CHAPTER IV

RESULTS AND THEORETICAL ANALYSIS OF TRANSFERENCE NUMBER DATA FOR DILUTE AQUEOUS ZINC CHLORIDE SOLUTIONS

4.1 Results

4.1.1 Conductivity Measurements of Aqueous $ZnCl_2$ Solutions

In this work the conductivity was corrected for solvent conductivity by equation (3.2)

$$K = K_{obs} - K_{solvent}$$

The magnitude of $K_{solvent}$ depends on the choice of the conductivity water used in solution preparation. In most cases, this correction was determined to within $\pm$ 0.5 - 1 % of the value of $K_{solvent}$. The uncertainty in conductance results attributed to the precision in the cell constants, the accuracy of the resistance measurements and the error in the solvent correction relative to the measured conductivity of the solution. The magnitude of uncertainty increases with decreasing solution concentration. The determination of cell constants is precise to 0.05% and 0.06% for the cells used with moderate and dilute concentration respectively. The resistance measurement was accurate within 0.05%. An error in solvent correction was small in most cases. The uncertainty of this correction contributed about $\pm$ 0.01% error in conductivity of most dilute solution. On this basis the conductance results are reported with an accuracy of 0.1% over the concentration of solution studied.

Results of conductivity vs. concentration for 0.001 - 0.1 mol dm^{-3} aqueous $ZnCl_2$ solution at 25° C are listed in Table 4.1. A plot of Λ as a function of $C^{1/2}$ over this concentration range is shown in Fig. 4.1. The same plot for M $<$ 1 x 10^{-2} mol dm^{-3} is also given in Fig. 4.2. The observed conductance of dilute $ZnCl_2$ solutions shown in Fig. 4.2 is an apparently linear function of $C^{1/2}$ (curve A). Linear extrapolation of this plot from the present data to infinite dilution by the least squares method gave $\Lambda^{\circ}_{ZnCl_2}$ = 131.34 $cm^2 \Omega^{-1}$ $equiv^{-1}$.. This result is somewhat higher than the value of $\Lambda^{\circ}_{ZnCl_2}$ = 129.35 $cm^2 \Omega^{-1}$ $equiv^{-1}$. obtained by using the literature data of $\lambda^{\circ}_{Zn^{2+}}$ = 53.0 $cm^2 \Omega^{-1}$ $equiv^{-1}$. (46) and $\lambda^{\circ}_{Cl^-}$ = 76.35 $cm^2 \Omega^{-1}$ $equiv^{-1}$. (25) . The Onsager limiting slopes calaulated from equation (2.8), Chapter 2, using $\Lambda^{\circ}_{ZnCl_2}$ = 129.35 $cm^2 \Omega^{-1}$ $equiv^{-1}$. and 131.34 $cm^2 \Omega^{-1}$ $equiv^{-1}$. are also included in Fig. 4.2 (B and C).

4.1.2 Transference Numbers of Zinc Ion-constituent

Transference numbers of zinc ion-constituent were calculated from equation (3.3) in section 3.6.3 . The error involved in T_H is small compared with other uncertainty in this experiment. External analysis of the following solution (m_{ZnCl_2})

Table 4.1

Equivalent Conductance of Zinc Chloride in Water at 25°C

$10^3 M_{ZnCl_2}$ / mol dm^{-3}	Λ_{ZnCl_2} / cm$^2 \Omega^{-1}$ equiv^{-1}.
98.378	76.15
93.369	77.25
84.909	78.71
74.943	81.58
74.102	81.87
63.306	84.79
50.003	88.75
48.187	89.50
37.291	93.53
28.835	97.12
18.700	103.69
9.1843	109.89
8.9436	110.23
8.6646	110.61
8.6298_6	110.55
8.0527	111.26
5.6558	114.61
4.7239	116.19
3.4341	118.18
2.7446	119.74
2.1915	121.14
1.2836	123.18
1.1539	123.28

Fig. 4.1 Concentration dependence of conductance, Λ_{ZnCl_2} vs. $C^{1/2}_{ZnCl_2}$ for 0.001 - 0.1 mol dm^{-3} aqueous $ZnCl_2$ solutions at 25° C

