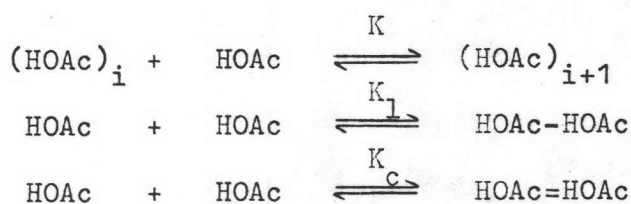


CHAPTER 5.

DISCUSSION AND CONCLUSION

In order to understand the on-going phenomena taking place in the system of various species like acetic acid in water, the equilibrium constants of the reversible reactions operating between the co-existing species are, almost always, the required quantity. In this work, equilibrium constants cannot be calculated by a simple method due to a large number of variables involved but they can be obtained from the fit of the proton chemical shift of aqueous acetic acid. It is quite a complicated task and needs an iterated calculation hence cannot be achieved without the aid of a computer. When a suitable computer program is applied to the following equilibrium model,



the corresponding values of K , K_1 and K_c are equal to 54.4 mf^{-1} , 141.7 mf^{-1} and 262.5 mf^{-1} respectively. It was found that these values may be well accepted in the concentration range of 50-85 %w/w. Beyond 85 %w/w (0.65 mf) a pronounced positive deviation due to the error of chemical shift was observed (Fig 5.1). This may be attributed to the fact that in the model used every acetic acid species is thought to be solvated with water molecules which is true for a fairly dilute solution

whereas at a higher concentration some acetic acid species may be left unsolvated. The possible existence of "ion-pair" at higher concentration is also thought to affect the chemical shift. It is interesting to look more closely into the tendency of changes in the values of equilibrium constants as a function of concentration at and above 85 %w/w in relation to changes in chemical shift. It can be seen from equation 2.18 that the chemical shift is influenced by $f(E)\delta(E)$, $f(I)\delta(I)$ and $f(C)\delta(C)$ hence in order to match the calculated chemical shift to the experimental one, $f(E)\delta(E)+f(I)\delta(I)+f(C)\delta(C)$ must increase proportionally. However, to conform to the restriction that the sum of the fraction of proton must always equal to unity, some influential terms cited above must increase while some decrease by an extent as much to conserve that restriction as to elevate the calculated chemical shift to the value comparable to that obtained by the experiment. Since $\delta(C) \gg \delta(E)$ and $\delta(I)$ (page 52), three possible patterns of changes in the calculated chemical shift can be proposed below.

| pattern | Elevating terms | Lowering terms |
|---------|-------------------------------|-------------------------------|
| 1 | $f(C)\delta(C)$ | $f(E)\delta(E)+f(I)\delta(I)$ |
| 2 | $f(I)\delta(I)+f(C)\delta(C)$ | $f(E)\delta(E)$ |
| 3 | $f(E)\delta(E)+f(C)\delta(C)$ | $f(I)\delta(I)$ |

To further discussion on the above proposed patterns, other informations are needed. Of particular interest in the present context is the viscosity measurement on aqueous acetic acid at various concentrations.⁽⁴⁵⁾ It shows one peak at 80 %v/v or 80.7 %w/w (Fig 5.4). The simplest interpretation of

this maximum is to ascribe it to the presence, predominantly, of the long chain polymers, The chains are broken at concentrations higher than 80 %v/v. These findings suggest that $f(I)$ decrease in parallel to the increase in the corresponding concentration above 80 %v/v. It is clear then, from the preceding discussion, that patterns 1 and 3 conform quite well with the viscosity data in the region of the high concentrations. Both patterns indicate that K_c becomes larger while K is proportionally smaller when concentration of the acid approaches that of concentrated acid.

Our main interest is now directed to the region of acid concentration of 0-85 %w/w where the amount of hydrogen-bonded species in mole percent is calculated from the values of equilibrium constants as shown numerically in Table 4.16 and graphically in Figs 5.5, 5.6 and 5.7. Figures 5.5 and 5.7 show the distinct predominant species in certain region of concentrations. Notably ones are listed below.

| <u>Range of concentration (%w/w)</u> | <u>Predominant species</u> |
|-------------------------------------------|----------------------------------|
| $1.6 \times 10^{-3} - 8.0 \times 10^{-3}$ | Monomer |
| 6.0 - 20.0 | Cyclic dimer |
| 10.0 - 25.0 | Cyclic dimer and linear dimer |
| 50.0 - 85.0 | Polymeric species |

It is thought worthwhile to show other evidence for the presence of cyclic dimer species as the major constituent at 6.0-10.0 %w/w. In the course of the present work, the author has conducted a complementary experiment on IR spectroscopy.

Samples under investigation were 10 %w/w acetic acid in water (sample I), 3 %w/w acetic acid in benzene (sample II) and in carbon tetrachloride (sample III). CaF_2 and ZnSe cells were used for every sample. IR spectra are attached as Figs 3.2, 3.3 and 3.4. Sample I yielded a combination absorption band at 1720 cm^{-1} which was comparable to the absorption bands of samples II and III which are known to contain mainly cyclic dimer (see page 65 for ΔH_{dimer} of acetic acid in benzene).

