CHAPTER V

ANALYSIS OF THE DATA

5.1 Method of Analysis

The complex formation constants of the aqueous zinc halide complexes were determined by the computational method which was introduced by Rielly and Stoke (9). The computational process requires the emf data from the cell of the type

$$\text{Zn-Hg} \;/\; ZnX_2\,(m_1),\; KX(m_2) \;/\; AgX, Ag \qquad \text{(I)}$$

the cell potential which is defined by

$$E_{cell} = E^{\circ}_{cell} - (k/2)\ \ln(m_1)(2m_1+m_2)^2\ \gamma^3 \qquad (17)$$

and is also given by

$$E_{cell} = E^{\circ}_{cell} - (k/2)\ \ln[\,Zn^{2+}\,][\,X^-\,]^2 \cdot \gamma^3_{21} \qquad (18)$$

where k equals RT/F , m_1 and m_2 are molal concentration and γ is the mean molal activity coefficient of the zinc and halide in the solution. This formal activity coefficient becomes the stoichiometric mean molal activity coefficient $\gamma_\pm$ of aqueous zinc halide when m_2 is zero (no potassium halide is present). $[\,Zn^{2+}\,]$

and [X^-] are the molal concentrations of the free ions at equilibrium (mol kg^{-1}) and γ_{21} is the activity coefficient of the non complexed zinc halides.

In aqueous solutions, a series of four complex equilibria occur, which are given by

$$Zn^{2+} + nX^- \underset{}{\overset{\beta_n}{\rightleftharpoons}} ZnX_n^{2-n} \qquad n = 1,2,3,4 \qquad (19)$$

The corresponding complex formation constants, β_n , are defined by

$$\beta_n = (ZnX_n^{2-n}) / (Zn^{2+})(X^-)^n \qquad (20)$$

(curve brackets indicate activities)

The corresponding concentration quotients Y_n are defined

$$Y_n = [ZnX_4^{2-n}] / [Zn^{2+}][X^-]^n \qquad (21)$$

It can be shown that

$$\beta_1 = Y_1 \gamma_{11}^2 / \gamma_{21}^3 \quad ; \quad \beta_2 = Y_2 \gamma_0 / \gamma_{21}^3$$
$$\beta_3 = Y_3 / \gamma_{21}^3 \quad ; \quad \beta_4 = Y_4 \gamma_{12}^3 / \gamma_{21}^3 \gamma_{11}^4 \qquad (22)$$

In eq.18 , γ_{ik} coefficients represent molal activity coefficients of the component dissociated electrolyte, with cationic valency i and anionic valency k and γ_0 is the coefficient of the neutral complex (ZnX_2).

There are several relations between the concentrations of the various species present in the solution.They are as followed. Firstly, the relations for the conservation of mass,

$$m_1 = \text{total zinc} = [Zn^{2+}] + \sum_{n=1}^{4} [ZnX_n^{2-n}] \qquad (23)$$

$$(2m_1 + m_2) = \text{total halide} = [X^-] + \sum_{n=1}^{4} n[ZnX_n^{2-n}] \qquad (24)$$

and

$$m_1 = [Zn^{2+}]\{1 + \sum_{n=1}^{4} Y_n [X^-]^n\} \qquad (25)$$

$$(2m_1 + m_2) = [X^-] + [Zn^{2+}] \sum_{n=1}^{4} nY_n [X^-]^n \qquad (26)$$

secondly for electroneutrality (neglecting the concentration of free hydrogen and hydroxyl ions and the small amounts of the hydrolysis products),

$$2[Zn^{2+}] + [ZnX^+] + m_2 = [X^-] + [ZnX_3^-] + 2[ZnX_4^{2-}] \qquad (27)$$

and thirdly, the ionic strength of the solution ,

$$I = 0.5(4[Zn^{2+}] + [ZnX^+] + [ZnX_3^-] + 4[ZnX_4^{2-}] + [X^-] + m_2) \qquad (28)$$

Equation 25 and 26 may be combined to give a fifth order polynomial, expressing free halide concentration in terms of concentration quotients and known concentrations

$$a[X^-]^5 + b[X^-]^4 + c[X^-]^3 + d[X^-]^2 + e[X^-] + f = 0 \qquad (29)$$

where

$$a = Y_4$$
$$b = Y_3 + Y_4 [\, 4m_1 - (\, 2m_1 + m_2 \,)\,]$$
$$c = Y_2 + Y_3 [\, 3m_1 - (\, 2m_1 + m_2 \,)\,]$$
$$d = Y_1 + Y_2 [\, 2m_1 - (\, 2m_1 + m_2 \,)\,]$$
$$e = 1 + Y_1 [\, m_1 - (\, 2m_1 + m_2 \,)\,]$$
$$f = -(\, 2m_1 + m_2 \,)$$

The values of free zinc and halide concentrations are restricted by the combined equation of 17 and 18, and one given as

$$m_1 (2m_1 + m_2)^2 \gamma^3 = [\, Zn^{2+}][\, X^-]^2 \gamma_{21}^3 \qquad (30)$$

It was assumed that activity coefficients may be expressed by extended Debye-Hueckel equations (eq.31a - d),

$$\log \gamma_{21} = -1.023I^{1/2} / (\, 1+A_{21} I^{1/2}) + BI + B'I^2 + B''I^3 \qquad (31a)$$

$$\log \gamma_{11} = -0.5115I^{1/2} / (\, 1+A_{11} I^{1/2}) + BI + B'I^2 + B''I^3 \qquad (31b)$$

$$\log \gamma_0 = BI + B'I^2 + B''I^3 \qquad (31c)$$

$$\log \gamma_{12} = -1.023I^{1/2} / (\, 1+A_{12} I^{1/2}) + BI + B'I^2 + B''I^3 \qquad (31d)$$

where $A_{21} = ba^{\circ}_{21}$, $A_{11} = ba^{\circ}_{11}$ and $A_{12} = ba^{\circ}_{12}$ with b= 0.3291 at 298.15°K and a°_{ik} the corresponding distance of closest approach (A).

The input parameters are E and the corresponding total concentrations of zinc and halide. Initially, the value of E° must be determined, the procedure of which is described in section 5.1.1. Then four complex formation constants of eq.20 and fifteen unknown parameters in the Debye-Hueckel activity coefficients (eq.31) are evaluated by the procedure described in section 5.1.2.

5.1.1 The Determination of the Standard Potential, E°, of the Cell (I)

For determination of E° ,the concentration of KX,m_2 was set to zero while the concentration of the zinc halide,m_1, was less than 0.1. In this concentration range, there is little possibility of self complexing of the salt. The square and the higher powers of the halide in equations 25 and 26 can thus be neglected, i.e., one needs only to consider the species Zn^{+}, ZnX^{+}, and X^{-}. Thus ,

$$m_1 = [\ Zn^{2+}\ ](\ 1 + \beta_1\ [\ X^-\ ]\ \gamma^3_{21}\ /\ \gamma^2_{11}\ ) \quad (32)$$

$$2m_1 = [\ X^-\ ](\ 1 + \beta_1\ [\ Zn^{2+}\ ]\ \gamma^3_{21}\ /\ \gamma^2_{11}\ ) \quad (33)$$

and
$$I = 0.5\ (\ 4\ [\ Zn^{2+}\ ] + [\ ZnCl^+\ ] + [\ Cl^-\ ]\ ) \quad (34)$$

The calculation procedure requires initial assumption about ionic strength. In this case, the ionic strength of fully dissociated 2:1 electrolyte at the same concentration was used as an initial guess. The chosen value of β_1 , and the starting values of the parameters in the extended Debye-Hueckel eqs.31a and 31b were used to calculate the approximate value of chloride concentration for each point (eqs.32 and 33). The concentration of Zn^{2+} and $ZnCl^{+}$ were computed from eq.24 and a new value of the ionic strength was obtained from eq.34. With this improved estimation of ionic strength, the calculation was repeated until the ionic strength was constant to 0.01%. The concentration of Zn^{2+} and Cl^{-} were then obtained and the value of E^{o} was evaluated from eq. 18. This procedure was applied to all data points and the standard deviation of the E^{o} values was calculated. All parameters were then optimized to give the appropriate value of E^{o} with the lowest standard deviation. The flow chart and the programme used for this procedure is given in Appendix (II).

5.1.2 The Determination of the Complex Formation Constants

In the system of ZnX_2 , each complex formation constant was adjusted separately, the procedure of which is described as followed.

1. The value of β_1 was obtained from the evaluation of E^{o} as described in section 5.1.1. The working concentration range was 0.001-0.1 $mol.kg^{-1}$.

2. By fixing the value of β_1, the value of β_2 was evaluated from the data of the solution concentration up to 0.5 $mol.kg^{-1}$. Within this limit, the effect of the anion complexes was assumed to be negligible. The initial guess of β_2, ionic strength and a,B parameters in the Debye-Hueckel expression (eq.31) were used

to calculate the halide concentration from the pentic equation (eq.29). The Bairstow's method (19) was employed, the procedure of which is shown in Appendix (I). The species concentrations were then computed from eq.(24) and the new value of ionic strength was obtained from eq.(28). The calculation was repeated until the ionic strength was constant to within 0.01%. The resulting values of zinc, halide concentrations and the activity coefficient values were then used in eq.(18) to calculate the emf. All parameters were optimized until the minimum standard deviation between the calculated and the measured emf.s (E) was obtained. The remaining, B' and B'' parameters in the extended Debye-Hueckel (eq. 31) were then adjusted to obtain the lower standard deviation. Finally the values of β_1 and β_2 were adjusted together.

