Zeitschrift: Archives des sciences [1948-1980]

Band: 13 (1960)

Heft: 9: Colloque Ampère

Artikel: Proton magnetic resonance study of hydrogen bonded systems

Autor: Dharmatti, S.S. / Govil, G. / Kanekar, C.R.

DOI: https://doi.org/10.5169/seals-738622

Proton Magnetic Resonance Study of Hydrogen Bonded Systems

S. S. DHARMATTI, G. GOVIL, C. R. KANEKAR and Y. P. VIRMANI

Tata Institute of Fundamental Research
and Atomic Energy Establishment Trombay, Bombay-1

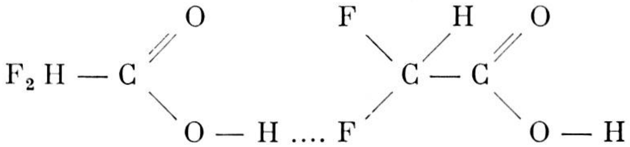
Résumé.

La technique de haute résolution pour le proton a été appliquée à l'étude de faibles interactions moléculaires. Cette communication présente les résultats obtenus pour les systèmes suivants: *a)* solutions d'acides formique, acétique et difluoracétique; *b)* mélanges eau-dioxane et eau-acétone; *c)* solutions de coumarine dans divers solvants.

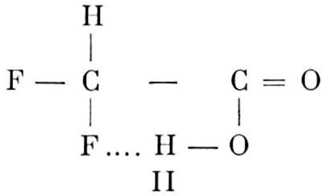
Le shift chimique δ du proton carboxylique dans les mélanges eau-acide formique a été mesuré en différentes concentrations. Les résultats montrent que l'acide formique est essentiellement monomère au-dessous d'une concentration correspondant à une fraction de 0,17 mole d'acide formique. Pour des fractions entre 0,2 et 0,4 mole la dimérisation de l'acide formique semble prépondérante. Il ne semble pas qu'il se forme un hydrate stable.

La variation du shift chimique du proton carboxylique dans les solutions aqueuses d'acide acétique a été examinée à nouveau puisque les premiers travaux sur ces mélanges n'étaient pas tout à fait concordants. Nos observations confirment les résultats de Bhar et Lindstrom [9]. L'anomalie dans la courbe donnant le shift en fonction de la concentration apparaît comme étant due à la formation d'un hydrate de l'acide acétique.

La résonance du proton de l'acide difluoracétique dans le dioxane et dans l'eau lourde a été étudiée. La dépendance des valeurs de δ du proton du groupe carboxylique vis-à-vis de la concentration montre que pour des fractions molaires dans le dioxane situées entre 1,0 et 0,80, l'acide difluoracétique se comporte comme un mélange de I et de II.



I



II

Pour des fractions molaires entre 0,8 et 0,35, c'est le monomère (II) qui existe; il donne lieu à une association avec le dioxane au-dessous de cette concentration. Des conclusions semblables ont été obtenues à partir de l'étude du système D_2O — acide difluoracétique. Nous avons trouvé que le shift chimique δ des protons de l'eau augmente avec la dilution dans l'acétone et le dioxane. L'eau est associée à toute concentration dans ces mélanges. Le changement de pente dans la courbe donnant δ en fonction de la concentration pour la fraction molaire 0,82, indique l'existence d'un hydrate de dioxane dans les mélanges eau-dioxane.

Nous avons observé que les shifts chimiques des protons en position 3 et 4 de la coumarine (III) sont indépendants de la concentration dans des solutions de coumarine dans le tétrachlorure, l'acétone et le dioxane. Ceci prouve que le groupe CH en position 3 ne donne pas lieu à des liaisons hydrogène. Cependant on trouve une association de la coumarine et de l'alcool méthylique, association due à la formation de liaisons hydrogène entre le groupe $C = 0$ de la coumarine et le groupe OH de l'alcool méthylique.

INTRODUCTION.

The technique of high resolution proton magnetic resonance has now been recognized as a powerful method for the study of molecular interactions such as those present in hydrogen-bonding systems [1]. The present paper deals with the results obtained on the following systems: *(a)* solutions of formic, acetic and difluoroacetic acids, *(b)* water-dioxane and water-acetone mixtures and *(c)* solutions of coumarin in different solvents. In all these systems, hydrogen bonds are formed and also broken at various concentrations and therefore it was thought that the dependence of the chemical shift of the relevant protons on concentrations in the solutions might yield fruitful results in the cases mentioned above.

Experimental.

The proton magnetic resonance in all these systems has been examined with the help of Varian Associates' V4300 High Resolution Spectrometer operating at a fixed frequency of 30 Mc/s coupled with their 12″ electromagnet. The chemical shifts were measured by the usual side band technique. The chemical shift parameter δ is the standard notation used in the literature defined as

$$\delta = \frac{H_i - H_r}{H_r} \times 10^6 = \frac{\nu_i - \nu_r}{\nu_r} \times 10^6$$

where H_r = reference proton resonance field.

H_i = resonance field for the proton taking part in hydrogen bonding.

In solutions of organic acids, the chemical shifts of the carboxyl group proton were measured relative to the protons of the alkyl group. In water-dioxane and water-acetone solutions, δ of protons in water was measured relative to the protons of the solvent. In coumarin-methanol system, δ was measured for hydroxyl proton relative to the protons in methyl group in methanol.

RESULTS AND DISCUSSION.

I. *Organic acids.*

1) Aqueous solutions of formic acid.

The spectra of these solutions should, in the absence of chemical exchange normally consist of three lines — one due to the aliphatic proton, another due to the carboxylic proton and the third due to the protons in water. But the spectra shows only two lines on account of the rapid exchange between the carboxyl proton and those of the water molecules. However, in an entirely separate experiment wherein water is taken in an internal co-axial tube within the tube containing the formic acid solution, the spectra shows the three independent lines of protons belonging to alkyl, carboxyl and water. It is customary to take the proton line in water as the standard with respect to which δ can be measured. As it was found that there was no shift of the alkyl proton with respect to water proton taken as external standard in the range of concentrations studied, the variation of the shift of carboxylic proton with respect to alkyl proton as internal standard, has been measured over the entire range of concentration. Figure 1 shows the concentration dependence of δ which increases continuously on dilution.

