Standard Molar Enthalpies of Formation of Ce(TCA)$_3$·3H$_2$O(s) and Ce(TCA)(C$_9$H$_6$NO)$_2$(s)

LI　Qiang-Guo[*]　　　　　　**YE　Li-Juan**[†]　　　　**SHOU　Meng-Juan**
Department of Chemistry，Xiangnan University，Chenzhou，Hunan 423000，China

The standard molar reaction enthalpies of two reactions，CeCl$_3$·7H$_2$O(s) + 3CCl$_3$COOH(s) = Ce(TCA)$_3$·3H$_2$O(s) + 3HCl(g) + 4H$_2$O(l)（1）and Ce(TCA)$_3$·3H$_2$O(s) + 2C$_9$H$_7$NO(s) = Ce(TCA)(C$_9$H$_6$NO)$_2$(s) + 2CCl$_3$COOH(s) + 3H$_2$O(l)（2）were investigated by classical solution calorimetry and an isoperibol calorimeter at 298.15 K. The standard molar enthalpies Δ$_s$$H_m^{\ominus}$ of solution of CeCl$_3$·7H$_2$O(s)，3CCl$_3$COOH(s)，Ce(TCA)$_3$·3H$_2$O(s)，Ce(TCA)$_3$·3H$_2$O(s)，2C$_9$H$_7$NO(s)，Ce-(TCA)(C$_9$H$_6$NO)$_2$(s) and 2CCl$_3$COOH(s) were determined to be 50.615 ± 0.028，23.431 ± 0.027，94.206 ± 0.010，54.151 ± 0.020，27.485 ± 0.045，106.392 ± 0.060 and −14.893 ± 0.026 kJ/mol respectively. The reaction enthalpies Δ$_r$$H_m^{\ominus}$ of reactions（1）and（2）were obtained to be 204.279 ± 0.023 and −9.863 ± 0.041 kJ/mol respectively. According to the above results and the data given in literature，through Hess′ law，the standard molar enthalpies Δ$_f$$H_m^{\ominus}$ of formation of Ce(TCA)$_3$·3H$_2$O(s) and Ce(TCA)(C$_9$H$_6$NO)$_2$(s) were estimated to be −3060.0 ± 0.087 and −1369.0 ± 0.292 kJ/mol respectively.

Keywords　　cerium choride seven-hydrate，trichloroacetic acid，8-hydroxyquinoline，thermochemistry

Introduction

Both rare earth ions[1] and 8-hydroxyquinoline are of antibacterial function [2] and their complexes have more powerful disinfection. Their binary complexes were reported as early as in 1963. At the same time，the research on their ternary complexes have become very active in recent years，and they are widely applied in many fields.[3-6] Dong[6] reported the synthesis and characterization of the complexes of rare earth trichloroacetic acid salts with 8-hydroxyquinoline. Its application in leather mouldy proof showed that the complexes have powerful disinfection. Obviously，it is very important to study the complexes of rare earth trichloroacetic acid salts with 8-hydroxyquinoline. It is necessary to obtain their basic thermodynamic data as the gist and basis for theoretical researches and industrial designing when two compounds are synthesized and developed industrially. However，the thermodynamic properties

of the complexes have not been reported yet. Therefore with solution calorimetry on a self-made and new type of isoperibol reaction calorimeter [7] the standard molar enthalpies of formation of Ce(TCA)$_3$·3H$_2$O(s) and Ce(TCA)·(C$_9$H$_6$NO)$_2$(s) were studied.

Experimental

Chemicals

The chemicals CeCl$_3$·7H$_2$O(s)，CCl$_3$COOH(s)，C$_9$H$_7$NO(s) and KCl used were of A.R. grade and were obtained from Shanghai Reagent Company.

CeCl$_3$·7H$_2$O(s) with a purity > 99% was dried in a desiccator containing sulphuric acid（60%）[8] at room temperature to constant mass prior to use. CCl$_3$COOH(s) with a purity > 99.5% was dried in a vacuum desiccator containing P$_4$O$_{10}$ until the mass became a constant prior to use. KCl（calorimetric primary standard）of purity > 99.99% was dried in a vacuum oven for 6 h at 135 ℃ prior to use. C$_9$H$_7$NO(s)（8-hydroxyquinoline）with a purity > 99.5% was used.

