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A THERMODYNAMIC INVESTIGATION OF THE NICKEL(II) CHLORIDE-ACETONITRILE SYSTEM

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ABSTRACT

Equilibrium vapor pressures were determined at temperatures between 294 K and 353 K for the $NiCl_2$–CH_3CN system.

Compositions studied ranged from molar ratios of CH_3CN to $NiCl_2$ of 0.27 to 1.90. Three stoichiometric compounds were identified: $NiCl_2(CH_3CN)_2$, $NiCl_2(CH_3CN)$, $NiCl_2(CH_3CN)_{0.88}$. Per mole of gaseous CH_3CN the values of ΔH° and ΔS° were calculated to be 52.0 ± 0.4 kJ mol^{-1} and 149.0 ± 1.3 J mol^{-1} K^{-1} for the decomposition of $NiCl_2(CH_3CN)_2$, and 25.9 ± 0.8 kJ mol^{-1} and 58.6 ± 2.1 J mol^{-1} K^{-1} for the decomposition of $NiCl_2(CH_3CN)$. Below a composition of $NiCl_2(CH_3CN)_{0.88}$ the phase diagram is complex and could not be interpreted in terms of specific stoichiometric compounds.

INTRODUCTION

There have been a number of investigations in the literature involving the preparation and characterization of complexes of the nickel halides with various aliphatic nitriles[1-4]. The nickel chloride–acetonitrile system is especially interesting in that it contains complexes with various stoichiometries. Hathaway and Holah[2] prepared complexes of the form $NiCl_2(CH_3CN)_2$ (yellow-green) and $NiCl_2(CH_3CN)_4$ (green). On the basis of spectral data these investigators concluded that the $NiCl_2(CH_3CN)_4$ contained both coordinated and uncoordinated acetonitrile and formulated the compound as $NiCl_2(CH_3CN)_2 \cdot 2CH_3CN$. Kern[5], using a rather unusual experimental procedure, reported a deep blue complex with the formula $NiCl_2(CH_3CN)_{3.5}$. Reedijk and Groeneveld[4] have prepared the $NiCl_2(CH_3CN)$ as well as verified the existence and properties of $NiCl_2(CH_3CN)_2$. Babaeva and Ikramov[3] reported the isolation of $NiCl_2(CH_3CN)_2$ but described it as forming sky blue crystals. On the other hand, Beach et al.[6] were unable to prepare aliphatic nitrile complexes of nickel chloride with sufficient stability for their thermochemical determinations.

As part of a study of the magnetic properties of a series of nickel halide complexes with different nitrile ligands, an investigation of the thermodynamics of the nickel chloride–acetonitrile system was undertaken to determine the range of stabilities of the various complexes in this system. This is especially important in view of the different stoichiometries reported, coupled with the conflicting statements as to the properties of some of these compounds.

EXPERIMENTAL

Chemicals

Anhydrous nickel chloride was prepared from finely ground $NiCl_2 \cdot 6H_2O$ (Baker's Analysed Reagent Grade) by heating at 300°C in a vacuum for 4–5 h. After the initial dehydration was completed the sample was reground and the dehydration process was repeated to insure complete removal of water. Completeness of dehydration was verified by differential thermal analysis (DTA), thermogravimetry (TG), and chemical analysis.

Acetonitrile (Eastman X488) was fractionated on a Todd Scientific Column and stored over a molecular sieve (Linde 3A). Analysis by GLPC showed water content to be less than 2 ppt and no other impurities were detectable by this method.

Preparation of compounds

$NiCl_2(CH_3CN)_2$ was prepared by the method of Hathaway and Holah[2] using a Soxhlet extractor protected by a phosphorus pentoxide drying tube. However, it was found necessary to carry out the extraction under reduced pressure (less than 10 cm of Hg) to obtain molar ratios of acetonitrile to nickel chloride greater than one. After cooling in the mother liquor the compound was filtered using a sintered glass crucible and sealed in glass ampoules. Filtering and handling of samples were done in a dry box to insure against moisture contamination.

$NiCl_2(CH_3CN)$ was prepared following the procedure of Reedijk and Groeneveld[4] by refluxing nickel chloride with excess acetonitrile. All processing and handling was done in a glove bag filled with dry nitrogen.

