A solution-reaction isoperibol calorimeter and standard molar enthalpies of formation of Ln(hq)$_2$Ac (Ln = La, Pr)[☆]

Hua-Guang Yu [a,b], Yi Liu [a,*], Zhi-Cheng Tan [b], Jia-Xin Dong [a], Teng-Jun Zou [a], Xiao-Ming Huang [a], Song-Sheng Qu [a]

[a] *Department of Chemistry, College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, PR China*
[b] *Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China*

Abstract

An on-line solution-reaction isoperibol calorimeter has been constructed. The performance of the apparatus was evaluated by measuring the molar enthalpy of solution of KCl in water at 298.15 K. The uncertainty and the inaccurary of the experimental results were within $\pm 0.3\%$ compared with the recommended reference data. Using the calorimeter, the molar enthalpies of reaction for the following two reactions: $LaCl_3 \cdot 7H_2O(s) + 2Hhq(s) + NaAc(s) = La(hq)_2Ac(s) + NaCl(s) + 2HCl(g) + 7H_2O(l)$ and $PrCl_3 \cdot 6H_2O(s) + 2Hhq(s) + NaAc(s) = Pr(hq)_2Ac(s) + NaCl(s) + 2HCl(g) + 6H_2O(l)$, were determined at $T = 298.15$ K, as $-(78.3 \pm 0.6)$ and $-(97.3 \pm 0.5)$ kJ mol^{-1}, respectively. From the above molar enthalpies of reaction and other auxiliary thermodynamic quantities, the standard molar enthalpies of formation of La(hq)$_2$Ac and Pr(hq)$_2$Ac, at $T = 298.15$ K, have been derived to be $-(1535.5 \pm 0.7)$ and $-(1536.7 \pm 0.6)$ kJ mol^{-1}, respectively.
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1. Introduction

Solution-reaction calorimetry is a broad and versatile technique, for example measurements may be done on liquid–liquid and liquid–solid systems to quantify heats of solution, dissolution, dilution, mixing, enthalpies of reaction, formation, and excess enthalpies [1–7]. Especially, solution-reaction calorimetry has become a classical method to obtain the standard molar enthalpies of formation of many inorganic compounds. The standard enthalpy of formation, together with the standard entropy, are equally important data in determining any chemical equilibria [8].

Solution calorimetry has been successfully employed to investigate differences in crystal formation and structure. These differences in crystal properties often correlate with an aspect of the behavior of drug/product, e.g. correlation of heats of solution with stability [9]. The solution calorimetry method was a rapid, accurate and convenient method to determine crystallinity of various systems for pharmaceutical dosage form development and for quality control

[10]. Solution calorimetry provided a good method to detect and quantify the amorphous composition of materials that have small amorphous contents. In addition, it has been shown capable of differentiating between samples of different moisture content and providing an indication of how moisture sorption contributes to the thermodynamics of the solution process [11]. Anthony et al. [12] illustrated what factors contribute to the exothermicity of circulating fluidized bed combustion (CFBC) ashes by using solution calorimetry. Reaction calorimetry provides both process design information and process safety information of chemical processes [7,13].

China is a country abundant in rare earth resources. 8-Hydroxyquinoline (Hhq) is an excellent ligand forming various coordination compounds. All of the rare earth elements, 8-hydroxyquinoline and acetic acid have bactericidal and fungicidal functions. Their solid ternary coordination compounds represent stronger biocidal functions than the free metal ions and the ligands alone [14,15]. The synergetic effect of rare earth with 8-hydroxyquinoline and acetic acid in stimulating the growth of plants is attracting increasing attention. The information about the role of metal complexes in biological systems, their presence and concentration in different equilibrium is of significant importance [16].

Coordination compounds of rare earth were widely used in many fields, however, few thermodynamic properties of the compounds have been reported. To further research on the compounds, it is necessary to determine their basic thermochemical parameters. According to Hess' law, we designed two thermochemical cycles, obtained the molar enthalpies of reaction for the two reactions: $LaCl_3 \cdot 7H_2O(s) + 2Hhq(s) + NaAc(s) = La(hq)_2Ac(s) + NaCl(s) + 2HCl(g) + 7H_2O(l)$ and $PrCl_3 \cdot 6H_2O(s) + 2Hhq(s) + NaAc(s) = Pr(hq)_2Ac(s) + NaCl(s) + 2HCl(g) + 6H_2O(l)$, and derived the standard molar enthalpies of formation of $Ln(hq)_2Ac$ (Ln = La, Pr).