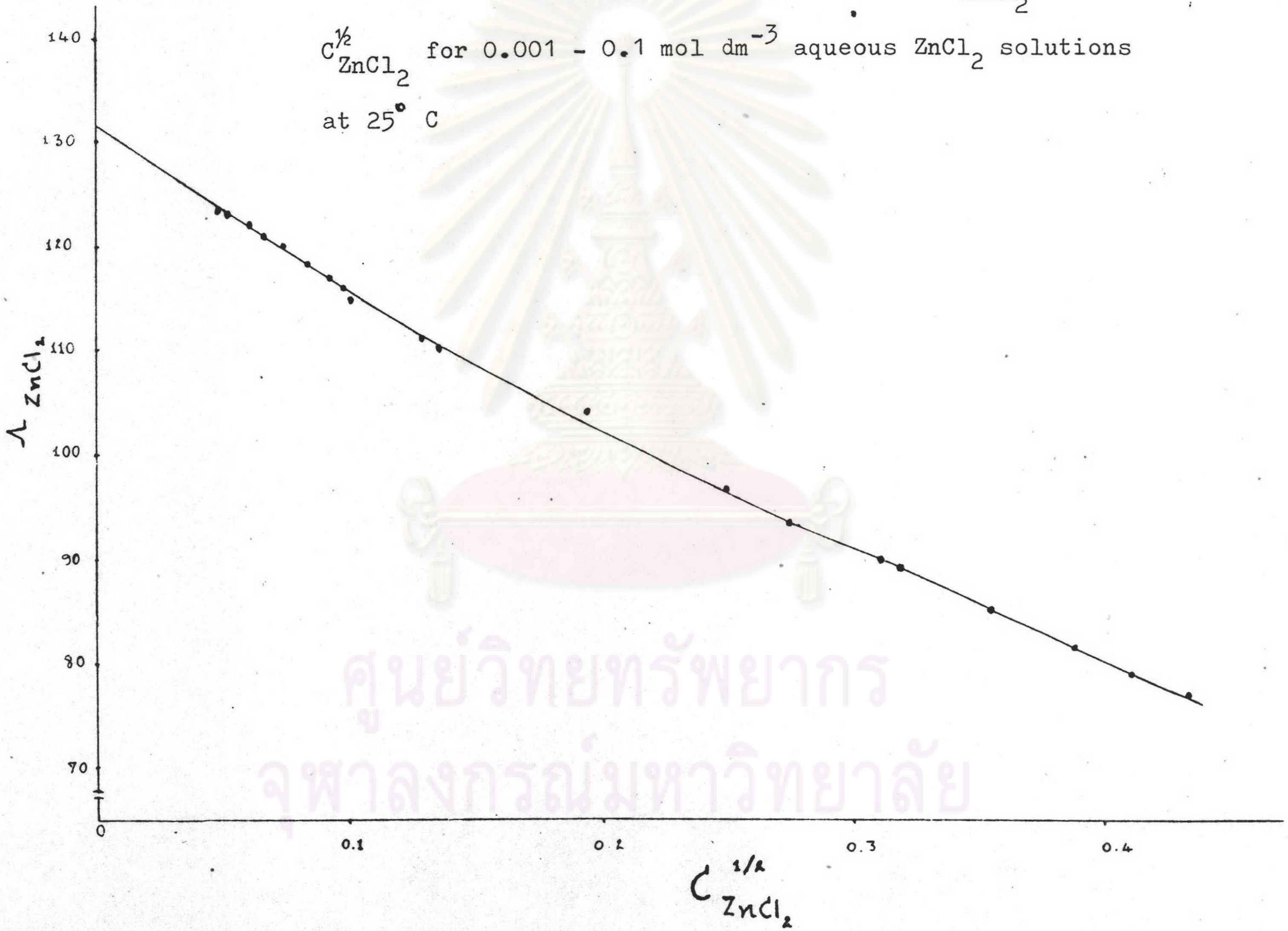
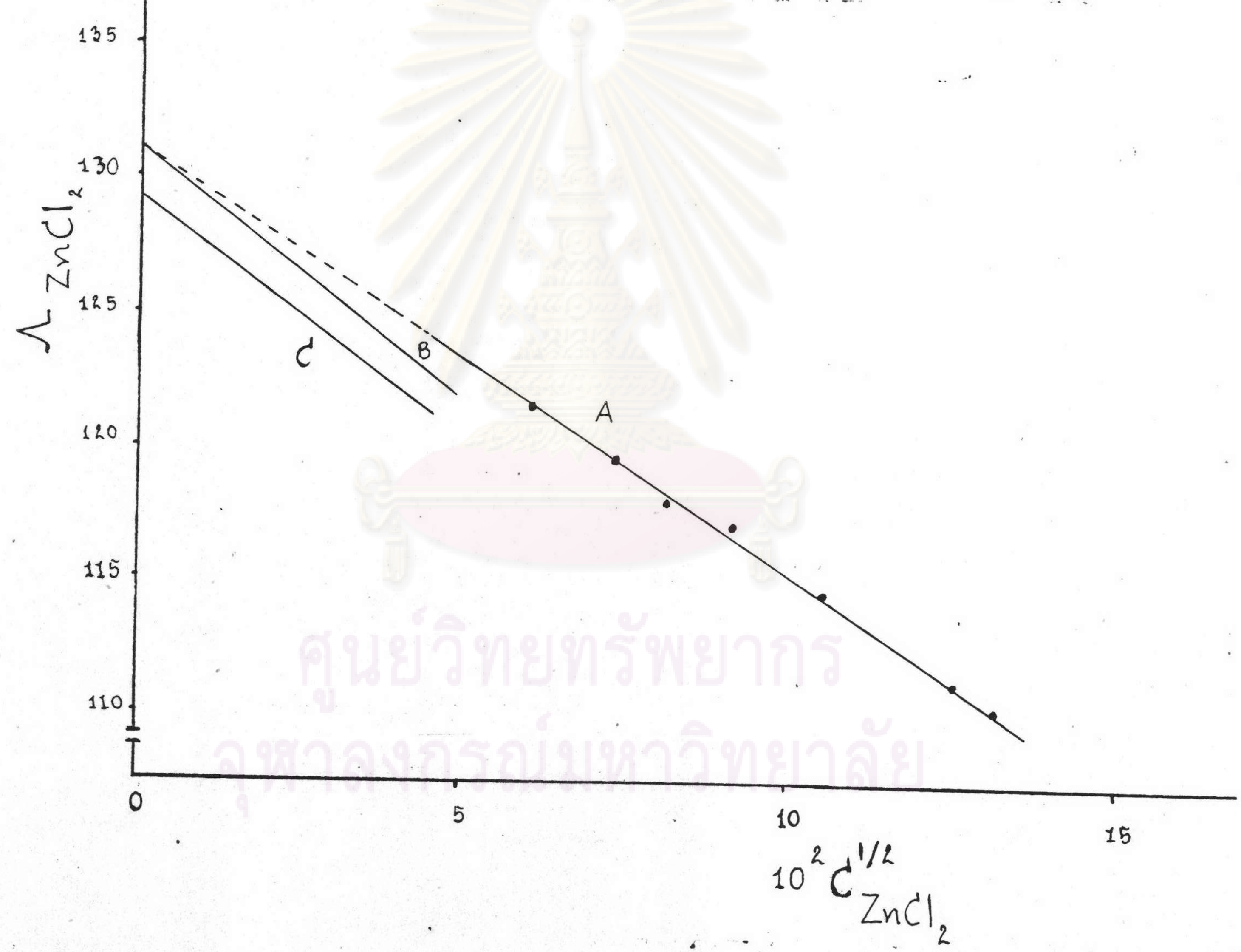


