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TG/DTA-based techniques for the determination of equilibrium vapour pressures of *N,N′*-propylenebis(2,4-pentanedion-iminoato)nickel(II) for CVD applications

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The Schiff's base complexes of nickel(II) prepared by condensing 1,2-diaminopropane (pn), 1,3-diaminopropane (trien), 1,4-diaminobutane (tren) or 1,2-diaminobenzene (opdn) with 2,4-pentanedione (acac) in a 1:2 mole ratio followed by chelation with nickel(II) were examined for their volatility/decomposition behaviour for CVD applications. Among the complexes screened, only one complex namely *N,N′*-propylenebis (2,4-pentanedion-iminoato) nickel(II) (designated as [Ni(acac)$_2$pn], Ni′) exhibited a single stepped volatilisation commencing from above its melting point (T_o) of 431.9 K and ending up with nil residue at about 570 K. Fast Atom Bombardment Mass Spectrometry was employed to determine the molecular mass of the vapour species to be 295 in accordance with the molecular mass for the monomeric Ni($C_{13}H_{20}O_2N_2$). The equilibrium vapour pressure (p_e) of Ni′ over the range of 434–498 K was determined to be $\log p_e/Pa = 13.771\ (\pm 0.574) – 4925.4\ (\pm 258.2)$ K/T by employing a TG-based transpiration technique, which yielded a value of 94.3±5.0 kJ mol^{-1} for its standard enthalpy of vapourisation (ΔH^o_{vap}). The DTA-based melting point depression (T_o–T) studies were carried out on four mixtures of Ni′ (as a volatile solvent) with bis(2,4-pentanedionato)nickel(II) (designated as Ni(acac)$_2$ or Ni″) as the non-volatile solute. The dependence of $\log X_{Ni'}$ against $1/T$(K) for the four mixtures with the solvent mole fraction $X_{Ni'} = 0.910$, 0.897, 0.881 or 0.849 exhibited near constant slope leading to an average value of 19.4±1.6 kJ mol^{-1} for the standard enthalpy of fusion(ΔH^o_{fus}). Combining ΔH^o_{vap} and ΔH^o_{fus}, a value of 113.7 ± 6.6 kJ mol^{-1} for standard enthalpy of sublimation(ΔH^o_{sub}) was derived to facilitate the estimation of vapour pressures for solid/vapour equilibrium below the melting point.

1. Introduction

Volatile Ni-organic complexes had been employed as precursors for Chemical Vapour Deposition (CVD) of Ni films on metallic [1–3] and non-metallic [4–6] substrates in industry and in technology. While developing tris(2,4-pentanedionato)chromium(III), Cr(acac)$_3$ (acac = acetylacetone) as a precursor for Plasma Assisted CVD (PACVD) of CrN film on stainless steel

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(SS) substrates for nuclear applications, Pankajavalli *et al.*[7] had highlighted the need for co-depositing Ni for improving adhesion/mechanical properties of CrN on SS substrates. To cater to this requirement, Premkumar *et al.* [8] had identified *N*,*N*′-ethylenebis(2,4-pentanedion-iminoato)nickel(II), [Ni(acac)$_2$en] as a candidate precursor for PACVD after the measurements of its equilibrium vapour pressures over both solid and liquid ranges by a TG-based transpiration technique. Since a Ni complex precursor with a wider temperature window for the single step volatilisation below about 500–600 K was deemed as more suitable for CVD according to Premkumar [9], a search for more smoothly vapourising Ni complexes was undertaken in this investigation.

Four complexes analogous in their coordination geometries to [Ni(acac)$_2$en] were screened for their suitability using non-isothermal TG runs under a dynamic inert atmosphere. The complex *N*,*N*′-propylenebis(2,4-pentanedion-iminoato)nickel(II) ([Ni(acac)$_2$pn] or Ni′) which emerged as the single suitable precursor was subjected to equilibrium vapour pressure measurements over its liquidus range by the same TG-based transpiration technique. This was further studied by a DTA-based melting point depression technique using an appropriate non-volatile solute to facilitate the assessment of vapour pressure at temperatures below its melting point owing to infeasibility of direct determination. The results of these studies are presented in this paper.

