THE APPLICATION OF THE INFRA RED ABSORPTION SPECTRUM OF THE HYDRONIUM ION TO DISSOCIATION STUDIES OF STRONG ACIDS IN AQUEOUS SOLUTIONS

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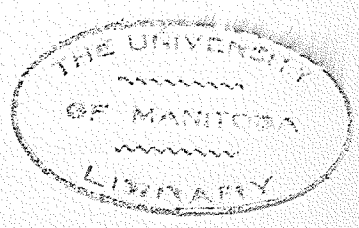

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ABSTRACT

An investigation of the infra red absorption spectrum of the hydronium ion in aqueous nitric and perchloric acid solutions was undertaken within the concentration range 0.01 to 4 molar. The purpose in view was to develop an auxillary method for the determination of the degree of dissociation of strong acids in aqueous solutions. The first overtone of the 2900 cm^{-1} absorption band was identified at 5800 cm^{-1}, and utilized for the present study.

It was found that for acid concentrations exceeding 0.3 molar there was an observed deviation from Beer's Law which could not be attributed to the degree of acid dissociation, values for which had been previously determined by Raman and Nuclear Magnetic Resonance investigations. This deviation precluded the use of the infra red absorption band as a suitable method for dissociation studies.

A theoretical discussion of the deviation is presented in terms of the effects of the hydronium ion hydration.

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INTRODUCTION

The problem of the dissociation of strong acids in water has become less formidable since spectroscopic methods have been employed to determine the variation in the degree of dissociation with concentration of acid (1, 2). These methods (Raman spectra, optical absorption spectra, and recently, nuclear magnetic resonance techniques) offer a direct approach to the identity and concentration of molecules, ions, or ion pairs which may be present in solution.

The Raman and optical absorption spectra have been used mainly to determine the anion concentration in aqueous acid solution. Only nuclear magnetic resonance has given investigators an opportunity to follow the concentration of H_3O^+ or hydronium ions in acid solutions with varying amounts of acid.

The absorption spectrum of the H_3O^+ ion in crystalline $HNO_3.H_2O$ and $HClO_4.H_2O$ has been observed in the infra red region and recently the H_3O^+ and $D3O^+$ absorption spectra have been reported for concentrated solutions of ordinary and deuterated acids in light and heavy water. Until now neither of these spectra has been investigated over a large concentration range of acid.

If the absorption spectrum of the H_3O^+ ion, or whatever entity is the cause of this spectrum in aqueous acid solution, obeys Beer's Law over a wide concentration range, a new method presents itself for the determination of the degree of dissociation of strong acids in water.

This thesis describes an attempt to verify Beer's Law for strong acid concentrations between 0.01 molar and 4 molar, to determine the apparent degree of dissociation from absorbance curves, and to compare the results with previously published data on the degrees of dissociation for HNO_3 and $HClO_4$.

REVIEW OF THE LITERATURE

A. RAMAN SPECTRA

When an intense beam of light traverses a transparent medium a detectable amount of the light is scattered by the molecules of the medium. Sir C. V. Raman discovered in 1928 that part of this scattered light differed in frequency from that of the incident light. This phenomenon is generally known as the Raman effect. It was realized in a short while that the frequency shifts were associated with the quantized changes in the rotational and vibrational energies of the molecules present.

Two ions possess six translational degrees of freedom, a molecule only three. At least one of the three lost translational modes of the ions is changed into a vibrational mode in the formation of a molecule. Thus the vibrational spectrum of the molecule must be different from that of the two ions, and may be used to identify molecules in the presence of ions and vice versa in a optical absorption or Raman study.

One should recognize that although the Raman frequency displacements and infra red absorption frequencies of a compound are somewhat similar, since both are associated with the vibration of the molecule, nevertheless the band intensities of the two kinds of spectra depend on different electrical characteristics. In molecules of high symmetry some bands may be strong in one type of spectrum and entirely absent from the other.

I. R. Rao (3) noticed that upon dilution of HNO_3 in water there was a change in the intensity of each of two sets of Raman lines: one set decreased in intensity upon dilution, the other set increased. The latter set is found also in solutions of nitrate salts. He concluded that the former set, the strongest line of which is Raman displacement frequency ($\Delta\nu$) 1299 cm^{-1} is due to the undissociated nitric acid molecule, the latter, the strongest of which is $\Delta\nu$ 1049 cm^{-1} is excited by the nitrate ion. By comparing intensities of these lines for different concentrations he was able to determine the relative degree of dissociation for nitric acid.

N. R. Rao (4) calculated the absolute degree of dissociation of the acid by comparing the intensities of the Raman lines in the spectrum of a solution of nitric acid with the spectrum of a solution of sodium nitrate giving Raman lines of equal intensity. Thus he was able to calculate the concentration of nitrate ion in the nitric acid solution.

The above investigators had to compare, on a photographic plate, the intensities of lines of unequal spectral width. Hence considerable error resulted due to this operation. A refined photographic technique was developed by Redlich and Bigeleisen (5) who reinvestigated the degree of dissociation of HNO_3 by utilizing the Raman spectrum of the nitrate ion in a manner similar to that of N. R. Rao.

The Raman technique awaited the use of a photoelectric cell to give very accurate results by eliminating the

comparison of intensities of spectral lines on a photographic plate.

In 1954 at the Symposium on solutions of electrolytes, held at Yale University, T. F. Young showed the results of his work with a photoelectric tube on the Raman lines of nitric acid (6, 7). These results agreed remarkably well with data obtained from nuclear magnetic resonance methods used by Redlich and others and described below. Young's work was also in good agreement with that of N. R. Rao.

