

RAMAN EFFECT AND HYDROGEN BONDS

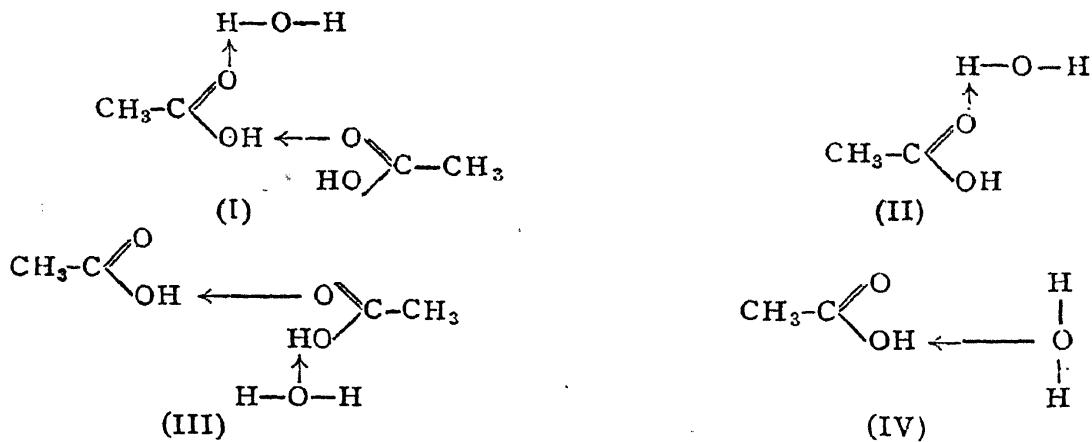
Part IV. Mixtures of Acetic Acid with Donor Substances

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IN Part III¹ of this series the Raman spectra of acetic acid and its solutions in water were studied and the results explained as due to the existence of ring dimers and open chain dimers in the pure liquid and to the changes in the molecular aggregation brought about in aqueous solutions by the attack of water molecules on the C=O groups, forming hydrogen bonds. This explanation was supported by the study of the mixture of acetic acid with a powerful acceptor solvent, phenol, which is known to co-ordinate with the C=O group very successfully. The possibility, however, of the attack of the water molecules on the hydroxyl groups of the acid dimers and monomers was not excluded. Water has both anionoid and cationoid centres and hence can form hydrogen bonds both with donors and acceptors as given below:—



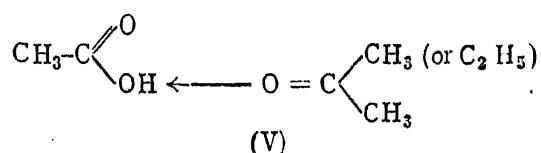
The aspect of the hydration of acetic acid molecules in which water behaves as the donor and acetic acid as the acceptor could not be independently followed in aqueous solution for the following reason namely: there is simultaneous attachment of the water molecules directly to the C=O groups of the acid; in this case water is the acceptor and the acid becomes the donor-molecule. Since our method of study involves the C=O frequency, hydration at the C=O becomes the observable and predominant effect. It is, however, possible to gain some idea of the influence of water as a donor on the changes taking place in acetic acid solutions by studying the effect of simple donor substances when mixed with acetic acid.

The carbonyl compounds employed in this investigation as donors and their C=O frequencies in the pure condition are presented in Table I.

TABLE I

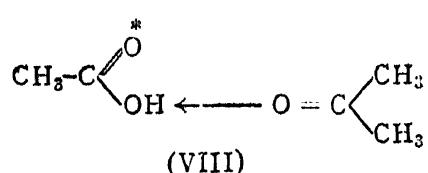
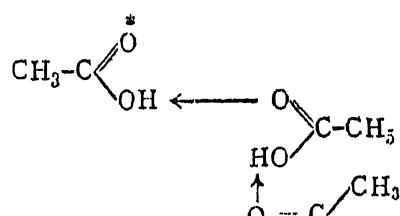
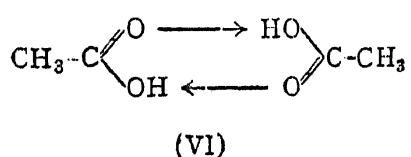
Name of the Compound	The C=O frequency recorded cm. ⁻¹
Acetone	1710
Methyl ethyl ketone	1712
Ethyl benzoate	1720
Ethyl cinnamate	1712
Ethyl acetate	1739
Coumarin	1742
Phenyl acetate	1766