2. Experimental

2.1. Chemicals

KCl, with a purity more than 99.99%, was purchased from Shanghai No. 1 Reagent Factory,

Shanghai, PR China. It was dried in a vacuum oven at 408 K for 6 h prior to use. The chemicals $LaCl_3 \cdot 7H_2O$, $PrCl_3 \cdot 6H_2O$, NaAc, and NaCl used were of analytical grade and obtained from Shanghai Reagent Factory, Shanghai, PR China. 8-Hydroxyquinoline was supplied by Shanghai No. 3 Reagent Factory and recrystallized from absolute alcohol for two times before being used. Double-distilled water was used to prepare all of the solutions.

2.2. Synthesis and characterisation of the coordination compounds

The synthesis and purification of $Ln(hq)_2Ac$ was carried out as previously described in literatures [14,15]. $LnCl_3 \cdot nH_2O$, an equivalent amount of NaAc with two equivalents of Hhq reacted in mixing solution of alcohol and double-distilled water (5:1) at 60 °C for 3–4 h (pH = 7–8). The yellow precipitates were filtered, and the products were subsequently washed with double-distilled water and then absolute alcohol for three times, respectively, and further dried in a vacuum oven at 60 °C for 24 h. Satisfactory results of elemental and spectroscopic analysis, and TG–DTA measurements were obtained for the two compounds.

2.3. Solution-reaction isoperibol calorimeter

On the basis of other calorimetric apparatus [1–5,13], and our previous work [17,18], an on-line solution-reaction isoperibol calorimeter (semi-adiabatic type), has been constructed in our laboratories. The schematic diagram of the calorimeter is shown in Fig. 1.

The calorimeter consisted of a water thermostat, a pyrex-glass Dewar, a glass sample cell, a heater for calibration and equilibration purposes, a glass-sheathed thermistor probe, an amplifier, a circuit used as an A/D converter and a personal computer for data acquisition and processing. The sample cell was a small glass cup, 2 mm thick, 14 mm high and 14 mm in diameter. The heater and the thermistor were placed in two glass tubes, in which silicone oil was filled as a heat transfer medium. The Dewar vessel with an internal volume of 100 ml, equipped with a twin-blade stirrer, served as a mixing chamber, was submerged in the water thermostat. The stirrer in the Dewar was set at 375 rpm. The vacuum jacket of the Dewar vessel
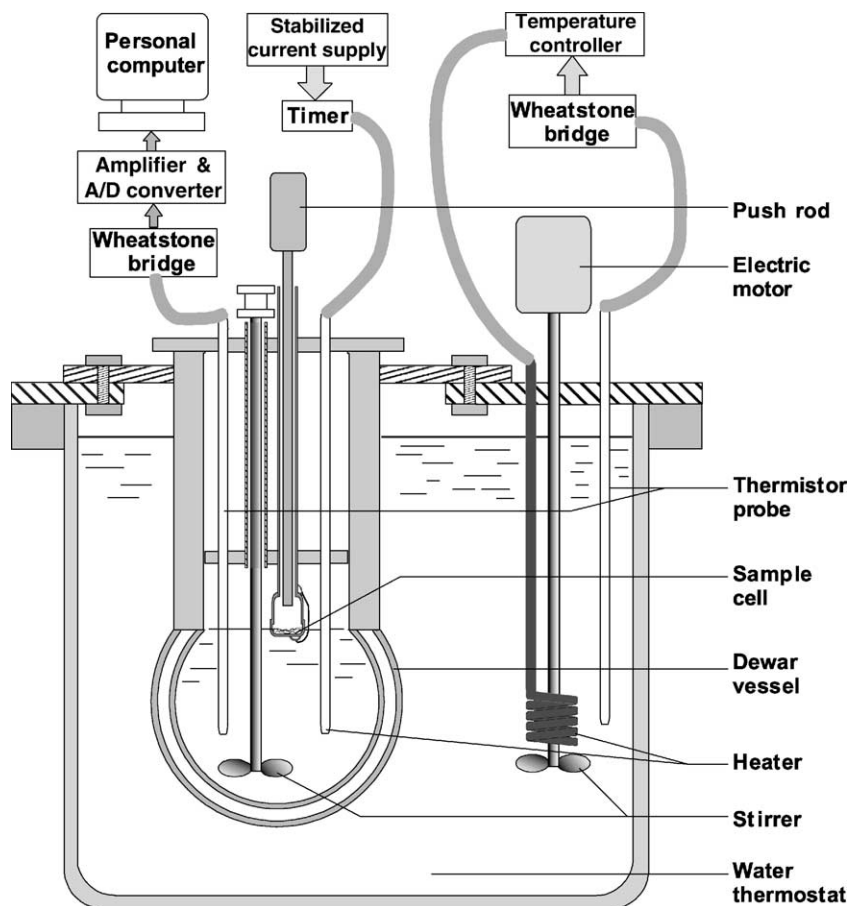
Fig. 1. The schematic diagram of a solution-reaction isoperibol calorimeter.

