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A thermochemical study on the coordination complex of lanthanum trichloroacetic acid with 8-hydroxyquinoline

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Abstract

The standard molar reaction enthalpies of two reactions, $LaCl_3{\cdot}7H_2O(s) + 3CCl_3COOH(s)$ (or TCA) $= La(TCA)_3{\cdot}3H_2O(s) + 3HCl(g) + 4H_2O(l)$ and $La(TCA)_3{\cdot}3H_2O(s) + 2C_9H_7NO(s) = La(TCA)(C_9H_6NO)_2(s) + 2CCl_3COOH(s) + 3H_2O(l)$, were studied by classical solution calorimetry. The molar dissolution enthalpies of the reactants and the products of the two reactions in certain solvent (for one reaction is in 1 mol/l HCl and another in a mixed solution consisting of absolute ethyl alcohol, dimethyl sulfoxide and 4 mol/l HCl) were determined by using an isoperibol calorimeter. From the results and other auxiliary quantities, the standard molar formation enthalpies of [$La(TCA)_3{\cdot}3H_2O$, s, 298.15 K] and [$La(TCA)(C_9H_6NO)_2$, s, 298.15 K] were determined to be $\Delta_f H_m^{\ominus}$[$La(TCA)_3{\cdot}3H_2O$, s, 298.15 K] $= -3063.3$ kJ/mol and $\Delta_f H_m^{\ominus}$[$La(TCA)(C_9H_6NO)_2$, s, 298.15 K] $= -1375.6$ kJ/mol.

Keywords: Lanthanum chloride; Trichloroacetic acid; 8-Hydroxyquinoline coordination complex; Thermochemical study

1. Introduction

Both rare earth ions [1] and 8-hydroxyquinoline possess disinfect function [2], their complexes have more powerful disinfection. Their binary complexes were reported as early as in 1963 [3]. The research on their triad complexes has become very active in recent years because of its wide application in many fields [4–7]. Synthesis and characterization of the complexes of rare earth trichloroacetic acid salts with 8-hydroxyquinoline were reported by Dong and Zhu [7], and its application research experiments in leather mouldyproof showed that the complexes have powerful disinfection properties. Obviously, it is very important to carry out research on the complexes of rare earth trichloroacetic acid salts and 8-hydroxyquinoline. In order to make a deep research on the complexes and provide for theory in living things mouldyproof mechanism, it is necessary to know their basic thermodynamics property. However, the thermochemical properties of their complexes have not been reported. Therefore, with solution calorimetry on the self-made and new type isoperibol reaction calorimeter [10], we determined the dissolution enthalpies of $LaCl_3{\cdot}7H_2O(s)$, $CCl_3COOH(s)$, and $La(TCA)_3{\cdot}3H_2O(s)$ in 1 mol/l HCl. According to Hess' Law, we designed a thermochemical cycle and through calculation got the reaction enthalpy of lanthanum chloride 7-hydrate with trichloroacetic acid and also estimated the standard formation enthalpy of $La(TCA)_3{\cdot}3H_2O(s)$. Meanwhile, we determined the dissolution enthalpy

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of $La(TCA)_3{\cdot}3H_2O(s)$, $2C_9H_7NO(s)$, $La(TCA)(C_9H_6NO)_2(s)$, and $2CCl_3COOH(s)$ in mixed solution consisting of absolute ethyl alcohol, dimethyl sulfoxide, and 4 mol/l HCl. And again according to Hess' Law, we designed a thermochemical cycle and through calculation got reaction enthalpy of lanthanum trichloroacetic acid with 8-hydroxyquinoline and also estimated the standard formation enthalpy of $La(TCA)(C_9H_6NO)_2(s)$.

2. Experimental

2.1. Chemicals

The chemicals $LaCl_3{\cdot}7H_2O(s)$, $CCl_3COOH(s)$, $C_9H_7NO(s)$, and KCl used were of A.R. grade and obtained from Shanghai Reagent Company.

$LaCl_3{\cdot}7H_2O(s)$ with a purity higher than 45% (calculate according to La_2O_3) was dried in a desiccator containing sulfuric acid of 60% [8] at room temperature to constant mass prior to use; $CCl_3COOH(s)$ with a purity higher than 99.5% was dried in a vacuum desiccator containing P_4O_{10} until constant mass prior to use; KCl (calorimetric primary standard) with a purity greater than 99.99% was dried in a vacuum oven for 6 h at 135°C prior to use; $C_9H_7NO(s)$ (8-hydroxyquinoline) with a purity higher than 99.5% was used.

