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Thermodynamic study of phase transitions of imidazoles and 1-methylimidazoles

Ana R.R.P. Almeida, Manuel J.S. Monte *

Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 687, P-4169-007 Porto, Portugal

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4,5-Dicyano-1-methylimidazole

ABSTRACT

The vapor pressures of imidazole, *N*-methylimidazole and of their dichloro and dicyano substituted compounds were measured at different temperatures, in the crystalline phase for two of them, and in crystalline and liquid phases for the other four. From these measurements, enthalpies and standard entropies of sublimation and vaporization were derived. The results allowed the determination of the triple points (p, T) coordinates of the four compounds studied in both condensed phases as well as the calculation of their enthalpy of fusion. Enthalpies and temperatures of fusion were also determined using d.s.c. The experimental results enabled the estimation of the enthalpy of the intermolecular N–H···N bonds in the imidazoles studied.

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1. Introduction

Imidazole and related compounds find quite a few practical applications. Several derivatives of imidazole are used as antibiotics and antifungal drugs [1], while *N*-methylimidazole is often used as precursor for the synthesis of several ionic liquids [2].

In previous works we estimated enthalpies of intermolecular hydrogen bonds N–H···O [3–5] and O–H···O [6] from sublimation vapor pressure measurements of selected compounds and of parent ones where the hydrogen atom participating in the hydrogen bond was replaced by a methyl group. In this work we decided to investigate the enthalpy of N–H···N intermolecular bond in crystalline imidazole and two imidazole derivatives by measuring their sublimation vapor pressures and the vapor pressures of the related *N*-methylderivatives. For four of the compounds studied we decided to extend the vapor pressure measurements to the liquid phase. Since the previously reported values of sublimation pressure of imidazole [7,8] were measured below 1 Pa inside a temperature range far from the melting temperature, we decided to use a much wider range of temperature to measure its sublimation vapor pressures.

2. Experimental

2.1. Materials and purity control

Imidazole (CAS No. 288-32-4), 1-methylimidazole (CAS No. 616-47-7), 4,5-dichloroimidazole (CAS No. 15965-30-7), and 4,5-dicyanoimidazole (CAS No. 1122-28-7) were obtained from Aldrich Chemical Co. with certified molar fraction purity of 0.9996, 0.997, 0.99+, and 0.998, respectively. 4,5-Dichloro-1-methylimidazole (CAS No. 1192-53-6) and 4,5-dicyano-1-methylimidazole (CAS No. 19485-35-9), were obtained from Alfa Aesar with assured minimum molar fraction purity of 0.97 and 0.98, respectively. Samples of the crystalline compounds were further purified by sublimation under reduced pressure while the liquid compound (1-methylimidazole) was studied without further purification. Final purity of the samples was investigated using an Agilent 4890D gas chromatograph equipped with HP-5 column, cross-linked, 5% diphenyl and 95% dimethylpolysiloxane (15 m long, 0.530 mm i.d., 1.5 μm film thickness) and a flame ionization detector. No molar fraction impurity higher than $1 \cdot 10^{-3}$ was observed.

2.2. Differential scanning calorimetry

A power compensated differential scanning calorimeter (Setaram 141) was used to detect possible phase transitions in

* Corresponding author. Tel.: +351 2608 2816; fax: +351 22 608 2959.
E-mail addresses: ana.figueira@fc.up.pt (A.R.R.P. Almeida), mjmonte@fc.up.pt (M.J.S. Monte).

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the crystalline phase and to determine the temperatures and enthalpies of fusion of the purified samples. Crystalline samples were sealed in aluminum crucibles while the liquid compound was studied in hermetically sealed steel crucibles. The calibration of the power scale of the calorimeter was performed using high-purity indium (mass fraction > 0.99999). The temperature scale of the calorimeter was calibrated by measuring the melting temperature of the following high purity reference materials [9]: naphthalene, benzoic acid, and indium. For each compound at least four independent scannings were performed under nitrogen atmosphere using a heating rate of $3.3 \cdot 10^{-2}$ K · s^{-1}. No crystalline transitions were detected between the temperature 298 K and the temperature of fusion of the compounds studied. Mean results and experimental uncertainties (calculated as the standard deviations) of the temperatures of fusion (observed at the onset of the calorimetric peaks) and of the molar enthalpies of fusion are presented in table 7.