diminished the heat transfer between the measurement system and the thermostatic system. Excellent thermal insulation was obtained with the Dewar fully silvered.

During experiment, the water thermostat was maintained at $T = (298.150 \pm 0.001)$ K through a circuit consisted of a Wheatstone bridge, a modified high-precision temperature controller (Model DWT-702, manufactured by No. 6 Plant of Automatic Meter of Shanghai) and a heater. The controller operated in the proportional-integral-derivative (PID) mode. The other thermistor probe was used as a sensor for temperature control of the thermostat. The ambient temperature of the laboratory, in which the calorimeter was placed, must be kept at between 10 and 18 °C and maintained steady. Any disturbances from air circulation in the laboratory should

be avoided. The water thermostat was well stirred, and excellent stability and uniformity of temperature in the thermostat was available.

Before the calorimetric test, temperature of solvent in the Dewar must reach the equilibrium temperature. Once equilibrium was obtained, the glass rod was depressed by hand to release the sample into the solvent. The calibration was carried out by Joule's heat using a stabilized dc current supply with a stability of 1×10^{-4} and a permanent precision resistor with a temperature coefficient of less than 10 ppm. The magnitudes of the current through the heater and the resistance of the heater were measured by a digital multimeter (Model 2000, Keithley, USA). The heating duration was accurately recorded using a digital electronic timer with a resolution of 0.01 s. The temperature (potential)–time

curve for each experiment included two parts, the solution (or reaction) part and the electric calibration part. Each part was divided into a fore-period about 5 min, a main-period about 6–15 min, and an after-period about 5 min. After the calorimetric test was completed, the Dewar and all components in it were completely cleaned and dried.

The change of temperature, ΔT against the surroundings—a thermostat at 298.150 K with a temperature constancy of 1×10^{-3} K—generated by the enthalpy of solution was measured with the thermistor probe. The thermistor with very large negative temperature coefficient of resistance, constituted one of the four arms of the Wheatstone bridge circuit. The thermistor had a nominal resistance of 80 kΩ at 298 K. The other resistors in the bridge circuit were manganin wire-wound component resistors with negligible temperature coefficient. A constant voltage supplied from a stabilized dry cell group was applied to the Wheatstone bridge. The unbalanced voltage signal was linear response to the change of temperature for a temperature range of ± 0.8 K. The signal was amplified, then recorded versus time typically with one entry every 1 or 2 s, and interfaced to a personal computer using the program Solution-Reaction Calorimetry System (SRCS) to control the calorimetric system. The entire circuit was very stable, and most of the "noise" could be traced to the stirring in the Dewar. The resolution of temperature measurement was ± 0.0001 K. The time constant of the calorimeter was about 3 s.

The inevitable heat transfer and heat generations due to friction were compensated and the corrected temperature change (the adiabatic temperature change) ΔT^* was obtained according to Dickinson's method (the equal area method) [19]. The heat of solution was finally calculated from the equation

$$\frac{Q_s}{\Delta T_s^*} = \frac{Q_E}{\Delta T_E^*}$$

where Q_s was the heat of solution, ΔT_s^* the adiabatic temperature change of the solution process, Q_E the heat of electric calibration, and ΔT_E^* the adiabatic temperature change of electric calibration.