2.2. Preparations

$La(TCA)_3{\cdot}3H_2O(s)$ (a white solid) was prepared according to the method given in [9] and the crystal was repeatedly crystallized in a mixed solution consisting of C_2H_5OH and $CHCl_3$ and then the crystals were put into a desiccator containing P_4O_{10} until the mass of the crystals became a constant. The chemical analysis proved that the composition of the complex was $La(TCA)_3{\cdot}3H_2O(s)$ and its purity was greater than 99.5%.

$La(TCA)(C_9H_6NO)_2(s)$ (a yellow solid) was prepared and analyzed according to the method given in [7].

2.3. Calorimeter and calibration

The isoperibol reaction calorimeter used for this study was constructed in the laboratory and was adapted to determine the enthalpies of solid–solid and liquid–liquid reaction [10]. The volume of the reaction vessel was 100 cm^3. The precision of temperature for control and determination were ±0.001 and ±0.0001 K, respectively.

The calorimeter was calibrated by determining the dissolution enthalpies of THAM (NBS742a, USA) in 0.1000 mol/l HCl and KCl (calorimetric primary standard) in water at 298.15 K. The mean dissolution enthalpies were -29776 ± 16 J/mol for THAM and 17597 ± 17 J/mol for KCl which are in conformity, respectively, compared with the published data (-29766 ± 31.5 J/mol for THAM [11] and 17536 ± 9 J/mol for KCl [12]). The uncertainties of both are less than 0.5%.

2.4. Determination of dissolution enthalpies

The method of dissolution enthalpies determination for the samples is the same as for the calibration of the calorimeter with THAM and KCl.

2.4.1. Reaction (1)

2.4.1.1. Determination of $\Delta_s H_m^\ominus[LaCl_3{\cdot}7H_2O(s)]$. The $LaCl_3{\cdot}7H_2O(s)$ was crushed in an agate bowl and then 0.37 g of the sample was put in the sampling device in calorimeter, and 100 cm^3 1 mol/l HCl was added into reaction cell, calorimeter was adjusted until constant temperature. Five readings were taken (see results in Table 1).

2.4.1.2. Determination of $\Delta_s H_m^\ominus[3CCl_3COOH(s)]$. A 0.49 g of crushed $CCl_3COOH(s)$ was put in the sampling device, and the solution (step mentioned in Section 2.4.1.1) was kept in the reaction cell. Five readings were taken (see results in Table 1).

2.4.1.3. Determination of $\Delta_s H_m^\ominus[La(TCA)_3{\cdot}3H_2O(s)]$. A 0.68 g of crushed $La(TCA)_3{\cdot}3H_2O(s)$ was put in the sampling device in calorimeter, and 100 cm^3 1 mol/l HCl was added into reaction cell, calorimeter was adjusted until constant temperature. Five readings were taken (see results in Table 1).

2.4.2. Reaction (2)

2.4.2.1. Choice of solvent. The properties of lanthanum trichloroacetic acid and 8-hydroxyquinoline are very

Table 1
Dissolution enthalpies of [$LaCl_3 \cdot 7H_2O$(s)], [$3CCl_3COOH$(s)], and [La(TCA)$_3 \cdot 3H_2O$(s)] in 1 mol/l HCl[a]