2. Experimental

2.1. Materials

For the identification of volatile metallo organic complexes of Ni(II) for its CVD, four complexes were chosen as candidate materials, and were synthesised using the ligands obtained by the condensation of acetylacetone (acac) (Loba Chemie, India, purity >99%) with propylenediamine (pn) (Lancaster, England, purity >99%), trimethylenediamine (trien) (Lancaster, England, purity >98%), tetramethylenediamine (tren) (Merck, Germany, purity >98%) or ortho-phenylenediamine (opdn) (S.D.Fine, India, purity >99%), the procedure of which was identical with that adapted by McCarthy *et al.* [10]. Out of the four complexes studied, only Ni[(acac)$_2$pn] showed 100% single step weight loss and hence, its synthesis is described in detail as follows though the other three were synthesised exclusively by refluxing the solution for 1 h.

The synthesis of Ni[(acac)$_2$pn] was a two stepped process, the first step being the condensation of its ligand constituents namely acetylacetone and propylenediamine in 1:2 mole ratio. The second step involved dissolving the ligand in absolute ethanol and chelating it with a saturated aqueous solution of $NiCl_2 \cdot 6H_2O$ (Loba Chemie, India, purity >99%) in a 1:2 mole ratio at the ambient temperature under magnetic stirring for about 1 h followed by controlled heating on a water bath at approximately 260 K for 0.5 h. The product was then separated out and dried under vacuum for 12 h. The sample so obtained is referred to as un-refluxed sample in the subsequent investigations.

The above procedure differed from that adapted by McCarthy *et al.* [10] in its second step by not resorting to refluxing. Hence, a second batch of [Ni(acac)$_2$pn] was synthesised by reproducing the refluxing step, but for a shorter time and is referred to as refluxed sample as well as Ni′ in the subsequent Sections of the text.

The preparation of Ni(acac)$_2$·4H$_2$O (used as a non-volatile solute in the DTA studies) involved the reaction between $NiCl_2 \cdot 6H_2O$ and acetylacetone followed by chemical characterisation as reported in the literature [9, 11].

2.2. Compositional analysis

The procedure for confirming the empirical formulae of the four Ni(II) complexes (excluding un-refluxed Ni(acac)$_2$pn samples) by elemental analysis namely the C, H, N (employing rapid elemental analyzer Model CARLO-ERBA-11008) and Ni, and that of O (by difference between the mass of aliquots taken and that accounted for by C, H, N and Ni analysis) was identical as reported elsewhere [8] employing the same set of equipment.

2.3. Melting point characterization

The melting point determinations on refluxed as well as un-refluxed [Ni(acac)$_2$pn] and on the other three complexes were carried out as per convention by sealing the samples in silica capillaries in contact with the bulb of a calibrated thermometer and subjected to gradual heating.

2.4. Non-isothermal TG

The TG-runs on refluxed as well as un-refluxed samples of Ni(acac)$_2$pn and on the other three complexes of Ni(II) were recorded at a linear heating rate of 0.17 K/s using a TG/DTA thermo analyzer (Model, Perkin Elmer, Pyris Diamond). High purity nitrogen (purity >99.99%) dried by passing through refrigerated molecular sieves (Linde 4A) was used as the carrier gas at a flow rate of 12 dm^3/h. The purpose of these runs is to observe the mass loss steps besides identifying the final temperature to attain nil residue or constant weight.

2.5. FABMS

The mass spectra of the refluxed and un-refluxed [Ni(acac)$_2$pn] samples were recorded using Fast Atom Bombardment Mass Spectrometer (FABMS) model JEOL SX 102/DA-6000 using argon/xenon as the FAB gas at an accelerating voltage of 10 kV with m-nitrobenzyl alcohol (NBA) as a matrix at ambient temperature.

2.6. Vapour pressure measurements

Based on dynamic TG runs only [Ni(acac)$_2$pn] (refluxed, Ni′) could be chosen for further vapour pressure measurements. The block diagram of the thermo analyzer, modification for its functioning in the transpiration mode including precise flow calibration for the carrier gas using a capillary glass flow meter and corrections for apparent weight losses in isothermal mode were the same as described earlier [9, 11]. The configuration of the horizontal dual arm single furnace thermo analyzer obviously eliminates/minimizes apparent weight changes caused by temperature gradients, convection currents within the furnace tube, buoyancy, thermo molecular drag and electrostatic effect. The arms of the thermo balance served as the temperature-cum-DTA sensors. The calibration of the *R* type thermocouple (Pt-13% Rh/Pt) so built-in was carried out using the recommended melting point standards in order to make the *T*-scale of the balance to conform to the International Practical Temperature Scale 1968 (IPTS-68) amended in 1975.

