CHAPTER V

DISCUSSION AND CONCLUSIONS

5.1 Discussion

The plots of the concentration dependence of $T_{Zn}^{ZnCl_2}$ from 0.003 - 0.4 mol kg^{-1} obtained by Partington (22), Harris (23) and the present work are shown in Fig. 4.4. These results are in good agreement in the dilute concentration (up to 0.07 mol kg^{-1}). However, the Partington's results shows more scattering than the present data. Above 0.07 mol kg^{-1}, the results of the present work are higher than Harris's and Partington's.

The transference number work on aqueous $ZnCl_2$ (23), $ZnBr_2$ (25), ZnI_2 (1) systems show a similar pattern of the concentration dependences of T_{Zn} (Fig. 5.1). That is T_{Zn} decreases slowly with increasing the concentration of electrolytes in the dilute range. At high concentrations T_{Zn} of these solutions decreases rapidly to zero, then became negative. This is due to the increasing concentration of the negative charge species arising from the association of metal and holide ions in these solutions. T_{Zn} was found to be negative at $\sim$ 2 mol kg^{-1} for $ZnCl_2$, $\sim$ 2.5 mol kg^{-1} for $ZnBr_2$ and $\sim$ 3.5 mol kg^{-1} for ZnI_2. This indicates that the ease of the complex formation is in the order
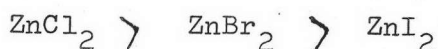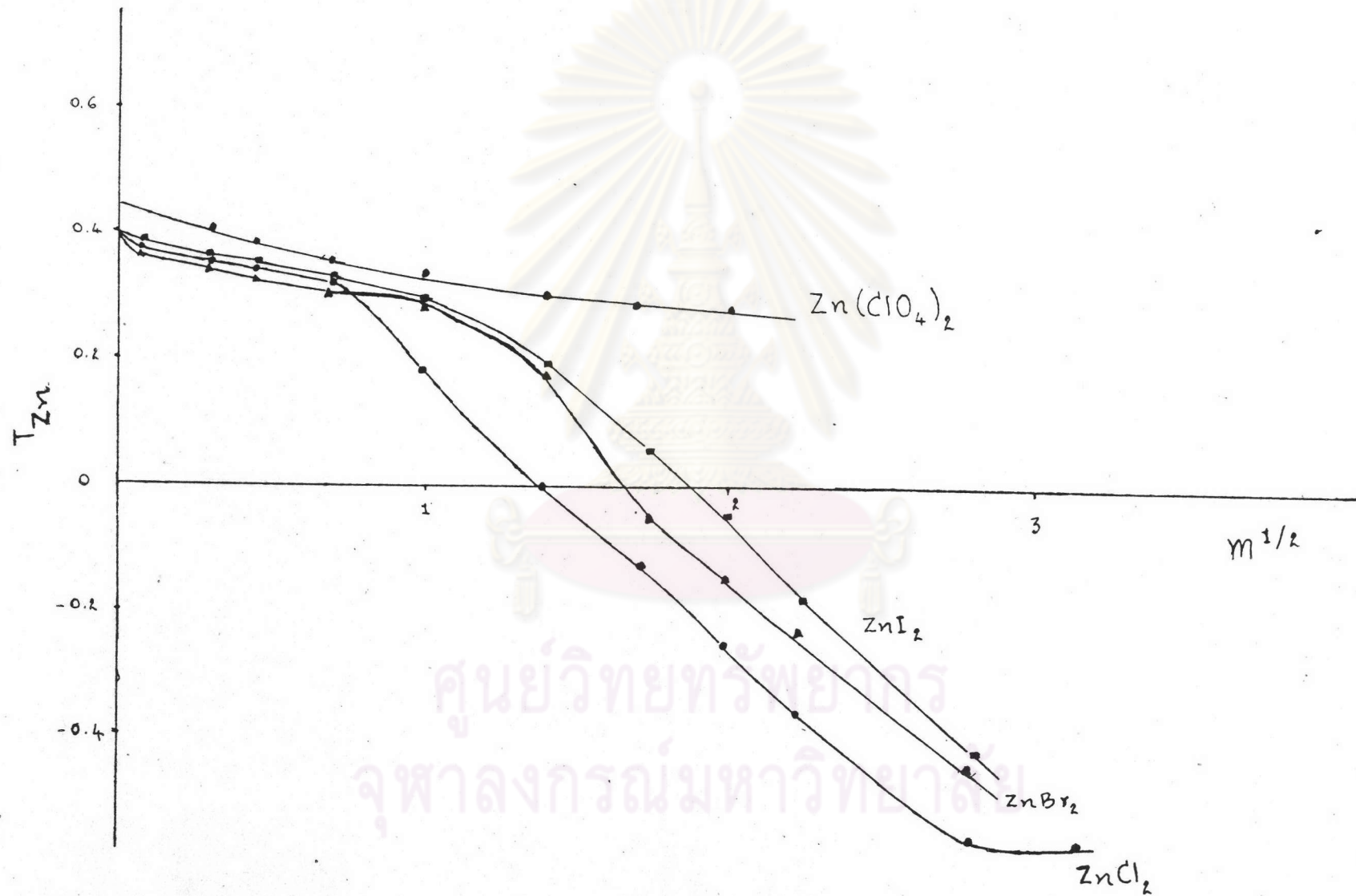
$$ZnCl_2 \, > \, ZnBr_2 \, > \, ZnI_2$$