B. OPTICAL ABSORBANCE SPECTRA

1). Ultra violet spectrum of HNO_3

Optical absorption experiments on the ultraviolet region of the spectrum have been used to estimate the extent of dissociation of nitric acid through the molecular extinction coefficient for the nitrate ion.

von Halban and Eisenbrand determined absorption curves for light of several wavelengths, showing the variation of the molecular extinction coefficients with concentration, for HNO_3 (8). The curves are complex, containing prominent points of inflexion whereas corresponding curves for potassium nitrate are comparatively simple. These points of inflexion have been ascribed to the rapid increase in the ratio of the concentration of undissociated acid, to dissociated acid, with increasing concentration of acid.

The absorption of light at 3180 Å in solutions of nitric

acid between 0.8 and 24.6 molar has been measured by Dalmon (9). At this wavelength both nitrate ion and the nitric acid molecule both absorb, but the latter not a significant amount, except perhaps at higher acid concentrations. Hence at lower concentrations his results should give approximate values for the nitrate ion concentrations and hence the degree of dissociation. But because of the fact that the extinction coefficient is not a function of the nitrate ion alone and because his work was done at $1^{o}C$ instead of room temperature his results are not strictly comparable with the other investigations mentioned above and below.

2). Infra Red Spectrum.

Bethell and Sheppard (10) observed the absorption spectrum of crystalline nitric acid monohydrate from 550 to 4000 cm^{-1} (18, 180 mu to 2500 mu). They found a series of absorption bands at 1134, 1650, and 3000 cm^{-1} which they assigned to the H_3O^+ ion. H_3O^+ is not only isoelectronic with NH_3^+ but also there is very little mass difference between the two. Because there is a great similarity in the frequency and intensity of the absorption bands of these two ions, Bethell and Sheppard felt justified in assigning the wave numbers given above to the H_3O^+ ion. The monohydrate was then melted and it was found that these absorption bands had disappeared, indicating that the liquid acid hydrate is essentially unionized.

However, Giguère and Falk (11) found for very thin films

of concentrated solutions of various acids a characteristic spectrum giving lines of 1200, 1750, and 2900 cm^{-1} (the latter intense and quite broad) which he assigned to the hydronium ion.

When the protons are replaced with deuterons the corresponding bands are at 950, 1400, and 2700 cm^{-1}.

C. NUCLEAR MAGNETIC RESONANCE

Many atomic nuclei are found to possess a magnetic moment which may be thought to arise from the angular momentum of the positively charged nucleus. This intrinsic angular momentum is specified by a spin quantum number I which, like the magnetic moment u of the nuclear magnet is a permanent, sharply defined characteristic of the nucleus. When such a nucleus is placed in a uniform magnetic field H_o, its energy is quantized and there are 2I + 1 energy levels or spin orientations which it may occupy on account of its interaction with the magnetic field. If an oscillating magnetic field is applied in a direction perpendicular to H_o, then for the proper frequency, transitions may be induced between the 2I + 1 energy levels of the nucleus (12, 13). For a proton, I = 1/2, and therefore, there are two spin orientations. These orientations are designated (+) or (-) depending upon whether the component of spin parallel to the static field H_o is in the same or reverse direction as H_o.

The probability of the induced transition is the same

for all spin orientations, i.e. from (+) -> (-) or from (-) -> (+), but since there will be a Boltzman distribution between all energy levels, a slight excess population of nuclei will be in a lower energy state favouring the induced transition.

Because of the different environment, a proton in chemical species A, will for a given static field H_o, have a slightly different resonant frequency than a proton in chemical species B; it is possible to distinguish proton resonance in H_2O from proton resonance in CH_3OH. For any given solution of say three compounds, containing protons, there will generally be, for a given H_o, three resonant frequencies. If, on the other hand, there is a fast exchange of protons between the different compounds, only a single proton resonance will be found.

Gutowsky and Saika (14) discovered that for a solution of strong acid in water there was only one resonant frequency, and moreover, that the deviation of the proton resonance line in the solution from that for proton resonance in water was given by

$$d = p' \, d_{H_3O^+}$$

where d = chemical shift of the resonance line

p' = fraction of protons in H_3O^+ ions

$d\ H_3O^+$ = proton resonance shift for H_3O^+

What is observed is the average of the energies of the protons in various molecular (or ionic) species present by weight i.e. a colligative property.

They accordingly were able to determine the degree of dissociation by measuring the d for a given concentration of acid (nitric and perchloric). It is important to note that there was no d for potassium nitrate or potassium sulfate which indicated, as they pointed out, that hydration of ions or molecules doesn't affect the resonance position of the protons involved.

Hood, Redlich and Reilly (15) refined the technique and extended the concentration range for HNO_3 and $HClO_4$, and also made measurements on HCl.

The agreement between their results and that of Young, who used a photoelectric tube with Raman measurements, is very good.

As a result of these investigations the thermodynamic dissociation constants at room temperature for HNO_3 and $HClO_4$ are K = 22 and K = 38 respectively.

The curves of concentration vs. dissociation for nitric and perchloric acid show that for concentrations up to about 5 molar, perchloric acid is not much stronger than nitric, but beyond this range, perchloric is more highly ionized than nitric acid.

The excellent agreement between the Raman and nuclear magnetic resonance work suggests that they may be used as a basis for correlating the data of other methods of investigation of the degree of dissociation.

For a comparison of previous work see Figure 4.

APPARATUS AND METHOD

Nitric acid and perchloric acid solutions were prepared using distilled water, which was additionally purified by running it through an ion exchange column, in the range from 0.01 to 4 molar and standardized against carbonate free NaOH using bromocresol purple (ph 5.2 - 6.8) as an indicator. The per cent transmittance of each solution was measured on a Beckman D. K. II spectrophotometer using stoppered 1.00 cm Corex cells. (corrections were made for cell mismatch). At least three trials were made at room temperature (22 - 26°C) on each solution on separate days. Also for each trial a minimum of two runs was made in order to check for reproducibility, which depended upon cleanliness of cells and absence of bubbles on the ground glass surfaces. Each time a new solution was put into the sample cell, fresh water was placed in the reference cell. This assured that both cells were at the same temperature. The scale expansion device on the spectrophotometer was used in order to determine the per cent transmittance for solutions less than 0.2 molar and greater than 1.3 molar. The accuracy of the readings is assumed to be within ome part in two hundred. This is the accuracy of the instrument as stated on the manufacturer's warranty.