2.3. Vapor pressures measurements

The vapor pressures of imidazole, 1-methylimidazole, 4,5-dichloro-1-methylimidazole, and 4,5-dicyano-1-methylimidazole were measured at different temperatures in both crystalline and liquid phases using a static apparatus, based on capacitance diaphragm gauges, that was previously described in detail [10]. For the other two compounds studied the amounts of available samples did not allow the measurement of their liquid vapor pressures. Sublimation vapor pressures of 4,5-dichloroimidazole and of 4,5-dicyanoimidazole were measured using the static apparatus and a Knudsen effusion apparatus, respectively. The two capacitance diaphragm absolute gauges available in the static apparatus were obtained from MKS Instruments, Inc. They operate at self-controlled constant temperatures: gauge 1, Baratron 631A01TBEH (T_{gauge} = 423 K) for measuring pressures in the range (0.4 to 133) Pa and in the temperature range (253 to 413) K; gauge 2, Baratron 631A11TBFP (T_{gauge} = 473 K) capable of measuring pressures in the range (3 to 1330) Pa and in the temperature range (253 to 463) K. A platinum resistance thermometer Pt100 class 1/10 (in a four wire connection) was used to measure the temperatures of the condensed samples. This thermometer was calibrated by comparison with a SPRT (25 Ω; Tinsley, 5187A). The metal tubing between the cell containing the condensed sample and the pressure gauge is kept at a temperature higher than the temperature of the sample and lower than the temperature of the gauge. The uncertainty of the temperature measurements is estimated to be better than ±0.01 K and the uncertainty in the pressure measurements is adequately described by the expressions $\sigma(p/\text{Pa}) = 0.01 + 0.0025\ (p/\text{Pa})$ for gauge 1 and $\sigma(p/\text{Pa}) = 0.1 + 0.0025\ (p/\text{Pa})$ for gauge 2.

The Knudsen effusion apparatus used to measure the vapor pressures of 4,5-dicyanoimidazole was also previously described in detail [11]. This apparatus enables the simultaneous operation of nine effusion cells, contained in cylindrical holes inside three temperature-controlled aluminum blocks. During an effusion experiment, each aluminum block, containing three effusion cells, is kept at a constant temperature, different from the other two blocks. Three different groups of effusion cells according to their different areas of effusion orifices were used: one "*small*" ($A_o \approx 0.5$ mm^2: series A), one "*medium*" ($A_o \approx 0.8$ mm^2: series B) and one "*large*" ($A_o \approx 1.1$ mm^2: series C). The temperature of each block is measured using a platinum resistance thermometer Pt100 class 1/10 (in a four wire connection) previously calibrated by comparison with an SPRT (25 Ω; Tinsley, 5187 A). The exact areas and Clausing factors of each used effusion orifice, made in platinum foil of 0.0125 mm thickness, are presented in the supporting information, table S1. In each effusion experiment, the mass loss of the crystalline sample, Δm, was measured by weighing the cells with samples, within ±0.01 mg, before and after a convenient effusion time period, t, in a system evacuated to a pressure near $1 \cdot 10^{-4}$ Pa. For the temperature T, measured with an accuracy of ±0.01 K, the vapor pressure p of the crystalline sample contained in each effusion cell is calculated by equation (1) where M is the molar mass of the effusing vapor, R is the gas constant, A_o represents the area of the effusion orifice and w_o is the respective Clausing factor. The accuracy of the measured pressures is estimated to be better than ±0.01 (p/Pa)

$$p = (m/A_o w_o t) \cdot (2\pi RT/M)^{1/2}. \quad (1)$$

3. Results and discussion

Tables 1 to 4 present the vapor pressure results measured using the static apparatus for both the crystalline and liquid phases, of imidazole, 1-methylimidazole, 4,5-dichloro-1-methylimidazole and 4,5-dicyano-1-methylimidazole, respectively. With the exception of 4,5-dichloro-1-methylimidazole, vapor pressures of metastable undercooled liquid were also measured. Table 5 shows the sublimation vapor pressure results of 4,5-dichloroimidazole, measured through the static apparatus, and the effusion sublimation vapor pressures of 4,5-dicyanoimidazole calculated for each

TABLE 1
Vapor pressure results for imidazole.[a]

T/K	p/Pa	$100\Delta p/p$	T/K	p/Pa	$100\Delta p/p$	T/K	p/Pa	$100\Delta p/p$[b]
				Crystalline phase				
303.99	0.58	0.8	324.96	4.69	0.0	342.84	22.89	0.6
306.97	0.79	0.1	327.95	6.21	0.5	345.83	29.23	0.3
309.99	1.08	0.0	330.92	8.19	1.2	348.80	37.01	−0.3
312.98	1.45	−1.1	333.90	10.63	0.7	351.77	46.93	−0.2
315.94	1.95	−1.0	336.88	13.77	0.5	354.75	59.20	−0.4
318.92	2.63	−0.3	339.86	17.82	0.7	357.72	73.94	−1.1
321.97	3.50	−1.0						
				Liquid phase				
333.90	14.85	−0.4	351.75	52.22	−0.1	369.63	159.6	−0.1
336.89	18.59	0.0	354.76	63.54	−0.2	372.60	191.2	0.7
339.86	23.11	0.3	357.72	76.82	−0.2	375.56	224.9	−0.1
342.84	28.48	0.1	360.69	92.88	0.1	378.51	265.5	−0.1
345.81	35.09	0.3	363.67	111.2	−0.4	381.51	313.4	−0.1
348.80	42.97	0.2	366.66	133.6	−0.2	384.48	368.8	0.1

[a] Estimated uncertainties are 0.01 K for the temperature, [0.01 + 0.0025 (p/Pa)] for pressures below 130 Pa (measured through gauge 1) and [0.1 + 0.0025 (p/Pa)] for the other pressures (measured through gauge 2).
[b] $\Delta p = p - p_{calc}$.

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