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Crystal structure and thermochemical properties of 1-dodecylamine hydrochloride ($C_{12}H_{28}NCl$)(s)

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ABSTRACT

Crystal structure of 1-dodecylamine hydrochloride ($C_{12}H_{28}NCl$)(s) has been determined by an X-ray crystallography. Lattice potential energy and the molar volumes of the solid compound and its cation were respectively obtained. The enthalpy of dissolution of the compound was measured by an isoperibol solution-reaction calorimeter at 298.15 K. The molar enthalpy of dissolution at infinite dilution was determined to be $\Delta_s H_m^\theta = 30.36\,\text{kJ}\,\text{mol}^{-1}$, and relative apparent molar enthalpies (Φ_L), relative partial molar enthalpies (L_2) of the compound and relative partial molar enthalpies (L_1) of the solvent (double distilled water) at different concentrations m (mol kg^{-1}) were obtained through fitted multiple regression equation by means of Pitzer's theory. Finally, hydration enthalpies of the substance and its cation were calculated by designing a thermochemical cycle in accordance with lattice potential energy and the molar enthalpy of dissolution at infinite dilution ($\Delta_s H_m^\theta$).

1. Introduction

1-Dodecylamine is an important intermediate in organic synthesis, which has great influence on our daily life. It can be used as accessory ingredients in the fields of rubber products and textile industry, and also as one of important compositions of mineral floatation agent. 1-Dodecylamine hydrochloride ($C_{12}H_{28}NCl$)(s) is indispensable for agricultural production as one of the important organic components of emulsifier and insecticide. In medicine, it has a special function on treating the skin burn as an antimicrobial. Meanwhile, it is the raw material of detergent in fine chemical industry.

In recent years, a great attention has been paid to the application of 1-dodecylamine hydrochloride and dodecyl ammonium salts in many fields, such as energy storage and textile industry. However, crystal structure, lattice potential energy, and thermodynamic properties of 1-dodecylamine hydrochloride have not been found in the literature. The enthalpy of dissolution of a substance in the water [1,2] is an important parameter. It is closely related to the structure and other properties of the substance, such as the physical, biological, physiological and chemical properties [3,4]. Lattice potential energy [5–7] is a vital measurement to weigh the bonding ability of the molecules or ions in the crystal structure, and in relationship with many significant physicochemical properties of substances. Hydration enthalpy [8] is the thermal effect of a solid substance in generating hydrated ion when the substance is dissolved in the water at infinite dilution, and is greatly related to lattice potential energy and the molar enthalpy of dissolution at infinite dilution. In the present work, crystal structure of the title compound has been determined by an X-ray crystallography, and the enthalpy of dissolution of the title compound in the water was measured by an isoperibol solution-reaction calorimeter. Lattice potential energy, various molar enthalpies of dissolution, and hydration enthalpy of the title compound were obtained based on the crystal structure and experimental enthalpies of dissolution at different concentrations.

2. Experimental

2.1. Synthesis and characterization of 1-dodecylamine hydrochloride ($C_{12}H_{28}NCl$)(s)

1-Dodecylamine and hydrochloric acid (37% in mass) chosen as the reactants and anhydrous ethyl alcohol (A.R.) used as the solvent were of analytical grade. 1-Dodecylamine was dissolved into right amount of the absolute alcohol in a three-neck flask, and the excessive amount of hydrochloric acid (37%) was gradually added to the above solution under sufficient stirring. The solution was boiled and refluxed for 2 h, whereafter the mixture was condensed by boiling off some of the liquid until crystal mem-

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brane emerged from the solution surface. The final solution was naturally cooled to room temperature, filtered, and white crystal was obtained. Then, the product was recrystallized for three times with anhydrous ethyl alcohol, white crystal was gained. Finally, the sample was placed in a vacuum desiccator at the temperature of 50 °C to dry in vacuum for 6 h, final product was put into a weighing bottle and preserved in a desiccator. Theoretical contents of Cl, C, H and N in the compound have been calculated to be 15.98%, 64.98%, 12.72%, 6.32%, respectively. Chemical and element analyses (model: PE-2400, PerkinElmer, USA) have shown that practical contents of Cl, C, H and N in the compound have been measured to be 16.00%, 64.96%, 12.75% and 6.29%, respectively. This showed that the purity of the sample prepared was higher than 99.50 mol%.