Mixtures of acetic acid with acetone and methyl ethyl ketone.—These mixtures were investigated by Koteswaram.² He noted a shift of the 1670 cm.⁻¹ line towards higher frequencies. This shift of the frequency was attributed to the existence of molecules of acetic acid associated with those of acetone (or methyl ethyl ketone) by the formation of hydrogen bonds according to the mechanism



the oxygen of the C=O in acetone or methyl ethyl ketone being the donor and the H of the OH in acetic acid the acceptor.

The results obtained by us show that the 1670 cm.⁻¹ line has become diffuse and that the 1745 cm.⁻¹ line has become brighter than in the pure acid. No useful information could be obtained from the 1710 cm.⁻¹ line because the C=O frequency of acetone also appears here. The diffuseness of the 1670 cm.⁻¹ line of the acid may not be due to any shift undergone by it but may be attributed to the presence, in this region, of frequencies corresponding to the C=O linkages of acetone that have been lowered as a result of hydrogen bond formation as in VII or VIII



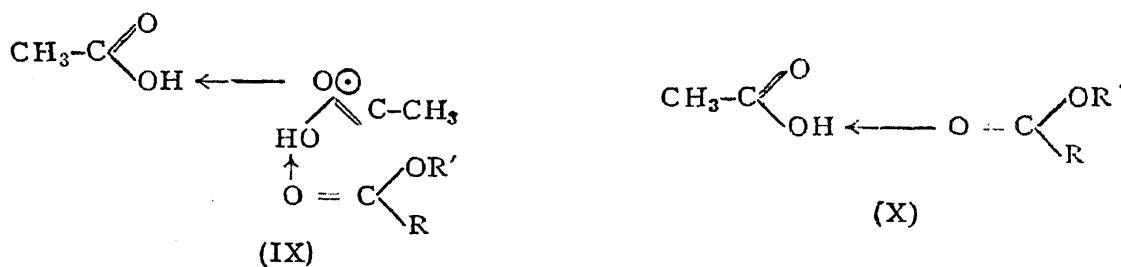
(VII)

The brightening up of the 1745 cm.⁻¹ frequency in the mixture is due to the formation of unco-ordinated C=O groups marked (*) in the above structures. This is obviously due to the attack of the carbonyl group of

acetone on the free hydroxyl of acetic acid leading to a stabilisation of the open dimers (*trans*) or the monomers and consequently shifting the equilibrium towards the right. It is quite possible that the monomers are very few but the results do not enable us to be very definite on this point. It may, however, be said that many of the original ring dimers exist and the change is only partial because the 1670 cm.^{-1} line of acetic acid continues to be bright in the spectrum of the mixture.

The mixture of acetic acid and methyl ethyl ketone yielded results which were quite similar to those of acetone mixture and consequently they lead to the same conclusions.

Acetic acid and ethyl benzoate.—Pure ethyl benzoate has the C=O frequency at 1720 cm.⁻¹ In the mixture of acetic acid and ethyl benzoate (1:1) it was noted that the 1745 cm.⁻¹ line of the acid had become brighter than that of the pure acid and the 1670 cm.⁻¹ line was not appreciably affected. It may be, therefore, concluded that though there is change in the molecular aggregation of acetic acid as a result of admixture with the ester leading to the formation of more of unco-ordinated C=O groups, *i.e.*, to the formation of open dimers and monomers, the change seems to be small. The new aggregates present in the ester mixture may be represented as below:



Acetic acid and ethyl cinnamate.—The spectrum of the mixture of acetic acid and ethyl cinnamate indicated that the 1745 cm.^{-1} line of the acid had become more intense in the mixture than in the pure acid. The 1670 cm.^{-1} line of the acid and the 1712 cm.^{-1} line of the ester had both become slightly diffuse. As in the previous case here also it can be concluded that some ring dimers of the acid get broken up by the formation of hydrogen bonds between the acid and ester molecules.