Preparations

Ce(TCA)$_3$·3H$_2$O(s) was prepared according to the reported method[6] and the crystal was obtained by repeated crystallization in a mixed solution consisting of C$_2$H$_5$OH and CHCl$_3$ and then the crystal was put into a desiccator containing P$_4$O$_{10}$ until the mass of the crystal became a constant. Its chemical analysis proved that composition of the complex was Ce(TCA)$_3$·3H$_2$O(s) and its purity was higher than 99.5%.

Ce(TCA)(C$_9$H$_6$NO)$_2$(s)（yellow solid）was prepared and analyzed according to the reported method.[6]

Calorimeter and calibration

The isoperibol reaction calorimeter was constructed in

the laboratory and adapted to determine the enthalpies of solid-liquid reaction and liquid-liquid reaction.[7] The volume of the reaction vessel was 100 mL. The precisions of temperature control and measurement were ± 0.001 and ± 0.0001 K respectively.

The calorimeter was calibrated by determining the dissolution enthalpy of KCl calorimetric primary standard in water at 298.15 K. The mean dissolution enthalpy was 17597 ± 17 J/mol which is in agreement with the reported datum 17536 ± 9 J/mol for KCl.[9] The uncertainty is less than 0.4%.

Determination of dissolution enthalpies of $CeCl_3 \cdot 7H_2O(s)$ *,* $3CCl_3COOH(s)$ *and* Ce TCA $_3 \cdot 3H_2O(s)$ *in reaction* 1

The determination method of dissolution enthalpy for the samples is the same as that for the calibration of the calorimeter with KCl. All were dissolved in 100 mL of 1 mol/L HCl solution.

$CeCl_3 \cdot 7H_2O(s)$ was ground in an agate mortar. $CeCl_3 \cdot 7H_2O(s)$ 0.372 g was put into a sampling cell in calorimeter and HCl 100 mL 1 mol/L was put into the reaction vessel. Calorimeter was adjusted to a constant temperature and the dissolution enthalpy was determined. Five readings were taken. The results are shown in Table 1.

The solution above was kept in the reaction vessel. Ground $CCl_3COOH(s)$ 0.49 g was put into the sampling cell. Five readings were taken. The results are shown in Table 1.

Ground Ce TCA $_3 \cdot 3H_2O(s)$ 0.68 g was put into the sampling cell in calorimeter and HCl 100 mL 1 mol/L was put into the reaction vessel. Calorimeter was adjusted to a constant temperature. Five readings were taken. The results are shown in Table 1.

Determination of dissolution enthalpies of Ce TCA $_3 \cdot 3H_2O(s)$ *,* $2C_9H_7NO(s)$ *,* Ce TCA $(C_9H_6NO)_2(s)$ *and* $2CCl_3COOH(s)$ *in reaction* 2

The determination method of dissolution enthalpies of the samples is the same as that for the calibration of the calorimeter with KCl. All were dissolved in 100 mL of mixed solution of dimethyl sulfoxide and absolute ethyl alcohol and 4 mol/L HCl.

The properties of cerium trichloroacetic acid and 8-hydroxyquinoline are different so it is hard to be dissolved in single solvent. Scores of the common solvents and the mixed solution in different proportions in many sorts of materials were examined. It was finally discovered that the mixed solvent **B*** of dimethyl sulfoxide and absolute ethyl

Table 1 Dissolution enthalpies $\Delta_s H_m^{\ominus}$ of $CeCl_3 \cdot 7H_2O(s)$, $3CCl_3COOH(s)$ and Ce TCA $_3 \cdot 3H_2O(s)$ in 1 mol/L HCl at 298.15 K $R = 1003.6\ \Omega$ $I = 20.123$ mA ^{a}