Fig. 4.2 Plot of Λ_{ZnCl_2} vs. $C^{1/2}_{ZnCl_2}$ for $M_{ZnCl_2} < 1 \times 10^{-2}$ mol dm^{-3}



was capable of giving a result with 0.1% uncertainty. Results of the transference number determination are shown in Table 4.2. In most cases, the results from the two samples agree within $\pm$ 0.1%. The results were reproducible, and independent of current within $\pm$ 0.15%. The values of $T_{Zn}^{ZnCl_2}$ obtained in this work are thus reported with 0.15% uncertainty over the concentration of solution studied.

Results of $T_{Zn}^{ZnCl_2}$ vs. concentration of aqueous $ZnCl_2$ solutions are summarised in Table 4.3.The mean deviation obtained by averaging the value from independent runs is given. A plot of $T_{Zn}^{ZnCl_2}$ as a function of $M^{1/2}_{ZnCl_2}$ is shown in Fig. 4.3. $T_{Zn}^{ZnCl_2}$ of the dilute concentration range (0.003 - 0.009 mol dm^{-3}) shown in Fig. 4.3 is an apparently linear function of $M^{1/2}_{ZnCl_2}$. Linear extrapolation of this plot to infinite dilution by the least squares method gave the intercept = 0.4079 with a mean diviation of $\pm$ 0.0006. That is $T_{Zn}^{ZnCl_2, o}$ = 0.4079 $\pm$ 0.0006 with a mean deviation comparable to the experimental uncertainty of $\pm$ 0.15% in the dilute range.

The results and plots of $T_{Zn}^{ZnCl_2}$ vs. concentration of aqueous $ZnCl_2$ solutions by Partington (22), Harris (23) and the present work are shown in Table 4.4 and Fig. 4.4 . Curve A combines the results at high concentration (0.05 - 0.4 mol kg^{-1} $ZnCl_2$) from Harris's e.m.f. measurements with the results at low concentration (0.003 - 0.09 mol kg^{-1} $ZnCl_2$) obtained by the indirect moving boundary method from the present work.

