A Thermodynamic Study on Hydrolytic Reactions of Lead(II) Ions in an Aqueous Solution and Dioxane-Water Mixtures. II. A Calorimetric Study

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(Received March 17, 1980)

The hydrolytic reactions of lead(II) ions were calorimetrically studied at 25 °C in an aqueous solution and dioxane-water mixtures (dioxane contents: 0.1 and 0.2 mole fractions, which correspond to 35.21 and 55.01 % w/w, respectively) both containing 3 mol dm^{-3} (Li)ClO$_4$ as a constant ionic medium. A fully automatic on-line system was used for the calorimetric titrations. Values of enthalpies and entropies for the formation of the $\mathrm{Pb_3(OH)_3}^{3+}$, $\mathrm{Pb_4(OH)_4}^{4+}$, $\mathrm{Pb_3(OH)_4}^{2+}$ and $\mathrm{Pb_6(OH)_8}^{4+}$ complexes in the aqueous solution, 0.1 and 0.2 mole fraction dioxane solutions were given. For the reaction $q\mathrm{Pb}^{2+}+p\mathrm{H_2O}=\mathrm{Pb}_q(\mathrm{OH})_p{}^{(2q-p)+}+p\mathrm{H}^+$, the values of ΔH^*_{pq}/kJ mol^{-1} and $T\Delta S^*_{pq}$/kJ mol^{-1} were determined as follows: $\mathrm{Pb_3(OH)_3}^{3+}$: 66.6, −20.7 (in aqueous solution); 72.1, −13.4 (in 0.1 mole fraction dioxane solution); 66.9, −17.7 (in 0.2 mole fraction dioxane solution); $\mathrm{Pb_4(OH)_4}^{4+}$: 81.4, −29.5; 84.1, −22.1; 94.7, −14.7; $\mathrm{Pb_3(OH)_4}^{2+}$: 61.6, −68.4; 83.4, −41.0, 99.8, −24.3; $\mathrm{Pb_6(OH)_8}^{4+}$: 242.8, 1.3, 243.2, 10.6; 236.7, 2.0. The solvent effects on ΔH^*_{pq} were discussed in terms of a function of the formal charge per metal ion of the complex, $z'=(2q-p)/q$. The thermodynamic parameters obtained for the $\mathrm{Pb_6(OH)_8}^{4+}$ complex were better explained by assuming the reaction, $2\mathrm{Pb_3(OH)_4}^{2+}=\mathrm{Pb_6O(OH)_6}^{4+}+\mathrm{H_2O}$, than the reaction, $2\mathrm{Pb_3(OH)_4}^{2+}=\mathrm{Pb_6(OH)_8}^{4+}$, and thus the $\mathrm{Pb_6(OH)_8}^{4+}$ complex formally written from the result of the potentiometric measurements will be described as $\mathrm{Pb_6O(OH)_6}^{4+}$ which has previously been proposed by X-ray diffraction.

In a previous paper,[1] we have discussed the Gibbs energy ΔG_{pq} of the hydrolytic reaction, $q\mathrm{M}^{z+}+p\mathrm{OH}^-=\mathrm{M}_q(\mathrm{OH})_p{}^{(zq-p)+}$, of divalent metal ions such as beryllium, copper, nickel, cadmium and lead in aqueous solutions and dioxane-water mixtures containing 3 mol dm^{-3} (Li)ClO$_4$ as an ionic medium. The Gibbs energy of transfer divided by p, $\Delta G^{t}_{pq}/p$ [$=\{\Delta G_{pq}(\mathrm{mix})-\Delta G_{pq}(\mathrm{aq})\}/p$], was found to be approximately independent of the composition of the complexes and the kind of the metal ions, and furthermore, the following relation was obtained:

$$\frac{1}{q}\Delta g^{t}_{pq} \approx \Delta g^{t}_{\mathrm{M}} + k(z-z'),$$

where Δg^{t}_{pq} and $\Delta g^{t}_{\mathrm{M}}$ denote the partial molar Gibbs energies of transfer of $\mathrm{M}_q(\mathrm{OH})_p{}^{(zq-p)+}$ and M^{z+}, respectively, and z' indicates the formal charge per metal ion of $\mathrm{M}_q(\mathrm{OH})_p{}^{(zq-p)+}$ [$z'=(zq-p)/q$], k being a constant. In the preceding work, on the other hand, we found that the enthalpies and entropies of transfer of the hydroxo complexes of beryllium ion strongly depend on the composition of the complexes.[2] In order to throw more light for elucidating solvent effects on thermodynamic parameters of hydrolytic reactions of metal ions, we examined a calorimetric study on hydrolytic reactions of lead(II) ion in an aqueous solution and dioxane-water mixtures.

Experimental

The calorimetric measurements were carried out in a room thermostated at 25 °C.[2] All the cells used were Dewar vessels, which were immersed in a water bath at (25.00±0.05) °C. Fluctuation of the temperature of the bath during one course of the measurement was within ±0.007 °C. About 150 cm^3 of a test solution which contained hydrolyzed lead(II) ions was placed in a titration vessel, then it was titrated with a standard perchloric acid solution. Initial concentrations of total lead ions in the test solution were changed from 0.005

Table 1. Determination of heat evolved per addition of the titrant

t/s	$Q_{\mathrm{ev}}(t)$/J	$C_pV\{\theta(t)-\theta_0\}$/J	$Q_{\mathrm{L}}(t)$/J
10	1.533	1.532	0.002
20	3.922	3.913	0.010
30	6.279	6.254	0.025
40	8.514	8.467	0.046
50	9.013	8.942	0.072
60	9.049	8.951	0.098
70	9.045	8.922	0.123
80	9.041	8.892	0.149
90	8.987	8.813	0.174
100	9.041	8.843	0.199
110	9.037	8.813	0.224
120	8.983	8.734	0.249
130	9.038	8.764	0.274
140	9.023	8.724	0.299
150	8.999	8.675	0.324
160	8.984	8.635	0.349
170	9.019	8.645	0.374
180	8.994	8.596	0.398
190	8.979	8.556	0.423
200	9.023	8.576	0.447
210	8.998	8.527	0.472
220	8.973	8.477	0.496
230	9.017	8.497	0.520
240	9.002	8.457	0.545
250	8.987	8.418	0.569
260	9.011	8.418	0.593
270	9.015	8.398	0.617
280	8.999	8.359	0.641
290	9.003	8.339	0.665
300	8.988	8.299	0.688
$q=(9.000\pm0.015)$ J[a]			

a) q is estimated by averaging $Q_{\mathrm{ev}}(t)$ values from 201 to 300 s (100 points).

to 0.2 mol dm^{-3}. Both the test solution and the titrant contained 3.0 mol dm^{-3} perchlorate ion as a constant ionic medium. The test solutions were prepared by mixing stock solutions of lead perchlorate and lithium hydroxide.

