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SYNTHESIS, CHARACTERIZATION AND STANDARD MOLAR ENTHALPY OF FORMATION OF $Nd(C_7H_5O_3)_2{\cdot}(C_9H_6NO)$[*]

L. Qiang-Guo[1**], *H. Yi*[1], *L. Xu*[1], *Y. Li-Juan*[1], *X. Sheng-Xiong*[1], *Y. De-Jun*[1] *and L. Yi*[1, 2]

[1]Department of Chemistry and Life Science, Xiangnan University, Chenzhou, Hunan 423000, China
[2]College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430062, China

The complex from reaction of neodymium chloride six-hydrate with salicylic acid and 8-hydroxyquinoline, $Nd(C_7H_5O_3)_2{\cdot}(C_9H_6NO)$, was synthesized and characterized by IR, elemental analysis, molar conductance, and thermogravimatric analysis. The standard molar enthalpies of solution of $[NdCl_3{\cdot}6H_2O(s)]$, $[2C_7H_6O_3(s)]$, $[C_9H_7NO(s)]$ and $[Nd(C_7H_5O_3)_2{\cdot}(C_9H_6NO)(s)]$ in a mixed solvent of anhydrous ethanol, dimethyl formamide (DMF) and perchloric acid were determined by calorimetry at 298.15 K. Based on Hess' law, a new chemical cycle was designed, and the enthalpy change of the reaction

$$NdCl_3{\cdot}6H_2O(s)+2C_7H_6O_3(s)+C_9H_7NO(s)=Nd(C_7H_5O_3)_2{\cdot}(C_9H_6NO)(s)+3HCl(g)+6H_2O(l) \quad (1)$$

was determined to be $\Delta_r H_m^\ominus=117.89\pm0.37$ kJ mol^{-1}. From data in the literature, through Hess' law, the standard molar enthalpy of formation of $Nd(C_7H_5O_3)_2{\cdot}(C_9H_7NO)(s)$ was estimated to be $\Delta_f H_m^\ominus[Nd(C_7H_5O_3)_2{\cdot}(C_9H_6NO)(s), 298.15\ K]=-2031.80\pm8.6$ kJ mol^{-1}.

Keywords: *8-hydroxyquinoline, neodymium chloride six-hydrate, salicylic acid, standard molar enthalpies of formation*

Introduction

It is known that rare earth ions, 8-hydroxyquinoline and salicylic acid have antibacterial properties [1–5]. Synthesis and characterization of the complexes of rare earth ions with salicylic acid and 8-hydroxyquinolin were reported by Yang and Li [6], and its application research experiments on actinomycete, the results shown that the inhibition of the ternary complexes of rare earth ions against actinomycete is more significant than of their ligand, salicylic acid and 8-hydroxyquinoline. Obviously, it is very important to carry out research on the complexes of rare earth ions with salicylic acid and 8-hydroxyquinolin. In order to make a deep research on the complexes, it is necessary to know their basic thermodynamics property.

In the present work, the synthesis and characterization of the complex of neodymium chloride six-hydrate with salicylic acid and 8-hydroxyquinoline, and determined the standard molar enthalpies of solution of $[NdCl_3{\cdot}6H_2O(s)]$, $[2C_7H_6O_3(s)]$, $[C_9H_7NO(s)]$ and $[Nd(C_7H_5O_3)_2{\cdot}(C_9H_6NO)(s)]$ in a mixed solvent of anhydrous ethanol, dimethyl formamide (DMF) and perchloric acid at 298.15 K are reported. By a thermochemical cycle, the molar enthalpy of the reaction:

$$NdCl_3{\cdot}6H_2O(s)+2C_7H_6O_3(s)+C_9H_7NO(s)= Nd(C_7H_5O_3)_2{\cdot}(C_9H_6NO)(s)+3HCl(g)+6H_2O(l) \quad (1)$$

and the standard molar enthalpy of formation of $Nd(C_7H_5O_3)_2{\cdot}(C_9H_6NO)(s)$ are obtained.