Table 4.2

Results of the Transference Numbers

Boundary System	Current / mA	Time / hr	$m^{(A)}_{ZnCl_2}$ /mol kg^{-1}	$m^{(B)}_{ZnCl_2}$ /mol kg^{-1}	$T^{ZnCl_2(A)}_{Zn}$	$T^{ZnCl_2(B)}_{Zn}$
0.4253 mHCl / 0.1200 m$ZnCl_2$	10	12.75	*0.09024	-	0.3550	-
	10	12.75	0.09029	0.09024	0.3552	0.3550
0.3758 mHCl / 0.1092 m$ZnCl_2$	10	11.00	*0.08035	-	0.3574	-
	10	11.00	0.08038	0.08036	0.3575	0.3574
0.3281 mHCl / 0.0892 m$ZnCl_2$	10	9.25	*0.07043	-	0.3587	-
	10	9.25	0.07031	0.07040	0.3581	0.3585
0.2664 mHCl / 0.0753 m$ZnCl_2$	10	8.75	*0.05792	-	0.3630	-
	10	8.75	0.05793	0.05794	0.3630$_6$	0.3631
0.2214 mHCl / 0.0618 m$ZnCl_2$	10	6.75	*0.04880$_5$	-	0.3676	-
	10	6.75	0.04876	0.048755	0.3673	0.3673

Table 4.2

Results of the Transference Numbers

Boundary System	Current / mA	Time / hr	$m^{(A)}_{ZnCl_2}$ /mol kg^{-1}	$m^{(B)}_{ZnCl_2}$ /mol kg^{-1}	$T^{ZnCl_2(A)}_{Zn}$	$T^{ZnCl_2(B)}_{Zn}$
0.1468 mHCl / 0.0409 $mZnCl_2$	8	4.75	0.03292	0.03289	0.3732	0.3729
0.1382 mHCl / 0.0409 $mZnCl_2$	10	4.50	0.03128	-	0.3765	-
	5	8.50	0.03121	0.03119	0.3757	0.3755
0.0926 mHCl / 0.0301 $mZnCl_2$	10	4.00	*0.02115	-	0.3796	-
	6	5.75	*0.02111_5	-	0.3790	-
0.0695 mHCl / 0.0210 $mZnCl_2$	10	2.00	*0.01616	-	0.3878	-
	10	2.75	*0.01615	-	0.3875	-
	8	2.75	0.01613	0.01611	0.3871	0.3866
0.0564 mHCl / 0.0196 $mZnCl_2$	8	2.50	*0.01321_3	-	0.3884	-
	5	3.50	*0.01322	-	0.3889	-

Table 4.2

Results of the Transference Numbers

Boundary System	Current / mA	Time / hr	$m^{(A)}_{ZnCl_2}$ /mol kg^{-1}	$m^{(B)}_{ZnCl_2}$ /mol kg^{-1}	$T_{Zn}^{ZnCl_2(A)}$	$T_{Zn}^{ZnCl_2(B)}$
0.0428 mHCl / 0.0151 $mZnCl_2$	4	3.25	$*0.01012_5$	-	0.3923	-
	4	3.25	0.01011	0.01012	0.3917	0.3921
	2	6.25	0.01010	0.01009	0.3913	0.3909
0.0348 mHCl / 0.0101 $mZnCl_2$	4	2.75	$*8.252_5 \times 10^{-3}$	-	0.3929	-
	4	2.75	8.250×10^{-3}	-	0.3928	-
	2	5.25	8.225×10^{-3}	8.230×10^{-3}	0.3916	0.3919
0.0380 mHCl / 0.0126 $mZnCl_2$	4	3.00	9.004×10^{-3}	-	0.3926	-
	4	3.00	8.996×10^{-3}	8.993×10^{-3}	0.3923	0.3921
	2	5.25	8.985×10^{-3}	8.974×10^{-3}	0.3918	0.3913

Table 4.2

Results of the Transference Numbers

Boundary System	Current / mA	Time / hr	$m^{(A)}_{ZnCl_2}$ /mol kg^{-1}	$m^{(B)}_{ZnCl_2}$ /mol kg^{-1}	$T^{ZnCl_2(A)}_{Zn}$	$T^{ZnCl_2(B)}_{Zn}$
0.0326 mHCl / 0.0097 m$ZnCl_2$	3	3.50	*7.779 x 10^{-3}	-	0.3953	-
	3	3.50	7.775 x 10^{-3}	7.767 x 10^{-3}	0.3951	0.3947
	2	4.50	7.746 x 10^{-3}	7.755_4 x 10^{-3}	0.3936	0.3941
0.0264 mHCl / 0.0081 m$ZnCl_2$	2	3.75	*6.330 x 10^{-3}	-	0.3967	-
	2	3.75	6.318 x 10^{-3}	6.320 x 10^{-3}	0.3963	0.3964
	1	7.00	6.305_6 x 10^{-3}	6.297 x 10^{-3}	0.3955	0.3950
0.0215 mHCl / 0.0069 m$ZnCl_2$	2	3.00	*5.164 x 10^{-3}	-	0.3975	-
	2	3.00	5.163 x 10^{-3}	5.163_4 x 10^{-3}	0.3973	0.3974
	1	6.00	5.147 x 10^{-3}	5.144 x 10^{-3}	0.3961	0.3959

