



CHAPTER 1.

INTRODUCTION

In 1890, Beckmann⁽¹⁾ postulated the existence of a monomer-dimer equilibrium in order to explain the anomalous freezing point depressions of solutions of carboxylic acids in inert solvents. Later, the electrolytic behaviours of acetic acid in water have received a widely interest, perhaps more than other carboxylic acids since its COOH group has the combined acid-base properties for C=O being a base whereas OH an acid. It is classified as aprotic solvent having static dielectric constant equal to 6.21. The protic behaviour tends to complicate the electrochemical reactions. One may find from literatures that many instrumental techniques have been employed in the study of the electrolytic behaviours of acetic acid in different physical states, crystalline, gaseous and solution (mainly in water) and a number of postulations concerning various forms of acetic acid have been proposed. Through the application of spectroscopic techniques and by assuming only the existence of a simple monomer-dimer equilibrium in the aqueous solutions of acetic acid, many group of workers^(2,3,4,5,6) were able to measure the hydrogen bonding equilibrium constants of the species in equilibrium. In 1944, Karle and Brockway⁽⁷⁾ used the electron diffraction method to study the structure of acetic acid in the gas phase and concluded that it existed mainly as a cyclic dimer.

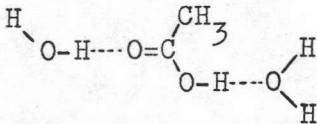
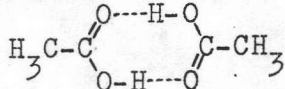
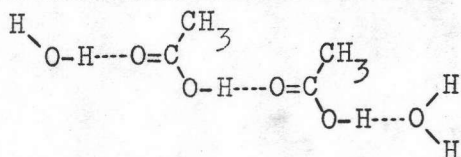
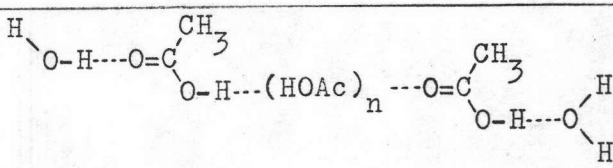
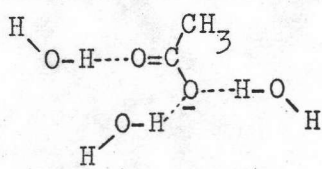
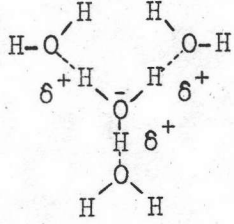
Later, when the nuclear magnetic resonance spectroscopy (NMR), has been developed and has become one of the powerful

techniques in detecting proton and protonated species, works on acetic acid have employed such a technique with some success. It has been known that the NMR chemical shift depends on the concentration of acid proton hence this method can be used to study hydrogen bonding system in the acetic acid solution. In 1956, Huggens, Pimentel, and Shoolery⁽⁸⁾ studied the NMR shift of acetic acid in carbon tetrachloride. About two years later, Reeves^(9,10) extended this work in which acetic acid in several other solvents were studied. Both teams came to the similar conclusion about the formation of the hydrogen bonding in the systems under study. In 1965, Maciel and Traficcate⁽¹¹⁾ used carbon-13 NMR to study acetic acid in several solvents in order to explain the existence of various hydrogen-bonded species of acetic acid in water.

The compilation of results of the work carried out during 1940-1970 enabled one to propose the possible co-existence of species other than monomer and dimer in acetic acid. For example, the observation of long chain linear polymers in crystalline acetic acid by the X-ray diffraction method⁽¹²⁾ along with cyclic dimers in the gas phase by the electron diffraction method⁽⁷⁾ led to the postulation of the equilibrium structures of acetic acid in the liquid state to be composed of a mixture of monomers, cyclic dimers, and linear polymers.⁽¹³⁾ On the other hand, evidence from Infrared and Raman spectra indicated the presence of chain linear polymers.^(14,15,16) Servantou and coworkers⁽¹⁷⁾ have shown that the NMR chemical shift of the acid proton could be accounted for quantitatively by equilibria between monomers, cyclic dimers, linear dimers,

and linear polymers, including hydrogen ions and water protons. In 1977, Panpa⁽¹⁸⁾ has studied the physical properties of aqueous acetic acid at various concentrations and confirmed the existence of cyclic dimers and chain polymers in equilibrium.

The purpose of the present work is to find a suitable quantitative model for solutions of acetic acid in water, taking into account the presence of free ionic species as well as the former postulated species. The species of interest are listed with their structures below.

Species	Structure
monomer	
cyclic dimer	
linear dimer	
linear polymer	
acetate ion	
hydrated hydrogen ion	

It was well realized that the set of equilibrium constants for the formation of cyclic dimers, linear dimers and linear polymers cannot be directly determined from the experiment and the evaluation of these constants are one of the most complicated tasks. In this work attempts have been made to combine the experimental results to the existing theoretical model in order to express the presence of those species quantitatively. Details of the theoretical treatments are outlined in Chapter 2.