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Thermochemistry on dodecylamine hydrochloride and *bis*-dodecylammonium tetrachlorozincate

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Abstract Dodecylamine hydrochloride $C_{12}H_{25}NH_3\cdot Cl(s)$ and *bis*-dodecylammonium tetrachlorozincate $(C_{12}H_{25}NH_3)_2ZnCl_4(s)$ were synthesized by the method of liquid phase reaction. The constant-volume energy of combustion of dodecylamine hydrochloride was measured by means of a RBC-II precision rotating-bomb combustion calorimeter at $T = (298.15 \pm 0.001)$ K. The standard molar enthalpy of formation of $C_{12}H_{25}NH_3\cdot Cl(s)$ was calculated to be $\Delta_f H_m^o(C_{12}H_{25}NH_3\cdot Cl, s) = -(706.79 \pm 3.97)$ kJ mol^{-1} from the constant-volume energy of combustion. In accordance with Hess' law, a reasonable thermochemical cycle was designed and the enthalpy change of the synthesis reaction of the complex $(C_{12}H_{25}NH_3)_2ZnCl_4(s)$ was determined by use of an isoperibol solution-reaction calorimeter. The standard molar enthalpy of formation of $(C_{12}H_{25}NH_3)_2ZnCl_4(s)$ was calculated as $\Delta_f H_m^o[(C_{12}H_{25}NH_3)_2ZnCl_4, s] = -(1862.14 \pm 7.95)$ kJ mol^{-1} from the standard molar enthalpy of formation of $C_{12}H_{25}NH_3\cdot Cl(s)$ and other auxiliary thermodynamic data.

Keywords Dodecylamine hydrochloride · *Bis*-dodecylammonium tetrachlorozincate · Constant-volume energy of combustion · Standard molar enthalpy of formation

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Introduction

The *bis*(*n*-alkylammonium) halometallates(II) (abbreviated as $C_{12}M$) [1–3] are important organometallic compounds of the general formula $(C_{12}H_{25}NH_3)_2MX_n$ ($n = 4$ or 6), where M is a divalent or trivalent metal ion (M = Zn^{2+}, Cu^{2+}, Mn^{2+}, Cd^{2+}, Co^{2+}, etc.) and X is a negative haloid ion. As a kind of solid–solid phase change materials (SSPCMs) [4, 5], $C_{12}M$ have been extensively investigated in the past decades since they show a variety of structural and magnetic phase transitions. They are also characterized by high enthalpy change and excellent reversibility of a solid–solid phase transition between two polymorphic forms in the temperature range of 273–393 K. As the necessary intermediate or raw material, dodecylamine hydrochloride $C_{12}H_{25}NH_3Cl(s)$ plays an important role in the formation of $C_{12}M$ in which the $C_{12}H_{25}NH_3^+$ cation bonds with the MX_n^{2-} anion through ionic bonds. As an advanced solid–solid phase change material, *bis*-dodecylammonium tetrachlorozincate $(C_{12}H_{25}NH_3)_2ZnCl_4(s)$ has some advantages such as small change in volume, no volatilization, high enthalpy, and low phase transition temperature.

Clark (in 1950), Pinto (in 1987), and Silver (in 1995) [6–8] investigated the crystal structure of *n*-dodecylammonium chloride. In 1953, Gordon et al. [9] investigated the crystal structures and some properties of *n*-dodecylammonium chloride and bromide. Kong (in 2009) [10, 11] has investigated crystal structure, phase transitions, and thermodynamic properties of 1-dodecylammonium chloride by X-ray crystallography, isoperibol solution-reaction calorimeter, and adiabatic calorimeter. Zhang et al. [12] reported the thermodynamic properties and phase change of $(C_{12}H_{25}NH_3)_2ZnCl_4(s)$ by means of adiabatic calorimetry over the temperature range from 280 to 500 K in 1988. In 2010, Kong et al. [13] investigated the crystal structure, phase transition, and thermodynamic properties of $(C_{12}H_{25}NH_3)_2ZnCl_4(s)$. Those researches were focused on crystal structure, solution thermodynamics, and phase transition. However, some basic thermochemical data such as the standard molar enthalpies of combustion and formation of $C_{12}H_{25}NH_3{\cdot}Cl(s)$, and the standard molar enthalpy of formation of $(C_{12}H_{25}NH_3)_2ZnCl_4(s)$ have not been reported until now, which restricts the progress of relevant theoretical studies and application development of $C_{12}M$. For the purpose of the application and theoretical researches concerned with the two substances, the standard molar enthalpies of formation of the two compounds are urgently needed.

