

Thermochemical Studies on Metal Complexes

IX. Free Energy, Enthalpy, and Entropy Changes for Stepwise Formation of Zinc(II) Halide Complexes in Aqueous Solution

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The enthalpy changes for the stepwise formation of zinc(II) halide complexes have been determined by a calorimetric titration procedure. From these enthalpy changes and the changes in free energy, computed from known stability constants, the entropy changes have been calculated by the relation:

$$T\Delta S_i^\circ = \Delta H_i^\circ - \Delta G_i^\circ$$

All data, except for those of the fluoride measurements at 1.00 M, refer to an aqueous sodium perchlorate medium of ionic strength 3.00 M and a temperature of 25.00°C.

In conformity with the cadmium(II) halide systems, $-\Delta H_1^\circ$ for the zinc(II) systems increases from fluoride to bromide and probably also to iodide — only an approximate value for the iodide system could be determined. The reversed order of the strength of the zinc(II) systems compared to the cadmium(II) systems is caused mainly by the entropy term.

The complex formation in aqueous solution between the zinc(II) ion and the fluoride, chloride, bromide, and iodide ions, respectively, has previously been studied by many investigators.¹⁻⁹ The tendency of complex formation was found to diminish from the fluoride to the iodide system. The present investigation was undertaken in order to determine the enthalpy and entropy changes for the stepwise formation of these complexes and to study how the stability depends on the two terms.

Apparently no calorimetric study has been reported for the stepwise formation of the zinc(II) systems investigated here. However, enthalpy values, calculated from stability constants measured at different temperatures, and entropy values are reported by Connick and Paul² for the fluoride system, $\Delta H_1 = 1.5$ (kcal·mole⁻¹), $\Delta S_1 = 8$ (cal·degree⁻¹·mole⁻¹), and by Shchukarev, Lilich, and Latysheva⁴ for the chloride system, $\Delta H_j = 0, 5.1, 14.1,$ and -18.1 (kcal·mole⁻¹), $\Delta S_j = -1.5, 18.4, 46,$ and -60 (cal·degree⁻¹·mole⁻¹), for the bromide system, $\Delta H_j = 0, 0, 26.4,$ and -28.4 (kcal·mole⁻¹), $\Delta S_j = 2.75, -1.7,$

85, and -87 ($\text{cal}\cdot\text{degree}^{-1}\cdot\text{mole}^{-1}$), and for the iodide system, $\Delta H_j=0, 2.9, 10.3,$ and -31.5 ($\text{kcal}\cdot\text{mole}^{-1}$), $\Delta S_j=-13.4, 15.4, 34,$ and -109 ($\text{cal}\cdot\text{degree}^{-1}\cdot\text{mole}^{-1}$), $j=1, 2, 3,$ and 4 .

The method used usually gives rather large errors, and thus no more could be stated from those measurements, than that ΔH_1 is near zero for all four systems and that ΔS_1 seems to decrease from the fluoride to the iodide system. Therefore, in this study a calorimetric method is used to determine the enthalpy changes. The calculations of the enthalpy values from the experimental data are described and a list of symbols and equations used is given in a previous paper.¹⁰

EXPERIMENTAL

C h e m i c a l s

Zinc(II) perchlorate was prepared according to Ref. 11 and the solutions analysed by EDTA using Erio-T as an indicator. To avoid hydrolysis the solutions used were acidified to $\text{pH} \approx 4$.^{12,13}

Sodium perchlorate with one mole of crystal water (Fluka, *p.a.*) was used to maintain the ionic strength in all solutions. The salt was analysed by a cation exchange procedure, and the solutions were then prepared by adding weighed amounts of it.

The ligand solutions of sodium fluoride, chloride, bromide, and iodide were prepared by dissolving the calculated weight of pure salt (Baker Analyzed or Merck, *p.a.*) in water. The fluoride solutions must be buffered in order to avoid hydrolysis of the zinc(II) ion and the ratio $C_A/C_{\text{HA}}=20$ was therefore maintained in all these solutions. The buffers were stored in polythene bottles until the calorimetric titrations were started. These were performed in a glass vessel and were completed within 2 h. When the buffers were investigated in a glass vessel by a fluoride electrode the drift of the emf during 2 h was very small, at most 0.2 mV. This means that the change of the fluoride ion concentration is less than 1 %.