Heating the furnace to 1173 K at a rate of 0.17 K/s under N_2 gas at the purge rate of 12 dm^3/h and then cooling under the same conditions to near-ambient temperature (about 323 K) was done for the heat cleaning of the furnace. After this, the sample finely powdered by using an agate mortar and pestle was spread out on a shallow alumina crucible mounted for vapour pressure measurements and was carefully flushed with N_2 at a rate of 6 dm^3/h at the ambient temperature. It was subsequently heated to isothermal temperatures in the range of 434–498 K in steps of approximately 10 K. The initial heating to say, 434 K was rather rapid (0.17 K/s) and after allowing for temperature stabilization, subsequent change in isothermal steps was done at the heating rate of 0.03 K/s. The choice of 6 dm^3/h for N_2 gas was made for the isothermal equilibrium vaporization on the basis of existence of a plateau in the plot of apparent vapour pressure (p') against the flow rate as described elsewhere [7, 8].

2.7. DTA studies

Four mixtures of Ni′ and Ni(acac)$_2$·4H$_2$O (referred to as Ni″ after resorting to *in situ* dehydration at about 390 K for sufficient time during DTA investigations) in the mole ratios of 1.000:0.099, 1.000:0.114, 1.000:0.135 and 1.000:0.177 were prepared by individually grinding each mixture in an agate mortar and pestle for one hour and compacting into thin pellets using a hydraulic press. The compositions corresponded to the values of 0.910, 0.897, 0.881 or 0.849 for the mole fraction $X_{\mathrm{Ni}'}$ in the binary system of Ni′ + Ni″.

The same thermo analyzer was used for recording the DTA-runs on the so compacted mixtures with an even weight of calcined α-alumina loaded in the reference pan. The typical sample weights were in the range of 1.8–2.1 mg. This Pyris Diamond model has the built in software (Pyris) for base line correction, with the help of which accurate inception temperatures for DTA endotherms could be identified with required accuracy and precision commensurate with *T*-scale calibration. DTA traces were recorded at a slow heating rate of 0.03 K/s.

3. Results and discussion

3.1. Compositional analyses

The results from the quantitative elemental analyses carried out on the four nickello organic complexes (excluding the un-refluxed one of [Ni(acac)$_2$pn]) confirmed the molecular formulae to be as given in column one of Table I (under Section 3.3) in agreement with the anticipated molecular formulae for these complexes. To evaluate the purity of the four refluxed samples conventional melting point determination was resorted to.

3.2. Melting point determination

The melting points of the refluxed and un-refluxed samples of [Ni(acac)$_2$pn] were found to be 431.9 and 430.9 ± 1 K respectively. Both the values are in good agreement with that of 430.6 K reported by McCarthy *et al.* [10]. The melting point of the refluxed sample being slightly higher (1 K) than the un-refluxed one could only be taken as a fortuitous indication of higher purity of the former (refluxed sample) because the difference between these two values are within the limits of experimental scatter. Still, a minor difference does exist with reference to the presence

TABLE I Thermal decomposition behaviour of nickel(II) complexes by TG[a] studies

						Mass of Ni $10^{-3} \times$ W(g) in the sample	
Sl. no	Complex	Initial weight $10^{-3} \times$ W(g)	Residue $10^{-3} \times$ W(g)	Nature	Final *T*(K)	Initial sample	Final residue
1	Ni[(acac)$_2$pn]	20.54	0.00	volatile; no end residue	570	4.09	0.00
2	Ni[(acac)$_2$trien]	35.80	6.13	decomposes	774	7.12	1.22
3	Ni[(acac)$_2$tren]	13.97	0.33	decomposes	771	2.66	0.06
4	Ni[(acac)$_2$opdn]	20.80	7.59	decomposes	674	3.71	1.35

[a] In dynamic nitrogen; flow rate: 12 dm^3/h; linear heating rate: 0.17 K/s; on samples referred to as refluxed in the text.
pn = Propylenediamine; trien = Trimethylenediamine; tren = Tetramethylenediamine; opdn = o-phenylenediamine.