Table 4.2

Results of the Transference Numbers

Boundary System	Current / mA	Time / hr	$m^{(A)}_{ZnCl_2}$ /mol kg^{-1}	$m^{(B)}_{ZnCl_2}$ /mol kg^{-1}	$T^{ZnCl_2(A)}_{Zn}$	$T^{ZnCl_2(B)}_{Zn}$
0.0159 mHCl / 0.0052 $mZnCl_2$	2	3.50	*3.843 $\times 10^{-3}$	-	0.3995	-
	2	3.50	3.839 $\times 10^{-3}$	3.841 $\times 10^{-3}$	0.3991	0.3993
	1	6.50	3.830 $\times 10^{-3}$	3.826 $\times 10^{-3}$	0.3981	0.3976
0.0126 mHCl / 0.0041 $mZnCl_2$	2	2.00	*3.043 $\times 10^{-3}$	-	0.3988	-
	2	2.00	3.042 $\times 10^{-3}$	3.043 $\times 10^{-3}$	0.3986	0.3988
	1	4.50	3.036 $\times 10^{-3}$	$3.031_5 \times 10^{-3}$	0.3978	0.3972

* refers to a single sample was to be analysed.

Table 4.3

Cation Transference Numbers* in Aqueous Zinc Chloride Solutions

m_{ZnCl_2} = 0.003 - 0.09 mol kg^{-1}

$10^2\ m_{ZnCl_2}$	$T_{Zn}^{ZnCl_2}$
0.3039 ± 0.0004	0.3982 ± 0.0005
0.3836 ± 0.0006	0.3987 ± 0.0006
0.5156 ± 0.0007	0.3968 ± 0.0006
0.6314 ± 0.0009	0.3959 ± 0.0006
0.7644 ± 0.0009	0.3945 ± 0.0005
0.8239 ± 0.0009	0.3923 ± 0.0006
0.8990 ± 0.0006	0.3920 ± 0.0003
1.011 ± 0.001	0.3916 ± 0.0004
1.322 ± 0.001	0.3886 ± 0.0002
1.614 ± 0.002	0.3872 ± 0.0005 **
2.113 ± 0.002	0.3793 ± 0.0003
3.123 ± 0.005	0.3759 ± 0.0006 **
4.877 ± 0.003	0.3674 ± 0.0002
5.793 ± 0.001	0.3630 ± 0.0001
7.038 ± 0.005	0.3584 ± 0.0003
8.036 ± 0.002	0.3574 ± 0.0001
9.025 ± 0.002	0.3551 ± 0.0001

* These results were obtained by averaging the values observed from independent runs.

