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HEATS OF FORMATION OF IODO-COMPLEXES OF ZINC(II), CADMIUM(II) AND MERCURY(II) IN AQUEOUS SOLUTIONS *

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ABSTRACT

Heats of formation of MeI^+, MeI_2, MeI_3^- and MeI_4^{2-} where $Me^{2+} = Zn^{2+}$, Cd^{2+} or Hg^{2+} were determined in acidic solutions by flow microcalorimetry. Some gaps in the literature data were filled. In particular, ΔH_3 for the mercury(II) complex was determined and the ΔH_1, $\Delta H_2 + \Delta H_3$, ΔH_4 for zinc(II) complexes were measured in sodium free solutions to avoid ionic couple formation. For cadmium(II) complexes, existing data were confirmed. Thermodynamic functions are discussed in term of hard/soft interactions.

INTRODUCTION

Incomplete calorimetric data exist for the iodo-complexes of transition metals in aqueous solutions. However, thermodynamic data in this field can be useful when considering the picture of iodo-complexes with respect to the soft character [1] of the donor molecule.

In the present work, heats of formation of iodo-complexes of the divalent ions of Group IIB, zinc, cadmium and mercury, have been determined.

Flow microcalorimetry was used for enthalpic measurements, thus allowing faster operating and mixing times. In such a way interference arising from side reactions, such as possible redox reactions, has been lowered. It was decided to study the heats of formations at 25°C ± 0.1 and at pH = 1.0. The acidity of the solutions avoided the formation of hydroxo-complexes. On the other hand a higher acidity value would produce a rapid iodide oxidation which was checked under our experimental conditions and found to be acceptably low.

EXPERIMENTAL

Chemicals

All chemicals were of analytical grade. Zinc, cadmium, lithium and sodium perchlorate solutions were obtained from the corresponding carbonates dissolved in perchloric acid. Zinc and cadmium solutions were standardized by complexometry [2]. Lithium and sodium iodide solutions were prepared

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from the dried salts and standardized with silver nitrate [2]. Mercurv perchlorate was prepared by dissolving HgO in perchloric acid [3].

Procedure .

Solutions of metal perchlorates were prepared in the appropriate ionic medium, lithium or sodium perchlorate, at pH = 1.0. Freshly prepared solutions of lithium or sodium iodide in the same ionic medium and at the same pH were also used to supply the ligand I^-. Both metal and ligand solutions were pumped into the mixing cell of a LKB Model 10700-1 flow microcalorimeter maintained at 25 ± 0.1°C. Reagent free solutions with the same ionic medium and pH were used as references so that the heats of dilutions due to the reagents mixing could be found and subtracted.

The heat of complexation was determined several times for each metal under consideration by varying the amount of iodide added. Concentrations were chosen approximately to optimize the calculations of the heats of formation with respect to the distributions of the MeI^+, MeI_2, MeI_3^- and MeI_4^{2-} species, where Me^{2+} represents Zn^{2+}, Cd^{2+} and Hg^{2+}. In Fig. 1, the species