P r o c e d u r e

The calorimeter and the titration procedure used were the same as described in a previous paper.¹⁴ This calorimeter was equipped with a device for the successive addition of known amounts of a titrant, T, into a calorimetric solution, S, initial volume 100.0 ml. The compositions of the solutions S and T were for the titrations of ligand solution into metal solution:

$$S \begin{cases} C_{\text{Zn}} & \text{M Zn}(\text{ClO}_4)_2 \\ (I-3C_{\text{Zn}}) & \text{M NaClO}_4 \end{cases} \quad T \begin{cases} C_{\text{X}} & \text{M NaX} \\ (I-C_{\text{X}}) & \text{M NaClO}_4 \end{cases}$$

or, for the titrations of metal into ligand:

$$S \begin{cases} C_{\text{X}} & \text{M NaX} \\ C_{\text{H}} & \text{M HX} \\ (I-C_{\text{X}}) & \text{M NaClO}_4 \end{cases} \quad T \begin{cases} C_{\text{Zn}} & \text{M Zn}(\text{ClO}_4)_2 \\ (I-3C_{\text{Zn}}) & \text{M NaClO}_4 \end{cases}$$

X = F, Cl, Br, or I

The solutions were buffered only for the fluoride system, for which also only the second type of titrations were used. Each titration series was repeated at least once.

The dilution heats of the ligands and the central ion were determined by similar titration series but without zinc or ligands, respectively. The dilution heat for one com-

ponent when adding a certain amount of a solution into another is taken directly as the correction of the reaction heat when the other component is also present at the titration. Often two correction heats, one for the central ion, and one for the ligand, had to be used in this study. It was assumed that the dilution heats of the various complexes could be neglected.

In this study the thermodynamic standard state for the solute species M, A, and MA_j , where M is the central ion and A the ligand, is a temperature of 25.00°C and a hypothetically ideal one molar solution having neutral salt to ionic strength 3.00 M (except for some measurements of the fluoride system with ionic strength 1.00 M). The zero superscript, when used with ΔG , ΔH , and ΔS , refers to the standard changes in these quantities.

MEASUREMENTS AND RESULTS

The electrical calibrations¹⁴ gave a linear dependence of the heat equivalent of the calorimetric system upon the total amount of titrant added. By use of a least squares method, the results were described by two relations:

$$-\varepsilon_v = 2.129 + 0.0197 v \quad (1)$$

$$-\varepsilon_v = 2.166 + 0.0198 v \quad (2)$$

Eqn. (1) is valid for the measurements performed at ionic strength 3.00 M and eqn. (2) for those at ionic strength 1.00 M. In both types of measurements a 5 ml pipette was used for the additions. The accuracy is better than $\pm 5 \times 10^{-3}$ cal ohm⁻¹ in the volume range used. No differences were observed between measurements on various systems.

The zinc(II) fluoride system. The formation constant of this system, for which only one complex species is reported, has been determined by Ahrlund and Rosengren¹ at 20°C and an ionic strength of 1 M and by Connick and Paul² at 25°C and 0.5 M. The value at 20°C can be recalculated to 25°C when an approximate value of ΔH_1° is determined. The agreement between the two constants, 5.6 and 5.4 M⁻¹, is then remarkably good in spite of the difference in ionic strength (*cf.* the cadmium(II) chloride and iodide systems¹⁵). The first value, 5.6 M⁻¹, is used for the calculations from calorimetric data of measurements at 1 M. In the measurements at 3 M a value of 7 M⁻¹, estimated from a comparison with the cadmium(II) systems studied earlier,^{10,15} is used.