3. Following the above procedure the value of β_3 was obtained by extending the concentration range of solution up to 1.5 $mol.kg^{-1}$. Above this concentration, the value of β_4 was determined.

4. Finally, the value of $\beta_1, \beta_2, \beta_3, \beta_4$ and all other parameters in eq.(31) were optimized simultaneously by using the Rosenbrock subroutine.

The above analysis was repeated for the data including the ZnX_2-KX systems. All parameters obtained from the analysis of ZnX_2 systems were used as initial guesses. The procedures for the calculation of the emf and for the evaluation of the complex formation constants were the same as previously described.

5.2 Results of Analysis

5.2.1 Zinc Chloride System

The standard potential of the cell

$$Zn\text{-}Hg\ /\ ZnCl_2\ (m)\ /\ AgCl,Ag \qquad (II)$$

was calculated by the method described in section 5.1.1. This gives $E^{\circ}_{cell} = 0.9838_7$ V. with $\sigma = 0.0002_5$ V. The standard electrode potential of zinc electrode, E°_{Zn} ($= E^{\circ}_{Ag,AgCl} - E^{\circ}_{cell}$) of -0.7616_3 V. is thus obtained. Using the same method, Lutfullah and Paterson (20) found these values to be 0.98428 V. and −0.76194 V., with σ =0.00015 V. They are in reasonable agreement.

Using our standard potential values in the analysis of the data, the complex formation constants were found to be

$$\beta_1 = 5.00 \pm 0.10 \qquad \beta_2 = 1.30 \pm 0.10$$
$$\beta_3 = 0.96 \pm 0.04 \qquad \beta_4 = 1.00 \pm 0.03$$

The parameters of the activity coefficients in the Debye-Hueckel equation are given in table 5.1.

Table 5.1 Activity coefficient parameters of the extended Debye-Hueckel equations in system of $ZnCl_2$.

log	a	B	B'	B''
γ_{21}	4.13	0.19551	0.00437	0.00025
γ_{11}	4.51	0.29374	0.00131	-0.00050
γ_0	-	0.31245	0.00140	0.00060
γ_{12}	4.85	0.41682	0.00175	-0.00120

The measured and calculated emf.s of the cell (II) as a function of $ZnCl_2$ concentrations are assembled in Table 5.2. The concentration of species in $ZnCl_2$ solutions are shown in Table 5.3. The graphical representation of the percentage* distribution of species as a function of total zinc concentrations is given in Fig 5.1 .

* percentage distribution of species = $[ZnX_n^{(2-n)}] \times 100 / m_{ZnX_2}$ %

Table 5.2 The measured and calculated emf.s of the cell (II) as a function of $ZnCl_2$ concentrations.

m_{ZnCl_2} mol.kg^{-1}	I mol.kg^{-1}	$E_{measd.}$ V.	$E_{cald.}$ V.	ΔE V.
0.00098	0.00293	1.2378	1.2377	-0.0001
0.00294	0.22871	1.1988	1.1985	-0.0003
0.00366	0.01081	1.1910	1.1909	-0.0001
0.00442	0.01303	1.1841	1.1844	0.0003
0.00508	0.01494	1.1793	1.1796	0.0003
0.00735	0.02148	1.1672	1.1671	-0.0001
0.00827	0.02411	1.1632	1.1631	-0.0001
0.01039	0.03014	1.1555	1.1556	0.0001
0.01204	0.03480	1.1504	1.1507	0.0003
0.01549	0.04446	1.1423	1.1424	0.0001
0.02052	0.05839	1.1331	1.1333	0.0002
0.02201	0.06248	1.1308	1.1311	0.0003
0.03017	0.08464	1.1206	1.1210	0.0004
0.04243	0.11731	1.1096	1.1101	0.0005
0.05913	0.16078	1.0993	1.0996	0.0003
0.06549	0.17708	1.0960	1.0963	0.0003
0.08327	0.22198	1.0883	1.0886	0.0003
0.09203	0.24376	1.0850	1.0854	0.0004
0.10352	0.27202	1.0812	1.0816	0.0004
0.15817	0.40201	1.0673	1.0675	0.0002
0.19300	0.48123	1.0604	1.0608	0.0004
0.23171	0.56626	1.0545	1.0545	0.0000
0.32792	0.76360	1.0433	1.0427	-0.0005

continue

m_{ZnCl_2} mol.kg^{-1}	I mol.kg^{-1}	$E_{measd.}$ V.	$E_{cald.}$ V.	ΔE V.
0.37307	0.84987	1.0386	1.0385	-0.0001
0.49003	1.05811	1.0300	1.0298	-0.0002
0.54438	1.14879	1.0270	1.0267	-0.0003
0.60653	1.24910	1.0233	1.0235	0.0002
0.68557	1.37261	1.0200	1.0200	0.0000
0.78735	1.52604	1.0158	1.0162	0.0004
0.84448	1.60997	1.0137	1.0142	0.0005
0.89037	1.67644	1.0124	1.0128	0.0004
0.93123	1.73494	1.0113	1.0115	0.0002
0.97995	1.80414	1.0096	1.0101	0.0005
1.09970	1.97069	1.0065	1.0069	0.0004
1.29993	2.24068	1.0017	1.0021	0.0004
1.40031	2.37245	0.9994	0.9999	0.0005
1.50247	2.50412	0.9970	0.9977	0.0007
1.60265	2.63108	0.9953	0.9957	0.0004
1.70085	2.75384	0.9935	0.9939	0.0004
1.89969	2.99624	0.9899	0.9903	0.0004
1.98896	3.10266	0.9886	0.9887	0.0001
2.07495	3.20383	0.9870	0.9873	0.0003
2.34061	3.50781	0.9830	0.9831	0.0001
2.61177	3.80660	0.9789	0.9791	0.0002
2.94767	4.16261	0.9743	0.9744	0.0001
3.22138	4.44181	0.9710	0.9709	-0.0001

The standard deviation of emf.(σ_{emf}) is 0.0003 V.

$$\Delta E = E_{cald.} - E_{measd.}$$

Table 5.3 The molal concentrations of the individual species in aqueous $ZnCl_2$ solutions.

m_{ZnCl_2} mol.kg^{-1}	$[Zn^{2+}]$	concentration of species (mol kg^{-1})				
		$[ZnCl^+]$	$[ZnCl_2]$	$[ZnCl_3^-]$	$[ZnCl_4^{2-}]$	$[Cl^-]$
0.00098	0.00097	0.00001	0.00C00	0.00000	0.00000	0.00000
0.00294	0.00288	0.00006	0.00000	0.00000	0.00000	0.00528
0.00366	0.00358	0.00008	0.00000	0.00000	0.00000	0.00724
0.00442	0.00430	0.00012	0.00000	0.00000	0.00000	0.00430
0.00508	0.00493	0.00015	0.00000	0.00000	0.00000	0.01001
0.00735	0.00706	0.00028	0.00000	0.00000	0.00000	0.01441
0.00827	0.00792	0.00035	0.00000	0.00000	0.00000	0.01519
0.01039	0.00987	0.00051	0.00000	0.00000	0.00000	0.02026
0.01204	0.01138	0.00066	0.00000	0.00000	0.00C00	0.02342
0.01549	0.01449	0.00100	0.00001	0.00000	0.00000	0.02997
0.02052	0.01894	0.00157	0.00001	0.00000	0.00000	0.03945
0.02201	0.02024	0.00176	0.00001	0.00000	0.00000	0.04224
0.03017	0.02725	0.00289	0.00003	0.00000	0.00000	0.05729
0.04243	0.03747	0.00489	0.00006	0.00000	0.00000	0.07982
0.05913	0.05090	0.00807	0.00014	0.00001	0.00000	0.10986
0.06549	0.05589	0.00939	0.00018	0.00002	0.00000	0.12116
0.08327	0.06953	0.01337	0.00032	0.00004	0.00001	0.15236
0.09203	0.07609	0.01546	0.00040	0.00006	0.00002	0.16755
0.10352	0.08456	0.01831	0.00053	0.00009	0.00003	0.18727
0.15817	0.12283	0.03329	0.00144	0.00039	0.00022	0.27812
0.19300	0.14586	0.04369	0.00230	0.00080	0.00054	0.33317
0.23171	0.16978	0.05567	0.00351	0.00153	0.00122	0.39127
0.32792	0.22418	0.08560	0.00763	0.00507	0.00543	0.51803
0.37307	0.24727	0.09895	0.01000	0.00775	0.00910	0.56753

