INTRODUCTION
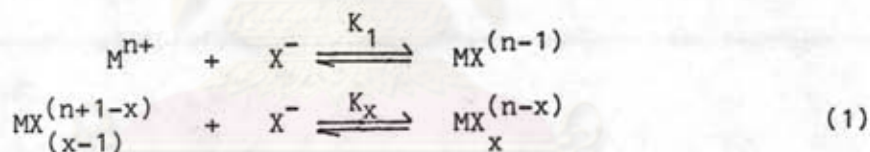
In many of the halides of heavy metals, particularly the halides of cadmium, zinc, copper, and mercury, ion-pair formation is followed by further association and negatively charged species is formed until the coordination shell is completed. The evidence for the existence of the complex species[1] of formula $MX_x^{(n-x)}$ (where x=1,2,..), has been shown by X-ray [2], Raman [3], and vapor pressure [4] studies. The complex formation is usually thought of as involving the following stepwise processes,

$$M^{n+} + X^- \underset{}{\overset{K_1}{\rightleftharpoons}} MX^{(n-1)}$$
$$MX_{(x-1)}^{(n+1-x)} + X^- \underset{}{\overset{K_x}{\rightleftharpoons}} MX_x^{(n-x)} \qquad (1)$$

M = Cd, Zn, Cu and Hg

$X^- = Cl^-, Br^-, I^-$ and F^-

For halide complexation of Cd, Zn, Cu and Hg, where n=2, the maximum halide coordination number (x) is 4. For example, $ZnCl_2$ in solution forms complex species $ZnCl^+$, $ZnCl_2$, $ZnCl_3^-$ and $ZnCl_4^{2-}$. Omitted from equation(1) are the hydrations associated with the ionic species in aqueous solutions, which normally complete the coordination sites up to about 4-6 around the ions.

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 for normal 2:1 electrolytes such as $CaCl_2$ and $BaCl_2$. At high concentrations of these solutions, the cation transference number decreases rapidly to zero, then becomes negative. This is again in marked contrast to the behavior of the transference numbers of normal 2:1 electrolytes such as $MgCl_2$, $CaCl_2$ and $Zn(ClO_4)_2$. The appearance of the negative cation constituent transference numbers in concentrated solutions can be explained if a large proportion of the metal is present as complex negative ions. Though no quantitative treatment of the effect can be given, it would appear that to give a negative transference number for the metal ion-constituent, the complex anion must have a higher mobility than the normal hydrated metal ion. This results in a net transfer of the metal ion-constituent towards the anode in transference number experiments.

In the dilute solutions, complex anions exist in a lesser proportion and the observed cation transference numbers of these electrolytes rise smoothly with decreasing concentration (5,6). Below certain concentrations, these values vary only slightly with concentration and either become constant or pass through a maximum. The latter behavior was found for some halides of cadmium and zinc (7).

The halide complexes of zinc are of interest as it represents an intermediate step in the transition from typical strong electrolytes, such as the alkaline earth halides to salts like cadmium halides in which ion association shows an important effect. Weingartner, et al. (8) have reinvestigated the transport properties such as conductance, viscosity and tracer-diffusion

coefficients (of cation, anion and water) of aqueous $ZnCl_2$ solutions. The effect of ion association in aqueous $ZnCl_2$ solutions are discussed by comparison with aqueous $MgCl_2$, and $CdCl_2$. It was found that the $ZnCl_2-H_2O$ system is characterized by the unexpectedly fast molecular motions and a " dip " in the concentration dependence of the equivalent conductance, viscosity, and self diffusion coefficient of water, which had not yet been observed for other systems. Furthermore, the onset of complex formation acts differently with various transport coefficients. The conductance and viscosity of this system showed no indication of complex formation at low concentration (< 0.1 M.), while the data of the cationic tracer diffusion was similar to those of $CdCl_2$ system implying some complexation.

Conventionally a set of complex formation constants for the complex equilibria

$$Zn^{2+} + nX^- \xrightleftharpoons{\beta_n} ZnX_n^{(2-n)} \qquad n=1,2,3,4$$
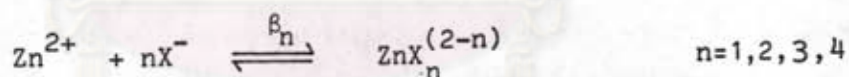
is used to describe complex formation. Using this convention, the complex formation constants of zinc chloride have been extensively studied by a variety of methods and under variable experimental conditions. Most of the works have been carried out in the presence of supporting electrolytes such as perchlorate ions, the assumption being that the activity coefficients of ionic species were kept constant, Therefore, these complex formation constants can only be compared with systems of the same ionic strength. In order to avoid this restriction, the thermodynamic complex formation constants are

required. The method of determination of these constants was introduced by Rielly and Stokes, and had been used for cadmium chloride system (9).

In the present work, the complex formation constants of zinc chloride and zinc bromide in aqueous solutions from 0.001 to 3.5 $mol.kg^{-1}$ were determined by the electromotive force measurements of the cell;

$$Zn-Hg \ / \ ZnX_2 \ (m) \ / \ AgX,Ag$$
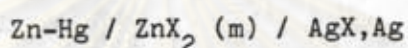
To allow for a higher complexation the solution of potassium halide (KX) was added into zinc halide solutions (ZnX_2) with Zn : X ratios from 1:2 to 1:20.

The method of analysis adopted by Rielly and Stokes was used to determine the complex formation constants of these systems.