The additional piece of information concerning the equilibrium structure of acetic acid in water at a low concentration (3 %w/w) is from the solvent extraction experiment. Based on a simple model (see page 58) which is found valid for acetic acid in water at low concentration, the heat of solvent transfer of acetic acid from benzene to water yields a reasonable value i.e. $\Delta H_{\text{benzene-H}_2\text{O}} = -22.46 \text{ KJ mole}^{-1}$ from which it suggests that monomer is formed in water in favour to benzene. This appears to support the finding shown in Fig 5.7, where monomer is the most abundance hydrogen-bonded species in dilute aqueous acetic acid solutions.

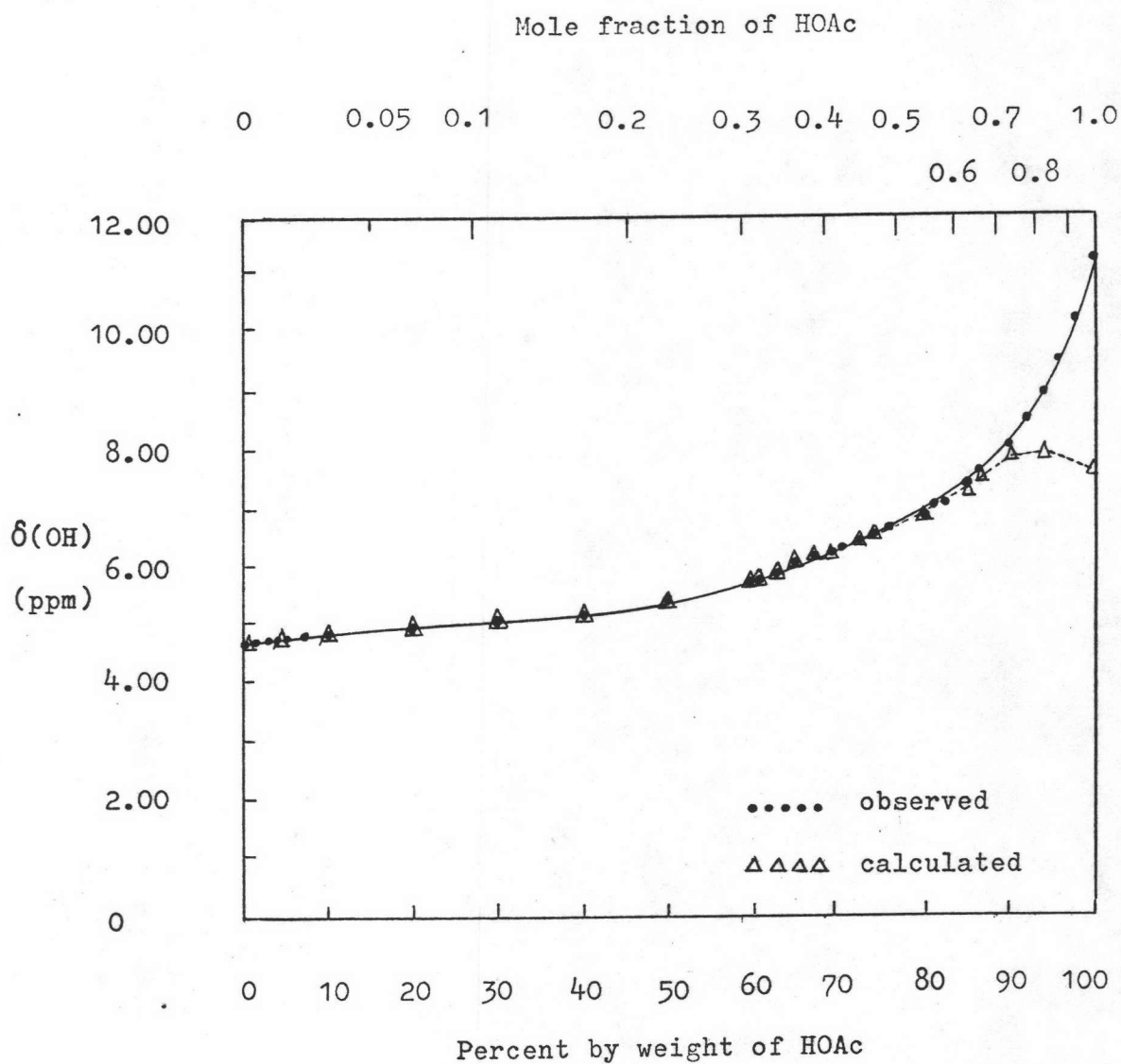


Figure 5.1 Calculated and observed chemical shifts at various concentrations (32°C).