2.2. *X-ray crystallography*

Single crystal suitable for X-ray analysis was mounted on a fiber. All diffraction data for the compound were collected on a Bruker Smart-1000 CCD area-detector diffractometer with graphite monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å) at 298(2) K using the program SMART and processed by SAINT-plus [9]. Absorption corrections were applied by SADABS. The structure was solved by direct methods and different Fourier synthesis using the SHELXTL-97 program, and refined with full-matrix least-squares technique on F^2. All non-hydrogen atoms were refined anisotropically. All H atoms were located theoretically and refined. The structural plots were drawn using the SHELXTL and OLEX programs.

2.3. *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 [10,11].

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 double distilled water at $T = (298.15 \pm 0.001)$ K. The average enthalpy of dissolution of KCl was (17,547 ± 13) J mol^{-1}, which compared with corresponding published data (17,536 ± 3.4) J mol^{-1} [12] under the same experimental conditions. It showed that the relative deviation between the literature value and the measuring value was within ±0.3%.

3. Results and discussion

3.1. *Crystal structural description*

The molecular structure of 1-dodecylamine hydrochloride is plotted in Fig. 1. The crystal parameters, data collection and refinement results for the compound are listed in Table 1. It is found from Table 1 that the crystal system of the compound is monoclinic, the space group is $P2_1/m$, unit cell dimensions are $a = 5.6680(8)$ Å; $b = 7.1783(5)$ Å; $c = 17.7385(18)$ Å; $\beta = 92.7740(10)°$, and $Z = 2$. Table 2 gives non-hydrogen atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$). Selected bond lengths and angles are listed in Table 3. The geometries of the hydrogen bonding are listed in Table 4.

As shown in Fig. 2, Hydrogen bonds of N(1)–H(1A)···Cl(1), N(1)–H(1B)···Cl(1) and N(1)–H(1C)···Cl(1) together with the Van der Waals forces exist in the crystal to stabilize the structure. All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atom (N), with bond

Table 1
Crystal data and structure refinement for the title compound $C_{12}H_{28}NCl(s)$.

Crystallographic data	Structure refinement
Empirical formula	$C_{12}H_{25}NH_3Cl$
Formula weight	221.80
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/m$
Unit cell dimensions	$a = 5.6680(8)$ Å, $b = 7.1783(5)$ Å, $c = 17.7385(18)$ Å; $\beta = 92.7740(10)°$
Volume	720.87(13) Å^3
Z	2
Calculated density	1.022 g/cm^3
Absorption coefficient	0.237 mm^{-1}
$F(000)$	248
Crystal size	0.43 mm × 0.39 mm × 0.25 mm
Theta range for data collection	2.30–25.00°
Limiting indices	$-6 \le h \le 6, -8 \le k \le 8, -13 \le l \le 20$
Reflections collected/unique	3488/1331 [R(int) = 0.0283]
Completeness to theta = 25.00	96.3%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1331/144/92
Goodness-of-fit on F^2	1.140
Final R indices [$I > 2$ sigma (I)]	$R_1 = 0.0895$, $wR_2 = 0.2569$
R indices (all data)	$R_1 = 0.1097$, $wR_2 = 0.2711$
Largest diff. peak and hole	0.493 and −0.420 eÅ^{-3}

Table 2
Non-hydrogen atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$).

Atom	x	y	z	U (equiv.)
Cl(1)	2,585(3)	2500	4650(1)	63(1)
N(1)	2,298(13)	6902(12)	4628(4)	60(3)
C(1)	1,902(13)	7500	3840(4)	57(2)
C(2)	3,885(15)	7120(20)	3359(4)	60(3)
C(3)	3,530(13)	7500	2551(4)	62(2)
C(4)	5,459(14)	7500	2049(4)	74(2)
C(5)	5,194(13)	7500	1243(4)	70(2)
C(6)	7,131(14)	7500	753(4)	71(2)
C(7)	6,916(14)	7500	−57(4)	74(2)
C(8)	8,847(14)	7500	−540(4)	75(2)
C(9)	8,660(13)	7500	−1352(4)	77(2)
C(10)	10,590(14)	7500	−1832(4)	85(3)
C(11)	10,436(15)	7500	−2636(4)	86(3)
C(12)	12,399(17)	7500	−3108(5)	109(4)

