Hepta - And Octa-Ammoniates of Nickel (II) Thiocyanate

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Summary: Nickel (II) thiocyanate reacts with ammonia at -35.4°C yielding solvated products Ni $(NCS)_2.NH_3$ (n = 7,8) with respective ammonia vapour pressures of 40 and 120 mm Hg at this temperature. The van't Hoff's method for the determination of dissociation enthalpies gave values of 30.8 and 29.4 kJ mol^{-1} for the seven - and eight - ammoniates respectively.

Introduction

The amminenickel (II) halide complexes NiX_2nNH_3 where n = 6 and X = Cl, Br, I have been reviewed in two excellent references [1,2] which also cover thermo-analytical properties of these complexes. Less is known concerning the reactions of nickel (II) thiocyanate with ammonia and $Ni(NCS)_24NH_3$ appears to be the only amminenickel (II) complex studied and characterised so far [4] presumably due to its room temperature stability. Recently we identified $Co(NCS)_2nNH_3$ (n = 7,8) in cobalt (II) thiocyanate - liquid ammonia systems at -35.4°C [5]. We report here a tensimetric re-investigation of the nickel(II) thiocyanate - liquid ammonia system under similar experimental conditions together with the results of dissociation enthalpy determinations according to the van't Hoff's method.

Experimental

Nickel (II) thiocyanate: The stock reagent (ex B.D.H.) was dried in vacuo at 100°C for 20 hours.

Liquid ammonia

Gaseous ammonia from a cylinder was condensed in a trap immersed in an acetone/solid CO_2 bath (-78°C) and dried by addition of metallic sodium.

The ammonia was distilled off and collected by re-condensation on the high vacuum apparatus and subsequently handled according to the procedure described earlier [2,5,6].

Tensimetric work

The high vacuum apparatus for measuring the ammonia vapour pressure over varying $NH_3:Ni(NCS)_2$ mole ratio reaction mixtures is detailed in reference [2]. The results obtained in this study are plotted in figure 1.

Thermostatic baths

Each of the following solvents was brought to the freezing point (indicated) by stirring with liquid nitrogen to give a solid/liquid equilibrium mixture. The solvents selected in this study were:

Dichlorobenzene (-45.6°C), 1,2-dichloroethane (-35.4°C), bromobenzene (-30.8°C), carbon tetrachloride (-23°C). An ice/water mixture was used for the 0°C point. The reaction mixture was immersed into each of these separate thermostatic

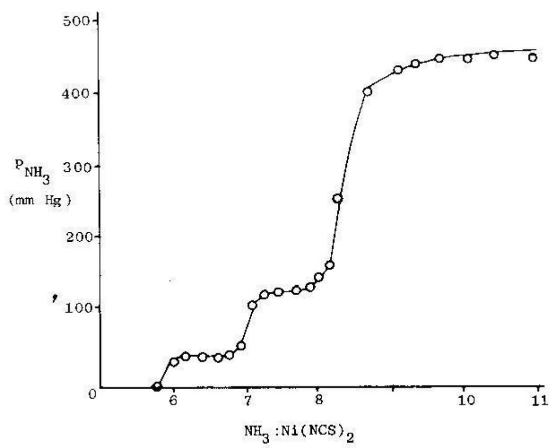

Fig.1: Tensimetric curve for the amonia nickel(II) thiocyanate system at -35.4°C.

baths during the enthalpy measurement experiments.

Dissociation enthalpy measurements: The ammonia vapour pressure for the dissociations

$$Ni(NCS)_2nNH_3(s) \longrightarrow Ni(NCS)_2 (n-1)NH_{3(s)} + NH_{3(g)}$$

was measured over a temperature range at selected fixed $NH_3:Ni(NCS)_2$ mole ratios at which the respective dissociative equilibria occur as determined from the -35.4° isotherm (see fig.1). For this work, the selected $NH_3:Ni(NCS)_2$ compositions were 7.44 and 6.64 for the octa- and hepta-ammoniates respectively. The results are plotted as log p_{NH3} versus reciprocal temperature (see fig. 2,3). From the integrated form of the van't Hoff's expression [7].

$$\log P_{NH3} = -\Delta H/2.303\ RT + C$$

the gradient of the linear plot equals $-\Delta H/_{2.303R}$ from which the value of ΔH can be determined.