The cell arrangement used was essentially the same as that described in the previous paper.$^{2)}$ All the procedures for the calorimetric titrations were carried out by using a fully automatic on-line system reported in the previous paper$^{2)}$ with a slight modification. In the present study, the titrant was automatically added from an automatic piston buret (Dosimat E535, Metrohm, Switzerland) controlled by an electronic computer. Other devices were the same as those used previously. The titrant was added stepwise and the volume of the titrant added in one step was about 0.5—1 cm^3 with an accuracy ± 0.001 cm^3.

We previously described the method of calorimetric determinations of heat evolved.$^{2)}$ However, the estimation of the heat escaping from the titration vessel was simple in the previous treatment, so that the method was applicable only to systems involving fast reactions which reached equilibria within a few minutes. In the present procedure, a more generalized treatment is adopted to evaluate the heat escaping during the measurement. The total heat which has escaped from the titration vessel until t seconds after the start of the addition of the titrant, $Q_L(t)$, is expressed by

$$Q_L(t) = C_p V \alpha \int_0^t \{\theta(\tau) - \theta_0\} d\tau, \qquad (1)$$

where C_p, V, and α stand for the heat capacity per unit volume of the test solution, the total volume of the solution in the vessel and the rate of heat escaping from the titration vessel, respectively. C_p and α were obtained by the same method as that used previously.$^{2)}$ θ_0 represents the temperature of the test solution at the initial stage where the solution is at the thermal equilibrium with the thermostated bath and $\theta(\tau)$ is the temperature of the test solution at time τ after

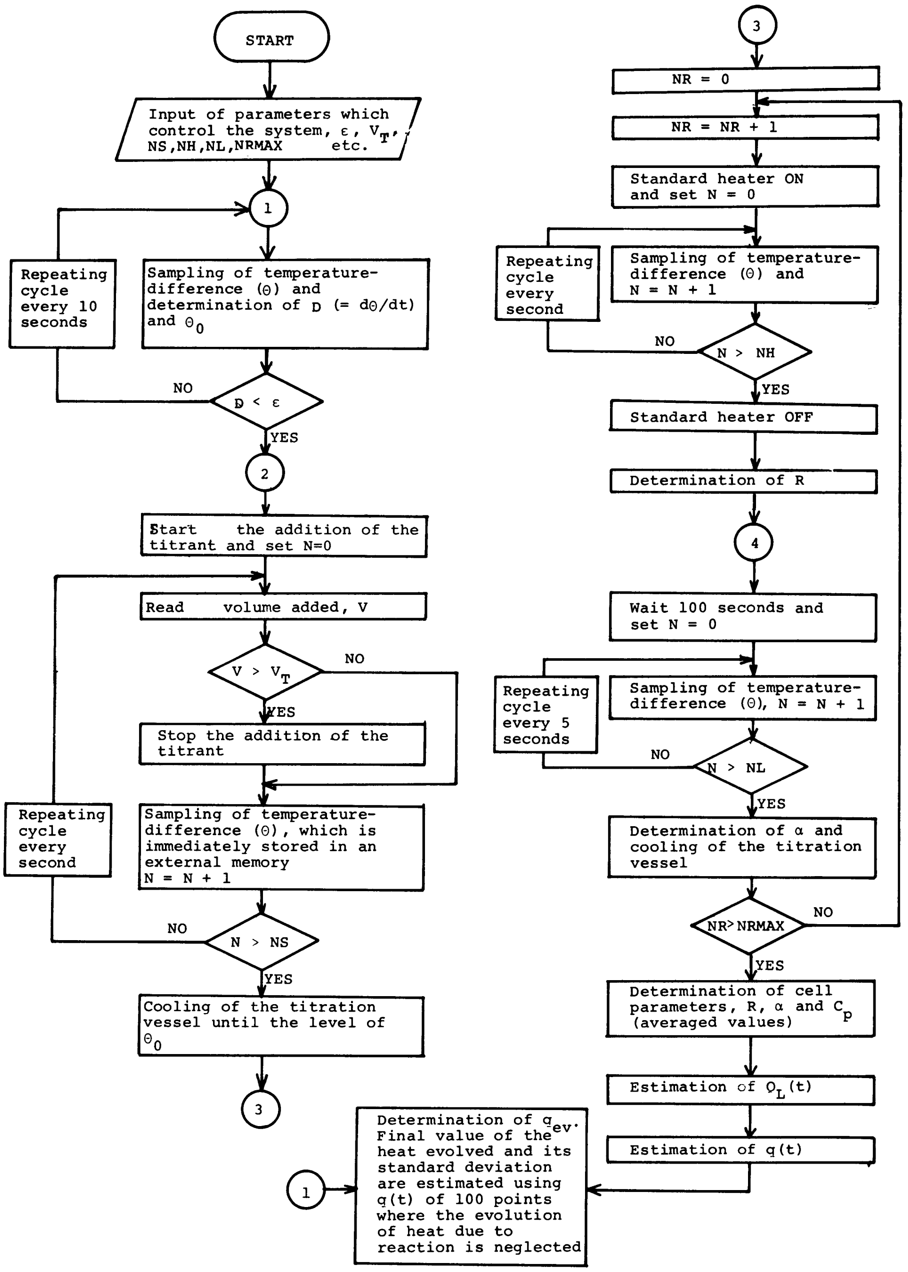

Fig. 1. The flow chart for determination of heat evolved per addition of the titrant.

