



CHAPTER I

INTRODUCTION

1.1 General Introduction

The basic transport properties of electrolytes are conductance and transference number. The concentration dependence of the transference numbers unlike that the conductances depend only on the electrophoretic effect and not the relaxation effect. Structural investigations from the transference numbers experiments alone or with the conductances measurements, have given certain information about the existence and properties of some complex ions (1-5).

There are three principle methods for determining transference numbers : the Hittorf method, the e.m.f. method and the moving boundary method. The Hittorf method requires great skill and precision for the analysis as well as time. The e.m.f. method, though useful, is often difficult to interpret the experimental data. It is however evident from the literature data that the moving boundary method is the most precise technique. Its significant improvement has been achieved by several developments of the apparatus and the recognition of certain influential experimental factors. In the early development of this method the emphasis was on a direct moving boundary technique. This technique was found to give transference numbers results accurate to $\pm 0.03\%$ (6). Certain limitations of the direct moving boundary method have subsequently increased the attraction of the indirect moving

boundary method whereby such limitations are eliminated. The accuracy of the results depends on the analysis of a small quantity of the following solution, thus depends on the precision of the analytical technique employed, and the justification of the use of the indirect moving boundary method. Most of the work done by the indirect moving boundary method has been limited to the development of the cell and technique for determining transference numbers of simple dissociated electrolytes.

1.2 Development of the Indirect Moving Boundary Technique

Cady and Longworth (7) were the first to investigate the extent of Kohlrausch concentration adjustment (a) from the change in the total resistance of their apparatus when a known length of leading solution had been displaced by indicator (or following solution), and (b) by measuring the conductivity just behind the boundary with two platinized microprobes. The condition, later known as Hartley correlation

$$\frac{C_B^{*\beta}}{C_A^{\alpha}} = \frac{T_B}{T_A}$$

was taken as the criterion for automatic adjustment. The first quantitative work using the indirect moving boundary was by Hartley, Drew and Collie (8) in 1934. After a few trials to design and construct a suitable apparatus for the determination of the Kohlrausch concentration, the so called "balanced boundary apparatus" with internal conductometric analysis, gave satisfactory results. The transference numbers of lithium ion-constituent in lithium chloride solutions were measured to about 1% precision

with KCl, NaCl and HCl as leading electrolytes. Hartley's cell made use of small air bubble and a controlled glass piston for the mechanism of the boundary formation.

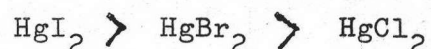
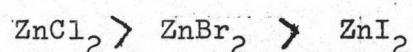
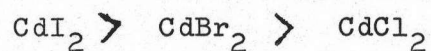
An improvement of the accuracy in determining adjusted indicator concentrations in the indirect moving boundary method was made in 1952 by Gordon and Kay (9). Cells for both rising and following boundaries were constructed in such a way that the middle section of the moving boundary tube (3cm long) could be separated from the rest of the apparatus after each run, and by appropriate insertion of two platinum electrodes converted into a small conductance cell filled with following solution. Several two-salt boundary system (KCl/LiCl, KCl/KIO₃, KCl/BaCl₂) were studied in these cells with the results obtained accurate to about $\pm 0.2\%$. They experimentally found that the equalisation of concentration under the density gradient in narrow channels (2.5 mm.i.d.) is an exceedingly slow process, analogous to diffusion. Therefore, with proper cell design this disturbing factor can be largely eliminated. A year later Muir, Graham and Gordon (10) described a method for determining following concentrations behind a moving boundary in dilute solutions with a precision comparable to that obtained in the direct moving boundary method. Their moving boundary cell was of the type used by Gordon and Kay(9) with shearing mechanism, except that in the middle channel was longer (30 cm). External conductometric analysis in a small conductance cell (0.8 cm³ capacity) was used in the determination of following concentration. The procedure was tested with the system KCl/NaCl at 25° C. The results agree with direct moving boundary data (11) within $\pm 0.03\%$. These results which in fact

apparent transference numbers, were later corrected for volume change during boundary movement by Spiro (12).

