J. Chem. Thermodynamics 43 (2011) 1058–1062

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Crystal structure and thermochemical properties of 1-decylammonium hydrochloride ($C_{10}H_{21}NH_3Cl$)(s)

Wen-Yan Dan, You-Ying Di *, Hai-Feng Yuan, Yu-Pu Liu, Dong-Hua He

College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, Shandong Province, PR China

ARTICLE INFO

Article history:
Received 16 September 2010
Received in revised form 20 October 2010
Accepted 14 February 2011
Available online 26 February 2011

Keywords:
1-Decylammonium hydrochloride
Pitzer's theory
Lattice potential energy
Hydration heat

ABSTRACT

The compound 1-decylammonium hydrochloride was synthesized by the method of liquid phase reflux. Chemical analysis, elemental analysis, and X-ray crystallography were applied to characterise its composition and structure. The lattice potential energy of the crystalline solid compound was calculated from data of the crystal structure. The values of the molar enthalpy of dissolution of 1-decylammonium hydrochloride at different concentrations (m) at $T = 298.15$ K were measured by means of an isoperibol solution–reaction calorimeter. According to the Pitzer electrolyte solution theory, the molar solution enthalpy of $C_{10}H_{21}NH_3Cl$(s) at infinite dilution ($\Delta_s H_m^{\infty}$) and Pitzer parameters ($\beta_{MX}^{(0)L}$ and $\beta_{MX}^{(1)L}$) were obtained. Then the apparent relative molar enthalpy ($^{\Phi}L$) of the title compound and relative partial molar enthalpies of solvent and solute ($\bar{L}_1$ and $\bar{L}_2$) were calculated, respectively. Hydration heats of the solid compound and its cation were derived from the molar solution enthalpy of the title compound at infinite dilution ($\Delta_s H_m^{\infty}$) and the lattice potential energy.

1. Introduction

The compound 1-decylamine is an important intermediate in organic synthesis, which has great influence on our daily life. In recent years, great attention has been paid to the application of 1-decylammonium salts in many fields such as energy storage. The complexes $(C_{10}H_{21}NH_3)_2CdCl_4$(s) and $(C_{10}H_{21}NH_3)_2CuCl_4$(s) were carefully investigated by Kind *et al.* [1] and Lee *et al.* [2]. These studies showed that these coordination compounds exhibited the high enthalpies of solid–solid phase transitions. Pinto *et al.* [3] investigated the crystal structure of 1-decylammonium hydrochloride. However, some thermodynamic properties of 1-decylamine hydrochloride such as lattice potential energy, molar solution enthalpy, Pitzer parameters, and hydration heat have not been found in the literature. The lattice potential energy [4–6] is a vital measurement to weigh the bonding ability of the molecules or ions in the crystal structure, and in relation with many significant physicochemical properties of substances. The enthalpy of dissolution of a substance in water [7,8] 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. Hydration heat [9] is the thermal effect of a solid substance in generating hydrated ion when the substance is dissolved in water at infinite dilution, and is 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. The enthalpy of dissolution of the compound in the water was measured by an isoperibol solution–reaction calorimeter. Lattice potential energy, various values of the molar enthalpy of dissolution, and hydration heat of the title compound were obtained based on the crystal structure and experimental enthalpies of dissolution at different concentrations.

2. Experimental

2.1. Synthesis of the compound $C_{10}H_{21}NH_3Cl$(s)

The 1-decylamine and hydrochloric acid (0.37 in mass fraction) used as the reactants were of analytical grade. The mass of 1-decylamine was accurately weighed at the mole ratio of $n(CH_3(CH_2)_9NH_2):n(HCl) = 1:1$. A certain amount of 1-decylamine (about 50 mmol) was firstly dissolved in a 250 cm^3 flask with 80 cm^3 of anhydrous methanol (A.R.) and then hydrochloric acid (about 50 mmol) was added slowly. The mixture was heated and stirred under reflux for 6 h. The above solution was heated and condensed on the electric furnace till crystal membrane appeared. The final solution was naturally cooled to room temperature, filtered, and the white product was washed by cool anhydrous methanol for three times. The white solid product was recrystallized using anhydrous methanol, and colourless crystals were obtained by natural evaporation of a solution of the title compound in anhydrous methanol at room temperature for the purpose of crystal growth. Finally, the sample was placed in a vacuum desiccator to dry in

* Corresponding author. Fax: +86 635 8239121.
E-mail addresses: diyouying@126.com, yydi@lcu.edu.cn (Y.-Y. Di).

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doi:10.1016/j.jct.2011.02.013

vacuum for 6 h. Theoretical contents of Cl, N, C, and H in the compound have been calculated to be 0.1830, 0.0723, 0.6199, and 0.1248, respectively. Chemical and elemental analyses (model: PE-2400, Perkin Elmer, USA) have shown that practical contents of Cl, N, C, and H in the compound have been measured to be 0.1827, 0.0725, 0.6201, and 0.1247, respectively. This shows that mass fraction purities of the sample prepared is greater than 0.995. The mass per cent content of the chlorine in the title substance was determined by gravimetry with AgCl.