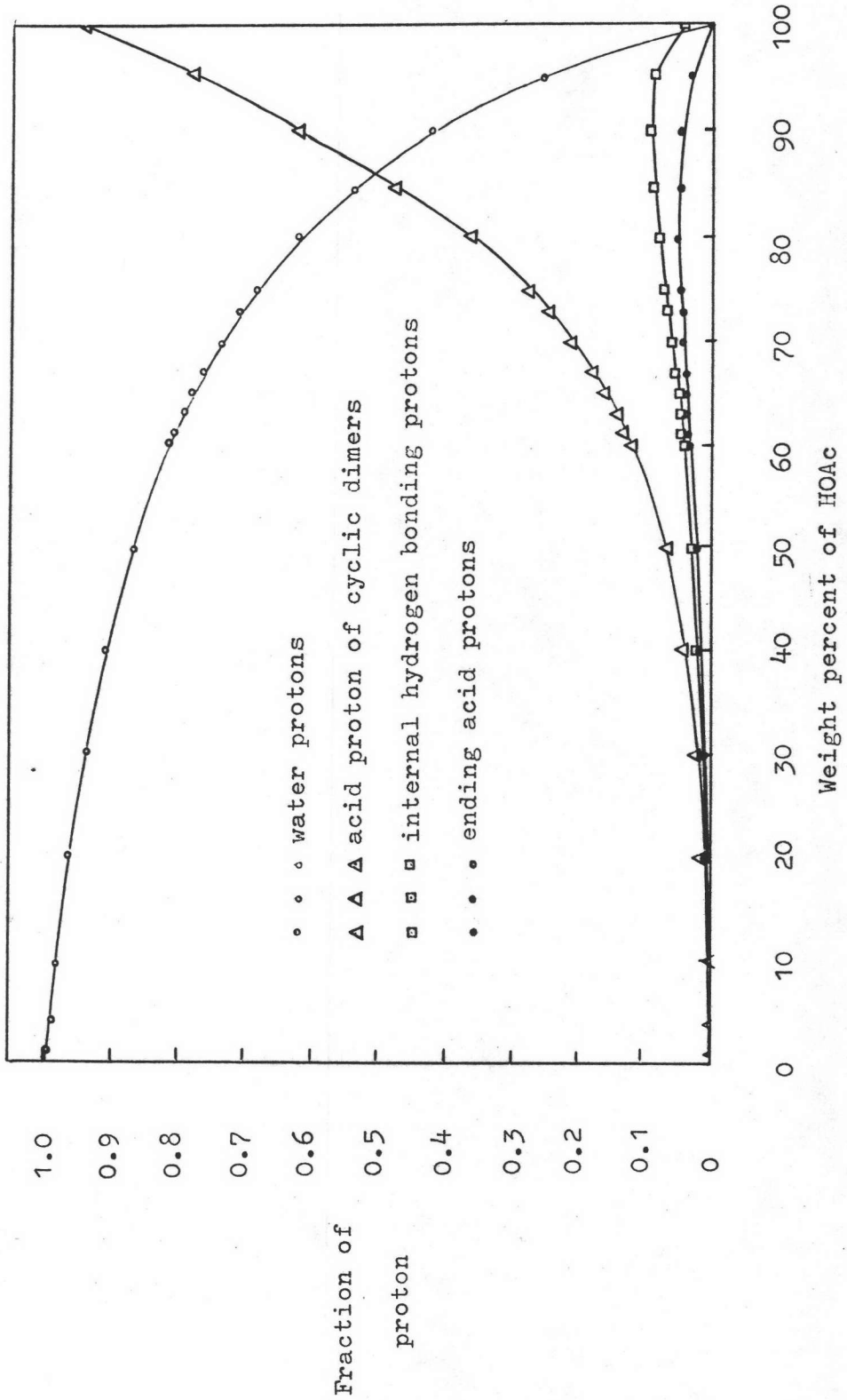


Figure 5.2 Fraction of proton of species groups at various concentrations

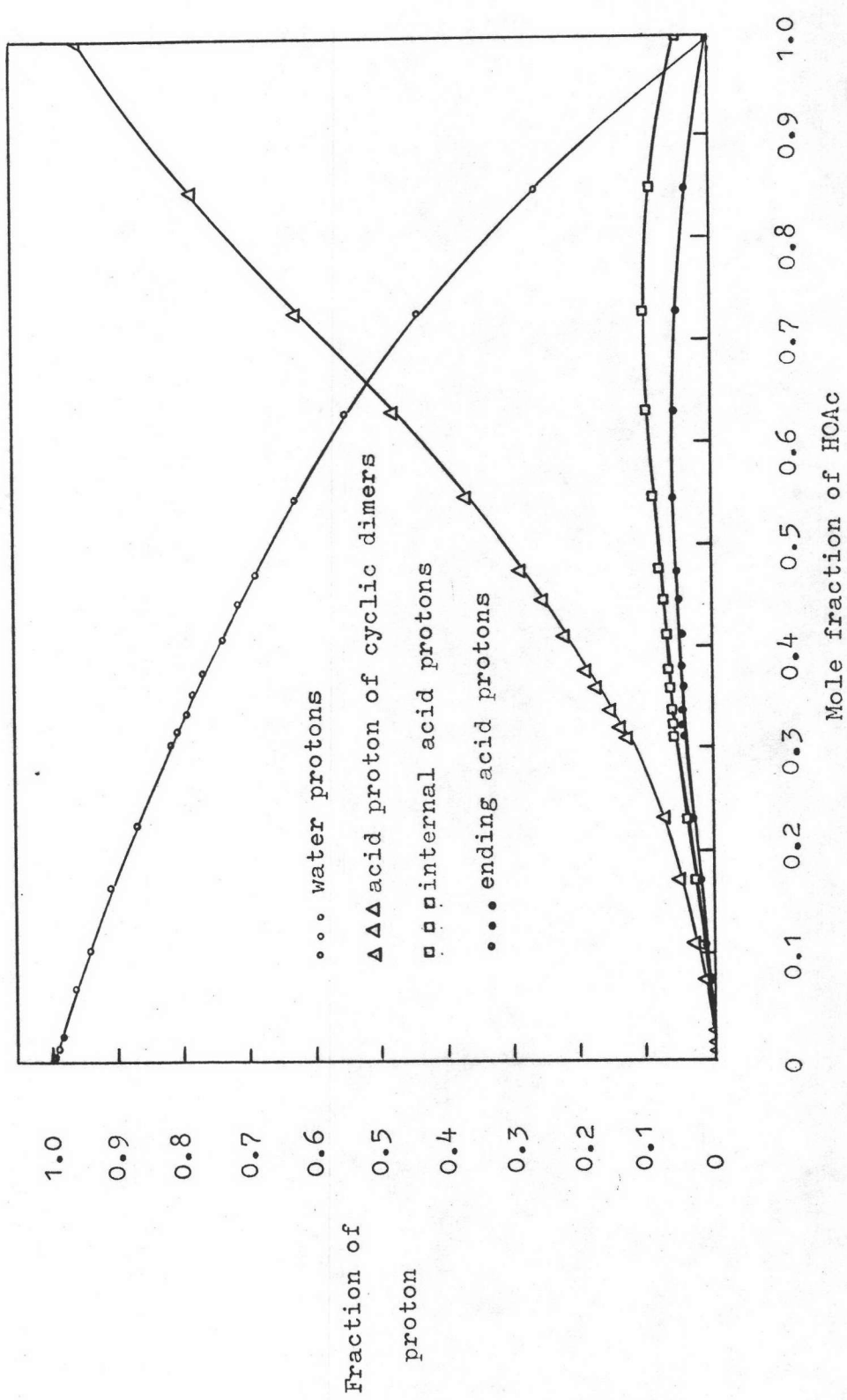


Figure 5.3 Fraction of proton