The following equation was used for Beer's Law plot:

$$\text{LOG}_{10}\ I_o/I = acl$$

where a = molar extinction coefficient

c = concentration in moles/liter

l = path length of cell

I_o = intensity of incident radiation

I = intensity of transmitted radiation

$\text{LOG}_{10} I_o/I$ = the absorbance

If a remains constant, a plot of $\text{LOG}_{10} I_o/I$ vs. concentration should give a straight line of slope a if the acid is completely dissociated. When association of the acid molecules becomes significant the line would be expected to curve.

The slit width was about .22 mm.

Solutions of HCl were prepared, but before quantitative measurements could be made on them, the spectrophotometer became inoperative.

DATA AND RESULTS

Nitric acid, perchloric acid and hydrochloric acid, all showed a broad absorption peak at 1750 - 1700 mu (5800 cm^{-1}), which is the first overtone of the 2900 cm^{-1} absorption band for acid solutions as reported by Giguere and Falk and assigned to the hydronium ion.

From the per cent transmittance (100 I/I_o) the absorbance was calculated for each trial for each solution (Table 1, 2) and a plot of absorbance vs. concentration was made (Figure 1, 2). Only for concentrations less than 0.3 molar did Beer's Law hold. The apparent degree of dissociation was calculated from this plot as follows:

$$\text{Degree of dissociation} = \frac{\text{concentration of } H_3O^+}{\text{concentration of acid}} = \frac{F}{B}$$

(see Table 3 and Figure 3)

The assumptions made were that the extinction coefficient remains constant for all concentrations and that only the H_3O^+ ion contributes to the extinction coefficient.

The maximum of the transmittance peak was used for the calculations. It was noticed that this peak maximum shifted, in a different way for HNO_3 and $HClO_4$, to a lower wavelength as the concentration of the acid increased (see Table 4 and Figure 5).

The results of the present work for the apparent degree of dissociation are compared with the literature data in Fig. 4.

TABLE 1

ABSORBANCE DATA FOR HNO_3

CONCENTRATION moles/liter	I/I_o	$LOG_{10}\ I_o/I$	CONCENTRATION moles/liter	I/I_o	$LOG_{10}\ I_o/I$
0.00928	0.979	0.0090	0.9534	0.187	0.728
	0.987	0.0056		0.185	0.733
	0.983	0.0073		0.187	0.728
0.01878	0.958	0.0183	1.171	0.136	0.866
	0.968	0.0141		0.138	0.860
	0.965	0.0158		0.137	0.863
0.04762	0.913	0.0394	1.581	0.079	1.102
	0.905	0.0430		0.082	1.087
	0.906	0.0426		0.082	1.087
0.09413	0.824	0.0839	2.005	0.052	1.284
	0.827	0.0824		0.056	1.257
	0.824	0.0839		0.056	1.252
0.1998	0.673	0.171	2.492	0.037	1.430
	0.672	0.173		0.040	1.400
	0.672	0.173		0.041	1.391
0.3839	0.474	0.324	3.044	0.030	1.520
	0.476	0.322		0.031	1.509
	0.473	0.325		0.032	1.489
0.5645	0.347	0.460	3.909	0.026	1.593
	0.348	0.458		0.026	1.585
	0.344	0.463		0.028	1.551
0.7433	0.259	0.587			
	0.250	0.585			
	0.259	0.587			

TABLE 2

ABSORBANCE DATA FOR $HClO_4$

CONCENTRATION moles/liter	I/I_o	$LOG_{10}\ I_o/I$	CONCENTRATION moles/liter	I/I_o	$LOG_{10}\ I_o/I$
0.009706	0.985	0.0064	0.2936	0.595	0.225
	0.983	0.0073		0.602	0.220
	0.985	0.0064		0.588	0.230
0.01948	0.963	0.0162	0.6303	0.348	0.458
	0.963	0.0162		0.347	0.460
	0.967	0.0145		0.349	0.457
0.02925	0.943	0.0253	0.7305	0.298	0.526
	0.946	0.0241		0.299	0.524
	0.942	0.0261		0.297	0.528
0.03912	0.931	0.0310	0.9358	0.224	0.650
	0.927	0.0330		0.225	0.649
	0.933	0.0302		0.223	0.652
0.04836	0.913	0.0394	1.233	0.150	0.824
	0.915	0.0386		0.151	0.821
	0.918	0.0370		0.150	0.824
0.05795	0.898	0.0469	1.562	0.105	0.979
	0.903	0.0442		0.102	0.991
	0.902	0.0449		0.105	0.979
0.06937	0.880	0.0554	1.967	0.069	1.161
	0.885	0.0531		0.072	1.146
	0.878	0.0565		0.071	1.149
0.7754	0.874	0.0584	2.423	0.053	1.277
	0.870	0.0603		0.053	1.276
	0.870	0.0603		0.049	1.314
0.09733	0.838	0.0770	2.933	0.041	1.387
	0.833	0.0792		0.041	1.387
	0.839	0.0763		0.042	1.378
0.1957	0.709	0.149	3.859	0.033	1.485
	0.710	0.149		0.034	1.471
	0.706	0.159			