Intermediate compositions were prepared by reacting weighed amounts of anhydrous nickel chloride and acetonitrile in sealed glass ampoules at temperatures of from 55 to 110°C for several days. At the end of this time the samples were ground, resealed in ampoules and tempered at 50°C for several additional days until the samples were homogeneous in appearance.

Analysis

To verify the compositions, the samples were analysed for nickel, chloride and acetonitrile. A total of 28 samples with molar ratios of acetonitrile to nickel chloride ranging from 0.27 to 1.9 were used in this investigation. The nickel and chloride contents were determined using standard analytical procedures given in Vogel[7]. Acetonitrile content was determined by weight loss using a DuPont 950 thermogravimetric analyser operated under a dry nitrogen atmosphere. For molar ratios of less than one, the acetonitrile content determined by difference, based on the nickel and chloride analysis, and that obtained by TG were in good agreement. For the higher molar ratios the TG results were generally lower than those obtained by difference. This was probably due to a loss of acetonitrile during the loading of the TG apparatus. In no case were the differences in composition given by the two methods found to be of importance in interpreting the phase diagram of the system.

Measurements

Vapor pressure measurements were made using glass isoteniscopes with mercury as the manometric liquid. The samples, mixed with washed and dried sand to increase surface area, were sealed in the isoteniscopes, cooled in a dry ice–isopropanol mixture and evacuated. The sample sizes were large enough so that the effect on the composition of the complexes due to the loss of nitrile in generating the vapor pressure was minimized. The isoteniscopes were completely immersed in an oil-bath thermostated to within ±0.02 °C of the desired temperature. The isoteniscopes were connected to an external pressure controlling system which could be adjusted so that the mercury levels in the isoteniscope manometers were approximately equal. The levels of the external and internal manometers were read to within 0.05 mm using a cathetometer and the pressures of the samples were calculated. The pressure readings in mm were converted to torr* using appropriate corrections[8]. Equilibrium was assumed to be reached when readings were constant to within ±0.2 mm for a period of two days and no trends were evidenced. To insure that the decompositions were reversible, after readings had been taken at high temperatures, the vapor pressures for selected samples were redetermined at lower temperatures and no significant differences were observed. The time required to reach equilibrium varied with both temperature and composition, being longer for the lower composition samples.

For some of the lower composition samples equilibration was so slow that an extrapolation method was used to estimate the equilibrium vapor pressure. This method consisted of taking readings at known time intervals and calculating the rate of change in pressure with time, $\Delta P/\Delta t$. This rate was then plotted as a function of pressure assuming either a first or a second order approach to equilibrium. The pressure at which $\Delta P/\Delta t$ was calculated to be zero was taken as the equilibrium vapor pressure. The choice between a first or a second order approach to equilibrium was based on the order yielding the smaller least-squares deviation. For samples with acetonitrile–nickel chloride molar ratios greater than one, the second order equation gave the lower standard deviation; for molar ratios less than one, a first order equation gave a smaller deviation.

This empirical relationship was checked using samples where equilibrium values were obtainable and it was found that the equilibrium pressures were the same within experimental indetermination. In general, the extrapolation method yielded equilibrium values with higher uncertainties. The average uncertainties in the equilibrium readings from static measurements were approximately ±0.2 mm for

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*Throughout this paper torr = (101.325/760) kPa.

pressures less than 100 torr and ±0.5 mm for pressures greater than 100 torr. The average uncertainties in the equilibrium values from extrapolation were approximately ±0.9 mm for pressures less than 100 torr and ±1.3 mm for pressures greater than 100 torr.

Differential thermal analysis curves were obtained using a DuPont Model 900 differential thermal analyser under a dry nitrogen atmosphere. Visible spectra of the solid complexes were measured on a Beckman DK-2A spectrophotometer using the nujol mull technique described by Lee et al.[9].

RESULTS AND DISCUSSION

Figure 1 shows plots of log$_e$ P versus 10^3 K/T where P is the equilibrium vapor pressure in torr for the different composition regions. Figure 2 shows log$_e$ P versus composition isotherms at 318.2, 328.2, and 338.2 K. The log$_e$ P and temperature data from which these plots were constructed are shown in Table 1. From these figures the regions of stability of the various phases can be delineated. At one atmosphere, $NiCl_2(CH_3CN)_2$ is stable up to a temperature of approximately 339 K where it decomposes to $NiCl_2(CH_3CN)$ and liquid CH_3CN. These findings are consistent with the fact that the $NiCl_2(CH_3CN)$ complex is obtained by reaction of nickel chloride and excess acetonitrile at the normal boiling point of acetonitrile, while lower temperatures are required for the formation of $NiCl_2(CH_3CN)_2$.