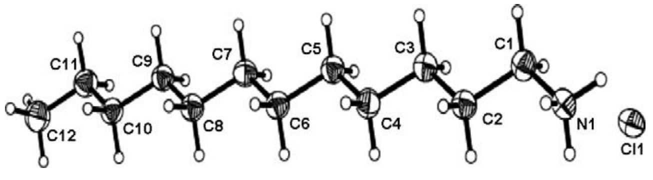


Fig. 1. Molecular structure of the title compound 1-dodecylamine hydrochloride.

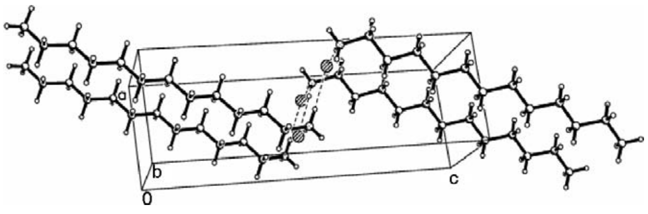


Fig. 2. Packing diagram of the compound 1-dodecylamine hydrochloride.

Table 3
Selected bond lengths [Å] and angles [°].

N(1)–C(1)	1.470(9)	C(3)–C(4)	1.443(10)	C(9)–C(10)	1.418(11)
N(1)–H(1A)	0.8900	C(4)–C(5)	1.431(10)	C(10)–C(11)	1.425(11)
N(1)–H(1B)	0.8900	C(5)–C(6)	1.433(10)	C(11)–C(12)	1.424(11)
N(1)–H(1C)	0.9272	C(6)–C(7)	1.436(10)	C(12)–H(12A)	0.9600
C(1)–C(2)	1.469(11)	C(7)–C(8)	1.422(10)	C(12)–H(12B)	0.9600
C(2)–C(3)	1.463(11)	C(8)–C(9)	1.439(10)	C(12)–H(12C)	0.9600
C(1)–N(1)–H(1A)	108.7	C(5)–C(4)–H(4B)	106.1	C(7)–C(8)–H(8B)	105.9
C(1)–N(1)–H(1B)	109.6	C(3)–C(4)–H(4B)	106.1	C(9)–C(8)–H(8B)	105.9
H(1A)–N(1)–H(1B)	109.5	C(4)–C(5)–C(6)	124.1(7)	C(10)–C(9)–C(8)	125.4(7)
C(1)–N(1)–H(1C)	107.5	C(4)–C(5)–H(5A)	106.3	C(10)–C(9)–H(9A)	106.0
H(1A)–N(1)–H(1C)	114.5	C(6)–C(5)–H(5A)	106.3	C(8)–C(9)–H(9A)	106.0
H(1B)–N(1)–H(1C)	106.9	C(4)–C(5)–H(5B)	106.3	C(10)–C(9)–H(9B)	106.0
C(2)–C(1)–N(1)	114.3(6)	C(6)–C(5)–H(5B)	106.3	C(8)–C(9)–H(9B)	106.0
C(3)–C(2)–C(1)	117.4(8)	C(5)–C(6)–C(7)	125.2(7)	C(9)–C(10)–C(11)	126.1(8)
C(3)–C(2)–H(2A)	109.4	C(5)–C(6)–H(6A)	106.0	C(9)–C(10)–H(10A)	105.8
C(1)–C(2)–H(2A)	109.3	C(7)–C(6)–H(6A)	106.0	C(11)–C(10)–H(10A)	105.8
C(3)–C(2)–H(2B)	106.5	C(5)–C(6)–H(6B)	106.0	C(9)–C(10)–H(10B)	105.8
C(1)–C(2)–H(2B)	106.5	C(7)–C(6)–H(6B)	106.0	C(11)–C(10)–H(10B)	105.8
C(4)–C(3)–C(2)	122.2(7)	C(8)–C(7)–C(6)	124.9(7)	C(12)–C(11)–C(10)	125.2(8)
C(4)–C(3)–H(3A)	106.8	C(8)–C(7)–H(7A)	106.1	C(12)–C(11)–H(11A)	106.0
C(2)–C(3)–H(3A)	105.3	C(6)–C(7)–H(7A)	106.1	C(10)–C(11)–H(11A)	106.0
C(4)–C(3)–H(3B)	106.9	C(8)–C(7)–H(7B)	106.1	C(12)–C(11)–H(11B)	106.0
C(2)–C(3)–H(3B)	108.2	C(6)–C(7)–H(7B)	106.1	C(10)–C(11)–H(11B)	106.0
C(5)–C(4)–C(3)	124.8(7)	C(7)–C(8)–C(9)	125.5(7)	C(11)–C(12)–H(12A)	109.5
C(5)–C(4)–H(4A)	106.1	C(7)–C(8)–H(8A)	105.9	C(11)–C(12)–H(12B)	109.5
C(3)–C(4)–H(4A)	106.1	C(9)–C(8)–H(8A)	105.9	C(11)–C(12)–H(12C)	109.5