continue

m_{ZnCl_2} mol.kg^{-1}	$[Zn^{2+}]$	concentration of species (mol kg^{-1})				
		$[ZnCl^{+}]$	$[ZnCl_2]$	$[ZnCl_3^{-}]$	$[ZnCl_4^{2-}]$	$[Cl^{-}]$
0.49003	0.30129	0.12972	0.01680	0.01778	0.02443	0.66566
0.54438	0.32420	0.14200	0.02010	0.02383	0.03425	0.69807
0.60653	0.34914	0.15458	0.02387	0.03171	0.04723	0.72667
0.68557	0.37937	0.16857	0.02860	0.04306	0.06598	0.75221
0.78735	0.41643	0.18390	0.03450	0.05965	0.09288	0.77134
0.84448	0.43655	0.19140	0.03771	0.06985	0.10896	0.77673
0.89037	0.45244	0.19695	0.04023	0.07850	0.12225	0.77883
0.93123	0.46677	0.20159	0.04241	0.08642	0.13404	0.77872
0.97995	0.48284	0.20672	0.04501	0.09650	0.14887	0.77816
1.09970	0.52250	0.21801	0.05114	0.12279	0.18527	0.76968
1.29993	0.58694	0.23361	0.06073	0.17231	0.24634	0.74249
1.40031	0.61858	0.24031	0.06526	0.19972	0.27644	0.72486
1.50247	0.65041	0.24658	0.06970	0.22935	0.30643	0.70520
1.60265	0.68131	0.25231	0.07389	0.26009	0.33505	0.68474
1.70085	0.71132	0.25758	0.07784	0.29186	0.36225	0.66887
1.89969	0.77136	0.26763	0.08538	0.36091	0.41441	0.62061
1.98896	0.79801	0.27195	0.08858	0.39393	0.43648	0.60108
2.07495	0.82353	0.27605	0.09155	0.42689	0.45693	0.58236
2.34061	0.90144	0.28861	0.10007	0.53548	0.51501	0.52600
2.61177	0.97959	0.30169	0.10774	0.65629	0.56646	0.47165
2.94767	1.07453	0.31895	0.11586	0.81846	0.61987	0.40981
3.22138	1.15042	0.33441	0.12138	0.95940	0.65577	0.36432

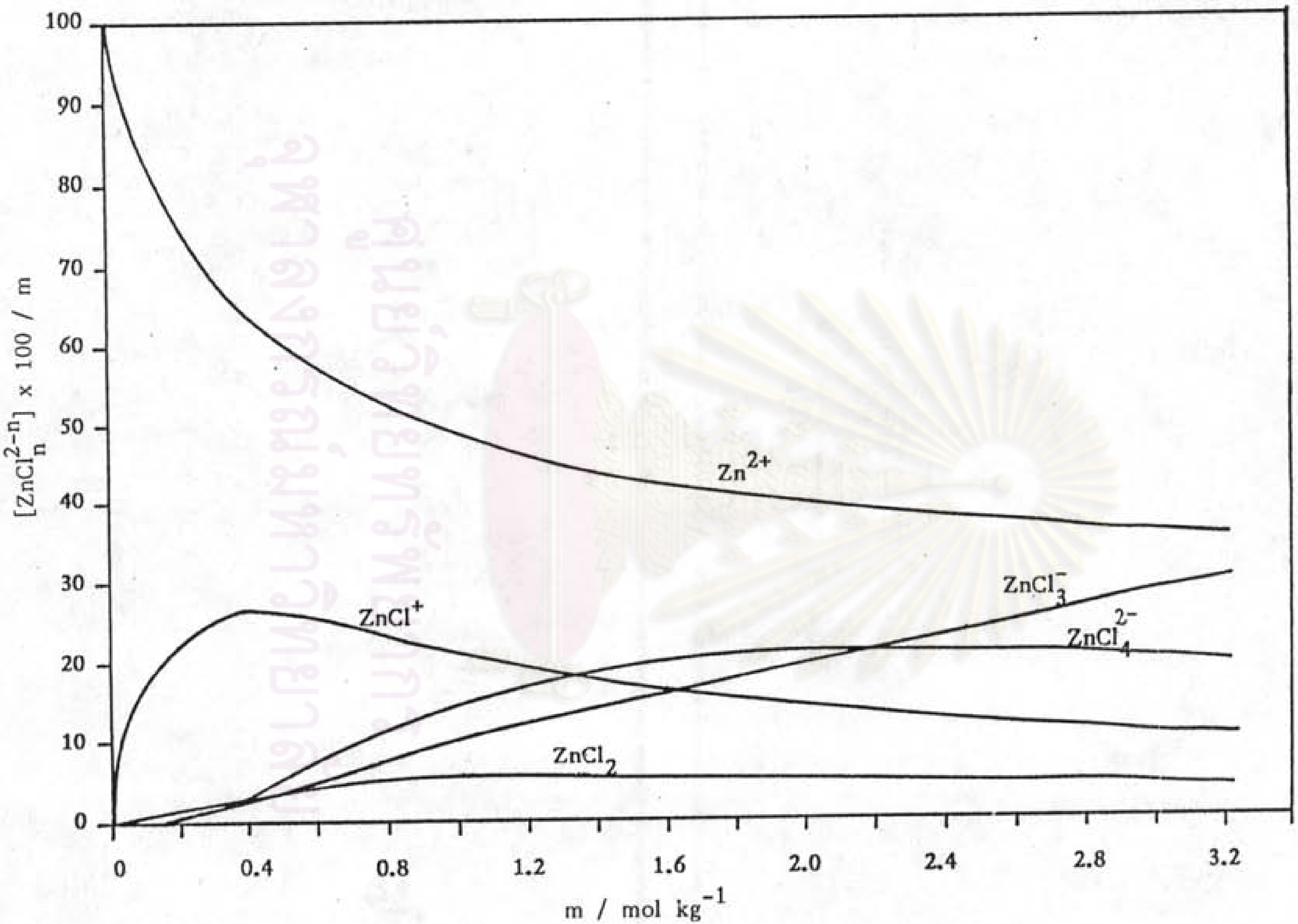

Figure 5.1 The percentage distribution of free and complexed zinc as a function of the molal concentration of zinc chloride

Including the data of $ZnCl_2$-KCl mixture in the analysis delivers the following complex formation constants

$$\beta_1 = 4.95 \pm 0.05 \qquad \beta_2 = 1.10 \pm 0.30$$

$$\beta_3 = 0.94 \pm 0.01 \qquad \beta_4 = 2.55 \pm 0.10$$

The parameters of the activity coefficients in the Debye-Hueckel equation are shown in table 5.4

Table 5.4 Activity coefficient parameters of the extended Debye-Hueckel equations in system of $ZnCl_2$ and $ZnCl_2$-KCl mixture.

log	a	B	B'	B''
γ_{21}	3.90	0.18000	0.00057	0.00025
γ_{11}	4.41	0.30000	0.00177	-0.00050
γ_0	-	0.47500	-0.00288	0.00060
γ_{12}	4.96	0.49844	0.00080	-0.00120

The measured and calculated emfs. of the cell Zn-Hg / $ZnCl_2$ (m_1), KCl (m_2) / AgCl,Ag are shown in table 5.5. The concentration of the species in $ZnCl_2$ solutions and $ZnCl_2$-KCl mixtures are shown in table 5.6. The graphical representation of the percentage distribution of species as a function of ionic strength is given in Fig.5.2.

Table 5.5 The measured and calculated emf.s of the cell

Zn-Hg / $ZnCl_2$ (m_1), KCl (m_2) / AgCl, Ag

m_1 mol kg^{-1}	$2m_1+m_2$ mol kg^{-1}	I mol kg^{-1}	$E_{measd.}$ V.	$E_{cald.}$ V.	ΔE V.
0.00098	0.00196	0.00293	1.2378	1.2378	-0.0000
0.00294	0.00588	0.00871	1.1988	1.1986	-0.0002
0.00366	0.00732	0.01081	1.1910	1.1910	-0.0000
0.00442	0.00884	0.01303	1.1841	1.1845	0.0004
0.00508	0.01016	0.01494	1.1793	1.1797	0.0004
0.00735	0.01470	0.02149	1.1672	1.1672	0.0001
0.00827	0.01654	0.02412	1.1632	1.1633	0.0001
0.01039	0.02078	0.03016	1.1555	1.1557	0.0002
0.01204	0.02408	0.03483	1.1504	1.1509	0.0005
0.01549	0.03098	0.04452	1.1423	1.1427	0.0004
0.02052	0.04104	0.05849	1.1331	1.1336	0.0005
0.02201	0.04402	0.06259	1.1308	1.1314	0.0006
0.03017	0.06034	0.08485	1.1206	1.1213	0.0007
0.04243	0.08486	0.11776	1.1096	1.1106	0.0010
0.05913	0.11826	0.16172	1.0993	1.1001	0.0008
0.06549	0.13098	0.17823	1.0960	1.0969	0.0009
0.08327	0.16654	0.22388	1.0883	1.0892	0.0009
0.09203	0.18406	0.24610	1.0850	1.0860	0.0010
0.10352	0.20704	0.27502	1.0812	1.0822	0.0010
0.15817	0.31634	0.40911	1.0673	1.0683	0.0010
0.19300	0.38600	0.49190	1.0604	1.0617	0.0013
0.23171	0.46342	0.58155	1.0545	1.0555	0.0010