TABLE 3

APPARENT DEGREE OF DISSOCIATION

CONCENTRATION moles/liter	DEGREE OF DISSOCIATION HNO_3	$HClO_4$
0.5	.980	.950
1.0	.900	.870
1.5	.833	.813
2.0	.750	.740
2.5	.668	.664
3.0	.593	.590
3.5	.529	.526
4.0	.470	.470

TABLE 4

WAVELENGTH OF PEAK MAXIMUM VS. CONCENTRATION

HNO_3		$HClO_4$	
Conc. moles/liter	Peak Maximum (mu)	Conc. moles/liter	Peak Maximum (mu)
0.05	1735 ± 4	0.03	1730 ± 4
0.10	1734	0.04	1738
0.20	1732	0.05	1738
0.38	1734	0.06	1741
0.56	1731	0.20	1736
0.74	1730	0.30	1738
0.95	1726	0.63	1738
1.17	1721	0.73	1735
1.58	1714	0.96	1732
2.00	1710	1.23	1727
2.49	1705	1.56	1723
3.04	1697	1.97	1715
3.90	1696	2.42	1712
		2.93	1708
		3.86	1700

DISCUSSION OF RESULTS

Several observations can be immediately made from the data and graphs:

1. The absorbance falls off too rapidly with concentration, thereby giving a smaller value for the degree of dissociation than that obtained from Raman and nuclear magnetic resonance methods.
2. The wavelength of the peak maximum shifts to a lower value as the concentration increases.
3. Nitric acid seems to be stronger than perchloric for low concentrations, whereas from other investigations, perchloric is the stronger, though not by a large degree at low concentrations.
4. The limiting value for the extinction coefficient a, is different for HNO_3 and $HClO_4$.

Since the data on the degree of dissociation for nitric acid from Raman and nuclear magnetic resonance works appears to be reliable, it seems that the following assumptions which were implicit in the calculations are invalidated:

1) The H_3O^+ ion alone is absorbing.

2) The extinction coefficient remains constant over the concentration range investigated.

Because the peak maximum shifts with concentration one would suspect that the entity observed does not retain its physical structure throughout the concentration range.

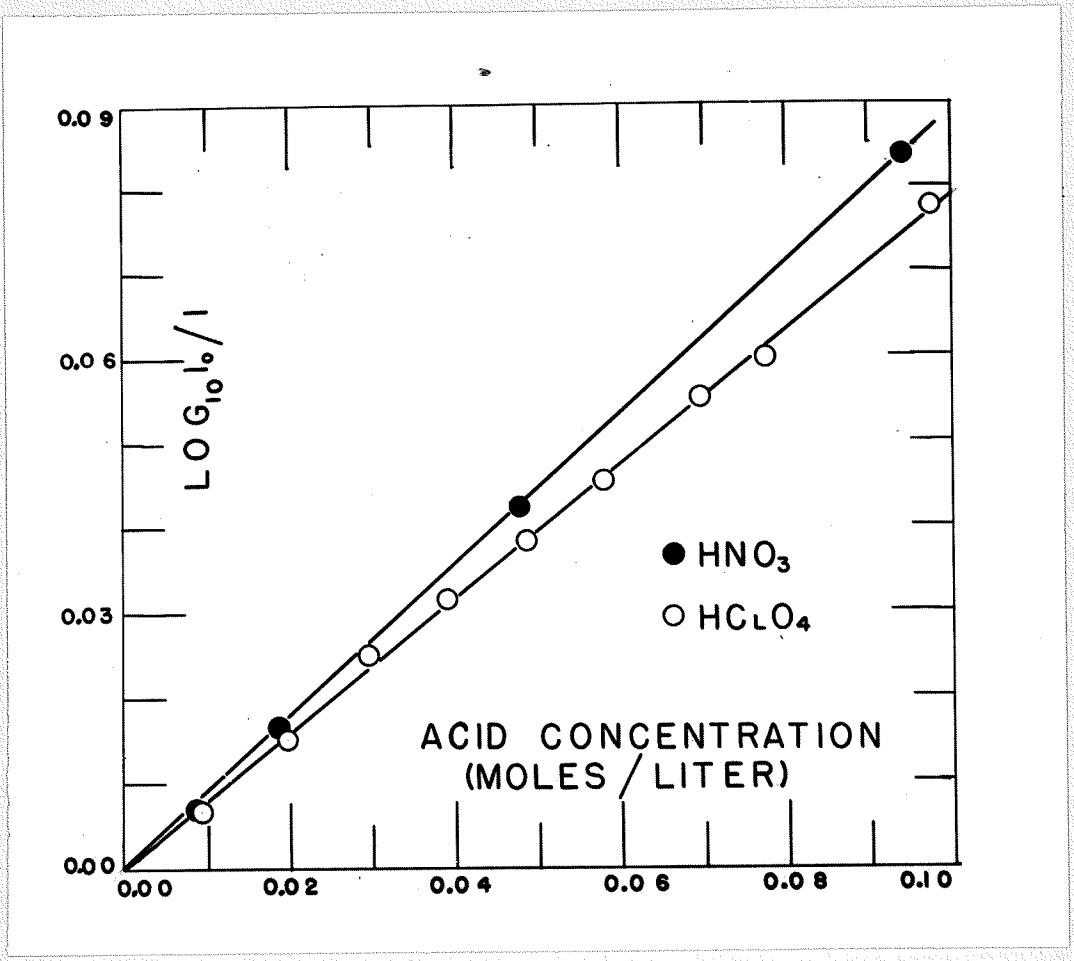

FIGURE 1. Absorbance vs. Concentration for low concentration acid solutions.