An aqueous solution of formic acid is a mixture of its own monomers and dimers which exchange rapidly with protons of the solvent water. One can, therefore, express the chemical shift δ of the carboxyl proton as an appropriate mean of the separate chemical shifts of monomer, dimer and water molecules as

$$\delta = p_m \, \delta_m + p_d \, \delta_d + p_{H_2O} \, \delta_{H_2O} \qquad (I)$$

where p_m, p_d and p_{H_2O} are the mole fractions of the exchanging protons in the monomer, dimer and water respectively and δ_m, δ_d and δ_{H_2O} are the corresponding chemical shifts for the monomer, dimer, and water.

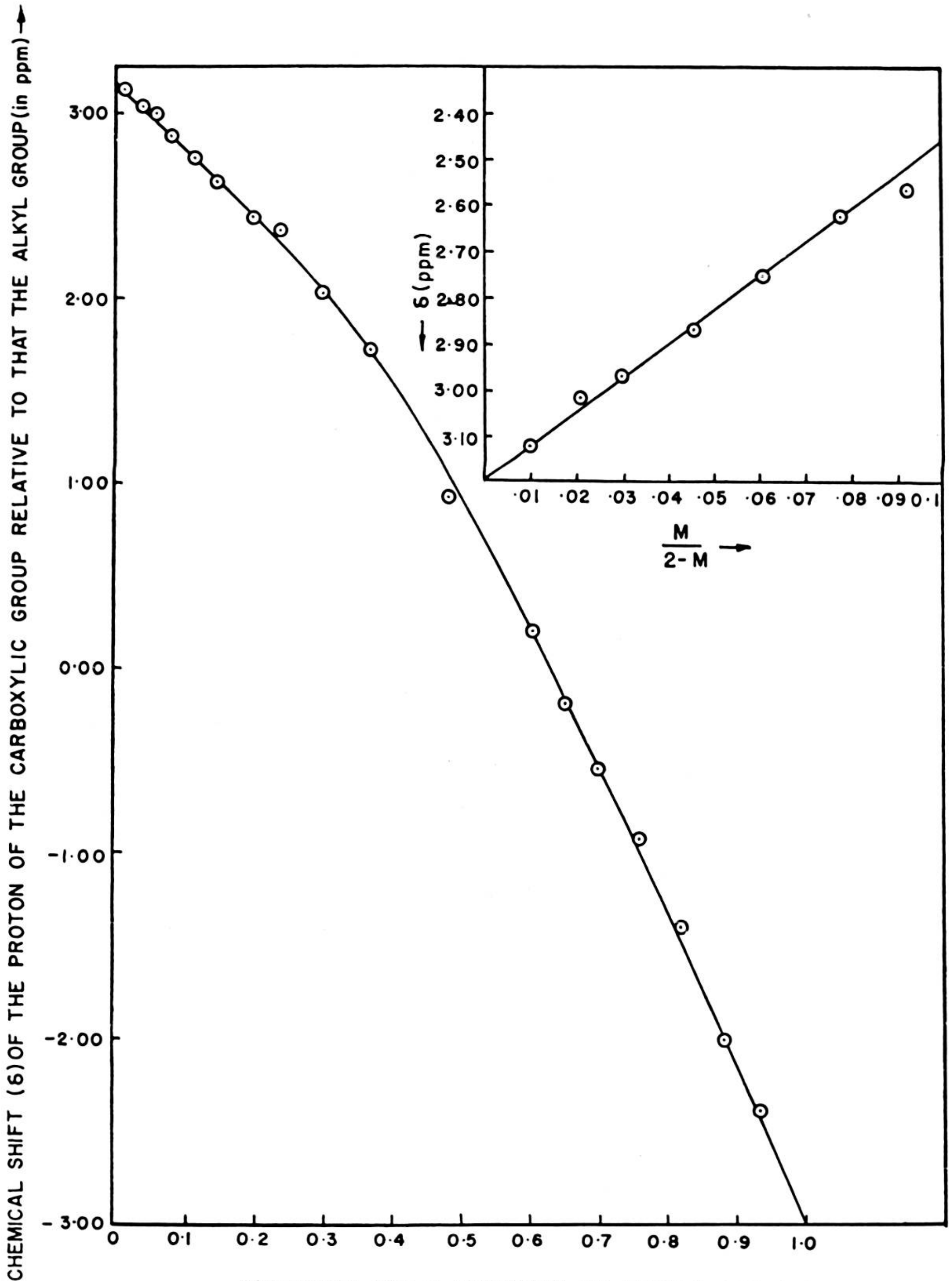


FIG. I.

If the shifts are measured relative to water, then $\delta_{H_2O} = 0$ and hence

$$\delta = p_m \, \delta_m + p_d \, \delta_d \qquad \text{(II)}$$

In high concentrations it is difficult to estimate the amount of the dimer and the equation (II) can only be qualitatively interpreted in terms of observed δ. It may also be mentioned here that other forms of interaction may have a role at higher concentrations and equation (II) may not hold true. However, at very low concentrations a simplified model can be considered with the assumptions

(a) that only monomers exist in which case

(II) becomes $\delta = p_m \, \delta_m$ (III)

and *(b)* there is no dissociation.