System	No.	m (g)	ΔE_s (mV)	ΔE_e (mV)	t (s)	Q_s (J)	$\Delta_s H_m^\Theta$ (kJ/mol)
{$LaCl_3 \cdot 7H_2O$(s) in 1 mol/l HCl}	1	0.3775	6.1933	4.7274	114.82	61.131	60.139
	2	0.3790	6.1987	5.9287	144.57	61.424	60.187
	3	0.3669	6.2153	6.9947	165.03	59.595	60.321
	4	0.3745	6.2082	6.4363	155.04	60.775	60.267
	5	0.3745	6.2131	6.8033	163.75	60.775	60.267
	$\Delta_s H_m^\Theta(1) = \Delta_s H_m^\Theta[LaCl_3 \cdot 7H_2O$, s, 298.15 K$] = 60.236 \pm 0.012$ kJ/mol						
{[$3CCl_3COOH$(s)] in $LaCl_3 \cdot 7H_2O$ and 1 mol/l HCl}	1	0.4946	2.5917	2.8643	73.66	27.086	26.843
	2	0.4965	2.6065	3.1791	82.11	27.359	27.010
	3	0.4935	2.6174	2.4535	62.61	27.145	26.961
	4	0.4810	2.5988	3.4141	85.04	26.307	26.808
	5	0.4922	2.6193	2.9330	75.05	27.238	27.125
	$\Delta_s H_m^\Theta(2) = \Delta_s H_m^\Theta[3CCl_3COOH$, s, 298.15 K$] = 26.949 \pm 0.014$ kJ/mol						
{[La(TCA)$_3 \cdot 3H_2O$(s)] in 1 mol/l HCl}	1	0.6785	8.8007	7.7081	218.23	101.260	101.497
	2	0.6816	8.8305	8.0123	227.74	102.005	101.779
	3	0.6803	8.7974	8.5275	241.95	101.440	101.409
	4	0.6809	8.8296	9.4888	269.20	101.803	101.682
	5	0.6816	8.8205	8.9802	255.46	101.973	101.747
	$\Delta_s H_m^\Theta(3) = \Delta_s H_m^\Theta$ [La(TCA)$_3 \cdot 3H_2O$, s, 298.15 K$] = 101.623 \pm 0.030$ kJ/mol						

[a] At 298.15 K, $R = 1003.6\ \Omega$, $I = 20.123$ mA; m: mass of sample; t: heating period of electrical calibration; Q_s: heat effect; ΔE_s: voltage change during the sample dissolution; ΔE_e: voltage change during the electrical calibration; $\Delta_s H_m^\Theta = (\Delta E_s/\Delta E_e) I^2 Rt(M/m)$, where R is the electroresistance, I the current, and M the molar mass.

different, so it is hard to dissolute in single solvent. The paper examined scores of common solvents and mixed solution in different proportions in many sorts of materials and finally discovered that the mixed solution of volume proportion of dimethyl sulfoxide and absolute ethyl alcohol and 4 mol/l HCl (V_{HCl}:V_{EtOH}:$V_{DMSO} = 1{:}0.5{:}0.5$) has the best effect. So, the experiments were done in it.

2.4.2.2. Determination of $\Delta_s H_m^\Theta$[La(TCA)$_3 \cdot 3H_2O$(s)]. La(TCA)$_3 \cdot 3H_2O$(s) was crushed in an agate bowl and then 0.68 g of the sample was put into the sampling device in calorimeter, and 100 cm^3 of the mixed solution of dimethyl sulfoxide and absolute ethyl alcohol and 4 mol/l HC1 was added into the reaction cell, then the calorimeter was adjusted until constant temperature. Five readings were taken (see results in Table 2).

2.4.2.3. Determination of $\Delta_s H_m^\Theta$[$2C_9H_7NO$(s)]. A 0.29 g of crushed C_9H_7NO(s) was put into the sampling device, and the solution was kept (step mentioned in Section 2.4.2.2) in the reaction cell. Five readings were taken (see results in Table 2).

2.4.2.4. Determination of $\Delta_s H_m^\Theta$[La(TCA)(C_9H_6NO)$_2$(s)]. A 0.59 g of crushed La(TCA)(C_9H_6NO)$_2$(s) was put in the sampling device in calorimeter, and 100 cm^3 of the mixed solution of dimethyl sulfoxide and absolute ethyl alcohol and 4 mol/l HCl were added to the reaction cell, and then the calorimeter was adjusted until constant temperature. Five readings were taken (see results in Table 2).

2.4.2.5. Determination of $\Delta_s H_m^\Theta$[$2CCl_3COOH$(s)]. A 0.32 g of crushed CCl_3COOH(s) was put in the sampling device, and 100 cm^3 of the mixed solution of dimethyl sulfoxide and absolute ethyl alcohol and 4 mol/l HCl were added to the reaction cell, and then the calorimeter was adjusted until constant temperature. Five readings were taken (see results in Table 2).