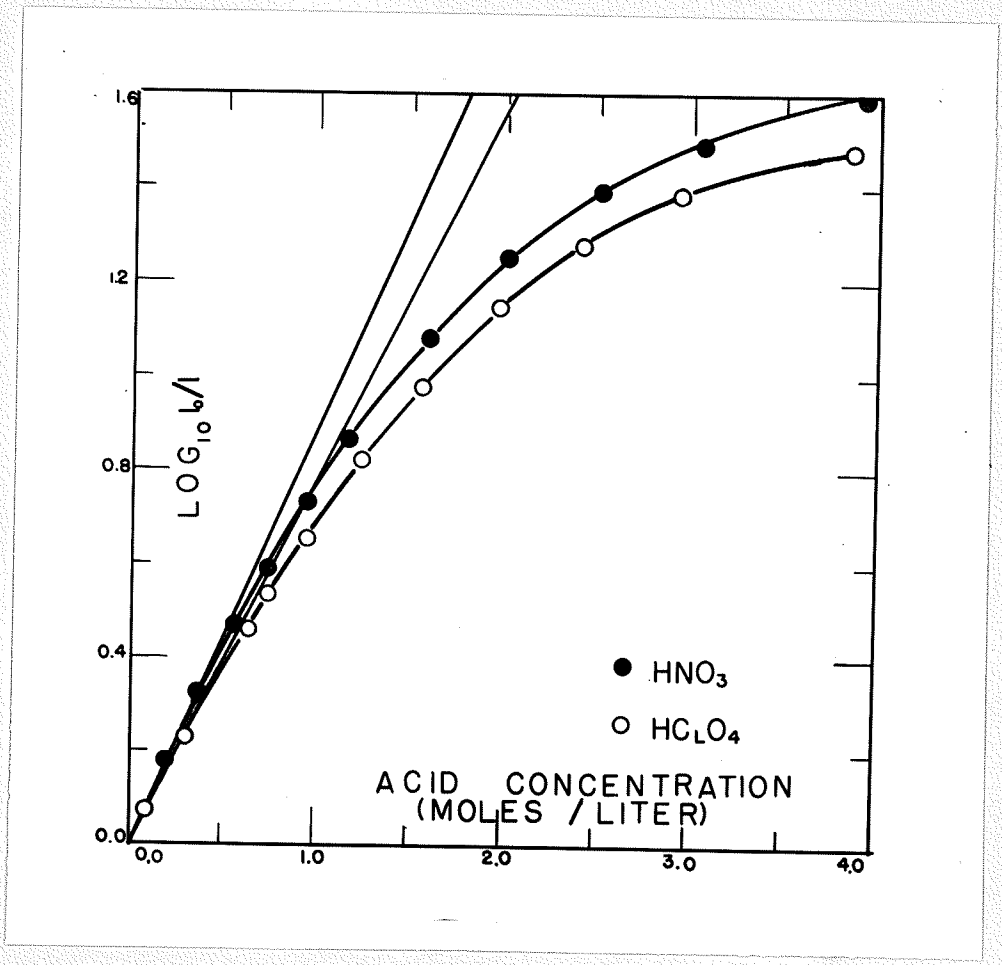

FIGURE 2. Absorbance vs. Concentration. The absorbance for both acids deviates from the limiting slopes (straight line).

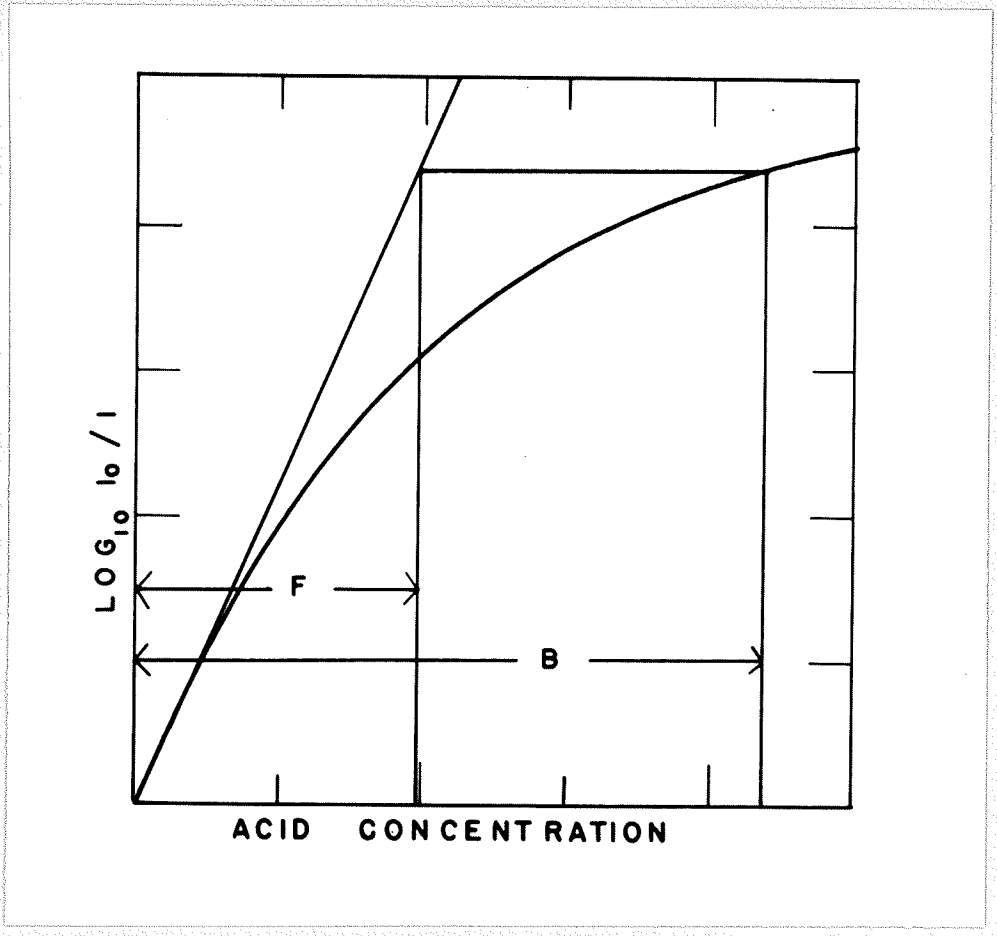

FIGURE 3. The degree of dissociation of the acid was calculated by dividing the hydronium ion concentration F by the concentration of acid B. It was assumed that Beer's Law was obeyed.