continue

m_1 mol kg^{-1}	$2m_1+m_2$ mol kg^{-1}	I mol kg^{-1}	$E_{measd.}$ V.	$E_{cald.}$ V.	ΔE V.
0.32792	0.65584	0.79358	1.0433	1.0438	0.0005
0.37307	0.74614	0.88817	1.0386	1.0395	0.0010
0.49003	0.98006	1.12015	1.0300	1.0309	0.0009
0.54438	1.08876	1.22301	1.0270	1.0277	0.0007
0.60653	1.21305	1.33721	1.0233	1.0245	0.0012
0.68557	1.37114	1.47826	1.0200	1.0208	0.0008
0.78735	1.57470	1.65382	1.0158	1.0168	0.0010
0.84448	1.68892	1.74993	1.0137	1.0147	0.0010
0.89037	1.78074	1.82601	1.0124	1.0138	0.0008
0.93123	1.86246	1.89296	1.0113	1.0119	0.0006
0.97995	1.95990	1.97149	1.0096	1.0104	0.0008
1.09970	2.19940	2.16081	1.0065	1.0070	0.0005
1.29993	2.59986	2.46606	1.0017	1.0020	0.0003
1.40031	2.80062	2.61445	0.9994	0.9997	0.0003
1.50247	3.00494	2.76279	0.9970	0.9976	0.0006
1.60265	3.20530	2.90550	0.9953	0.9956	0.0003
1.70085	3.40170	3.04406	0.9935	0.9937	0.0002
1.89969	3.79938	3.31973	0.9899	0.9902	0.0003
1.98896	3.97792	3.44235	0.9886	0.9887	0.0001
2.07495	4.14990	3.55957	0.9870	0.9873	0.0003
2.34061	4.68122	3.92196	0.9830	0.9833	0.0003
2.61177	5.22354	4.29525	0.9789	0.9795	0.0006
2.94767	5.89534	4.78084	0.9743	0.9751	0.0008
3.22138	6.44276	5.21267	0.9710	0.9716	0.0006

continue

m_1 mol kg^{-1}	$2m_1+m_2$ mol kg^{-1}	I mol kg^{-1}	$E_{measd.}$ V.	$E_{cald.}$ V.	ΔE V.
*0.02889	0.57676	0.58574	1.0747	1.0749	0.0002
*0.03265	0.58623	0.59620	1.0730	1.0730	0.0000
*0.03730	0.59692	0.60811	1.0709	1.0710	0.0001
*0.04353	0.61069	0.62344	1.0686	1.0686	0.0000
*0.06551	0.65628	0.67398	1.0620	1.0620	0.0000
*0.07512	0.68174	0.70292	1.0596	1.0596	0.0000
*0.08762	0.70125	0.72296	1.0571	1.0571	0.0000
*0.10538	0.73905	0.76312	1.0539	1.0538	-0.0001
*0.13224	0.79484	0.82137	1.0498	1.0497	-0.0002
*0.17737	0.88717	0.91843	1.0442	1.0440	-0.0002
*0.25838	1.03489	1.06138	1.0371	1.0369	-0.0002
*0.29268	0.87823	0.94992	1.0381	1.0387	0.0001
*0.58117	2.11513	1.90076	1.0153	1.0161	0.0008
*0.74772	1.99442	1.88104	1.0130	1.0137	0.0007
*0.90005	2.29549	2.11439	1.0088	1.0091	0.0004

The standard deviation of emf (σ_{emf}) is 0.0004 V.

$$\Delta E = E_{cald.} - E_{measd.}$$

* $ZnCl_2$-KCl mixture solutions

Table 5.6 The molal concentrations of individual species in $ZnCl_2$ and $ZnCl_2$-KCl mixture solutions.

m_1 mol kg^{-1}	I mol kg^{-1}	concentration (mol kg^{-1})					
		$[Zn^{2+}]$	$[ZnCl^{+}]$	$[ZnCl_2]$	$[ZnCl_3^-]$	$[ZnCl_4^{2-}]$	$[Cl^-]$
0.00098	0.00293	0.00097	0.00001	0.00000	0.00000	0.00000	0.00195
0.00294	0.00871	0.00288	0.00006	0.00000	0.00000	0.00000	0.00582
0.00366	0.01081	0.00358	0.00008	0.00000	0.00000	0.00000	0.00724
0.00442	0.01303	0.00430	0.00012	0.00000	0.00000	0.00000	0.00872
0.00508	0.01494	0.00493	0.00015	0.00000	0.00000	0.00000	0.01001
0.00735	0.02149	0.00707	0.00028	0.00000	0.00000	0.00000	0.01442
0.00827	0.02412	0.00793	0.00034	0.00000	0.00000	0.00000	0.01620
0.01039	0.03016	0.00989	0.00050	0.00000	0.00000	0.00000	0.02027
0.01204	0.03483	0.01140	0.00064	0.00000	0.00000	0.00000	0.02343
0.01549	0.04452	0.01452	0.00097	0.00000	0.00000	0.00000	0.03000
0.02052	0.05849	0.01889	0.00152	0.00001	0.00000	0.00000	0.03950
0.02201	0.06259	0.02030	0.00170	0.00001	0.00000	0.00000	0.04229
0.03017	0.08485	0.02736	0.00279	0.00002	0.00000	0.00000	0.05750
0.04243	0.11776	0.03769	0.00468	0.00005	0.00000	0.00000	0.08706
0.05913	0.16172	0.05135	0.00765	0.00011	0.00001	0.00001	0.11033
0.06549	0.17823	0.05645	0.00888	0.00014	0.00002	0.00001	0.12174
0.08327	0.22388	0.07044	0.01253	0.00024	0.00004	0.00002	0.15332
0.09203	0.24610	0.07721	0.01443	0.00029	0.00006	0.00004	0.16872
0.10352	0.27502	0.08597	0.01701	0.00038	0.00008	0.00006	0.18875
0.15817	0.40911	0.12614	0.03028	0.00098	0.00037	0.00041	0.28137
0.19300	0.49190	0.15056	0.03923	0.00150	0.00074	0.00097	0.33766
0.23171	0.58155	0.17671	0.04929	0.00221	0.00141	0.00209	0.39713

continue

m_1 mol kg^{-1}	I mol kg^{-1}	concentration (mol kg^{-1}) $[Zn^{2+}]$	$[ZnCl^{+}]$	$[ZnCl_2]$	$[ZnCl_3^{-}]$	$[ZnCl_4^{2-}]$	$[Cl^{-}]$
0.32792	0.79358	0.23734	0.07321	0.00436	0.00465	0.00837	0.52650
0.37307	0.88817	0.26380	0.08329	0.00547	0.00708	0.01343	0.57694
0.49003	1.12015	0.32744	0.10504	0.00836	0.01631	0.03288	0.67786
0.54438	1.22301	0.35511	0.11305	0.00962	0.00200	0.04460	0.71204
0.60653	1.33721	0.38560	0.12078	0.01096	0.02955	0.05964	0.74311
0.68557	1.47826	0.42293	0.12869	0.01250	0.04073	0.08071	0.77241
0.78735	1.65382	0.46491	0.13625	0.14243	0.05759	0.11010	0.79680
0.84448	1.74993	0.49442	0.13940	0.01508	0.06824	0.12732	0.80523
0.89037	1.82601	0.51435	0.14145	0.01570	0.07742	0.14146	0.80982
0.93123	1.89296	0.53190	0.14294	0.01621	0.08623	0.15416	0.81239
0.97995	1.97149	0.55257	0.14438	0.01677	0.09681	0.16942	0.81388
1.09970	2.16081	0.60242	0.14646	0.01793	0.12573	0.20717	0.81123
1.29993	2.46606	0.68328	0.14631	0.01319	0.18116	0.26986	0.79197
1.40031	2.61445	0.72289	0.14497	0.01977	0.21197	0.30071	0.77735
1.50247	2.76279	0.76271	0.14292	0.02011	0.24515	0.33159	0.76000
1.60265	2.90550	0.80134	0.14040	0.02033	0.27924	0.36134	0.74117
1.70085	3.04406	0.83888	0.13746	0.02044	0.31407	0.39000	0.72115
1.89969	3.31973	0.91417	0.13049	0.02042	0.38784	0.44667	0.67746
1.98896	3.44235	0.94776	0.12699	0.02032	0.42207	0.47183	0.65678
2.07495	3.55957	0.98005	0.12347	0.02017	0.45542	0.49583	0.63649
2.34061	3.92196	1.07982	0.11180	0.01944	0.55951	0.57004	0.57186
2.61177	4.29525	1.18269	0.09902	0.01835	0.66324	0.64847	0.50421
2.94767	4.78084	1.31397	0.08231	0.01658	0.77822	0.75659	0.41886
3.22138	5.21267	1.42712	0.06863	0.01483	0.84824	0.86308	0.34798

continue

m_1 mol kg^{-1}	I mol kg^{-1}	concentration (mol kg^{-1})					
		$[Zn^{2+}]$	$[ZnCl^{+}]$	$[ZnCl_2]$	$[ZnCl_3^-]$	$[ZnCl_4^{2-}]$	$[Cl^-]$
*0.02889	0.58574	0.01940	0.00764	0.00048	0.00044	0.00093	0.56312
*0.03265	0.59620	0.02182	0.00862	0.00055	0.00052	0.00109	0.57057
*0.03730	0.60811	0.02487	0.00986	0.00064	0.00062	0.00132	0.57867
*0.04353	0.62344	0.02890	0.01149	0.00076	0.00076	0.00163	0.58889
*0.06551	0.67398	0.04286	0.01717	0.00120	0.00133	0.00296	0.62090
*0.07512	0.70292	0.04867	0.01962	0.00141	0.00165	0.00376	0.63929
*0.08762	0.72296	0.05650	0.02276	0.00167	0.00203	0.00466	0.65040
*0.10538	0.76312	0.06709	0.02713	0.00206	0.00273	0.00637	0.67414
*0.13224	0.82137	0.08266	0.03351	0.00268	0.00395	0.00944	0.70736
*0.17737	0.91843	0.10764	0.04355	0.00375	0.00651	0.01592	0.75292
*0.25838	1.06138	0.15084	0.05967	0.00560	0.01221	0.03006	0.80715
*0.29268	0.94992	0.18943	0.06877	0.00545	0.00904	0.01999	0.69145
*0.58117	1.90076	0.22892	0.07889	0.01153	0.07937	0.18246	1.04493
*0.74772	1.88104	0.36642	0.11166	0.01424	0.08427	0.17113	0.19695
*0.90005	2.11439	0.42676	0.11781	0.01589	0.11853	0.22147	0.90607