of species groups at various concentrations

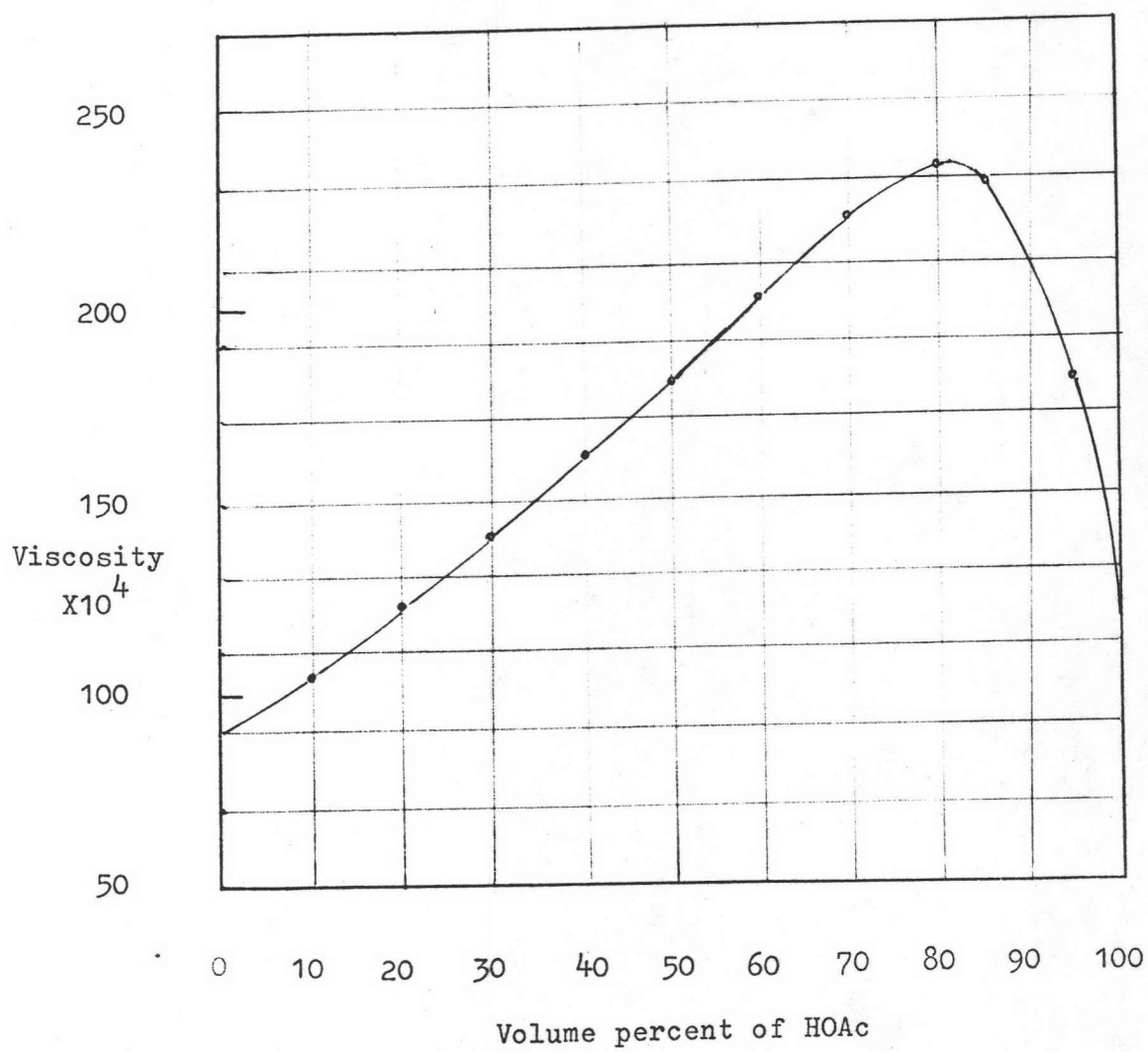


Figure 5.4 Viscosities of aqueous acetic acid at various concentrations, at 25°C (from reference 45).