Experimental

Materials

Chemicals

The purity of chemicals $NdCl_3{\cdot}6H_2O(s)$ (>99%), $C_7H_6O_3(s)$ (>99.5%), $C_9H_7NO(s)$ (>99.5%) and KCl is greater than 99.99% and were obtained from Shanghai Reagent Company. $NdCl_3{\cdot}6H_2O(s)$ was dried in a desiccator containing sulphuric acid (60%) [1] at room temperature and $C_7H_6O_3(s)$ and $C_9H_7NO(s)$ were dried in a vacuum desiccator containing P_4O_{10} to constant mass. KCl (calorimetric primary standard) with the purity of greater than 99.99% was dried in a vacuum oven for 6 h at 135°C prior to use.

Preparations of $Nd(C_7H_5O_3)_2{\cdot}(C_9H_6NO)(s)$

A mass of 0.02 mol of powdered $C_7H_6O_3(s)$ was dissolved in 40 cm^3 of anhydrous ethanol (solution A). Sodium salicylate solution was formed when an aqueous solution of 10% NaOH (0.02 mol of NaOH) was added into the solution A (solution B). A mass of 0.01 mol of powdered 8-hydroxyquinoline was dis-

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[**] Author for correspondence: liqiangguo@163.com

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solved in 40 cm^3 of anhydrous ethanol (solution C). A mixture solution was obtained when the solution B was added into the solution C (solution D). A mass of 0.01 mol of powdered $NdCl_3·6H_2O$ was dissolved in 40 cm^3 of anhydrous ethanol (solution E). Primrose yellow crystals were separated out when the solution E was added slowly into the solution D at 37.5°C after 3 h of magnetic stirring. The solution was left to settle down at pH=6.5–7.0 during 12 h. Finally the primrose yellow solid complex was obtained by filtration in vacuum, washed with several portions of distilled water many times, washed with anhydrous ethanol and washed with acetone. The product was put into a desiccator in vacuum at 37.5°C for 24 h and kept until the mass of the crystals became a constant. The chemical composition of the synthetic sample was determined by elemental analysis for C, H and N, by EDTA titration for Nd^{3+} [7], by mercury salt titration for Cl^- and by difference and TG-DTG curve for H_2O. The analysis results proved that the composition of the complex was $Nd(C_7H_5O_3)_2·(C_9H_6NO)(s)$ and its purity was >99.56%.

Methods

Elemental analyzer (Perkin-Elmer 2400 CHN, USA), FTIR spectrometer (Avatar 360, with KBr pellet, USA), thermogravimetry analyzer (Perkin-Elmer TG6, at a heating rate of 10°C min^{-1} in flowing N_2, USA), Abbe refractometer (WAY, Shanghai, China), Ultraviolet-Visible spectrophotometer (U-3010, HITACHI, Japan), Solution-Reaction Isoperibol Calorimeter (SRC 100, constructed by the thermochemical laboratory of Wuhan University, China)[TCA401], conductance (DDS-12A, Shanghai, China) were used for sample analysis.

The solution–reaction isoperibol calorimeter and calibration

The solution–reaction isoperibol calorimeter (SRC 100) was described in detail elsewhere [8]. A Dewar vessel with an internal volume of 100 mL, equipped with a twin-blade stirrer, was submerged in the water of thermostat. The precisions of temperature control and temperature measurement were ±0.001 and ±0.0001 K, respectively.

The calibration of the calorimeter was carried out by measuring the dissolution enthalpies of THAM (NBS 742a, USA) in 0.0001 mol cm^{-3} HCl and KCl (calorimetric primary standard) in water at 298.15 K. The mean dissolution enthalpies were –29776±16 J mol^{-1} for THAM and 17597±17 J mol^{-1} for KCl, which is in agreement with published data (–29766±31.5 J mol^{-1} for THAM [9] and 17536±9 J mol^{-1} for KCl [10]).

Determination of dissolution enthalpies

$Nd(C_7H_5O_3)_2·(C_9H_6NO)(s)$ can be regarded as the product of the following reaction (1), and the thermochemical cycle was designed as Fig. 1.

The UV spectra and refractive indexes of the final solutions of both the reactants and the products can be used to determine if they have the same thermodynamic state. In the present experiments, we determined the spectrum and refractive indexes of solutions C and F in Fig. 1, and found for both of them the same UV spectrum (Fig. 2) and equal refractive index ($\eta_{25°C}$=1.3445). It proves that both have the same thermodynamics state and that the thermochemical cycle of the reaction (1) is reliable.

