



CHAPTER VI

DISCUSSION AND CONCLUSION

6.1 Discussion

6.1.1 Zinc Chloride System

Table 6.1 compares the complex formation constants obtained in this work with the literature values using the same method.

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Table 6.1 Comparison of the literature values of β for the zinc chloride complexes with the present results.

(a) Electrodes	Temp °C	Medium	β_1	β_2	β_3	β_4	Ref.
Zn-Hg, Ag/AgCl	25	ZnCl ₂ var. (0.0004-0.1 mol.kg ⁻¹)	4.50	-	-	-	(20)
Zn-Hg, Ag/AgCl	25	ZnCl ₂ var. (0.0009-3.2 mol.kg ⁻¹)	5.00±0.20	1.30±0.10	0.96±0.04	1.00±0.03	**
(b) Electrode	Temp °C	Medium	β_1^c	β_2^c	β_3^c	β_4^c	Ref.
Zn-Hg	25	3(NaClO ₄) (I= 3 M)	0.65±0.10	0.25±0.25	1.40±0.30	-	(22)
Zn-Hg, Ag/AgCl	25	ZnCl ₂ var. (0.0009-3.2 mol.kg ⁻¹)	0.56±0.01	0.29±0.02	1.96±0.08	3.51±0.10	**

** Present work

From Table 6.1a, it is obvious that the value of $\beta_1 = 5.00 \pm 0.10$, obtained here is slightly higher than that ($\beta_1 = 4.50$) obtained by Lutfullah & Paterson (20). The authors had admitted that there was considerable ambiguity concerning their value being due to the non-unique solution obtained from the determination of E° . Aduldecha & Korbratna (21) found that this value ($\beta_1 = 4.50$) gave $\lambda_{Zn^{2+}}^\circ$ value of $ZnCl_2$ inconsistent with those obtained from the completed dissociated salts.

Sillén & Liljéquist (22) had investigated the complex formation constants of zinc chloride by potentiometric titrations using liquid zinc amalgam electrodes at constant ionic strength ($I = 3 \text{ mol dm}^{-3}$). Their results, in Table 6.1b, are given in terms of the concentration complex formation constants, β_n^c , defined by

$$\beta_n^c = [ZnCl_n^{(2-n)}] / [Zn^{2+}][Cl^-]^n$$

To compare these values, our thermodynamic complex formation constants were converted to the concentration complex formation constants at the same ionic strength using eq.(23). They are listed in Table 6.1b. The two sets of results are in fairly good agreement. The β values have the following trend, $\beta_1 > \beta_2 > \beta_3 < \beta_4$. The values of $\beta_2 \sim \beta_3 \sim \beta_4$ are about 1.

From the results of the species concentrations as a function of salt concentrations (table 5.3, Fig.5.1), it is obvious that in the dilute concentration range up to about 0.1 mol kg^{-1} the major species are Zn^{2+} (81.6%) and $ZnCl^+$ (17.6%). Initially, there is a sharp increase in the amount of $ZnCl^+$ species with a maximum at

about 0.45 mol kg^{-1} . Above this concentration the anion complex species become significant. The decrease in the amount of ZnCl^+ is compensated by the increase in ZnCl_3^- and ZnCl_4^{2-} concentrations. The onset of ZnCl_4^{2-} concentration is more rapid than that of ZnCl_3^- which makes ZnCl_4^{2-} a dominant anion complex (a maximum concentration of 22% at 2 mol kg^{-1}) up to the concentration of 2.2 mol kg^{-1} . Above this concentration the amount of ZnCl_4^{2-} decreases and the ZnCl_3^- complex anion becomes more significant. This could be due to the values of β_3 and β_4 being comparable ($\beta_3 = 0.96$, $\beta_4 = 1.00$). For the whole range of concentration, the amount of neutral ZnCl_2 species is always very low, < 5% of the total zinc concentration.

Including the data of ZnCl_2 -KCl system in the analysis, the same set of B values were obtained except for the larger β_4 value (see section 5.2.1). This effect may be due to additional amount of chloride in the solution , especially for anion complexes. The species distribution in the concentration range studied is also similar to that of the ZnCl_2 system (Fig.5.2). However, the amount of the individual species of the former is larger than that of the latter.

It might be worthwhile to compare the result of ZnCl_2 system with other systems of similar nature, viz., the CdCl_2 and CdI_2 systems. Fig.6.1 shows the species distribution of the CdCl_2 system calculated from Rielly & Stoke's data (9). The same plot for CdI_2 system was obtained by Paterson & co-workers (23) and was shown in Fig.6.2 . The appearance of the distribution curve of ZnCl_2 system is generally similar to that of CdI_2 system, but quite different from that of CdCl_2 system. The distribution of monohalide