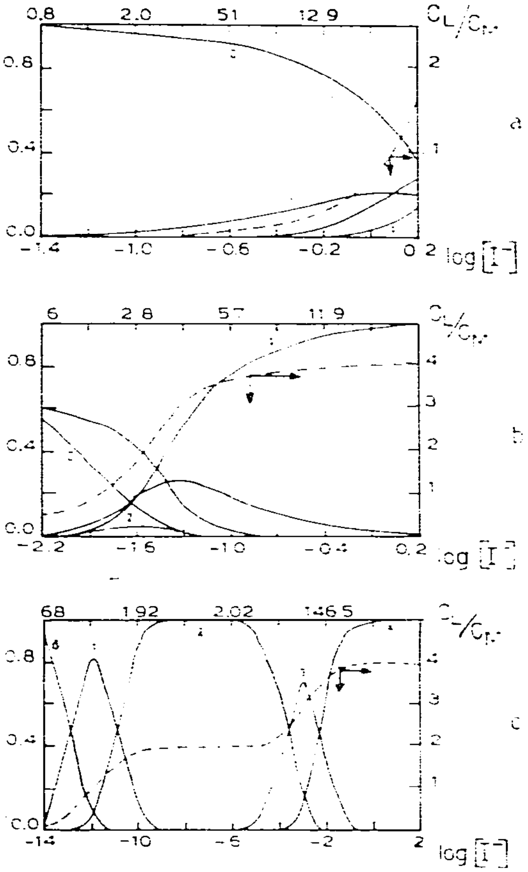

Fig. 1. Species distribution and $\bar{n}$ vs. free iodide concentration and C_L/C_M (total iodide/total metal) ratio. Temperature 25°C; pH = 1.0; (a) Zn^{2+}—I^- system: $C_{Zn} = 5.0 \times 10^{-2}$ M, $LiClO_4$ 4 M; (b) Cd^{2+}—I^- system: $C_{Cd} = 5.0 \times 10^{-2}$ M, $NaClO_4$ 3 M; (c) Hg^{2+}—I^- system: $C_{Hg} = 7.0 \times 10^{-5}$ M, $NaClO_4$ 0.4 M; - - - - - -, $\bar{n}$ formation function; ———, 0: Me^{2+}, 1: MeI^+, 2: MeI_2, 3: MeI_3^-, 4: MeI_4^{2-}.

distribution of the systems under consideration are shown as a function of the free iodide concentration related to the C_L/C_M iodide/metal ratio, as calculated for the experimental conditions used. Reported curves were obtained by using small computer programs on an HP 1000 system.

Values for the heats of formation were calculated by a least-squares method applied to properly chosen sets of experimental measurements. From a theoretical point of view, this empirical approach is equivalent to the definition of a weight matrix in the general best-fit problem. In fact the set

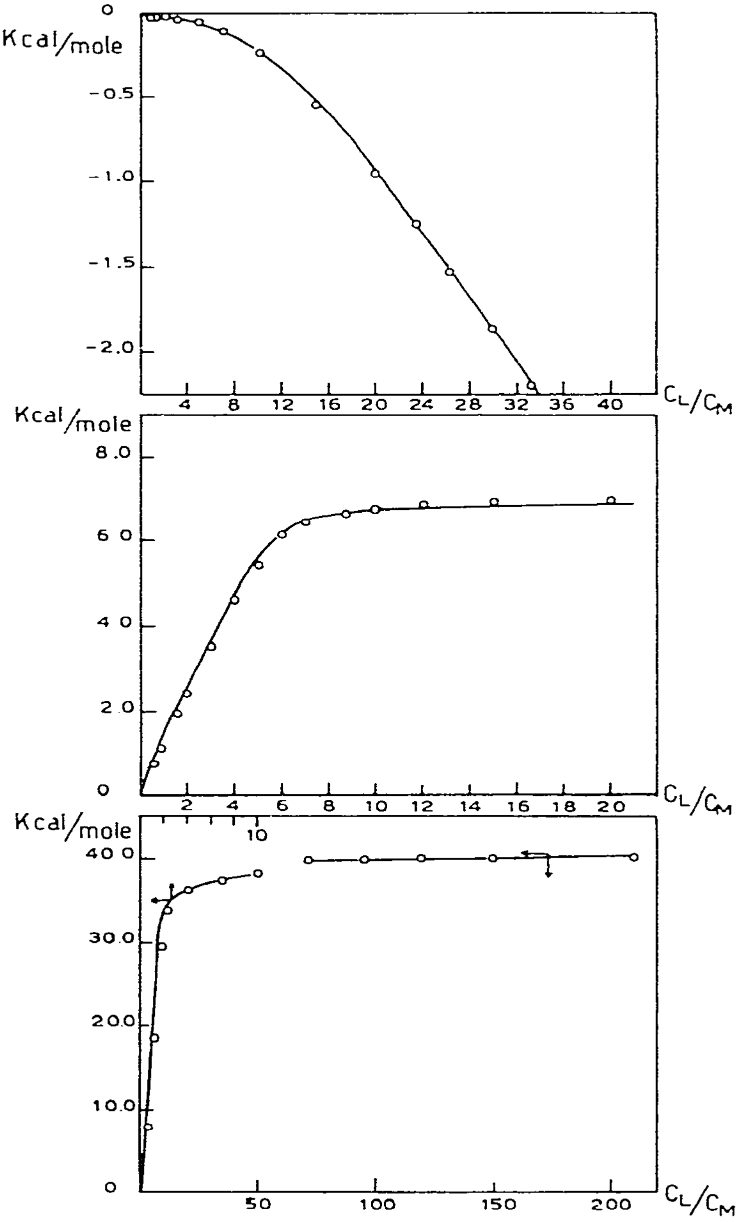

Fig. 2. Heats of reactions per mole of metal ion vs C_L/C_M (total iodide/total metal) ratio. Temperature 25°C; pH = 1.0; (a) Zn^{2+}—I^- system: $C_{Zn} = 5.0 \times 10^{-2}$ M, $LiClO_4$ 4 M; (b) Cd^{2+}—I^- system: $C_{Cd} = 5.0 \times 10^{-2}$ M, $NaClO_4$ 3 M; (c) Hg^{2+}—I^- system: $C_{Hg} = 7.0 \times 10^{-5}$ M, $NaClO_4$ 0.4 M. Circles represent experimental data and continuous lines are calculated from β's and ΔH's.

of values obtained is not sensitive to small numerical changes in experimentally obtained calorimetric data while theoretical curves, calculated from used β's and determined ΔH_{β}'s ($\Delta H_{\beta_i} = \Sigma_1^i{}_j \Delta H_j$) fit very well with the experimental data as shown in Fig. 2.