** The high uncertainties of these results were due to the effect of 50% variation of current used for electrolysis.

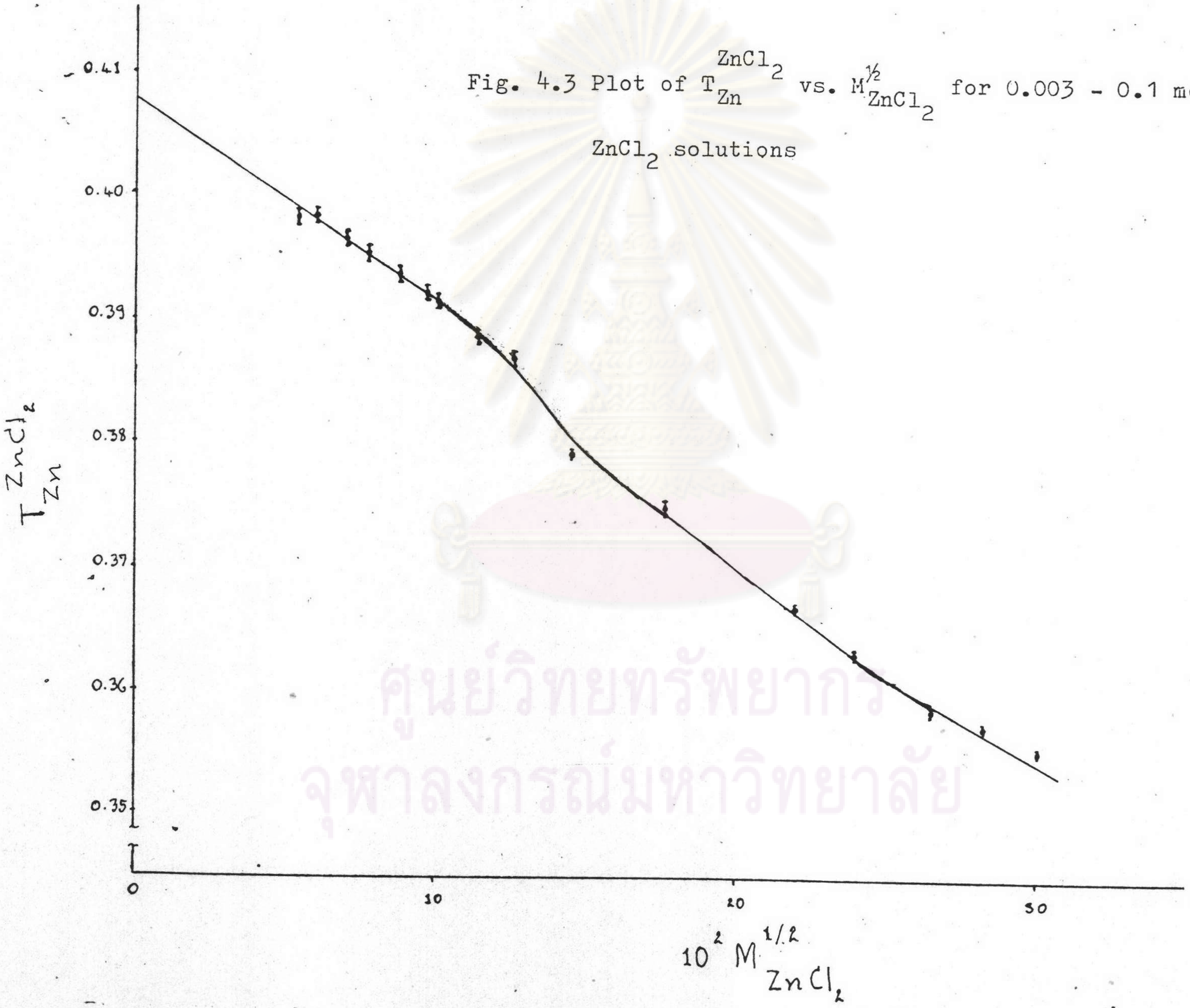


Fig. 4.3 Plot of $T_{Zn}^{ZnCl_2}$ vs. $M^{1/2}_{ZnCl_2}$ for 0.003 - 0.1 mol dm^{-3} $ZnCl_2$ solutions

Table 4.4

Cation Transference Numbers in Aqueous Zinc Chloride Solutions

$m = 0.003 - 5.0 \text{ mol kg}^{-1}$

$m^{(1)}_{ZnCl_2}$	$T^{ZnCl_2(1)}_{Zn}$	$m^{(2)}_{ZnCl_2}$	$T^{ZnCl_2(2)}_{Zn}$
0.003039	0.3982		
0.003836	0.3987		
0.005156	0.3968		
0.006314	0.3959		
0.007644	0.3945		
0.008239	0.3923		
0.008990	0.3920		
0.01011	0.3916	0.0097	0.390
0.01322	0.3886	0.0210	0.379
0.01614	0.3872	0.0327	0.372
0.02113	0.3793	0.0431	0.369
0.03123	0.3759	0.0500	0.365
0.04877	0.3674	0.0581	0.363
0.05793	0.3630	0.0672	0.361
0.07038	0.3584	0.0750	0.355
0.08036	0.3574	0.0862	0.351
0.09025	0.3551	0.0986	0.347
0.1	0.350	0.1344	0.342
0.2	0.335	0.1500	0.341

Table 4.4

Cation Transference Numbers in Aqueous Zinc Chloride Solutions

$m = 0.003 - 5.0 \text{ mol kg}^{-1}$

$m^{(1)}_{ZnCl_2}$	$T^{ZnCl_2(1)}_{Zn}$	$m^{(2)}_{ZnCl_2}$	$T^{ZnCl_2(2)}_{Zn}$
0.5	0.331	0.1724	0.338
1.0	0.171	0.2102	0.337
2.0	0.000	0.2800	0.333
3.0	-0.137	0.3271	0.330
4.0	-0.256		
5.0	-0.364		

$m^{(1)}_{ZnCl_2}$ vs. $T^{ZnCl_2(1)}_{Zn}$ are results obtained from the present work by the indirect moving boundary method for dilute $ZnCl_2$ solutions (0.003 - 0.09 mol kg^{-1}) and those obtained by Harris from the concentration cell transference number measurements for $ZnCl_2$ solution above 0.09 mol kg^{-1}.

$m^{(2)}_{ZnCl_2}$ vs. $T^{ZnCl_2(2)}_{Zn}$ are Partington's results obtained by Hittorf measurement.