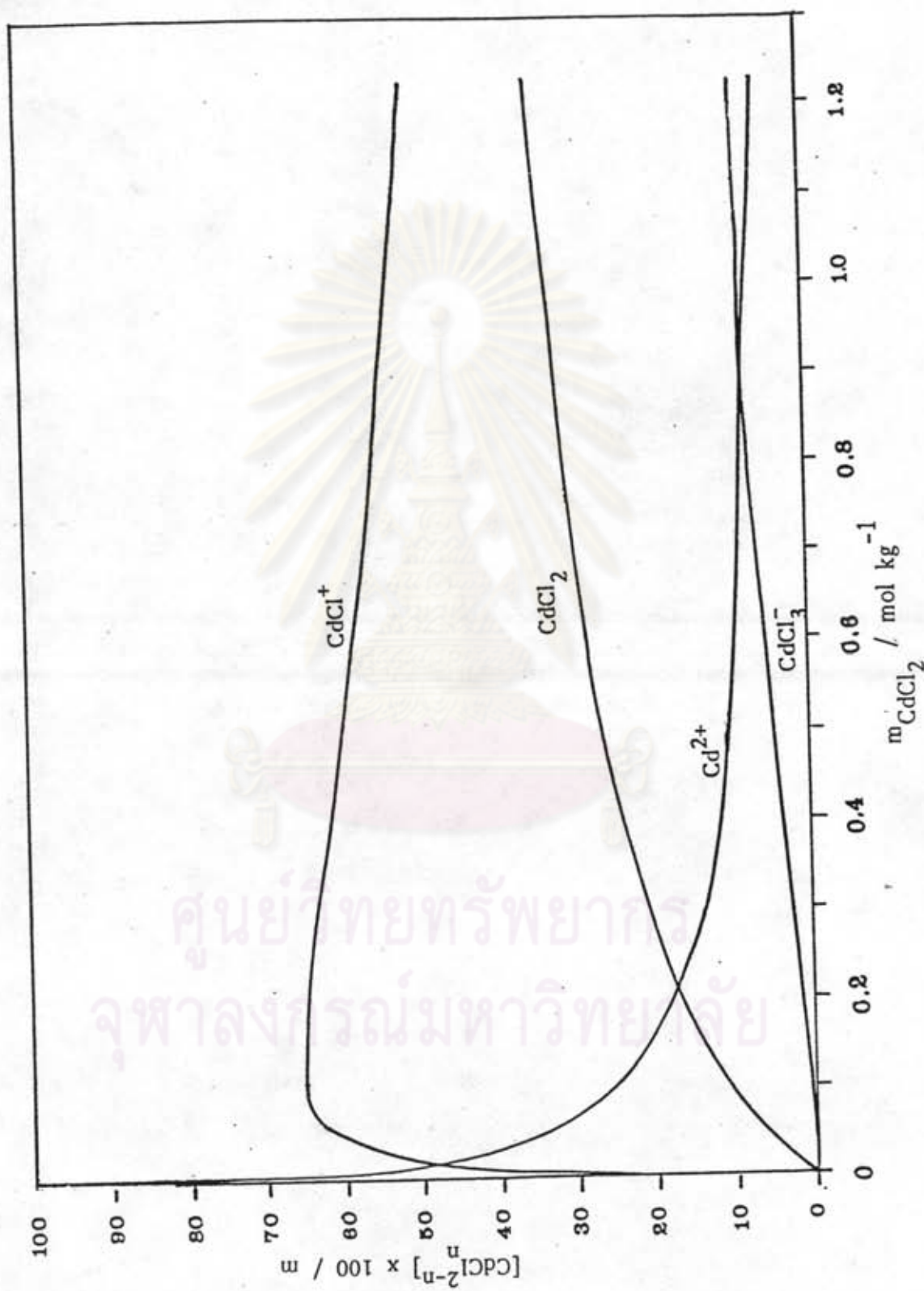


Figure 6.1 The percentage distribution of free and complexed cadmium as a function of the molar concentration of cadmium chloride