The performance and accuracy of the calorimetric system was tested by measuring the molar enthalpy of solution of KCl (Standard Reference Material 1655, the National Institute of Standards and Technology) in double-distilled water. Six independent

Table 1
The molar enthalpy of solution of KCl in water at 298.15 K

| No.	m (g)	$\Delta_s H_m^{\ominus}$ (kJ mol^{-1})
1	0.3795	17.586
2	0.3742	17.533
3	0.3825	17.542
4	0.3673	17.571
5	0.3851	17.577
6	0.3669	17.552
Mean		17.560 ± 0.021

experiments were carried out, and the results are presented in Table 1. The molar enthalpy of solution of KCl in double-distilled water was 17560 ± 21 J mol^{-1} at 298.15 K, which was in good agreement with the published values in literatures [20,21]. The uncertainty and the inaccuary of the experimental results were within $\pm 0.3\%$ compared with the recommended reference data.

The calorimeter was adapted for measuring enthalpies of solid–liquid, liquid–liquid interactions. The necessary amount of sample without loss of general accuracy was 0.2–0.6 g per experiment.

### 2.4. Determination of the molar enthalpies of dissolution

The Reactions (1) and (2) are depicted in Figs. 2 and 3, respectively.

Samples of 0.5 mmol [LaCl$_3$·7H$_2$O(s), 2Hhq(s), and NaAc(s)] were dissolved in 100.0 ml 2.500 mol l^{-1} HCl(aq) at 298.15 K

$$\{LaCl_3 \cdot 7H_2O(s) + 2Hhq(s) + NaAc(s)\} + S_1$$
$$\rightarrow \text{solution A} \qquad (3)$$
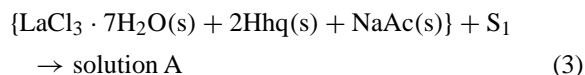
where S$_1$ was the calorimetric solvent.

Samples of 0.5 mmol [La(hq)$_2$Ac(s) and NaCl(s)] were dissolved in [100.0 ml 2.500 mol l^{-1} HCl (aq) + 1.0 mmol HCl + 3.5 mmol H$_2$O] at 298.15 K

$$\{La(hq)_2Ac(s) + NaCl(s)\} + S_2 \rightarrow \text{solution B} \qquad (4)$$
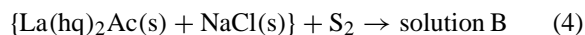
where S$_2$ was the calorimetric solvent.

The calorimetric results of Reactions (3) and (4) are listed in Tables 2 and 3.

Samples of 0.5 mmol [PrCl$_3$·6H$_2$O(s), 2Hhq(s), and NaAc(s)] were dissolved in 100.0 ml 2.500 mol l^{-1}
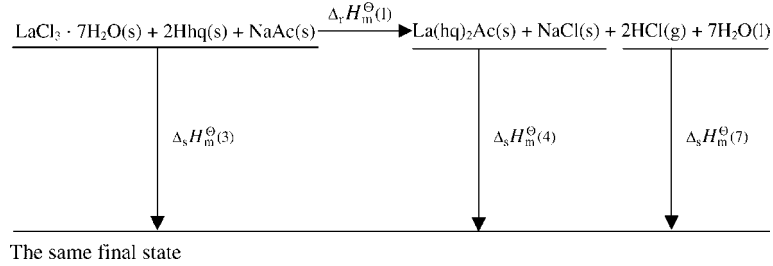
Fig. 2. Thermochemical cycle for measuring the molar enthalpy of reaction for Reaction (1).
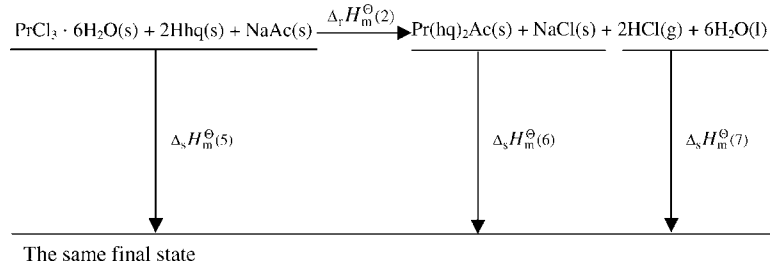

Fig. 3. Thermochemical cycle for measuring the molar enthalpy of reaction for Reaction (2).