If M is the mole fraction of the formic acid, the number of molecules of formic acid in N molecules of the solution will be NM and of water molecules N (1 — M). Hence the fraction of carboxylic protons in the monomer

$$p_m = \frac{\mathrm{NM}}{\mathrm{NM} + 2\mathrm{N}\,(1 - \mathrm{M})} = \frac{\mathrm{M}}{2 - \mathrm{M}} \qquad \text{(IV)}$$

and therefore from (III)

$$\delta = \frac{\mathrm{M}}{2 - \mathrm{M}} \, \delta_m \qquad \text{(V)}$$

The values of δ have been plotted against $\frac{\mathrm{M}}{2 - \mathrm{M}}$ in the inset in figure 1. The plot indicates that at concentrations below 0.17 mole fraction the points lie on a straight line. The slope of this straight line gives the value of the chemical shift δ_m of the monomer. This was found to be — 7.37 ppm (relative to water). The chemical shift of 100% formic acid can be obtained by extrapolating the curve in figure 1 to M = 1. This value when expressed relative to water comes to be — 6.17 ppm. We observed a shift of — 6.0 ppm relative to water for carboxyl proton in formic acid for 80 and 90% solutions of formic acid in chloroform where formic acid is expected to be present as dimer. Correcting for the effect of self association of chloroform (0.25 ppm) which can be estimated from the work of Korinek and Schneider [2], the shift of the dimer comes out to be — 5.7 ppm. This value is not far from the extrapolated shift of — 6.17 ppm. The slight difference in the two values may be due to approximations involved in extrapolation. Open chain polymers as postulated by Schneider [3] for acetic acid may also be present and may be responsible for this difference.

The proton magnetic resonance spectra were also obtained for mixtures of formic acid in D_2O and the nature of the curve for δ against M was found to be almost the same in both the cases. The value of δ was the same for

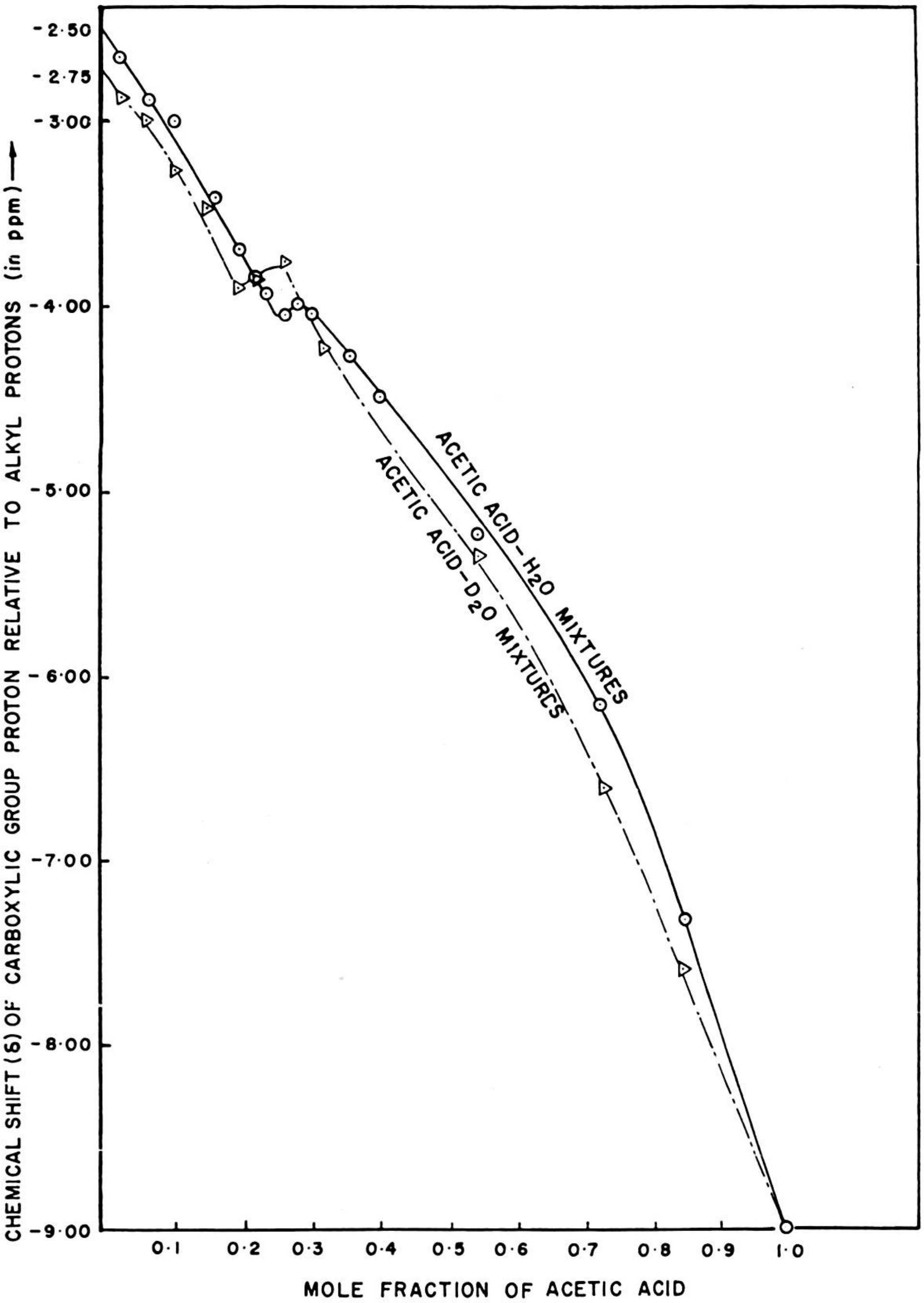


FIG. 2.

solutions of the same concentration in both ordinary water and heavy water, within experimental errors.

Rao and coworkers [4] from the data of magnetic susceptibility and other physical properties postulated the existence of a stable monohydrate of formic acid at a concentration of about 0.5 mole fraction. We do not observe any sudden change in the plot of δ against M. The formation of such a hydrate has been disputed by other workers too [5, 6].

The results thus indicate that formic acid is essentially monomeric below the concentration of 0.17 mole fraction. Beyond this concentration the curve is no linear but shows greater changes of δ with M between 0.2 mole fraction to 0.6 mole fraction, and then again the linearity sets in. In this range dimerisation seems to be a predominant process. It does not appear that a stable hydrate is formed.