The compositions of the solutions S and T were for the measurements at $I=1.00$ (M):

$$S \begin{cases} 0.200, & 0.0500 \text{ M NaF} \\ 0.010, & 0.0025 \text{ M HF} \\ 0.800, & 0.950 \text{ M NaClO}_4 \end{cases} \quad T \begin{cases} 0.100 \text{ M Zn(ClO}_4)_2 \\ 0.700 \text{ M NaClO}_4 \end{cases}$$

and for the measurements at $I=3.00$ (M):

$$S \begin{cases} 0.100 \text{ M NaF} \\ 0.005 \text{ M HF} \\ 2.900 \text{ M NaClO}_4 \end{cases} \quad T \begin{cases} 0.200 \text{ M Zn(ClO}_4)_2 \\ 2.400 \text{ M NaClO}_4 \end{cases}$$

The heats of dilution were measured by titrations of T into I M NaClO₄, $Q_{\text{dil., T}}$, and of I M NaClO₄ into S, $Q_{\text{dil., S}}$, $I=1$ and 3 (M), respectively. However, the dilution heats of 0.050 M NaF, $I=1$ (M), and 0.100 M NaF,

Table 1. The heats of reaction and dilution for the titrations of the fluoride system at $I=1.00$ (M). Titrations of type I are performed with $C_{\text{NaF}}=0.200$ (M) and those of type II with $C_{\text{NaF}}=0.0500$ (M). $C_{\text{Zn}(\text{ClO}_4)_2}=0.100$ (M) in both types.

| Titration type | v (ml) | $[\text{F}^-]$ (M) | Q_X (cal) | $Q_{\text{dil., T}}$ (cal) | $Q_{\text{dil., S}}$ (cal) | $Q_{\text{corr.}}$ (cal) |
|----------------|-------------|-----------------------|----------------|-------------------------------|-------------------------------|-----------------------------|
| I | 5.02 | 0.185 | -0.501 | -0.009 | 0.011 | -0.503 |
| | 10.05 | 0.174 | -0.475 | 0.002 | 0.009 | -0.486 |
| | 5.02 | 0.185 | -0.505 | (-0.032) | 0.025 | -0.521 |
| | 10.05 | 0.174 | -0.487 | -0.009 | 0.017 | -0.495 |
| II | 5.02 | 0.046 | -0.183 | -0.009 | — | -0.174 |
| | 10.05 | 0.043 | -0.191 | 0.002 | — | -0.193 |
| | 5.02 | 0.046 | -0.193 | (-0.032) | — | -0.184 |
| | 10.05 | 0.043 | -0.182 | -0.009 | — | -0.173 |

Table 2. The heats of reaction and dilution for the titrations of the fluoride system at $I=3.00$ (M). $C_{\text{Zn}(\text{ClO}_4)_2}=0.200$ (M).

| v (ml) | $[\text{F}^-]$ (M) | Q_X (cal) | $Q_{\text{dil., T}}$ (cal) | $Q_{\text{corr.}}$ (cal) |
|-------------|-----------------------|----------------|-------------------------------|-----------------------------|
| 5.02 | 0.090 | -0.818 | -0.109 | -0.709 |
| 10.05 | 0.083 | -0.735 | -0.093 | -0.642 |
| 5.02 | 0.090 | -0.818 | -0.096 | -0.722 |
| 10.05 | 0.083 | -0.714 | -0.084 | -0.630 |

$I=3$ (M) are assumed to be negligible. Corresponding values of v , $[\text{F}^-]$, Q_X , $Q_{\text{dil., T}}$, $Q_{\text{dil., S}}$, and $Q_{\text{corr.}}$ are given in Tables 1 and 2. In the calculations of $[\text{F}^-]$ corrections are made not only for the formation of the zinc complex but also for the formation of HF_2^- according to the equilibrium reported by Ahrlund *et al.*¹⁶ To check the possible change of fluoride ion concentration while in the glass vessel of the calorimeter, one titration was performed after 4 h. No difference in the measured data was observed.

The enthalpy values obtained at $I=1$ (M) for different ligand concentrations, agreed within the experimental errors, and in the range used the formation of one complex species can describe the data found. The small difference between the values obtained at $I=1$ (M) and at $I=3$ (M) is of the order expected from measurements of the cadmium(II) fluoride system.¹⁰ In Table 5 the values of ΔG_1° , ΔH_1° , and ΔS_1° with their estimated errors are given.

