

## MOLECULAR ASSOCIATION IN OXYACIDS

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**ABSTRACT.** In the present paper, molecular association in solutions of oxyacids is studied with the help of Raman effect. On comparing the associating nature of these substances with their strength, it is found that the stronger the acid the smaller is the tendency for its molecules to polymerise. To study this point further, a comparative study of molecular association in solutions of acetic and chloroacetic acids, which are known to be of increasing order of strength but of quite similar structure, is made and the above point is confirmed.

It is also found that increase in the hydrogen-ion concentration in these solutions will have the effect of diminishing the molecular association contrary to what is to be expected from the law of mass action.

## INTRODUCTION

Koteswaram (1910) successfully employed Raman effect to study molecular association in a number of associated liquids and arrived at the conclusions that substances must have both a donor and an acceptor atom for association to take place in pure state, *e.g.*, water, fatty acids. From this it appears as if oxyacids, which contain both H and O atoms, form ideal substances for molecular association. It is well known that in the oxyacids, the hydrogen-ion is attached to the oxygen atom forming the OH link which on dissociation breaks off. Thus, nitric acid is considered to be having the formula  $\text{NO}_2\text{OH}$ , sulphuric acid  $\text{SO}_2(\text{OH})_2$ , iodic acid  $\text{IO}_2\text{OH}$  and so on. This contention has been further verified by the Raman spectra of these acids in the pure state by Venkateswaran (1936) and Dadieu and Kohorusch (1931) who observed the OH band in these spectra. Also, all these molecules must necessarily be polar because of their unsymmetrical structures. Thus, the condition for molecular association is satisfied and one must expect associated molecules in solutions of these oxyacids. But a study of the solutions of  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HClO}_4$  or  $\text{H}_3\text{PO}_4$  does not show any evidence of the existence of associated molecules of the type  $(\text{HNO}_3)_2$  or  $(\text{H}_2\text{SO}_4)_2$ , etc., though in solutions of acetic acid the determination of molecular weights of  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$  and  $\text{HClO}_4$  revealed the existence of unstable dimers, which were found to be very unstable and to decompose with time. In solutions of iodic acid, evidence for associated molecules could be found in higher concentrations (Rao, N. R., 1942). Its Raman spectra in different concentrations show lines which are found to vary with concentration, which was interpreted on the basis of the splitting up of polymerised molecules into normal molecules with dilution. In trichloroacetic acid also, evidence for polymers, which split up very fast on dilution, was found from a study

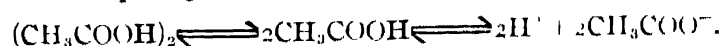
of its Raman spectrum in different concentrations and temperatures.\* But in acetic acid, studied in detail by Koteswaram (1938), associated molecules were found even in dilute solutions.

In the present paper, the association of the oxyacids and its dependence on their strengths will be studied, by making a comparative study of the acetic and chloroacetic acids, which are known to be of increasing order of strength.

#### ACETIC ACID

Koteswaram observed that the Raman spectrum of acetic acid consists of sharp lines of frequencies 446, 601, 620, 872, 893, 1010, 1270, 1368, 1433, 2889, 2946, 2996 and a band which can be regarded as composed of components at 1673, 1700, 1720 and 1770. On examining the intensities and the changes in the frequencies of the lines 872, 893, 1010 and the band at 1700 in the spectra of this acid in different concentrations in water and other polar liquids and at different temperatures, he observed that (1) the line at 872 appears only in the spectrum of the pure acid, (2) the second line 893 gets diffuse on dilution and increase of temperature, (3) the line at 1010, which he attributed to the C-O band, shifts to a higher Raman frequency on dilution and temperature and (4) the lower frequency components of the 1700 band disappear under these conditions. He attributed these changes to the depolymerisation of the acid molecules.