2) *Acetic acid in aqueous and heavy water solutions.*

Hydrogen bonding in acetic acid has been investigated by Huggins, Pimental and Schoolery [7] in acetone, by Schneider and Reeves [8] in several nonpolar solvents, and by Bhar and Lindstrom [9] and Gutowsky and Saika [10] in aqueous solutions. The work on aqueous solutions has been repeated by us since the earlier reports already mentioned are not in complete agreement. Gutowsky et al found a linear dependence of the chemical shift of carboxyl group proton with concentration while Bhar and Lindstrom reported a hump in the shift concentration curve at a concentration of about 50% V/V (0.23 mole fraction). The results obtained for aqueous solutions of acetic acid in the present work, shown in figure 2, confirm the presence of a hump near about the same concentration as that of Bhar and Lindstrom. We believe that it may be due to the formation of a hydrate of acetic acid.

The solutions of acetic acid in D_2O gives a similar hump at a slightly lower mole fraction. The values of δ for solutions of acetic acid in deuterium oxide are consistently lower than those for solutions in protium oxide except near the hump. This observation supports Bhar's results. The inversion of the two curves at the hump is probably a consequence of the deuterate of acetic acid being formed at a slightly lower concentration due to the different polar nature of D_2O and H_2O or due to isotopic effect. In this connection the infra red work is in progress.

3) *Difluoroacetic acid in dioxane and water.*

The proton resonance was studied in difluoroacetic acid where there is the possibility of formation of both intermolecular as well as intramolecular hydrogen bonds.

A typical high resolution spectrum for proton magnetic resonance obtained in dioxane solution is shown in figure 4. The peak occurring at the lowest field is identified as being due to the carboxyl proton; that at the highest field is due to dioxane. The line due to the alkyl proton is split into a triplet owing to its coupling with fluorine nuclei (J_{HF} observed $= 53$ c/s). The chemical shifts of the alkyl and carboxyl protons measured in terms of an internal standard, cyclohexane, are respectively — 4.43 and — 6.75 ppm. The observed shift for the carboxyl proton in this acid is compared with the corresponding values for other lower fatty acids in Table I.

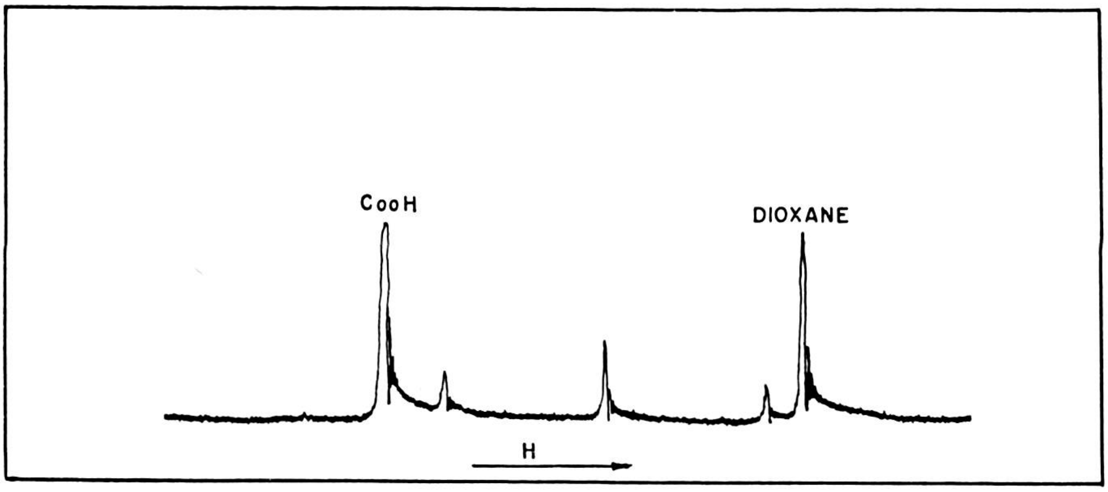
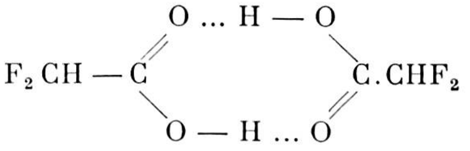


FIG: 4. DIFLUOROACETIC ACID IN DIOXANE (0·9 MOLE FRACTION)

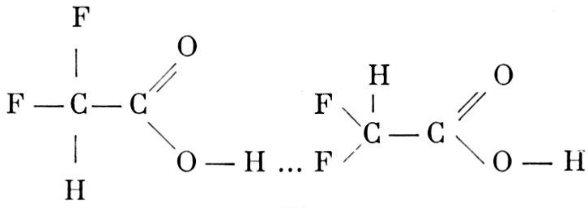
TABLE I.

Acid	Carboxyl proton shift relative to cyclohexane (ppm)	O^{17} shift in carboxyl group group relative to H_2O^{17} (11) $\sigma \times 10^4$
HCOOH	— 9.55	— 2.7
CH_3COOH	— 9.70	— 2.2
CH_3CH_2COOH	— 10.0	— 2.1
CHF_2COOH	— 6.75	—

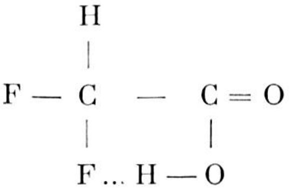
It is seen that whereas the proton shifts decrease as the chain length increase, the o^{17} shifts increase. It is a significant fact to note however, that the carboxyl proton in difluoroacetic acid resonates at a much higher field than in any other acid. Three types of structures are possible for the associated and unassociated difluoroacetic acid as shown below



I



II



III

Structure I is similar to cyclic dimers in formic and acetic acids. The existence of such dimers appears improbable in pure difluoroacetic acid, firstly because structure II and III involve O — H ... F bonds which are stronger than O — H ... O bonds in structure I; secondly, the δ value for difluoroacetic acid would be expected to be close to that of other acids shown in table I if similar cyclic dimers were present.

It, therefore, appears that in the pure acid, dimers and monomers representing structures II and III are both present. The variation in δ for the proton of carboxyl group relative to the alkyl proton with concentration for the solutions of difluoroacetic acid is shown in figure 3. Here δ decreases with dilution between 1.0 to 0.8 mole fraction of the acid, remains practically constant between 0.8 and 0.35 mole fraction, and then increases as the acid is further diluted with dioxane.