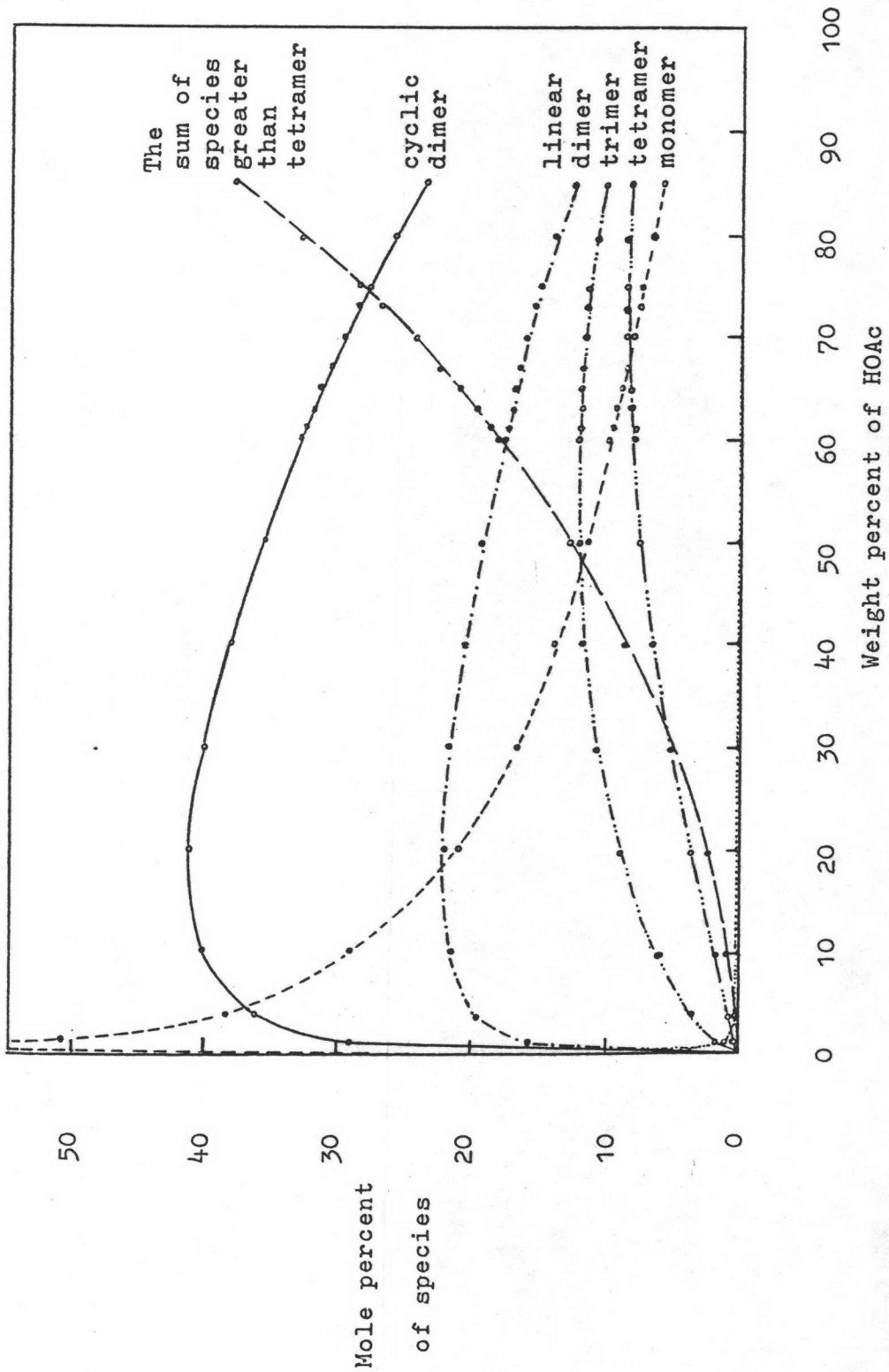