Table 4
Hydrogen bonds [Å and °].

D–H···A	*d* (D–H) (Å)	*d* (H···A) (Å)	<DHA (°)	*d* (D···A) (Å)	Symmetry code
N(1)–H(1A)–Cl(1)	0.890	2.274	178.92	3.164	–
N(1)–H(1B)–Cl(1)	0.890	2.282	160.38	3.135	[$-x, -y+1, -z+1$]
N(1)–H(1C)–Cl(1)	0.927	2.291	152.42	3.142	[$-x+1, -y+1, -z+1$]

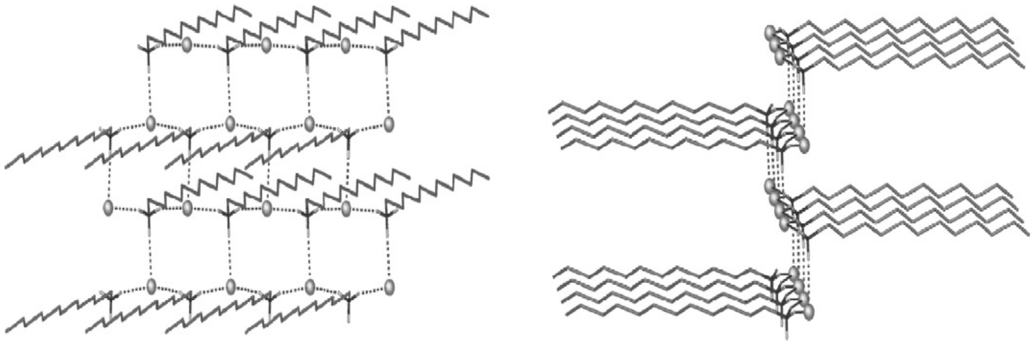
lengths of N(1)–H(1A), N(1)–H(1B), and N(1)–H(1C) are 0.890 Å, 0.890 Å, and 0.927 Å, respectively. The formation of the intermolecular hydrogen bonds, which makes the lone pair electron of chlorine atom move towards to hydrogen atom, and increased density of electron clouds around H. Accordingly, bond lengths of N(1)–H(1A), N(1)–H(1B), and N(1)–H(1C) are slightly lengthened, and bond energies are weakened, and then, additional bond energies are obtained by N(1)–H(1A)···Cl(1), N(1)–H(1B)···Cl(1), and N(1)–H(1C)···Cl(1). These hydrogen bonding and intermolecular forces form a configuration with two-dimensional layer that can be clearly identified from Fig. 3, in which the crystal structures were arranged along *ab* and *bc* axial planes, respectively. The results reveal that the hydrogen bonds play important roles in stabilizing the whole structure of title compound.

3.2. Lattice potential energy of the compound and volume of the cation $C_{12}H_{25}NH_3^+$

Eq. (1) used to estimate lattice potential energy for the general type of the salts of M_pX_q is obtained from the literature [6]:

$$U_{\mathrm{POT}} = \sum n_i z_i^2 \left(\frac{\alpha'}{V_m^{1/3}} + \beta' \right) \qquad (1)$$

where α' and β' are appropriate fitted cofficients chosen according to the stoichiometry of the salt, n_i is the number of ions with a charge z_i in the formula unit, V_{m} is the molecular volume.