Table 2
Dissolution enthalpies of [La(TCA)$_3$·3H$_2$O(s)], [2C$_9$H$_7$NO(s)], [La(TCA)(C$_9$H$_6$NO)$_2$(s)], and 2CCl$_3$COOH(s)] in a mixed solvent consisting of 4 mol/l HCl, dimethyl sulfoxide, and absolute ethyl alcohol[a]

System	No.	m (g)	ΔE_s (mV)	ΔE_e (mV)	t (s)	Q_s (J)	$\Delta_s H_m^\Theta$ (kJ/mol)
La(TCA)$_3$·3H$_2$O(s) in B	1	0.6816	9.8084	9.0351	136.55	60.244	60.111
	2	0.6803	9.7971	8.5325	128.71	60.061	60.042
	3	0.6818	9.8055	8.6235	130.36	60.240	60.089
	4	0.6797	9.8158	8.7802	132.28	60.100	60.135
	5	0.6820	9.7926	8.6857	131.35	60.184	60.015
	$\Delta_s H_m^\Theta(1') = \Delta_s H_m^\Theta$[La(TCA)$_3$·3H$_2$O, s, 298.15 K] = 60.078 ± 0.006 kJ/mol						
2C$_9$H$_7$NO(s) in [La·3TCA·3H$_2$O·B]	1	0.2923	4.4990	3.8137	57.93	27.774	27.586
	2	0.2906	4.5053	3.8810	58.58	27.637	27.610
	3	0.2912	4.4961	3.7085	56.11	27.646	27.562
	4	0.2894	4.4889	3.8369	57.67	27.420	27.507
	5	0.2912	4.4615	3.7843	57.27	27.440	27.357
	$\Delta_s H_m^\Theta(2') = \Delta_s H_m^\Theta$[2C$_9H_7$NO, s, 298.15 K] = 27.524 ± 0.028 kJ/mol						
[La(TCA)(C$_9$H$_6$NO)$_2$(s)] in B	1	0.5905	12.7805	12.6108	280.81	115.657	115.479
	2	0.5854	12.7666	12.7767	282.21	114.600	115.381
	3	0.5894	12.7343	12.7443	283.39	115.079	115.116
	4	0.5816	12.7632	12.8342	281.62	113.817	115.381
	5	0.5878	12.7489	13.0398	289.10	114.869	115.219
	$\Delta_s H_m^\Theta(3') = \Delta_s H_m^\Theta$[La(TCA)(C$_9H_6$NO)$_2$, s, 298.15 K] = 115.315 ± 0.026 kJ/mol						
2CCl$_3$COOH(s) in [La·TCA·2C$_9$H$_6$NO·B]	1	0.3288	2.3953	2.3555	35.39	−14.625	−14.535
	2	0.3273	2.3764	2.3714	35.50	−14.457	−14.434
	3	0.3305	2.4028	2.8379	42.87	−14.751	−14.585
	4	0.3274	2.4006	2.3607	35.30	−14.588	−14.560
	5	0.3290	2.3989	2.4237	36.41	−14.646	−14.547
	$\Delta_s H_m^\Theta(4') = \Delta_s H_m^\Theta$[2CCl$_3$COOH, s, 298.15 K] = −14.532 ± 0.017 kJ/mol						

[a] At 298.15 K, $R = 1003.6\ \Omega$, $I = 20.123$ mA; solvent B was mixed solvent consisting of 4 mol/l HCl and dimethyl sulfoxide and absolute ethyl alcohol.

3. Results and discussion

3.1. Reaction (1)

3.1.1. Thermochemical cycle of reaction (1)

According to Hess' Law, a thermochemical cycle was designed as shown in Table 3.

3.1.2. Evaluation of the standard molar formation enthalpy of La(TCA)$_3$·3H$_2$O(s)

According to thermochemical cycle in Table 3, standard reaction enthalpy (in kJ/mol)

$$\begin{aligned}\Delta_r H_m^\Theta(1) = {} & \Delta_s H_m^\Theta(1) + \Delta_s H_m^\Theta(2) - \Delta_s H_m^\Theta(3) \\ & - \Delta_s H_m^\Theta(4) \\ & - \Delta_s H_m^\Theta(5) = 210.091\end{aligned}$$

According to thermodynamics principle, we know

$$\begin{aligned}\Delta_r H_m^\Theta(1) = {} & \Delta_f H_m^\Theta[\mathrm{La(TCA)_3 \cdot 3H_2O, s, 298.15\,K}] \\ & + 3\Delta_f H_m^\Theta[\mathrm{HCl, g, 298.15\,K}] \\ & + 4\Delta_f H_m^\Theta[\mathrm{H_2O, l, 298.15\,K}] \\ & - \Delta_f H_m^\Theta[\mathrm{LaCl_3 \cdot 7H_2O, s, 298.15\,K}] \\ & - 3\Delta_f H_m^\Theta[\mathrm{CCl_3COOH, s, 298.15\,K}]\end{aligned}$$