Fig. 5.1 Plot of T_{Zn} vs. $m^{\frac{1}{2}}$ for $Zn(ClO_4)_2$, ZnI_2, $ZnBr_2$ and $ZnCl_2$ system

For $Zn(ClO_4)_2$ system, T_{Zn} hardly changes at all with concentration (Fig. 5.1). This is the usual behavior of complete dissociated electrolyte.

When compare the concentration dependence of cation-constituent transference number of $ZnCl_2$ with that of $CdCl_2$ which are both halides of Group II B metal, it was found that the two patterns are different in dilution range. For $CdCl_2$ system (14) the cadmium ion-constituent transference number increases with decreasing concentration of the electrolyte, passes through a maximum, and decreasingly approach the limiting value. This is different from $T_{Zn}^{ZnCl_2}$ pattern which has no maximum (see Fig. 5.2) and apparently approach the limiting value from above.

From the present data, linear extrapolation of $T_{Zn}^{ZnCl_2}$ to infinite dilution (see Fig. 4.3) gave $T_{Zn}^{ZnCl_2, o} = 0.4079 \pm 0.0006$. This result may be compared with those estimated from some conductivity results. Using $\lambda^o_{Zn^{2+}} = 53.0$ cm$^2 \Omega^{-1}$ equiv^{-1}. from Owen's (46) conductance measurements on $ZnSO_4$ solutions, and the accepted value of $\lambda^o_{Cl^-} = 76.35$ cm$^2 \Omega^{-1}$ equiv^{-1}. given by Robinson and Stokes (25) a value of $T_{Zn}^{ZnCl_2, o} = 0.409$ is obtained. Extrapolation of Purser's (47) e.m.f. work on $ZnSO_4$ solution gave $T_{Zn}^{ZnSO_4, o} = 0.398$. Using $\lambda^o_{SO_4^{2-}} = 80.02$ cm$^2 \Omega^{-1}$ equiv^{-1}. (25) the value of $\lambda^o_{Zn^{2+}} = 52.64$ cm$^2 \Omega^{-1}$ equiv^{-1}. is obtained. This value gives $T_{Zn}^{ZnCl_2, o} = 0.408$ for $ZnCl_2$.