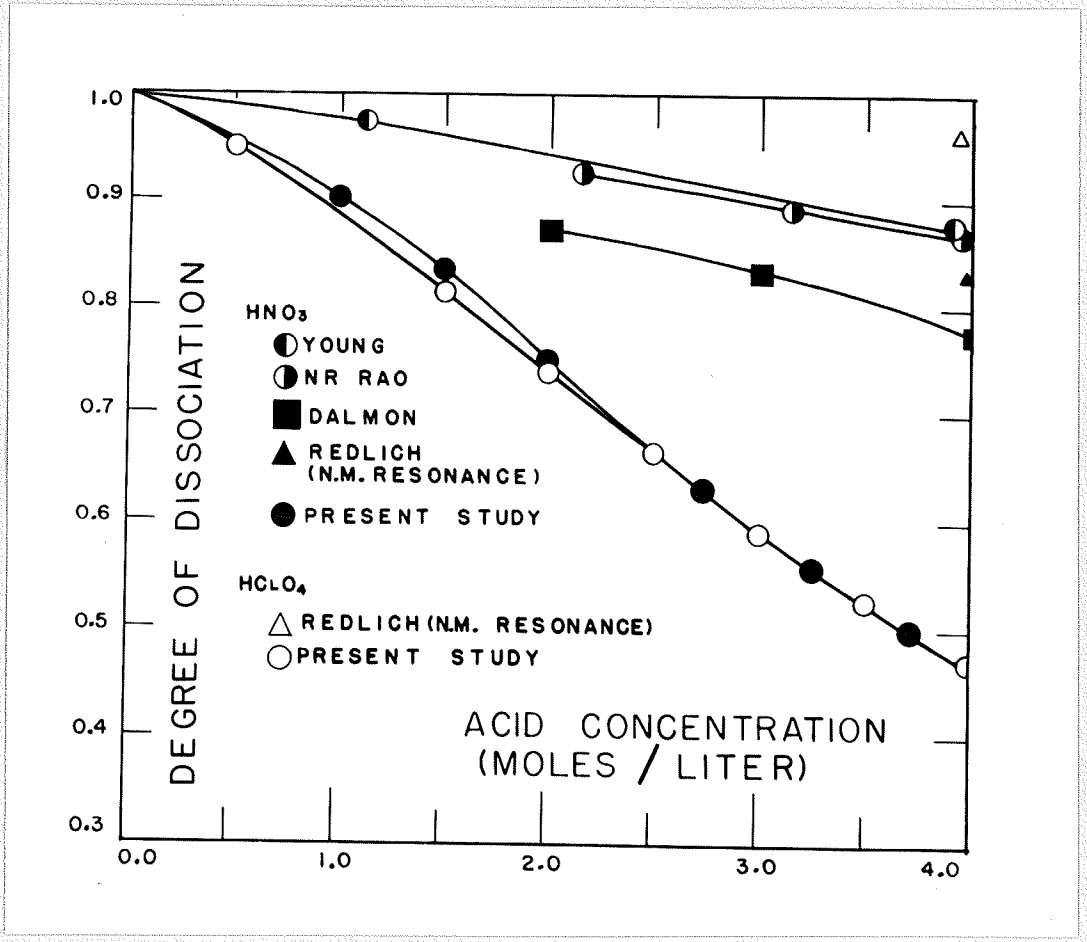

FIGURE 4. The results for the degree of dissociation of nitric and perchloric acid are compared with previous investigations.

It is reasonable to assume that the H_3O^+ ion, which has three hydrogen atoms available for bonding to oxygen atoms and a positive charge, is connected to the surrounding water molecules. Raman studies of liquid water by Cross, Burnham, and Leighton (16) have shown that at low temperatures water has a four fold co-ordination structure (each water molecule is surrounded by four neighbors). Moreover, between 26°C and 90°C there is a two fold co-ordination structure. The structure of course is a dynamic one; over a long range there would appear to be no repetition of units, nevertheless there is a structure over a short range. Hence the co-ordination or hydration sphere of the H_3O^+ ion would include not free water molecules but a structure intimately connected with that of water itself, and would therefore be subject to any change in the structure of the solvent which would be reflected by a change in the co-ordination or hydration of the hydronium ion.

If this picture is close to the true model of a dissociated acid in water one would expect a change in the nature of the $H_3O^+.nH_2O$ hydrate with concentration. At higher concentrations hydronium ions would compete for available water molecules in order to form co-ordination spheres. Once these co-ordination spheres are formed they would be subject to any change in the structure of the solvent.