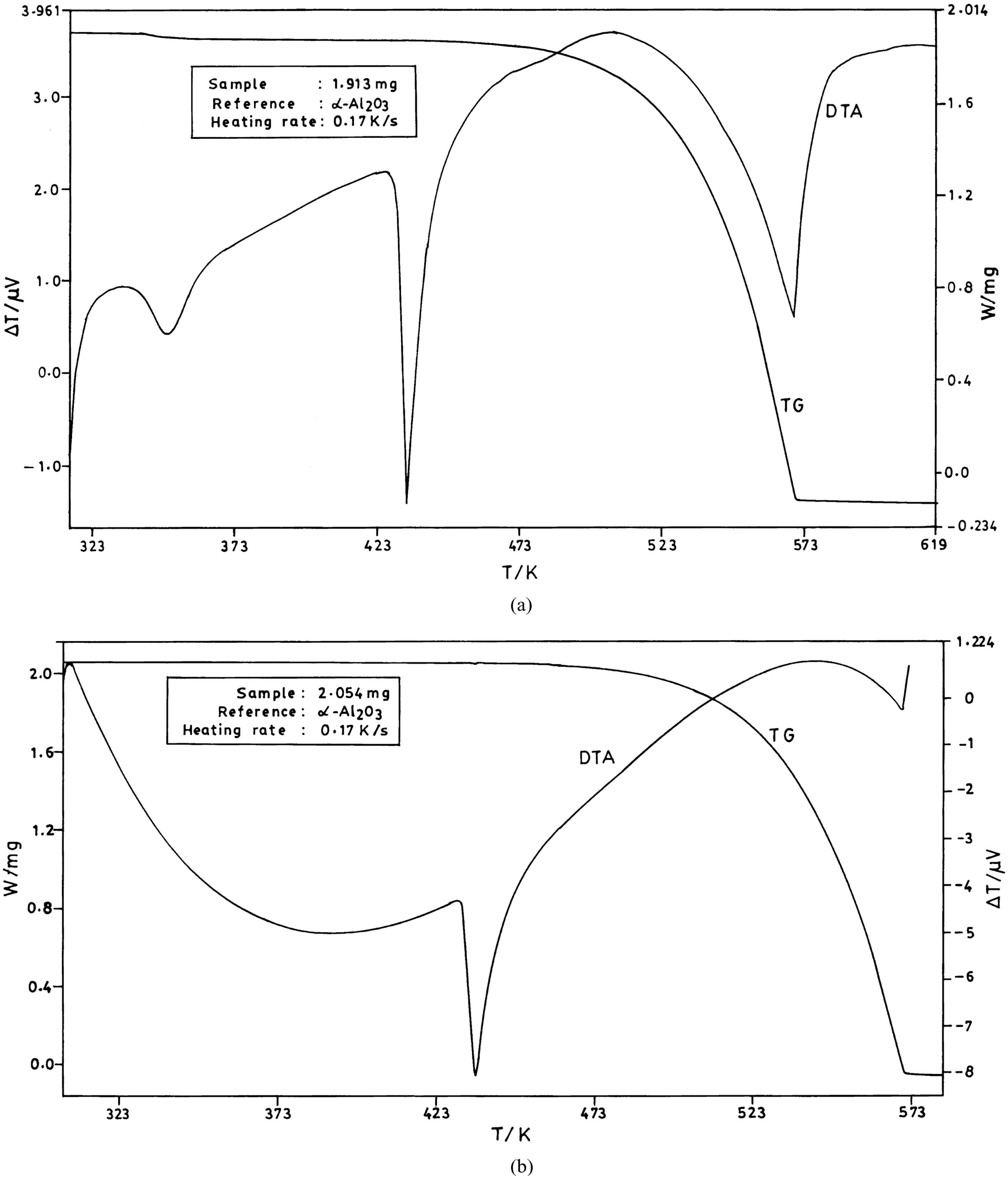
of physisorbed water in the latter sample as discerned by TG studies (c.f. Section 3.3) endorsing the higher purity of the refluxed specimen. The other three Ni(II) complexes decomposed without sharp melting which necessitated the use of dynamic TG runs to assess their melting/decomposition/volatilisation behaviour.

3.3. Non-isothermal TG

The TG runs on the un-refluxed as well as refluxed one (Ni′) are reproduced in Figs. 1A and B respectively. It could be noted that the un-refluxed sample exhibited a minor weight change corresponding to loss of physisorbed water at around 340 K which weight loss was absent in the refluxed sample. These runs revealed that the major weight loss occurred in a single step commencing mainly from about 473 K (presumably due to vapourisation and not decomposition) ending up with the total weight loss at around 570 K during the time span dictated by the heating rate of 0.17 K/s. This single stage weight loss (providing a wide enough temperature window for volatilization) occurring after the melting of the refluxed sample helped to identify the complex Ni′ as a potential precursor for CVD of metallic Ni films for technological applications.