System	No.	n 10^{-3} mol	ΔE_s mV	ΔE_e mV	t s	Q_s J	$\Delta_s H_m^{\ominus}$ kJ/mol
	1	1.0165	5.2037	5.2919	128.53	51.364	50.530
	2	1.0205	5.2285	5.3113	129.00	51.609	50.572
A	3	1.0001	5.1356	5.3565	130.10	50.692	50.687
	4	1.0085	5.1741	5.3627	130.25	51.072	50.641
	5	1.0130	5.1973	5.3524	130.00	51.301	50.643
1* $CeCl_3 \cdot 7H_2O(s)$							50.615 ± 0.028
	1	1.0091	2.2758	2.4033	61.33	23.602	23.388
	2	1.0129	2.2929	2.4483	62.50	23.788	23.484
B	3	1.0068	2.2757	2.2638	57.77	23.601	23.441
	4	1.0018	2.2559	2.4727	63.10	23.395	23.352
	5	1.0052	2.2769	2.4100	61.50	23.613	23.490
2* $3CCl_3COOH(s)$							23.431 ± 0.027
	1	0.9976	9.3631	9.3421	230.67	93.955	94.181
	2	1.0030	9.4187	9.3476	230.80	94.511	94.228
C	3	0.9985	9.3720	9.3555	231.00	94.044	94.185
	4	1.0012	9.4004	9.3191	230.10	94.328	94.215
	5	1.0022	9.4104	9.3373	230.55	94.429	94.222
3* Ce TCA $_3 \cdot 3H_2O(s)$							94.206 ± 0.010

^{a} n molal number 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 $\Delta_s H_m^{\ominus} = \Delta E_s / \Delta E_e \cdot I^2 R t \cdot 1/n$ where R is the resistance of the heater I current A solution obtained when $CeCl_3 \cdot 7H_2O(s)$ was dissolved in 1 mol/L HCl solution **B** thesolution obtained when $3CCl_3COOH(s)$ was dissolved in solution **A** **C** the solution obtained when Ce TCA $_3 \cdot 3H_2O(s)$ was dissolved in 1 mol/L HCl solution.

alcohol and 4 mol/L HCl $V_{DMSO}:V_{EtOH}:V_{HCl}=0.5:0.5:1$ is the most appropriate solvent. And the mixed solvent $\mathbf{B}^*$ was selected in the experiment.

     The Ce TCA $_3$ 3H$_2$O s was ground in an agate mortar and a sample 0.68 g was put into a sampling cell in calorimeter and 100 mL of $\mathbf{B}^*$ was put into a reaction vessel $\mathbf{A}'$. Calorimeter was adjusted to a constant temperature. Five readings were taken. The results are shown in Table 2.

     Ground C$_9$H$_7$NO s 0.29 g was put into the sampling cell and the solution $\mathbf{A}'$ above was kept in the reaction vessel $\mathbf{B}'$. Five readings were taken. The results are shown in Table 2.

     Ground Ce TCA C$_9$H$_6$NO $_2$ s 0.59 g was put into a sampling cell in calorimeter and 100 mL of solvent $\mathbf{B}^*$ was put into the reaction vessel $\mathbf{C}'$. Calorimeter was adjusted to a constant temperature. Five readings were taken. The results are shown in Table 2.

     Ground CCl$_3$COOH s 0.32 g was put into a sam-

pling cell and the solution $\mathbf{C}'$ above was kept in the reaction vessel $\mathbf{D}'$. Five readings were taken. The results are shown in Table 2.

Results and discussion

Evaluation of the standard molar enthalpy of formation of Ce TCA $_3$ 3H$_2$O s

     According to Hess's law a thermochemical cycle was designed as shown in Fig. 1.

     The standard reaction enthalpy is obtained

$$\Delta_r H_m^{\ominus}\ 1 = \Delta_s H_m^{\ominus}\ 1^* + \Delta_s H_m^{\ominus}\ 2^* -$$
$$\Delta_s H_m^{\ominus}\ 3^* - \Delta_s H_m^{\ominus}\ 4^* - \Delta_s H_m^{\ominus}\ 5^*$$
$$= 204.279 \pm 0.023\ \text{kJ/mol}$$

According to thermodynamic principle at 298.15 K

Table 2 Dissolution enthalpies $\Delta_s H_m^{\ominus}$ of Ce TCA $_3$ 3H$_2$O s 2C$_9$H$_7$NO s Ce TCA C$_9$H$_6$NO $_2$ s and 2CCl$_3$COOH s in a mixed solvent $\mathbf{B}^*$ at 298.15 K $R = 1003.6\ \Omega$ $I = 20.123\ \text{mA}$ ^{a}

