

Short communication

# Heat capacities and molar enthalpies and entropies of fusion for anhydrous 1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline

M.G. Bonicelli\*, A. Catalani, G. Mariano, S. Vecchio\*\*

*Dipartimento di Ingegneria Chimica Materiali e Ambiente, Università di Roma "La Sapienza", Via del Castro Laurenziano 7, 00161 Rome, Italy*

Received 2 August 2007; received in revised form 1 October 2007; accepted 4 October 2007

Available online 10 October 2007

## Abstract

Heat capacities ( $C_{p,m}$ ) of solid anhydrous 1,10-phenanthroline (phen) and 2,9-dimethyl-1,10-phenanthroline (dmphen) were determined by differential scanning calorimetry using the three step method over the temperature range from 298 K to about 5 K (for phen) and 40 K (for dmphen) below their melting temperatures. No further solid–solid phase transition occurs in the temperature range examined. In addition, the average melting temperature, molar enthalpy and molar entropy of fusion for phen and dmphen were also determined to be  $(391.1 \pm 0.1 \text{ K}, 11.8 \pm 0.1 \text{ kJ mol}^{-1}, \text{ and } 30.0 \pm 0.3 \text{ J K}^{-1} \text{ mol}^{-1})$  and  $(435.9 \pm 0.3 \text{ K}, 17.6 \pm 0.3 \text{ kJ mol}^{-1}, \text{ and } 40.3 \pm 0.6 \text{ J K}^{-1} \text{ mol}^{-1})$ , respectively. The experimental heat capacity data were obtained and the respective second-order polynomial fitting equations were derived:

$$C_{p,m}(\text{phen, cr})/(\text{J K}^{-1} \text{ mol}^{-1}) = (-3905 \pm 16) + (22.0 \pm 1.0)(T/\text{K}) - (0.0289 \pm 0.0015)(T/\text{K})^2 \text{ from } 298.2 \text{ to } 360.2 \text{ K}, R^2 = 0.9935;$$

$$C_{p,m}(\text{dmphen, cr})/(\text{J K}^{-1} \text{ mol}^{-1}) = (-2808 \pm 14) + (17.1 \pm 1.0)(T/\text{K}) - (0.0229 \pm 0.0014)(T/\text{K})^2 \text{ from } 298.2 \text{ to } 393.2 \text{ K}, R^2 = 0.9953.$$

In particular the  $C_{p,m}$  values at  $T = 298.15 \text{ K}$  for phen and dmphen were found to be  $(115 \pm 18 \text{ and } 253 \pm 30) \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively, where the associated uncertainties are twice the standard deviations of the mean.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** 1,10-Phenanthroline; 2,9-Dimethyl-1,10-phenanthroline; Heat capacity; Differential scanning calorimetry; Three step method

## 1. Introduction

In the last decades, differential scanning calorimetry (DSC) was extensively used to determine some important thermodynamic properties of pure organic substances [1–4]. Many thermodynamic studies in the field of thermochemistry, solution chemistry, biochemistry and biophysics use heat capacity data of pure compounds to obtain enthalpies of vaporization and sublimation at 298.15 K from measurements at different temperatures higher than 298.15 K. For the sake of example, some authors used the enthalpies of vaporization and sublimation corrected at 298.15 K using capacity data obtained in suitable temperature ranges, to derive the standard enthalpies of solvation [5] or the enthalpies of formation [6] using the enthalpies of solution

at infinite dilution or the enthalpies of combustion at 298.15 K, respectively. However, the accuracy of the heat capacity data obtained by DSC measurements usually varies from about 5 to 1% or less, depending on the apparatus, the experimental method, and the data processing procedure used [7].

In this study, some thermophysical properties of two nitrogen-coordinating compounds, which are able to form a series of mono- to tris-ligand complexes with transition metals [8–10] have been examined: 1,10-phenanthroline (CAS: 66-71-7, phen) and 2,9-dimethyl-1,10-phenanthroline (CAS: 484-11-7, dmphen), often denoted as neocuproine. They are widely used in metallocene industry for coordination of organometallic-complexes and in connection with DNA–protein interactions [9,10], as well as in catalysis for the oxidation of alcohols in solution [11]. In addition, phen is used as an oxidation–reduction indicator due to its characteristic colour change (it turns to faint blue when oxidized) and as an indicator for iron as it forms a complex compound with ferrous ions (ferroin) [12]; dmphen is used as a clinical reagent in blood glucose assay and in the spec-

\* Corresponding author. Tel.: +39 06 4976 6732; fax: +39 06 4976 6749.