the start of the addition of the titrant. The temperature change was measured at every second. Then, the heat evolved $Q_{\mathrm{ev}}(t)$ until a time t after the start was determined by the following equation:

$$Q_{\mathrm{ev}}(t) = k_1 C_{\mathrm{p}} V\{\theta(t) - \theta_0\} + Q_{\mathrm{L}}(t) + k_2, \tag{2}$$

where k_1 and k_2 denote empirical constants (k_1 is close to unity and k_2 is nearly zero joule) which had been determined by separate experiments by using a standard heater. $Q_{\mathrm{ev}}(t)$ approaches a constant value q when the evolution of heat due to the reactions becomes negligible. A typical set of $Q_{\mathrm{ev}}(t)$ and $Q_{\mathrm{L}}(t)$ as functions of time is shown in Table 1. The heat evolved q was finally estimated by averaging $Q_{\mathrm{ev}}(t)$ values of the last 100 points (data from 201 to 300 s in Table 1). The standard deviation was usually within ±0.03 J.

The flow chart for determination of heat evolved per addition of the titrant is presented in Fig. 1. A least-squares method was employed for the analysis of the set of the data obtained.

Reagents. Stock solutions were prepared by similar ways described in the previous paper.[1)]

Results

The total heat evolved Q by complex formation involving several species is expressed as follows:

$$Q = \sum_j q_j = \sum_i \Delta H_i \cdot \delta n_i, \tag{3}$$

where ΔH_i and δn_i stand for the enthalpy of formation of the complex species i and the amount of the complex species decomposed by the addition of the standard acid solution at each step of titration, respectively. j represents the number of portions of the titrant added in one course of the titation.

We have previously reported that four hydroxo complexes of lead(II) ions, $\mathrm{Pb_3(OH)_3}^{3+}$, $\mathrm{Pb_4(OH)_4}^{4+}$, $\mathrm{Pb_3(OH)_4}^{2+}$, and $\mathrm{Pb_6(OH)_8}^{4+}$ are formed in both an aqueous solution and dioxane–water mixtures,[1)] and thus, the total heat evolved in the solvent systems is represented in terms of the enthalpy ΔH^*_{pq} of the reaction, $q\mathrm{Pb}^{2+} + p\mathrm{H_2O} = \mathrm{Pb}_q(\mathrm{OH})_p{}^{(2q-p)+} + p\mathrm{H}^+$, as follows:

$$Q = \Delta H^*_{33} \cdot \delta n_{33} + \Delta H^*_{44} \cdot \delta n_{44} + \Delta H^*_{43} \cdot \delta n_{43} + \Delta H^*_{86} \cdot \delta n_{86}. \tag{4}$$

δn_{pq} is calculated on the basis of the formation constants previously determined.[1)] Since only $\mathrm{Pb_3(OH)_3}^{3+}$ and $\mathrm{Pb_4(OH)_4}^{4+}$ complexes are predominant in solutions of pH<6, the total heat evolved in the solutions is approximately written as follows:

$$Q = \Delta H^*_{33} \cdot \delta n_{33} + \Delta H^*_{44} \cdot \delta n_{44}, \tag{5}$$

and hence

$$Q/\delta n_{33} = \Delta H^*_{33} + \Delta H^*_{44}(\delta n_{44}/\delta n_{33}). \tag{6}$$

Therefore, plots of $Q/\delta n_{33}$ against $\delta n_{44}/\delta n_{33}$ should be a straight line with the slope of ΔH^*_{44} and the intercept ΔH^*_{33}. As is seen from Fig. 2, the plots are straight for all the solvent systems examined. The values of ΔH^*_{33} and ΔH^*_{44} are then inserted into Eq. 7 in order to determine the values of ΔH^*_{43} and ΔH^*_{86} by assuming that the four complexes coexist in the region of pH>6.

$$(Q - \Delta H^*_{33} \cdot \delta n_{33} - \Delta H^*_{44} \cdot \delta n_{44})/\delta n_{43} = \Delta H^*_{43} + \Delta H^*_{86}(\delta n_{86}/\delta n_{43}) \tag{7}$$

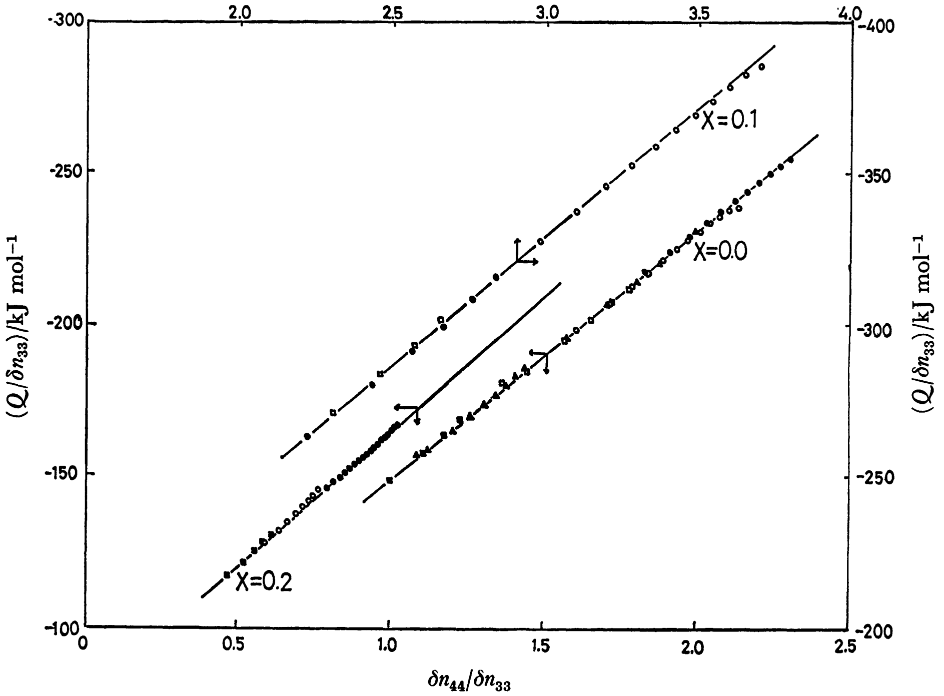

Fig. 2. Determination of the enthalpies, ΔH^*_{33} and ΔH^*_{44} for the hydrolytic reactions of lead (II) ions in the aqueous solution and dioxane–water mixtures containing 3 mol dm^{-3} (Li)ClO$_4$ as an ionic medium. X denotes the mole fraction of dioxane in the mixtures. Initial concentrations (mol dm^{-3}) of the total lead (II) ions are as follows: Aqueous; ● 0.2040, ○ 0.1503, △ 0.1005, □ 0.07913, ▲ 0.04149, ■ 0.02151: 0.1 mole fraction dioxane; ○ 0.07990, ● 0.05690, □ 0.03756: 0.2 mole fraction dioxane; ● 0.1585, ○ 0.07941, □ 0.04218.