System	No.	n 10^{-3} mol	ΔE_s mV	ΔE_e mV	t s	Q_s J	$\Delta_s H_m^{\ominus}$ kJ/mol
	1	1.0022	8.5642	8.4929	132.50	54.300	54.181
	2	1.0003	8.5381	8.3313	129.98	54.135	54.119
$\mathbf{A}'$	3	1.0025	8.5635	8.4608	132.00	54.296	54.161
	4	0.9994	8.5436	8.3326	130.00	54.170	54.202
	5	1.0028	8.5555	8.4993	132.60	54.245	54.094
1′ Ce TCA $_3$ 3H$_2$O s							54.151 ± 0.020
	1	1.0068	4.3632	4.0024	62.60	27.734	27.547
	2	1.0010	4.3419	3.9832	62.30	27.599	27.571
$\mathbf{B}'$	3	1.0030	4.3431	3.9967	62.51	27.606	27.523
	4	0.9968	4.3076	3.9641	62.00	27.380	27.468
	5	1.0030	4.3107	3.9960	62.50	27.400	27.318
2′ 2C$_9$H$_7$NO s							27.485 ± 0.045
	1	1.0015	11.8075	11.6511	259.08	106.703	106.543
	2	0.9930	11.6973	11.7091	260.37	105.708	106.453
$\mathbf{C}'$	3	1.0001	11.7539	11.7581	261.46	106.219	106.208
	4	0.9865	11.6208	11.6700	259.50	105.016	106.453
	5	0.9970	11.8385	11.7158	260.52	106.984	106.303
3′ Ce TCA C$_9$H$_6$NO $_2$ s							106.392 ± 0.060
	1	1.0052	2.4522	2.3295	35.00	−14.973	−14.896
	2	1.0006	2.4222	2.3043	34.65	−14.802	−14.793
$\mathbf{D}'$	3	1.0014	2.4514	2.3375	35.12	−14.968	−14.947
	4	1.0019	2.4485	2.3429	35.20	−14.950	−14.922
	5	1.0058	2.4558	2.3362	35.10	−14.995	−14.908
4′ 2CCl$_3$COOH s							−14.893 ± 0.026

^{a} $\mathbf{B}^*$ the mixed solvent of dimethyl sulfoxide and absolute ethyl alcohol and 4 mol/L HCl $V_{DMSO}:V_{EtOH}:V_{HCl}=0.5:0.5:1$ $\mathbf{A}'$ the solution obtained when Ce TCA $_3$ 3H$_2$O s was dissolved in solution $\mathbf{B}^*$ $\mathbf{B}'$ the solution obtained when C$_9$H$_7$NO s was dissolved in solution $\mathbf{A}'$ $\mathbf{C}'$ the solution obtained when Ce TCA C$_9$H$_6$NO $_2$ s was dissolved in solution $\mathbf{B}^*$ $\mathbf{D}'$ the solution obtained when CCl$_3$COOH s was dissolved in solution $\mathbf{C}'$.

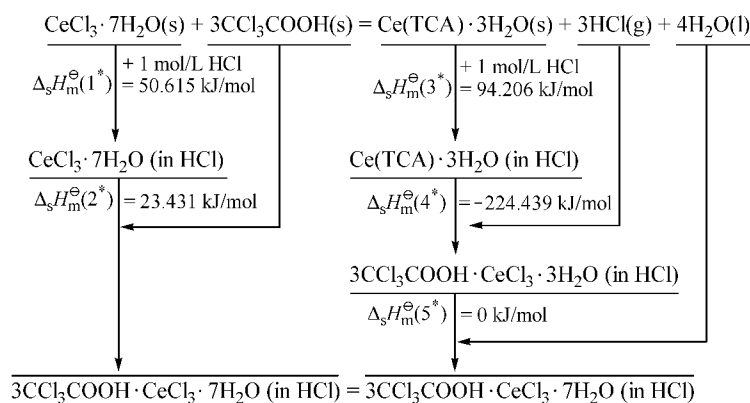$$CeCl_3 \cdot 7H_2O(s) + 3CCl_3COOH(s) = Ce(TCA) \cdot 3H_2O(s) + 3HCl(g) + 4H_2O(l)$$

