

CHAPTER I
INTRODUCTION



1.1 General Introduction

Aspects of ion-solvent and ion-ion interactions have been studied by the investigation of the transport processes of electrolytes in solution. Ion-ion interaction can be understood by the study of the concentration dependence of the transport properties of electrolytes. Solvation and ion-solvent interaction can be dealt with if some properties of the individual ions can be determined. The basic measurable quantities of the transport properties of electrolytes are the conductivity and transference number. Practical techniques for conductance measurements have been well established. Conductance data for completely dissociated, and associated electrolyte systems are abundant. The interpretation of the conductivity in terms of electrolyte theories has improved the understanding of the behaviour of electrolytes in solution. It also allows, when applicable, the estimation of the structure and dimension of the ions in the electrolyte solution.

1.2 Conductivity Equations

Early conductance equations such as those proposed by Onsager and Shedlovsky are restricted to dilute solutions and are mostly successful for simple electrolytes. The conductance equations derived for these systems are based on the primitive model where the ions are represented as charged, rigid unpolarisable spheres of a finite size moving in a dielectric continuum. The solvent is assumed to be structureless, dielectric saturation in the close proximity of the ions is ignored, and only the hard core electronic forces are considered in the short range interaction. In the Fuoss - Onsager equation (1) ion association is simply considered as two ions in contact with a pairwise ion association constant, K_A .

For multicomponent electrolytes, an improvement in the analysis as well as the model of numerical computation was made by Onsager and

Kim (2). An extension of the Fuoss and Onsager (1) equation to cover mixed electrolytes was made by Quint and Villard (3). Both conductance equations derived for these systems use the primitive model. It was not until 1974 that a new model for ions in solutions was proposed by Fuoss (4). This model is based on the concept of the Gurney cosphere which makes an allowance for dielectric saturation in the close vicinity of the ion and the existence of solvent-separated ion pair (SSIP) for ion association. Fuoss used this model to derive conductance equation for multi-component system. Recently Lee and Wheaton (5, 6, 7), in a series of papers on the derivation of conductance equations in terms of statistical thermodynamics based on this new model have described transport in solutions containing any number of ionic species, of any valence type and hence its extension to symmetrical, unsymmetrical and mixed electrolytes.

1.3 The Present Work

The validity of the Lee and Wheaton equation for the analysis of associated unsymmetrical electrolyte, CdCl_2 (3) is still questionable. Further investigation was considered to be carried out for associated symmetrical CdSO_4 and completely dissociated unsymmetrical $\text{Cd}(\text{ClO}_4)_2$ electrolytes for which less assumptions would be involved. The application of the Lee and Wheaton equation to the electrolytes of zinc which have similar properties to the above solutions of cadmium, viz. ZnCl_2 , ZnSO_4 , and $\text{Zn}(\text{ClO}_4)_2$ will also be investigated.

Most of the early conductance data for the above systems were observed within limited concentration range. Some are of high concentration or inconsistent. From a literature survey, a summary of the conductivity work for these systems is as follow.

The conductance measurement of $2.5 \times 10^{-5} - 3.0 \times 10^{-3} \text{ mol dm}^{-3}$ aqueous $\text{Zn}(\text{ClO}_4)_2$ solutions was carried out at 25°C in 1960 by Dye, Faber and Karl (8). The effect of self complexing in $\text{Zn}(\text{ClO}_4)_2$ solution was assumed and the value of $\Lambda_{\text{Zn}(\text{ClO}_4)_2}$ was found to be $122.7 \text{ cm}^2 \Omega \text{ equiv}^{-1}$ which gave $\lambda_{\text{Zn}^{2+}} = 55.34 \text{ cm}^2 \Omega \text{ equiv}^{-1}$. In 1978, Agnew and Paterson (9) measured the conductance of $0.1-3.0 \text{ mol dm}^{-3}$ aqueous $\text{Zn}(\text{ClO}_4)_2$ solutions. Their results showed significant complete dissociation and no effect of the association as reported by the above authors. The data

