Standard enthalpy of fusion of N,N′-ethylenebis (2,4-pentanedion-iminoato)nickel(II) complex by DTA-based melting point depression studies

S. Arockiasamy[a], P. Antony Premkumar[a], O.M. Sreedharan[a,1], C. Mallika[b], V.S. Raghunathan[b], K.S. Nagaraja[a,*]

[a]Department of Chemistry, Loyola Institute of Frontier Energy (LIFE), Loyola College, Chennai TN-600 034, India
[b]Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam TN-603 102, India

Abstract

Determination of T–X'_{Ni} diagram for a binary system of N,N′-ethylenebis(2,4-pentanedion-iminoato)nickel(II) (designated as Ni′) and anhydrous bis(2,4-pentanedionato)nickel(II) (designated as Ni″) over the range 1.000–0.749 for the mole fraction (X'_{Ni}) of the volatile solvent by employing DTA revealed the system to resemble an ideal eutectic exhibiting lowering of the melting point of the volatile complex Ni′ with the addition of the non-volatile solute Ni″. The thermodynamic correlation between T and X'_{Ni} yielded an average value of 35.0 ± 4.0 kJ mol^{-1} for the standard enthalpy of fusion of the complex Ni′, upholding the value of 34.70 ± 3.95 kJ mol^{-1} reported earlier using the TG-based transpiration technique.
© 2005 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, there is an increasing trend in the chemical vapour deposition (CVD) of nickel thin films on metallic, ceramic, and non-metallic substrates owing to their special characteristics such as high oxidation-cum-corrosion resistance, luster, low electrical resistivity and selective absorption. Thus, the deposition of Ni thin films was resorted to on ferrites and n-type SiC for electronic applications [1–4], on graphite and uranium blocks in nuclear industry [5,6] and on decorative ceramics [1,4]. Despite the promising advantages of such protective coatings, CVD of metals (including metallic Ni) were limited

due to the non-availability of suitable metallo-organic precursors [7]. To cater to this need, Antony Premkumar et al. [8] had synthesized and reported the equilibrium vapour pressures (p_e) as well as standard enthalpies of sublimation (ΔH°_{sub}) and vaporization (ΔH°_{vap}) of solid phase and liquid phase, respectively, of N,N′-ethylenebis (2,4-pentanedion-iminoato)nickel(II) (designated as Ni[(acac)$_2$en] or Ni′) by employing a TG-based transpiration method. The standard enthalpy of fusion (ΔH°_{fus}) of Ni[(acac)$_2$en] was derived by these authors from the change in the slope of Clausius–Clapeyron type (i.e logarithm of vapour pressure against $1/T$) plots.

In order to widen the temperature range of vaporization of the liquid phase for a better control of the CVD process, Arockiasamy et al. [9] had synthesized a Ni complex precursor wherein, 1,2-diaminopropane (pn) substitutes 1,2-diaminoethane (en) in the formula Ni[(acac)$_2$pn]. Although the p_e values of Ni[(acac)$_2$pn] [9] were substantially higher than those for the Ni[(acac)$_2$en] [8] complex for their liquid

* Corresponding author. Tel.: +91 44 28178200x374; fax: +91 44 28175566.
E-mail address: ksnagi@vsnl.net (K.S. Nagaraja).
1 Former Head, Thermodynamics and Kinetics Division, IGCAR, Kalpakkam, India.

phases at commensurate temperatures, the rates of solid sublimation for the former appeared to be too low to preclude the direct determination of ΔH°_{sub} since equilibrium could not be achieved in its sublimation. Hence, a method has to be identified for the direct determination of ΔH°_{sub} or ΔH°_{fus}, which again has to be validated by conducting such studies on Ni[(acac)$_2$en].

Fortunately, Antony Premkumar et al. [10] had devised a DTA-based melting point depression technique for the determination of ΔH°_{fus} of a volatile Cr(acac)$_3$ complex (acac=acetylacetone) using a non-volatile solute Ni(acac)$_2$ (with the common ligand acac). Therefore, this investigation was undertaken by adopting the same DTA technique for the determination of ΔH°_{fus} of Ni[(acac)$_2$en] using the same non-volatile solute as in the case of Cr(acac)$_3$. To justify the use of DTA-based technique for ΔH°_{fus} determination of complex precursors, mention must be made of the unsuitability of the conventional but more reliable calorimetric methods. This unsuitability stems from the rather high volatility of such complexes as well as the lower magnitude of their numerical values (<40 kJ mol^{-1}) of ΔH°_{fus}.