$\Delta_s H_m^\ominus(1^*)$ | + 1 mol/L HCl = 50.615 kJ/mol

$\Delta_s H_m^\ominus(3^*)$ | + 1 mol/L HCl = 94.206 kJ/mol

$CeCl_3 \cdot 7H_2O$ (in HCl)

$\Delta_s H_m^\ominus(2^*)$ = 23.431 kJ/mol

$Ce(TCA) \cdot 3H_2O$ (in HCl)

$\Delta_s H_m^\ominus(4^*)$ = −224.439 kJ/mol

$3CCl_3COOH \cdot CeCl_3 \cdot 3H_2O$ (in HCl)

$\Delta_s H_m^\ominus(5^*)$ = 0 kJ/mol

$$3CCl_3COOH \cdot CeCl_3 \cdot 7H_2O \text{ (in HCl)} = 3CCl_3COOH \cdot CeCl_3 \cdot 7H_2O \text{ (in HCl)}$$

Fig. 1   Thermochemical cycle of reaction 1 .

$\Delta_r H_m^\ominus$ 1 $= \Delta_f H_m^\ominus$ Ce TCA $_3$ $3H_2O$ s +
$\quad 3\Delta_f H_m^\ominus$ HCl g $+ 4\Delta_f H_m^\ominus$ H_2O l −
$\quad \Delta_f H_m^\ominus$ $CeCl_3$ $7H_2O$ s $- 3\Delta_f H_m^\ominus$ CCl_3COOH s

According to Ref. 10

$\Delta_f H_m^\ominus$ HCl g   298.15 K = − 92.307 kJ/mol

$\Delta_f H_m^\ominus$ H_2O l   298.15 K = − 285.830 kJ/mol

$\Delta_f H_m^\ominus$ $CeCl_3$ $7H_2O$ s   298.15 K = − 3169.4 kJ/mol

$\Delta_f H_m^\ominus$ CCl_3COOH s   298.15 K = − 505.0 kJ/mol

and the above-mentioned values

$\Delta_r H_m^\ominus$ 1 =   204.279 ± 0.023   kJ/mol

The standard molar enthalpy is obtained

$\Delta_f H_m^\ominus$ Ce TCA $_3$ $3H_2O$ s   298.15 K
$\quad$ = − 3060.0 ± 0.087   kJ/mol.

Evaluation of the standard molar enthalpy of formation of
Ce TCA C_9H_6NO $_2$ s

According to Hess′s law a thermochemical cycle was

designed as shown in Fig. 2. The standard reaction en-
thalpy is obtained

$\Delta_r H_m^\ominus$ 2 $= \Delta_s H_m^\ominus$ 1′ $+ \Delta_s H_m^\ominus$ 2′ $- \Delta_s H_m^\ominus$ 3′ −
$\quad \Delta_s H_m^\ominus$ 4′ $- \Delta_s H_m^\ominus$ 5′ = − 9.863 ± 0.041 kJ/mol

According to thermodynamics principle at 298.15 K

$\Delta_r H_m^\ominus$ 2 $= \Delta_f H_m^\ominus$ Ce TCA C_9H_6NO $_2$ s +
$\quad 2\Delta_f H_m^\ominus$ CCl_3COOH s $+ 3\Delta_f H_m^\ominus$ H_2O l −
$\quad \Delta_f H_m^\ominus$ Ce TCA $_3$ $3H_2O$ s $- 2\Delta_f H_m^\ominus$ C_9H_7NO s

According to Ref. 11

$\Delta_f H_m^\ominus$ C_9H_7NO s   298.15 K = − 83.3 kJ/mol

and the following values

$\Delta_f H_m^\ominus$ CCl_3COOH s   298.15 K = − 505.0 kJ/mol

$\Delta_f H_m^\ominus$ Ce TCA $_3$ $3H_2O$ s   298.15 K = − 3060.0 kJ/mol

$\Delta_f H_m^\ominus$ H_2O l   298.15 K = − 285.830 kJ/mol

$$Ce(TCA)_3 \cdot 3H_2O(s) + 2C_9H_7NO(s) = Ce(TCA)(C_9H_6NO)_2(s) + 2CCl_3COOH(s) + 3H_2O(l)$$