Table 2
The molar enthalpy of dissolution of 0.5 mmol [LaCl$_3$·7H$_2$O(s), 2Hhq(s), and NaAc(s)] in 100.0 ml 2.500 mol l^{-1} HCl(aq) at 298.15 K[a]

| No.	m (g)			Q_s (J)	$\Delta_s H_m^{\ominus}$ (kJ mol^{-1})
	LaCl$_3$·7H$_2$O(s)	2Hhq(s)	NaAc(s)		
1	0.1854	0.1453	0.0414	−24.988	−49.975
2	0.1861	0.1456	0.0411	−25.034	−50.068
3	0.1860	0.1453	0.0412	−24.959	−49.918
4	0.1861	0.1454	0.0412	−25.359	−50.718
5	0.1860	0.1454	0.0414	−25.339	−50.678
Mean					−50.271 ± 0.352

[a] Q_s: heat of dissolution; $\Delta_f H_m^{\ominus}$: the molar enthalpy of dissolution.

Table 3
The molar enthalpy of dissolution of 0.5 mmol [La(hq)$_2$Ac(s) and NaCl(s)] in [100.0 ml 2.500 mol l^{-1} HCl(aq) + 1.0 mmol HCl + 3.5 mmol H$_2$O] at 298.15 K

No.	m (g)		Q_s (J)	$\Delta_s H_m^{\ominus}$ (kJ mol^{-1})
	La(hq)$_2$Ac(s)	NaCl(s)		
1	0.2432	0.0291	−57.585	−115.171
2	0.2433	0.0292	−57.998	−115.998
3	0.2433	0.0291	−57.305	−114.611
4	0.2435	0.0291	−57.924	−115.847
5	0.2434	0.0296	−57.602	−115.203
Mean				−115.366 ± 0.503

HCl (aq) at 298.15 K

$$\{PrCl_3 \cdot 6H_2O(s) + 2Hhq(s) + NaAc(s)\} + S_1$$
$$\rightarrow solution\ C \qquad (5)$$
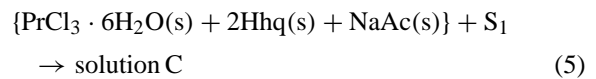
where S$_1$ was the calorimetric solvent.

Samples of 0.5 mmol [Pr(hq)$_2$Ac(s) and NaCl(s)] were dissolved in [100.0 ml 2.500 mol l^{-1} HCl (aq) + 1.0 mmol HCl + 3.0 mmol H$_2$O] at 298.15 K

$$\{Pr(hq)_2Ac(s) + NaCl(s)\} + S_3 \rightarrow solution\ D \qquad (6)$$
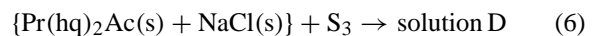
where S$_3$ was the calorimetric solvent.

The calorimetric results of Reactions (5) and (6) are shown in Tables 4 and 5.

Table 4
The molar enthalpy of dissolution of 0.5 mmol [PrCl$_3$·6H$_2$O(s), 2Hhq(s), and NaAc(s)] in 100.0 ml 2.500 mol l^{-1} HCl(aq) at 298.15 K

No.	m (g)			Q_s (J)	$\Delta_s H_m^{\Theta}$ (kJ mol^{-1})
	PrCl$_3$·6H$_2$O(s)	2Hhq(s)	NaAc(s)		
1	0.1776	0.1454	0.0411	−28.172	−56.344
2	0.1780	0.1455	0.0411	−27.976	−56.029
3	0.1779	0.1456	0.0411	−28.524	−57.047
4	0.1778	0.1453	0.0412	−28.232	−56.465
5	0.1780	0.1454	0.0412	−28.005	−56.010
Mean					−56.379 ± 0.378

Table 5
The molar enthalpy of dissolution of 0.5 mmol [Pr(hq)$_2$Ac(s) and NaCl(s)] in [100.0 ml 2.500 mol l^{-1} HCl (aq) + 1.0 mmol HCl + 3.0 mmol H$_2$O] at 298.15 K

No.	m (g)		Q_s (J)	$\Delta_s H_m^{\Theta}$ (kJ mol^{-1})
	Pr(hq)$_2$Ac(s)	NaCl(s)		
1	0.2443	0.0295	−51.228	−102.457
2	0.2444	0.0292	−51.192	−102.382
3	0.2443	0.0294	−51.391	−102.784
4	0.2444	0.0295	−51.015	−102.031
5	0.2443	0.0294	−51.473	−102.947
Mean				−102.520 ± 0.321