(I) (II)

Fig. 3. The structure linked by hydrogen bonds along axial planes of *ab* (I) and *bc* (II).

Table 5
Enthalpy of dissolution of 1-dodecylamine hydrochloride in double distilled water at 298.15 K.

W (mg)	$10^3 m$ (mol kg^{-1})	$\Delta_s H_m$ (kJ mol^{-1})	Φ_L (kJ mol^{-1})	$10^{-6}\ (\partial\Phi_L/\partial m)_{T,P}$	L_1 (kJ mol^{-1})	L_2 (kJ mol^{-1})
5.3574	0.2415	31.234	0.8725	3.3928	−0.00357	1.6919
10.682	0.4816	32.048	1.6866	2.8673	−0.01198	3.0675
15.325	0.6909	32.599	2.2369	2.5200	−0.02168	3.9780
20.845	0.9398	33.255	2.8938	2.1754	−0.03462	4.9382
25.391	1.1447	33.677	3.3149	1.9276	−0.04552	5.5214
30.066	1.3555	33.963	3.6013	1.6968	−0.05618	5.9012
35.424	1.5970	34.384	4.0224	1.4553	−0.06688	6.3465
40.554	1.8283	34.704	4.3424	1.2422	−0.07482	6.6135
45.002	2.0289	34.839	4.4772	1.0691	−0.07930	6.6462
50.067	2.2572	35.092	4.7298	0.8831	−0.08108	6.7233
55.295	2.4929	35.226	4.8646	0.7018	−0.07860	6.6142
60.165	2.7125	35.469	5.1072	0.5413	−0.07177	6.5754
65.782	2.9657	35.614	5.2520	0.3649	−0.05784	6.3342
70.231	3.1662	35.670	5.3082	0.2311	−0.04175	6.0399

For the particular type of the salts of MX (1:1), MX_2 (1:2), and M_2X (2:1), Eq. (1) is changed to

$$U_{\mathrm{POT}} = |z_+||z_-|\nu\left(\frac{\alpha'}{V_{\mathrm{m}}^{1/3}} + \beta'\right) \tag{2}$$

where z_+ and z_- are the respective charges on the cation and anion of the compound, ν is the number of ions per molecule and is equals to $(p+q)$. For the case of salts of formula MX with charge ratio (1:1) such as 1-dodecylamine hydrochloride, $z_+ = 1$, $z_- = 1$, $p = q = 1$, $\nu = 2$, $\alpha' = 117.3$ kJ mol^{-1} nm, $\beta' = 51.9$ kJ mol^{-1}, and V_{m} is in units of nm^3 (which is the most convenient in reference to crystal structures) [7]:

$$V_{\mathrm{m}}\,(\mathrm{nm}^3) = \frac{M_{\mathrm{m}}}{\rho N_{\mathrm{A}}} = 1.66045 \times 10^{-3}\frac{M_{\mathrm{m}}}{\rho} \tag{3}$$

where N_{A} is the Avogadro's constant, 6.02245×10^{23} molecule mol^{-1}, the density ρ (g cm^{-3}) and molar mass M_{m} (g mol^{-1}) are obtained from the title compound's crystal structure information of Table 1 that $\rho = 1.022$ g cm^{-3}, and $M_{\mathrm{m}} = 221.80$ g mol^{-1}, respectively. V_{m} is calculated as 0.36036 nm^3 according to Eq. (3), consequently lattice energy of 1-dodecylamine hydrochloride is determined to be $U_{\mathrm{POT}} = 433.47$ kJ mol^{-1}.

In addition, since for a salt of M_pX_q, [6]:

$$V_{\mathrm{m}} = pV_+ + qV_- \tag{4}$$

where V_- and V_+ are the volumes of the anion and cation, $p = 1$ and $q = 1$ for MX (1:1), and $V_{\mathrm{Cl}^-} = 0.0298$ nm^3 in terms of Ref. [13]. In view of $V_{\mathrm{m}} = 0.36036$ nm^3, the V_+ (the volume of the cation $C_{12}H_{25}NH_3{}^+$) is estimated to be 0.33056 nm^3.