The oxygen-bomb combustion calorimeter is one of the basic devices necessary in some thermochemical research, especially useful for the determination of the combustion energies of some elements, organic compounds, metal organics, etc. [14]. The combustion calorimetry is often applied to determine the standard molar enthalpies of formation of many important organic substances in industry and scientific research based on the data of enthalpies of combustion and some auxiliary thermodynamic quantities. In this study, the constant-volume energy of combustion $(\Delta_c U)$ of dodecylamine hydrochloride is determined by means of a RBC-II precision rotating-bomb combustion calorimeter and standard molar enthalpies of combustion $\left(\Delta_c H_m^o\right)$ and formation $\left(\Delta_f H_m^o\right)$ are calculated.

Solution-reaction calorimetry is one of the classical methods used to obtain the standard molar enthalpies of formation of many organic and inorganic compounds, especially useful for the determination of liquid–liquid and liquid–solid systems to quantify the enthalpies of dissolution, the standard molar enthalpy of reaction and formation, the standard molar enthalpy at infinite dilution, and the dissociation enthalpy of coordination ion. In this study, the standard molar dissolution enthalpies of reactants and product of the designed reaction are determined by an isoperibol solution reaction calorimeter. The standard molar enthalpy of formation of $(C_{12}H_{25}NH_3)_2ZnCl_4(s)$ is determined based on these experimental results.

Experimental

Synthesis of the title complexes

Dodecylamine, hydrochloric acid (37 mass%), and zinc chloride chosen as the reactants and anhydrous ethyl alcohol used as the solvent were all of analytical grade. The reactants were weighed accurately at the molar ratios of $n(C_{12}H_{25}NH_2)$:$n(HCl)$:$n(ZnCl_2)$ = 2:2:1 and $n(C_{12}H_{25}NH_2)$:$n(HCl)$ = 1:1, and slowly dissolved into anhydrous ethyl alcohol under sufficient stirring. The mixtures were heated and stirred under refluxing for 6 h, respectively. After both solutions were boiled and refluxed for 6 h, the mixtures were condensed by boiling off some of the liquid until crystal membrane emerged from the solution surface. The final solutions were naturally cooled to room temperature, filtered, and colorless crystals were obtained. The products were re-crystallized for three times with anhydrous ethyl alcohol, and colorless crystals were gained. Finally, the samples were placed in a vacuum desiccator at $T = 303.15$ K to dry in vacuum for 12 h, the final products were placed in weighing bottles and preserved in a desiccator, respectively. The mass fraction purity of the two compounds was determined to be >0.994 by HPLC. The contents of the chloride and zinc in the compounds were determined by chemical analysis, respectively. Elemental analysis (C, H, and N) was carried out on a Vario EL III CHNOS instrument made in Germany. These results showed that the mass fraction purities of the two compounds were >0.994.

Rotating-bomb combustion calorimetry

The constant-volume energy of combustion of dodecylamine hydrochloride was measured by a precision rotating-bomb combustion calorimeter (model: RBC-II type, made in Northwest University, China). The structure and principle of the calorimeter had been described in detail previously elsewhere [15]. The initial temperature of the combustion reaction was automatically maintained at $T = (298.15 \pm 0.001)$ K. The uncertainty of results of the constant-volume energy of combustion obtained from the calorimeter could reach ±0.05%.

The sample was burned under an oxygen pressure of 2.5 MPa in the presence of 0.001 dm^3 of double distilled water in the bomb to ensure equilibrium in the final state after the combustion. The mole fraction purity of the oxygen used in the experiment was of research grade (>0.99998). The mass of the sample had been calibrated from the air buoyancy on the basis of determination of the density for a pellet of the sample. At $T = (298.15 \pm 0.001)$ K, the differential quotient of the constant-volume energy of combustion with the oxygen pressure, $(\partial U/\partial P)_T$, for the solid was assumed to be -0.2 J g^{-1} MPa^{-1}, a typical value for organic solids [16].