$\Delta_s H_m^\ominus(1')$ | + **B*** = 54.151 kJ/mol

$\Delta_s H_m^\ominus(3')$ | + **B*** = 106.392 kJ/mol

$Ce(TCA)_3 \cdot 3H_2O$ (in **B***)

$\Delta_s H_m^\ominus(2')$ = 27.485 kJ/mol

$Ce(TCA)(C_9H_6NO)_2$ (in **B***)

$\Delta_s H_m^\ominus(4')$ = −14.893 kJ/mol

$Ce(TCA)_3(C_9H_6NO)_2$ (in **B***)

$\Delta_s H_m^\ominus(5')$ = 0 kJ/mol

$$Ce(TCA)_3(C_9H_6NO)_2 \cdot 3H_2O \text{ (in B}^*) = Ce(TCA)_3(C_9H_6NO)_2 \cdot 3H_2O \text{(in B}^*)$$
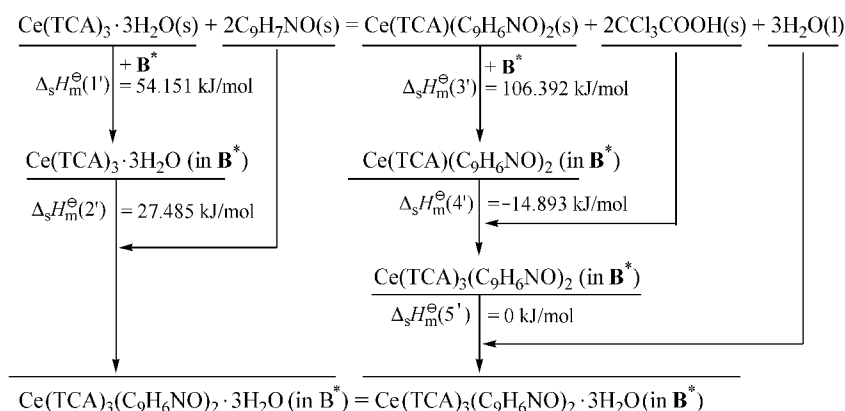
Fig. 2   Thermochemical cycle of reaction 2 .

$\Delta_r H_m^{\ominus}(2) = -9.863 \pm 0.041$ kJ/mol

the standard molar enthalpy is obtained

$\Delta_f H_m^{\ominus}[Ce(TCA)(C_9H_6NO)_2, s, 298\ K]$
　　$= -1369.0 \pm 0.292$ kJ/mol.

Discussion

　　The spectra and refractive indexes of dissolution product of $[CeCl_3 \cdot 7H_2O(s) + 3CCl_3COOH(s)]$ and $[Ce\text{-}TCA \cdot 3H_2O(s) + 3HCl(g) + 4H_2O(l)]$ in 1 mol/L HCl were determined. It is found that their UV spectra are quite similar (Fig. 3) and their refractive indexes are equal ($\eta_{25\ \text{°C}} = 1.3431$). It proves that both have the same thermodynamic states and the thermochemical cycle of reaction (1) is reliable.
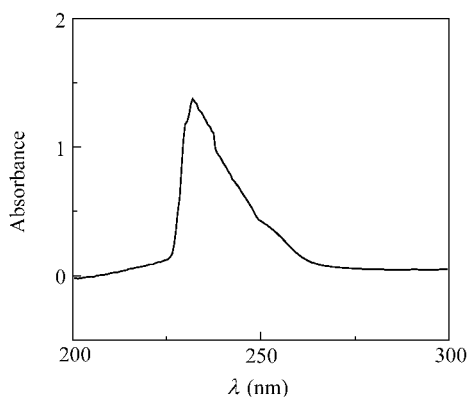
Fig. 3 UV spectrum of the final dissolution state of the reactants and products.