* results of $ZnCl_2$-KCl mixture solutions

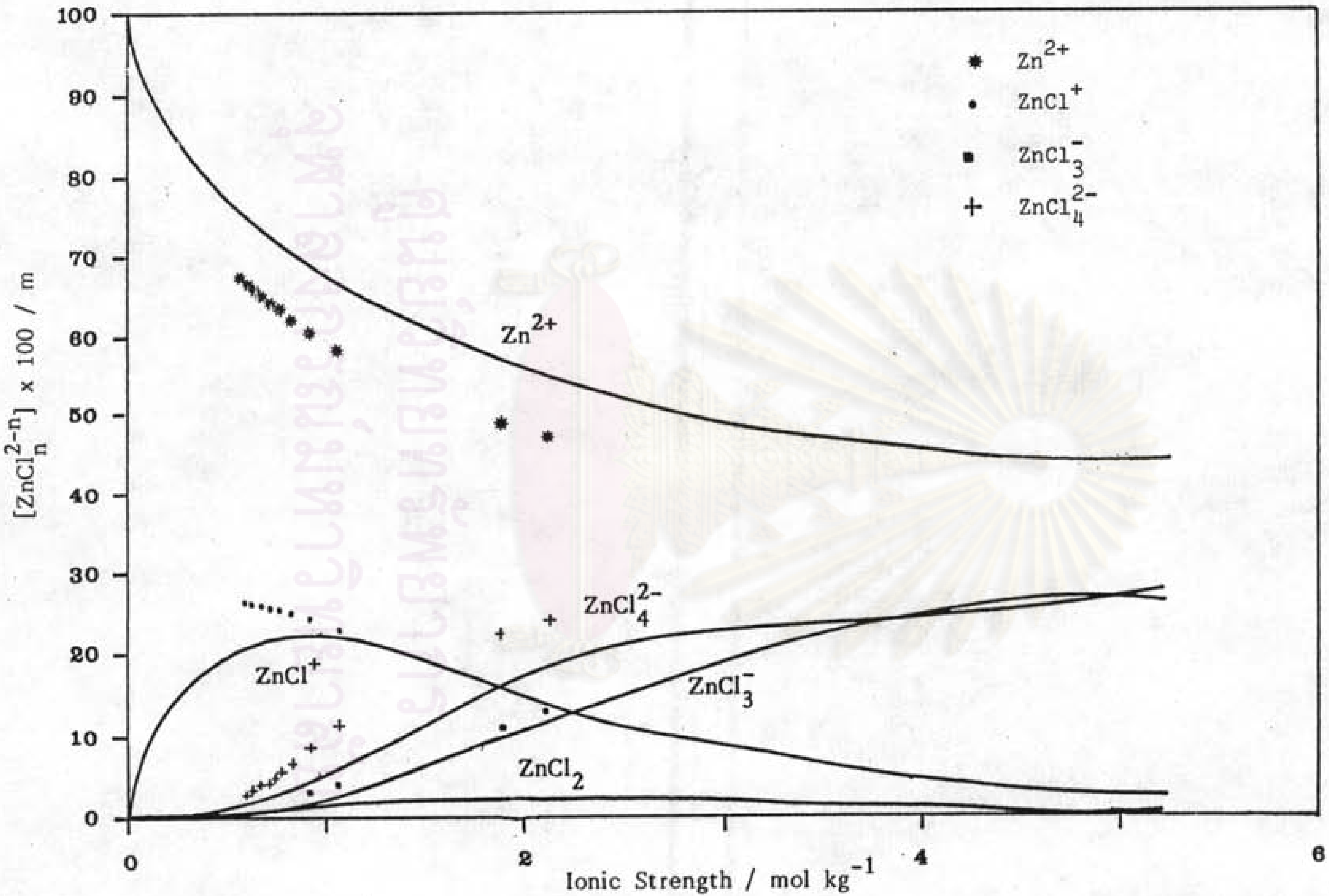

Figure 5.2 The percentage distribution of free and complexed zinc as a function of ionic strength in $ZnCl_2$ and $ZnCl_2$-KCl solutions
(the solid curves belong to the data of the pure $ZnCl_2$ solutions while the specified points are those of $ZnCl_2$-KCl system)

5.2.2 Zinc Bromide System

The standard potential of the cell

$$Zn\text{-}Hg \; / \; ZnBr_2 \; (m) \; / \; AgBr,Ag \qquad (III)$$

was found to be 0.8323_6 V., with $\sigma = 0.0001_9$ V. The standard potential electrode of zinc electrode, E°_{Zn} ($E^\circ_{Ag,AgBr} - E^\circ_{cell}$) of -0.7615_3 V. was thus obtained. This result agrees with that obtained for $ZnCl_2$ system.

Using the standard potential of the cell in the analysis of the data, the thermodynamic complex formation constants were found to be

$$\beta_1 = 2.45 \pm 0.05 \qquad \beta_2 = 1.25 \pm 0.05$$
$$\beta_3 = 0.036 \pm 0.00 \qquad \beta_4 = 0.43 \pm 0.01$$

The parameters of the activity coefficients in the Debye-Hueckel equation are given in Table 5.7

Table 5.7 Activity coefficient parameters of the extended Debye-Hueckel equations in system of $ZnBr_2$.

log	a	B	B'	B''
γ_{21}	4.45	0.17420	0.00094	0.00035
γ_{11}	4.73	0.31338	-0.00287	0.00041
γ_{0}	-	0.47520	0.00164	0.00041
γ_{12}	5.33	0.53379	0.00200	-0.00040

The measured and calculated emf.s of the cell (III) as a function of $ZnBr_2$ concentrations are listed in Table 5.8. The concentration of species in $ZnBr_2$ solutions are shown in Table 5.9. The graphical representation of the percentage distribution of species as a function of total zinc concentrations is given in Fig.5.3 .

* percentage distribution of species = $[ZnX_n^{(2-n)}] \times 100 / m_{ZnX_2}$ %

Table 5.8 The measured and calculated emf.s of the cell (III) as a function of $ZnBr_2$ concentrations.

m_{ZnBr_2} mol.kg^{-1}	I mol.kg^{-1}	$E_{measd.}$ V.	$E_{cald.}$ V.	ΔE V.
0.00100	0.00299	1.0854	1.0855	0.0001
0.00203	0.00606	1.0596	1.0600	0.0004
0.00325	0.00968	1.0432	1.0434	0.0002
0.00400	0.01190	1.0361	1.0361	0.0001
0.00510	0.01515	1.0274	1.0277	0.0003
0.00762	0.02255	1.0135	1.0140	0.0005
0.00822	0.02431	1.0110	1.0114	0.0004
0.01281	0.03768	0.9960	0.9965	0.0005
0.01887	0.05517	0.9832	0.9837	0.0005
0.02500	0.07271	0.9740	0.9744	0.0004
0.03210	0.09288	0.9660	0.9663	0.0003
0.04000	0.11513	0.9590	0.9592	0.0001
0.05000	0.14307	0.9515	0.9518	0.0003
0.05705	0.16263	0.9470	0.9475	0.0005
0.07289	0.20672	0.9390	0.9394	0.0004
0.09000	0.25276	0.9320	0.9324	0.0004
0.10000	0.27973	0.9278	0.9288	0.0010
0.15000	0.41260	0.9145	0.9148	0.0003
0.20269	0.54912	0.9033	0.9040	0.0003
0.28113	0.74687	0.8910	0.8916	0.0006
0.33976	0.89025	0.8844	0.8841	-0.0003
0.38082	0.98850	0.8797	0.8796	-0.0002
0.45553	1.16262	0.8724	0.8723	-0.0001
0.48207	1.22305	0.8697	0.8700	0.0003

continue

m_{ZnBr_2} mol.kg^{-1}	I mol.kg^{-1}	$E_{measd.}$ V.	$E_{cald.}$ V.	ΔE V.
0.52198	1.31256	0.8664	0.8667	0.0003
0.56246	1.14074	0.8631	0.8637	0.0006
0.58149	1.44314	0.8617	0.8623	0.0006
0.64224	1.57340	0.8579	0.8583	0.0004
0.67096	1.63351	0.8563	0.8565	0.0002
0.70318	1.70050	0.8541	0.8546	0.0005
0.80044	1.89818	0.8492	0.8494	0.0002
0.92025	2.13383	0.8432	0.8438	0.0006
0.99049	2.26832	0.8401	0.8409	0.0008
1.01024	2.30569	0.8397	0.8401	0.0004
1.30092	2.83489	0.8295	0.8298	0.0003
1.49993	3.17545	0.8235	0.8239	0.0004
1.65193	3.42465	0.8192	0.8199	0.0007
1.82372	3.69481	0.8158	0.8158	-0.0000
1.97743	3.92664	0.8124	0.8124	-0.0001
2.13239	4.15208	0.8093	0.8092	-0.0001
2.24645	4.31279	0.8072	0.8070	-0.0002
2.48530	4.63630	0.8028	0.8027	-0.0001
2.69102	4.90338	0.7991	0.7994	0.0003
2.61177	3.80660	0.9789	0.9791	0.0002
2.89758	5.16280	0.7962	0.7963	0.0001
3.09691	5.40685	0.7929	0.7935	0.0006
3.30599	5.65839	0.7901	0.7907	0.0006
3.55661	5.95578	0.7861	0.7875	0.0014