The corrected value of the heat exchange between the calorimetric tube and its surroundings was calculated by means of the following equation according to the Linio-Pyfengdelel-Wsava formula [15, 16]:

$$\Delta(\Delta T) = nV_0 + \left[(V_n - V_0)/(\overline{T_n} - \overline{T_0})\right] \cdot \left[(T_0 + T_n)/2 + \sum_{i=1}^{n-1} T_i - n\overline{T_0}\right], \qquad (1)$$

where $\Delta(\Delta T)$/K denoted the corrected value of the heat exchange; n, the number of readings in the main (or reaction) stage; V_0 and V_n/K min^{-1}, the temperature drifted rates in the initial and final stages, respectively (V was positive when the temperature decreases); $\overline{T_0}$ and $\overline{T_n}/\mathrm{K}$, the average temperatures of the calorimeter during the initial and final stages, respectively; T_0 and T_n/K, the first and last readings of the main stage; $\sum_{i=1}^{n-1} T_i$, the sum of all the temperature readings of the main stage except for the last one; $(V_n - V_0)/\left(\overline{T_n} - \overline{T_0}\right)$, a constant related to the performance of the calorimeter.

After the experiment ended, the analytical methods for the final products (gas, liquid, and solid) of the combustion reaction were the same as those in reference [15]. The combustion products were analyzed mainly for carbon dioxide by the Rossini method [16]. No soot was observed in the sample crucible after each of combustion experiments. During the determination of the energy equivalent of the combustion calorimeter and measurements of constant-volume energy of combustion of the sample, mole ratios of real amounts of carbon dioxide produced in the combustion to the theoretical amounts were determined to be >0.9992. This demonstrated that the combustion of the sample in the oxygen bomb was complete. Qualitative tests for CO with indicator tubes were negative within the limits of their sensitivity {mole fraction x (CO) $< 1{\cdot}10^{-6}$}. As a result, either carbon deposits or carbon monoxide formed during the combustion and the amount of NO_x in the final gas phase was negligible.

The energy equivalent of the calorimeter was determined from seven combustion experiments using benzoic acid with a mole fraction purity (0.99998), which was purified three times by the sublimation before using and its certified constant-volume energy of combustion $\Delta_c U = -26434$ J g^{-1} at $T = 298.15$ K was recommended by NIST. The energy equivalent of the combustion calorimeter was determined to be $\varepsilon = (18604.99 \pm 8.14)$ J K^{-1} by the following formula [17] under the same experimental conditions:

$$\varepsilon = (Q \cdot W + q_c + q_N)/\Delta T, \tag{2}$$

where ε/(J K^{-1}) was the energy equivalent of the calorimeter; Q/(J g^{-1}), the energy of combustion of benzoic acid; W/g, the mass of benzoic acid; q_c/J, calibrated heat of combustion of wire {$q_c = G \cdot b$, in which G/(J cm^{-1}) was the combustion enthalpy of Ni–Cr wire for ignition and $G = 0.9$ J cm^{-1}; b/cm, the length of the actual Ni–Cr wire consumed in ignition}; q_N/J, correction value of total acid {$q_N = 5.97c$, in which 5.97/(J mol^{-1}) was the enthalpy of dissolution and formation of nitric acid corresponding to 1 cm^3 of 0.1000 mol dm^{-3} sodium hydroxide solution; c/cm^3, the volume of the consumed 0.1000 mol dm^{-3} sodium hydroxide solution}; ΔT/K, the corrected temperature rise of the combustion reaction. The calibration results of the energy equivalent of rotating bomb combustion calorimeter are tabulated in the Table 1.