According to [13]

$$\begin{aligned}\Delta_f H_m^\Theta[\mathrm{HCl, g, 298.15\,K}] & = -22.062\,\mathrm{kcal/mol} \\ & = -92.307\,\mathrm{kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta_f H_m^\Theta[\mathrm{H_2O, l, 298.15\,K}] & = -68.315\,\mathrm{kcal/mol} \\ & = -285.830\,\mathrm{kJ/mol}\end{aligned}$$

Table 3
The reaction scheme for the standard molar reaction enthalpy of [$LaCl_3{\cdot}7H_2O(s) + 3CCl_3COOH(s)$] at 298.15 K[a]

No.	Reaction	$\Delta_s H_m^{\Theta}$ (kJ/mol)
1	$LaCl_3{\cdot}7H_2O(s) + A = LaCl_3{\cdot}7H_2O$ (in A)	60.236
2	$3CCl_3COOH(s) + LaCl_3{\cdot}7H_2O$ (in A) $= 3CCl_3COOH{\cdot}LaCl_3{\cdot}7H_2O$ (in A)	26.949
3	$La(TCA)_3{\cdot}3H_2O(s) + A = La{\cdot}3TCA^-{\cdot}3H_2O$ (in A)	101.623
4	$3HCl(g) + La{\cdot}3TCA^-{\cdot}3H_2O$ (in A) $= 3CCl_3COOH{\cdot}LaCl_3{\cdot}3H_2O$ (in A)	−224.529
5	$4H_2O(l) + 3CCl_3COOH{\cdot}LaCl_3{\cdot}3H_2O$ (in A) $= 3CCl_3COOH{\cdot}LaCl_3{\cdot}7H_2O$ (in A)	0
6	$LaCl_3{\cdot}7H_2O(s) + 3CCl_3COOH(s) = La(TCA){\cdot}3H_2O(s) + 3HCl(g) + 4H_2O(l)$	210.091

[a] Solvent A was 1 mol/l HCl.

$$\Delta_f H_m^{\Theta}[LaCl_3 \cdot 7H_2O, s, 298.15\,K] - 759.7\,kcal/mol = -3178.6\,kJ/mol$$

$$\Delta_f H_m^{\Theta}[CCl_3COOH, s, 298.15\,K] = -505.0\,kJ/mol$$

and the above-mentioned values,

$$\Delta_r H_m^{\Theta}(1) = 210.091\,kJ/mol$$

So that

$$\Delta_f H_m^{\Theta}[La(TCA)_3 \cdot 3H_2O, s, 298.15\,K] = -3063.3\,kJ/mol$$

3.1.3. Discussion

With Japanese UV-160 UV spectrophotometer and WZS-1 refractometer, we determined the spectrum and refractive index of dissolution product of [$LaCl_3 \cdot 7H_2O(s) + 3CCl_3COOH(s)$] and [$La(TCA){\cdot}3H_2O(s) + 3HCl(g) + 4H_2O(l)$] in 1 mol/l HCl, and discovered the duplicate UV spectroscopy (Fig. 1) and equal refractive index ($\eta_{25^\circ C} = 1.3431$). It proves, both have same thermodynamics state and thermochemical cycle.

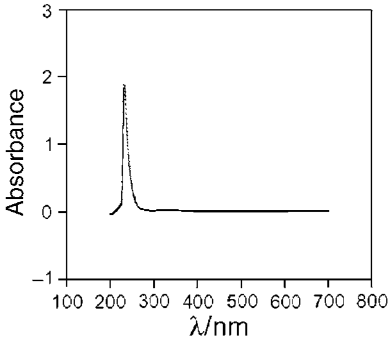

Fig. 1. UV spectrum of the final dissolution state of the reactants and products.