The standard deviation of emf (σ_{emf}) is 0.0003 V.

$$\Delta E = E_{cald.} - E_{measd.}$$

Table 5.9 The molal concentrations of the individual species in aqueous $ZnBr_2$ solutions.

m_{ZnBr_2} mol.kg^{-1}	$[Zn^{2+}]$	concentration of species (mol kg^{-1})				
		$[ZnBr^+]$	$[ZnBr_2]$	$[ZnBr_3^-]$	$[ZnBr_4^{2-}]$	$[Br^-]$
0.00100	0.00100	0.00000	0.00000	0.00000	0.00000	0.00199
0.00203	0.00202	0.00001	0.00000	0.00000	0.00000	0.00405
0.00325	0.00322	0.00003	0.00000	0.00000	0.00000	0.00647
0.00400	0.00395	0.00005	0.00000	0.00000	0.00000	0.00795
0.00510	0.00502	0.00008	0.00000	0.00000	0.00000	0.01012
0.00762	0.00747	0.00015	0.00000	0.00000	0.00000	0.01509
0.00822	0.00804	0.00017	0.00000	0.00000	0.00000	0.01627
0.01281	0.01243	0.00037	0.00000	0.00000	0.00000	0.02524
0.01887	0.01815	0.00071	0.00001	0.00000	0.00000	0.01815
0.02500	0.02386	0.00112	0.00002	0.00000	0.00000	0.04884
0.03210	0.03040	0.00167	0.00003	0.00000	0.00000	0.06246
0.04000	0.03758	0.00236	0.00006	0.00000	0.00000	0.07752
0.05000	0.04657	0.00334	0.00010	0.00000	0.00000	0.09647
0.05705	0.05283	0.00408	0.00013	0.00000	0.00000	0.10974
0.07289	0.06674	0.00590	0.00024	0.00000	0.00000	0.13938
0.09000	0.08152	0.00807	0.00040	0.00000	0.00001	0.17111
0.10000	0.09006	0.00941	0.00051	0.00000	0.00001	0.18951
0.15000	0.13181	0.01680	0.00131	0.00002	0.00007	0.28024
0.20269	0.17434	0.02539	0.00262	0.00005	0.00029	0.37345
0.28113	0.23530	0.03889	0.00554	0.00018	0.00122	0.50686
0.33976	0.27910	0.04900	0.00846	0.00039	0.00281	0.60120
0.38082	0.30889	0.05587	0.01086	0.00061	0.00459	0.66386
0.45553	0.36117	0.06759	0.01584	0.00124	0.00969	0.76931
0.48207	0.37914	0.07144	0.01777	0.00155	0.01217	0.80386

continue

m_{ZnBr_2} $mol.kg^{-1}$	$[Zn^{2+}]$	concentration of species (mol kg^{-1})				
		$[ZnBr^+]$	$[ZnBr_2]$	$[ZnBr_3^-]$	$[ZnBr_4^{2-}]$	$[Br^-]$
0.52198	0.40561	0.07687	0.02077	0.00212	0.01662	0.85273
0.56246	0.43176	0.08191	0.02391	0.00283	0.02205	0.89851
0.58149	0.44384	0.08410	0.02541	0.00322	0.02493	0.91871
0.64224	0.48157	0.09041	0.03025	0.00469	0.03551	0.97783
0.67096	0.49877	0.09299	0.03252	0.00551	0.04117	1.00267
0.70318	0.51788	0.09561	0.03507	0.00655	0.04807	1.02867
0.80044	0.57364	0.10185	0.04256	0.01046	0.07193	1.09428
0.92025	0.63899	0.10644	0.05117	0.01704	0.10661	1.15417
0.99049	0.67586	0.10781	0.05583	0.02192	0.12906	1.17943
1.01024	0.68895	0.10805	0.05675	0.02314	0.13335	1.17943
1.30092	0.82867	0.10563	0.07274	0.05417	0.23972	1.22921
1.49993	0.92022	0.09985	0.08052	0.08526	0.31408	1.22300
1.65193	0.98560	0.09421	0.08515	0.11533	0.37164	1.20680
1.82372	1.05741	0.08726	0.08904	0.15570	0.43431	1.17777
1.97743	1.11926	0.08086	0.09153	0.19759	0.48818	1.14543
2.13239	1.17956	0.07444	0.09320	0.24517	0.54002	1.10837
2.24645	1.22243	0.06982	0.09398	0.28347	0.57674	1.07924
2.48530	1.31052	0.06067	0.09454	0.37139	0.64818	1.01398
2.69102	1.38360	0.05340	0.09407	0.45481	0.70541	0.95550
2.89758	1.45516	0.04672	0.09288	0.54442	0.75840	0.89581
3.09691	1.52290	0.04085	0.09118	0.63530	0.80667	0.83802
3.30599	1.59297	0.03527	0.08891	0.73412	0.85471	0.77767
3.55661	1.67627	0.02933	0.08568	0.85523	0.91011	0.70642

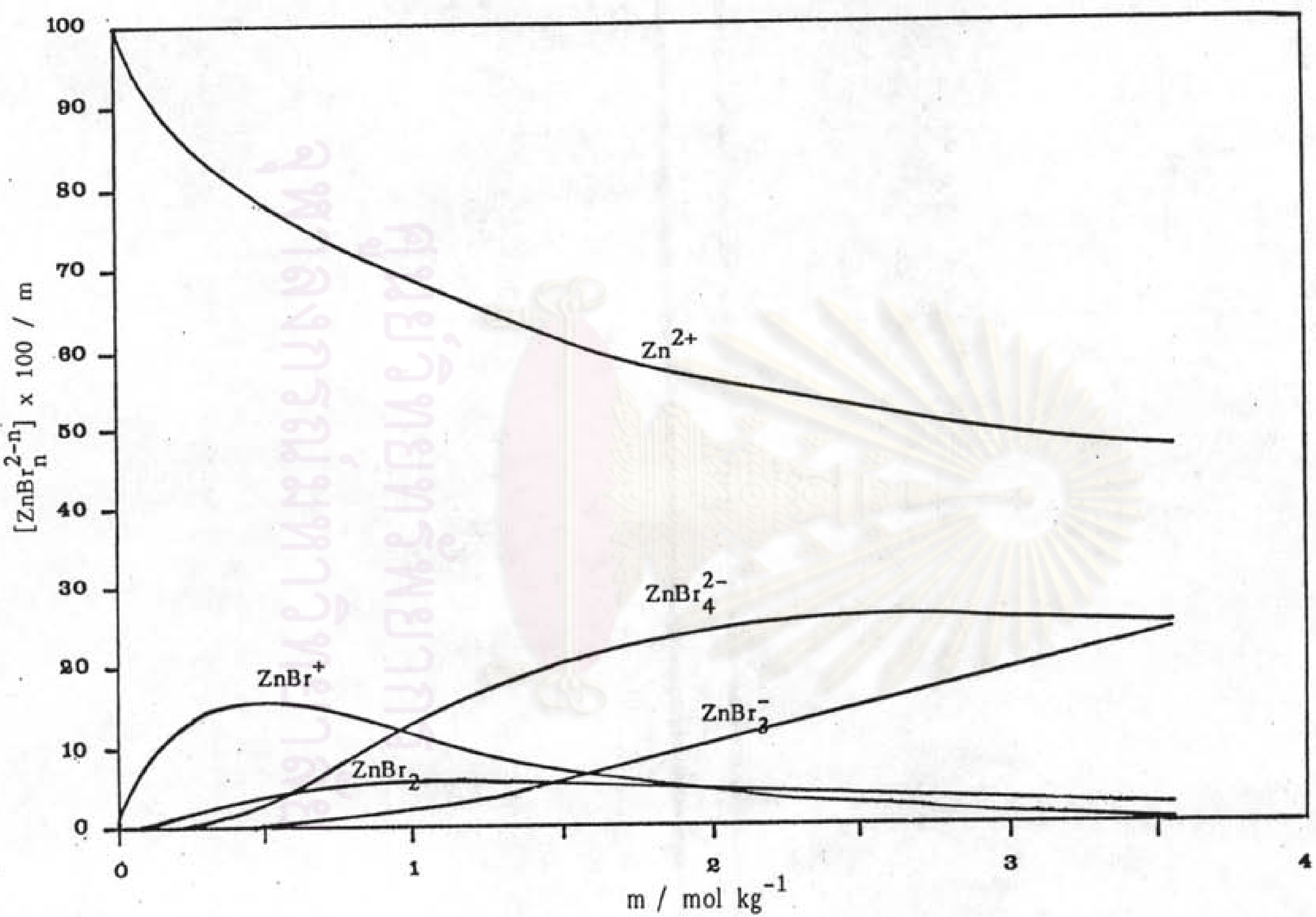

Figure 5.3 The percentage distribution of free and complexed zinc as functions of a molal concentration of zinc bromide