In all the four cases dealt with above, *i.e.*, the two ketone mixtures and the two ester mixtures, the C=O line in which changes could be easily observed is the one at 1745 cm.⁻¹ and the information indicates that there is greater formation of unco-ordinated C=O due either to open dimer or monomer associates.

Acetic acid and ethyl acetate.—The 1670 cm.⁻¹ of the acid and 1739 cm.⁻¹ line of the ester were not appreciably affected. It is difficult to say anything about the 1745 cm.⁻¹ line of the acid since it was masked by the brighter line

of the ester falling in that region. On the other hand, the very interesting observation was made that the 1710 cm.^{-1} line of the pure acid had brightened up considerably in the mixture. This increase may be due to two causes, namely,

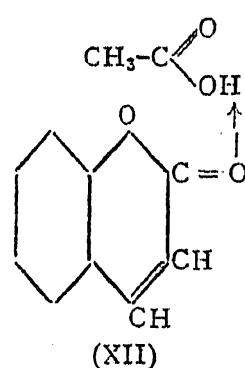
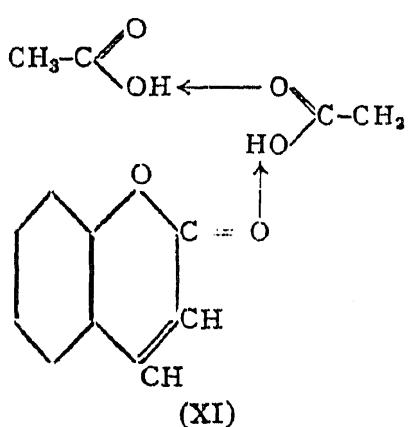
(1) the greater formation of the open dimers having linearly co-ordinated $\text{C}=\text{O}$ marked \odot in formula IX and

(2) the co-ordination of the ester $\text{C}=\text{O}$ groups with the hydroxylic hydrogen of the open dimers or the monomers.

Both, however, arise from the partial breakdown of the ring structures and may be expected to give almost the same $\text{C}=\text{O}$ frequency because of structural similarity.

Coumarin dissolved in acetic acid.—The $\text{C}=\text{O}$ frequencies recorded in the spectrum of a solution of coumarin in acetic acid corresponded to 1670 , 1715 and 1740 cm.^{-1} . The second of these lines was definitely more intense than the last. For purposes of analysing the results it was assumed that the 1710 and 1745 cm.^{-1} lines of the pure acid are indistinguishable from 1715 and 1740 cm.^{-1} of the mixture. In the same way the co-ordinated ($\text{C}=\text{O}$ of coumarin and HO of acetic acid) and unco-ordinated $\text{C}=\text{O}$ frequencies of coumarin could not be distinguished from the second line (1715 cm.^{-1}) and the last line (1740 cm.^{-1}) respectively of the mixture. From general considerations and analogies the assumption seems to be justified.

The association of coumarin and acetic acid molecules could take either of the two forms given below:



For each coumarin molecule that enters into association according to the mechanism XI two linearly co-ordinated $\text{C}=\text{O}$ groups (1715 cm.^{-1}) and one unco-ordinated $\text{C}=\text{O}$ (1740 cm.^{-1}) are formed. Consequently the 1715 cm.^{-1} line should be brighter than the other. This leads to the conclusion that mechanism XI is the one that is prevailing in the mixture and further that almost all the coumarin molecules have associated with acetic acid. Otherwise, if appreciable number of molecules should exist free, they will contribute to the relative brightening up of the 1740 cm.^{-1} line. In this

connection may be recalled our findings described in Part I³ relating to the extraordinary anionoid capacity of the C=O groups of coumarin which undergo almost complete association even with chloroform.

The alternative mechanism XII cannot satisfactorily explain the observations. According to this for each co-ordinated C=O of coumarin whose frequency is lowered from 1740 to 1715 there would be one unco-ordinated C=O of acetic acid with a frequency of 1740 cm.⁻¹. Hence even if all the coumarin molecules are involved in the hydrogen bond formation the 1715 cm.⁻¹ cannot become brighter than the 1740 cm.⁻¹. It could therefore be concluded that there is ample evidence for the existence of the open dimers and for their co-ordination with coumarin as represented by the mechanism XI. The results, however, do not rule out the possibility of the existence of a few associated molecules represented by the formula XII. The relative diminution of the intensity of the 1670 cm.⁻¹ line shows that an appreciably large number of ring dimers of acetic acid are attacked and thus opened out by coumarin molecules.