　　Treatment of $\Delta_s H_m^{\ominus}(4^*)$ According to the relationship of dissolution enthalpy and dilution enthalpy[12]

$\Delta_d H_m^{\ominus} = \Delta_s H_m^{\ominus}(\text{diluted}) - \Delta_s H_m^{\ominus}(\text{concentrated})$

So that

$\Delta_s H_m^{\ominus}(m = 1.030\ \text{mol/L})$
$= \Delta_s H_m^{\ominus}(m = 1.000\ \text{mol/L}) - \Delta_d H_{1.030\to1.000}^{\ominus}$

According to Ref. 11

$\Delta_s H_m^{\ominus}[HCl(g), 298.15\ K] = -74.843$ kJ/mol

According to the relationship between the infinitively diluted integral enthalpy of dilution and the relatively apparent molar enthalpy[13]

$\Delta_d H_{m\to0}^{\ominus} = -\Phi_{L2}$

According to the data in Ref. 10

$\Delta_d H_{1.030\to1.000}^{\ominus}$
$= \Delta_d H_{1.030\to0}^{\ominus} - \Delta_d H_{1.000\to0}^{\ominus}$
$= -\Phi_{L\ 1.030} - (-\Phi_{L\ 1.000})$
$= -1.72 - (-1.69)$ kJ/mol
$= -0.03$ kJ/mol

So that

$\Delta_s H_m^{\ominus}(m = 1.030\ \text{mol/L})$
$= \Delta_s H_m^{\ominus}(m = 1.000\ \text{mol/L}) - \Delta_d H_{1.030\to1.000}^{\ominus}$
$= -74.843 - (-0.03)$ kJ/mol
$= -74.813$ kJ/mol

And

$\Delta_s H_m^{\ominus}(4^*)$
$= 3 \times \Delta_s H_m^{\ominus}(m = 1\ \text{mol/L})$
$= 3 \times (-74.813)$ kJ/mol
$= -224.439$ kJ/mol

　　Treatment of $\Delta_s H_m^{\ominus}(5^*)$ Because of low concentration of $CeCl_3$ and $3CCl_3COOH$ in the solution **C**, the dilution enthalpies of $CeCl_3$ and $3CCl_3COOH$ are small when "$4H_2O$" is put into the solution and the dilution enthalpy is also very small when "$4H_2O$" is put into 1 mol/L HCl. In the system the overall dilution enthalpy is much smaller than those of materials, which can be neglected, and so $\Delta_s H_m^{\ominus}(5^*) \approx 0$.

　　The spectra and refractive indexes of dissolution product of $[Ce(TCA)_3 \cdot 3H_2O(s) + 2C_9H_7NO(s)]$ and $[Ce\text{-}TCA(C_9H_6NO)_2(s) + 2CCl_3COOH(s) + 3H_2O(l)]$ in the solution **B*** were determined. It is found that their UV spectra are quite similar (Fig. 4) and their refractive indexes are equal ($\eta_{25\ \text{°C}} = 1.4000$). It proves that both have the same thermodynamic state and thermochemical cycle of the reaction (2) is reliable.
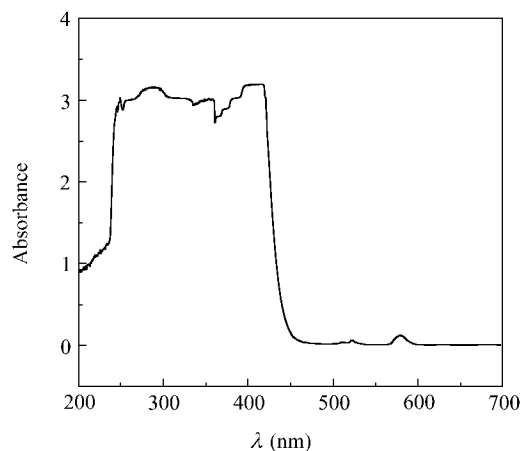
Fig. 4 UV spectrum of the final dissolution state of the reactants and products.

Treatment of $\Delta_s H_m^{\ominus}$ 5′   Because of small concentration of Ce TCA $C_9H_6NO_2$ and CCl_3COOH in the solution **D**′ the dilution enthalpies of Ce TCA $C_9H_6NO_2$ and CCl_3COOH are small when″ $3H_2O$″ is put into the solution **D**′. And the dilution enthalpy is also very small when″ $3H_2O$″ is put into the solution **B***. In the system the overall dilution enthalpy is much smaller than those of materials which can be neglected and so $\Delta_s H_m^{\ominus}$ 5′ $\approx$ 0.

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