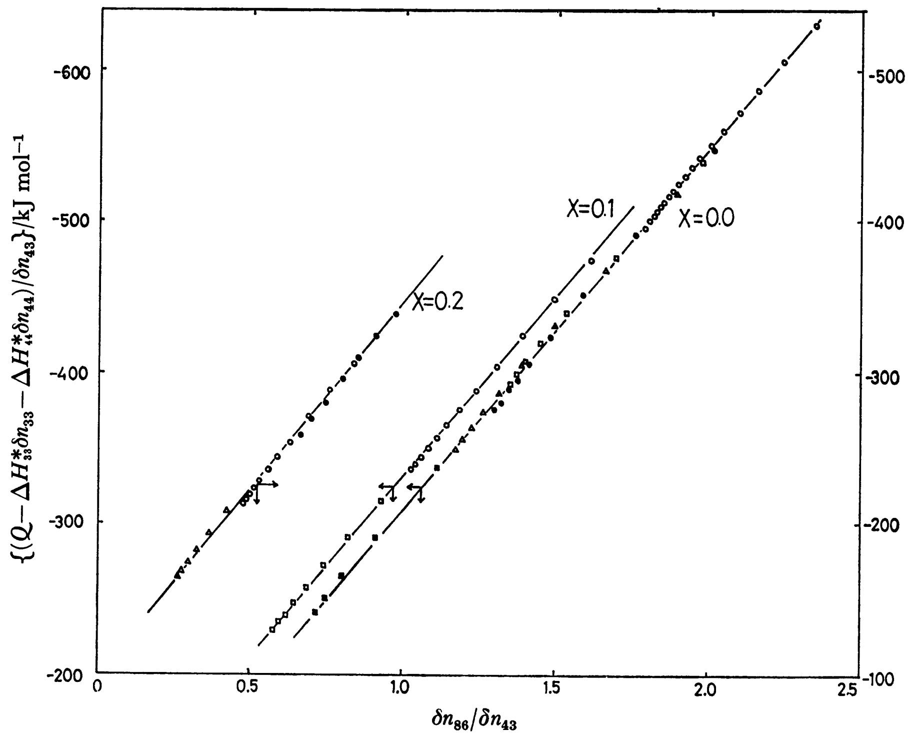

Fig. 3. Determination of the enthalpies, ΔH^*_{43} and ΔH^*_{86} for the hydrolytic reactions of lead (II) ion in the aqueous solution and dioxane–water mixtures containing 3 mol dm^{-3} (Li)ClO$_4$ as an ionic medium. X denotes the mole fraction of dioxane in the mixtures. Initial concentrations (mol dm^{-3}) of the total lead (II) ions are as follows: Aqueous; ○ 0.04149, △ 0.02151, □ 0.01234, ● 0.01039, □ 0.00564: 0.1 mole fraction dioxane: ○ 0.03756, □ 0.02028: 0.2 mole fraction dioxane; ● 0.04218, ○ 0.02061, △ 0.01042.

Table 2. The formation constants ($^*\beta_{pq}$) and the enthalpies (ΔH^*_{pq}/kJ mol^{-1}) and entropies ($T\Delta S^*_{pq}$/kJ mol^{-1}) of the hydrolytic reactions of lead(II) ion in the aqueous solution and dioxane–water mixtures

$q\mathrm{Pb}^{2+}+p\mathrm{H_2O}=\mathrm{Pb}_q(\mathrm{OH})_p{}^{(2q-p)+}+p\mathrm{H}^+$

		Mole fraction of dioxane		
		0.0	0.1	0.2
$\mathrm{Pb_3(OH)_3}^{3+}$	$-\log {}^*\beta_{33}$	−15.29(0.01)$^{a)}$	−14.98(0.01)$^{a)}$	−14.81(0.01)$^{a)}$
	ΔH^*_{33}	66.6 (1.8)	72.1 (2.9)	66.9 (1.3)
	$T\Delta S^*_{33}$	−20.7 (1.9)	−13.4 (3.0)	−17.7 (1.4)
$\mathrm{Pb_4(OH)_4}^{4+}$	$-\log {}^*\beta_{44}$	−19.42(0.01)$^{a)}$	−18.60(0.01)$^{a)}$	−19.17(0.01)$^{a)}$
	ΔH^*_{44}	81.4 (0.4)	84.1 (1.0)	94.7 (1.6)
	$T\Delta S^*_{44}$	−29.5 (0.5)	−22.1 (1.1)	−14.7 (1.7)
$\mathrm{Pb_3(OH)_4}^{2+}$	$-\log {}^*\beta_{43}$	−22.78(0.02)$^{a)}$	−21.79(0.02)$^{a)}$	−21.74(0.02)$^{a)}$
	ΔH^*_{43}	61.6 (2.0)	83.4 (2.5)	99.8 (2.0)
	$T\Delta S^*_{43}$	−68.4 (2.1)	−41.0 (2.6)	−24.3 (2.1)
$\mathrm{Pb_6(OH)_8}^{4+}$	$-\log {}^*\beta_{86}$	−42.33(0.01)$^{a)}$	−40.75(0.01)$^{a)}$	−41.12(0.01)$^{a)}$
	ΔH^*_{86}	242.8 (1.1)	243.2 (2.3)	236.7 (3.6)
	$T\Delta S^*_{86}$	1.3 (1.2)	10.6 (2.4)	2.0 (3.7)

Uncertaities are given in parentheses as the standard deviation. a) Ref. 1.