Table 1 The calibration result of energy equivalent of the rotating bomb combustion calorimeter, where W was the mass of benzoic acid; ΔT was the corrected temperature rise; q_N was corrected heat of total acid; q_c was the calibrated heat of combustion wire; ε was the energy equivalent of calorimeter

No.	W/g	ΔT/K	q_N/J	q_c/J	ε/J K^{-1}
1	0.98450	1.4004	25.90	12.60	18610.95
2	0.86320	1.2301	19.96	12.60	18576.04
3	1.10295	1.5658	19.49	12.60	18640.61
4	1.11940	1.5924	25.99	12.60	18606.39
5	0.82615	1.1764	23.82	12.60	18594.75
6	0.93520	1.3317	19.31	11.70	18586.83
7	0.84385	1.1999	22.46	12.60	18619.38
$(\bar{x} \pm \sigma_a)$	$\varepsilon = (18604.99 \pm 8.14)$ J K^{-1}				

$\bar{x}$, the mean value of a set of measurement results; $\sigma_a = \sqrt{\sum_{i=1}^{n} (x - \bar{x})^2 / n(n-1)}$, n was the experimental number; x_i, a single value in a set of measurements

In this study, after the experiment ended, the fittings and the inside wall of the bomb were washed using distilled water, then the washing solution was cooled to the room temperature and transferred to a volumetric flask. The total amount of acid was obtained by titrating the solution to a phenolphthalein end-point with 0.1000 mol dm^{-3} sodium hydroxide solution. Because $C_{12}H_{25}NH_3{\cdot}Cl(s)$ contained chlorine and nitrogen, the final bomb-solution would contain HCl (aq) and HNO_3 (aq). In the analysis, the total amount of HNO_3 was determined by using the Devarda's alloy method [15]. The total amount of HCl (aq) in the solution was determined according to the difference between the total amount of acid and the amount of HNO_3 (aq) in solution. The results demonstrated that mole ratio of real amount of HCl (g) produced in the combustion to the theoretical amounts was determined to be >0.9991.

Isoperibol solution-reaction calorimetry

The isoperibol solution-reaction calorimeter consisted primarily of a precision temperature controlling system, an electric energy calibration system, a calorimetric body, an electric stirring system, a thermostatic bath made from transparent silicate glass, a precision temperature measuring system, and a data acquisition system. The principle and structure of the calorimeter were described in detail elsewhere [18, 19].

The reliability of the calorimeter was verified previously by measuring dissolution enthalpy of KCl (calorimetrically primary standard) in double distilled water. According to the molar ratio of KCl to water,$n_{\mathrm{KCl}} : n_{\mathrm{H_2O}} \approx 1 : 1110$, a certain amount of KCl was dissolved in 100 mL of double distilled water at $T = (298.15 \pm 0.001)$ K. The average enthalpy of dissolution of KCl was (17547 ± 13) J mol^{-1}, which compared with corresponding published data (17536 ± 3.4) J mol^{-1} [20] under the same experimental conditions. This showed that the relative deviation between the literature value and the measuring value was within ±0.3%.

Results and discussion

Constant-volume energy of combustion of dodecylamine hydrochloride

The method for determining the constant-volume energy of combustion of dodecylamine hydrochloride was the same as that used in the calibration of the calorimeter with benzoic acid. The constant-volume energy of combustion of dodecylamine hydrochloride according to the Eq. 2 could be calculated to be:

$$-\Delta_{\mathrm{c}}U = (\varepsilon \cdot \Delta T - q_{\mathrm{c}} - q_N)/W, \tag{3}$$

where $\Delta_{\mathrm{c}}U$/(J g^{-1}) was the constant-volume energy of combustion of the sample; W/g was the mass of the sample; the physical meanings of other symbols were the same as those in Eq. 2.

