Available online at www.sciencedirect.com

SCIENCE DIRECT®

J. Chem. Thermodynamics 37 (2005) 271–279

JCT

www.elsevier.com/locate/jct

Thermodynamic study of the sublimation of six halobenzoic acids

Manuel A.V. Ribeiro da Silva *, José M.S. Fonseca,
Rui P.B.M. Carvalho, Manuel J.S. Monte

Department of Chemistry, Faculty of Science, University of Porto, Centro de Investigação em Química, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal

Received 3 August 2004; received in revised form 7 September 2004; accepted 9 September 2004

Abstract

The Knudsen mass-loss effusion technique was used to measure the vapour pressures at different temperatures of the following halobenzoic acids: 2-chlorobenzoic acid, between T = (320.16 and 339.15) K, 3-chlorobenzoic acid, between T = (320.13 and 340.13) K, 4-chlorobenzoic acid, between T = (333.15 and 356.14) K, 2-bromobenzoic acid, between T = (327.56 and 347.68) K, 3-bromobenzoic acid, between T = (327.67 and 347.60) K and 4-bromobenzoic acid, between T = (348.67 and 366.65) K. From the temperature dependence of the vapour pressure of the crystalline compounds, the standard, $p^\circ = 10^5$ Pa, molar enthalpies, entropies and Gibbs energies of sublimation at T = 298.15 K, were derived. A d.s.c. study of the fusion of the crystals is also presented.

Keywords: Knudsen effusion; Vapour pressures; Enthalpies of sublimation; Entropies of sublimation; Enthalpies of fusion; Halobenzoic acids; Chlorobenzoic acids; Bromobenzoic acids

1. Introduction

The present work is a continuation of a thermodynamic study of our laboratory on the sublimation of several substituted benzoic acids recently published [1–4], which included the fluorobenzoic and iodobenzoic acids [1]. In order to study the influence of the halogen substituent on the volatility of the different halobenzoic acids, it was decided to extend the previous study to the three chlorobenzoic and to the three bromobenzoic acids for which vapour pressure–temperature data were not known. Furthermore, literature calorimetric values of the standard molar enthalpies of sublimation for some of those compounds, published by different authors, showed significant disagreement.

2. Experimental

The 4-bromobenzoic acid [CAS 586-76-5] was obtained from BDH Chemicals Ltd. with high purity grade (organic analytical standard). All the other compounds are commercial products from Aldrich Co: 2-chlorobenzoic acid [CAS 118-91-2], 0.999 mass fraction (g.c.), 3-chlorobenzoic acid [CAS 535-80-8], mass fraction >0.99, 4-chlorobenzoic acid, [CAS 74-11-3], 0.999 mass fraction (g.c.), 2-bromobenzoic acid [CAS 88-65-3], 0.994 mass fraction (g.c.), 3-bromobenzoic acid CAS [585-76-2], 0.999 mass fraction (g.c.).

All the samples of the studied compounds were further purified by sublimation under reduced pressure prior to the experimental measurements. The temperature and the enthalpy of fusion of the sublimed samples (hermetically sealed in steel crucibles) were measured using a Setaram DSC 141 calorimeter under a heating rate of $3.3 \cdot 10^{-2}$ K $\cdot$ s^{-1}. The calibration of the power scale of the calorimeter was performed using high-purity

---

* Corresponding author. Tel.: +351 22 6082 821; fax: +351 22 6082 822.

E-mail address: risilva@fc.up.pt (M.A.V. Ribeiro da Silva).

0021-9614/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jct.2004.09.005

indium (mass fraction >0.99999) and its temperature scale was calibrated by measuring the melting temperature of the following high purity reference materials [5]: naphthalene, benzoic acid and indium. For each compound, at least four independent runs were performed. Mean results and standard deviations of the temperatures (observed at the onset of the calorimetric peaks) of fusion, T_{fus}, and of the molar enthalpies of fusion, $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\circ}(T_{\mathrm{fus}})$ are presented in table 1 together with the mass fractions of impurity, x, calculated through a fractional fusion technique [6].

The vapour pressures of the crystalline samples were measured at several temperatures using the Knudsen mass-loss effusion technique. The used experimental apparatus enables the simultaneous operation of three Knudsen cells, with three different effusion orifices, making it possible to check the absence of any dependence of the measured pressures on the area of the effusion orifice. A full description of the main features of the apparatus, procedure, technique and the results obtained with ferrocene and benzoic acid have been reported [7]. The consistency of the measured vapour pressures was also checked by comparing the results obtained for benzoic acid and for copper(II) β-diketonates using this apparatus, with the results obtained for these compounds by using different experimental apparatuses and different techniques [8]. A few minor changes have been introduced to the original apparatus design and several other tests have been performed with other reference substances such as benzophenone, dibenzothiophene and naphthalene.