The plot of $(Q-\Delta H^*_{33}\cdot\delta n_{33}-\Delta H^*_{44}\cdot\delta n_{44})/\delta n_{43}$ against $\delta n_{86}/\delta n_{43}$ was a straight line in each solvent as shown in Fig. 3, from which the values of ΔH^*_{86} and ΔH^*_{43} were determined.

The enthalpies were finally evaluated by the least-squares method by minimizing $U=\sum(Q-Q_{\mathrm{calcd}})^2$ over the whole points measured in a system. The results obtained are summarized in Table 2. Typical calorimetric data obtained for the hydrolytic reactions of lead(II) ion in aqueous solution and the differences between the measured heats and the calculated ones are shown in Table 3.

TABLE 3. TYPICAL HEAT DATA OBTAINED FOR THE HYDROLYTIC REACTIONS OF LEAD(II) IONS IN AN AQUEOUS SOLUTION CONTAINING 3 mol dm^{-3} (Li)ClO$_4$ AT 25 °C

V_{add}/cm^3	Q/J	$(Q-Q_{\mathrm{calcd}})$/J
1) $c_{\mathrm{Pb}}=0\ 2040$ mol dm^{-3}		
$c_{\mathrm{H}}=-0.06259$ mol dm^{-3}		
0.801	16.45	−0.01
1.604	33.02	0.04
2.407	49.01	0.10
3.210	66.20	0.34
4.012	82.81	0.25
4.814	99.52	0.43
5.616	116.15	0.52
6.418	132.18	0.66
7.221	149.54	0.68
8.023	166.40	0.92
8.827	183.39	1.19
2) $c_{\mathrm{Pb}}=0.1502$ mol dm^{-3}		
$c_{\mathrm{H}}=-0.04793$ mol dm^{-3}		
0.604	12.31	−0.11
1.210	24.79	−0.11
1.816	37.23	−0.16
2.421	49.75	−0.11
3.025	62.18	−0.13
3.629	74.71	−0.07
4.234	87.27	−0.00
4.840	99.80	0.00
5.445	112.32	−0.05
6.050	124.89	−0.03
6.657	137.62	0.08
7.264	150.80	0.62
3) $c_{\mathrm{Pb}}=0.07912$ mol dm^{-3}		
$c_{\mathrm{H}}=-0.07056$ mol dm^{-3}		
0.817	18.78	−0.34
1.634	36.35	−0.19
2.435	53.24	−0.10
3.235	69.81	−0.11
4.036	86.34	−0.12
4.837	102.78	−0.18
5.638	119.17	−0.29
6.437	135.59	−0.36
7.239	151.98	−0.56
8.041	168.48	−0.63
8.842	184.96	−0.73
9.643	201.52	−0.79
10.444	218.24	−0.78
4) $c_{\mathrm{Pb}}=0.04148$ mol dm^{-3}		
$c_{\mathrm{H}}=-0.04452$ mol dm^{-3}		
0.164	9.00	−0.90
1.227	17.80	−1.15
1.843	26.16	−0.97
2.455	33.67	−0.65
3.067	40.36	−0.36
3.672	46.34	−0.14
4.283	51.94	−0.00
4.894	57.32	0.14
5.499	62.45	0.19
6.111	67.55	0.24
6.716	72.56	0.28
7.321	77.50	0.29
7.927	82.44	0.29
8.539	87.40	0.28
9.151	92.37	0.28
9.756	97.27	0.27
10.361	102.19	0.27
10.966	107.05	0.22
11.572	111.94	0.18
12.183	116.87	0.15
12.795	121.81	0.11
13.405	126.75	0.08
14.018	131.67	0.01
14.629	136.61	−0.03
15.234	141.55	−0.05
15.846	146.53	−0.08
16.451	151.47	−0.11
17.061	156.54	−0.08
5) $c_{\mathrm{Pb}}=0.02150$ mol dm^{-3}		
$c_{\mathrm{H}}=-0.02224$ mol dm^{-3}		
0.740	9.54	−0.14
1.345	16.22	0.08
1.951	22.04	0.30
2.563	27.37	0.44
3.175	32.45	0.44
3.784	37.42	0.42
4.395	42.37	0.40
5.006	47.27	0.33
5.610	52.09	0.34
6.221	57.04	0.19
6.830	61.90	0.08
7.440	66.80	−0.00
8.044	71.67	−0.09
8.654	75.93	−0.26
6) $c_{\mathrm{Pb}}=0.01233$ mol dm^{-3}		
$c_{\mathrm{H}}=-0.01479$ mol dm^{-3}		
0.512	7.67	−0.34
1.021	14.60	−0.30
1.534	20.53	0.00
2.044	25.46	0.27
2.558	29.47	−0.03
3.072	33.56	−0.15
3.585	37.71	−0.18
4.100	41.80	−0.27
4.614	45.87	−0.39
5.128	49.97	−0.49
5.639	54.12	−0.56

c_{Pb} denotes the total concentration of lead(II) ion in a test solution. c_{Pb} decreases by dilution by adding the titrant in the course of titration. c_{H} represents the concentration of analytical excess of hydrogen ion in the test solution. The negative values show that the solutions contain the corresponding excess amounts of hydroxide ions. The initial volume of the test solution is 149.83 cm^3. Concentrations of hydrogen ions in the titrant are 0.9887 mol dm^{-3} for runs 1—3 and 0.3887 mol dm^{-3} for runs 4—6. Q_{calcd} is calculated by using the enthalpies listed in Table 2. V_{add} stands for the total volume of the titrant added.

Discussion

The enthalpies and entropies for the hydrolytic reactions of lead(II) ions in the aqueous solution containing 3 mol dm^{-3} (Li)ClO$_4$ listed in Table 2 may be compared with those obtained by Carell and Olin[3] in an aqueous solution containing 3 mol dm^{-3} (Na)ClO$_4$. They have reported the enthalpies, ΔH^*_{44}, ΔH^*_{43}, and ΔH^*_{86}, which are 83.97 110.9 and 206.9 kJ mol^{-1}, respectively. Their ΔH^*_{44} value coincides well with our result, whilst their ΔH^*_{43} and ΔH^*_{86} are appreciably different from ours.