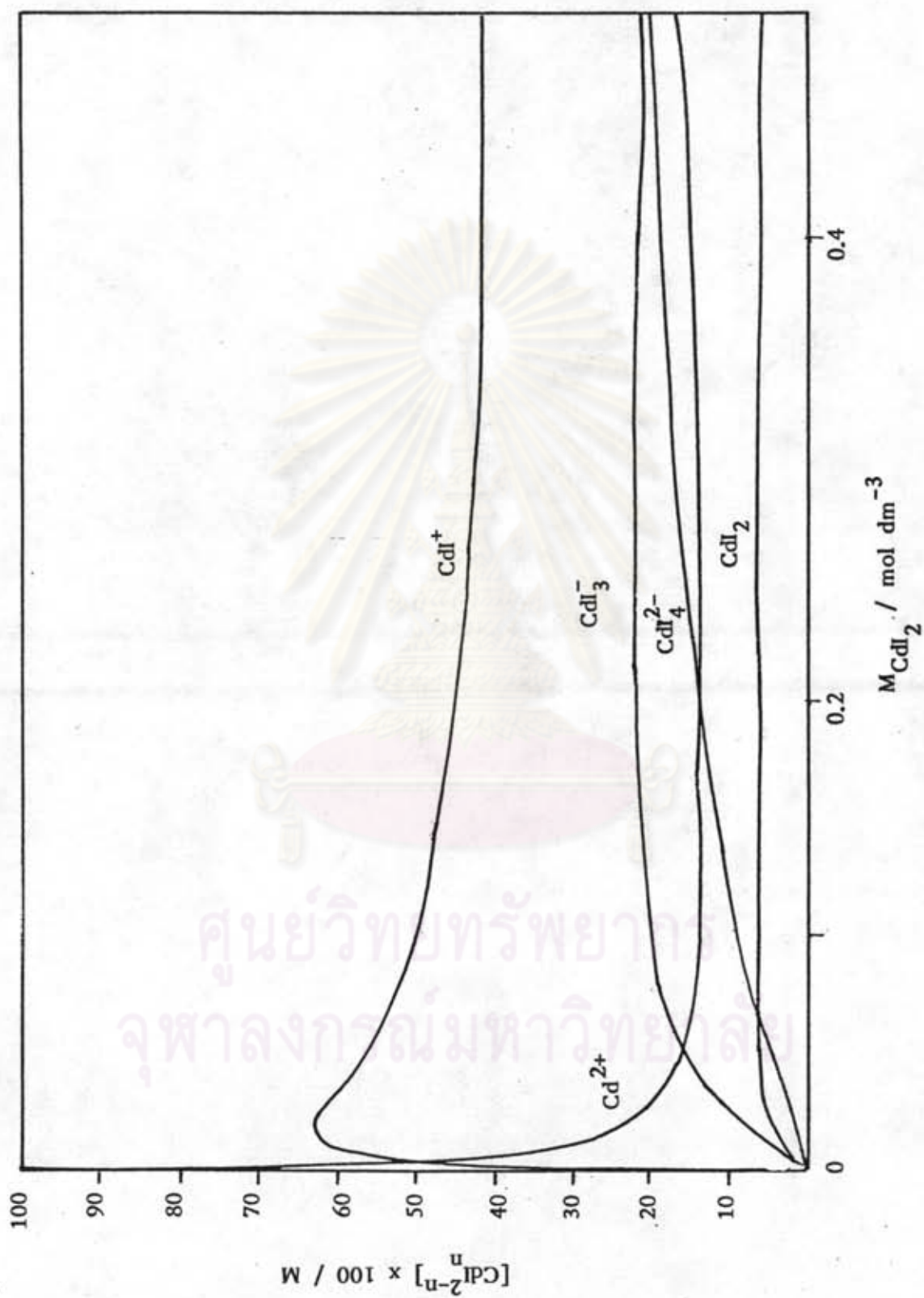


Figure 6.2 The percentage distribution of free and complexed cadmium as a functions of the molar concentration of cadmium iodide

cation complex in these systems all show the maxima in the low concentration range. For the system of ZnCl_2 , however, the maximum occurs at somewhat higher concentration due to the lower value of β_1 . The concentration of the neutral complex in CdCl_2 solution becomes as high as 50% of the total complex distribution while those of ZnCl_2 and CdI_2 systems are always very low. In most cases, the anion complexes predominate in the higher concentration range. For the CdCl_2 system, however, the concentration of CdCl_4^{2-} is virtually zero. It might be noted that, in the same concentration range, although the monovalent anion complex in CdI_2 system contributed more significantly than the divalent species, the reverse was true for the ZnCl_2 system. The amount of monovalent cation complex in CdCl_2 system is persistently high (50%) while those in ZnCl_2 and CdI_2 solutions decrease more abruptly.

It should be possible now to discuss the equilibrium and transport properties of the ZnCl_2 system in terms of the species distribution obtained in this work. Figs. 6.3, 6.4 and 6.5 are the plots of equivalent conductance, viscosity and tracer diffusion coefficients as a function of concentration for ZnCl_2 , CdCl_2 and MgCl_2 compiled by Wiengartner & co-workers (8). Fig. 6.6 shows the cation transference numbers as a function of concentration for CdCl_2 , ZnCl_2 , ZnBr_2 and ZnI_2 systems obtained by McQuillan (24), Harris (25), Parton (26) and Robin & Stokes (27) respectively. By comparing the data of ZnCl_2 and CdCl_2 with those of MgCl_2 (complete dissociated 2:1 electrolyte), several remarks can be made.