Structure II involves two molecules of difluoroacetic acid and hence will be less stable at lower concentration of the acid. Structure III will be invariant of concentration. Hence the decrease in δ between 1.0 to 0.8 mole fraction is due to the breaking up of dimers (II) into monomers (III).

The non-variation of δ from 0.8 to 0.35 mole fraction of the acid is an indication of the existence of structure III in this range. However, the

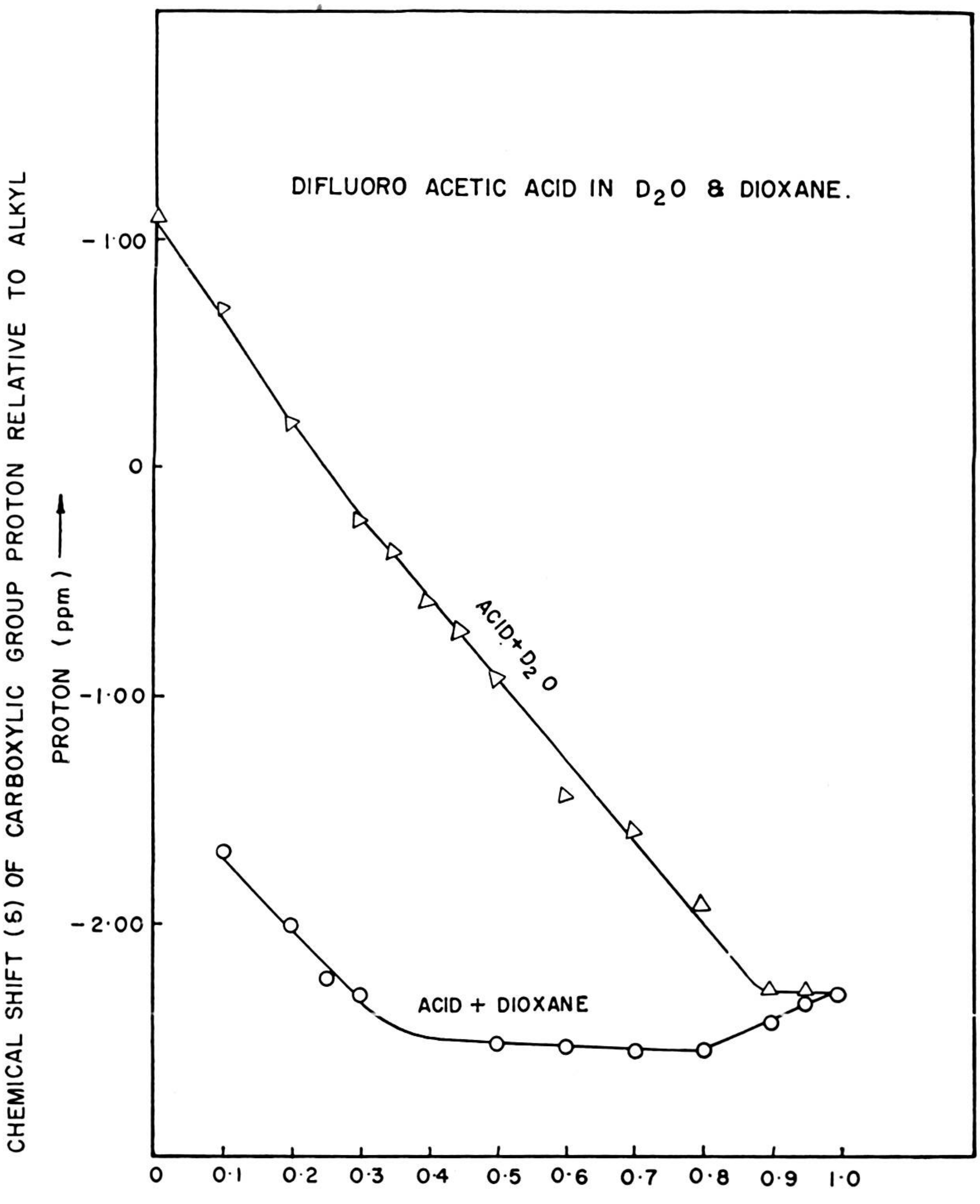


FIG 3

interaction of the solvent with the monomer becomes prominent as the concentration of dioxane increases. The increase in carboxyl proton shift beyond 0.35 mole fraction concentration is, therefore, due to the association of difluoroacetic acid with the solvent.

It appears, therefore, that between 1.0 and 0.80 mole fraction in dioxane, difluoroacetic acid occurs as a mixture of II and III. Between

