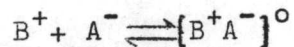


## CHAPTER I

### INTRODUCTION

The concept of ionic association arises when ions of opposite charges are close together. The electrostatic forces between ions will cause ions of unlike charges to attract one another. Although there is a continual interchange of ions, the result is the formation of a new entity in the solution, the ion-pair, persisting through a number of collisions with solvent molecules. In solution of a weak electrolyte, the free ions and its ion-pair may be separated by one or more solvent molecule. A definite amount of energy is required to separate the two approaching unlike ions. If this energy is much less than the kinetic energy of the solvent molecules, thermal agitation will dissociate the ion-pair while if the energy is greater, the ion-pair will exist for sometime.

In solution of an electrolyte the formation of ion-pairs may be expressed by the equilibrium:



The equilibrium constant of this reaction is called the association constant and its reciprocal value is the dissociation constant of an ion-pair. In general the association depends on the size and the charge of the ions, and on the size and structure of the solvent molecule. In a high dielectric constant medium, the ions interact

preferably with polar solvent molecules and become solvated, thus ion association occurs only at high concentration. On the other hand, in the solvent of low dielectric constant, ion association is enhanced as the ion-solvent interaction is weak, and can take place at low concentration.

The relationship of association constant,  $1/K$  of the ion-ion-pair equilibrium with the dielectric constant,  $D$  and absolute temperature,  $T$  is represented by the following equation (1)

$$\frac{1}{K} = \frac{4 \pi N}{1000} \left[ \frac{|z_1 z_2| e^2}{DkT} \right]^3 Q(b)$$

where  $Q(b) = \int_2^b x^{-4} e^x dx$

$$b = \frac{|z_1 z_2| e^2}{aDkT}$$

$$2 = \frac{|z_1 z_2| e^2}{qDkT}$$

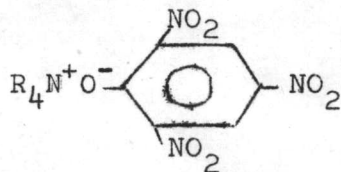
and  $x = - \frac{z_1 z_2 e^2}{DkTr}$

Here  $q$  is critical distance;  $z_1, z_2$  are valence of cation and anion respectively,  $N$  is Avogadro's number,  $e$  is the protonic charge,  $r$  is the distance between the center of two charges and "a" is an empirical parameter which interpreted as the distance between centers of charge of the ions in the ion-pairs when the ions are in contact and is termed distance of closest approach. It can be seen from the equation that, in the solvent of low dielectric constant,  $K$  will increase with temperature, while in the solvent of high dielectric constant it will decrease. Thus, the evaluation of  $1/K$ , association constant will lead to the understanding of association taking place in the system under study.

Methods<sup>(2)</sup> used in the study of association are simply those capable of yielding  $K$  in terms of concentration, either ionic or neutral concentration. In order to obtain ionic concentration ion exchange method, polarography, potentiometry or measurement of conductivity and solubility are usually employed, whereas spectrophotometry, the measurement of freezing point and viscosity are used for the determination of concentration of neutral species.

Although several studies of association of a number of electrolytes in various solvents have been made, scarcely any data on the study of the rate of such reaction exist. This might be due to the fact that, the change in the concentration with time of either ionic or neutral species involved in the association reaction was so small, that the existing techniques and instruments were not feasible. The early investigation<sup>(3)</sup> of association in any solvent seemed to confine to the determination of " $a$ " and  $K$  where " $a$ " is the distance of closest approach and  $K$  the dissociation constant respectively. These values were studied as a function of dielectric constant, size of ions and temperature dependence. In order to furnish informations about the association reaction taking place in systems, which have already been subjected to investigation on other aspects of association reaction, such as that of Mercier and Kraus,<sup>(4)</sup> a certain kinetic studies of tetraalkylammonium picrates in dioxane-water mixture were chosen for the work reported here.

The tetraalkylammonium picrates are of great interest because of their structure which is composed of tetraalkylammonium ion and picrate ion. The structure<sup>(5,6,7)</sup> is believed to be  $R_4N^+Pi^-$ .



The tetraalkylammonium ion can be associated with other anion because of the large size with low charge and symmetrical shape, factors which unfavour solvation of the ions. Some of their salts are soluble in quite a number of solvents besides water. For the high homologous member, the association will decrease and will be difficult to obtain.<sup>(8)</sup> Although the unsymmetrical screening effect of trinitrobenzene group of the picrate ion to the localization of negative charge will decrease the tendency of ion pair formation, once it is formed this localization will increase the stability of the ion-pair. Thus, picrate is an ideal counter ion for tetramethyl and tetraethyl group in the study of the association reaction.

Among mixed solvents dioxane-water seems to be one of the popular solvents. Dioxane has low dielectric constant, neutral character and is completely miscible with water. The dielectric constant of dioxane-water mixture can be varied over a wide range from 78.6 to 2.21. Consequently one should be able to study reaction in a variety of dielectric constants by only changing percentage of water in the mixture. It has been found that the dielectric constant of dioxane-water mixture decrease almost linearly with the increase in dioxane content in the mixture containing less than 50% by weight of dioxane, above 60%, however the decrease shows deviation from linearity.<sup>(9)</sup>

After thorough investigation, 80% dioxane-water was chosen in this work as a solvent for tetraalkylammonium picrate simply because its

dielectric constant is high enough to prevent the formation of the higher aggregate of ions such as ion triplets but low enough to facilitate the union of the ion-pair.