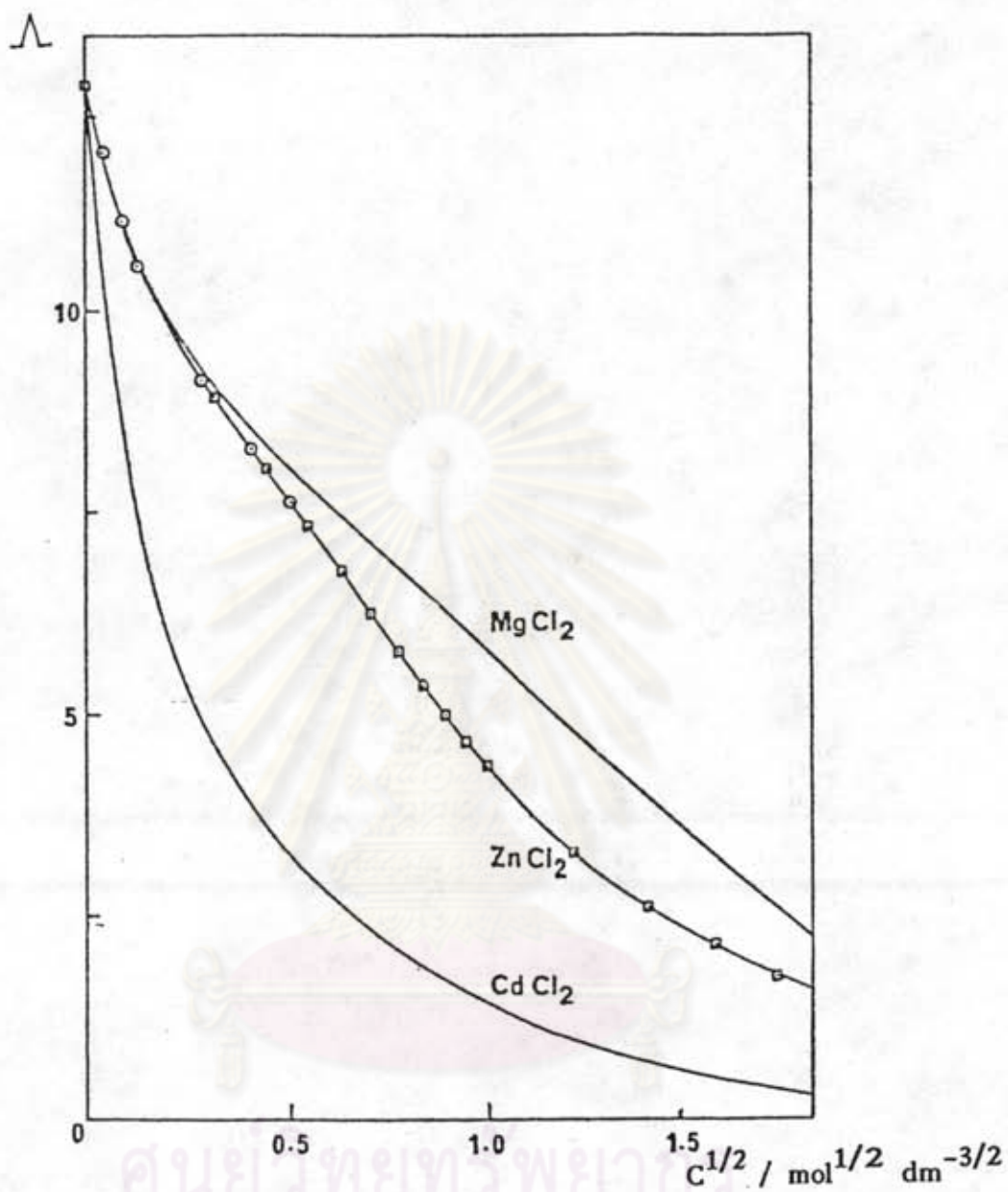


Figure 6.3 Plot of equivalent conductance (Λ) as a function of $C^{1/2}$ for aqueous $ZnCl_2$ solution at 25°C in comparison with values of values of $MgCl_2$ and $CdCl_2$