The measured results of the constant-volume energy of combustion of dodecylamine hydrochloride ($C_{12}H_{25}NH_3$·Cl)(s), $\Delta_{\mathrm{c}}U_1$/(J g^{-1}), are indicated in Table 2. At $T = 298.15$ K, the differential quotient of the constant-volume energy of combustion with the oxygen pressure $(\partial U/\partial P)_T = -0.2$ J g^{-1} MPa^{-1} [16]. Considering that the pressure in the oxygen-bomb in the combustion of the sample was corrected from 2.50 to 0.1 MPa (standard pressure), $\Delta P = -2.49$ MPa, the change of the constant-volume energy of combustion of the sample $\Delta(\Delta_{\mathrm{c}}U)$ was calculated to 0.50 J g^{-1}. Therefore, the real constant-volume energy of combustion of dodecylamine hydrochloride was corrected to be $\Delta_{\mathrm{c}}U^{\mathrm{o}}_{\mathrm{m}} = -(36184.91 \pm 16.27)$ J g^{-1} + 0.50 J g^{-1} = $-(36184.41 \pm 16.27)$ J g^{-1} = $-(8025.70 \pm 3.61)$ kJ mol^{-1} based on $\Delta_{\mathrm{c}}U$ (kJ mol^{-1}) = $\Delta_{\mathrm{c}}U$ (J g^{-1}) M (g mol^{-1}) 10^{-3}.

Table 2 The measured results of the constant-volume energies of combustion of $C_{12}H_{25}NH_3$·Cl at $T = 298.15$ K, where W was the mass of the sample; $\Delta_{\mathrm{c}}U$ was the constant-volume energy of combustion of $C_{12}H_{25}NH_3$·Cl; the physical meanings of other symbols were the same as those in Table 1

Compounds	No.	W/g	$\Delta_{\mathrm{c}}T$/K	q_N/J	q_{c}/J	$-\Delta_{\mathrm{c}}U$/J g^{-1}
$C_{12}H_{25}NH_3$·Cl	1	0.50065	0.9788	90.12	12.60	36168.67
	2	0.51230	1.0006	92.61	12.60	36133.01
	3	0.51785	1.0120	92.98	11.70	36156.36
	4	0.50490	0.9877	90.68	12.60	36191.06
	5	0.50675	0.9925	91.09	12.60	36234.36
	6	0.50845	0.9955	91.35	10.80	36226.02
$(\bar{x} \pm \sigma_a)$	$\Delta_{\mathrm{c}}U = -(36184.91 \pm 16.27)$ J g^{-1}					

Standard molar enthalpy of combustion of dodecylamine hydrochloride

The standard molar enthalpy of combustion of dodecylamine hydrochloride,$\Delta_{\mathrm{c}}H^{\mathrm{o}}_{\mathrm{m}}$, referred to the combustion enthalpy change of the following combustion reaction at $T = 298.15$ K and $P = 100$ kPa based on the definition of combustion enthalpy of dodecylamine hydrochloride:

$$\begin{aligned} &C_{12}H_{25}NH_3 \cdot Cl(s) + 75/4O_2(g) \\ &\quad = 12CO_2(g) + 27/2H_2O(l) + 1/2N_2(g) + HCl(l). \end{aligned} \tag{4}$$

The standard molar enthalpy of combustion of dodecylamine hydrochloride could be derived from the constant-volume energy of combustion at $T = 298.15$ K by means of the following formula:

$$\Delta_{\mathrm{c}}H^{\mathrm{o}}_{\mathrm{m}} = \Delta_{\mathrm{c}}U^{\mathrm{o}}_{\mathrm{m}} + \Delta n \cdot RT, \tag{5}$$

$$\Delta n = \sum n_i\,(\text{products, g}) - \sum n_i\,(\text{reactants, g}), \tag{6}$$

where $\sum n_i$ was the total amount (in mole) of the gases in products or reactants, $\Delta n = -25/4$ mol, $R = 8.314$ J K^{-1} mol^{-1}, $T = 298.15$ K. The calculated standard molar enthalpy of combustion of dodecylamine hydrochloride was derived to be: $\Delta_{\mathrm{c}}H^{\mathrm{o}}_{\mathrm{m}}(C_{12}H_{25}NH_3\text{·Cl, s}) = -(8041.19 \pm 3.61)$ kJ mol^{-1}.

Standard molar enthalpy of formation of dodecylamine hydrochloride

The standard molar enthalpy of formation of dodecylamine hydrochloride, $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$, was calculated by a designed Hess thermochemical cycle according to the reaction 4 as followed:

$$\begin{aligned} \Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}(C_{12}H_{25}NH_3 \cdot Cl,s) = {} & 12\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}(CO_2,g) \\ & + 27/2\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}(H_2O,l) \\ & + \Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}(HCl,l) \\ & - \Delta_{\mathrm{c}}H^{\mathrm{o}}_{\mathrm{m}}(C_{12}H_{25}NH_3 \cdot Cl,s), \end{aligned} \tag{7}$$

where $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}(CO_2,\ g) = -393.51 \pm 0.13$ kJ mol^{-1} [21], $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}(H_2O,\ l) = -285.83 \pm 0.04$ kJ mol^{-1} [21], $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ (HCl, l) = −167.15 kJ mol^{-1} [22].