3. Results

3.1. Evaluation of the enthalpy of dissolution

The molar enthalpy of dissolution of [2 mol HCl (g) + 7 mol H$_2$O (l)] or [2 mol HCl (g) + 6 mol H$_2$O (l)] in [2000 × 100.0 ml] 2.500 mol l^{-1} HCl (aq) at 298.15 K was calculated

$$\Delta_s H_m^{\Theta}(7)$$
$$= 2\Delta_s H_{\infty}^{\Theta}[\text{HCl(g)}] - 2\Delta_d H_m^{\Theta}[\text{HCl(aq)}(2.500 \rightarrow 0)]$$
$$= 2[74.772 - 3.060] = 143.424 \text{ kJ mol}^{-1}$$

3.2. The molar enthalpies of reaction for the two reactions

$$\Delta_r H_m^{\Theta}(1)$$
$$= \Delta_s H_m^{\Theta}(3) - \Delta_s H_m^{\Theta}(4) - \Delta_s H_m^{\Theta}(7)$$
$$= [-50.271] - [-115.36] - [143.424]$$
$$= -78.3 \pm 0.6 \text{ kJ mol}^{-1}$$

$$\Delta_r H_m^{\Theta}(2)$$
$$= \Delta_s H_m^{\Theta}(5) - \Delta_s H_m^{\Theta}(6) - \Delta_s H_m^{\Theta}(7)$$
$$= [-56.379] - [-102.520] - [143.424]$$
$$= -97.3 \pm 0.5 \text{ kJ mol}^{-1}$$

3.3. The standard molar enthalpies of formation of the two compounds

From the molar enthalpies of reaction obtained for the two reactions and using various ancillary data, the standard molar enthalpies of formation of the two co-ordination compounds were calculated

$$\Delta_f H_m^{\Theta}[\text{La(hq)}_2\text{Ac(s)}]$$
$$= \Delta_f H_m^{\Theta}[\text{LaCl}_3 \cdot 7\text{H}_2\text{O(s)}] + 2\Delta_f H_m^{\Theta}[\text{Hhq(s)}]$$
$$+ \Delta_f H_m^{\Theta}[\text{NaAc(s)}] - \Delta_f H_m^{\Theta}[\text{NaCl(s)}]$$
$$- 2\Delta_f H_m^{\Theta}[\text{HCl(g)}] - 7\Delta_f H_m^{\Theta}[\text{H}_2\text{O(l)}]$$
$$+ \Delta_r H_m^{\Theta}(1)$$

$$\Delta_f H_m^{\Theta}[\text{La(hq)}_2\text{Ac(s)}]$$
$$= -[-3178.6] + 2[-83.3] + [-708.13]$$
$$- [-410.76] - 2[-92.31] - 7[-285.830]$$
$$+ [-78.3] = -1535.5 \pm 0.7 \text{ kJ mol}^{-1}$$

$$\Delta_f H_m^{\Theta}[\text{Pr(hq)}_2\text{Ac(s)}]$$
$$= \Delta_f H_m^{\Theta}[\text{PrCl}_3 \cdot 6\text{H}_2\text{O(s)}] + 2\Delta_f H_m^{\Theta}[\text{Hhq(s)}]$$
$$+ \Delta_f H_m^{\Theta}[\text{NaAc(s)}] - \Delta_f H_m^{\Theta}[\text{NaCl(s)}]$$
$$- 2\Delta_f H_m^{\Theta}[\text{HCl(g)}] - 6\Delta_f H_m^{\Theta}[\text{H}_2\text{O(l)}]$$
$$+ \Delta_r H_m^{\Theta}(2)$$

Table 6
The molar enthalpies of reaction for the two reactions

Reaction	$\Delta_f H_m^{\ominus}$ (kJ mol^{-1})
LaCl$_3$·7H$_2$O(s) + 2Hhq(s) + NaAc(s) → La(hq)$_2$Ac(s) + NaCl(s) + 2HCl(g) + 7H$_2$O(l)	-78.3 ± 0.6
PrCl$_3$·6H$_2$O(s) + 2Hhq(s) + NaAc(s) → Pr(hq)$_2$Ac(s) + NaCl(s) + 2HCl(g) + 6H$_2$O(l)	-97.3 ± 0.5

Table 7
The standard molar enthalpies of formation of the two compounds

Compound	$\Delta_f H_m^{\ominus}$ (kJ mol^{-1})
La(hq)$_2$Ac(s)	-1535.5 ± 0.7
Pr(hq)$_2$Ac(s)	-1536.7 ± 0.6

$\Delta_f H_m^{\ominus}[\text{Pr(hq)}_2\text{Ac(s)}]$

$= [-2875.00] + 2[-83.3] + [-708.13]$

$\quad - [-410.76] - 2[-92.31] - 6[-285.830]$

$\quad + [-78.3] = -1536.7 \pm 0.6 \, \text{kJ mol}^{-1}$

The final results of the molar enthalpies of reaction and the standard molar enthalpies of formation are summarized in Tables 6 and 7.