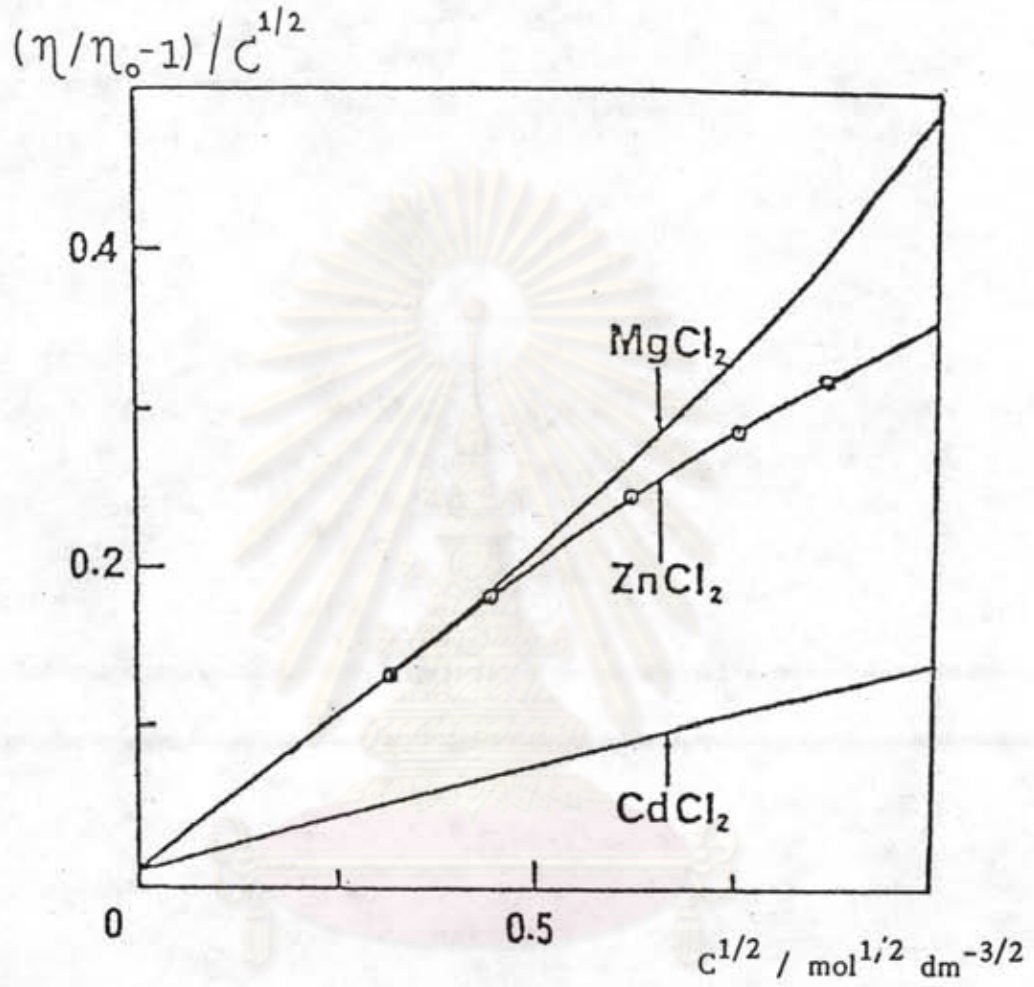


Figure 6.4 Plot of viscosity function against $c^{1/2}$ for aqueous ZnCl_2 solution in comparison with values of MgCl_2 and CdCl_2

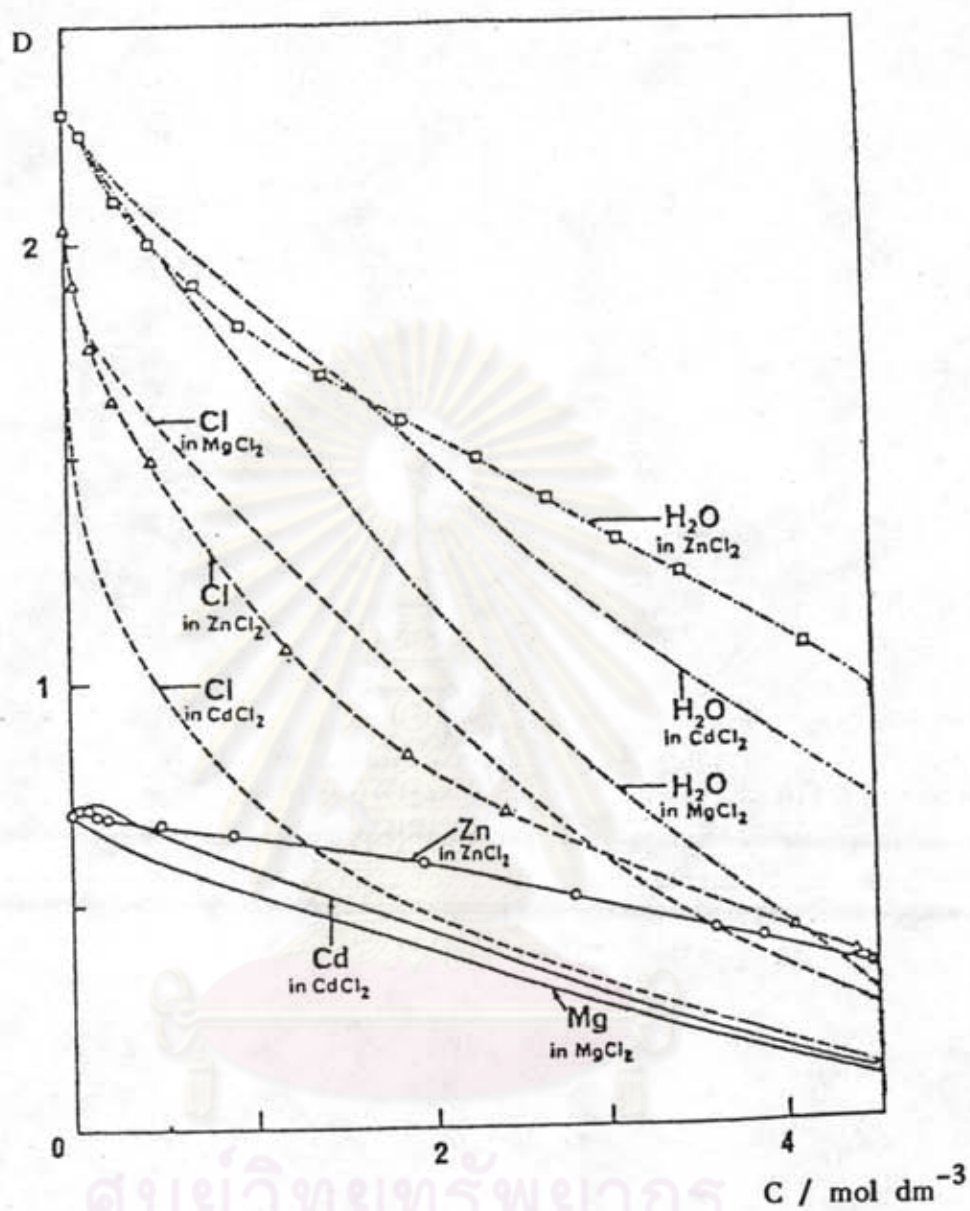


Figure 6.5 Plot of the self-diffusion coefficient (D) of H_2O , Zn and Cl constituent in aqueous ZnCl_2 solution against concentration (C) at 25°C in comparison with MgCl_2 and CdCl_2

1. In dilute concentration ($< 0.1 \text{ mol dm}^{-3}$) the equivalent conductance of ZnCl_2 system shows no indication of incomplete dissociation whereas that of CdCl_2 system obviously indicates ion association even in dilute concentration range.

2. Two points of inflection were observed at 0.1 mol dm^{-3} and 1 mol dm^{-3} , resulting in a small 'dip' in the conductivity curve of ZnCl_2 system.