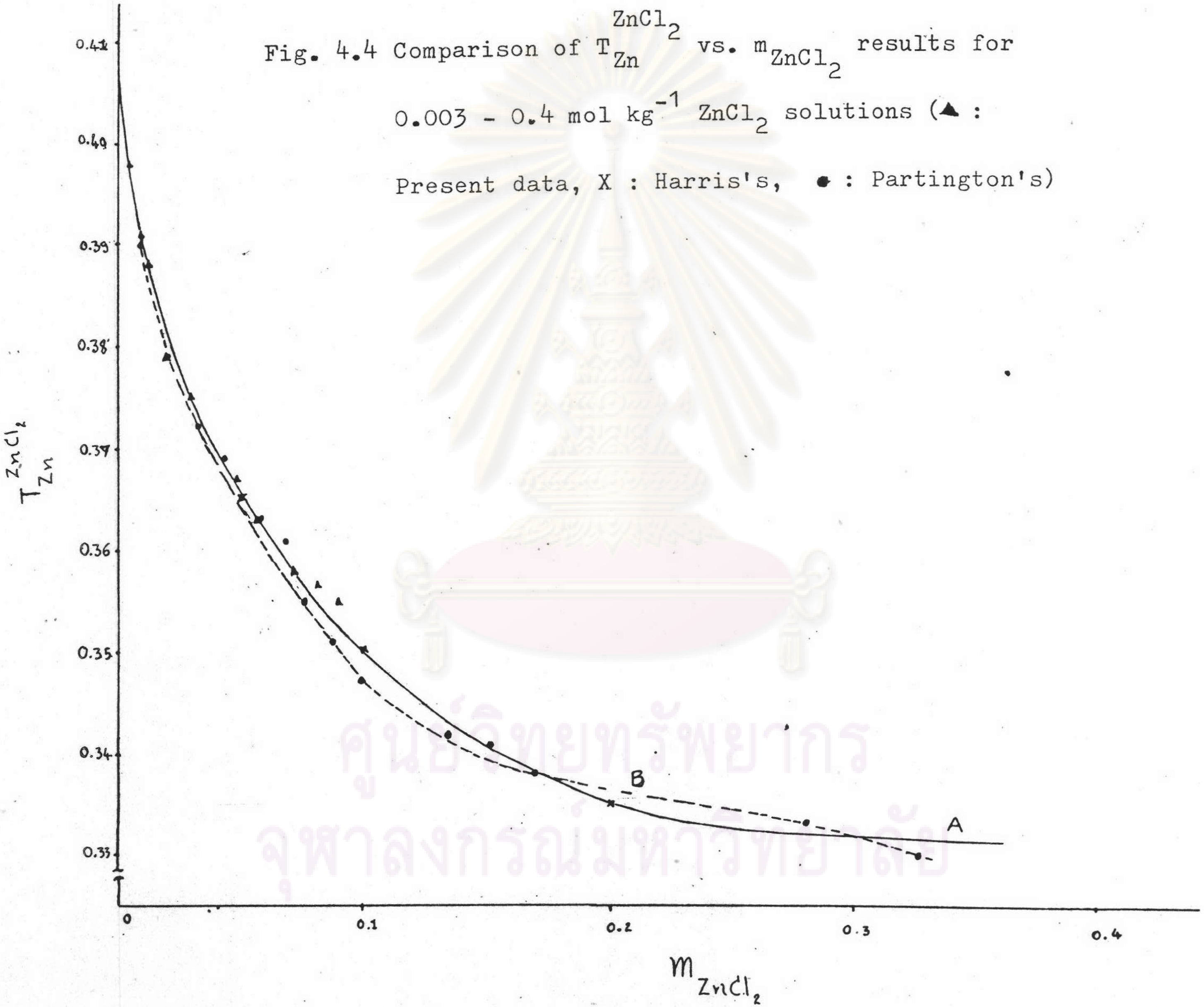


Fig. 4.4 Comparison of $T_{Zn}^{ZnCl_2}$ vs. m_{ZnCl_2} results for $0.003 - 0.4$ mol kg^{-1} $ZnCl_2$ solutions (▲ : Present data, X : Harris's, ● : Partington's)

Partington's results for the concentration range 0.009 - 0.3 mol kg^{-1} are plotted as curve B.

4.2 Theoretical Analysis of Transference Numbers for Dilute Aqueous Zinc Chloride Solutions

The relationship between the cation-constituent transference number and the equivalent conductances of ionic species present in solution is given by equation (2.6) (Chapter 2) The Lee and Wheaton conductance equation, which has the usual form,

$$\Lambda = f(\lambda_1^{o}, ---, \lambda_s^{o}, R, C, K_A^1, ---, K_A^X)$$

allows the equivalent conductances of several ionic species, λ_i (i = 1, 2, - - -) at any concentration in dilute solutions to be evaluated from known λ_i^{o} values. These data thus permit the calculation of $T_{Zn}^{ZnCl_2}$ at different $ZnCl_2$ concentrations by equation (2.6). Owing to the limitation of the application of the theory, the analysis of the transference number data were considered up to about 0.01 mol dm^{-3} solution.