obtained from the Raman studies (26), activity coefficients (23), transport numbers (23), and conductance measurements (25) also support this conclusion (9). In 1938 Owen and Gurry (10) made conductance measurements of ZnSO_4 solutions in the concentration range $5 \times 10^{-3} - 0.1 \text{ mol dm}^{-3}$. The values of Λ_{ZnSO_4} and K_A were found to be $132.8 \text{ cm}^2 \Omega^{-1} \text{ equiv}^{-1}$ and $204 \text{ dm}^3 \text{ mol}^{-1}$ respectively. Katayama (11) in 1976, also made the conductance measurements of $(2-30) \times 10^{-4} \text{ mol dm}^{-3}$ ZnSO_4 solutions. His results for Λ_{ZnSO_4} and K_A were $134.30 \text{ cm}^2 \Omega^{-1} \text{ equiv}^{-1}$ and $165 \text{ dm}^3 \text{ mol}^{-1}$ respectively. The conductance of ZnCl_2 solutions in concentration range $0.1-3.5 \text{ mol dm}^{-3}$ was studied by Agnew and Paterson (12) in 1978. The effect of self complexing in zinc chloride solutions was illustrated by comparison with the solutions of zinc perchlorate and other group II B metal halides. In 1976, Lutfullah, Dunsmore and Paterson (13) used e.m.f measurements to determine the ion association constant of ZnCl_2 solutions. The solutions showed significant complex formation at concentrations above 0.01 mol kg^{-1} and K_A was found to be 4.5 kg mol^{-1} .

The conductance measurement of aqueous $\text{Cd}(\text{ClO}_4)_2$ solutions was carried out in the concentration range $5 \times 10^{-4} - 5 \times 10^{-2} \text{ mol dm}^{-3}$ by Matheson (14) in 1962. It was considered to be completely dissociated in dilute concentration range and $\Lambda_{\text{Cd}(\text{ClO}_4)_2}$ was found to be $120.87 \text{ cm}^2 \Omega^{-1} \text{ equiv}^{-1}$. In 1976, Katayama (11) measured the conductance of $(2-30) \times 10^{-4} \text{ mol dm}^{-3}$ aqueous CdSO_4 solutions and determined the ion association constant from this data. His results gave $\Lambda_{\text{CdSO}_4} = 113.15 \text{ cm}^2 \Omega^{-1} \text{ equiv}^{-1}$ and $K_A = 212 \text{ dm}^3 \text{ mol}^{-1}$. Conductance measurement of aqueous CdCl_2 solutions was carried out by Indaratna (3) in 1980 for the concentration range $1 \times 10^{-4} - 0.1 \text{ mol dm}^{-3}$. The analysis of the data by Lee and Wheaton equation gave $\lambda_{\text{Cd}^{2+}} = 53.94 \text{ cm}^2 \Omega^{-1} \text{ equiv}^{-1}$ and $\lambda_{\text{CdCl}^+} = 22 \text{ cm}^2 \Omega^{-1} \text{ equiv}^{-1}$ using $K_A = 85 \text{ kg mol}^{-1}$ obtained by Reilly and Stokes (15).

In the present work conductance measurements were carried out at 25°C for

- (i) 0.0003 to 0.1 mol dm^{-3} aqueous ZnCl_2 solutions
- (ii) 0.0003 to 0.1 mol dm^{-3} aqueous ZnSO_4 solutions

(iii) 0.0002 to 0.1 mol dm⁻³ aqueous Zn(ClO₄)₂ solutions

(iv) 0.0003 to 0.1 mol dm⁻³ aqueous CdSO₄ solutions

The analysis of these conductance data was made by graphical extrapolation using Onsager and Shedlovsky functions and by the multiparameter manual fitting method using Lee and Wheaton equation. Some of the literature data were also analysed by the latter method.

The normal procedure of the multiparameter manual optimisation is to minimise the standard deviation $\delta(\Lambda)$ between the calculated and measured conductances over a range of concentrations of the electrolyte by adjusting the unknown parameters. The Algol programme used for CdCl₂ system by indaratna was converted into Fortran. This programme which calculates equivalent conductivity values as a function of the fitting parameters was modified for the use with the present study.