The enthalpy ΔH_D of the reaction

$$2Pb_3(OH)_4^{2+} = Pb_6(OH)_8^{4+} \tag{8}$$

was estimated as $\Delta H_D = \Delta H^*_{86} - 2\Delta H^*_{43}$, and the values in various solvents are shown in Table 4 together with the corresponding Gibbs energies and entropies. The enthalpies and entropies of the reaction were all largely positive. These results are in contrast to those obtained by Carell and Olin,[3] who reported that the enthalpy of reaction (8) was negative.

Table 4. The gibbs energy (ΔG_D/kJ mol^{-1}), enthalpy (ΔH_D/kJ mol^{-1}) and entropy ($T\Delta S_D$/kJ mol^{-1}) of the reaction, $2Pb_3(OH)_4^{2+} = Pb_6(OH)_8^{4+}$, in the aqueous solution and dioxane–water mixtures and the thermodynamic parameters of transfer from the aqueous solution to dioxane–water mixtures (indicated by a superscript t)

Mole fraction of dioxane	ΔG_D	ΔH_D	$T\Delta S_D$	ΔG^t_D	ΔH^t_D	$T\Delta S^t_D$
0.0	−18.47	119.6	138.1	—	—	—
0.1	−16.13	76.4	92.6	2.34	−43.2	−45.5
0.2	−13.44	37.1	50.6	5.03	−82.5	−87.5

In recent years, structural information of the hydroxo complexes of lead(II) ions in aqueous solutions has been obtained by means of X-ray diffraction.[4–7] According to Olin and Söderquist,[6,7] in the $Pb_6(OH)_8^{4+}$ complex one oxygen atom is located at the center of four lead atoms which are tetrahedrally arranged and the other two lead atoms are located outside the tetrahedral unit. If the complex formally written as $Pb_6(OH)_8^{4+}$ exists in the form of $Pb_6O(OH)_6^{4+}$ in solution, the dimerization reaction given in Eq. 8 should be written as Eq. 9:

$$2Pb_3(OH)_4^{2+} = Pb_6O(OH)_6^{4+} + H_2O. \tag{9}$$

The reaction involves a heterolysis of an O–H bond which may be largely endothermic. Thus, reaction (9) can appropriately account for our result that the enthalpy is largely positive. The positive enthalpies of transfer from an aqueous solution to dioxane–water mixtures for reaction (9) can be expected as we will discuss in the following section.

The Solvent Effects on the Thermodynamic Parameters of the Hydrolytic Reactions of Lead(II) Ion. The hydrolytic reaction of lead(II) ions may be expressed as follows:

$$qPb^{2+} + pH_2O = Pb_q(OH)_p^{(2q-p)+} + pH^+, \tag{10}$$

or

$$qPb^{2+} + (p+r)H_2O = Pb_qO_r(OH)_p^{(2q-p-2r)+} + (p+2r)H^+. \tag{11}$$

Combination of the thermodynamic parameters for reaction (10) given in Table 2 with those for the reaction, $H_2O = H^+ + OH^-$,[1,2] leads to Gibbs energies, enthalpies and entropies, ΔG_{pq}, ΔH_{pq} and ΔS_{pq}, respectively, for the following reaction:

$$qPb^{2+} + pOH^- = Pb_q(OH)_p^{(2q-p)+}. \tag{12}$$

The enthalpy of transfer for reaction (12), ΔH^t_{pq}, from an aqueous solution to a dioxane–water mixture is represented as follows:

$$\begin{aligned} \Delta H^t_{qp} &= \Delta H_{pq}(\text{mix}) - \Delta H_{pq}(\text{aq}) \\ &= \Delta h^t_{pq} - q\Delta h^t_{Pb} - p\Delta h^t_{OH}, \end{aligned} \tag{13}$$

where Δh^t_i denotes the partial molar enthalpy of transfer of species i. The Gibbs energies, enthalpies and entropies of transfer for the hydrolytic reactions of lead(II) ions from an aqueous solution to dioxane–water mixtures examined are summarized in Table 5, together with those quantities divided by the number of hydroxide ions, $\Delta G^t_{pq}/p$, $\Delta H^t_{pq}/p$, and $T\Delta S^t_{pq}/p$. In this table, $Pb_6O(OH)_6^{4+}$ is formally written as $Pb_6(OH)_8^{4+}$ according to reaction (10).

A question whether a complex is a hydroxo or an oxo-hydroxo complex always arises when we discuss the composition of $M_q(OH)_p^{(2q-p)+}$ type complexes. For lead(II)-hydroxo complexes, all of the complexes found, except the $Pb_6(OH)_8^{4+}$ complex, are believed to have only hydroxide ions as the ligands. Therefore,

Table 5. The thermodynamic parameters of transfer (ΔG^t_{pq}/kJ mol^{-1}, ΔH^t_{pq}/kJ mol^{-1}, and $T\Delta S^t_{pq}$/kJ mol^{-1}) for the hydrolytic reactions of lead(II) ions from the aqueous solution to dioxane–water mixtures: $qPb^{2+} + pOH^- = Pb_q(OH)_p^{(2q-p)+}$

	0.1 mole fraction of dioxane			0.2 mole fraction of dioxane		
	ΔG^t_{pq}	ΔH^t_{pq}	$T\Delta S^t_{pq}$	ΔG^t_{pq}	ΔH^t_{pq}	$T\Delta S^t_{pq}$
$Pb_3(OH)_3^{3+}$	−14.40(−4.83)	1.0(0.3)	15.5(5.2)	−28.59(−9.53)	−13.5(−4.5)	15.1(5.0)
$Pb_4(OH)_4^{4+}$	−21.63(−5.41)	−3.3(−0.8)	18.3(4.6)	−35.84(−8.96)	−5.0(−1.2)	30.8(7.7)
$Pb_3(OH)_4^{2+}$	−22.60(−5.65)	15.8(4.0)	38.4(9.6)	−40.35(−10.1)	19.8(5.0)	60.2(15.0)
$Pb_6(OH)_8^{4+}$	−42.92(−5.37)	−11.6(−1.5)	31.3(3.9)	−75.85(−9.48)	−42.9(−5.4)	33.0(4.1)

Values in parentheses give thermodynamic parameters per hydroxide ion, $\frac{1}{p}\Delta G^t_{pq}$, $\frac{1}{p}\Delta H^t_{pq}$, and $\frac{T}{p}\Delta S^t_{pq}$.

the discussion about the composition of the complexes on the basis of the thermodynamic quantities will be focused on the $\mathrm{Pb_6(OH)_8{}^{4+}}$ complex in the following section.