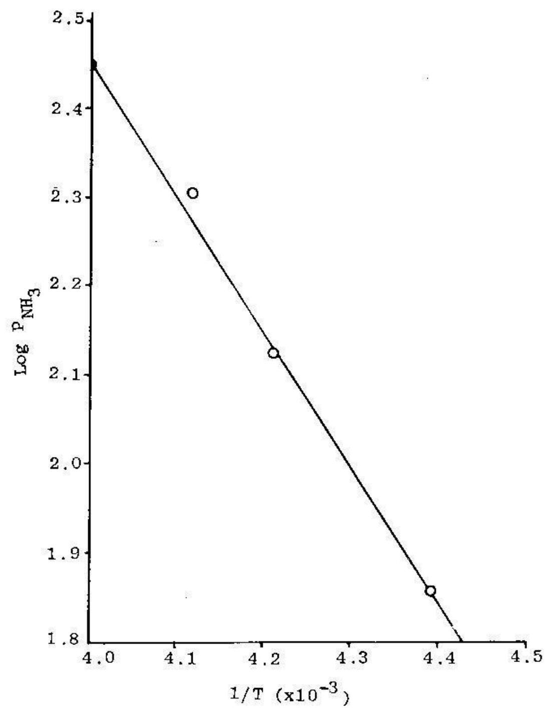

Fig.2: Isochore plots for the dissociation of the eight-ammoniate of nickel(II) thiocyanate.

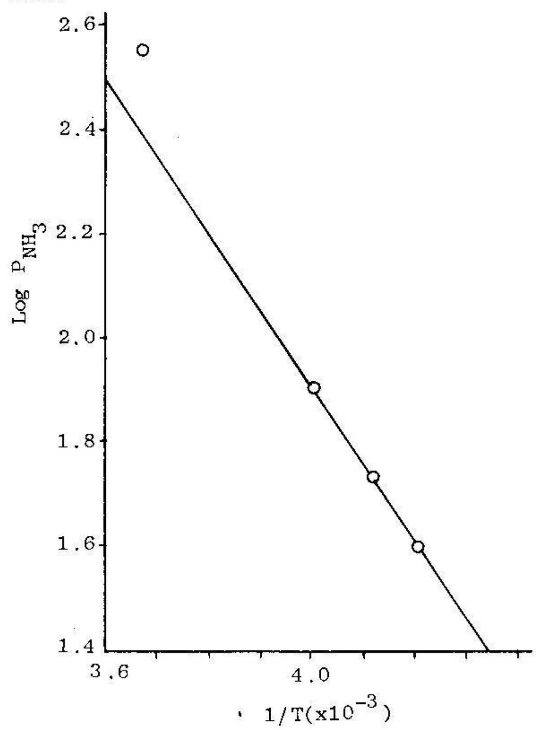

Fig.3: Isochore plots for the dissociation of the seven-ammoniate of nickel(II) thiocyanate.

Results and Discussion

In figure 1 are plotted the results of varying the NH_3:$Ni(NCS)_2$ mole composition versus P_{NH3} at -35.4°C. In the upper NH_3:$Ni(NCS)_2$ reaches, the isotherm shows characteristic lowering of solvent ammonia pressure as the solution becomes enriched with solute $Ni(NCS)_2$ in conformity to Raolt's law. At infinite dilution the pressure of the system approaches the value for pure solvent ammonia of about 680 mm Hg at -35.4°C [5]. The stepwise dissociative equilibria for the eight- and seven - ammoniates are characterised by a one-unit univariant mole ratio interval each showing a P_{NH3} value governed by the magnitude of the equilibrium constant for the dissociation. At -35.4°C the dissociation P_{NH3} values are 130 and 40 mm Hg for the octa- and hepta-ammoniates respectively. The octa - ammoniate has a violet colour while the hepta-ammoniate is light pink. The isotherm does not show evidence of ammonolytic reaction as often encountered in some systems containing multi-positive metallic species [2].

The $\Delta H/2.303$ R values (i.e slopes) of the linear log P_{NH3} vs NH_3:$Ni(CNS)_2$ plots (see figure 2 and 3) are -1.51×10^{-3} and -1.48×10^{-3} for the seven-and eight-ammoniates respectively yielding corresponding ΔH values of 30.4 and 29.4 kJ mol^{-1}. These low enthalpy magnitudes are characteristic of weak ion-dipole bonding forces indicating attachment of the seventh and eighth ammonia molecules to the octahedral hexammine species $[Ni(NH_3)_6]^{2+}$ by weak electrostatic forces. This situation is comparable to that reported for certain titanium (III) ammoniates by other workers[8]. The seven ammoniate has the higher dissociation enthalpy in accord with stability predictions since this is the species incorporating fewer ligands.

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