Now on dilution, the polymerised molecules split up into simple ones which on further dilution split up into ions. They can be represented by the equation :



Now if, in a dilute solution, the hydrogen ion concentration is increased, the backward reactions must be favoured resulting in an increase of the polymerised molecules. To test this, 3 sets of aqueous solutions, 82% acetic acid, and 82% acetic acid + 1N HCl, 50% acetic acid, and 50% acetic acid + 1N HCl and 25% acetic acid + 1N HCl are prepared and their Raman spectra are obtained with times of exposure inversely proportional to the concentration of acetic acid in them. For each pair of solutions, the weight of acetic acid per 100 c.c. of solution was the same, so that the spectra for any pair should be identical for equal exposures under identical conditions, if the acetic acid is unaffected by HCl. The changes in the spectra of the mixture compared to the pure solutions are very slight and of uncertain nature. Only there is a slight indication that the lower frequency components of the band at 1700 are further diminished in intensity in the mixture with HCl. This is surprising in view of the above expectation, which is expected to show an increase in the intensity of components which correspond to the polymers.

#### MONOCHLOROACETIC ACID

Due to substitution of one of the hydrogen atoms in the  $\text{CH}_3$  group of acetic acid by chlorine, this acid is known to be stronger than acetic acid. In

\* Unpublished work of the author.

the following pages are given the results on the molecular association of this acid on lines similar to those in the case of acetic acid.

The Raman spectrum of this acid in the solid and the molten states has been studied by a few authors including Parthasarathy (1934), Thatte and Ganesan (1931), Cheng (1929), and Dadiou and Kohlrausch (1929). All the above authors reported that their spectra were superposed by an intense continuous background. Parthasarathy seems to have obtained a fairly good spectrum of the acid in the solid state. Thatte and Ganesan recorded only two feeble lines of frequencies 433 and 2994. Cheng made a comparative study of the infra-red and the Raman spectra of the acid. Kohlrausch seems to have obtained the best spectrum with the molten acid, though he reported to have observed intense continuum superposed on this spectrum. But, so far, no attempt was made to study its molecular association by this method.

#### EXPERIMENTAL

The Raman spectra of this acid are usually superposed by an intense continuum, making it sometimes difficult to observe the lines clearly. In order to avoid this, the acid is distilled a number of times and the final distillate is collected direct into the Wood's tube. The spectrum of the molten acid is taken by maintaining the copper jacket at about 60°C and exposing the acid for about 2 hours. Aqueous solutions of concentrations 10.5N, 5N, 2.5N, 1.25N and 0.5N are prepared and treated with pure carbon while hot. The solution is filtered through a quantitative filter paper in a sintered glass funnel. In a similar way, a 2.5N solution of the sodium salt of this acid is also prepared. To study the effect of increasing the hydrogen-ion concentration, two solutions, one of normality 1.35 and another a mixture of 1.25N of this acid and 1N of HCl, are prepared with the weight of  $\text{CH}_3\text{COOH}$  per 100 c. c. of solution in both being the same.

The experimental arrangement is the same as that employed in the previous work. Spectra of the acid of different concentrations are photographed with times of exposures nearly inversely proportional to the concentration of the acid. Spectra of concentrations 10.5N, 5N, 2.5N and 1.25N are photographed at 80°C also, to study the temperature effect.

#### RAMAN LINES

Raman lines in spectra obtained by the previous authors are given in Table I and those obtained by the author in Table II.