Various sets of $\lambda^{o}_{Zn^{2+}}$, $\lambda^{o}_{ZnCl^+}$ and R were used to calculate values of $T_{Zn}^{ZnCl_2}$ over a range of concentration. By comparing the experimental $T_{Zn}^{ZnCl_2}$ vs. M_{ZnCl_2} curve with those obtained from the calaulations the set of $\lambda^{o}_{Zn^{2+}}$ and $\lambda^{o}_{ZnCl^+}$ values which gave the best fit between the experimental and predicted $T_{Zn}^{ZnCl_2}$ vs. M_{ZnCl_2} curve was obtained.The predicted zinc ion-constituent transference numbers are listed in Table4.5.These plots are shown in Fig. 4.5. From this analysis, using $\lambda^{o}_{Zn^{2+}} = 53.5_7$ $cm^2 \Omega^{-1} equiv^{-1}$. which is the best value, curve II was obtained. Curve I was obtained by using the values of 56.2 and 35.0 $cm^2 \Omega^{-1} equiv^{-1}$. for $\lambda^{o}_{Zn^{2+}}$ and $\lambda^{o}_{ZnCl^{+}}$ respectively. This set gives the best fit for conductance analysis by the Lee and Wheaton equation. Curve III was obtained by using the literature $\lambda^{o}_{Zn^{2+}}$ value of 53.0 $cm^2 \Omega^{-1} equiv^{-1}$. and the value of $\lambda^{o}_{ZnCl^{+}} = 35.0$ $cm^2 \Omega^{-1} equiv^{-1}$. . Using $\lambda^{o}_{Zn^{2+}} = 53.5_7$ $cm^2 \Omega^{-1} equiv^{-1}$. the value of $T^{ZnCl_2, o}_{Zn}$ was calculated to be 0.4121. The limiting slope of the zinc ion-constituent transference number was then calculated from these values using equation (2.9), Chapter 2, and is included in Fig. 4.5 .

Table 4.5

Predicted $T_{Zn}^{ZnCl_2}$ vs. M_{ZnCl_2}

$10^3 M_{ZnCl_2}$ / mol dm^{-3}	Predicted $T_{Zn}^{ZnCl_2}$		
	I	II	III
0.3044	0.4247	0.4125	0.4098
1.283	0.4181	0.4045	0.4107
1.915	0.4173	0.4032	0.4004
2.199	0.4166	0.4023	0.3994
2.744	0.4159	0.4011	0.3952
3.434	0.4151	0.3997	0.3967
4.724	0.4136	0.3973	0.3943
5.656	0.4126	0.3957	0.3938
8.053	0.4100	0.3916	0.3882
8.271	0.4098	0.3912	0.3881
8.630	0.4094	0.3906	0.3874
8.944	0.4090	0.3901	0.3866
9.185	0.4088	0.3897	0.3865

(I) $\lambda^{o}_{Zn^{2+}} = 56.2\ cm^2 \Omega^{-1} equiv^{-1}$.; $\lambda^{o}_{ZnCl^{+}} = 35.0\ cm^2 \Omega^{-1} equiv^{-1}$.

(II) $\lambda^{o}_{Zn^{2+}} = 53.5_7\ cm^2 \Omega^{-1} equiv^{-1}$.; $\lambda^{o}_{ZnCl^{+}} = 35.0\ cm^2 \Omega^{-1} equiv^{-1}$.

(III) $\lambda^{o}_{Zn^{2+}} = 53.0\ cm^2 \Omega^{-1} equiv^{-1}$.; $\lambda^{o}_{ZnCl^{+}} = 35.0\ cm^2 \Omega^{-1} equiv^{-1}$.

Fig. 4.5 Experimental and Predicted $T_{Zn}^{ZnCl_2}$ vs. M_{ZnCl_2} for 0.0003 - 0.01 mol dm^{-3} $ZnCl_2$ solutions at 25° C (• : Experimental data, I : using $\lambda^\circ_{Zn^{2}} = 56.2\ cm^2\Omega^{-1}$ equiv^{-1}. and $\lambda^\circ_{ZnCl^+} = 35.0\ cm^2\Omega^{-1}$ equiv^{-1}. , II : using $\lambda^\circ_{Zn^{2+}} = 53.5_7\ cm^2\Omega^{-1}$ equiv^{-1}. and $\lambda^\circ_{ZnCl^+} = 35.0\ cm^2\Omega^{-1}$ equiv^{-1}. , III : using $\lambda^\circ_{Zn^{2+}} = 53.0\ cm^2\Omega^{-1}$ equiv^{-1}. and $\lambda^\circ_{ZnCl^+} = 35.0\ cm^2\Omega^{-1}$ equiv^{-1}.)