The TG runs on the other three Ni(II) complexes under the same heating rate and purge gas flow rate showed decomposition patterns leading to residues with significant Ni contents and hence, were rejected as candidate materials for CVD. The salient inferences from the dynamic TG runs made on the four refluxed Ni(II) complexes are given in Table I.

As the objective of this investigation was to evaluate the equilibrium vapour pressures by a TG-based transpiration technique, apriori knowledge of the molecular weight of



(a)

(b)

Figure 1 TG/DTA scan of [Ni(acac)$_2$pn] (a) un-refluxed; (b) refluxed.

the vapourising species is required. For this purpose, the refluxed and un-refluxed [Ni(acac)$_2$pn] specimens were subjected to FABMS studies.

3.4. FABMS

The FABMS spectrum of the Ni′ (refluxed specimen) is reproduced in Fig. 2. From the cluster peak associated with the isotopic abundances of natural Ni, the peak at m/z = 295 could be accounted for by the molecular weight of the complex of maximum intensity. This value corresponds to the molecular formula of the complex Ni[(acac)$_2$pn] with the theoretical molecular weight of $m/z = 294.7$ taken as a monomeric molecule. The peaks at $m/z = 279$ and 265 would closely correspond to consecutive fragmentation of $(CH_3)^+$ from the monomer as interpreted earlier [8] in the case of Ni[(acac)$_2$en] complex.

The loss of the fragment $(CH_3–CH–CN–CH_3)^+$ from the cluster peak at $m/z = 265$ would account for the cluster peak at $m/z = 196$; likewise, the loss of a ligand fragment $(CH_3–CO–CH–CN–)^+$ from the cluster fragment with $m/z = 265$ would result in the cluster peak at $m/z = 183$. Further, the loss of the fragment $(CH_2–CH–)^+$ from that at $m/z = 196$ would account for the cluster peak at $m/z = 169$. On a similar basis, the loss of fragments $(CH_3–CO–CH–CN–CH_3)^+$ and $(CH_3–CO–CH–CN–)^+$ from that at $m/z = 279$ would closely correspond to the cluster peak at $m/z = 149$ which on further loss of the fragment $(CH_3–CO–)^+$ would give rise to the cluster peak at $m/z = 106$. The peak at $m/z = 136$ is ignored being a matrix peak.

The corresponding spectrum of the un-refluxed specimen was almost identical with that for the refluxed one (Ni′) and is not reproduced here to avoid redundancy. The conditions for recording the mass spectrum of the un-refluxed one were conducive for the removal of physisorbed water thereby making it equivalent to that for the refluxed one.

3.5. Vapour pressure measurements

If W is the mass loss of the sample at the isothermal temperature T(K), which was caused by the flow of V_c dm^3 of the carrier gas, the vapour pressure, p' could be calculated using Dalton's law of partial pressure for ideal gas mixtures as given by

$$p' = WRT/MV_c \tag{1}$$

where M is the molar mass of Ni′. The numerical value of M is inferred to be 295 from the FABMS spectrum in accordance with the molecular formula assigned to it earlier.

To demonstrate the equilibrium nature of the vapourisation process in this TG-based transpiration technique, a chair shaped curve was established when an apparent vapour pressure p' was plotted as a function of flow rate of the carrier gas N_2 as mentioned elsewhere [7, 8], and hence, it is not shown here. However, all isothermal TG runs for vapour pressure measurements were carried out using a flow rate of nearly 6 dm^3/h of N_2 (well within the plateau region) to ensure equilibrium vapourisation (i.e. to facilitate the designation of apparent vapour pressure p' as equilibrium vapour pressure, p_e). The values of observed mass loss, T and the calculated ones of p_e (using Equation 1) are listed in Table II, and are also plotted as $\log p_e$ against 1/T(K) in Fig. 3. This temperature range so covered in the measurement of p_e encompasses only the liquidus range of Ni′.