The $NiCl_2(CH_3CN)$ complex remained stable up to the highest temperature at which pressure measurements were made (371 K). By extrapolation, it is estimated

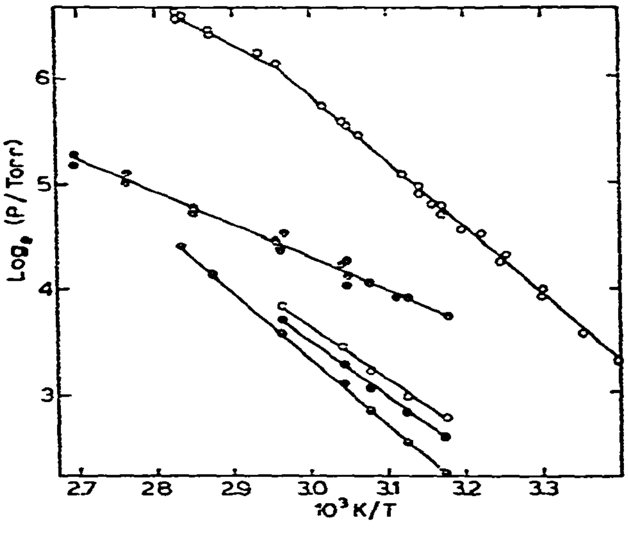

Fig. 1. A plot of the equilibrium values of log$_e$ (P/torr) versus reciprocal temperature for the composition regions in the nickel chloride–acetonitrile system. ○ = samples with acetonitrile to nickel chlorides between 1.04 and 1.90; ◓ = samples between 0.88 and 0.99; ◑ = molar ratio of 0.72; ● = molar ratio of 0.48; ◒ = molar ratio of 0.27.

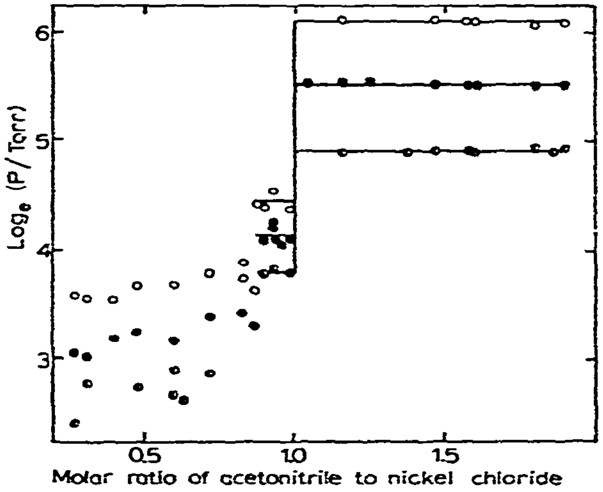

Fig. 2. A plot of the equilibrium values of $\log_e$ (*P*/torr) versus molar ratio of acetonitrile to nickel chloride at selected temperatures. ◐ = 318 K; ● = 328 K; ○ = 338 K.

TABLE 1

EQUILIBRIUM VAPOR PRESSURE DATA FOR
THE ACETONITRILE-NICKEL(II) CHLORIDE SYSTEM

Torr = (101.325/760) k Pa.

Molar ratios $CH_3CN/NiCl_2$	*T/K*	$\log_e$ (*P/torr*)	*Molar ratios* $CH_3CN/NiCl_2$	*T/K*	$\log_e$ (*P/torr*)
0.27	315.1	2.224	0.99	362.2	5.091
	320.2	2.527		371.2	5.259
	324.9	2.834	1.04	328.2	5.522
	329.0	3.093	1.16	318.2	4.904
	338.0	3.588		328.6	5.561
	348.2	4.110		338.3	6.119
	353.2	4.359		348.4	6.400
0.31	318.2	2.773		353.5	6.553
	328.2	3.007	1.25	328.1	5.532
	338.2	3.557	1.38	294.3	3.291
0.40	328.2	3.169		298.5	3.571
	338.2	3.546		303.3	3.901
0.48	315.2	2.589		308.3	4.252
	320.2	2.818		313.1	4.542
	324.9	3.049		317.0	4.813
	328.8	3.282	1.47	318.4	4.920
	337.7	3.707		328.5	5.555
0.60(I)	318.2	2.674		338.4	6.123
0.60(II)	318.2	2.889		348.6	6.444
	328.2	3.162		353.6	6.528
	338.2	3.694	1.58	320.6	5.071