The chosen calorimetric solvent must dissolve the chemicals in the sample cell completely and very rapidly. The calorimetric solvent (S) of dimethyl

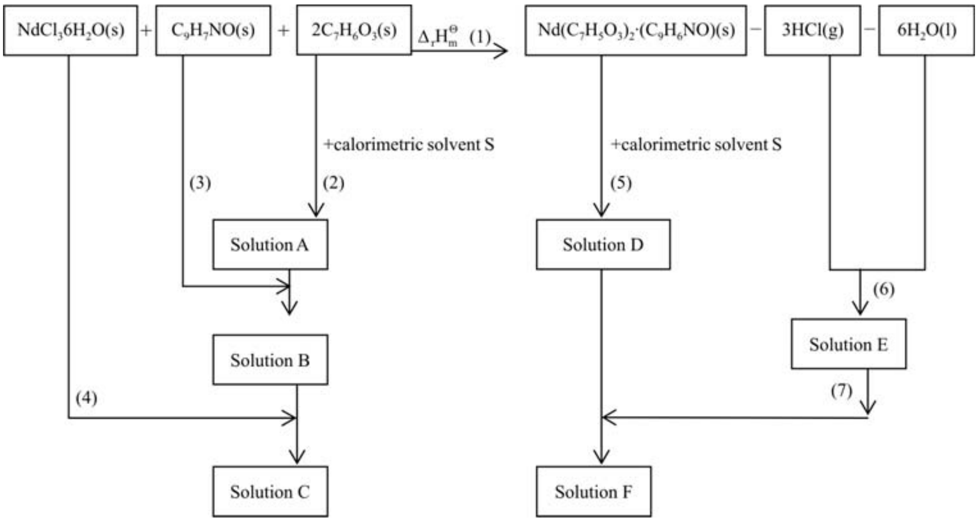

Fig. 1 Thermochemical cycle of the reaction (1)

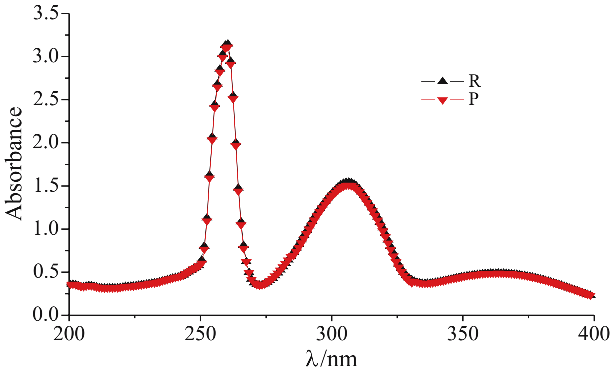

Fig. 2 UV spectrum of the final dissolution state of the reactants and products in the calorimetric solvent S

formamide (DMF) and anhydrous ethanol and perchloric acid (V_{DMF}:V_{EtOH}:V_{HClO_4}=1:1:0.5) is the most appropriate solvent for this experiment. Rigorous control of the stoichiometry was maintained through each series of experiments to ensure that the final solutions resulting from the dissolution of the reactants were of the same composition as those from the dissolution of the products.

The $C_7H_6O_3(s)$ was grinded in an agate mortar and a sample (0.138 g) was placed into a sample cell in calorimeter. The calorimetric solvent (100 cm^3) was added into the reaction vessel. Calorimeter was adjusted to a constant temperature of 298.15 K and the dissolution enthalpy was determined. Five parallel experiments were performed at the same time for the sake of obtaining accurate results.

$$2C_7H_6O_3(s)+S\rightarrow\text{solution A} \quad (2)$$

where S is the calorimetric solvent (100 cm^3). The above solution A was kept in the reaction vessel. Powdered $C_9H_7NO(s)$ (0.072 g) was put into the sample cell. Five parallel experiments were also made.

$$C_9H_7NO(s)+\text{solution A}\rightarrow\text{solution B} \quad (3)$$

The above solution B was kept in the reaction vessel. Powdered $NdCl_3{\cdot}6H_2O(s)$ (0.179 g) was put into the sample cell. Five parallel experiments were carried out.

$$NdCl_3{\cdot}6H_2O(s)+\text{solution B}\rightarrow\text{solution C} \quad (4)$$