TABLE I

Author	Raman frequencies in $\text{cm}^{-1}$
Parthasarathy	242 (3), 294 (3), 333 (3), 426 (4), 575 (4), 648 (0), 789 (2), 991 (1), 1235 (2), 1366 (1b).
Thatte and Ganesan	433 (w), 2994 (m).
Raman lines	794, 868, 920, 1191, 1437
Cheng	12.58, 11.52, 10.85, 8.39, 6.96.
Infra Red	168 (2b, c), 232 (3b, e, c), 411 (6sb), 561 (3b), 669 (1sb), 790 (10 sb), 901 (3sb), 1181 (1), 1405 (3sb), 1670-1760 (3), 2957 (3b).
Kohlrausch	

TABLE II

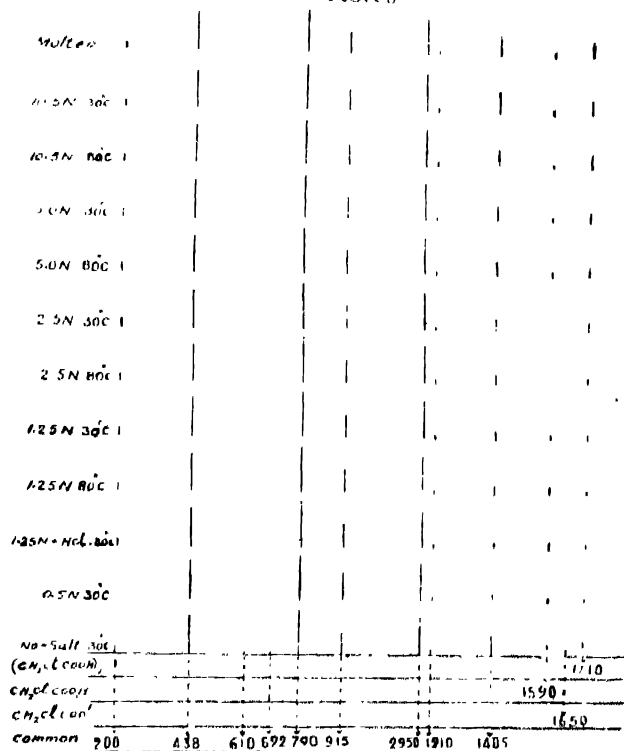
Molten 60°C	10.5N 30°C	10.5N 80°C	5.0N 30°C	5.0N 80°C	2.5N 30°C	2.5N 80°C	1.25N 30°C	1.25N 80°C	1.25N in HCl	0.5N 30°C	Salt 3N
230	242	242	242	242	242	242	242	242	242	242	242
414	438	438	438	438	438	438	438	438	438	438	450
560	610	610	610	610	610	610	610	610	610	610	610
670	682	682	682	682	682	682	682	682	682	682	682
790	790	790	790	790	790	790	790	790	790	790	790
900	915	915	920	920	920	920	920	920	920	930	930
1180	1200	1200	1200	1200	1200	1200	1200	1200	1200	1200	1200
1415	1405	1405	1405	1405	1405	1405	1405	1405	1405	1405	1405
1710	1710	1710	1710	1710	1710	1710	1710	1710	1710	1710	1710
2950	2950	2950	2950	2950	2950	2950	1650	1650	1650	1650	1650

DISCUSSION

The Raman spectrum of this acid is in many respects similar to that of acetic acid. The lines 242, 438, 610, 682, 790, 1205 and 2950 undergo very little change on dilution. On comparing the assignment of the lines for acetic acid studied by Koteswaram it can be seen that the lines of frequencies 790, 915, 1405 and 1590-1710 can be attributed respectively to C-C, C-O, CH<sub>2</sub> and C-O bonds. The other lines are due to some external oscillations.

The line at 915 changes in frequency from 900 in molten acid to 930 in the salt, similar to the C-O lines in acetic acid, probably for similar reasons, i.e., due to the splitting up of the polymers into simple molecules. The band at 1590-1710 and the line 1405 undergo conspicuous changes on dilution and variation of temperature.

Diagrammatic representation of Raman frequencies of monochloroacetic acid in different states.