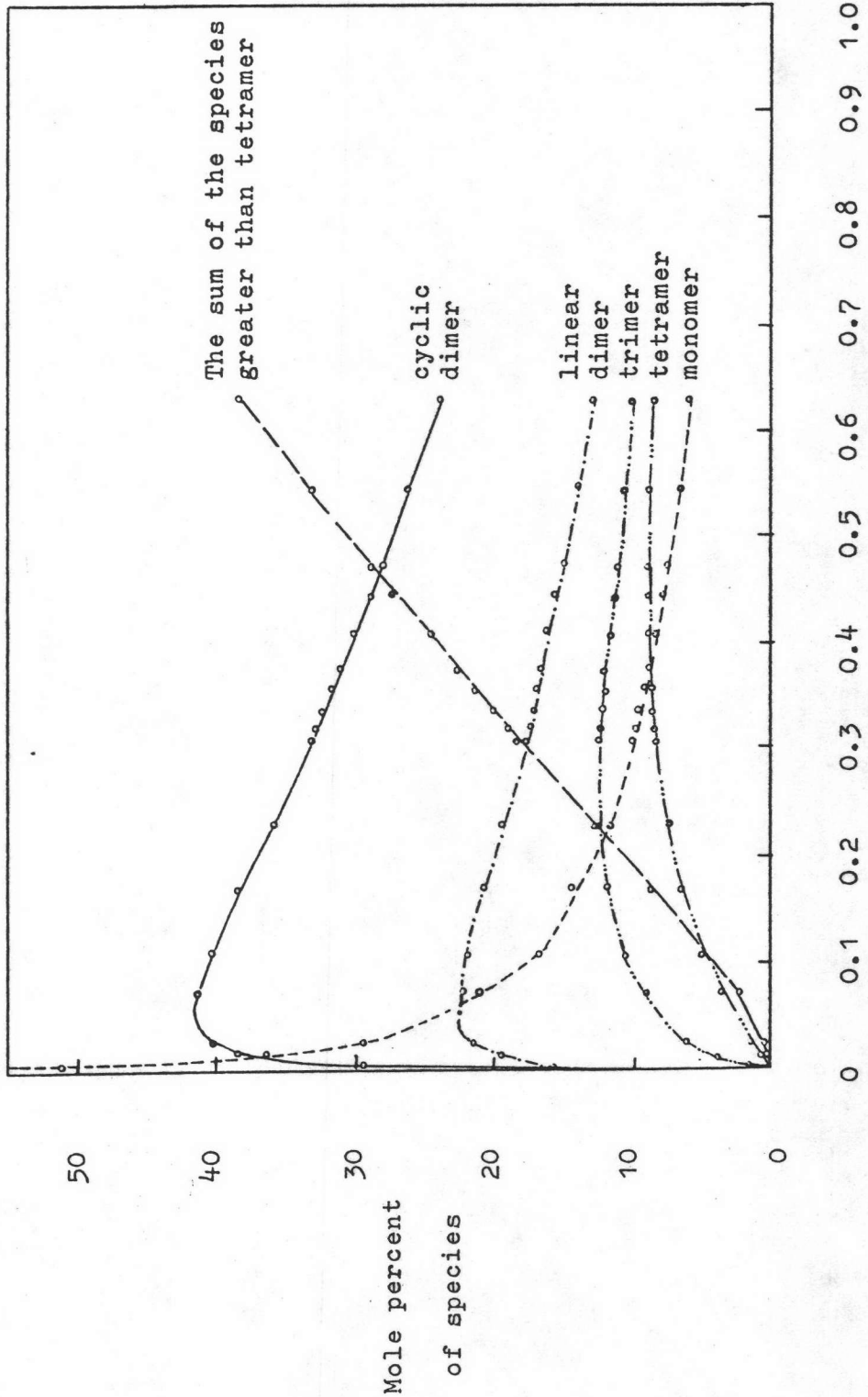