3.3. Enthalpies of dissolution

The title compound is soluble in double distilled water. The experimental values of enthalpy of dissolution ($\Delta_s H_m$) of 1-dodecylamine hydrochloride in double distilled water are given in Table 5, and the curvilinear relationship of $\Delta_s H_m$ (kJ mol^{-1}) with molality $10^3 m$ (mol kg^{-1}) is shown in Fig. 4. The relative apparent molar enthalpy (Φ_L, calculated), relative partial molar enthalpy (L_2, calculated) of the compound ($C_{12}H_{28}NCl$)(s) and relative partial molar enthalpy (L_1, calculated) of the solvent of double distilled water are also given.

The relationship between $\Delta_s H_m$ and Φ_L can be expressed as [14,15]:

$$\Delta_s H_m = \Delta_s H_m^{\theta} + \Phi_L \tag{5}$$

$\Delta_s H_m^{\theta}$ is the molar enthalpy of dissolution at infinite dilution, and the relative apparent molar enthalpy (Φ_L) in accordance with Pitzer's theory [14] can be expressed as

$$\Phi_L = 2\left(\frac{A_H}{2.4}\right)\ln(1 + 1.2I^{1/2}) - 2RT^2\left(m\beta_{\mathrm{MX}}^{(0)L} + my'\beta_{\mathrm{MX}}^{(1)L} + \frac{m^2 C_{\mathrm{MX}}^{\Phi_L}}{2}\right) \tag{6}$$

where I is ionic strength, m is molality (mol kg^{-1}) of the sample, R is molar gas constant, and $\beta_{\mathrm{MX}}^{(0)L}$, $\beta_{\mathrm{MX}}^{(1)L}$, and $C_{\mathrm{MX}}^{\Phi_L}$ are Pitzer's parameters for enthalpies, $\beta_{\mathrm{MX}}^{(0)L} = (\partial\beta_{\mathrm{MX}}^{(0)}/\partial T)_P$, $\beta_{\mathrm{MX}}^{(1)L} = (\partial\beta_{\mathrm{MX}}^{(1)}/\partial T)_P$, $C_{\mathrm{MX}}^{\Phi_L} = (\partial C_{\mathrm{MX}}^{\Phi}/\partial T)_P$, $\beta_{\mathrm{MX}}^{(0)L}$ and $\beta_{\mathrm{MX}}^{(1)L}$ represent all kinds of short-range interaction between ions, $C_{\mathrm{MX}}^{\Phi_L}$ is the third virial coefficient and only shows its effection in high concentration. $C_{\mathrm{MX}}^{\Phi_L}$ can be overlooked because the molality of the sample in this experiment is relatively low. A_{H} is the Debye-Huckel parameter for enthalpy [14], $A_{\mathrm{H}} = 1986$ J mol^{-1} at 298.15 K.

From above equations, the working equation [16] to determine Pitzer's parameter is shown as

$$Y = \frac{\Delta_s H_m - 2(A_{\mathrm{H}}/2.4)\ln(1 + 1.2I^{1/2})}{2RT^2} = \alpha_0 - m\beta_{\mathrm{MX}}^{(0)L} - my'\beta_{\mathrm{MX}}^{(1)L} \tag{7}$$

where Y is the extrapolation function, $\alpha_0 = \Delta_s H_m^{\theta}/2RT^2$, and $y' = [1 - (1+2I^{1/2})\exp(-2I^{1/2})]/2I$. Regression of Y against $-m$ and $-my'$ was made by least-squares to obtain $\alpha_0 = 0.02054$, $\beta_{\mathrm{MX}}^{(0)L} = 24.68999$, and $\beta_{\mathrm{MX}}^{(1)L} = -27.79341$ with a standard deviation of fit 3.76737×10^{-5} and correlation coefficient 0.99861. The molar