Including the data of $ZnBr_2$ mixture in the analysis, the following complex formation constants

$$\beta_1 = 2.40 \pm 0.10 \qquad \beta_2 = 1.80 \pm 0.05$$

$$\beta_3 = 0.041 \pm 0.02 \qquad \beta_4 = 0.38 \pm 0.01$$

are obtained. The complex coefficient parameters in the Debye-Hueckel equation are listed in table 5.10

Table 5.10 Activity coefficient parameters of the extended Debye-Hueckel equations in system of $ZnBr_2$ and $ZnBr_2$-KBr mixture.

log	a	B	B'	B''
γ_{21}	4.13	0.18104	0.00094	0.00035
γ_{11}	4.73	0.32086	0.00221	0.00041
γ_0	-	0.63434	-0.00323	0.00091
γ_{12}	5.38	0.52135	0.00170	-0.00040

The measured and calculated emfs. of the cell Zn-Hg / $ZnBr_2$ (m_1), KBr (m_2) / AgBr,Ag are assembled in table 5.11. The concentration of the species in $ZnBr_2$ solutions and $ZnBr_2$-KBr mixtures are shown in table 5.12. The graphical representation of the percentage distribution of species as a function of ionic strength is given in Fig.5.4.

Table 5.11 The measured and calculated emf.s of the cell $Zn\text{-}Hg / ZnBr_2 (m_1), KBr (m_2) / AgBr, Ag$

m_1 mol kg^{-1}	$2m_1+m_2$ mol kg^{-1}	I mol kg^{-1}	$E_{meas.}$ V.	E_{cal} V.	ΔE V.
0.00100	0.00200	0.00299	1.0854	1.0854	0.0000
0.00203	0.00406	0.00606	1.0596	1.0600	0.0004
0.00400	0.00800	0.01190	1.0361	1.0361	0.0001
0.00510	0.01020	0.01515	1.0274	1.0277	0.0003
0.00762	0.01524	0.02256	1.0135	1.0140	0.0005
0.00822	0.01644	0.02432	1.0110	1.0114	0.0004
0.01281	0.02562	0.03770	0.9960	0.9966	0.0006
0.01887	0.03774	0.05521	0.9832	0.9838	0.0006
0.02500	0.05000	0.07279	0.9740	0.9746	0.0006
0.03210	0.06420	0.09299	0.9660	0.9665	0.0005
0.04000	0.08000	0.11530	0.9590	0.9594	0.0004
0.05000	0.10000	0.14333	0.9515	0.9522	0.0007
0.05705	0.11410	0.16297	0.9470	0.9479	0.0009
0.07289	0.14578	0.20674	0.9390	0.9399	0.0009
0.09000	0.18000	0.25354	0.9320	0.9329	0.0009
0.10000	0.20000	0.28069	0.9278	0.9293	0.0015
0.15000	0.30000	0.41457	0.9145	0.9154	0.0009
0.20269	0.40538	0.55276	0.9033	0.9046	0.0013
0.28113	0.56226	0.75361	0.8910	0.8921	0.0011
0.33976	0.67952	0.90019	0.8844	0.8846	0.0002
0.38082	0.76164	1.00251	0.8797	0.8798	0.0001
0.45553	0.91106	1.18032	0.8724	0.8725	0.0001

continue

m_1 mol kg^{-1}	$2m_1+m_2$ mol kg^{-1}	I mol kg^{-1}	$E_{meas.}$ V.	E_{cal} V.	ΔE V.
0.48207	0.96414	1.24274	0.8697	0.8702	0.0005
0.52198	1.04396	1.33534	0.8664	0.8669	0.0005
0.56246	1.12492	1.42774	0.8631	0.8638	0.0007
0.58149	1.16298	1.47066	0.8617	0.8624	0.0007
0.64224	1.28488	1.60598	0.8579	0.8583	0.0004
0.67096	1.34192	1.66284	0.8563	0.8565	0.0002
0.70318	1.40636	1.73781	0.8541	0.8546	0.0005
0.80044	1.60088	1.94330	0.8492	0.8494	0.0002
0.92025	1.84050	2.18833	0.8432	0.8438	0.0006
0.99049	1.98818	2.32740	0.8401	0.8409	0.0008
1.01024	2.02048	2.36613	0.8397	0.8402	0.0005
1.30092	2.60184	2.91393	0.8295	0.8300	0.0005
1.49993	2.99986	3.26558	0.8235	0.8242	0.0007
1.65193	3.30386	3.52190	0.8192	0.8202	0.0010
1.82372	3.64744	3.79845	0.8158	0.8160	0.0002
1.97743	3.95486	4.03542	0.8124	0.8126	0.0002
2.13239	4.26478	4.26419	0.8093	0.8093	0.0000
2.24645	4.49290	4.42582	0.8072	0.8071	-0.0001
2.48530	4.97060	4.74944	0.8028	0.8027	-0.0001
2.69102	5.38204	5.01126	0.7991	0.7993	0.0002
2.89758	5.79516	5.26158	0.7962	0.7961	-0.0001
3.09691	6.19382	5.49076	0.7929	0.7932	0.0003
3.30599	6.61198	5.71977	0.7901	0.7904	0.0003
3.55661	7.11322	5.98163	0.7861	0.7872	0.0011

continue

m_1 mol kg^{-1}	$2m_1+m_2$ mol kg^{-1}	I mol kg^{-1}	$E_{meas.}$ V.	E_{cal} V.	ΔE V.
*0.02339	0.57921	0.59296	0.9232	0.9223	-0.0009
*0.02941	0.55729	0.57503	0.9201	0.9203	0.0003
*0.03301	0.56695	0.58664	0.9190	0.9185	-0.0005
*0.04098	0.58164	0.60596	0.9148	0.9151	0.0003
*0.06249	0.62481	0.66128	0.9083	0.9080	-0.0003
*0.07026	0.64086	0.68161	0.9051	0.9058	0.0007
*0.09970	0.69967	0.75613	0.9001	0.8991	-0.0010
*0.14946	0.79890	0.87991	0.8901	0.8904	0.0010
*0.20753	0.91517	1.02155	0.8801	0.8825	0.0014
*0.29614	1.10789	1.24384	0.8734	0.8727	-0.0007
*0.44097	1.38203	1.55364	0.8624	0.8615	-0.0009
*0.55054	1.80120	1.93412	0.8520	0.8519	-0.0001
*0.60742	1.87387	2.01721	0.8493	0.8496	0.0003
*0.72267	1.94524	2.13248	0.8451	0.8462	0.0011
*0.85016	2.40079	2.50819	0.8382	0.8390	0.0008

The standard deviation of emf (σ_{emf}) is 0.0006 V.

$$\Delta E = E_{cald.} - E_{measd.}$$

* $ZnBr_2$-KBr mixture solutions

Table 5.12 The molal concentrations of individual species in $ZnBr_2$ and $ZnBr_2$-KBr mixture solutions.

m_1 mol kg^{-1}	I mol kg^{-1}	concentration (mol kg^{-1}) $[Zn^{2+}]$	$[ZnBr^{+}]$	$[ZnBr_2]$	$[ZnBr_3^{-}]$	$[ZnBr_4^{2-}]$	$[Br^{-}]$
0.00100	0.00299	0.00100	0.00000	0.00000	0.00000	0.00000	0.00200
0.00203	0.00606	0.00202	0.00001	0.00000	0.00000	0.00000	0.00405
0.00400	0.01190	0.00395	0.00005	0.00000	0.00000	0.00000	0.00795
0.00510	0.01515	0.00503	0.00007	0.00000	0.00000	0.00000	0.01013
0.00762	0.02256	0.00147	0.00015	0.00000	0.00000	0.00000	0.01509
0.00822	0.02432	0.00805	0.00017	0.00000	0.00000	0.00000	0.01627
0.01281	0.03770	0.01245	0.00036	0.00000	0.00000	0.00000	0.02525
0001887	0.05521	0.01818	0.00068	0.00001	0.00000	0.00000	0.03704
0.02500	0.07279	0.02391	0.00107	0.00003	0.00000	0.00000	0.04888
0.03210	0.09299	0.03047	0.00159	0.00005	0.00000	0.00000	0.06252
0.04000	0.11530	0.03769	0.00223	0.00008	0.00000	0.00000	0.07761
0.05000	0.14333	0.04673	0.00314	0.00013	0.00000	0.00000	0.09660
0.05705	0.16297	0.05305	0.00383	0.00018	0.00000	0.00000	0.10991
0.07289	0.20674	0.06708	0.00550	0.00031	0.00000	0.00000	0.13965
0.09000	0.25354	0.08202	0.00747	0.00050	0.00000	0.00001	0.17150
0.10000	0.28069	0.09066	0.00869	0.00063	0.00000	0.00001	0.18999
0.15000	0.41457	0.13306	0.01532	0.00153	0.00002	0.00007	0.28129
0.20269	0.55276	0.17651	0.02295	0.00292	0.00006	0.00026	0.37538
0.28113	0.75361	0.23921	0.03481	0.00575	0.00020	0.00116	0.51069
0.33976	0.90019	0.28460	0.04361	0.00837	0.00043	0.00276	0.60686
0.38082	1.00251	0.31519	0.04974	0.01049	0.00069	0.00472	0.67493
0.45553	1.18032	0.37020	0.05955	0.01428	0.00140	0.01010	0.77836
0.48207	1.24274	0.38902	0.06277	0.01569	0.00176	0.01283	0.81339