RESULTS

Numerical values obtained in this work are summarized in Table 1, where the sets of constants used and available literature data are also reported. Owing to minor differences in operating procedures each system will be described separately.

System Zn(II)—I⁻

Values for β_1—β_4 and ΔH_1—ΔH_4 are available from chemical literature in a $NaClO_4$ ionic medium [4]. However, some criticism was aimed at these values [5] suggesting that the presence of Na^+ ions increases the formation of ionic couples with ZnI_4^{2-} complexes. On the other hand, the same behaviour is not in evidence (or at least the stability of ionic couples is strongly reduced) when the ionic medium is $LiClO_4$. Therefore calorimetric measurements were carried out in 4 M $LiClO_4$ solutions. Enthalpic values were determined on the basis of the species distribution calculated from reported β values [5]. The species distribution shown in Fig. 1(a) accounts for the absence of the ZnI_2 species over the whole concentration range examined. Because the maximum degree of formation for this species is about 1%, it was not possible to calculate either the corresponding enthalpic value, or the β set. The ΔH_{β}'s obtained are reported in Table 1 and the calculated calorimetric curve is shown in Fig. 2(a) together with the experimental measurements.

System Cd(II)—I⁻

The set of stability constants for this system is known as are the enthalpic values in 3 M $NaClO_4$ at pH = 4 [2]. Both for a procedure check and to reduce possible metal hydrolysis the same data were recalculated at pH = 1.0. The β values were obtained by applying the method of corresponding solutions [6] to two sets of measurements, the first with $C_M = 5.0 \times 10^{-2}$ M and the second with $C_M = 1.0 \times 10^{-2}$ M. The species distribution curves shown in Fig. 1(b) were calculated on the basis of the β values obtained. Enthalpic values were determined as reported in Table 1. In this case, as for the Zn(II)—I⁻ system, the greatest difficulty was the calculation of the CdI_2 values because of their small contribution to the species distribution. However, even with the highest standard error, when these values are used to draw the calculated calorimetric curves there is a good agreement with the experimental points as shown in Fig. 2(b).

System Hg(II)—I⁻

For this system K_1, ΔH_1 and K_2, ΔH_2 were known in 0.4 M $NaClO_4$ and 0.1 M $HClO_4$ ionic media [3,7]. Values of K_3 and K_4 under the same conditions were also reported [8] and ΔH_{β_4} was determined without details of the

TABLE 1

Data at 25°C for $MeI_i^{(2-i)+}$ complexes with i = 1—4

Rows without references show data obtained in this work. Standard errors reported for these values only. Acidity was created by $HClO_4$ addition in all cases. Units of ΔH_{β_i} are kcal $mole^{-1}$ and units of β_i are $mole^{-i}\ l^i$

Me^{2+}	Ionic medium	Ionic strength (mole l^{-1})	pH	Ref.	β_1	β_2	β_3	β_4	$-\Delta H_{\beta_1}$	$-\Delta H_{\beta_2}$	$-\Delta H_{\beta_3}$	$-\Delta H_{\beta_4}$
Zn^{2+}	$NaClO_4$	4.5	3	4	1.0×10^{-3}	2.0×10^{-2}	1.5×10^{-2}	4.0×10^{-3}	0	−2.9	−13.2	−18.3
Zn^{2+}	$LiClO_4$	4.0	3	5	3.4×10^{-1}	1.0×10^{-2}	1.8×10^{-2}	5.6×10^{-2}				
Zn^{2+}	$LiClO_4$	4.0	1						−0.4 ± 0.1		−8.4 ± 0.1	0.7 ± 0.2
Cd^{2+}	$NaClO_4$	3.0	4	2	1.2×10^{2}	6.0×10^{2}	8.2×10^{4}	3.3×10^{6}	2.3	2.5	3.2	7.0
Cd^{2+}	$NaClO_4$	3.0	1		1.1×10^{2} $\pm 0.1 \times 10^{2}$	7.0×10^{2} $\pm 1.0 \times 10^{4}$	8.0×10^{6} $\pm 1.0 \times 10^{4}$	3.5×10^{6} $\pm 0.3 \times 10^{6}$	2.3 ± 0.2	2.5 ± 0.6	3.2 ± 0.3	6.9 ± 0.1
Hg^{2+}	$NaClO_4$	0.5	1	3,7	7.2×10^{12}	6.5×10^{23}			18.6	34.2		
Hg^{2+}	$NaClO_4$	0.5	2	8			3.0×10^{27} *	6.3×10^{29} *				
Hg^{2+}				9								43.0
Hg^{2+}	$NaClO_4$	0.5	1						18.2 ± 0.8	34.5 ± 0.9	39.6 ± 0.5	40.6 ± 0.5