(*Table continued on p. 382*)

TABLE 1 (*continued*)

Molar ratios $CH_3CN/NiCl_2$	T/K	$\log_e$ $(P/torr)$	*Molar ratios* $CH_3CN/NiCl_2$	T/K	$\log_e$ $(P/torr)$
0.63	318.2	2.634		326.7	5.432
0.72	315.0	2.777		331.6	5.711
	320.2	2.992		338.1	6.099
	325.0	3.223	1.59	307.4	4.295
	329.1	3.428		310.6	4.496
	337.7	3.817		317.0	4.780
0.83 (I)	328.2	3.419		320.6	5.076
	338.2	3.745		326.7	5.432
0.83 (II)	328.2	3.427		331.6	5.718
	338.2	3.898		338.1	6.100
0.87	328.2	3.300	1.60	303.1	3.983
	338.2	3.627		318.4	4.890
0.88	338.3	4.426		328.5	5.533
0.90	321.5	3.894		338.4	6.107
	338.1	4.386		348.6	6.451
	351.1	4.745		353.6	6.609
	362.2	5.022	1.80	318.5	4.967
	371.2	5.186		328.6	5.534
0.93	314.7	3.732		338.4	6.082
	320.2	3.899		348.6	6.440
	324.9	4.049		353.0	6.594
	328.2	4.250	1.86	314.7	4.684
	328.8	4.220	1.90	307.4	4.292
	337.4	4.511		310.6	4.503
0.94	328.2	4.091		315.5	4.780
0.96	328.2	4.027		320.6	5.071
0.99	321.5	3.909		326.7	5.432
	338.1	4.368		331.6	5.712
	351.1	4.724		338.1	6.093
				340.9	6.215

that its decomposition pressure would achieve one atmosphere at a temperature greater than 444 K. This phase also has a low temperature limit of stability of about 259 K, at which it disproportionates to $NiCl_2(CH_3CN)_2$ and some lower complex.

Below an acetonitrile to nickel chloride molar ratio of one, the phase regions become more complex. There is good evidence for the existence of a compound whose stoichiometry is close to $NiCl_2(CH_3CN)_{.88}$ or $(NiCl_2)_8(CH_3CN)_7$ (see Fig. 2). Below this composition the results are more difficult to interpret in terms of definite stoichiometric compounds.

The 318 K isotherm (Fig. 2) appears to have steps at molar ratios of about 0.6 and 0.3 acetonitriles per nickel chloride. The 328 K isotherm shows steps at about the same molar ratios but the differences in pressure are smaller than at 318 K. At 338 K the experimental scattering has obscured any stepwise changes. Even at 318 K the change in pressure with composition is small enough so that, taking into account the experimental indetermination, it is not possible to state unambiguously what compounds may exist. Indeed, the isotherms could be interpreted in terms of a solid solution region where the vapor pressure decreases systematically with composition. It is difficult to visualize, however, how a solid solution could be formed between a compound such as $NiCl_2(CH_3CN)_{.88}$ and $NiCl_2$, especially in view of the polymeric structure of $NiCl_2$. Difficulties in determining equilibrium vapor pressures for composition with low ligand content have previously been reported in the literature. For example, Broers and van Welie[10] in an investigation of the $CoSO_4$–H_2O system could not obtain reproducible equilibrium vapor pressures for the $CoSO_4 \cdot H_2O(s) \rightarrow CoSO_4(s) + H_2O(g)$ decomposition.

Because of the suggestion that several stoichiometric phases may exist in the lower composition regions, vapor pressure measurements were made at additional temperatures for compositions with acetonitrile to nickel chloride ratios of 0.72, 0.48 and 0.27. These data are also shown in Fig. 1. It is interesting to note that the pressure curves of the $NiCl_2(CH_3CN)_{.88}$ and the three lower compositions all intersect at about the same temperature, just below 373 K. Above that temperature the only stable complex that exists is the $NiCl_2(CH_3CN)$.