In 1969 a new method was described by Kay, Vidulich and Fratiello (13) in which transference numbers for both leading and following ion-constituents could be determined in the same moving boundary experiment. The boundary movement was detected by the change in potential across platinum microprobes sealed in series into the moving boundary cell. Their method permits transference numbers measurements of electrolyte as dilute as 1×10^{-4} mol dm⁻³ with low current density. Recently, Indaratna (14) has developed the technique and apparatus for the indirect moving boundary method. External conductometric analysis was used in the determination of the following concentration. The transference numbers of cadmium ion-constituent in 0.003 - 0.1 mol dm⁻³ aqueous CdCl₂ solutions were measured to 0.1 - 0.2 % precision.

1.3 Zinc Chloride in Aqueous Solution

Literature survey reveals that zinc ion is remarkable as a divalent d¹⁰ cation with pronounced complex forming tendencies. This behavior was also found in many halides of heavy metal such as cadmium, copper and mercury. The evidence for the existence of complex species in an aqueous solution has been made from X-ray (15), raman (16), e.m.f. (17) and vapour pressure (18) studies. The ease of formation of complex ions is in the order



Owing to the association of the metal and halide ions, fewer conducting species are present. The observed conductivities of these solutions are therefore substantially lower than those of normal 2:1 electrolytes such as CaCl_2 , MgCl_2 and BaCl_2 (19). At high concentrations the cation transference numbers of these solutions decrease rapidly to zero, then became negative. This is again in marked contrast to the behavior of the transference numbers of normal 2:1 electrolytes such as CaCl_2 (20) and $\text{Zn}(\text{ClO}_4)_2$ (21). Activity coefficients of these electrolytes are very low compared with those of non-associated electrolytes.

The transference numbers of dilute aqueous ZnCl_2 solutions have not been well established. Hittorf work done by Partington (22) in 1945 gave a value of $t_{\text{Zn}}^{\text{ZnCl}_2} = 0.347$ at 25°C for 0.09 mol kg^{-1} solution of ZnCl_2 . At this concentration, Harris's (23) e.m.f. measurement gave the value of 0.350. In 1978, Paterson (24) reported transference measurements of ZnCl_2 solutions from 0.1 to 3.5 mol dm^{-3} by Hittorf and concentration cell method. His two sets of results were in good agreement and also agree with the Harris's data.

1.4 Present Work

For most work, the transference numbers determined by Hittorf method was found to be at best $\pm 0.1\%$ (6), usually for the work with concentrated solution and the lowest concentration limit of about 0.01 mol dm^{-3} . The e.m.f. method using cell with transference give results with precision of about $\pm 0.2\%$ owing to the approximate differential forms used for the computation of the transference numbers. Therefore, the results obtained are

rarely more accurate than $\pm 1\%$ (6). The moving boundary method, on the other hand, has been regarded as the most precised technique for the determination of the transference numbers, with no upper limit of concentration. The direct moving boundary technique usually gives results with precision of about $\pm 0.03\%$ for most electrolyte systems (6). However, it normally requires complicated experimental set up and the observed transference numbers are subject to volume correction. The complementary indirect moving boundary method, is somewhat relatively easier to employ due to its practical simplicity. The application of this technique to $0.004 - 0.1 \text{ mol dm}^{-3}$ aqueous CdCl_2 solutions was found to give results within $\pm 0.1 - 0.2 \%$ provided that the cell used was suitably designed. The technique has therefore given much insight for its further application. Chemistry of aqueous ZnCl_2 solution is somewhat similar to that of aqueous CdCl_2 solution in that they form complex and have low cation-constituent mobility. In concentrated solution it may also hydrolyse. Regarding these similarities, together with the former consideration for the methods of transference number determination, the indirect moving boundary method using cell and technique developed by Indaratna(14) was employed in this work. The transference numbers measurements were carried out at 25°C for $0.003 - 0.1 \text{ mol dm}^{-3}$ of aqueous ZnCl_2 solutions.

The transference numbers of zinc ion-constituent in ZnCl_2 solutions, which was calculated from the analysis of the Lee and Wheaton conductance equation was also included in this work.