3. At a higher concentration the conductance of ZnCl_2 passes a maximum at 2.5 mol dm^{-3} with $\kappa_{\text{max}} = 0.105 \Omega^{-1} \text{ cm}^{-1}$. This value is lower than those obtained for normal 2:1 electrolyte e.g. $\kappa_{\text{max}} (\text{MgCl}_2) = 0.340 \Omega^{-1} \text{ cm}^{-1}$ but higher than of CdCl_2 ($0.025 \Omega^{-1} \text{ cm}^{-1}$).

4. In the concentration range up to 0.1 mol dm^{-3} the viscosity for ZnCl_2 and MgCl_2 systems have identical slopes while that of CdCl_2 differs markedly.

5. The tracer diffusion coefficients of H_2O and of Cl^- for ZnCl_2 system are similar to those of MgCl_2 in the dilute concentration range whereas those of CdCl_2 show some departures.

6. A similar maximum was found for the cationic tracer diffusion coefficient in ZnCl_2 as in CdCl_2 system.

7. At 4 mol dm^{-3} the tracer diffusion coefficient of Zn and Cl constituents in ZnCl_2 are almost equal implying that the motion of the ionic constituents are strongly coupled (i.e., Zn and Cl in some complex).

8. The cationic transference number in ZnCl_2 becomes negative at 2 mol.kg^{-1} whereas in CdCl_2 , it occurs at a higher concentration (4 mol.kg^{-1}).

From these observations the following interpretation can be made. At 0.1 mol kg^{-1} ZnCl_2 solution the percentage distribution of species of Zn^{2+} , ZnCl^+ , ZnCl_2 , ZnCl_3^- and ZnCl_4^{2-} are 81.6%, 17.6%, 0.51%, 0.08% and 0.03% respectively. Within this concentration range the major species are therefore Zn^{2+} and ZnCl^+ . In the system of CdCl_2 , on the other hand, Cd^{2+} , CdCl^+ and CdCl_2 are the major species with percentage distribution of 23.2%, 65.2% and 11.0% respectively. It might thus be expected that in the dilute concentration range up to 0.1 mol kg^{-1} , the reduction in the conductivity of CdCl_2 system due to the production of the monovalent cation and the neutral complex species would be more pronounced than that in the ZnCl_2 system, where the neutral species amount to only 0.5%. Within this dilute concentration range, therefore, the observed conductance of ZnCl_2 does not show much effect due to autocomplexation and behaves more closely to the complete dissociated system. This also reflects in the viscosity as well as the water and ionic tracer diffusion coefficient for the concentration $< 0.1 \text{ mol dm}^{-3}$. From the cationic tracer diffusion experiment, however, the maximum at 0.05 mol dm^{-3} ZnCl_2 solution was found, which indicates the existence of the faster moving ZnCl^+ complex. This could be due to the different sensitivity of the methods in sensing the formation of complex.

Above this concentration up to 0.45 mol.kg^{-1} the concentration of ZnCl^+ rises to a maximum of 26.4% and then falls to 19.6% at 1.0 mol.kg^{-1} . This variation of ZnCl^+ concentration could be responsible for the small 'dip' and the two inflection points in the conductance curve of ZnCl_2 due to the partial reduction of charge.

At a higher concentration (above 1.0 mol kg^{-1}), the reduction of ZnCl^+ concentration is compensated by the production of the complex anions, ZnCl_3^- and ZnCl_4^{2-} . The conductance of the system thus rises to a maximum at 2.5 mol dm^{-3} and the cationic transference number also becomes negative at 2 mol kg^{-1} as a consequence of the high mobility of these complex anions. At this concentration the amount of ZnCl_4^{2-} complex reaches the maximum of 22%, while that of ZnCl_3^- is 20%. For CdCl_2 system, however, the percentage distributions of the anion complexes are considerably low being 9.2% for CdCl_3^- and virtually zero for CdCl_4^{2-} at 1.2 mol kg^{-1} CdCl_2 solution. At this concentration of ZnCl_2 solution, the percentage distribution of ZnCl_3^- and ZnCl_4^{2-} are 12% and 18% respectively. Therefore the cation transference number of CdCl_2 becomes negative at the concentration as high as 4 mol kg^{-1} . At this concentration, therefore one would expect most of Zn^{2+} to form complexes with the Cl^- , thus resulting in the almost equal value of tracer diffusion coefficient of the two constituents.

6.1.2 Zinc Bromide System

Sillén & Liljéquist (22) had also investigated the complex formation constants of zinc bromide by potentiometric method using liquid zinc amalgam electrode at constant ionic strength ($I = 3 \text{ mol dm}^{-3}$). Only the β_1^c value was obtained and was found to be 0.25 ± 0.04 . Converting our thermodynamic complex formation constant to the concentrationz constant at the same ionic strength gives $\beta_1^c = 0.10 \pm 0.01$. There was no indication of why the other complex formation steps has not been considered in the literature.

However, the author had anticipated that there should be higher complexes formed as in the case of ZnCl_2 system. Therefore the discrepancy of these data could be partly due to the omission of the other β^c values in obtaining the value of β_1^c in the literature.