\*\* Corresponding author. Tel.: +39 06 4976 6906; fax: +39 06 4976 6749.

E-mail addresses: [mariagrazia.bonicelli@uniroma1.it](mailto:mariagrazia.bonicelli@uniroma1.it) (M.G. Bonicelli), [stefano.vecchio@uniroma1.it](mailto:stefano.vecchio@uniroma1.it) (S. Vecchio).

trophotometric determination of copper [13]. Their molecular structures are reported in [supplementary Fig. 1](#).

The melting temperatures of anhydrous phen and dmphen taken from the literatures [14,15] are 390.2 and 432.7 K, respectively. However, to the best of our knowledge little is known about thermodynamic data of these compounds. Therefore, in order to fill this gap in view of requirements for theoretical research studies and practical applications concerning the compound examined, their melting temperatures, the molar heat capacities ( $C_{p,m}$ ), the molar enthalpies and entropies as well as their chemical purities (using the DSC peak profile method [16]) were determined.

## 2. Experimental

High-pure indium (supplied by Perkin-Elmer), synthetic sapphire ( $\alpha\text{-Al}_2\text{O}_3$ ) and copper (reference material supplied by Rheometric Scientific), naphthalene and benzoic acid (supplied by Fluka) have mass fraction  $\geq 0.994$ . Phen and dmphen samples were supplied by Riedel-de Haën and Fluka, respectively. Purities (expressed as mole fractions), determined from the fractional melting DSC experiments using the Van't Hoff equation, were 0.9961 and 0.9930, respectively. Consequently, phen and dmphen were not further purified. In order to eliminate hydration and crystallization water and avoid re-hydration of both organic bases, sapphire, benzoic acid, phen and dmphen were dried in an oven at 378 K for 24 h and kept in a dessicator until the moment of their use.

DSC measurements were carried out with a Perkin-Elmer Pyris I calorimeter equipped with an intracooler unit from 298.15 to 368.15 K under a stream of nitrogen of  $0.67\text{ cm}^3\text{ s}^{-1}$  using hermetically sealed Al pans. For the heat capacity determinations, four DSC experiments were carried out with masses in the range 4–6 mg and fresh samples were used for each run. The change of pressure in the sealed crucibles is usually small and the heat capacity measured is nearly the same as that under room normal pressure ( $p^\circ \sim 0.1\text{ MPa}$ ). The temperature sensors were chromel–alumel for the sample thermocouples and platinel II for the control of temperature of the sample and reference. The temperature scale, whose uncertainty is  $\pm 0.1\text{ K}$ , was calibrated using recommended high purity reference materials: benzoic acid and indium [17,18]. The heat flux scale was calibrated by measuring the enthalpy of fusion of benzoic acid and indium determined by means of the above-mentioned DSC experiments. The experimental melting temperatures as well as the enthalpies of fusion of benzoic acid and indium (whose associated uncertainties are twice the standard deviations of the respective means) were found to be in a good agreement with the recommended literature values [18]: within 0.2% for the former and about 2% for the latter ([supplementary Table 1](#)).

The heat capacities were determined as a function of temperature using synthetic sapphire ( $\alpha\text{-aluminium oxide}$ ) as reference material [17–19] by means of the following equation:

$$C_{p,m}(\text{J K}^{-1}\text{ mol}^{-1}) = \left( \frac{\phi(\text{sam}) - \phi(\text{blk})}{\phi(\text{ref}) - \phi(\text{blk})} \right) \left( \frac{m(\text{ref})}{m(\text{sam})} \right) C_{p,m}(\text{ref}), \quad (1)$$