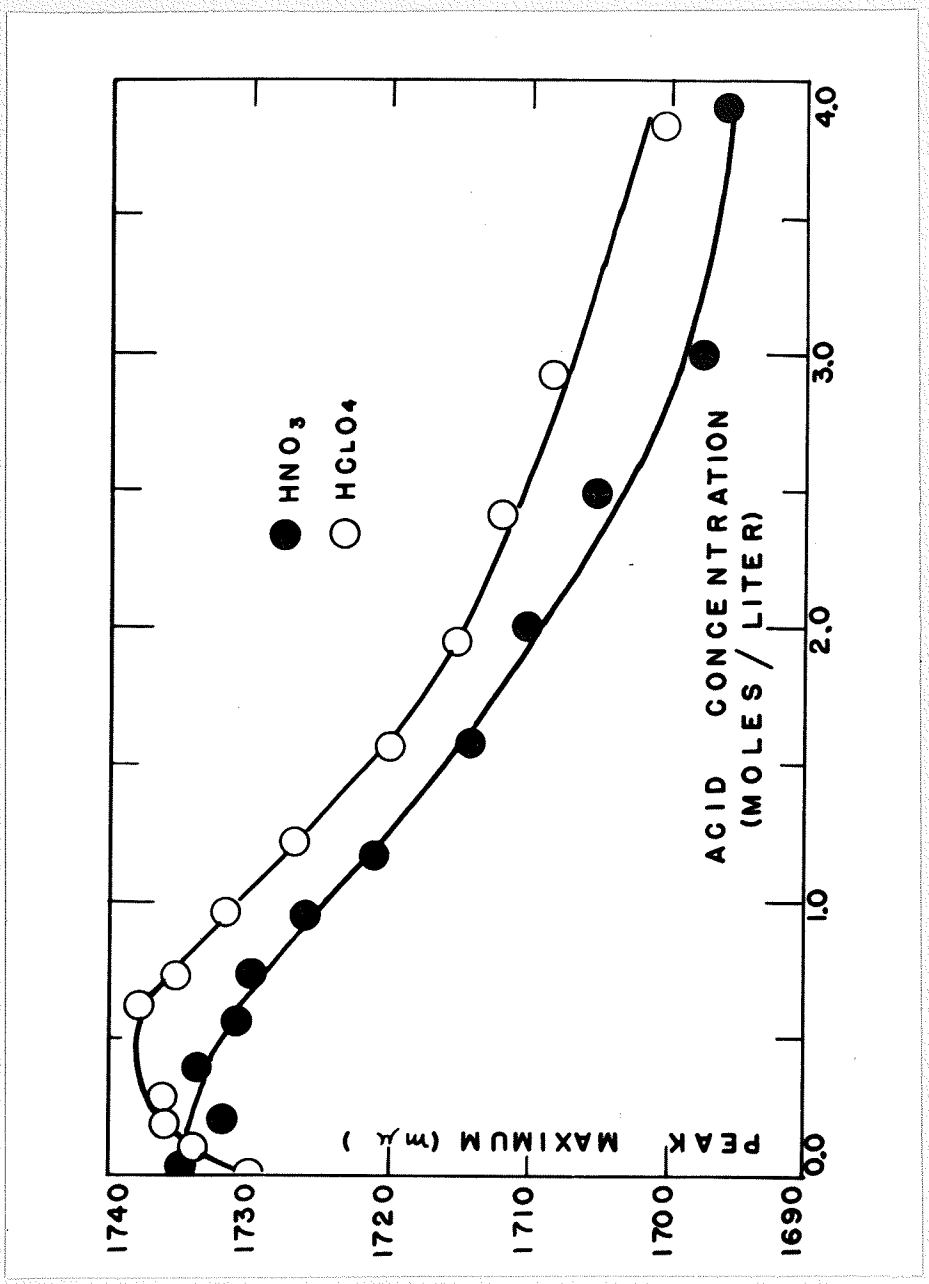

FIGURE 5. Absorption peak maximum vs. concentration of acid.

It is well known that the association of water is disturbed by an electrolyte. It was Bernal and Fowler (12) who first suggested that electrolyte ions cause a rearrangement of the structure of liquid water. Leighton, and Burnham (18), showed that $ZnCl_2$ dissolved in water causes a shift in the short frequency component of a main Raman absorption band. Using the x-ray diffraction curves of LiCl, NaCl and KCl in aqueous solution at 15°C Stewart (19) demonstrated that:

1) with increasing ionic concentration the amount of four fold co-ordination of water structure is lessened.
2) that the alteration in structure is apparently similar to that produced by increasing the temperature. When the temperature is increased, the structure of water begins to break up.

There is also additional evidence that the addition of an electrolyte breaks up water structure. A study of the relative partial molal entropies (20) for a number of strong electrolytes in solution showed a general type of concentration dependence which can be reasonably explained on the basis of a few simple assumptions. One of these is thatthe entropy of a solution is affected through breaking down of the structure of water, and that individual differences among entropy concentration curves for different electrolytes are related mainly to the nature of the ions themselves and the particular way in which they may influence the water structure.

Now, if through hydration of the water molecules by ions, or through dissociation of the associated structure of water, the solution absorbs less light than that of pure water at the same wavelength (negative absorbance) due either to destruction of some degree of freedom of the water molecules, or by shifting the absorption band of pure water, it is possible that the absorbance curves for the hydronium ion would appear too low. That is to say, in order for the absorbance results to agree with other data, they should not be so low. This assumes that a negative absorptiom mechanism acts simultaneously with the positive absorbance by the hydronium ion.

What is true for the hydronium ion must also be true for small positively charged ions like Li^+, Na^+, K^+, which it is generally accepted, are hydrated. This would imply then that these ions should give negative absorbance (or a transmittance value over 100%)in the spectral region around 1700 - 1750 mμ. With this in mind solutions of $NaNO_3$, NaCl and $LiNO_3$ were run in the spectrophotometer from 1900 to 800 mμ. The results were as predicted. All of the solutions gave negative absorbance in the region of the absorbance peak for the acids (see Figure 6). As previously mentioned nuclear magnetic resonance was not influenced by hydration of the H_3O^+ ion. Also Raman work did not consider hydration effects at all. Thus it is quite probable that the reason why the results of the present work for the degree of dissociation of nitric and perchloric acid differed from that of the literature, was because of interference due to hydration effects. It might be