Powdered $Nd(C_7H_5O_3)_2{\cdot}(C_9H_6NO)(s)$ (0.281 g) was put into the sample cell in calorimeter, and the calorimeter solvent (100 cm^3) was added into the reaction vessel. Calorimeter was adjusted to a constant temperature of 298.15 K and the dissolution enthalpy was determined. Five repetitive experiments were performed.

$$Nd(C_7H_5O_3)_2{\cdot}(C_9H_6NO)(s)+S\rightarrow\text{solution D} \quad (5)$$

where S is the calorimetric solvent (100 cm^3). A mass of 1.5 mmol $HCl(g)$ was dissolved into 3.0 mmol $H_2O(l)$

$$1.5\text{ mmol }HCl(g)+3.0\text{ mmol }H_2O(l)\rightarrow\text{solution E} \quad (6)$$

The solution D above was kept in the reaction vessel. The solution E was put into the sample cell. Five repetitive experiments were performed.

$$\text{solution D}+\text{solution E}\rightarrow\text{solution F} \quad (7)$$

The calorimetric results of reactions (2)–(5) and (7) are listed in Table 1.

Results and discussion

Composition and electrolytic character of the complex

The elemental analysis data (observed/% (calculated/%)): C 48.79 (49.10), H 2.55 (2.87), N 2.40 (2.49) and Nd 25.62 (25.63) showed that the complex has the stoichiometry of $Nd(C_7H_5O_3)_2{\cdot}(C_9H_6NO)$. It is insoluble in water, acetone, ether and benzene and slightly soluble in anhydrous ethanol. It is soluble in dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). The molar conductance of the complex is 0.00055 S m^2 mol^{-1} in DMF, indicating that the complex is a non-electrolyte and exists as neutral molecule in DMF [11].

IR spectra

There are five characteristic bands that are observed for the salicylic acid [12]: ν_{OH}^{COOH} (hydrogen bond intra-molecular, 3237 cm^{-1}, s), ν_{OH}^{COOH} (hydrogen bond intermolecular, 2857 cm^{-1}, s), ν_{O-H}(COOH, 2598 cm^{-1}, s), ν_{C-O}(COOH, 1663 cm^{-1}, vs) and δ_{O-H}(phenol, 1483 cm^{-1}, s). All these bands disappeared after complex formation except by the band due to the angular deformation of the OH group. At the same time two new absorption bands due to the carboxylate group (COO^-), ν_{as} (1593 cm^{-1}, s) and ν_s (1385 cm^{-1}, s) appeared, indicating that the oxygen atoms of the carboxylate group are coordinated to the metal ion. These observed frequencies in the complex shifted to higher values when compared with the frequencies observed for the sodium salicylate salt but, $\Delta\nu(\nu_{as}-\nu_s)$ stated the same (208 cm^{-1}). According with these results, it can be concluded that the carboxylate group is coordinated to the metal ion through the two oxygen atoms, as a symmetrical bidentate group.

There are four characteristic absorption bands that are observed for 8-hydroxyquinoline: ν_{O-H} (3188 cm^{-1}, m), ν_{C-O} (1094 cm^{-1}, w), $\nu_{C=N}$

(1578 cm^{-1}, w) and δ_{O-H} (1223 cm^{-1}, s). After complex formation, both ν_{O-H} and δ_{O-H} disappeared and ν_{C-O} (1103 cm^{-1}, m) shift towards higher frequencies.

DTA-TG analysis

The thermal analysis was made in the temperature range from room temperature to 800°C at a heating rate of 10°C min^{-1} in atmosphere of N_2. The results indicating that salicylic acid is melted at 158°C and is gasified to be decomposed at 211°C, 8-hydroxyquinoline is melted at 72°C and is gasified to be decomposed at 207°C and the complex showed one endothermic weak peak at 198–280 °C and one or two decomposition exothermic strong peaks at 370–520°C, respectively, and at one time with association of a mass loss (Fig. 3).