Figure 5.5 Mole percent of hydrogen-bonded species at various concentrations



Mole fraction of HOAc

Figure 5.6 Mole percent of hydrogen-bonded species at various concentrations

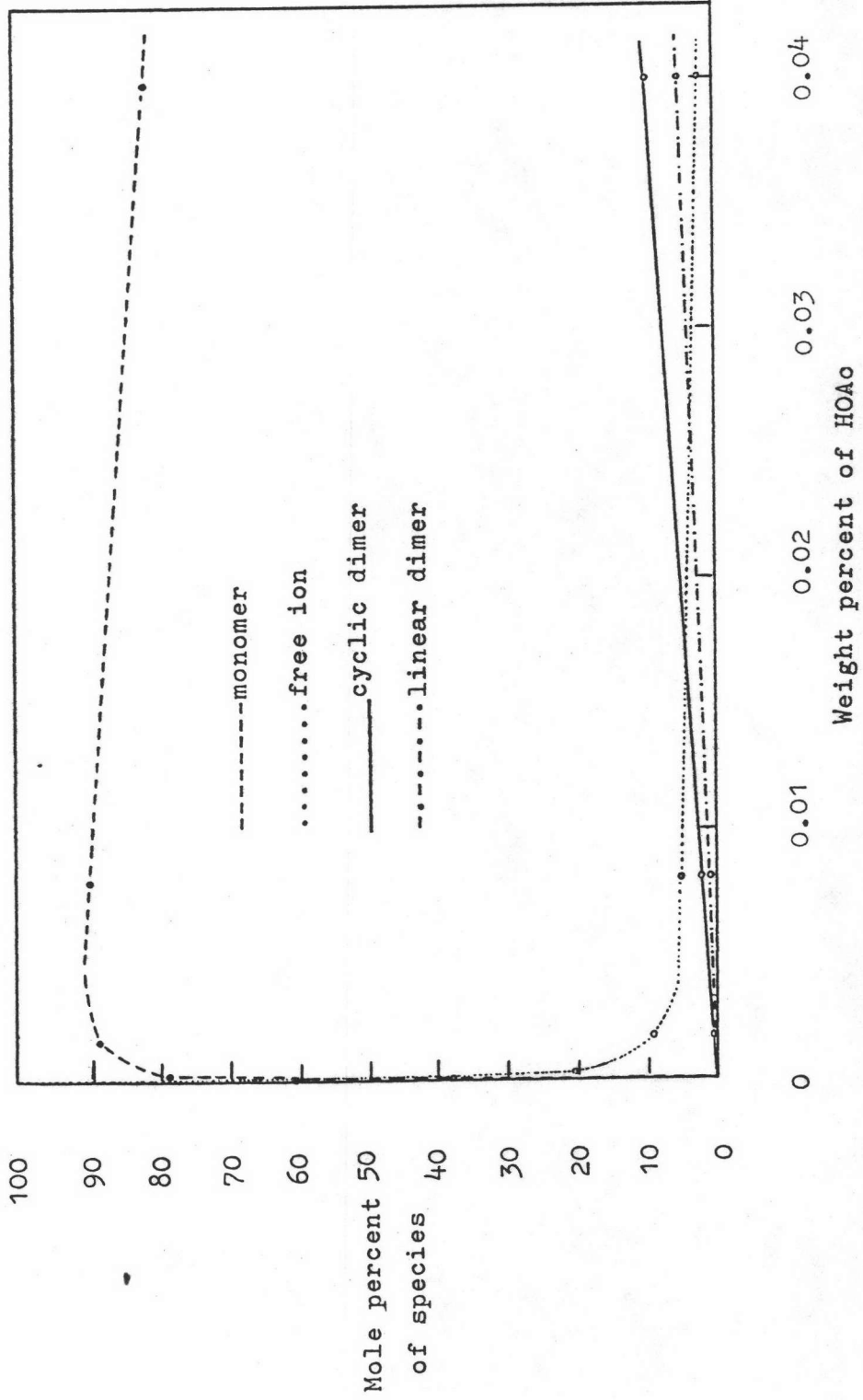


Figure 5.7 Mole percent of hydrogen-bonded species at dilute concentrations

Concluding Remarks

Results of the work reported here provide a significant contribution to the understanding of an aqueous acetic acid that, as a solvent, it can complicate the system by the presence of various hydrogen-bonded species. The concentration of the acid affects both type and amount of such species and this research work is able to assign the species that predominate at a certain range of concentration. A similar work reported by Goldman and Emerson⁽¹³⁾ have been found useful in forming a basis computational method of this work. It should be noted, however, that while Goldman and Emerson's work was confined to the system of acetic acid in CCl_4 which is an inert diluent, the present work dealt with acetic acid in water which is itself an ionizing solvent causing a more complicated situation. A modified computational method was therefore developed whereby the above mentioned results generated.

This work can also be exemplified as one of the work that blending the experimental part to that of the theoretical one and this should be expanded to accommodate a similar investigation in the future.

Suggestion for the future work

In order to furnish the knowledge of the behaviour of acetic acid in water over the entire range of concentrations, it seems that only one theoretical model is not adequate. The future work should be directed to the development of a suitable working model for the region of a high concentration of acetic acid i.e. above 85 %w/w. The effect of, for example, the ion

association, solvent-solute interaction should be thoroughly investigated. Figures 5.8 and 5.9 show peculiar patterns which cannot be understood clearly at present hence it is recommended that at high concentration of acid, a study of hydrogen-bonded species should be made by taking into consideration of the carbon shift which is due to carbonyl carbon and methyl carbon. It is hoped that with more informations, an appropriate interpretation can be made on the unconventional patterns exhibited in both Figures.