3.3.1. Ancillary data

The following data were used:

Compound	Enthalpies (kJ mol^{-1})	References
$\Delta_f H_m^{\ominus}[\text{H}_2\text{O(l)}]$	-285.830 ± 0.042	[22]
$\Delta_f H_m^{\ominus}[\text{HCl(g)}]$	-92.31 ± 0.13	[22]
$\Delta_f H_m^{\ominus}[\text{NaCl(s)}]$	-410.76	[23]
$\Delta_f H_m^{\ominus}[\text{LaCl}_3 \cdot 7\text{H}_2\text{O(s)}]$	-3178.6	[23]
$\Delta_f H_m^{\ominus}[\text{PrCl}_3 \cdot 6\text{H}_2\text{O(s)}]$	-2875.00	[24]
$\Delta_f H_m^{\ominus}[\text{Hhq(s)}]$	-83.3	[25]
$\Delta_f H_m^{\ominus}[\text{NaAc(s)}]$	-708.13	[23]
$\Delta_s H_{\infty}^{\ominus}[\text{HCl(g)}]$	74.772	[23]
$\Delta_d H_m^{\ominus}[\text{HCl(aq, } 2.500 \to 0)]$	3.060	[23]

4. Discussion

Li et al. [26] have reported the standard molar enthalpy of formation of a similar inorganic compound, coordination compound of lanthanum with 8-hydroxyquinoline and trichloroacetic acid (TCA), La(hq)$_2$(TCA), and $\Delta_f H_m^{\ominus}$[La(hq)$_2$(TCA), s,

298.15 K] was determined as $-1375.6 \, \text{kJ mol}^{-1}$. In present work, the standard molar enthalpy of formation of coordination compound of rare earth with 8-hydroxyquinoline and acetic acid, $\Delta_f H_m^{\ominus}$[La(hq)$_2$ (AC), s, 298.15 K] and $\Delta_f H_m^{\ominus}$[Pr(hq)$_2$(AC), s, 298.15 K] were obtained to be $-1535.5 \pm 0.7 \, \text{kJ mol}^{-1}$ and $-1536.7 \pm 0.6 \, \text{kJ mol}^{-1}$, respectively. The difference of $\Delta_f H_m^{\ominus}$ between La(hq)$_2$(TCA) and La(hq)$_2$(AC) probably resulted from the difference of the abilities of trichloroacetic acid and acetic acid to form coordination compounds with rare earth. The little difference between the $\Delta_f H_m^{\ominus}$[La(hq)$_2$(AC), s, 298.15 K] and $\Delta_f H_m^{\ominus}$[Pr(hq)$_2$(AC), s, 298.15 K] may be attributed to the fact that the atom of Pr has smaller radius than that of La due to lanthanide contraction.

The chosen calorimetric solvent must dissolve the chemicals in the sample cell completely and relatively rapidly. So the choice of the calorimetric solvent is very important in the calorimetric experiments. Rigorous control of the stoichiometry was maintained through each series of experiments to ensure that the final solutions resulting from dissolution of the reactants were of the same composition of those from dissolution of the products. This was tested by releasing the sample cell containing the final solution from the dissolution of the reactants, into the final

solution from the products in the calorimeter, and no enthalpy change being detected [3]. The UV-Vis spectrums and refractive indexes of the final solution of the reactants and the final solution of the products, can also be used to determine whether they have the same thermodynamic state [26]. In the present experiments, the solution A had the same composition with the solution B, and the solution C was of the same composition with the solution D. Thus, we believed that the values of $\Delta_f H_m^{\ominus}$ determined by solution-reaction calorimetry was reliable.

5. Conclusion

An on-line solution-reaction isoperibol calorimeter has been developed and used to determine the molar enthalpy of reaction for two reactions and the standard molar enthalpy of formation of Ln(hq)$_2$Ac (Ln = La, Pr). In general, a solution-reaction calorimeter is very useful tool in the thermochemical studies, which is capable of providing accurate thermodynamic quantities of many important substances in industry and scientific research. This type of study may also potentially benefit the research and development of the coordination compounds of rare earth.

Acknowledgements

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