximum of the band, as well as in the band as a

whole, towards the greater frequency side as we pass from lithium chloride to sodium nitrate and from hydrochloric to sulphuric and nitric acids, that in the case of nitric acid being the greatest.

(9) With the same water content, both with acids and salts, the bands become more and more similar, the differences noticed in (8) tending to vanish.

(10) The water band in solutions of sodium nitrate is much sharper than that for nitric acid, even when the latter is taken at a much higher concentration.

6. *Discussion.*

These changes in the intensity distribution of the Raman band of water with addition of electrolytes are similar to those observed by Ramakrishna Rao[22] with change of temperature. To explain the latter phenomena, Ramakrishna Rao put forward the hypothesis that the three components in the water band corresponding to Raman frequencies equal to 3610, 3413 and 3195 cm^{-1} are due respectively to the three types of molecules, namely (H_2O), $(H_2O)_2$ and $(H_2O)_3$, which are supposed to be present in water. The change with temperature in the intensity distribution of the band is attributed by him to changes in their relative proportions.

On account of the close similarity between the two sets of phenomena, *viz.,* changes in the structure of the water band with temperature on the one hand and with addition of electrolytes on the other, the explanation of the latter appears, to a large extent, to be most probably the same as for the former. The predominance of the central component at about 3400 cm^{-1} in the water band in most electrolytic solutions and the general weakening of the other two components, compared to the band for pure water, shows that, on the above hypothesis, the double

[22] *Loc. cit.*

$(H_2O)_2$ molecules in water increase in proportion when an electrolyte is added to it, the number of the other two types at the same time diminishing.

This is at once clear from the greater sharpness of the curves for the solutions of dissolved electrolytes than that for pure water as well as from the slightly concave nature of their intensity curves, as compared with the curve for pure water which has a decidedly convex shape, particularly on the side of greater frequency shift : also the positions of the maxima in all the cases very nearly correspond to that of the double molecules in the water band. This indicates that the $(H_2O)_2$ molecules persist in solutions of electrolytes while the H_2O and $(H_2O)_8$ type molecules are comparatively unstable, particularly at the higher concentrations of the electrolytes, and as such tend to gradually disappear, the triple molecules perhaps dissociating and recombining amongst themselves or with the single molecules to form the simpler type, $(H_2O)_2$ molecules. Thus the increased sharpness of the water band in solutions of electrolytes and the relative shift in the shape and position of the band to different degrees in the different cases to the side of greater frequency may be due to a change in the water equilibrium, consequent upon the partial dissociation and recombination of the more complex $(H_2O)_8$ molecules amongst themselves and with the single molecules to form the stabler type of $(H_2O)_2$ molecules.

Bancroft and Gould in a recent paper,[28] made a similar suggestion as to the possibility of a more satisfactory explanation of the phenomena, so far ascribed to ionic hydration, on the basis of a displacement in the water equilibrium between the monohydrol, dihydrol and trihydrol. This explanation of the observed effect as due to a change in the proportion of the three types of water molecules appears, at least in part, to be the true interpretation when one considers the observed result of an increasing similarity and blending together of the intensity

[28] Jour. Phys. Chem., Vol. 38, 2, p. 197 (1934).

curves when the water content is equalised in the numerous cases studied (refer figs. 8 to 12). This interpretation of the phenomenon is also supported by the conclusion arrived at by Ramakrishna Rao that the $(H_2O)_2$ molecules are decidedly more stable in the liquid state of water as is evidenced by their greater preponderance over the other two types in this state. Addition of electrolytes seems to contribute to enhance the instability of the latter types.

In addition to the possibility of the above effect, there may also be hydrates formed by the combination of the two unstable types, (H_2O) and $(H_2O)_3$, with the ions of the electrolyte in solution. That such an effect takes place in aqueous solutions, as well as with some non-aqueous solvents, has been inferred from other methods in which some physical property or other of the binary system, water and solute, has been investigated. Thus, from a study of the freezing point curves of nitric acid and water the existence of at least two hydrates of nitric acid, the monohydrate HNO_3, H_2O and the trihydrate $HNO_3, 3H_2O$ has been established, while the possibility of the existence of other hydrates has been inferred.[24] Similarly for hydrochloric acid the presence of the three hydrates, $HCl; 3H_2O$, $HCl, 2H_2O$ and HCl, H_2O with increasing concentration of HCl has been pointed out;[25] and for sulphuric acid[26] of a number of hydrates. $H_2SO_4, 2H_2O$ and H_2SO_4, H_2O among others.

Thus, in cases where the hydrates formed have either two or a multiple of two as the number of molecules of water of hydration, then the band due to this water of hydration falls more or less in the same position as that due to the double molecules and hence contributes to intensify the latter. As most of the intensity curves for the electrolytic solutions studied

[24] Mellor : Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. VIII, p. 563.

[25]   ,,   ,,   ,   Vol. II, p. 183.

[26]   ,,   ,,   ,,   Vol. X, p. 861.

exhibit a sharpening of the band in the region where the component due to the $(H_2O)_2$ molecules is found to be present, it may be that, in many of them, hydrates with an even number of associated molecules predominate. But in cases where hydrates with an odd number of molecules are present it may happen that the band due to the water of hydration shifts either to the side of greater or smaller frequency depending on the number of molecules of hydration, whether single or triple. Thus the appearance of a slight convexity noticed in the shape of the intensity curves on the smaller frequency side with increasing dilution in the case of nitric and sulphuric acids is perhaps due to the formation of complex hydrates, particularly those with three associated molecules of water, that is, $H_2SO_4, 3H_2O$ and $HNO_3, 3H_2O$. This is also supported by the observations of the earlier workers on the freezing point curves of the acid water mixtures referred to before.