The standard molar enthalpy of formation of dodecylamine hydrochloride could be derived to be: $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ ($C_{12}H_{25}NH_3$·Cl, s) = $-(706.79 \pm 3.97)$ kJ mol^{-1} based on these values and standard molar enthalpy of combustion of dodecylamine hydrochloride. It showed that dodecylamine hydrochloride was stable in thermodynamics.

From the result of specific energy of combustion, the standard molar enthalpies of combustion and formation of dodecylamine hydrochloride were derived. They are tabulated in Table 3.

The enthalpy change for the reaction of $(C_{12}H_{25}NH_3{\cdot}Cl)(s)$ with $ZnCl_2(s)$

The designed reaction is shown in the following reaction:

$$\begin{aligned}&2C_{12}H_{25}NH_3 \cdot Cl(s) + ZnCl_2(s)\\&\quad = (C_{12}H_{25}NH_3)_2ZnCl_2(s).\end{aligned} \tag{8}$$

The standard molar enthalpies of dissolution of the reactants and product of the reaction 8 in the selected solvent (1.0 mol dm^{-3} C_2H_5OH) were measured by an isoperibol solution-reaction calorimeter, respectively. The enthalpy change of the reaction was calculated from the data of above standard molar enthalpies of dissolution. Before measuring the standard molar enthalpies of dissolution, the solid reactants ($C_{12}H_{25}NH_3{\cdot}Cl$ and $ZnCl_2$) and product $\{(C_{12}H_{25}NH_3)_2ZnCl_4\}$ were, respectively, ground within an agate mortar into a fine powder and placed in a vacuum desiccator at $T = 300$ K to dry in vacuum for 6 h.

Table 3 Derived standard ($P^0 = 0.1$ MPa) molar enthalpy of combustion and standard molar enthalpy of formation for $C_{12}H_{25}NH_3{\cdot}Cl$ at $T = 298.15$ K

Compound	$-\Delta_c U^o_m$/ kJ mol^{-1}	$-\Delta_c H^o_m$/ kJ mol^{-1}	$-\Delta_f H^o_m$/ kJ mol^{-1}
$C_{12}H_{25}NH_3{\cdot}Cl$	8025.70 ± 3.61	8041.19 ± 3.61	706.79 ± 3.97

About 5.0×10^{-4} mol of $ZnCl_2(s)$ was accurately weighed and dissolved in 100 cm^3 of 1.0 mol dm^{-3} C_2H_5OH solution at $T = 298.15$ K. The experimental results of the process are shown in Table 4. If "s" represented 100 cm^3 of 1.0 mol dm^{-3} C_2H_5OH solution, the dissolution process may be expressed as:

$$\{ZnCl(s)\} + \text{``s''} = \text{Solution A}.$$

The stoichiometric number of $C_{12}H_{25}NH_3{\cdot}Cl(s)$ $\{n(C_{12}H_{25}NH_3{\cdot}Cl):n(ZnCl_2) = 2:1\}$ in the reaction 8 was regarded as a norm for sample weighing, about 1.0×10^{-3} mol of $C_{12}H_{25}NH_3{\cdot}Cl(s)$ was dissolved in the solution A at $T = 298.15$ K. The experimental results of the process are shown in Table 4 and the dissolution process may be expressed as:

Table 4 Dissolution enthalpies of reactants and product of the reaction 8 in the selected solvent