* Only values of K_3 and K_4 are extracted from reference: β's are obtained using K_1 and K_2 of refs 3 and 7.

TABLE 2

Stepwise thermodynamic functions for iodo-complexes at 25°C as obtained from data reported in Table 1

Me^{2+}	I (mole l^{-1})	i	ΔG_i (kcal mole^{-1})	ΔH_i (kcal mole^{-1})	ΔS_i (e.u.)
Zn^{2+}	4	1	0.64	0.4	−0.8
		2	2.08		
		3	−1.71	8.0 *	25.7 *
		4	0.70	−9.1	−32.9
Cd^{2+}	3	1	−2.82	−2.3	1.7
		2	−0.95	−0.2	2.5
		3	−2.90	−0.7	7.4
		4	−2.18	−3.7	−5.1
Hg^{2+}	0.5	1	−17.47	−18.2	−2.4
		2	−14.88	−16.3	−4.8
		3	−4.98	−5.1	−0.4
		4	−3.16	−1.0	7.2

* Sum of the second and third step.

experimental conditions being given [9]. Values for the heats of formation were determined by using a total mercury(II) concentration low enough to avoid HgI_2 precipitation [3]. This was carried out by taking into account that the species distribution, calculated from reported β's and shown in Fig. 1(c), allows for the separation of the two couples HgI^+, HgI_2 and HgI_3^- and HgI_4^{2-} by the appropriate choice of ligand concentrations. The enthalpic values obtained are reported in Table 1; the calculated curve with the corresponding experimental points for the two ligand concentration ranges are shown in Fig. 2(c).

DISCUSSION

The values obtained in this work fill some gaps existing in the literature data for the iodo-complexes of Zn(II), Cd(II) and Hg(II) as shown in Table 1. The agreement with existing values is very good except for the Zn(II)—I^- system, this being explained by the difference in the ionic medium. The problem of ionic couple formation with Na^+ ions seems to be specific to zinc(II) iodo-complexes while those of cadmium(II) and mercury(II) are not affected [5]. Enthalpic data collected in this work offer a good picture of the behaviour of the iodo-complexes of the divalent ions of Group IIB. These data are related very closely to those for standard states so a comparison may be not hazardous. When considering the d^{10} acceptors of Group IIB, it is known the softness decreases from the markedly soft Hg^{2+} to the mildly soft Cd^{2+} to the hard Zn^{2+}. Stepwise thermodynamic values are reported in Table 2 for complexes with the soft donor I^-. The stability, i.e. free energy release, decreases in the order $Hg^{2+} > Cd^{2+} > Zn^{2+}$ corresponding to the formation of soft—soft, soft—mildly soft and soft—hard complexes. For mercury(II) complexes, an abrupt change in ΔH_i occurs as the third ligand is taken up with a corresponding increase in ΔS_i, thus accounting for a change from linear to tetrahedral configuration as observed for chloro- and bromo-complexes [1]. For cadmium(II) complexes, no abrupt change of the same magnitude takes place, probably due to the mildly soft character exhibited by the acceptor. In this case, the greatest ΔS_i increase occurring at the $i = 3$ level seems to be in agreement with a change from octahedral to tetrahedral configuration when the third donor enters the coordination sphere of the acceptor. However, looking at the chloro- and bromo-complexes of cadmium(II), it can be observed that a markedly greater increase in ΔS_i and ΔH_i occurs [1] at the same level $i = 3$. Thus it can be suggested that configurational change for iodo-complexes is spread out over the second and third steps of formation. The very low stability of the ZnI_2 complex did not allow the determination of separate values for ΔH_2 and ΔH_3. The marked increase in $\Delta H_2 + \Delta H_3$ and $\Delta S_2 + \Delta S_3$, however, most probably accounts for a configurational change taking place at the $i = 2$ and/or $i = 3$ level.

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