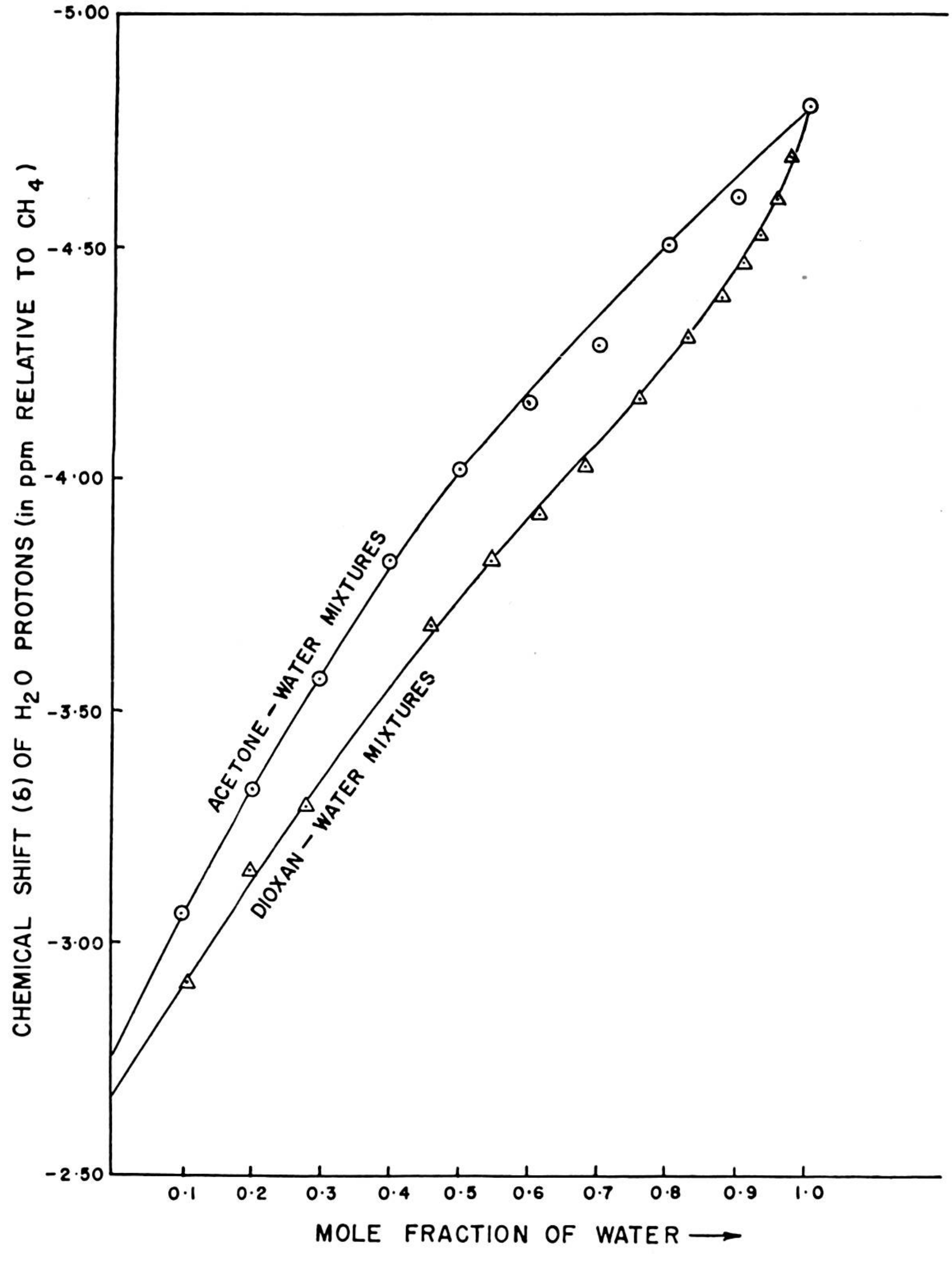


FIG. 5.

0.8 and 0.35 mole fraction only the monomer exists which gets associated with dioxane below this concentration.

The concentration dependence of δ values for the carboxyl group proton in D_2O solutions of difluoro acetic acid is also shown in figure 3. The curve does not show the hump similar to that observed in acetic acid solutions. The curve represents the breaking up of the dimers and the association of monomers of the type discussed above on dilution. However since D_2O is a much more polar solvent than dioxane, it is more effective in breaking the dimers at a much lower concentration of the solvent than dioxane.

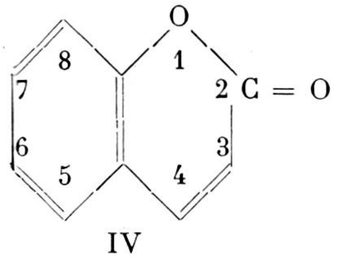
II. *Water-acetone and water dioxane mixtures.*

Figure 5 shows the plot of the chemical shift of water protons (δ) against concentration in acetone and dioxane solutions of H_2O. For the sake of convenience of the discussion which follows the δ values which were measured relative to the solvent protons have been expressed relative to protons in methane gas. This conversion has been made from the known chemical shift of methane gas relative to CH_3 and CH_2 protons in ethyl alcohol [1 *(b)*]. Both the curves in figure 5 show that δ for water protons shifts continuously towards higher field with dilution. The value of the chemical shift for water in the gas phase relative to methane has been found to be — 0.60 ppm [Schneider et al (12)]. The extrapolated values of δ for the two mixtures at infinite dilution were found to be — 2.7 ppm in acetone and — 2.57 in dioxane. These results indicate that water is associated at all concentrations in both these mixtures, either with itself or with the solvent.

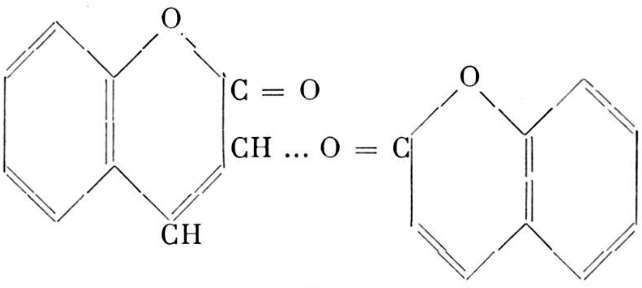
A number of workers have studied water dioxane mixtures by various physical methods such as refractometry [Pesce and Lago (13)], dielectric constant measurements [Gerald Oster (14)], Viscosity [Geddes (15) and Mariani (16)] and X-ray diffraction [Cennamo and Tartaglione (17)]. All of them have observed a remarkable change in the behaviour of these mixtures at a concentration of about 0.8 mole fraction of water. Geddes has postulated the formation of a pentahydrate and Mariani, a tetrahydrate to account for the unusual behaviour in viscosity at this concentration. Cennamo and Tartaglione attribute it to complete depolymerisation of water at and beyond this concentration. The curve for water-dioxane mixtures in the present studies show a change in slope at 0.82 mole fraction of water. The change in slope cannot be attributed to complete depolymerisation of water at this concentration since we have already seen that water is associated even at infinite dilution. Hence the view of Mariani and Geddes appears to be more probable.