As we have already described in the previous paper,[1] the $\Delta G^{\mathrm{t}}_{pq}/p$ values of various metal ions such as beryllium(II), copper(II), nickel(II), cadmium(II), and lead(II) have been found to be approximately independent of not only the composition but also the kind of metal ions of the hydroxo complexes.[1] However, the $\Delta H^{\mathrm{t}}_{pq}$ values are strongly dependent on the composition of the hydroxo complexes. The solvent effects on the enthalpies of the hydrolytic reactions of beryllium ion from an aqueous solution to dioxane–water mixtures have been previously discussed in terms of the solvent structure of the bulk, the structure of the solvated ions involved in the reactions and the charge distribution within the hydroxo complexes.[2] A similar consideration can be made for interpreting the enthalpies of transfer from an aqueous solution to dioxane–water mixtures for the reactions of lead(II) ions.

As seen from Table 5, the $\Delta H_{44}/4$ value becomes more negative with the increase in the content of dioxane in the mixtures. However, the reverse is found for $\Delta H^{\mathrm{t}}_{43}/4$, which is positive. Therefore, the relation $\Delta H^{\mathrm{t}}_{44}/4 < \Delta H^{\mathrm{t}}_{43}/4$ holds in the solvent systems examined. By using Eq. 13, the relation is rewritten in terms of the partial molar enthalpies of transfer of the relevant species involved in the reactions as follows:

$$\frac{1}{4}\Delta h^{\mathrm{t}}_{44} - \Delta h^{\mathrm{t}}_{\mathrm{Pb}} < \frac{3}{4}\left(\frac{1}{3}\Delta h^{\mathrm{t}}_{43} - \Delta h^{\mathrm{t}}_{\mathrm{Pb}}\right). \qquad (14)$$

As seen in Table 2, the enthalpies of transfer for the reaction, $q\mathrm{Pb}^{2+} + p\mathrm{H_2O} = \mathrm{Pb}_q(\mathrm{OH})_p{}^{(2q-p)+} + p\mathrm{H}^+$, are zero or positive $[\Delta H^{*\mathrm{t}}_{pq} = \Delta H^{*}_{pq}(\mathrm{mix}) - \Delta H^{*}_{pq}(\mathrm{aq}) = \Delta h^{\mathrm{t}}_{pq} + p\Delta h^{\mathrm{t}}_{\mathrm{H}} - q\Delta h^{\mathrm{t}}_{\mathrm{Pb}} - p\Delta h^{\mathrm{t}}_{\mathrm{OH}}]$. The partial molar enthalpy of transfer of a neutral water molecule will be less than those of the ions involved in reaction (10), and thus the value $q\Delta h^{\mathrm{t}}_{\mathrm{Pb}}$ will be more negative than the values $\Delta h^{\mathrm{t}}_{pq}$ and $p\Delta h^{\mathrm{t}}_{\mathrm{H}}$. Therefore, both sides of Eq. 14 will be positive, thus:

$$\frac{1}{4}\Delta h^{\mathrm{t}}_{44} < \frac{1}{3}\Delta h^{\mathrm{t}}_{43} < 0. \qquad (15)$$

The formal charge per metal ion of the $\mathrm{Pb_4(OH)_4{}^{4+}}$ and $\mathrm{Pb_3(OH)_4{}^{2+}}$ complexes are +1 and +0.67, respectively. Therefore, the result obtained in Eq. 15 is consistent with what is expected from the consideration based on the formal charge per metal ion of the complexes, which has been discussed in the previous paper.[2]

Since the formal charge per metal ion z' of the $\mathrm{Pb_3(OH)_3{}^{3+}}$ and $\mathrm{Pb_4(OH)_4{}^{4+}}$ complexes are both +1, the relation $\Delta h^{\mathrm{t}}_{33}/3 \simeq \Delta h^{\mathrm{t}}_{44}/4$ will approximately hold, if we assume as the first approximation that the local charges per metal ion within the complexes are the same. The values of $\Delta H^{\mathrm{t}}_{33}/3$ were +0.3 and −4.5 kJ mol^{-1} for the dioxane systems containing 0.1 and 0.2 mole fraction of dioxane, respectively. If we take into account the uncertainties in ΔH^{*}_{33} listed in Table 2, it appears that $\Delta H^{\mathrm{t}}_{33}$ tends to monotonously decrease as the dioxane content increases (see Table 5). The same trend is also seen in $\Delta H^{\mathrm{t}}_{44}$. Although the value $\Delta H^{\mathrm{t}}_{33}/3$ is more negative than that of $\Delta H^{\mathrm{t}}_{44}/4$ in the 0.2 mole fraction dioxane system, the difference is not significant, and we can assume $\Delta H^{\mathrm{t}}_{33}/3 \simeq \Delta H^{\mathrm{t}}_{44}/4$. The values $\Delta H^{\mathrm{t}}_{33}/3$ of the $\mathrm{Be_3(OH)_3{}^{3+}}$ complex are −2.3 and −5.5 kJ mol^{-1} for 0.1 and 0.2 mole fraction dioxane systems, respectively,[2] which are more negative than the corresponding values of the $\mathrm{Pb_4(OH)_4{}^{4+}}$ or $\mathrm{Pb_3(OH)_3{}^{3+}}$ complex. This seems to be attributed to stronger solvation of beryllium(II) ions than that of lead(II) ions.