DIAGRAM

As in the case of acetic acid, this band can be regarded as composed of components due to the polymers, simple molecules and ions. With increasing dilution and temperature, this band shifts to a lower frequency due to increase in the intensity of the component 1590 attributed to  $\text{CH}_2\text{ClCOOH}$  molecules, due to splitting up of the polymers  $(\text{CH}_2\text{ClCOOH})_2$ . On further dilution, *i.e.*, from 2.5 to 1.25 and from 1.25 to 0.5N, the band shifts to a higher frequency due to the increase in the intensity of the component 1650, which is the frequency of the band in the spectrum of the salt solution. This shows the evidence for the electrolytic dissociation of the acid. Since the band is very diffuse and is composed of components very close to it, a quantitative determination of the degree of dissociation is not possible.

The line at 1405 behaves in a peculiar way. It is found to be common in all the solutions, but its intensity falls off rapidly on dilution and rise in temperature. In the salt solution, however, it is very intense. Probably, the line is common to all the radicals but its specific intensity corresponding to the normal molecules is perhaps very small. The feebleness of this line even in 0.5N solution shows that the dissociation of the acid in this solution also is small.

On adding HCl, the band at 1590-1710 shows (1) an increase in the intensity on the lower frequency and (2) a diminution in intensity on the higher frequency side indicating a large increase in the number of normal  $\text{ClCH}_2\text{COOH}$  molecules due to (1) a decrease in the dissociation and (2) a large splitting of the polymers. The latter result is in conformity with that obtained in the case of acetic acid, and the former with those reported in a previous paper by the author "On the effect of common ion on the dissociation of strong electrolytes" (Rao, N. R., 1941).

#### IODIC AND TRICHLORACETIC ACIDS

Studies on these acids are given in detail in the previous papers of the author (Rao, N. R., 1942). But a brief account of the results obtained will be given below, as far as it relates to the present paper. In iodic acid, concentrated solutions show diffuse Raman lines at 636 and 790. The latter was regarded as composed of components at 770 and 825 characteristic of  $(\text{HIO}_3)_2$  and  $\text{HIO}_3$ , respectively. With dilution, the former diminished in intensity with a corresponding increase in the intensity of the latter, indicating gradual splitting up of the polymers into monomers. The effect of increasing the hydrogen-ions on the molecular association of this acid could not be studied as it does not dissolve to a sufficiently large extent in solutions of other acids.

In trichloroacetic acid, the C-O band at about 1700 shows similar behaviour as in acetic acid, with this difference that in this case the diminution in the intensity of the component due to the polymers is very rapid and is almost absent even in 6N solution.

#### GENERAL CONCLUSIONS

From the foregoing work, the following conclusions can be drawn as regards molecular association in oxyacids:—

1. No evidence for polymerisation could be found in solutions of strong acids, *viz.*,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HClO}_4$  and  $\text{H}_3\text{PO}_4$ .

2. Weak oxyacids like acetic, formic and benzoic acids show the presence of polymerised molecules in their solutions. Evidence for this can be gathered from the work of previous authors, *e.g.*, Koteswaram, already referred to in the course of this paper.

3. Oxyacids of intermediate strength, *e.g.*, iodic, monochloroacetic, and trichloroacetic acids, contain polymers in their solutions.

4. From the above results, it can be seen that the weaker the acid, the larger the tendency for the molecules to polymerise. This can also be seen on examining acetic, monochloroacetic and trichloroacetic acids which have similar structures but have a decreasing tendency for exhibiting association and increasing tendency for dissociation.

5. These results show that while the presence of donor and acceptor atoms is essential for the formation of polymers, this is not the only factor. The nature of both the solvent and the solute plays a great part in determining the degree of association.

6. Addition of hydrogen ions will diminish polymerisation. This could be definitely tested only in the case of monochloroacetic acid.

It is likely that due to the supply of a large number of ions by  $\text{HCl}$ , the dielectric constant of the solutions is increased, exerting more electrical pressure on the polymers and hence the suppression of association on the addition of ions.

In conclusion, the author takes great pleasure in recording his grateful thanks to Dr. I. Ramakrishna Rao, under whose direction the present work was done.

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