Acetic acid and Phenyl acetate.—In the Raman spectrum of this mixture it was found that the 1670 cm.⁻¹ line had diminished in intensity whereas the other two lines 1710 and 1745 cm.⁻¹ of the acid had brightened up. There was thus indication that the ring dimers had been broken down by this ester and the mixture contains considerable amount of molecules of the types IX and X.

The intensity relations of the C=O frequencies that have been dealt with in this paper are diagrammatically presented below:

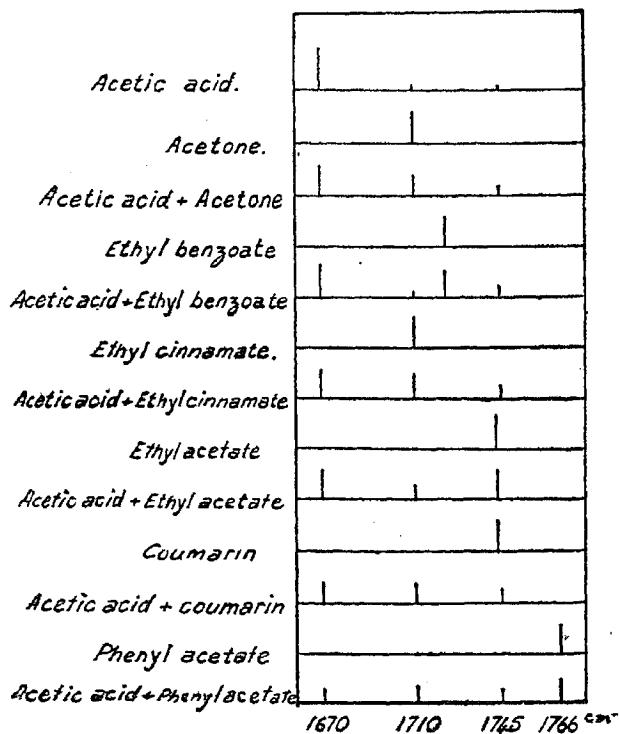


FIG. 1

Discussions

From the results presented in this paper it can be concluded that solvents having anionoid groups are capable of forming associates with acetic acid molecules and effecting change in the state of aggregation. It has been shown that ring dimers are broken down and associated linear dimers and finally associated molecules of monomeric acetic acid are formed. Definite evidence has further been adduced to prove the existence of linear dimers that were first described in connection with the spectra of aqueous solutions of acetic acid.¹ In this connection particular mention should be made of the study of coumarin and acetic acid mixture. Another conclusion that could be arrived at from the results presented in this paper is that the stronger the anionoid characteristic of the C=O present in the solvent the larger the percentage of the ring dimers broken due to association. This agrees with the generalisations arrived at earlier in this series^{3, 4} regarding the conditions controlling hydrogen bond formation. Since as a general rule anionoid solvents affect acetic acid dimers it could be concluded that in aqueous solutions also water molecules may similarly reinforce the breakdown of the ring dimers, though the cationoid attack is predominantly existing. It should, however, be noted that unlike the case of aqueous solutions, acetic acid mixtures with carbonyl compounds do not indicate complete breakdown of the ring dimers as evidenced from the persistence of the 1670 cm.⁻¹ line. Thus these mixtures contain the ring dimers and co-ordinated linear dimers and probably co-ordinated monomers also.

Summary

Raman spectra of mixtures of acetic acid with a number of carbonyl compounds have been studied. It is shown that anionoid solvents affect the molecular aggregation of acetic acid, the effect being prominent with those having strong anionoid C=O groups such as coumarin and phenyl acetate. The breakdown of the ring dimers is not, however, complete in these cases. Definite evidence has been given for the presence of open dimers. There is justification for the view that water molecules serve also as anionoid molecules in effecting the breakdown of the ring dimers of acetic acid.

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Current Science, 1939, **8**, 70; *Ind. J. Phys.*, 1940, **14**, 341.
3. Murty and Seshadri .. *Proc. Ind. Acad. Sci., (A)*, 1941, **14**, 593.
4. _____ .. *Ibid.*, 1942, **15**, 154.