System	Solvent	No.	W/g	$\Delta E_s/\Delta E_e$	t_e/s	Q_s/J	$\Delta_{sol}H^o_m$/kJ mol^{-1}
$ZnCl_2$	1.0 mol dm^{-3} C_2H_5OH	1	0.03475	0.77401	40.719	−15.293	−59.98
		2	0.03445	0.92526	34.031	−15.279	−60.45
		3	0.03440	0.87946	35.328	−15.076	−59.73
		4	0.03432	0.93423	33.469	−15.172	−60.26
		5	0.03400	0.92125	33.219	−14.853	−59.65
$(\bar{x} \pm \sigma_a)$ $\Delta_s H^o_{m(ZnCl_2)}$ $= -(60.01 \pm 0.15)$ kJ mol^{-1}							
$C_{12}H_{25}NH_3{\cdot}Cl$	Solution A	1	0.11041	1.1187	49.141	26.675	53.59
		2	0.11039	1.39176	39.281	26.528	53.30
		3	0.11015	1.36155	40.266	26.603	53.57
		4	0.11096	1.12044	48.859	26.511	53.02
		5	0.11033	1.38638	39.281	26.425	53.13
$(\bar{x} \pm \sigma_a)$ $\Delta_s H^o_{m(C_{12}H_{28}NCl)}$ $= (53.32 \pm 0.11)$ kJ mol^{-1}							
$(C_{12}H_{25}NH_3)_2ZnCl_4$	1.0 mol dm^{-3} C_2H_5OH	1	0.14490	1.17264	35.422	20.155	80.66
		2	0.14455	1.15535	35.500	19.917	79.90
		3	0.14406	1.14515	35.375	19.657	79.44
		4	0.14452	1.16306	35.250	19.894	79.82
		5	0.14493	1.17669	35.401	20.216	80.86
$(\bar{x} \pm \sigma_a)$ $\Delta_s H^o_{m(C_{12}H_{28}N)_2ZnCl_4}$ $= (80.14 \pm 0.27)$ kJ mol^{-1}							

W Mass of sample; t_e Heating period of electrical calibration; $Q_s = -(\Delta E_s/\Delta E_e)\, I^2 R\, t$ Heat effect during the sample dissolution; ΔE_s The voltage change during the sample dissolution; ΔE_e The voltage change during the electrical calibration; $\Delta_s H^o_m = Q_s/n = -(\Delta E_s/\Delta E_e)\, I^2 R\, t_e (M/m)$, where R was the electro-resistance ($R = 1213.09\ \Omega$ at $T = 298.15$ K), I was the current ($I = 20.015$ mA), and M was the molar mass of the sample. $\sigma_a = \sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2 / n(n-1)}$

Table 5 Reaction scheme used to determine the standard molar enthalpy of formation of $(C_{12}H_{28}N)_2ZnCl_4(s)$

No.	Reactions	Formed solution	$\Delta_f H_m^o$ or $\left(\Delta_{Sol} H_m^o \pm \sigma_a\right)/\text{kJ mol}^{-1}$
1	$ZnCl_2(s)$ + “s” =	A	$\Delta_s H^o_{m(ZnCl_2)} = -(60.01 \pm 0.15)$ kJ mol^{-1}
2	$C_{12}H_{25}NH_3{\cdot}Cl(s)$ + solution A =	A_1	$\Delta_s H^o_{m(C_{12}H_{28}NCl)} = (53.32 \pm 0.11)$ kJ mol^{-1}
3	$(C_{12}H_{28}N)_2ZnCl_4(s)$ + “s” =	B	$\Delta_s H^o_{m(C_{12}H_{28}N)_2ZnCl_4} = (80.14 \pm 0.27)$ kJ mol^{-1}
4	$12C(s) + 14H_2(g) + 0.5N_2(g) + 0.5Cl_2(g) = C_{12}H_{28}NCl(s)$		$\Delta_f H^o_{m(C_{12}H_{28}NCl,s)} = -(706.79 \pm 3.97)$ kJ mol^{-1}
5	$Zn(s) + Cl_2(g) = ZnCl_2(s)$		$\Delta_f H^o_{m[ZnCl_2,s]} = -415.05$ kJ mol^{-1}
6	$24C(s) + 28H_2(g) + N_2(g) + 2Cl_2(g) + Zn(s) = (C_{12}H_{28}N)_2ZnCl_4(s)$		$\Delta_f H^o_{m\left[(C_{24}H_{56}N)_2ZnCl_4,s\right]} = -(1862.14 \pm 7.95)$ kJ mol^{-1}

$$\text{Solution A} + \{C_{12}H_{25}NH_3 \cdot Cl(s)\} = \text{Solution } A_1.$$

The dissolution enthalpies of the product of the reaction in the selected solvent (1.0 mol dm^{-3} C_2H_5OH solution) were measured under the same condition as the above. The experimental results of the process are listed in Table 4 and the dissolution process may be expressed as:

$$\left\{(C_{12}H_{25}NH_3)_2ZnCl_4(s)\right\} + \text{``s''} = \text{Solution B}.$$

