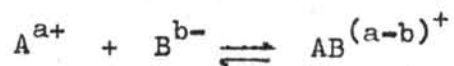


CHAPTER I
INTRODUCTION

During recent years it has become increasingly apparent that the use of non-aqueous solvent media provides an important means of investigating ion-ion and ion-solvent interactions under extremely varied conditions. The growing interest in this area of study is due mainly to the fact that the short range ion-solvent and the long-range coulombic attractions account for the peculiarity in the property of electrolyte solutions both in aqueous and non-aqueous solvent. New ions or uncharged molecules resulting from the various kind of interactions in the electrolyte solution usually behave quite differently from the constituent ions of the electrolyte. The chemists try to understand these phenomena and achieve only partially both in theory and in practice so far. One of the chief difficulties encountered in trying to identify the species present in the bulk solution is that there is no method by which structures of them can be readily obtained. It is however well known that in an electrolyte solution, many kinds of solute entities are present: ions-solvated or unsolvated, electrostatically associated group of ions (ion-pair), covalently bound molecules and complex ions.

In the reaction of



the thermodynamic equilibrium constant is given by

$$K = \frac{[A^{a+}][B^{b-}]}{[AB^{(a-b)+}]} \cdot \frac{f_A \cdot f_B}{f_{AB}}$$

Hence

$$\frac{1}{K} = \frac{[AB^{(a-b)+}]}{[A^{a+}][B^{b-}]} \cdot \frac{f_{AB}}{f_A f_B}$$

which known in various terms such as stability, association, complexity and formation constants, The term from which informations concerning the type and the extent of the above mentioned interactions can be obtained. It is worth noted here that the usages of the terms ion-pair and complex vary and cause confusion. The term ion-pair is restricted to an associated pair of ions in which association occurs as a result of purely electrostatic attraction between oppositely charged ions and in some property behave in a manner distinct from the free constituent ions. It is sometimes called an outer-sphere complex by contrast with an inner-sphere complex where there is no interposed layer of solvent separate the two ions.

It is therefore the primary aim of those who are interested to understand more of the actual kinetic entities in solutions to seek for a technique capable of giving an accurate and reliable value of association constants ($\frac{1}{K}$).

There are some general points to consider in planning a study of the state of a solute in an electrolyte solution. First, it may be possible to use a number of complementary methods such as conductometry and solubility, thus simplifying considerably the calculation of the concentrations of ionic species. Next, it is necessary to decide whether to study the system at low concentrations so that activity corrections can be made in the calculation of thermodynamic association constants, or whether to use a medium of constant ionic strength. The choice will depend upon how the results are to be

related to the work done. Experimental data at constant ionic strength are directly comparable only with similar data at the same ionic strength. When a very high, constant ionic strength is used, it may be necessary to consider the extent of association of the medium with the ions under study. At relatively low constant ionic strengths, these medium effects are minimized and it may be possible to make reasonable estimates of activity coefficients. Hence, when it is possible by a suitable control of concentrations, to limit the number of new species in the solution, it is desirable to work at low concentrations so that thermodynamic constant such as association constant may be derived.

There are many general methods for study of association constants such as conductometry, solubility, potentiometry, NMR spectra, Raman spectra, reaction kinetics, solvent extraction, colligative properties of solute, viscosity etc: all of which enable the concentration of species in the system become determinable and hence is the association constants.

Among these techniques, electrolytic conductance seems to be the most direct evidence for the existence of ions in solution, and in solution of a single electrolyte its variation with concentration is the most obvious way of studying ionic equilibria. For electrochemical study of a non-aqueous system usually begins with conductivity measurements which throw light on the condition of the solute and mode of ionisation. Measurements of high precision of conductivity can be made on very dilute solutions. The degree of dissociation into ions of a neutral species at a concentration c, α , is given by the simple relation

$$\alpha = \frac{\Lambda}{\Lambda_i}$$

where Λ is the measured equivalent conductance of the solution.

Λ_i is the hypothetical equivalent conductance.

The electrolyte would have if it were completely dissociated ions at a concentration αc . For the reaction



the association constant, $\frac{1}{K}$, is then calculated from

$$\frac{1}{K} = \frac{(1-\alpha)}{\alpha^2 c_f^2}$$

It is important to realise that complex formation relates to competition for the cation between the ligand and solvent molecules. The same competition for the cation between the solvent and ligand also governs solubility equilibria and there are often parallels between such equilibria and complex ion equilibria in a homogeneous solution. Thus solubility measurement is one of the popular methods in the studying of the incomplete dissociation of electrolyte.

The measurements of solubilities of a sparingly soluble salt in the presence of another electrolyte can be used to study of ion-pair formation and was first used by Davies.⁽¹⁾ Solubility studies of sparingly soluble salts can yield information concerning the formation of complexes in solution.

The work reported in this thesis is in fact a part of the major project namely "The Study of Electrolyte—Solvent Interactions in Non-aqueous Solvent" which has been carried out by a team of

staff member and graduate students of this department for some years. Here, the extent of ion-association and the ion-size parameter, "a", of ions in the solvent of low dielectric constant are the topics of interest. Amongst many known methods usually employed in such studies conductivity and solubility measurement are chosen in this work owing to their ease in manipulation, the facilities available and the capabilities of the methods to yield the quantities of interest with sufficient certainty.

Literature survey reveals that the thalious ion is remarkable as a univalent d^{10} cation with pronounced complex forming tendencies. The complex of this cation has been thoroughly investigated in an aqueous solution. There are some experimental evidences for example from Raman studies,⁽²⁾ although non-conclusive, that complex formation may occur with Tl (I) ions. However, similar studies in the low dielectric constant solvents have not yet been reported. It is known among electrochemists that complex formation tendency is enhanced in the low dielectric constant medium. The solution of thallium salt in glacial acetic acid ($\epsilon = 6.21$ at 25°C)⁽³⁾ is therefore chosen for a system of study in this work.

It is hoped also that the ion-size parameter "a" obtained from this study will be used further in the correction of the redox potential of Tl (III)/Tl (I) electrode in glacial acetic acid thus studied by S.Ho-ampawanwong.⁽⁴⁾

The following four chapters will present a summary of theories, previous work involving in conductivity and solubility studies. The experimental details will be described along with the analysis of the data obtained by means of ^{the} theory.