The zinc(II) chloride system. Sillén and Liljeqvist³ report three mononuclear complexes all of which are very weak. At low ligand concentration, ΔH_1 is determined by titrations with solutions S and T of composition:

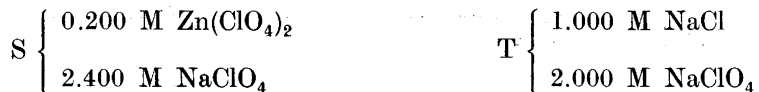
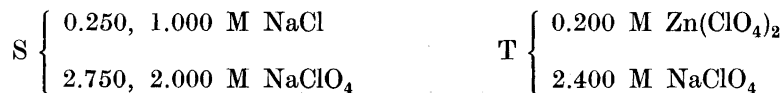


Table 3. The heats of reaction and dilution for the titrations of the chloride system. Titrations of type I are performed with ligand solution into metal solution, type II with metal into ligand, $C_{\text{NaCl}}=0.25$ (M), and type III with metal into ligand, $C_{\text{NaCl}}=1.00$ (M). $C_{\text{Zn(ClO}_4)_2}=0.200$ (M) in all types.

| Titration type | v (ml) | $[\text{Cl}^-]$ (M) | Q_x (cal) | $Q_{\text{dil., T}}$ (cal) | $Q_{\text{dil., S}}$ (cal) | $Q_{\text{corr.}}$ (cal) |
|----------------|----------|---------------------|-------------|----------------------------|----------------------------|--------------------------|
| I | 5.02 | 0.043 | -0.909 | 0.004 | -0.102 | -0.811 |
| | 10.05 | 0.081 | -1.031 | 0.014 | -0.102 | -0.943 |
| | 5.02 | 0.043 | -0.893 | 0.011 | -0.076 | -0.828 |
| | 10.05 | 0.081 | -1.024 | -0.016 | -0.088 | -0.920 |
| | 5.02 | 0.238 | -0.573 | -0.109 | — | -0.464 |
| | 10.05 | 0.227 | -0.458 | -0.093 | — | -0.365 |
| II | 5.02 | 0.238 | -0.559 | -0.096 | — | -0.463 |
| | 10.05 | 0.227 | -0.461 | -0.084 | — | -0.377 |
| | 5.02 | 0.954 | -4.839 | -0.109 | 0.011 | -4.741 |
| | 10.05 | 0.909 | -4.058 | -0.093 | 0.019 | -3.984 |
| | 5.02 | 0.954 | -4.868 | -0.096 | 0.000 | -4.772 |
| | 10.05 | 0.909 | -4.084 | -0.084 | -0.005 | -3.995 |

The dilution heats were measured by titrations of T into 3.00 M NaClO₄ and 3.00 M NaClO₄ into S. Corresponding values of v , $[\text{Cl}^-]$, $Q_{\text{dil., T}}$, $Q_{\text{dil., S}}$, and $Q_{\text{corr.}}$ are collected in Table 3. From these data it is found that at least two complex species are formed. To obtain higher ligand concentrations, the following compositions of solutions S and T were used:



Data from these measurements are well described if the three constants suggested by Sillén and Liljeqvist are used.³ Other sets of constants⁴⁻⁷ do not give such a good fit. The experimental values are given in Table 3. The values of ΔG_j° , ΔH_j° , and ΔS_j° with their estimated errors are collected in Table 5.

The zinc(II) bromide system. Sillén and Liljeqvist³ suggested two or three complexes for this system, but only for the first one could an accurate value of the formation constant be given. The calorimetric titrations were performed at both low and high ligand concentration. At low concentrations the compositions of S and T were:



and at high concentrations:



The values of v , Q_x , $Q_{\text{dil., T}}$, $Q_{\text{dil., S}}$, and $Q_{\text{corr.}}$ are tabulated in Table 4.