where  $\Phi(\text{sam}) - \Phi(\text{blk})$  is the blank corrected net heat flow into the sample,  $\Phi(\text{ref}) - \Phi(\text{blk})$  the blank corrected net heat flow of the reference,  $m(\text{ref})$  and  $m(\text{sam})$  the masses of the sapphire and the sample, respectively, and  $C_{p,m}(\text{ref})$  is the heat capacity of sapphire in  $\text{J K}^{-1}\text{ mol}^{-1}$ , whose temperature dependence was taken from the literature [18]. The adopted procedure requests firstly the determination of the heat flow rate of the blank using empty Al pans of practically equal masses in the sample and reference sides. This zero line reflects the asymmetry of the instrument. Subsequently, a weighed amount of sapphire is placed in the sample side and the DSC experiment is repeated under identical conditions. After putting the sample and reference at their respective places in the DSC assembly the selected protocol performs the following steps: (i) isothermal run at room temperature for at least 1800 s, (ii) heating to 373 K at a heating rate of  $33\text{ mK s}^{-1}$  and (iii) isothermal run at 373 K for 1800 s. Three to five DSC experiments were carried out for reference and tested compounds and the reported values are the average of the results obtained. In order to check the accuracy of the experimental heat capacity measurements under the selected operating conditions identical experiments were carried out using high purity fresh samples of benzoic acid, copper and naphthalene, which are recommended as heat flow calibrants [18,20]. Percentages of deviation of experimental from literature  $C_{p,m}$  values for benzoic acid are reported in [supplementary Fig. 2](#) up to 373 K, while those of copper and naphthalene listed are given in [supplementary Table 2](#) at the selected temperatures. The agreement between experimental and recommended literature values is very good in all the cases, thus demonstrating that the accuracy of the procedure applied is good. The thermodynamic enthalpies and entropies of solid phen and dmphen relative to the reference temperature of 298.15 K were calculated from the heat capacity data according to Eqs. (2) and (3), respectively:

$$H_T - H_{298.15}(\text{J mol}^{-1}) = \int_{298.15}^T C_{p,m}(\text{s})dT, \quad (2)$$

$$S_T - S_{298.15}(\text{J K mol}^{-1}) = \int_{298.15}^T (C_{p,m}(\text{s})/T)dT, \quad (3)$$

where  $C_{p,m}(\text{s})$  is the heat capacity of the solid sample.

## 3. Results and discussion

The DSC curves of phen and dmphen ([supplementary Fig. 3A and B](#), respectively) show a single sharp endothermic peak ascribable to melting and no solid–solid phase transition processes was observed for both compounds in the investigated temperature ranges. Mean values of temperature, molar enthalpy and molar entropy of fusion obtained from these measurements and the associated errors estimated as standard deviations for phen and dmphen are  $391.1 \pm 0.1\text{ K}$ ,  $11.8 \pm 0.1\text{ kJ mol}^{-1}$ ,  $30.0 \pm 0.3\text{ J K}^{-1}\text{ mol}^{-1}$  and  $435.9 \pm 0.3\text{ K}$ ,  $17.6 \pm 0.3\text{ kJ mol}^{-1}$ ,  $40.3 \pm 0.6\text{ J K}^{-1}\text{ mol}^{-1}$ , respectively. By comparing all the fusion characteristic values it is evident that values for dmphen are rather higher than those of phen. Furthermore, from the DSC-peak profile method [16] the purity of the samples investigated was evaluated in order to establish if a purification treatment

should be considered before the heat capacity measurements. To this purpose, the sample temperatures during the occurrence of melting for phen and dmphen were reported as a function of the reciprocal of the melting fractions ( $1/F$ ) in [supplementary Fig. 4A and B](#), respectively. From the extrapolation of the corresponding straight line to  $1/F=0$  and  $1/F=1$  the corresponding melting temperatures of the theoretically absolute pure phen and dmphen samples,  $T_0$ , (391.4 and 436.5 K, respectively) as well as those of the impure real phen and dmphen samples,  $T_1$ , (390.9 and 435.9 K, respectively) were determined. From these experiments a final purity of phen and dmphen, expressed in terms of mole fraction, was found to be 0.9961 and 0.9930, respectively. As a consequence of the high purity values of the samples investigated, no further purification treatment was adopted before the heat capacity measurements.

The mean values of the different sets of experimental heat capacity measurements for phen (in the temperature range from 298 to 360 K at 2 K intervals) and dmphen (in the temperature range from 298 to 393 K at 5 K intervals) are given in [supplementary Tables 3 and 4](#), respectively. The experimental  $C_{p,m}$  values for phen and dmphen (32 and 20 data points, respectively) were fitted to the following second-order polynomial equations:

$$C_{p,m}(\text{phen, cr})/(\text{J K}^{-1} \text{ mol}^{-1}) \\ = (-3905.1 \pm 16) + (22.0 \pm 1.0)(T/\text{K}) \\ - (0.0289 \pm 0.0015)(T/\text{K})^2 \text{ from } 298.2 \text{ to } 360.2 \text{ K,} \\ R^2 = 0.9935;$$