The least squares analysis of $\log p_e$ against the reciprocal of T(K) yielded the expression

$$\log p_e/Pa = 13.771(\pm 0.574) - 4925.4(\pm 258.2)\ K/T; \quad (434 - 498\,\text{K}) \tag{2}$$

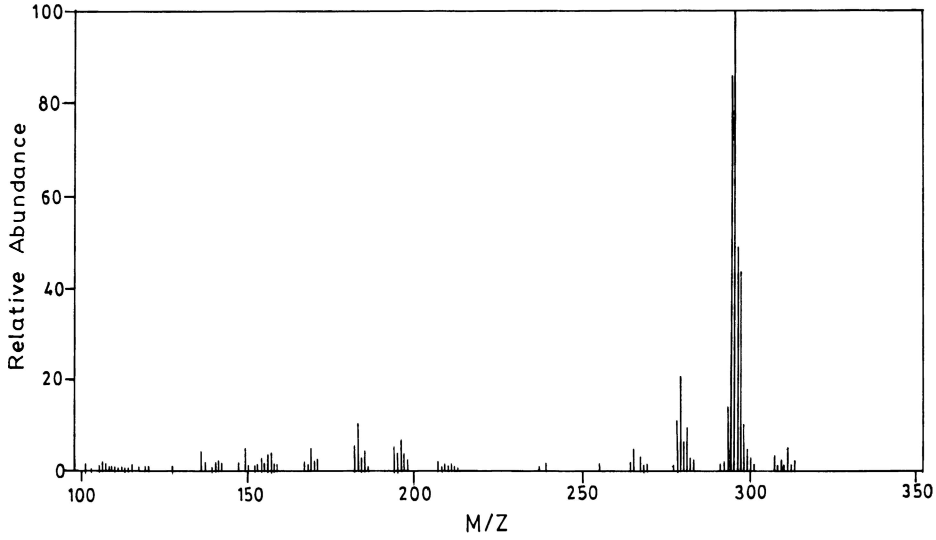


Figure 2 Fast Atom Bombardment Mass Spectra of [Ni(acac)$_2$pn].

TABLE II Mass loss and equilibrium vapour pressure (p_e) for liquid vapourisation of Ni′ by the TG-based transpiration method

Sl. no	T/K	Mass loss/mg	p_e/Pa
1	434.47	0.092	281.6
2	445.25	0.160	501.9
3	456.05	0.290	931.8
4	466.82	0.524	1723.5
5	477.68	0.879	2958.4
6	488.42	1.448	4982.9
7	498.62	2.293	8055.7

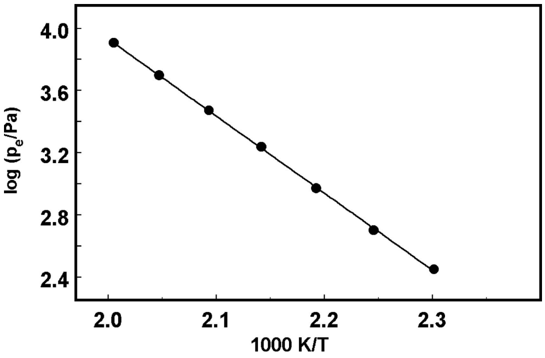


Figure 3 The plot of equilibrium vapour pressure (p_e) of [Ni(acac)$_2$pn] against 1000 K/T for liquid vapourisation.

Multiplying the slope of Equation 2 by−2.303 R, a value of 94.3 ± 5.0 kJ mol^{-1} could be derived for the standard enthalpy of vapourisation, $\Delta H^{\text{o}}_{\text{vap}}$ of liquid Ni′.

As no direct measurements of equilibrium vapour pressures could be made on the solid state of Ni′ below its T_{o} (431.9 K), it had to be evaluated indirectly by determining its standard enthalpy of fusion ($\Delta H^{\text{o}}_{\text{fus}}$). Though the TG-based transpiration measurements were feasible [8] down to $p_e = 0.1$ *Pa*, as in the case of [Ni(acac)$_2$en] the rather low rates of vapourisation of Ni′, presumably due to kinetic reasons restricted the direct measurements. Therefore, a cryoscopic technique similar to that adapted by Arockiasamy *et al.* [12] for estimating the $\Delta H^{\text{o}}_{\text{fus}}$ of [Ni(acac)$_2$en] was resorted to. The results so obtained on [Ni(acac)$_2$pn] by using a non-volatile solute are discussed in the following Section.

3.6. DTA studies

As in the case of [Ni(acac)$_2$en], the determination of $\Delta H^{\text{o}}_{\text{fus}}$ of Ni′ is possible only if the mixtures of Ni′ + Ni″ exhibit near ideal eutectic behaviour. Since, the thermally stable as well as non volatile Ni” complex exhibits tetrahedral geometry in contrast to the square planar geometry of the solvent Ni′ (similar to its [Ni(acac)$_2$en] analogue) it could manifest solid-solid immiscibility. In case the mixture of these two immiscible solids exhibit ideal solution behaviour in the single liquidus phase after fusion of the Ni′ complex, then the mixtures of these two solids should give rise to an ideal eutectic phase diagram as in the earlier investigation [8]. The results of such studies are presented in Table III and in Fig. 4.