III. *Coumarin solutions in CCl_4 and methyl alcohol.*

Coumarin is represented by IV



IV

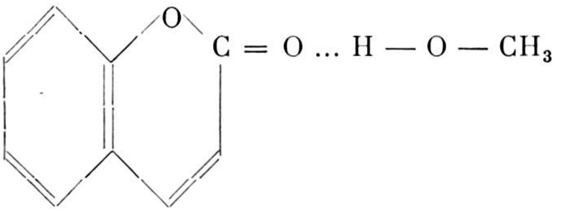


V

Narasimhamurty and Sheshadri [18] found from the Raman spectrum that this compound occurs as a hydrogen bonded dimer V. Measurements of magnetic susceptibility, dielectric constants and molecular weight determination [19] do not indicate such a dimerisation. Proton magnetic resonance study of coumarin was therefore undertaken to ascertain the existence of hydrogen bonding in this compound. A solution of coumarin in CCl_4 gives a five line proton magnetic resonance spectrum. Four of these arise from the two protons attached to carbon atoms in position 4 and 3 which form an AB system. The chemical shifts of these protons are — 6.14 and — 4.75 ppm relative to cyclohexane and $J_{34} = 9.2$ c/s. The phenyl protons give an intense line with poorly resolved structure and which has a chemical shift of — 5.75 ppm relative to cyclohexane.

Solutions ranging in concentration from 0.7 molar to .07 molar in CCl_4 were made and the variation of the chemical shift of the AB protons over this concentration range was studied. No variation in shift was observed. This indicates that the dimers of coumarin do not exist within the range of concentration of 0.7 mole and .07 mole. Solutions in acetone and dioxane also did not show any variation in the shift of these protons thus indicating that C-H group at position 3 does not form hydrogen bonds. It may be pointed out here that Mathur [19] has also shown that coumarin occurs only as monomer.

However Coumarin has been known to associate with methyl alcohol [18]. In these solutions the association occurs as shown in VI.



VI

To study the intermolecular hydrogen bonding of this type solutions of both coumarin and methyl alcohol (0.657 m) were made in CCl_4. The two solutions were mixed in different proportions and the shift of the OH proton with respect to methyl protons was determined for each concentration. A typical spectrum of coumarin in methyl alcohol is shown in figure 6, in which the peak at the highest field corresponds to the OH proton. Since methyl alcohol itself is an associated liquid and the chemical shift of the OH proton in methyl alcohol solutions in CCl_4 is concentration dependent [20], separate blank experiments were made to determine the variation of δ for OH proton in alcohol without the addition of coumarin for the concentrations corresponding to the coumarin methyl alcohol mixtures. Figure 7 shows the plots of δ against concentration for the two systems. It is seen that whereas the extrapolated δ for OH proton to zero concentrations of methyl alcohol is 2.8 ppm in methyl alcohol-CCl_4 mixtures, it is only 1.53 ppm in coumarin solutions in methyl alcohol. The difference is indicative of hydrogen bond formation between methyl alcohol and coumarin. The curve for δ against concentration for coumarin-methyl alcohol system lies below that for the methyl alcohol solutions. Infra red spectroscopic measurements and NMR work [2] have amply indicated that the dilution of methyl alcohol with CCl_4 results in the breaking of various polymers. This is shown by our curve also. In the coumarin-methyl alcohol-CCl_4 system, however, both the breaking and formation of hydrogen

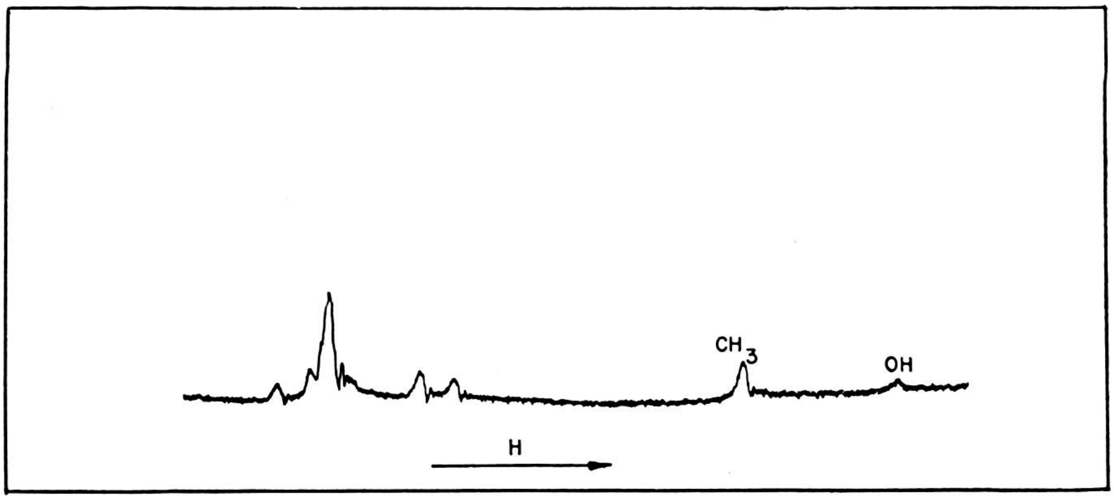


FIG. 6. COUMARIN + METHYL ALCOHOL.