Fig. 5.2 Comparison of $T_{Zn}^{ZnCl_2}$ vs. m_{ZnCl_2} with $T_{Cd}^{CdCl_2}$ vs. m_{CdCl_2}
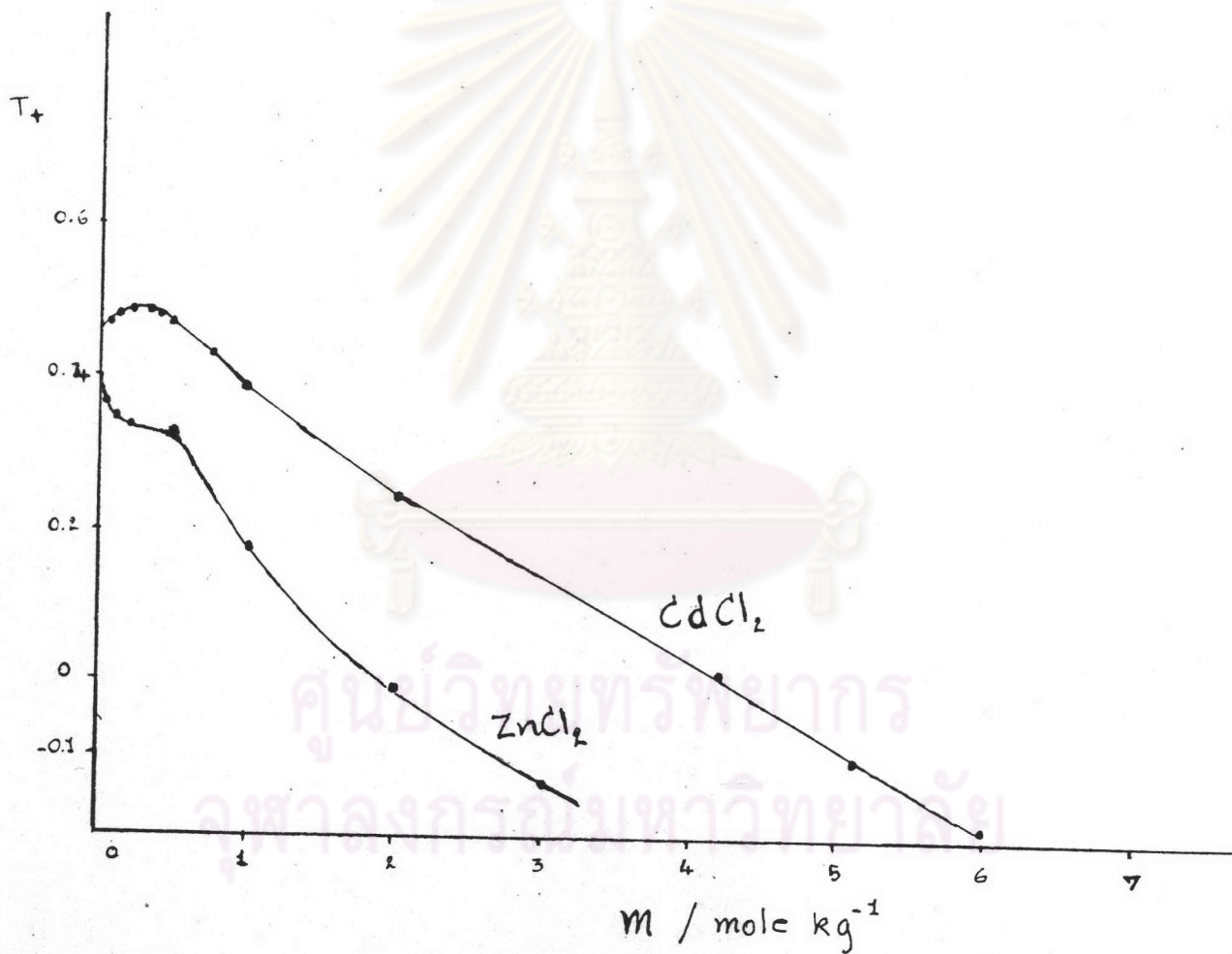
The limiting zinc ion-constituent transference number of ZnI_2 solution (1) was found to be 0.408 by e.m.f. method. Since the value of $\lambda^o_{I^-}$ is not very different from that of $\lambda^o_{Cl^-}$ ($\lambda^o_{I^-}$ = 76.84 cm$^2 \Omega^{-1}$ equiv^{-1}., $\lambda^o_{Cl^-}$ = 76.35 cm$^2 \Omega^{-1}$ equiv^{-1}.), it may be expected that $T^{ZnI_2, o}_{Zn}$ may also be almost the same as $T^{ZnCl_2, o}_{Zn}$. This result is in close proximity to the value $T^{ZnCl_2, o}_{Zn}$ obtained in this work and it agrees with that obtained by the above estimated values.

The concentration dependence of $T^{ZnCl_2}_{Zn}$ obtained from the theoretical analysis follows the general trend observed in the transference number experiments. $T^{ZnCl_2}_{Zn}$ continues to increase for the concentration of $ZnCl_2$ below 1×10^{-3} mol dm^{-3}. The set of $\lambda^o_{Zn^{2+}}$ = 56.2 cm$^2 \Omega^{-1}$ equiv^{-1}. and $\lambda^o_{ZnCl^+}$ = 35.0 cm$^2 \Omega^{-1}$ equiv^{-1}., which gave the best fit for conductance analysis by the Lee and Wheaton equation, gives the results for transference numbers (curve I Fig. 4.5) about 3% higher than the experimental data for the whole concentration range. This may be due to the assumption made to derive the relaxation term for unsymmetrical electrolyte (14) used to obtained the values of the ionic equivalent conductance which was then used to calculate the transference number at each concentration. The best fit values of $\lambda^o_{Zn^{2+}}$ = 53.5$_7$ cm$^2 \Omega^{-1}$ equiv^{-1}. and $\lambda^o_{ZnCl^+}$ = 35.0 cm$^2 \Omega^{-1}$ equiv^{-1}. gave II (Fig. 4.5) with steeper slope when compared with the experimental curve. Using the literature value of $\lambda^o_{Zn^{2+}}$ = 53.0 cm$^2 \Omega^{-1}$ equiv^{-1}. and the value of $\lambda^o_{ZnCl^+}$ = 35.0

$cm^2\Omega^{-1}$ equiv^{-1}., the predicted transference numbers (curve III Fig. 4.5) were about 1% less than the experimental data.