2. Experimental

2.1. Materials

The complex Ni[(acac)$_2$en] (for brevity hereafter referred to as Ni′) was synthesized as reported elsewhere [8,11]. The synthesis of Ni[(acac)$_2$en] is a two-step process. In the first step, the ligand [(acac)$_2$en] was prepared by mixing reagent grade ethylenediamine and acetylacetone (both from Loba Chemie, India; purity>99.9%) in 1:2 mole ratio to obtain [(acac)$_2$en] [11]. In the second step, the alcoholic solution of ligand and a saturated aqueous solution of NiCl$_2$·6H$_2$O (Loba Chemie, India; purity>99.9%) were mixed in a 2:1 mole ratio and stirred at ambient temperature for about half an hour. Further characterization of Ni′ including elemental (C, H, N) analyses, estimation of Ni content, and FABMS characterization of molecular weight as well as fragmentation of the complex were identical with the earlier report [8] and confirmed the composition. The preparation of Ni(acac)$_2$·4H$_2$O involved the interaction of NiCl$_2$·6H$_2$O with acetylacetone (both from Loba Chemie, India; purity>99.9%) which was characterized as reported earlier [12,13].

The mixtures of Ni′ and Ni(acac)$_2$·4H$_2$O (referred to as Ni″ after in situ dehydration at about 390 K during DTA investigation) in the mole ratios of 1.000:0.055, 1.000:0.115, 1.000:0.171, 1.000:0.251, and 1.000:0.335 were prepared by individually grinding each mixture in an agate mortar and pestle for one hour and subsequently compacting into thin pellets using a hydraulic press. This procedure was also adopted for grinding approximately 100 mg of the pure Ni′ for an even time for reproducing the particle size as in the case of the mixtures, followed by compaction and was used for DTA scanning for its melting point determination.

2.2. Procedure

A horizontal TG–DTA analyzer (Perkin Elmer, Pyris Diamond) was used for recording the DTA traces of the mixtures making use of differential type R (Pt-13% Rh/Pt) thermocouple serving both as dual arms of the balance and for temperature sensing. Since this model has the additional facility for baseline correction of DTA endotherms for more accurate melting point determination, the temperature scale of this analyzer was calibrated by using the recommended melting point standards and inferring the inception of melting with the help of baseline corrected by Pyris software.

The melting point determination of Ni′ (freshly synthesized and characterized for this investigation) was repeated at least 5 times to establish its reproducibility. For pure Ni′ and for the mixtures of Ni′ and Ni″ (generated in situ by dehydration of Ni(acac)$_2$·4H$_2$O at 390 K), 0.4–2.6 and 2–4 mg of the compacted samples, respectively, were taken in the sample pan with an even weight of calcined α-alumina packed into the reference pan. High purity (99.99%) N$_2$ was used as the purge gas at a flow rate of about 10 dm^3/h to provide an inert atmosphere. For the in situ dehydration of Ni″, initially the samples were heated to 390 K at a heating rate of 10 K/min followed by isothermal heating for a few minutes. Subsequently, DTA traces were recorded at a heating rate of 2 K/min.

3. Results and discussion

The melting point peaks recorded on different samples of Ni′ presented in Fig. 1 had led to an average value of 474.6±0.5 K. The melting point reported by Antony Premkumar et al. [8] for Ni′ was 469±3 K making use of the thermal analyzer without adequate facility for instrumental baseline correction and hence, could be the cause of the larger scatter (±3 K). However, the earliest report [14] cited by McCarthy et al. [11] had presented the standard melting point (T_o) to be 473 K (200 °C).

The weight ratio and mole ratio of the mixtures of Ni′ and Ni″ employed for DTA studies are summarized in the first two columns of Table 1, along with the mole fraction of the volatile solvent Ni[(acac)$_2$en] (Ni′) (after in situ drying of the non-volatile solute Ni(acac)$_2$·4H$_2$O) are given in the third column of this table. The melting points inferred from the DTA endotherms presented in Fig. 2 are also listed in Table 1. A plot of the liquidus temperatures T (K) inferred from Fig. 2 against the corresponding mole fractions X'_{Ni} is shown in Fig. 3 (shown by the symbol ○), along with the best fit curve depicting the partial phase diagram of this binary system (shown as a continuous curve).

For a thermodynamic correlation of the depression in the melting point of a volatile nickel precursor Ni′ by an non-volatile solute Ni″, an a priori knowledge of the mutual solid–solid as well as liquid–liquid solubility behaviour is warranted. For this purpose, cue was taken from the earlier