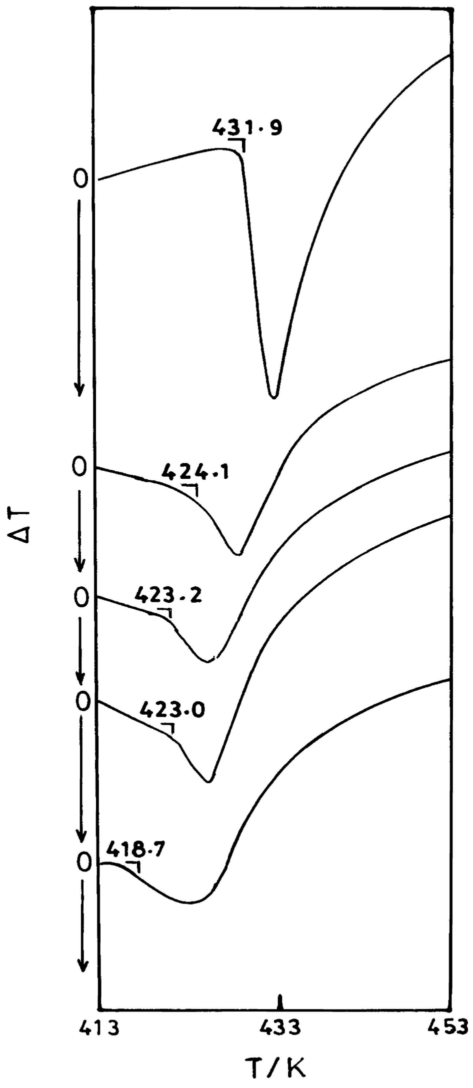


Figure 4 DTA endotherms of Ni′ + Ni″ for $X_{\text{Ni}}{}'$ of (a) 1.000, (b) 0.910, (c) 0.897, (d) 0.881 and (e) 0.849.

The weight ratio, mole ratio and the volatile solvent mole fraction, $X_{\text{Ni}\prime}$ of the four mixtures are listed in the first three columns of Table III. The DTA traces of these mixtures are depicted in Fig. 4. A typical DTA-based standard melting point (T_{o}) curve of the pure refluxed Ni′ is also included in this figure. The value of $T_{\text{o}}(K)$ and the instantaneous melting points, T(K) of the mixtures inferred from Fig. 4 are given under column 4 of this table.

By making use of the thermodynamic correlation between the solvent mole fraction ($X_{\text{Ni}}{}'$) and the melting temperatures

$$\log X_{Ni'} = [-\Delta H^{\text{o}}_{\text{fus,Ni}'}/2.303R][1/T - 1/T_{\text{o}}] \quad (3)$$

derived for ideal eutectic system by Reisman *et al.* [13], $\Delta H^{\text{o}}_{\text{fus}}$(Ni′) values were calculated for each mixture of this binary system and are listed in the last column of

TABLE III DTA based liquidus temperatures of volatile [Ni(acac)$_2$pn] (refluxed) with [Ni(acac)$_2$] as the non-volatile solute

Sl. no	Weight ratio (mg:mg) of Ni′/hydrated Ni″	Mole ratio of Ni′/Ni″	$X_{\mathrm{Ni}'}$	Liquidus T(K)	$\Delta H^{\mathrm{o}}_{\mathrm{fus}}$ (kJ mol^{-1})
1	100.00:0.00	1.000:0.000	1	431.9	–
2	53.60:5.90	1.000:0.099	0.910	424.1	18.39
3	53.30:6.80	1.000:0.114	0.897	423.2	18.93
4	53.00:8.00	1.000:0.135	0.881	423.0	21.68
5	50.30:9.90	1.000:0.177	0.849	418.7	18.52

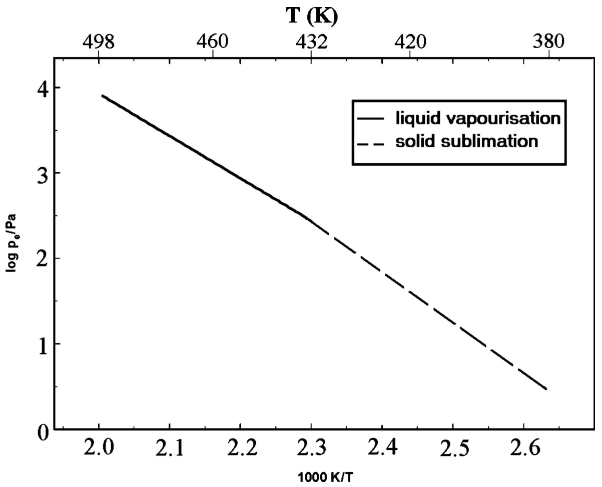


Figure 5 The plot of equilibrium vapour pressure (p_e) of [Ni(acac)$_2$pn] against 1000 K/T for solid sublimation.