Table 4. The heats of reaction and dilution for the titrations of the bromide system. Titrations of type I are performed with ligand solution into metal solution, type II with metal into ligand. $C_{\text{Zn(ClO}_4)_2} = 0.200$ (M) and $C_{\text{NaBr}} = 1.000$ (M) in both types.

| Titra- tion type | v (ml) | $[\text{Br}^-]$ (M) | Q_x (cal) | $Q_{\text{dil., T}}$ (cal) | $Q_{\text{dil., S}}$ (cal) | $Q_{\text{corr.}}$ (cal) |
|------------------------|-------------|------------------------|----------------|-------------------------------|-------------------------------|-----------------------------|
| I | 5.02 | 0.046 | -0.125 | 0.049 | -0.069 | -0.105 |
| | 10.05 | 0.088 | -0.161 | 0.051 | -0.079 | -0.133 |
| | 5.02 | 0.046 | -0.154 | 0.038 | -0.096 | -0.096 |
| | 10.05 | 0.088 | -0.177 | 0.044 | -0.105 | -0.116 |
| II | 5.02 | 0.952 | -0.967 | 0.096 | -0.069 | -0.994 |
| | 10.05 | 0.906 | -0.787 | 0.042 | -0.079 | -0.750 |
| | 5.02 | 0.952 | -0.978 | 0.087 | -0.096 | -0.969 |
| | 10.05 | 0.906 | -0.763 | 0.056 | -0.105 | -0.714 |

The experimental data at low ligand concentration give a value of ΔH_1 and also indicate that the formation of the second complex is small or has a ΔH_2° -value near zero. The data at high ligand concentration are explained with three complex species, the second one formed only to a very small extent, in agreement with one of the two sets of constants calculated by Sillén and Liljeqvist.³ Other sets of reliable constants^{4,7,9} give similar enthalpy values. In Table 5 the values of ΔG_j° , ΔH_j° , and ΔS_j° are given with their estimated errors.

The zinc(II) iodide system. This system is the weakest one of the four investigated and the most reliable suggestion of its formation constants is that none of them is larger than 0.05 M^{-1} .³ Preliminary calorimetric measure-

Table 5. The stability constants used and the values of the free energy, enthalpy, and entropy changes for the stepwise reactions of three of the zinc(II) halide systems tabulated with their estimated errors. Ionic strength 3.00 M if not otherwise stated.

| Ligand | | F ⁻ I=1 (M) | F ⁻ | Cl ⁻ | Br ⁻ |
|--|-------------|---------------------------|----------------|-----------------|-----------------|
| β_j (M ^{-j}) | <i>j</i> =1 | 5.6 ± 0.3 | 7 ± 1 | 0.65 ± 0.10 | 0.27 ± 0.04 |
| | 2 | | | 0.25 ± 0.10 | 0.04 ± 0.02 |
| | 3 | | | 1.4 ± 0.3 | 0.13 ± 0.05 |
| -Δ <i>G</i> _{<i>j</i>} [°] × 10 ⁻³ (cal · mole ⁻¹) | 1 | 1.02 ± 0.07 | 1.15 ± 0.09 | -0.26 ± 0.10 | -0.78 ± 0.10 |
| | 2 | | | -0.57 ± 0.32 | -1.13 ± 0.53 |
| | 3 | | | 1.02 ± 0.33 | 0.70 ± 0.50 |
| -Δ <i>H</i> _{<i>j</i>} [°] × 10 ⁻³ (cal · mole ⁻¹) | 1 | -1.99 ± 0.07 | -1.83 ± 0.08 | -1.32 ± 0.03 | -0.35 ± 0.03 |
| | 2 | | | - 9 ± 2 | - 10 ± 2 |
| | 3 | | | 0 ± 2 | 2 ± 2 |
| Δ <i>S</i> _{<i>j</i>} [°] (cal · mole ⁻¹ · degree ⁻¹) | 1 | 10.1 ± 0.3 | 10.0 ± 0.5 | 3.6 ± 0.4 | -1.4 ± 0.4 |
| | 2 | | | 27 ± 8 | 30 ± 7 |
| | 3 | | | 2 ± 8 | - 4 ± 8 |