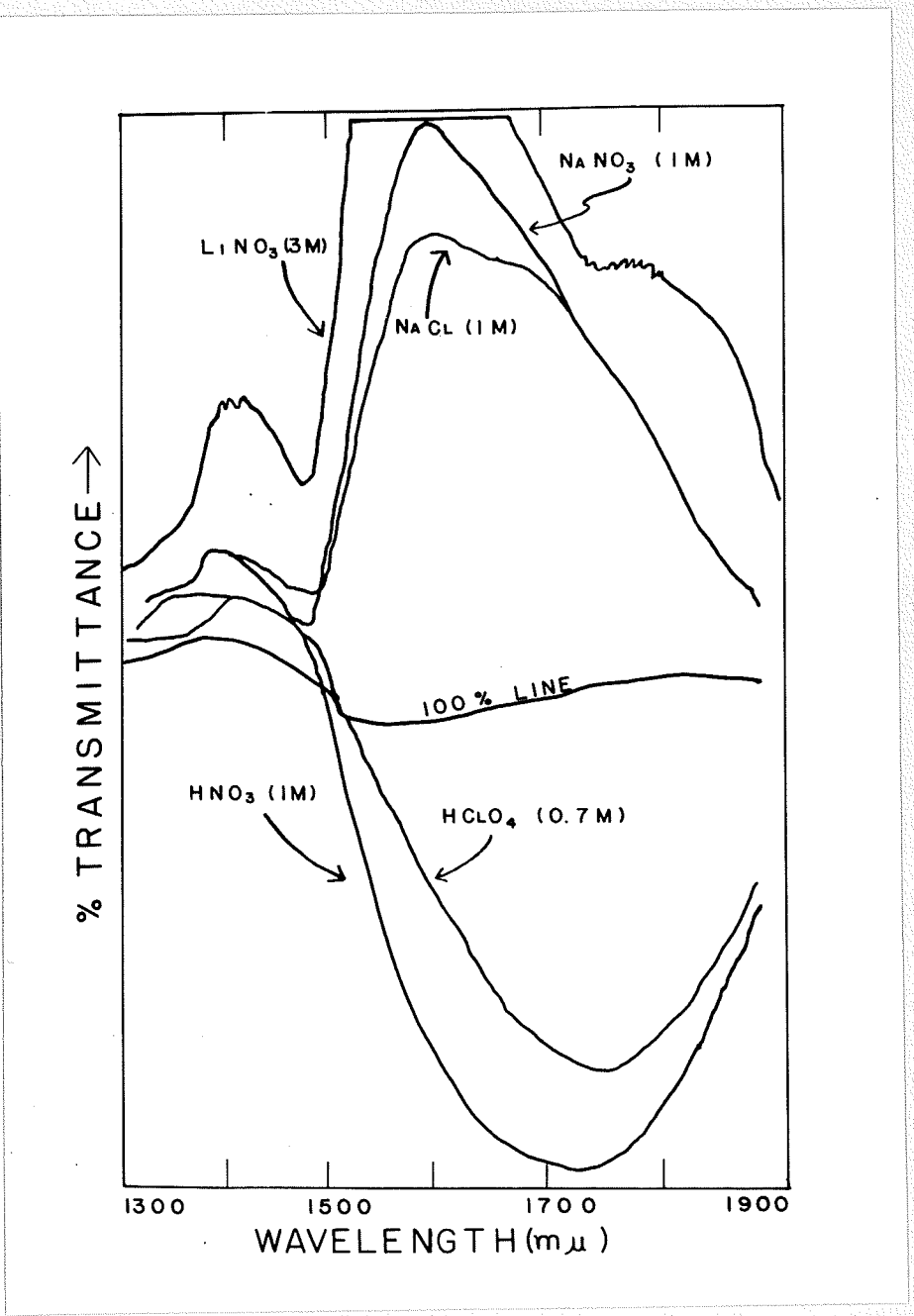

FIGURE 6. The absorption spectra for solutions of HNO_3, $HClO_4$, $NaNO_3$, NaCl $LiNO_3$ are compared. The spectrum for 3 molar $LiNO_3$ went off scale. Notice that the salt solutions give a per cent transmittance greater than 100.

suggested that the high transparency of the acid solutions was due to the fact that as the acid concentration increases, fewer water molecules are in the beam path: less light is absorbed by the solvent. However, the strong bands of the salt soltuions in the 1700 mμ region discount this as being of primary importance, if of importance at all. It would be interesting not only to verify Beer's Law for the other two peaks reported by Giguere but also to study the infra red spectrum of salts with highly charged small ions.

In explaining the properties of electrolytes in aqueous solution one should, as given evidence here, always take into account the structure of the solvent itself.

Because only a property which is exclusively due to the hydronium ion may be used to estimate the degree of dissociation of an acid, and since many effects contribute to the spectrum of a strong acid in water around 1750 mμ, the absorption spectrum in this region may not be used to give the true degree of dissociation for the acid.

CONCLUSION

The discovery by Giguère and Falk of the infra red absorption of the hydronium ion suggested as a succeeding step the application of its spectrum to an investigation of the dissociation of acids in aqueous solutions. However, a Beer's Law plot of the first overtone of one of the primary absorption bands showed that the use of the spectrum for an acid dissociation study was not as promising as one might have anticipated. No doubt the same results would be had if the primary absorption band was used.

A qualitative explanation of the observed deviation from Beer's Law is difficult. A quantitative explanation in terms of the co-ordination or hydration sphere of the hydronium ion and a perturbation or shift of the absorption bands of water from their normal positions would be even more difficult. Although one can give a reasonable explanation for many of the properties of extremely dilute solutions, fairly concentrated ones still present a difficult and complex problem to the theoretical chemist or physicist.

This investigation of the infra red absorption of the hydronium ion serves in its own way to add to our knowledge of concentrated solution. Eventually, when more data are accumulated for higher concentrations, a more lucid picture of electrolytic solutions may be obtained.

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