The measurements were extended through a temperature interval of *ca.* 20 K chosen to correspond to measured vapour pressures in the range 0.1 to 1 Pa. In a typical effusion experiment, the crystalline sample is placed at the base of each cylindrical effusion cell. After being weighed to within ±0.01 mg, the cells containing the samples are placed in aluminium blocks inside glass tubes connected to the vacuum system. These tubes are immersed in a thermostatically controlled to ±0.001 K silicone oil bath during the experiment. The vapour effuses through the orifice coaxially located at the top of each cell into the outside space evacuated to a pressure of 10^{-4} Pa. The temperature of the bath is measured using Amarell mercury thermometers, calibrated by Eichamt Wertheim (Germany) and graduated to 0.01 K.

TABLE 1
Temperatures of fusion, T_{fus}/K, enthalpies of fusion, $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\circ}(T_{\mathrm{fus}})$, and mass fraction of impurities, x, of the studied compounds

Compound	$10^3 \cdot x$	T_{fusion}/K	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}/\mathrm{kJ \cdot mol^{-1}}$
2-Chlorobenzoic acid	0.3	413.95 ± 0.06	25.25 ± 0.06
3-Chlorobenzoic acid	0.7	427.87 ± 0.21	23.67 ± 0.13
4-Chlorobenzoic acid	0.8	512.50 ± 0.23	30.91 ± 0.34
2-Bromobenzoic acid	2.1	421.60 ± 0.22	24.83 ± 0.34
3-Bromobenzoic acid	0.7	430.08 ± 0.14	24.91 ± 0.10
4-Bromobenzoic acid	2.3	526.34 ± 0.38	30.87 ± 0.08

The effusion time period of each experiment was usually longer than 10^4 s in order to allow sublimed masses of the samples from each effusion cell greater than 10 mg. After the effusion process is complete, the cells are weighed again and the sublimed masses, Δm, are calculated. At the temperature T of each effusion experiment, the vapour pressure p is calculated by the Knudsen equation:

$$p = (\Delta m / A_{\mathrm{o}} w_{\mathrm{o}} t) \cdot (2\pi R T / M)^{1/2}, \tag{1}$$

where M is the molar mass of the effusing vapour (assumed to be monomeric for all the studied compounds), t is the effusion time period, R is the gas constant, A_{o} is the area of the effusion orifice and w_{o} is the respective Clausing factor, calculated by equation (2), with l being the thickness of the orifice and r its radius:

$$w_{\mathrm{o}} = \{1 + (3l/8r)\}^{-1}. \tag{2}$$

In this work, circular effusion orifices made in platinum foil of 0.0125 mm thickness were used. Their areas and Clausing factors are as follows: orifice 1, $A_{\mathrm{o}}/\mathrm{mm}^2 = 0.663$, $w_{\mathrm{o}} = 0.990$; orifice 2, $A_{\mathrm{o}}/\mathrm{mm}^2 = 0.785$, $w_{\mathrm{o}} = 0.991$; orifice 3, $A_{\mathrm{o}}/\mathrm{mm}^2 = 0.996$, $w_{\mathrm{o}} = 0.992$.

3. Results and discussion

The Clausius–Clapeyron equation (3), where $p^{\circ} = 1$ Pa, was used to determine the molar sublimation enthalpy at the mean temperature $\langle T \rangle$ of the experiments, $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(\langle T \rangle)$, for each compound studied:

$$d\{\ln(p/p^{\circ})\}/d(1/T) = -\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(\langle T \rangle)/R. \tag{3}$$

The plots of $\ln(p/p^{\circ})$ against $1/T$ for the global results obtained for the studied compounds are presented in figure 1. Table 2 presents, for each compound and for each effusion orifice used, the results of the vapour pressure obtained from each effusion experiment during the effusion time period t, at the temperature T, together with the residuals of the values calculated through equation (4), where a is a constant and $b = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(\langle T \rangle)/R$,

$$\ln(p/\mathrm{Pa}) = a - b \cdot (T/\mathrm{K})^{-1}. \tag{4}$$

Table 3 presents, for each effusion orifice used and for the global treatment of all the (p,T) results obtained for each studied compound, the parameters of equation (4) together with the calculated standard deviations and the standard molar enthalpies of sublimation at the mean temperature of the experiments $\langle T \rangle$. For the global treatment, the equilibrium pressure at the mean temperature $p(\langle T \rangle)$ and the entropies of sublimation at equilibrium conditions, $\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}\{\langle T \rangle, p(\langle T \rangle)\} = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(\langle T \rangle)/\langle T \rangle$ are also presented. For each compound, the calculated enthalpies of sublimation obtained from each individual orifice are in agreement, within experimental error, with the values obtained using the global treatment.