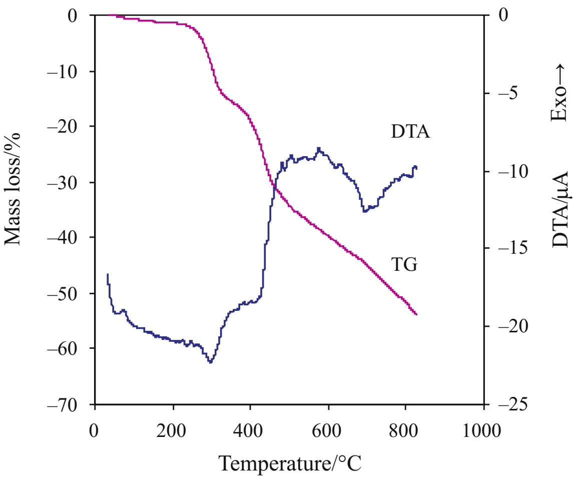

Fig. 3 TG-DTA curve of Nd(Hal)$_2$·hq

Results of calorimetric experiment

The results of the calorimetric measurements are given in Table 1.

Estimation of $\Delta_s H_m^\Theta$ *(6)*

According to the reaction (6)

1.5 mmol HCl(g)+3.0 mmol H_2O(l)⟶solution E

$$\begin{aligned}\Delta_s H_m^\Theta(6) &= \Delta_s H_m^\Theta(m=0.0278\ \text{mol cm}^{-3}) \quad [13]\\ &= \Delta_s H_m^\Theta(m=0.0010\ \text{mol cm}^{-3})\\ &\quad -\Delta_d H_m^\Theta(27.78\rightarrow 1.000)\\ &= [-74.843-(-25.388)]\ \text{kJ mol}^{-1}\\ &= -49.46\ \text{kJ mol}^{-1}\end{aligned}$$

The molar enthalpy of reaction (1)

According to the Hess' Law, the standard molar reaction enthalpy of the reaction (1) is obtained:

$$\begin{aligned}\Delta_r H_m^\Theta(1) &= \Delta_s H_m^\Theta(2)+\Delta_s H_m^\Theta(3)+\Delta_s H_m^\Theta(4)\\ &\quad -\Delta_s H_m^\Theta(5)-\Delta_s H_m^\Theta(6)-\Delta_s H_m^\Theta(7)\\ &= [15.98-5.33-35.24+86.51+49.46+6.52]\\ &\quad \pm[\sqrt{(0.09)^2+(0.28)^2+(0.08)^2+(0.16)^2+(0.14)^2}]\\ &= 117.89\pm 0.37\ \text{kJ mol}^{-1}\end{aligned}$$

Evaluation of $\Delta_f H_m^\Theta$*[La($C_7H_5O_3$)$_2$·(C_9H_6NO)(s)]*

According to Hess' law:

$$\begin{aligned}\Delta_r H_m^\Theta(1) &= \Delta_f H_m^\Theta[\text{Nd}(\text{C}_7\text{H}_5\text{O}_3)_2\cdot(\text{C}_9\text{H}_6\text{NO}(s),\ 298.15\ \text{K}]\\ &\quad +3\Delta_f H_m^\Theta[\text{HCl}(g),\ 298.15\ \text{K}]\\ &\quad +6\Delta_f H_m^\Theta[\text{H}_2\text{O}(l),\ 298.15\ \text{K}]\\ &\quad -\Delta_f H_m^\Theta[\text{NdCl}_3\cdot 6\text{H}_2\text{O}(s),\ 298.15\ \text{K}]\\ &\quad -2\Delta_f H_m^\Theta[\text{C}_7\text{H}_6\text{O}_3(s),\ 298.15\ \text{K}]\\ &\quad -\Delta_f H_m^\Theta[\text{C}_9\text{H}_7\text{NO}(s),\ 298.15\ \text{K}]\end{aligned}$$

According to [14]

$$\Delta_f H_m^\Theta[\text{HCl}(g),\ 298.15\ \text{K}] = -92.31\pm 0.10\ \text{kJ mol}^{-1}$$

$$\Delta_f H_m^\Theta[\text{H}_2\text{O}(l),\ 298.15\ \text{K}] = -285.830\pm 0.040\ \text{kJ mol}^{-1}$$

According to [15]

$$\begin{aligned}&\Delta_f H_m^\Theta[\text{NdCl}_3\cdot 6\text{H}_2\text{O}(s),\ 298.15\ \text{K}] =\\ &= -2874.4\pm 8.0\ \text{kJ mol}^{-1}\end{aligned}$$

where ±8.0 is calculated according to the data in [14] and [16].