As is discussed above, at least at the first step of approach, the formal charge per metal ion of a hydroxo complex is an important factor which controls solvent effects on hydrolytic reactions of metal ions. The formal charge per metal ion of the $\mathrm{Pb_6(OH)_8{}^{4+}}$ complex is +0.67, which is the same as that of the $\mathrm{Pb_3(OH)_4{}^{2+}}$ complex. Therefore, if the approach so far examined for the estimation of the partial molar enthalpy of transfer of a hydroxo complex is applicable to the case of the $\mathrm{Pb_6(OH)_8{}^{4+}}$ complex, the value $\Delta H^{\mathrm{t}}_{86}/8$ would be similar to $\Delta H^{\mathrm{t}}_{43}/4$, that is, it would be positive. In fact, the values $\Delta H^{\mathrm{t}}_{86}/8$ obtained are −1.5 and −5.4 kJ mol^{-1} for the 0.1 and 0.2 mole fraction dioxane systems, respectively. Thus, the value $\Delta H^{\mathrm{t}}_{86}/8$ becomes more negative with an increase in the dioxane content in the mixtures in contradiction to that of $\Delta H^{\mathrm{t}}_{43}/4$. This fact can be explained by assuming the formation of the $\mathrm{Pb_6O(OH)_6{}^{4+}}$ complex instead of the $\mathrm{Pb_6(OH)_8{}^{4+}}$ complex.

The hydrolytic reaction of formation of the $\mathrm{Pb_6O(OH)_6{}^{4+}}$ complex is represented as follows:

$$6\mathrm{Pb}^{2+} + 7\mathrm{OH}^- = \mathrm{Pb_6O(OH)_6{}^{4+}} + \mathrm{H}^+. \qquad (16)$$

The enthalpy of transfer for the reaction (16) is written as follows:

$$\Delta H^{\mathrm{t}}_{616} = \Delta h^{\mathrm{t}}_{616} - 8\Delta h^{\mathrm{t}}_{\mathrm{OH}} - 6\Delta h^{\mathrm{t}}_{\mathrm{Pb}} + (\Delta h^{\mathrm{t}}_{\mathrm{H}} + \Delta h^{\mathrm{t}}_{\mathrm{OH}}), \qquad (17)$$

which may be compared with that for the reaction, $6\mathrm{Pb}^{2+} + 8\mathrm{OH}^- = 2\mathrm{Pb_3(OH)_4{}^{2+}}$,

$$2\Delta H^{\mathrm{t}}_{43} = 2\Delta h^{\mathrm{t}}_{43} - 8\Delta h^{\mathrm{t}}_{\mathrm{OH}} - 6\Delta h^{\mathrm{t}}_{\mathrm{Pb}}. \qquad (18)$$

Here $\Delta H^{\mathrm{t}}_{616}$ and $\Delta h^{\mathrm{t}}_{616}$ represent the quantities defined by Eq. 13 for the $\mathrm{Pb_6O(OH)_6{}^{4+}}$ complex.

The formal charge per metal ion of the $\mathrm{Pb_6O(OH)_6{}^{4+}}$ complex is +0.67, and thus, the value $\Delta h^{\mathrm{t}}_{616}$ will be similar to that of $2\Delta h^{\mathrm{t}}_{43}$. The term $\Delta h^{\mathrm{t}}_{\mathrm{H}} + \Delta h^{\mathrm{t}}_{\mathrm{OH}}$ in Eq. 17 is negative.[2] Therefore, even if the value $\Delta h^{\mathrm{t}}_{616} - 8\Delta h^{\mathrm{t}}_{\mathrm{OH}} - 6\Delta h^{\mathrm{t}}_{\mathrm{Pb}}$ is as largely positive as that $2\Delta H^{\mathrm{t}}_{43}$, the value $\Delta H^{\mathrm{t}}_{616}$ will remain negative owing to the term $\Delta h^{\mathrm{t}}_{\mathrm{H}} + \Delta h^{\mathrm{t}}_{\mathrm{OH}}$ which is more negative than $\Delta h^{\mathrm{t}}_{616} - 8\Delta h^{\mathrm{t}}_{\mathrm{OH}} - 6\Delta h^{\mathrm{t}}_{\mathrm{Pb}}$.

The enthalpy of transfer for reaction (9), $\Delta H^{\mathrm{t}}_{\mathrm{D}}$, is expressed as follows:

$$\Delta H^{\mathrm{t}}_{\mathrm{D}} = \Delta h^{\mathrm{t}}_{616} + \Delta h^{\mathrm{t}}_{\mathrm{H_2O}} - 2\Delta h^{\mathrm{t}}_{43}. \qquad (19)$$

If we assume that

$$\frac{1}{6}\Delta h^{\mathrm{t}}_{616} \simeq \frac{1}{3}\Delta h^{\mathrm{t}}_{43}, \qquad (20)$$

we obtain the following equation:

$$\Delta H^{\mathrm{t}}_{\mathrm{D}} \simeq \Delta h^{\mathrm{t}}_{\mathrm{H_2O}}. \qquad (21)$$

The values $\Delta H^{\mathrm{t}}_{\mathrm{D}}$ were found to be −43.2 and −82.5 kJ mol^{-1} for the systems of the dioxane contents of 0.1 and 0.2 mole fractions, respectively (Table 4). Although the values of $\Delta h^{t}_{\mathrm{H_2O}}$ estimated by using Eq. 21 may be too largely negative because of the oversimplified assumption given as Eq. 20, we can conclude that the partial molar enthalpies of transfer of water $\Delta h^{t}_{\mathrm{H_2O}}$ from an aqueous solution to dioxane–water mixtures will be negative. This result is consistent with that derived in the previous paper.[2] The hydrogen bonded structure of water in an aqueous solution is broken down by the addition of dioxane,[8,9] and thus, the value of $\Delta h^{t}_{\mathrm{H_2O}}$ will be negative by enhancement of the intramolecular O–H bonds within water molecules in dioxane–water mixtures.

The work has been partially supported by a Grant-in-Aid for Scientific Research No. 343011 from the Ministry of Education, Science and Culture.

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