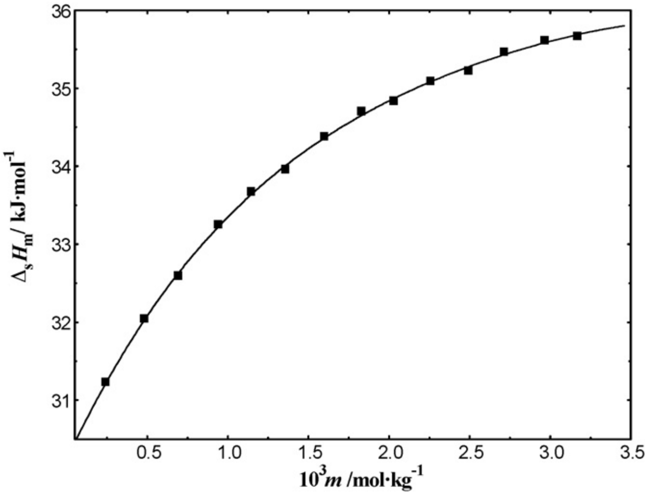


Fig. 4. Measured dissolution enthalpy $\Delta_s H_m$ for 1-dodecylamine hydrochloride as a function of molality $10^3 m$ at 298.15 K.

enthalpy of dissolution for the title compound at infinite dilution was determined to be $\Delta_s H_m^\theta = 30.36\,\mathrm{kJ\,mol^{-1}}$.

According to the relationship shown in Eq. (5), the relative apparent molar enthalpy (Φ_L) with two ingredients for the title compound is obtained and listed in Table 5.

The formula to determine the relative partial molar enthalpy (L_2) of $C_{12}H_{28}NCl$ (s) is

$$L_2 = \Phi_L + m\left(\frac{\partial \Phi_L}{\partial m}\right)_{T,P} \tag{8}$$

The partial derivative of Eq. (6) ($C_{\mathrm{MX}}^{\Phi_L}$ is neglected) against molality under constant temperature and pressure is expressed as

$$\left(\frac{\partial \Phi_L}{\partial m}\right)_{T,P} = \frac{A_{\mathrm{H}}}{2(m^{1/2}+1.2m)} - 2RT^2\left[\beta_{\mathrm{MX}}^{(0)L} + \beta_{\mathrm{MX}}^{(1)L}\exp(-2m^{1/2})\right] \tag{9}$$

and the relative partial molar enthalpy (L_1) of the solvent of double distilled water is expressed as

$$L_1 = -M_{\mathrm{H_2O}} m^2\left(\frac{\partial \Phi_L}{\partial m}\right)_{T,P} \tag{10}$$

All the results calculated above are listed in Table 5. From the values of enthalpy of dissolution, it can be found that the dissolution of 1-dodecylamine hydrochloride in the water is a typical endothermic process. It may ascribe to the existence of a hydrophobic dodecyl group in the compound, which leads to the weakening of hydration effect of the compound when met with the solvent of double distilled water. What's more, the breaking of hydrogen bonds existing in the substance need to absorb additional heat. Such, the endothermic process takes place because the heat quantity given out from the hydration of the compound is smaller than that absorbed due to the breaking of ionic bonds and hydrgen bonds in the solid compound. Therefore, the experimental values of dissolution enthalpies of the compound at different concentrations are increased with the concentration.

3.4. Hydration enthalpy

A thermodynamic cycle is designed to calculate the hydration enthalpy [8] of the compound ($C_{12}H_{28}NCl$)(s), which is exactly be expressed as $C_{12}H_{25}NH_3Cl$(s), is shown as follow:

$$\begin{tikzcd}
C_{12}H_{25}NH_3Cl(s) + \infty H_2O(l) & & C_{12}H_{25}NH_3^+(aq) + Cl^-(aq) \\
& C_{12}H_{25}NH_3^+(g) + Cl^-(g) &
\arrow[from=1-1, to=1-3, "\Delta_s H_m^\theta"]
\arrow[from=1-1, to=2-2, "U_{\mathrm{POT}} + 2RT"']
\arrow[from=2-2, to=1-3, "\Delta H_+ + \Delta H_-"']
\end{tikzcd}$$

The thermal effect in the process of generating $C_{12}H_{25}NH_3^+$(aq) and Cl^-(aq) from $C_{12}H_{25}NH_3^+$(g) and Cl^-(g) is the sum of hydration enthalpies of corresponding ions, respectively. Therefore, according to the thermochemical cycle, the calculation of hydration enthalpy is expressed as

$$(\Delta H_+ + \Delta H_-) = \Delta_s H_m^\theta - (U_{\mathrm{POT}} + 2RT) \tag{11}$$