The trend of the β values of ZnBr_2 is similar to those of ZnCl_2 . For ZnBr_2 system, however, the value of β_3 is very low (0.036). Both β_3 and β_4 values ($\beta_3 = 0.036$, $\beta_4 = 0.43$) are considerably lower than the value of β_2 (1.25). The value of β_1 of ZnBr_2 system (2.45) is also smaller than that of ZnCl_2 system (5.0).

The species distribution concentration of ZnBr_2 system (Fig.5.3) is generally similar to that of ZnCl_2 system. The percentage distribution of the complex species is somewhat lower due to the smaller values of β . In the dilute concentration range up to 0.1 mol kg^{-1} the major species are Zn^{2+} and ZnBr^+ . At this concentration the percentage distribution of Zn^{2+} , ZnBr^+ , ZnBr_2 , ZnBr_3^- , and ZnBr_4^{2-} are 90.2%, 9.4%, 0.5%, 0.03%, 0.01%, respectively. The amount of ZnBr^+ complex reaches a maximum of 14.8% at 0.45 mol kg^{-1} ZnBr_2 solution. At this concentration of ZnCl_2 solution the amount of ZnCl^+ complex is also at a maximum but with a larger proportion (26.4%). Above this concentration the amount of higher complexes become significant, whereas that of ZnBr^+ decreases.

At $\sim 1.0 \text{ mol kg}^{-1}$ the ZnBr_4^{2-} complex species predominates. The percentage species distribution of ZnBr^+ , ZnBr_2 , ZnBr_3^- and ZnBr_4^{2-} are 10.7%, 5.6%, 2.3% and 13% respectively. While the amount of ZnBr_3^- rises almost linearly with concentration, the

concentration of ZnBr_4^{2-} increases more rapidly until the maximum concentration is obtained at 2.7 mol kg^{-1} . At this concentration the species distribution of ZnBr^+ , ZnBr_2 , ZnBr_3^- and ZnBr_4^{2-} are 1.9%, 3.5% 16.9% and 26.2% respectively. This results from the β_4 value (0.43) being larger than the β_3 value (0.036). Similar behavior was found for ZnCl_2 system but at a lower concentration (2.0 mol kg^{-1}). Above 3.5 mol kg^{-1} one might expect a decrease in ZnBr_4^{2-} concentration and a continuous increase in ZnBr_3^- concentration. This behavior was found for ZnCl_2 system at the concentration above 2.2 mol kg^{-1} . The concentration of the neutral ZnBr_2 complex is consistently low for the whole concentration range studied as also observed in the ZnCl_2 system.

Including the data of the ZnBr_2 -KBr system in the analysis, the similar set of β values were obtained except for the slightly higher β_2' value. The concentration of the individual species in the plot of percentage distribution as a function of ionic strength (Fig.5.4) are somewhat higher than that for the ZnBr_2 system due to additional amount of bromide .

No data of the physical properties of aqueous ZnBr_2 system were found in the literature except for the cation transference number data (26). Fig. 6.6 compares the cationic transference number data as a function of $m^{1/2}$ for ZnCl_2 , ZnBr_2 , ZnI_2 and CdCl_2 systems. The three curves of the zinc systems are very similar. One might thus expect that the trend of the β values could also be the same. The fact that the cationic transference number of ZnBr_2 becomes negative at a higher concentration ($\sim 2.7 \text{ mol kg}^{-1}$) than that of ZnCl_2 ($\sim 2 \text{ mol kg}^{-1}$), normally implies that there is a