ments supported this assumption. When 5 ml 1.000 M NaI is added to 100 ml 0.200 M Zn(ClO₄)₂, *I*=3.00 (M), the heat evolved after correction for dilution is *ca.* 0.03 cal. This indicates a negative enthalpy change. $\beta_1=0.03$ (M⁻¹) and $-\Delta H_1^\circ=1$ (kcal·mole⁻¹) explain the experimental data. For the addition of 5 ml 0.200 M Zn(ClO₄)₂ into 1.000 M NaI, *I*=3.00 (M), the heat taken up after correction for dilution is *ca.* 0.1 cal. This can be accounted for by a β_2 or β_3 -value of 0.03 M^{-j} and a ΔH_2° or ΔH_3° -value, respectively, of about 10 kcal·mole⁻¹.

DISCUSSION

In spite of the uncertain values of the stability constants three facts about the zinc(II) halide systems can be concluded from these calorimetric measurements: (i) enthalpy changes can be determined even for such very weak complex systems. (ii) the stepwise formation of the zinc(II) chloride, bromide, and iodide complexes is confirmed, and the particularly weak second step for the chloride and the bromide systems suggested by Sillén and Liljeqvist³ (*cf.* the cadmium(II) halide systems¹⁷) is supported. (iii) the decreasing stability of the first step from the fluoride to the iodide system is caused by the entropy term, the enthalpy term being most stabilizing for the iodide system as for cadmium(II)¹⁰ and mercury(II).¹⁸

Zinc(II), cadmium(II), and mercury(II) are all three *d*¹⁰-ions, but in their complex formation with fluoride, chloride, bromide, and iodide it has been found in aqueous solutions that the zinc(II) ion,¹⁻⁹ contrary to the cadmium(II)¹⁷ and mercury(II)¹⁹ ions, forms the strongest complex with the fluoride ion and the weakest one with the iodide ion. The zinc(II) ion consequently is a class (a)²⁰ or "hard" acceptor²¹ and it can be assumed that its halide systems

are held by bonds of an essentially electrostatic character. This must influence not only the strength of the systems but also the enthalpy and entropy changes of the complex formation compared to the cadmium(II) and mercury(II) halide systems.

Earlier papers have pointed out that for halide complexes with class (b) or "soft" acceptors $-\Delta H_1^\circ$ increases in the order fluoride to iodide, see *e.g.* the cadmium(II),¹⁰ mercury(II),¹⁸ and (between chloride and bromide) thallium(III)²² systems. ΔS_1° is reported to increase from fluoride to chloride but to decrease from chloride to iodide, see *e.g.* the cadmium(II) and mercury(II) systems. For halide complexes with iron(III), which is a class (a) or "hard" acceptor, the variation in the enthalpy and the entropy terms from the fluoride to the chloride systems is opposite to systems with "soft" acceptors, *i.e.* both $-\Delta H_1^\circ$ and ΔS_1° are less for chloride than for fluoride systems.^{23,24} No data are available for the bromide and iodide systems of iron(III).

This study indicates a correlation between the variation of the entropy term of the formation of halide complexes and the (a) and (b) character of the central ion; ΔS_1° decreases from the fluoride to the chloride system for the zinc(II) ion as for the iron(III) ion but contrary to the cadmium(II) and mercury(II) ions, and furthermore the differences between the fluoride and the chloride system depend on the degree of (a) and (b) character. The variation of the enthalpy term, however, can not be directly correlated with the character of the central ion. For the zinc(II) systems the increase in $-\Delta H_1^\circ$ when going from fluoride to bromide (see Table 5), and presumably also to iodide, is about the same as for the cadmium(II) systems, but considerably smaller than for the mercury(II) systems and for the thallium(III) chloride and bromide systems. On the other hand, the enthalpy terms for the systems of each halide ion depend on the "softness" of the central ion; $-\Delta H_j^\circ$ increases in the order zinc(II), cadmium(II), and mercury(II).

The large negative values of $-\Delta H_2^\circ$ and the associated large positive values of ΔS_2° for the zinc(II) chloride and bromide systems may be explained by a considerable loss of water molecules from the hydration sphere of the zinc(II) ion at this reaction step, *cf.* the third step for the cadmium(II) chloride, bromide, and iodide systems.

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