Several complexes with acetonitrile to nickel chloride ratios greater than two have been reported. Hathaway and Holah[2] noted the existence of an unstable $NiCl_2(CH_3CN)_2 \cdot 2CH_3CN$ in which only two of the four acetonitriles were coordinated. Kern[5] reported the isolation of a royal blue $NiCl_2(CH_3CN)_{3.5}$ complex that was not characterized but was stable enough for analysis. Kern's procedure is quite similar to that of Hathaway and Holah for the preparation of $NiCl_2(CH_3CN)_2$ except that zinc metal is mixed with the nickel chloride in the extraction thimble. An attempt to repeat Kern's procedure resulted in the formation of blue crystals which were very unstable and decomposed on handling to give $NiCl_2(CH_3CN)_2$.

Table 2 lists the near infrared and visible spectral data obtained for compositions ranging from $NiCl_2(CH_3CN)_{1.9}$ to $NiCl_2(CH_3CN)_{0.27}$. The data for $NiCl_2(CH_3CN)_{1.9}$ and $NiCl_2(CH_3CN)$ are in agreement with values obtained by

TABLE 2

SPECTRAL ENERGIES (cm^{-1}) OF TRANSITIONS IN THE NICKEL CHLORIDE–ACETONITRILE SYSTEM

Composition	$^3A_{2g} \rightarrow {}^2T_{2g}$	$^3A_{2g} \rightarrow {}^3T_{1g}$, ^1E_g		$^3A_{2g} \rightarrow {}^3T_{1g}(D)$	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
$NiCl_2$	7250	12 300	13 100	19 400	22 200
$NiCl_2(CH_3CN)_{0.4}$	7350	12 200	13 000	19 400	22 200
$NiCl_2(CH_3CN)_{0.7}$	7600	12 200	12 800	19 400	22 500
$NiCl_2(CH_3CN)_{1.0}$	7650	12 200	13 300	19 200	23 000
$NiCl_2(CH_3CN)_{1.6}$	8350	12 700	13 700	—	23 400
$NiCl_2(CH_3CN)_{1.9}$	8350	12 500	13 700	—	23 900
$Ni(CH_3CN)_6^{2+}$ [a]	9250	14 600	17 000	—	27 800

[a] Data obtained from solution measurements.

other investigators for the di- and monoacetonitrile complexes and are consistent with an octahedral configuration about the nickel[2,3]. There is a general trend downward in the energy of the $^3T_{2g} \leftarrow {}^3A_{2g}$ transition on going from high to low acetonitrile content as would be expected from the relative positions of chloride and acetonitrile in the spectrochemical series[11] and the rule of average environment[12]. This would indicate that the nickel ions remain octahedrally coordinated when nitrile is lost with chloride ions replacing acetonitrile molecules in the coordination sphere of the nickel. For compositions with acetonitrile to nickel chloride ratios less than one, it is impossible for all nickel ions to have the same environment and one would expect to see some spectral evidence for this fact. However, the $^3T_{2g} \leftarrow {}^3A_{2g}$ peak is quite broad and of such low intensity that using our technique it is not possible to resolve peaks that are close together.

Differential thermal analysis has been used in identifying phases and obtaining enthalpy data on phase transitions and decompositions. Extensive DTA data were obtained on samples covering the entire composition range of the acetonitrile–nickel chloride system. However, due to the slowness of the kinetics of the decompositions involved, these data are of little use in clarifying or supporting the thermodynamic data obtained from vapor pressure measurements. DTA peak temperatures did not correspond to those predicted from the vapor pressure measurements. A study of DTA peak areas per gram of nickel chloride as a function of composition indicated that some of the peaks probably corresponded to transitions involving metastable intermediates that were kinetically slow in their decomposition.

Thermodynamic parameters for the various decompositions are shown in Table 3. If one assumes that only two and three coordinated chlorides exist in any phase, then the contribution to ΔH per mole of nitrile due to bond rupture and bond formation, ΔH_b, is given by:

$$\Delta H_b = \varepsilon_N + 2\varepsilon_2 - 3\varepsilon_3 \qquad (1)$$

where ε_N is the nickel–nitrile bond energy, ε_2 is the nickel–chloride bond energy for a two coordinated halide, and ε_3 is the nickel–chloride bond energy for a three coordinated halide. This expression is valid only when the influence of the group *trans* to a particular ligand on the nickel–ligand bond energy is negligible. Under these conditions, ΔH_b should be approximately the same for all decompositions since they involve replacing a nickel–nitrile bond with a nickel–chloride bond, thereby converting a two coordinated chloride into a three coordinated one. In addition to ΔH_b there are contributions due to changes in Van der Waals forces holding the polymeric units together. These forces will vary from one stoichiometric phase to another and are primarily responsible for the variations in the values of ΔH° shown in Table 3. The large difference in ΔH° is between the decomposition of the diacetonitrile complex to the monoacetonitrile complex and the decomposition of $NiCl_2(CH_3CN)$ to $NiCl_2(CH_3CN)_{.88}$ indicates that the $NiCl_2(CH_3CN)_{.88}$ may be more stabilized by favorable Van der Waals interactions than either the mono- or the diacetonitrile complexes. If one substracts the enthalpy of vaporization of acetonitrile[13] (33.1 kJ

TABLE 3

STANDARD ENTHALPY AND ENTROPY CHANGES PER MOLE OF GASEOUS ACETONITRILE FOR DECOMPOSITIONS IN THE DIFFERENT PHASE REGIONS OF THE NICKEL CHLORIDE-ACETONITRILE SYSTEM CALCULATED FROM DATA IN TABLE 1

Phase region	*No. of points*	$\Delta H^{\circ a}$ *(kJ mol^{-1})*	$\Delta S^{\circ a}$ *(J mol^{-1}K^{-1}*
$NiCl_2(CH_3CN)_2$ and $NiCl_2(CH_3CN)$	41	52.0 ± 0.4	149.0 ± 1.3
$NiCl_2(CH_3CN)$ and $NiCl_2(CH_3CN)_{0.88}$	19	25.9 ± 0.8	58.6 ± 2.1
Average composition $NiCl_2(CH_3CN)_{0.72}$	5	41.0 ± 0.8	97.5 ± 2.5
Average composition $NiCl_2(CH_3CN)_{0.45}$	5	44.4 ± 0.8	107.1 ± 2.9
Average composition $NiCl_2(CH_3CN)_{0.27}$	7	51.9 ± 0.4	127.6 ± 1.3

[a] Values of ΔH° and ΔS° are per mole of gaseous CH_3CN. Uncertainties are standard deviations.

mol^{-1}), the value of ΔH° for the decomposition of the $NiCl_2(CH_3CN)$ to form $NiCl_2(CH_3CN)_{.88}$ and liquid CH_3CN is -7.1 kJ mol^{-1}, indicating an exothermic process.

Reedijk and Groeneveld[4] have proposed polymeric structures of octahedrally coordinated nickel for $NiCl_2(CH_3CN)_2$ and $NiCl_2(CH_3CN)$ with chloride bridges existing between adjacent nickel ions. Although X-ray structure determinations have not been made, one can speculate as to the possible polymeric units that could give rise to the various stoichiometries. In $NiCl_2(CH_3CN)_2$ the most probable structure would consist of rows of nickel ions held by double chloride bridges with two nitriles occupying the axial positions above and below each nickel to complete its octahedral coordination. The $NiCl_2(CH_3CN)$ could arise from a condensation of two rows of octahedra where nitriles are replaced by halide bridges. Such structures have been proposed by Brown et al.[14] for $NiCl_2Q_2$ and $NiCl_2Q$ (Q = quinoline, C_9H_7N) and by Lee et al.[9] for $NiCl_2(bipy)_2$ and $NiCl_2(bipy)$ (bipy = 2,2'bipyridine, $C_{10}H_8N_2$). These investigators also report compounds of lower, fractional stoichiometries ($NiCl_2Q_{.67}$ and $NiCl_2(bipy)_{.50}$) which presumably were formed by further condensation of polymeric units. The apparent steps in the acetonitrile–nickel chloride isotherms shown in Fig. 2 could be the result of such polymeric condensation. However, no simple model along these lines can be used to explain the existence of the $NiCl_2(CH_3CN)_{.88}$ compound.

It is possible that with the $NiCl_2(CH_3CN)_{.88}$ a transition from linear polymeric units to extended layer structures may begin and that this may account for the unusually small value of ΔH°. Without more information as to the structures of the different compositions, little more can be said by way of interpretation of the thermodynamic results.

Compositions with nitrile content below that of $NiCl_2 \cdot CH_3CN$ were poorly crystallized, giving very weak powder diffraction patterns. Therefore, it is doubtful that X-ray diffraction procedures would be successful in providing data for the elucidation of the structures in this phase region.

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