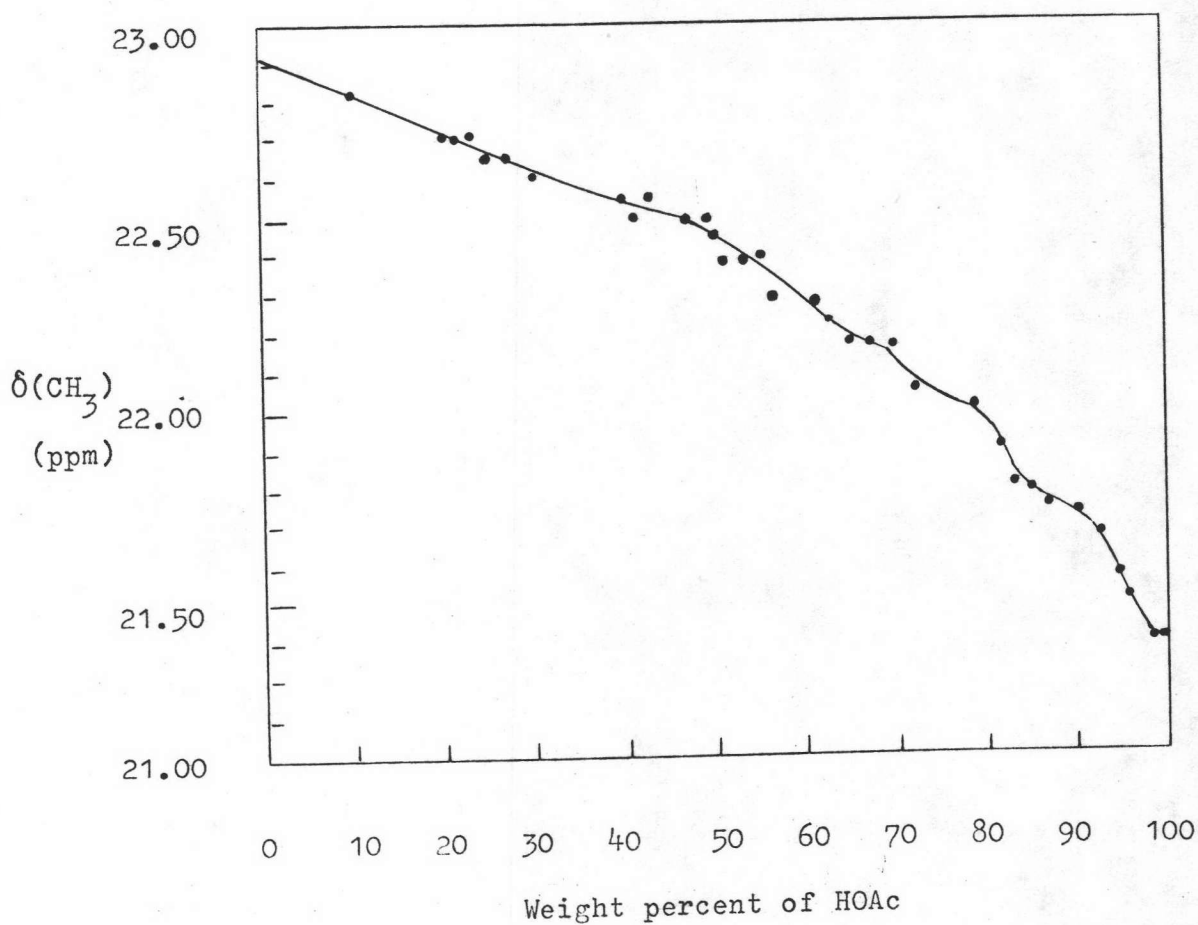


Figure 5.8 The curve of methyl carbon shift against the concentration of aqueous acetic acid at 32 °C

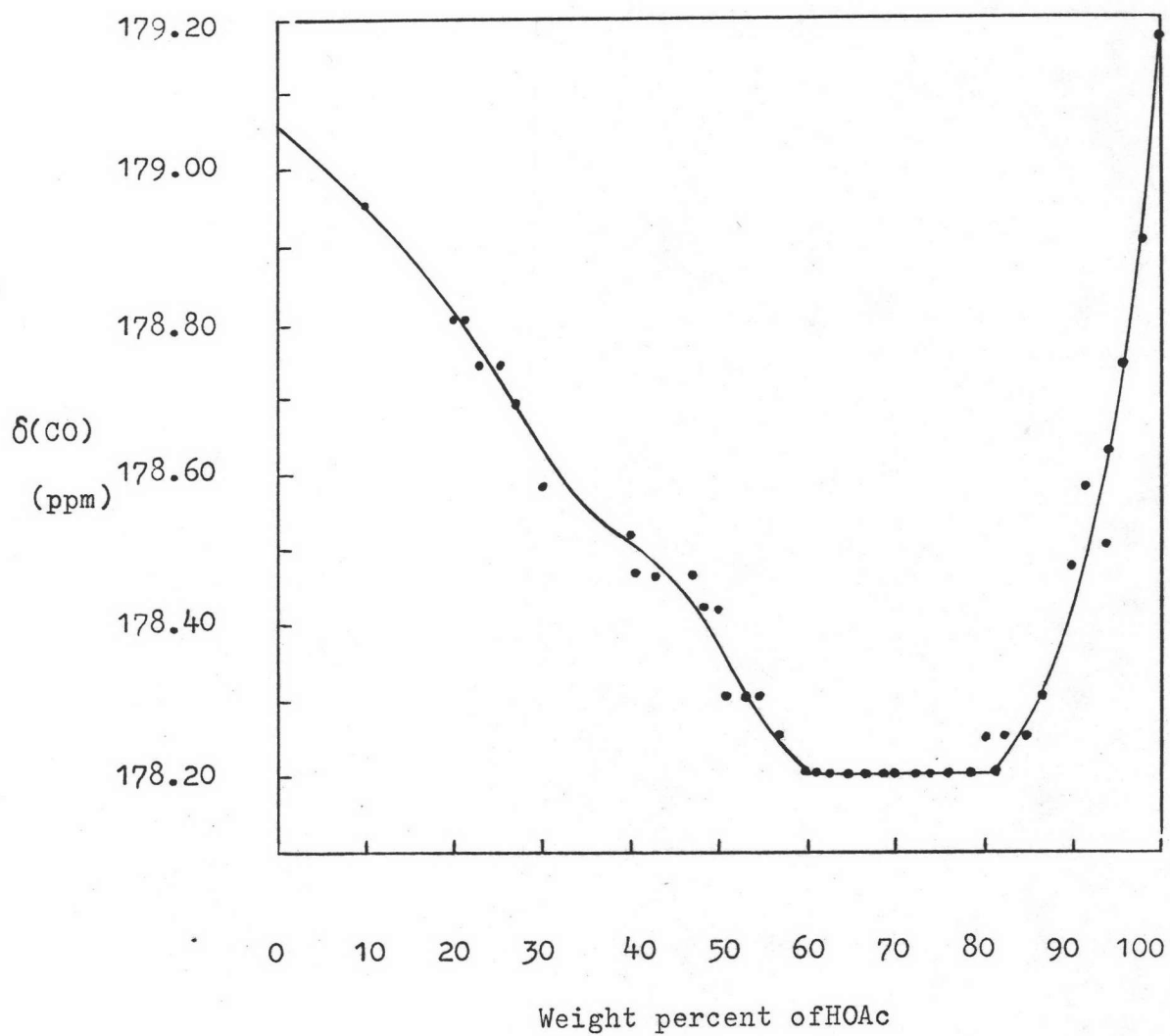


Figure 5.9 The curve of carbonyl carbon shift against the concentration of aqueous acetic acid at 32°C