2.2. X-ray crystallography

All X-ray crystallographic data were collected on a Bruker SMART CCD 1000 diffractometer with Mo Kα radiation, λ = 0.071073 nm. A criterion of observability was used for the solution and refinement. The intensity data were collected at T = 298(2) K. The structure was solved by direct methods and expanded using Fourier techniques with SHELXL-97 program [10]. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2. The hydrogen atoms were added theoretically, riding on the concerned atoms and not refined.

2.3. Isoperibol solution–reaction calorimetry

The isoperibol solution–reaction calorimeter consisted primarily of a precise temperature controlling system, an electric energy calibration system, a calorimetric body, an electric stirring system, a thermostatic bath made from transparent silicate glass, a precise temperature measuring system and a data acquisition system. The principle and structure of the calorimeter were described in detail elsewhere [11,12].

The reliability of the calorimeter was verified previously by measuring the dissolution enthalpy of KCl (calorimetrically primary standard) in double distilled water. According to the mole ratio of KCl to H_2O, $n_{KCl} : n_{H_2O} \approx 1 : 1110$, the KCl was dissolved in 100 cm^3 of double-distilled water at T = (298.15 ± 0.001) K. The mean dissolution enthalpy was (17,547 ± 13) J · mol^{-1}, which compares with the corresponding published data, (17,536 ± 3.4) J · mol^{-1} [13].

3. Results and discussion

3.1. Crystal structure of 1-decylammonium hydrochloride

The X-ray crystallography showed that the compound was 1-decylamine hydrochloride. The molecular structure of $C_{10}H_{21}NH_3Cl$(s) is shown in figure 1. Crystal data and refinement details are summarised in table 1. The selected bond lengths and angles of 1-decylammonium hydrochloride are listed in table 2. The information on the hydrogen bonds is given in table 3. The cation ($[C_{10}H_{21}NH_3]^+$) and anion (Cl^-) are held together by electrovalent bond in the compound. Weak van der Waals forces act between the alkyl chains. The compound is composed of the regular alternation of inorganic and hydrocarbon regions through the hydrogen bonding viewing along b–c plane, as shown in figure 2. The alkyl chains of molecules of 1-decylammonium hydrochloride are perfectly ordered in the all trans conformation and form an intercalated bilayer in figure 2. A two-dimensional network of the title compound was formed through hydrogen bonding viewing along a–b plane, as shown in figure 3.

The crystal data and the structure of the title compound determined are almost consistent with the previously reported results [3].

3.2. Lattice potential energy

The lattice potential energy (U_{POT}) is calculated by the following formula [14],

$$U_{POT} = \gamma\left(\frac{\rho_m}{M_m}\right)^{1/3} + \delta, \quad (1)$$

where M_m/g · mol^{-1} is the molar mass of the ionic material; ρ_m/g · cm^{-3} is the density of the substance; coefficients γ and δ take the following values for MX (charger ratio 1:1), γ = 1981.2 kJ · mol^{-1} · cm and δ = 103.8 kJ · mol^{-1} [14]. The values of ρ_m and M_m are found in table 1. The lattice potential energy of the complex is calculated to be 449.01 kJ · mol^{-1}.

3.3. Ionic radius

The volume of the ionic material can be obtained by using equation (2):

$$V = V_{cell}/Z \quad (2)$$

in which V denotes the volume of one molecule (formula unit), V_{cell} represents the volume of molecules per unit cell, and Z is the number of molecules per unit cell. The values of V_{cell} and Z can be found in table 1.

For a salt, M_pX_q, in accordance with the additive property of the volumes, the total molar volume should equal the sum of those of the cation and anion, namely,

$$V = pV_+ + qV_-, \quad (3)$$

where V_+ is the effective volume of cation, V_- is the corresponding effective volume of the anion. Like the title complex, p = 1 and q = 1. The volume of Cl^- is (0.047 ± 0.013) nm^3 [5]. From equations (2) and (3), the value of V_+ can be calculated to be (0.267 ± 0.013) nm^3. The ionic radius of the cation, r_+, of 1-decylammonium

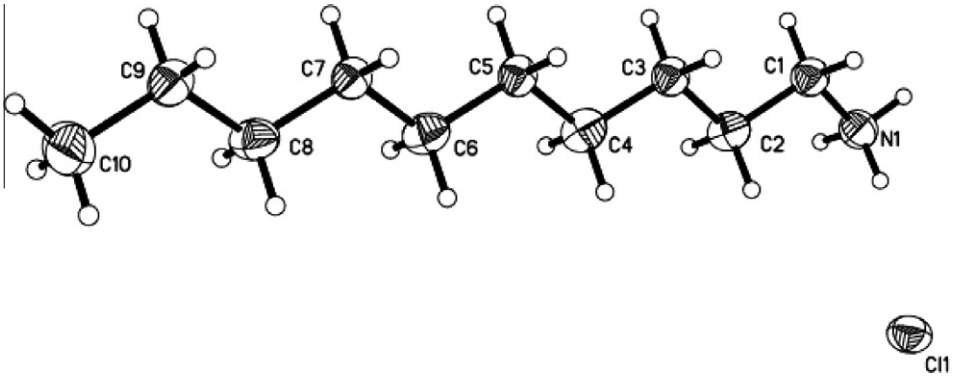

FIGURE 1. Molecular structure of $C_{10}H_{21}NH_3Cl$(s).