ΔH_+ is the hydration enthalpy of the cation, ΔH_- is that of the anion, and ($\Delta H_+ + \Delta H_-$) is the sum of hydration enthalpies of corresponding ions and can be derived from Eq. (11) to be $-408.07\,\mathrm{kJ\,mol^{-1}}$. Therefore, based on hydration enthalpy of chloridion [17] $\Delta H_- = -350\,\mathrm{kJ\,mol^{-1}}$, hydration enthalpy of $C_{12}H_{25}NH_3^+$ is calculated to be $\Delta H_+ = -58.07\,\mathrm{kJ\,mol^{-1}}$, which prove that hydration action of $C_{12}H_{25}NH_3^+$(g) in the water is very weak.

4. Conclusions

The paper reported crystal structure, lattice potential energy, molar volumes of the compound and its cation, and a series of thermodynamic properties of the compound 1-dodecylamine hydrochloride. The data and geometries of the structure, lattice energy, and the molar enthalpy of dissolution at infinite dilution, relative apparent molar enthalpy (Φ_L), relative partial molar enthalpy (L_2) of the compound ($C_{12}H_{28}NCl$)(s), and relative partial molar enthalpy (L_1) of the solvent of double distilled water were derived, respectively. Hydration enthalpy of ($C_{12}H_{28}NCl$)(s) and its cation were also obtained from lattice potential energy and the molar dissolution enthalpy at infinite dilution. These results have shown that the existence of a hydrophobic dodecyl group in the compound is an important reason why the thermodynamic properties of the title compound ($C_{12}H_{28}NCl$)(s) are different from those of the molecules without hydrophobic groups.

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References

[1] L. Yang, Q. Pei, Y.L. Cao, T.L. Zhang, W. He, Chin. J. Energ. Mater. 15 (2007) 224–227.
[2] Z.F. Zhang, H. Wang, D.W. Fang, J.Z. Yang, Chem. J. Chin. Univ. 29 (2008) 569–572.
[3] Z.C. Tan, Y.Y. Di, Prog. Chem. 18 (2006) 1234–1251.
[4] Y.Y. Di, Y.X. Kong, W.W. Yang, Z.C. Tan, Chin. Phys. 17 (2008) 3276–3283.
[5] L. Glasser, Thermochim. Acta 421 (2004) 87–93.
[6] H.D.B. Jenkins, H.K. Roobottom, J. Passmore, L. Glasser, Inorg. Chem. 38 (1999) 3609–3620.
[7] H.D.B. Jenkins, L. Glasser, Inorg. Chem. 41 (2002) 4378–4388.
[8] W. Guan, L. Li, H. Wang, W.G. Xu, J.Z. Yang, Chem. J. Chin. Univ. 27 (2006) 310–313.
[9] X.K. Gao, J.M. Dou, D.C. Li, F.Y. Dong, D.Q. Wang, J. Mol. Struct. 733 (2005) 181–186.
[10] Y.Y. Di, J.T. Chen, Z.C. Tan, Thermochim. Acta 471 (2008) 70–73.
[11] Y.X. Kong, Y.Y. Di, Y.D. Qi, W.W. Yang, Z.C. Tan, Thermochim. Acta 488 (2009) 27–32.
[12] R. Rychly, V. Pekarek, J. Chem. Thermodyn. 9 (1977) 391–396.
[13] L. Glasser, H.D.B. Jenkins, Inorg. Chem. 47 (2008) 6195–6202.
[14] K.S. Pitzer, in: K.S. Pitzer (Ed.), Activity Coefficients in Electrolyte Solutions, Revised, CRC, Boca Raton, 1991 (Chapter 3).
[15] L.F. Silvester, K.S. Pitzer, J. Phys. Chem. 81 (1977) 1822–1828.
[16] W. Guan, H. Wang, L. Li, Q.G. Zhang, J.Z. Yang, Thermochim. Acta 437 (2005) 196–197.
[17] L.Z. Zhou, J.Y. Zou, Handbook of Rare Metals, Central South Industrial University Press, Changsha, 1993, pp. 180–181.