The effect may be also partly due to an increase in the proportion of triple molecules that results with increased water content in the solution. Again, the decreasing sharpness is observed in the shape of the band with increasing dilution in the case of sulphuric acid, nitric acid and nitrates, as indicated in their intensity curves, figs. 2, 3, 5 and the slight shift noticeable in the curves to the smaller frequency side as dilution of the acid increases appears to be also due to the same two causes. Both these effects, namely, the formation of complex hydrates (particularly those with three molecules of water of hydration) and the formation of an increased proportion of triple molecules at higher dilutions, tend to shift the resultant curve to the smaller frequency side, the region corresponding to the component of the triple molecules in the band for pure water.

The anomalous results observed in the case of hydrochloric acid, *viz.*, an increased broadening of the band at the higher concentration of the acid, a slight shift in the band to the smaller frequency side at the larger concentration as compared

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with that at the smaller concentration, do not seem to be easily explicable on the above hypotheses, as it is very improbable that more complex hydrates, which alone could shift the band to the short frequency side, could form at greater concentrations of the acid or with less quantity of water present. This problem is expected to be cleared by further work, which is in progress at present.

The greater sharpness in the intensity curves of sodium nitrate as compared with those of nitric acid, fig. 13, even when the latter is taken at much higher concentrations seems to be partly due to the formation of more complex hydrates in nitric acid and partly due to the superposition of the narrow diffuse band at 3420 cm^{-1} due to NO_2OH molecule, found by Kohlrausch[27] to be present in pure nitric acid, over that due to water. The latter cause also appears to be the real explanation of the appearance of a second band observed by Ramakrishna Rao[28] in nitric acid solutions at concentrations higher than 76%, and not the formation of hydrates as put forward by him.

Passing on to the curves for the same concentration of the different electrolytes, figs. 6 and 7, the shift in the position of the band to the larger frequency side, as we pass from hydrochloric to sulphuric and nitric acids indicates the gradual decrease in the proportion of triple molecules and at the same time a slight increase in the proportion of single molecules. These results are, to some extent, in conflict with the hypothesis of Bancroft and Gould,[29] who postulate, from their observations on the Hofmeister series of certain anions, that for equivalent concentrations the amount of monohydrol is less with nitrate ion than with chloride ion. If that were the case, the intensity curve for hydrochloric acid must be shifted *more* to the larger frequency side than that of nitric acid, indicating thereby a

27 Naturwiss., Vol. 19, p. 690 (1931).
28 Roy. Soc., Proc., A, Vol. 130, p. 489 (1931).
29 loc. cit.

greater preponderance of the single molecules or monohydrol in hydrochloric acid than in nitric acid, but actually the reverse is found to be the case. Again, their assumption in the same connection that the sulphate ion tends to convert trihydrol and monohydrol into dihydrol must lead one to expect that the water band in sulphuric acid would be narrower than in the other cases, thus indicating the comparatively low proportion of the single and triple molecules, but this again is found to be at variance with the experimental results obtained by the author.

Thus, the changes in the intensity distribution of the water band with addition of electrolytes may be not only due to changes in the relative proportions of the three types of molecules present in water, but may also arise out of formation of hydrates by combination of the ions with the water molecules.

The striking similarity of the curves with solutions of the three acids when the amount of water they contain is equalized, figs. 9 and 10, leads one to the conclusion that the differences noticed in the curves for different electrolytes are only due to a difference in their water content, and when it is the same in all the cases the nature of the electrolyte has not much influence anyway on the constitution of water and in consequence on the structure of its band. This is quite an unexpected result.

Thus the marked similarity between the several intensity curves taken with solutions having the same water content, leads one to expect that the effect of dissolved electrolytes is similar to that of a change of temperature of water, viz., a change in the water equilibrium due to variation in the proportions of the three types of water molecules. Otherwise the result is not easily explained unless one makes the highly improbable assumption that at the same water content the amount and nature of hydrates formed are identical for the several substances.

Though the above curves are very similar, there are small but yet definite secondary differences between them which cannot be explained away as arising out of experimental errors, as they

are much more than the probable differences which may arise in the estimation of intensities. They therefore remain to be explained. These differences are to be attributed either to variations in the water equilibrium to different amounts for the different electrolytes or to formation of hydrates which may be different for the different electrolytes. That the latter cause explains the differences between the curves of sodium nitrate and lithium chloride (fig. 12), that still persist even when their water content is equalized, as also the greater sharpness of the band in sodium nitrate solution than in that of lithium chloride, can also be inferred from the fact that lithium salts are known to crystallize with a large amount of water of crystallization while sodium salts do not; and it is but natural that those salts, which crystallize with a larger amount of water, also associate with water molecules to a much greater extent in solution. With the results thus far available it is difficult to decide more definitely between the two alternatives set forth above as to the probable cause of the observed results. Both, however, seem to be equally probable and co-existent.

Finally, the cation seems to exert little characteristic influence on the constitution of water as can be inferred from the similarity of results obtained with acids and salts.

In conclusion, it is a pleasure to express my best thanks to Dr. I. Ramakrishna Rao for his very keen interest and helpful guidance throughout the progress of the work.

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SCIENCE AND TECHNOLOGY, WALTAIR,
        18th Sept., 1934.