3.1.3.1. Treatment of $\Delta_s H_m^{\Theta}(4)$.

According to the relationship of dissolution enthalpy and dilution enthalpy,

$$\Delta_d H_m^{\Theta} = \Delta_s H_m^{\Theta}\,(\text{dilute}) - \Delta_s H_m^{\Theta}\,(\text{concentrated})$$

so that

$$\Delta_s H_m^{\Theta}\,(\text{concentrated}) = \Delta_s H_m^{\Theta}\,(\text{dilute}) - \Delta_d H_m^{\Theta}$$

or

$$\Delta_s H_m^{\Theta}\,(m = 1\,mol/l) = \Delta_s H_\infty^{\Theta}\,(m = 0\,mol/l) - \Delta_d H_m^{\Theta}$$

According to [13], the infinite dilution dissolution enthalpy of hydrogen chloride

$$\Delta_s H_\infty^{\Theta}(HCl, g, 298.15\,K) = -17,888\,cal/mol$$

According to the data in [13], through calculation

$$\begin{aligned}\Delta_d H_{1.000\to 0}^{\Theta} &= \Delta_d H_{1.000\to 0}^{\Theta} - \Delta_d H_{0\to 0}^{\Theta}\\ &= -\Phi_{L(1.000)} - [-\Phi_{L(0)}]\\ &= [-405 + 0]\,cal/mol = -405\,cal/mol\end{aligned}$$

So that

$$\begin{aligned}\Delta_s H_m^{\Theta}\,(m = 1\,mol/l) &= \Delta_s H_\infty^{\Theta}\,(m = 0\,mol/l) - \Delta_d H_m^{\Theta}\\ &= [-17,888 - (-405)]\,cal/mol\\ &= -74.483\,kJ/mol\end{aligned}$$

and so

$$\begin{aligned}\Delta_s H_m^{\Theta}(4) &= 3 \times \Delta_s H_m^{\Theta}\,(m = 1\,mol/l)\\ &= 3 \times (-74.483\,kJ/mol)\\ &= -224.529\,kJ/mol)\end{aligned}$$

3.1.3.2. Treatment of $\Delta_s H_m^{\Theta}(5)$.

Because of small concentration of $LaCl_3$ and $3CCl_3COOH$ in [1 mol/l $HCl{\cdot}LaCl_3{\cdot}3CCl_3COOH$] solution, the dilution

Table 4
The reaction scheme for the standard molar reaction enthalpy of $[La(TCA)_3 \cdot 3H_2O(s) + 2C_9H_7NO(s)]$ at 298.15 K[a]

No.	Reaction	$\Delta_s H_m^{\Theta}$/(kJ/mol)
1′	$[La(TCA)_3{\cdot}3H_2O(s)] + B = [La{\cdot}3TCA{\cdot}3H_2O]$ (in B)	60.078
2′	$2C_9H_7NO(s) + [La{\cdot}3TCA{\cdot}3H_2O]$ (in B) $= [La{\cdot}3TCA{\cdot}2C_9H_6NO{\cdot}3H_2O]$ (in B)	27.524
3′	$La(TCA)(C_9H_6NO)_2(s) + B = [La{\cdot}TCA{\cdot}2C_9H_6NO]$ (in B)	115.315
4′	$2CCl_3COOH(s) + [La{\cdot}TCA{\cdot}2C_9H_6NO]$ (in B) $= [La{\cdot}3TCA{\cdot}2C_9H_6NO]$ (in B)	−14.532
5′	$3H_2O(l) + [La{\cdot}3TCA{\cdot}2C_9H_6NO]$ (in B) $= [La{\cdot}3TCA{\cdot}2C_9H_6NO{\cdot}3H_2O]$ (in B)	0
6′	$La(TCA)_3{\cdot}3H_2O(s) + 2C_9H_7NO(s) = La(TCA)(C_9H_6NO)_2(s) + 2CCl_3COOH(s) + 3H_2O(l)$	−13.181

[a] Solvent B was mixed solvent consisting of 4 mol/l HCl and dimethyl sulfoxide and absolute ethyl alcohol.

enthalpy of $LaCl_3$ and $3CCl_3COOH$ when putting "$4H_2O$" into the solution is small. And the dilution enthalpy is also very small when putting "$4H_2O$" into 1 mol/l HCl. In the system, the overall dilution enthalpy is much smaller than dissolution enthalpies of materials. The overall dilution enthalpy is small, which can be neglected. So that $\Delta_s H_m^{\Theta}(5) \approx 0$.

3.2. Reaction (2)

3.2.1. Thermochemical cycle of reaction (2)

According to Hess' Law, a thermochemical cycle was designed as shown in Table 4.