The summary of the results of $\lambda^o_{Zn^{2+}}$ and $T^{ZnCl_2,\ o}_{Zn}$ is given in Table 5.1. The value of the limiting zinc ion-constituent transference number obtained from theoretical analysis of 0.4121 is somewhat higher than the value of 0.4079 obtained from linear extrapolation of experimental transference number data and the value of 0.409 calulated from the literature value ($\lambda^o_{Zn^{2+}}$ = 53.0 $cm^2\Omega^{-1}$ equiv^{-1}.). The value of $T^{ZnCl_2,\ o}_{Zn}$ = 0.4239 obtained by using $\lambda^o_{Zn^{2+}}$ = 56.2 $cm^2\Omega^{-1}$ equiv^{-1}. (the best fit of conductance analysis) is however too high, owing to large discrepancy between the predicted and experimental transference numbers as shown in Fig. 4.5.

Table 5.1 Summary of Results

Analysis	$\lambda^o_{Zn^{2+}}$ $cm^2\Omega^{-1}$ equiv^{-1}.	$T^{ZnCl_2,\ o}_{Zn}$
Theoretical Analysis of Transference Number Data	53.57 $\pm$ 0.01	0.4121 $\pm$ 0.0002
Linear Extrapolation of Experimental Transference Number	52.67 $\pm$ 0.10	0.4079 $\pm$ 0.0006
Conductance Analysis	56.20 $\pm$ 0.01	0.4239 $\pm$ 0.0002
Literature	53.0	0.409

5.2 Conclusion

It is now evident that the indirect moving boundary technique using the same cell as developed by Indaratna (14) for transference number determination of $CdCl_2$ solutions could be well applied to the determination of zinc ion-constituent transference numbers in $ZnCl_2$ solutions with the same precision (0.15%). The results of the present work agree with those obtained by Harris (23) and Partington (22) for the $ZnCl_2$ concentrations below 0.07 mol kg^{-1}. Above this concentration the results of the indirect moving boundary technique were higher than those obtained by the e.m.f. and Hittorf methods. The further study of the application of this technique to the transference number determination for the more concentrated solutions would seem to be appropriate. The concentration dependence of $T_{Zn}^{ZnCl_2}$ follows a similar trend found for $ZnBr_2$ (25) and ZnI_2 (1) systems. Linear extrapolation of $T_{Zn}^{ZnCl_2}$ vs. $M_{ZnCl_2}^{1/2}$ to infinite dilution gave $T_{Zn}^{ZnCl_2, o} = 0.4079 \pm 0.0006$.

Theoretical analysis of the transference number data for dilute aqueous $ZnCl_2$ solutions has been carried out up to about 0.01 mol dm^{-3}. The best fit transference number results was obtained when $\lambda_{Zn^{2+}}^o = 53.5_7$ $cm^2 \Omega^{-1}$ $equiv^{-1}$. and $\lambda_{ZnCl^+}^o = 35.0$ $cm^2 \Omega^{-1}$ $equiv^{-1}$.. This analysis gave $T_{Zn}^{ZnCl_2, o} = 0.4121$. The values of $T_{Zn}^{ZnCl_2, o}$ in Table 5.1 given in section 5.1 would suggest that $T_{Zn}^{ZnCl_2, o}$ should have the value of 0.410 ± 0.002. The limiting zinc ion-constituent transference number of ZnI_2

system (0.408) also support this conclusion. It would be, however, worthwhile to further investigate the concentration dependence of the transference number in very dilute concentration range using a better analytical technique for the analysis of the following solution e.g. atomic absorption method and ion chromatography technique.

The experimental and predicted transference numbers of $ZnCl_2$ solutions seem to approach the limiting value from above and do not approach the limiting slope even at extreme dilution. Similar behavior was found for the solution of ZnI_2 and $ZnBr_2$. No maximum occurred in the dilute region as found for $CdCl_2$ (14) and CdI_2 (48) systems.