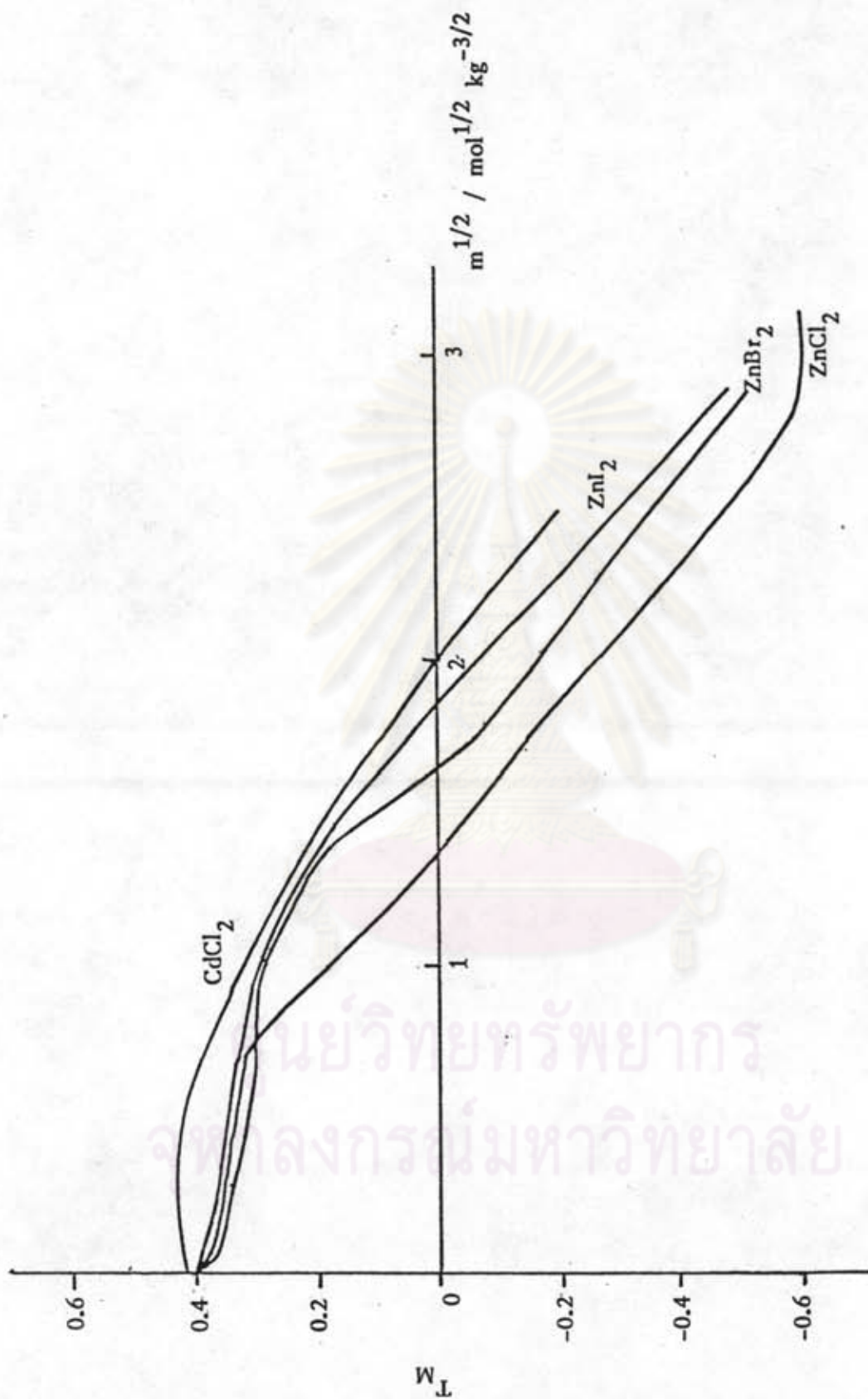


Figure 6.6 Plot of T_M ($M=\text{Cd}, \text{Zn}$) vs $m^{1/2}$ for CdCl_2 , ZnBr_2 , ZnCl_2 , ZnBr_2 , and ZnCl_2 system

lesser extent of complex anions formed in ZnBr_2 solution. This is conformed with the observed species distribution found in this work. The same argument can be applied for ZnI_2 system. It should also be noted that the concentration at which the cation transference numbers become negative coincides with the concentration maxima of the divalent anion complexes of the corresponding salts.

6.2 Conclusion

In the present work, the complex formation of ZnCl_2 and ZnBr_2 systems were investigated by potentiometric method. From the analysis of the data, the values of the complex formation constants of the systems were evaluated and were found to be,

$\beta_1 = 5.00 \pm 0.10$, $\beta_2 = 1.30 \pm 0.10$, $\beta_3 = 0.96 \pm 0.04$, $\beta_4 = 1.00 \pm 0.03$
for ZnCl_2 system and

$\beta_1 = 2.45 \pm 0.05$, $\beta_2 = 1.25 \pm 0.05$, $\beta_3 = 0.36 \pm 0.00$, $\beta_4 = 0.43 \pm 0.01$
for ZnBr_2 system.

It is now obvious that similar trends were found for the β values of ZnCl_2 and ZnBr_2 systems .i.e.,

$$\beta_1 > \beta_2 > \beta_3 < \beta_4$$

The species distributions of the two systems also have similar features. However the complex formation of ZnBr_2 system occurs in a lesser extent. In a dilute concentration up to 0.1 mol kg^{-1} the major species are Zn^{2+} , ZnX^+ and X^- ($\text{X}^- = \text{Cl}^-$, Br^-). Moreover, the concentration of the neutral ZnX_2 species is always very low. The

contributions of the complex formations to the solution properties (conductance, viscosity, etc.) are thus less than those normally observed for associated salts. Consequently, the solutions of ZnX_2 may well behave more like a complete dissociated salts in this concentration range. At a higher concentration, the amount of the monovalent cation rises to a maximum, which occurs at about the same concentration ($\sim 0.45 \text{ mol kg}^{-1}$). This could be responsible for the small 'dip' in the conductivity curve. Above 1.0 mol kg^{-1} the anion complexes are the dominating species. The divalent anion complex (ZnX_4^{2-}) predominates in the lower concentration range while the monovalent anion complex (ZnX_3^-) becomes more significant at a high concentration. The substantial production of these complex anions causes the cation transference numbers to be negative. From our results, the maximum concentrations of the divalent anion complexes for both systems occur at the salt concentrations where the cationic transference numbers become negative, i.e., 2.0 mol kg^{-1} for $ZnCl_2$ and 2.7 mol kg^{-1} for $ZnBr_2$.

Including the data of ZnX_2 - KX systems in the analysis delivers the same values of β_1 , β_2 and β_3 as for ZnX_2 alone. The value of β_4 for $ZnCl_2$ system, however shows a considerable shift. This could imply the inadequacy of the model used in the analysis of the data for the evaluation of the β_4 . It should thus be worthwhile to further investigate the system with a larger X:Zn ratios and allowing for the formation of higher complex in the analysis.