3.2.2. Evaluation of the standard molar formation enthalpy of $La(TCA)(C_9H_6NO)_2(s)$

According to thermochemical cycle in Table 4, standard reaction enthalpy

$$\begin{aligned}\Delta_r H_m^{\Theta}(2) = \Delta_s H_m^{\Theta}(6') &= \Delta_s H_m^{\Theta}(1') + \Delta_s H_m^{\Theta}(2') \\ &\quad - \Delta_s H_m^{\Theta}(3') - \Delta_s H_m^{\Theta}(4') - \Delta_s H_m^{\Theta}(5') \\ &= -13.181\,\text{kJ/mol}\end{aligned}$$

According to thermodynamics principle, we know

$$\begin{aligned}\Delta_r H_m^{\Theta}(2) = {} & \Delta_f H_m^{\Theta}[La(TCA)(C_9H_6NO)_2, s, 298.15\,K] \\ & + 2\Delta_f H_m^{\Theta}[CCl_3COOH, s, 298.15\,K] \\ & + 3\Delta_f H_m^{\Theta}[H_2O, l, 298.15\,K] \\ & - \Delta_f H_m^{\Theta}[La(TCA)_3 \cdot 3H_2O, s, 298.15\,K] \\ & - 2\Delta_f H_m^{\Theta}[C_9H_7NO, s, 298.15\,K]\end{aligned}$$

According to [14],

$$\begin{aligned}\Delta_f H_m^{\Theta}[C_9H_7NO, s, 298.15\,K] &= -19.9\,\text{kcal/mol} \\ &= -83.3\,\text{kJ/mol}\end{aligned}$$

and the above-mentioned values

$$\Delta_f H_m^{\Theta}[CCl_3COOH, s, 298.15\,K] = -505.0\,\text{kJ/mol}$$

$$\Delta_f H_m^{\Theta}[La(TCA)_3 \cdot 3H_2O, s, 298.15\,K] = -3063.3\,\text{kJ/mol}$$

$$\Delta_f H_m^{\Theta}[H_2O, l, 298.15\,K] = -285.830\,\text{kJ/mol}$$

$$\Delta_r H_m^{\Theta}(2) = -13.181\,\text{kJ/mol}$$

so that

$$\Delta_f H_m^{\Theta}[La(TCA)(C_9H_6NO)_2, s, 298.15\,K] = -1375.6\,\text{kJ/mol}$$

3.2.3. Discussion

With Japanese UV-160 UV spectrophotometer and WZS-1 refractometer, we determined the spectrum and refractive index of dissolution product of $[La(TCA)_3 \cdot 3H_2O(s) + 2C_9H_7NO(s)]$ and $[La(TCA)(C_9H_6NO)_2(s) + 2CCl_3COOH(s) + 3H_2O(l)]$ in 1 mol/l HCl, dimethyl sulfoxide, and absolute ethyl alcohol discovered the duplicate UV spectroscopy (Fig. 2) and equal refractive index ($\eta_{25^\circ C} = 1.4001$). It proves, both have same thermodynamics state and thermochemical cycle.

3.2.3.1. Treatment of $\Delta_s H_m^{\Theta}(5')$. Because of small concentration of $La(TCA)(C_9H_6NO)_2$ and CCl_3COOH in $[4\,mol/l\ HCl{\cdot}(CH_3)_2SO{\cdot}C_2H_5OH{\cdot}La(TCA)(C_9H_6NO)_2{\cdot}2CCl_3COOH]$ solution, the dilution enthalpy of $La(TCA)(C_9H_6NO)_2$ and CCl_3COOH when putting "$3H_2O$" into the solution is small. And the dilution enthalpy is also very small when putting "$3H_2O$" into $4\,mol/l\ HCl{\cdot}(CH_3)_2SO{\cdot}C_2H_5OH$. In the system, the overall dilution enthalpy is much smaller than dissolution enthalpies of materials.

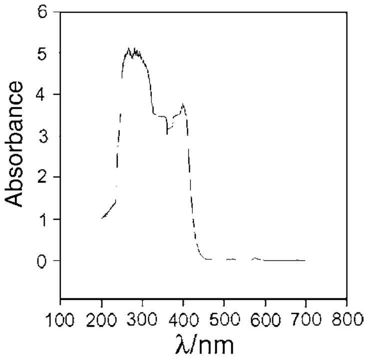

Fig. 2. UV spectrum of the final dissolution state of the reactants and products.

The overall dilution enthalpy is small, which can be neglected. So that $\Delta_s H_m^{\Theta}(5') \approx 0$.

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