Then the enthalpy change of the reaction 8 could be calculated in accordance with the experimental results as follows:

$$\begin{aligned}\Delta_r H_m^o &= \sum \Delta_s H_m^o\,(\text{reactants}) - \sum \Delta_s H_m^o\,(\text{product}) \\ &= \Delta_s H^o_{m(ZnCl_2)} + 2 \times \Delta_s H^o_{m(C_{12}H_{28}NCl)} - \Delta_s H^o_{m(C_{12}H_{28}N)_2ZnCl_4} \\ &= -60.01 + 2 \times 53.32 - 80.14 = -(33.51 \pm 0.38)\,\text{kJ mol}^{-1}.\end{aligned}$$

The standard molar enthalpy of formation of the compound $(C_{12}H_{25}NH_3)_2ZnCl_4(s)$

One reaction scheme used to derive the standard molar enthalpy of formation of $(C_{12}H_{25}NH_3)_2ZnCl_4(s)$ is given in Table 5. The experimental values of the dissolution enthalpies of the reactants and product of the reaction 8 were combined with some auxiliary thermodynamic data, $\Delta_f H_m^o\,(C_{12}H_{25}NH_3 \cdot Cl, \cdot s) = -(706.79 \pm 3.97)$kJ mol^{-1} and $\Delta_f H_m^o(ZnCl_2, s) = -415.05\,\text{kJ mol}^{-1}$ [22], and the standard molar enthalpy of formation of $(C_{12}H_{25}NH_3)_2ZnCl_4(s)$ was determined to be:

$$\begin{aligned}&\Delta_f H_m^o\left[(C_{12}H_{28}N)_2ZnCl_4, s\right] = \Delta_r H_m^o + 2 \times \Delta_f H_m^o \\ &(C_{12}H_{25}NH_3 \cdot Cl,s) + \Delta_f H_m^o(ZnCl_2, s) = (-33.51) + 2 \\ &\times (-706.79) + (-415.05) = -(1862.14 \pm 7.95)\,\text{kJ mol}^{-1}\end{aligned}$$

The results of refractive indexes were important information used to detect whether the difference of the structure and composition between two kinds of solution existed. In this article, the measured values of the refractive indexes of solution A_1 and B were (1.6912 ± 0.0002) and (1.6910 ± 0.0001), respectively. The result indicated that solution A_1 was consistent with solution B, and there was no difference in the structure, chemical components, and physicochemical properties between the two solutions. Therefore, the designed thermochemical cycle was reasonable and reliable, and could be used to calculate the standard molar enthalpy of formation of $(C_{12}H_{25}NH_3)_2ZnCl_4(s)$.

Conclusions

Dodecylamine hydrochloride $(C_{12}H_{25}NH_3{\cdot}Cl)(s)$ and $(C_{12}H_{25}NH_3)_2ZnCl_4(s)$ were synthesized. The standard molar enthalpy of formation $(C_{12}H_{25}NH_3{\cdot}Cl)(s)$ was calculated to be $\Delta_f H_m(C_{12}H_{25}NH_3{\cdot}Cl, s) = -(706.79 \pm 3.97)$ kJ mol^{-1}. The standard molar enthalpy of formation of $(C_{12}H_{25}NH_3)_2ZnCl_4(s)$ was calculated as $\Delta_f H_m[(C_{12}H_{25}NH_3)_2ZnCl_4, s] = -(1862.14 \pm 7.95)$ kJ mol^{-1} from the standard molar enthalpy of formation of $C_{12}H_{25}NH_3{\cdot}Cl(s)$.

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