According to [16]

$$\Delta_f H_m^\Theta[\text{C}_7\text{H}_6\text{O}_3(s),\ 298.15\ \text{K}] = -592.1\pm 1.3\ \text{kJ mol}^{-1}$$

According to [17]

$$\Delta_f H_m^\Theta[\text{C}_9\text{H}_7\text{NO}(s),\ 298.15\ \text{K}] = -83.0\pm 1.5\ \text{kJ mol}^{-1}$$

and the above-calculated values of

$$\Delta_r H_m^\Theta = 117.89\pm 0.37\ \text{kJ mol}^{-1}$$

So that

$$\begin{aligned}&\Delta_f H_m^\Theta[\text{Nd}(\text{C}_7\text{H}_5\text{O}_3)_2\cdot(\text{C}_9\text{H}_6\text{NO})(s),\ 298.15\ \text{K}]\\ &= [117.89-3(-92.31)-6(-285.830)\\ &\quad +(-2874.4)+2(-592.1)+(-83.0)]\\ &\quad \pm\sqrt{0.37^2+(3\cdot 0.10)^2+(6\cdot 0.040)^2+(8.0)^2+(2\cdot 1.3)^2+(1.5)^2}\\ &= -2031.80\pm 8.6\ \text{kJ mol}^{-1}\end{aligned}$$

Table 1 Dissolution enthalpies of [$2C_7H_6O_3$(*s*)], [C_9H_7NO(*s*)], [$NdCl_3\cdot6H_2O$(*s*)] and [$Nd(C_7H_5O_3)_2\cdot(C_9H_6NO)$(*s*)] in the calorimetric solvent S at 298.15 K

System	No.	*m*/g	*t*/s	$\Delta_s H_m^\ominus$/kJ mol^{-1}
$2C_7H_6O_3$(*s*) in S	1	0.1384	36.25	15.8122
	2	0.1381	35.67	16.1599
	3	0.1387	30.12	15.9056
	4	0.1376	34.62	16.1996
	5	0.1384	34.84	15.7996
$\Delta_s H_m^\ominus(2)=\Delta_s H_m^\ominus[2C_7H_6O_3(s)$, 298.15 K]=15.98±0.09 kJ mol$^{-1\ a}$				
C_9H_7NO(*s*) in the solution A	1	0.0731	5.25	–5.2815
	2	0.0736	8.19	–5.6287
	3	0.0726	4.29	–5.3840
	4	0.0733	5.16	–5.2705
	5	0.0724	4.15	–5.0840
$\Delta_s H_m^\ominus(3)=\Delta_s H_m^\ominus[C_9H_7NO(s)$, 298.15 K]= –5.33±0.28 kJ mol^{-1}				
$NdCl_3\cdot6H_2O$(*s*) in the solution B	1	0.1792	47.26	–35.3310
	2	0.1798	38.01	–35.4560
	3	0.1800	40.08	–34.9758
	4	0.1800	40.04	–35.1698
	5	0.1795	40.12	–35.2498
$\Delta_s H_m^\ominus(4)=\Delta_s H_m^\ominus[NdCl_3\cdot6H_2O(s)$, 298.15 K]= –35.24±0.08 kJ mol^{-1}				
$Nd(C_7H_5O_3)_2\cdot(C_9H_6NO)$(*s*) in S	1	0.2813	65.77	–86.8333
	2	0.2814	65.99	–86.1244
	3	0.2813	65.55	–86.2895
	4	0.2816	65.95	–86.3440
	5	0.2816	66.25	–86.9357
$\Delta_s H_m^\ominus(5)=\Delta_s H_m^\ominus[Nd(C_7H_5O_3)_2\cdot(C_9H_6NO)(s)$, 298.15 K]= –86.51±0.16 kJ mol^{-1}				
Solution D + solution E	1	0.1478	45.41	–6.0703
	2	0.1485	45.54	–6.7700
	3	0.1478	45.98	–6.4971
	4	0.1484	45.72	–6.3724
	5	0.1480	45.59	–6.8766
$\Delta_s H_m^\ominus(7)$= –6.52±0.14 kJ mol^{-1}				

n – molar number of sample; *t* – heating period of electrical calibration

[a] Uncertainty was estimated as twice the standard deviation of the mean of the results

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