this table. An average value of 19.4 ± 1.6 kJ mol^{-1} could be arrived at for the$\Delta H^{\mathrm{o}}_{\mathrm{fus}}$(Ni′). Making use of the correlation,$\Delta H^{\mathrm{o}}_{\mathrm{sub}} = \Delta H^{\mathrm{o}}_{\mathrm{fus}} + \Delta H^{\mathrm{o}}_{\mathrm{vap}}$, a value of 113.7 ± 6.6 kJ mol^{-1} could be derived for$\Delta H^{\mathrm{o}}_{\mathrm{sub}}$(Ni′) to facilitate the estimation of p_e for the solid/vapour equilibrium.

Making use of the equality of p_e of the solid and liquid Ni′ at 431.9 K in conjunction with Equation 2 along with the value of $\Delta H^{\mathrm{o}}_{\mathrm{sub}}$(Ni′), p_e for the solidus range could be derived as

$$\log(p_e/Pa) \pm 0.80 = 16.1 - 5940.4K/T \quad (380 - 432\,\mathrm{K}) \qquad (4)$$

The Equation 4 is plotted as a dotted line in Fig. 5. The instantaneous melting points for the four mixtures of Ni′ + Ni″ along with the value of T_o (431.9 K) facilitated the construction of a partial $T - X^{Ni'}$ diagram as shown in Fig. 6 along with the best fit curve shown as a continuous curve.

4. Conclusion

A stream lined method of synthesis and assessment of volatilization/decomposition behaviour by non-isothermal TG under inert purge gas were demonstrated using four analogous Ni(II) complexes with similar coordination geometries. Only the complex *N,N*′-propylenebis(2,4-pentanedion-iminoato)nickel(II) (Ni′) was identified as an ideal precursor for CVD of nickel films. The equilibrium vapour pressures of Ni′ measured over its liquidus range of 434–498 K by using a TG-based transpiration technique yielded the value of 94.3 ± 5.0 kJ mol^{-1} for its $\Delta H^{\mathrm{o}}_{\mathrm{vap}}$. Making use of the ideal eutectic behaviour exhibited by the binary mixtures of Ni′ with Ni″ [anhydrous Ni(acac)$_2$], the $\Delta H^{\mathrm{o}}_{\mathrm{fus}}$(Ni′) was determined to be 19.4 ± 1.6 kJ mol^{-1} by a DTA-based melting point depression technique. This has led to a value of 113.7 ± 6.6 kJ mol^{-1} for the$\Delta H^{\mathrm{o}}_{\mathrm{sub}}$(Ni′). This value could be used in predicting log p_e for the solidus range of Ni′ by making use of the equality of p$_e$ of the solid and liquid phases at the standard melting point of Ni′.

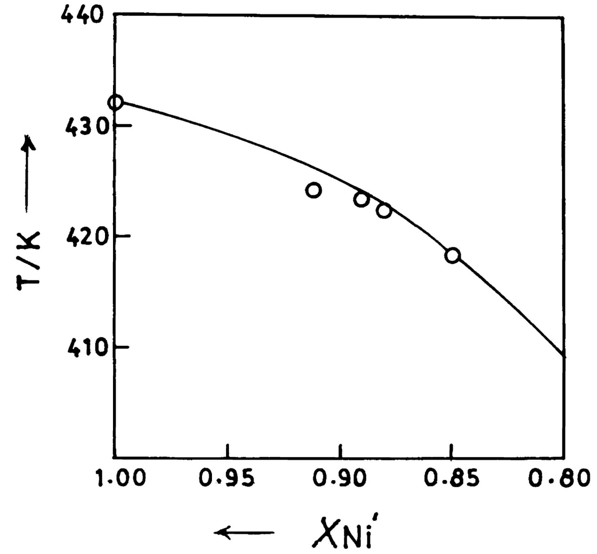


Figure 6 Partial T$-X_{Ni}$′ diagram for the binary system Ni′ + Ni″.

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