continue

m_1 mol kg^{-1}	I mol kg^{-1}	concentration (mol kg^{-1})					
		$[Zn^{2+}]$	$[ZnBr^{+}]$	$[ZnBr_2]$	$[ZnBr_3^-]$	$[ZnBr_4^{2-}]$	$[Br^-]$
0.52198	1.33534	0.41673	0.06725	0.01777	0.00241	0.01782	0.86266
0.56246	1.42774	0.44411	0.07132	0.01981	0.00323	0.02399	0.90833
0.58149	1.47066	0.45674	0.07305	0.02073	0.00367	0.02729	0.92829
0.64224	1.60598	0.49617	0.07788	0.02351	0.00536	0.03953	0.98577
0.67096	1.66284	0.51410	0.07976	0.02470	0.00630	0.04611	1.00944
0.70318	1.73781	0.53399	0.08160	0.02595	0.00748	0.05416	1.03378
0.80044	1.94330	0.59186	0.08553	0.02912	0.01187	0.08206	1.09325
0.92025	2.18833	0.65857	0.08753	0.03189	0.01918	0.12308	1.14351
0.99049	2.32740	0.69712	0.08753	0.03291	0.02439	0.14854	1.16030
1.01024	2.36613	0.70743	0.08742	0.03315	0.02603	0.15621	1.16456
1.30092	2.91393	0.85275	0.08124	0.03434	0.05812	0.27447	1.17968
1.49993	3.26558	0.94440	0.07438	0.03357	0.08988	0.35769	1.15850
1.65193	3.52190	1.01116	0.06867	0.03255	0.12004	0.41950	1.13197
1.82372	3.79845	1.08333	0.06223	0.03121	0.16059	0.48637	1.09557
1.97743	4.03542	1.14534	0.05664	0.02991	0.20288	0.54266	1.05914
2.13239	4.26419	1.20566	0.05135	0.02861	0.25124	0.59553	1.02037
2.24645	4.42582	1.24882	0.04771	0.02768	0.29040	0.63183	0.99128
2.48530	4.74944	1.33600	0.04078	0.02583	0.38230	0.70039	0.92970
2.69102	5.01126	1.40817	0.03560	0.02438	0.47137	0.75149	0.87759
2.89758	5.26158	1.47819	0.03103	0.02306	0.56978	0.79553	0.82656
3.09691	5.49076	1.54387	0.02721	0.02191	0.67226	0.83166	0.77936
3.30599	5.71977	1.61105	0.02372	0.02083	0.78708	0.86331	0.73212
3.55661	5.98163	1.68950	0.02014	0.01968	0.95392	0.89337	0.67848

continue

m_1 mol kg^{-1}	I mol kg^{-1}	concentration (mol kg^{-1})					
		$[Zn^{2+}]$	$[ZnBr^{+}]$	$[ZnBr_2]$	$[ZnBr_3^{-}]$	$[ZnBr_4^{2-}]$	$[Br^{-}]$
*0.02339	0.59296	0.01892	0.00360	0.00069	0.00002	0.00015	0.57356
*0.02941	0.57503	0.02394	0.00446	0.00083	0.00002	0.00016	0.55052
*0.03301	0.58664	0.02683	0.00501	0.00094	0.00003	0.00019	0.55920
*0.04098	0.60596	0.03326	0.00623	0.00119	0.00004	0.00026	0.57187
*0.06249	0.66128	0.05047	0.00953	0.00191	0.00007	0.00050	0.60922
*0.07026	0.68161	0.05664	0.01073	0.00219	0.00008	0.00062	0.62303
*0.09970	0.75613	0.07980	0.01526	0.00332	0.00015	0.00117	0.67264
*0.14946	0.87991	0.11813	0.02283	0.00545	0.00034	0.00272	0.75330
*0.20753	1.02155	0.16141	0.03133	0.02823	0.00069	0.00586	0.84186
*0.29614	1.24384	0.22332	0.04309	0.01289	0.00173	0.01511	0.97338
*0.44097	1.55364	0.31848	0.05803	0.01971	0.00470	0.04006	1.11026
*0.55054	1.93142	0.35963	0.06122	0.02441	0.01152	0.09376	1.28155
*0.60742	2.01721	0.39520	0.06450	0.02595	0.01379	0.10798	1.28418
*0.72267	2.13248	0.47798	0.07187	0.02861	0.01749	0.12672	1.25680
*0.85016	2.50819	0.51009	0.06724	0.02984	0.03270	0.21030	1.33459

* results of $ZnBr_2$-KBr mixture solutions

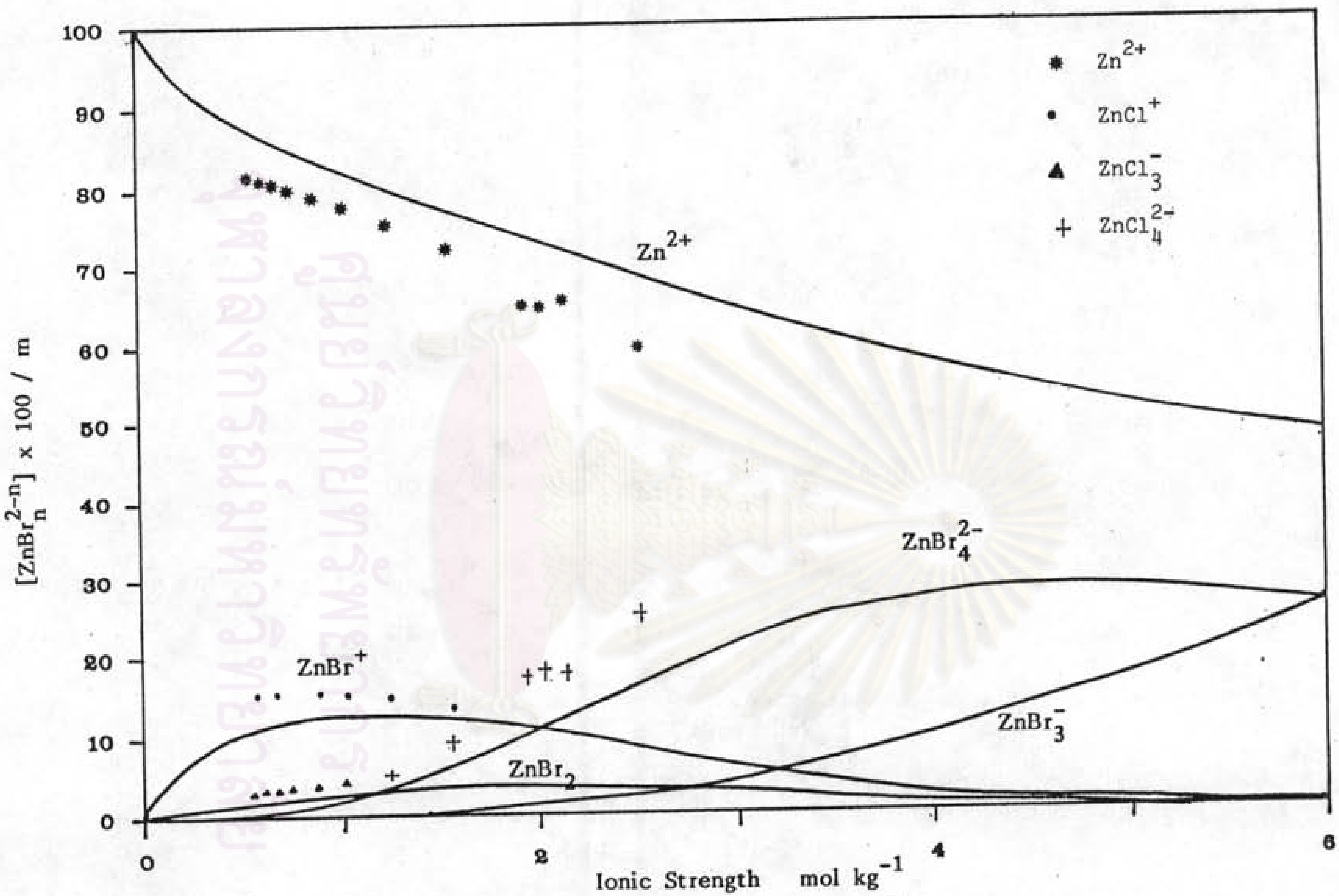

Figure 5.4 The percentage distribution of free and complexed zinc as a function of ionic strength in $ZnBr_2$ and $ZnBr_2$-KBr solutions
(the solid curves belong to the data of the pure $ZnBr_2$ solutions while the specified points are those of $ZnBr_2$-KBr system).