$$C_{p,m}(\text{dmphen, cr})/(\text{J K}^{-1} \text{ mol}^{-1}) \\ = (-2808 \pm 14) + (17.1 \pm 1.0)(T/\text{K}) \\ - (0.0229 \pm 0.0014)(T/\text{K})^2 \text{ from } 298.2 \text{ to } 393.2 \text{ K,} \\ R^2 = 0.9953,$$

where the associated errors are standard deviations. Since to the best of our knowledge no experimental heat capacity data are published concerning phen and dmphen the only comparison possible was between the experimental and predicted values obtained using the selected fitted equations. In [supplementary Fig. 5](#) the percentage of the relative deviation of the experimental values from the predicted ones for phen and dmphen was reported as a function of temperature in the respective experimental temperature range. From these plots it is evident that the deviation of experimental data from the predicted values does not exceed the 8% for phen and 3% for dmphen.

The values of the thermodynamic functions  $H_T - H_{298.15}$  and  $S_T - S_{298.15}$  for phen and dmphen are listed in [supplementary](#)

[Tables 5 and 6](#), respectively as a function of the temperature in the same temperature range considered for the  $C_{p,m}$  measurements.

### Acknowledgements

This work was financially supported by MIUR. The authors wish to thank Mr. Fabio Raimondi for his contribution to this work.

### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tca.2007.10.001](https://doi.org/10.1016/j.tca.2007.10.001).

### References

- [1] P. Jiménez, M.V. Roux, J.Z. Davalos, M. Temprado, *Thermochim. Acta* 394 (2002) 25–29.
- [2] M. Ahrens, J. Maier, *Thermochim. Acta* 443 (2006) 189–196.
- [3] L. Abate, B. Palecz, C. Giancola, G. Della Gatta, *J. Chem. Thermodyn.* 29 (1997) 359–368.
- [4] J. Pak, Q.M. Pyda, E. Nowak-Pyda, B. Wunderlich, *J. Therm. Anal. Cal.* 82 (2005) 565–574.
- [5] G. Della Gatta, G. Barone, V. Elia, *J. Solution Chem.* 15 (1986) 157–167.
- [6] M.A.V. Ribeiro da Silva, M.D.M.C. Ribeiro da Silva, L.M.P.F. Amaral, J. Elguero, P. Jiménez, M.V. Roux, J.Z. Davalos, M. Temprado, P. Cabildo, R.M. Claramunt, O. M6, M. Yanez, *J. Chem. Thermodyn.* 37 (2005) 1168–1176.
- [7] T.M.V.R. de Barros, R.C. Santos, A.C. Fernandes, M.E. Minas de Piedade, *Thermochim. Acta* 269/270 (1995) 51–60.
- [8] D.V. Scaltrito, D.W. Thompson, J.A. O'Callaghan, G.J. Meyer, *Coord. Chem. Rev.* 208 (2000) 243–266.
- [9] Q.-X. Zhen, Q.-L. Zhang, J.-G. Liu, L.-N. Ji, L. Wang, *J. Inorg. Biochem.* 78 (2000) 293–298.
- [10] H. Deng, J. Li, K.C. Zheng, Y. Yang, H. Chao, L.N. Ji, *Inorg. Chim. Acta* 358 (2005) 3430–3440.
- [11] S. Meenakshisundaram, R. Markkandan, *Trans. Met. Chem.* 29 (2004) 136–143.
- [12] S. Budavari (Ed.), *The Merck Index*, 13th ed., Merck & Co., Inc., Whitehouse Station, NY, 2001.
- [13] B. Nebesar, *Anal. Chem.* 36 (1964) 1961–1965.
- [14] R.C. Weast (Ed.), *CRC Handbook of Chemistry and Physics*, 64th ed., CRC Press, Inc., Boca Raton, FL, USA, 1983.
- [15] F.H. Case, *J. Am. Chem. Soc.* 70 (1948) 3994–3996.
- [16] C. Plato, *Anal. Chem.* 44 (1972) 1531–1534.
- [17] R. Sabbah, A. Xu-wu, J.S. Chickos, M.L. Planas Leitão, M.V. Roux, L.A. Torres, *Thermochim. Acta* 331 (1999) 93–204.
- [18] G. Della Gatta, M.J. Richardson, S.M. Sarge, S. Stølen, *Pure Appl. Chem.* 78 (2006) 1455–1476.
- [19] T. Hatakeyama, Z. Liu (Eds.), *Handbook of Thermal Analysis*, John Wiley & Sons Ltd., Baffins Lane, Chichester, UK, 1998.
- [20] R. Stevens, J. Boerio-Goates, *J. Chem. Thermodyn.* 36 (2004) 857–863.