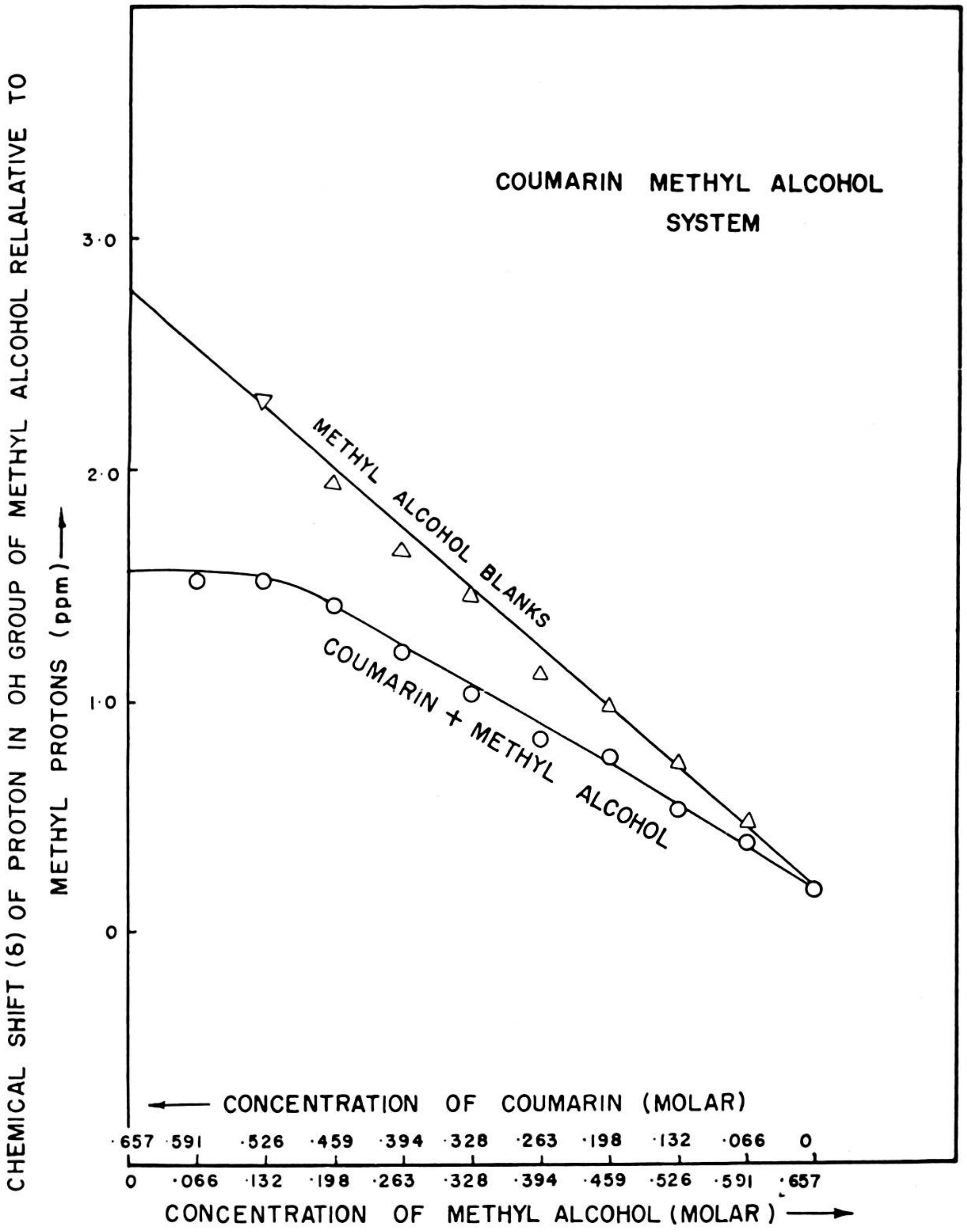


FIG: 7.

bonds occur. Firstly the various polymers of methyl alcohol are broken with successive dilution; secondly the association of methyl alcohol with coumarin takes place. At higher concentrations of coumarin the curve between δ and concentration becomes flat which indicates that the association of CH_3OH and coumarin goes nearly to completion in very concentrated solutions.

CONCLUSION.

The study of proton magnetic resonance has given interesting information about the hydrogen bonded systems. Although the interpretation of data becomes more difficult on account of the complexity of the various hydrogen bonded species in mixtures such as those studied here, coupled with infra red study and other physical properties, NMR may enable one to get a reasonably good physical picture of such systems.

ACKNOWLEDGEMENTS.

Our sincere thanks are due to Sri R. Vijayaraghvan for many helpful discussions.

REFERENCES

1 *(a)*. PIMENTAL and MCCLELLAN, *The Hydrogen Bond* (Freeman and Company), p. 143.
(b). POPLE, BERNSTEIN and SCHNEIDER, *High resolution nuclear magnetic resonance* (McGraw Hill Publications), p. 400-421.
2. KORINEK and SCHNEIDER, *Can. J. Chem.*, *35*, 1157, 1957.
3. SCHNEIDER, *Hydrogen Bonding* (Papers presented to Ljubljana Symposium on hydrogen bonding), edited by Hadzi (Pergamon Press Ltd.), p. 55.
4 *(a)*. RAO and SRIRAMAN, *J. Annamalai Univ.*, *7*, 187-93, 1938.
(b). RAO and NARAYANASWAMI, *Proc. Indian Acad. Sci.*, *9A*, 35-66, 1939.
5. KOTESWARAM, *Z. Physik*, *112*, 395-406, 1939.
6. ANGUS and TILSTON, *Trans. Faraday Soc.*, *43*, 221, 1947.
7. HUGGINS, PIMENTAL and SCHOOLERY, *J. Phys. Chem.*, *23*, 1244, 1955.
8. SCHNEIDER and REEVES, *Trans. Faraday Soc.*, *54*, 314, 1958.
9. BHAR and LINDSTROM, *J.C.P.*, *23*, 1958, 1955.
10. GUTOWSKY and SAIKA *J.C.P.*, *21*, 1688, 1953.
11. DHARMATTI, SUNDARA RAO and VIJAYARAGHAVAN, *Il Nuovo Cimento 11 (X)* 656-669, 1959.
12. SCHNEIDER, BERNSTEIN and POPLE, *J.C.P.*, *28*, 601, 1958.
13. PESCE and LAGO, *C.A.*, *41*, 1143f, 1947.
14. Gerald OSTER, *J.A.C.S.*, *68*, 2036, 1946.
15. GEDDES, *J.A.C.S.*, *55*, 4832, 1933.
16. MARIANI, *C.A.*, *37*, 2979^4, 1943.
17. CENNAMO and TARTAGLIONE, *Il Nuovo Cimento*, *11 (3)*, 401, 1959.
18. SHESHADRI and NARASIMHAMURTI, *Proc. Ind. Aca. Sci.*, *8A*, 519, 1938.
19. MATHUR, Thesis. Bombay University, 1955.
20 *(a)*. COHEN and REID, *J.C.P.*, *25*, 790, 1956.
(b). LIDDEL and BECKER, *Spectrochim. Acta*, *10*, 70-84, 1956.